DYNAMICS OF SURFACE MELTING

FINAL

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Appendix A: List of Publications Resulting From DOE Support

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I. Introduction

The research supported by this DOE grant deals with the study of the dynamics of surface melting. Both conventional surface probes and picosecond time-resolved surface electron diffraction are used in our studies. The goal is to develop a better understanding of the nature of the order-disorder phase transformation that the top few atomic layers undergo with the increase in temperature. We have studied the temperature induced disorder of the surface of single-crystals of metals and epitaxially grown metal thin films. In the following we summarize work performed on this grant.

II. Picosecond Electron Diffraction Facility

The work started on a previous DOE grant at the University of Rochester was reestablished at Old Dominion University. The time-resolved electron diffraction facility at ODU is housed in a 2,400 sq. ft. laboratory within the Physical Electronics Research Institute. Significant cost and effort was put to bring this facility to full operation. We have made use of this facility to study a range of problems of interest, as described in the following sections of this report. ODU has allocated about \$200,000 of capital equipment in addition to all costs associated with the infrastructure and preparation of the laboratory space. One UHV system was brought from Rochester in addition to some laser systems. Other equipment purchases were made using DOE funds. We have also been fortunate enough to receive a sizable equipment donation from Xerox-Webster which included two UHV systems. All three systems are presently operating in the low 10^{-10} Torr range and have been used to conduct experiments reported upon here. This facility is presently used by a postdoctoral research associate, three Ph.D. students, and one M.S. student working on this DOE project. The following is a description of the main components of this facility. A more detailed description is given in Appendix A of our renewal application.

Ultrahigh Vacuum Systems:

UHV System #1: This contains the picosecond reflection high-energy electron diffraction system originally built at the University of Rochester. This system is pumped by a Perkin-Elmer 300-l/s ion pump and a titanium sublimation pump to achieve a pressure in the low 10^{-10} Torr. A precision manipulator with a heating and cooling stage is used to position the specimen. A temperature controller maintains the sample temperature to ± 1 degree. Surface cleaning is performed by argon ion bombardment and annealing on a hot stage. Surface cleanliness is checked by Auger spectroscopy using a cylindrical electron energy analyzer with an internal electron gun (Omicron). An auxiliary chamber pumped by a 270 l/s turbomolecular pump is used for instrumentation testing and fabrication of photocathodes for the time-resolved RHEED electron gun. This chamber is separated from the main chamber by an ultrahigh vacuum valve. A microchannel plate assembly is used for time-resolved RHEED detection. The diffraction patterns are routinely acquired by a computer-controlled, two-dimensional CCD detector and stored for data analysis (EG&G Princeton Applied Research). This system is presently used to study superheating of free surfaces of single-crystals.

UHV System #2: This system is used for studying the melting of thin films grown *insitu* on inert substrates, such as lead microcrystallites on graphite. It is pumped with 300 l/s ion pump (Varian) and a titanium sublimation pump. A 75 l/s turbomolecular pump is used to rough the system. It contains a precision manipulator with heating and cooling capabilities and a temperature controller. A commercial RHEED gun and screen made by PHI are incorporated in the system, plus a dedicated home-built photoactivated RHEED system for time-resolved work. A thermal evaporator and a quartz crystal thickness monitor plus controller are used for thin film deposition. A separate two-dimensional image analysis system (K-Space) is used for RHEED pattern acquisition and analysis. This image analysis system and software were specifically designed for RHEED image acquisition and analysis.

UHV System #3: This system is shared between this DOE project and another project to study high-yield photocathode development. It is pumped by a 220 l/s ion pump. A 75 l/s turbomolecular pump is used for roughing the system. A precision manipulator with a heating stage is incorporated in the chamber. DOE related work on this chamber include instrumentation development for a RHEED system with a few ps temporal resolution based on the design we previously developed in Rochester [Aeschliman et. al., 1995]. We plan to use this chamber for the time-resolved photoemission microscopy, which we are proposing in our renewal application.

Laser Systems:

The main laser system used in this work is based on a Quantronix Nd:YAG actively mode-locked oscillator providing ~90-ps pulses with a repetition rate of 82 MHz. The average power of this laser is 17 W. This oscillator is used to seed a home-built Nd:YAG regenerative amplifier. The regenerative amplifier uses a Quantronix 117 laser head and a Medox Pockels cell driver. The Pockels cell assembly and the optical design of the cavity was done at ODU. This regenerative amplifier provides more than 1.5 mJ, $\lambda = 1.06 \mu\text{m}$, with a pulse width of ~ 90 ps at a repetition rate of 82 MHz. This performance is slightly better than a commercial regenerative amplifier system, and was achieved with a fraction of the cost of the commercial system. The stability of the regenerative amplifier is better than 5 % over an extended period of time (sometimes in hours, especially during weekend and night operation). A home-made autocorellator based on a LiIO_3 crystal and a computer controlled delay line is used to check the pulse width.

Some of the experiments require the use of ~20 mJ pulse energies, in order to uniformly heat a relatively large single-crystal surface since the electron beam in the RHEED geometry interacts with a few millimeters on the surface. Therefore, we added a single-pass amplifier (Kigre) that allowed us to obtain ~30 mJ per pulse at a repetition rate of 50 Hz. We developed a discriminator circuit to allow us to synchronize the injection of the regenerative amplifier pulse to the firing of the single-pass amplifier flashlamp. In this circuit a detector monitors the amplifier flashlamp pulse and, at a particular light level, gives a signal to fire the regenerative amplifier. Using this method the stability of the amplified laser was almost the same as the output of the regenerative amplifier.

The Nd:YAG laser system we are using provides a robust, relatively easy to maintain, and highly stable laser for applications requiring a temporal resolution longer than ~ 100 ps. This has been the case in several of the systems we studied and we expect that this system will continue to serve our research program for a long time. However, for some applications, such as the melting of open surfaces, identifying the limits of superheating, certain surface reconstructions, and many other surface phenomena, better temporal resolution is needed. In the past few years a significant progress has been accomplished using Ti:sapphire lasers. For that purpose, we have initiated a parallel program to build an amplified Ti:sapphire laser system with ~ 100 fs temporal resolution and a few millijoule pulse energy at 50 Hz repetition rate. Using university funds we purchased an Ar-ion laser capable of delivering 18 Watts for all lines. A femtosecond Ti:sapphire laser was assembled based on designs provided to us by Dr. Margaret Murnane of the University of Michigan. We are at the present time finalizing some tests on that unamplified system. For amplification, we have acquired a 50-Hz, Q-switched Nd-YAG laser delivering 150 mJ pulses with ~ 7 ns FWHM. We plan to frequency double this laser and use it to pump a Ti:sapphire regenerative amplifier. The Pockels cell and driver for this amplifier are available in our laboratory.

III. Anomalous Expansion of Pb(100)

We have conducted a set of experiments aiming to understanding temperature-dependent structural properties of surfaces. Pb(100) is one of the surfaces we studied using both conventional static RHEED and time-resolved RHEED. We have observed anomalous surface expansion of about 4% for Pb(100) in the temperature range between room temperature to about 500 K [Tang and Elsayed-Ali, 1994]. This surface expansion is 7-8 times larger than that in the bulk. Surface expansion was measured using temperature dependent shifts in the peak position of the RHEED streaks in the in-phase condition, where the in-phase condition is that obtained when constructive interference occurs for the ongoing electron wave which contains contributions deep within the crystal. An example of this shift in RHEED peak intensity with temperature is shown in Fig. 1 where normalized RHEED profiles are plotted at various temperatures. By comparing the ratio of the background intensity to peak intensity we conclude that a high density of vacancies appears at temperatures above ~ 500 K. These results are in general agreement with those of Yang et. al. [1991].

Fig. 1 A set of normalized RHEED profile intensities for the 01 streak of Pb(100) plotted at various temperatures.

IV. Pb ON Si(111)

A. STM STUDIES

Through a collaboration with Dr. Wendelken and coworkers at Oak Ridge National Laboratory, we studied temperature and coverage dependence of the structure of Pb on Si(111)7x7 surface using scanning-tunneling microscopy [Tang et. al., 1995]. Our results showed that for low Pb coverage, the Pb atoms favored the faulted sites. The ratio between the number of Pb atoms on faulted to unfaulted sites increased after sample annealing. Using the temperature dependence of this ratio, we estimated an energy difference of 0.05 eV associated with a Pb atom on these two sites. High mobility of Pb atoms on Si(111) was observed at temperatures as low as 260 °C for a coverage of 0.1 and 1 monolayer.

B. RHEED STUDIES

We used reflection high-energy electron diffraction to study the temperature-dependent structure of Pb on Si(111)7x7 surface. Three different phases giving $\sqrt{3}\times\sqrt{3}$ -R30 ° Pb diffraction patterns were observed. These are the 1 ML incommensurate (IC) phase, the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30 ° phase, and the 1/6 ML $\sqrt{3}\times\sqrt{3}$ -R30 ° mosaic phase. A phase transformation resulting in the disappearance of the $\sqrt{3}\times\sqrt{3}$ -R30 ° diffraction streaks into the background is observed at 300 °C and 570 °C for the 1 ML IC phase and the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30 ° phase respectively. Through quantitative analysis of the temperature dependent diffraction streak intensity, the Debye temperature of the 1 ML IC phase is measured to be 55 ± 15 K, whereas that

for the $1/3 \text{ ML } \sqrt{3} \times \sqrt{3} - \text{R}30^\circ$ phase is $80 \pm 10 \text{ K}$. Details are given in the attached manuscript (Appendix C).

V. Superheating of Bi(0001)

We observed substantial laser superheating for Bi(0001) using time-resolved RHEED with ~ 200 -ps time resolution. Bi was chosen because of its relatively low melting temperature ($T_m = 544 \text{ K}$) and low vapor pressure ($\sim 2 \times 10^{-10} \text{ Torr}$) at T_m , and the fact that previous slow-heating experiments have demonstrated superheating of Bi crystallites. Some of these Bi crystallites melted after a time delay of about 30 min. when held at T_m and after 10 min. when held at $T_m + 5 \text{ K}$ [Blackman et. al., 1972; Peppiatt, 1975]. Bi, contrary to most metals, undergoes a negative volume change upon melting. This is thought to induce surface stress during melting that might cause substantial superheating. Using time-resolved RHEED with ~ 200 -ps resolution we are able to achieve heating rates of $\sim 10^{11} \text{ K/s}$, approximately 13 order of magnitude larger than that used in the Bi crystallite experiments.

Superheating of Bi(0001) by about 90 K was observed [Murphy et. al., 1993]. Larger temperature excursions above T_m result in melting and irreversible laser damage to the surface. Scanning electron microscopy (SEM) images show the presence of a laser-induced periodic surface structure in the damaged region of the sample, the spacing of which is approximately the heating laser wavelength ($\lambda = 1.06 \mu\text{m}$). One of these SEM images is shown in Fig. 2. Significant and irreversible reduction in surface quality was observed, both as a decrease in RHEED streak intensity and in the reflectivity of the surface.

Fig.2 Scanning electron microscopy (SEM) images of Bi(0001) showing periodic surface structure produced after irradiation with a fluence that raises the surface temperature by more than 90 K above the bulk melting temperature.

In order to relate a given decrease in RHEED streak intensity to a temperature rise ΔT , an intensity versus temperature calibration was obtained as shown in Fig. 3. These data are normalized to the streak intensity at the lowest temperature studied. The intensity of the diffraction pattern is consistent with Debye-Waller behavior up to the highest temperature studied, 523 K (i.e., the diffraction streak intensity attenuation is exponential with temperature indicating that no surface disordering occurs). From the slope of the calibration a surface Debye temperature of 42 ± 9 K can be extracted.

Fig. 3 RHEED streak intensity of Bi(0001) normalized to that at 300 K obtained as a function of temperature plotted on a semilogarithmic scale. The intensity was measured near the peak of the 01 streak. The reduction in RHEED streak intensity with temperature follows a Debye-Waller behavior with a Debye temperature of 49 ± 9 K.

To determine the maximum superheating temperature, the behavior of $I/I(T_{\text{bias}})$ versus peak laser intensity I_p for $T_{\text{bias}} = 523$ K at different time delays was observed. Figure 4 shows $\ln[I/I(T_{\text{bias}})]$ versus I_p for $t = t_0$ and $t = t_0 + 4.0$ ns, respectively, where t_0 is the time of maximum modulation of $I/I(T_{\text{bias}})$ due to heating. The linear regions in Fig. 4 show exponential decay consistent with Debye-Waller behavior. Deviation from this linear behavior is due to melting. From Fig. 4, the value of $\ln[I/I(T_{\text{bias}})]$ corresponding to the maximum I_p before deviation from linear behavior is extracted and converted to a peak temperature rise, ΔT , using the calibration in Fig. 3. For $T_{\text{bias}} = 523$ K, observation of melting occurs for $I_p = 2.0 \pm 0.2 \times 10^7 \text{ W/cm}^2$. This corresponds to $\Delta T = 110 \pm 25$ K or equivalently, a superheating temperature of 90 ± 25 K. When the maximum superheating temperature is exceeded, melting occurs. This is indicated by a strong deviation from the behavior predicted by heat-diffusion model. The earliest visual observations of damage was observed to coincide with the point at which $\ln[I/I(T_{\text{bias}})]$ versus I_p deviates from linear behavior.

Fig. 4 The logarithm of the ratio of the heated streak intensity to the intensity at $T_{\text{bias}} = 523 \text{ K}$ is plotted versus peak laser intensity for (a) $t = t_0$, and $t = t_0 + 4.0 \text{ ns}$. Deviation from Debye-Waller behavior is seen, which corresponds to the onset of melting. Superheating of Bi(0001) occurs up until the break from the line fit that occurs at $2.0 \pm 0.2 \times 10^7 \text{ W/cm}^2$ corresponding to a superheating temperature of $90 \pm 25 \text{ K}$.

After damage has occurred, the RHEED streaks were still visible but their intensities were diminished, indicating a reduction in the surface quality. SEM images, Fig. 2, of the laser-damaged surface indicate that the surface has melted. The SEM images show formation of a periodic structure with periodicity about equal to the wavelength of the laser. This periodic structure forms in a hexagonal arrangement of melt puddles, which in some regions coalesce into parallel rows. The spacing between puddles and rows is approximately equal to the wavelength of the heating laser.

Previous pulsed-laser melting experiments on the (0001), $(\bar{1}010)$, and $(2\bar{1}\bar{1}0)$ surfaces of Bi using a ruby laser with a 30-ns pulse width have shown defect formation on the $(\bar{1}010)$, and $(2\bar{1}\bar{1}0)$ surfaces resulting from mechanical stress induced by slip planes parallel to the (0001) surface. In these experiments, the Bi(0001) surface regrew epitaxially from the liquid with no laser-induced periodic surface structure observed [Helms et. al., 1988]. The different behavior observed in our experiment may be related to the two-orders-of-magnitude difference in laser pulse width.

In our previous superheating experiments on Pb(111) [Herman and Elsayed-Ali, 1992], surface damage was only induced by the laser for an I_p much larger than that which corresponded to maximum superheating. For Pb(111) the threshold for pulsed-laser melting is lower than the threshold for pulsed-laser damage although for Bi(0001) these two thresholds appear to be comparable.

VI. Time-Resolved RHEED Study of Pb(100)

We used time-resolved reflection high-energy electron diffraction to study the structural behavior of Pb(100) subjected to 200-ps laser pulses. These experiments were performed just prior to moving the time-resolved RHEED system to ODU. Data analysis and some further experiments were performed at ODU. Measurement of the electron diffraction intensity indicates that residual order is present on the surface at a temperature of 615 ± 20 K, where the bulk melting temperature of Pb is 600.7 K. This implies that the disordered film that forms on Pb(100) is stable up to the bulk melting temperature and above.

A medium energy ion scattering (MEIS) study on Pb(100) and vicinal surfaces showed that a limited amount of disorder began to form on Pb(100) at temperatures above 500 K, where T_m for Pb is 600.7 K [van Pijxteren and Frenken, 1992]. The disordered layer thickness on Pb(100) was observed to increase logarithmically up to 2-3 K below T_m and then saturates at 1.3 monolayer, measured up to $T_m - 0.05$ K. A model has been developed that includes the effect of the substrate on the disordered layer [Chernov and Mikheev, 1988; 1989]. In this model, the ordered substrate induces a periodic density modulation in the disordered layer in a direction parallel to the solid-disordered layer interface. This modulation makes it energetically favorable for the surface to form disordered films with the thickness being an integral multiple of $2\pi/k_1$, where k_1 is the wavenumber corresponding to the first maximum of the structure factor of the bulk liquid. For Pb, $2\pi/k_1$ is approximately 2.86 Å [van Pijxteren and Frenken, 1992]. The disordered layer that forms is stable up to T_m and does not act as a nucleus for further melting.

RHEED streak intensity measurement, normalized to that at a given bias temperature, T_{bias} , was obtained for various peak laser intensities. Results are shown in Fig. 5 for four experiments representing bias temperatures successively closer to T_m , where the set in Fig. 5(d) is biased just 11 K below T_m . These sets were obtained at the time t_0 . In each of the sets, the normalized streak intensity is observed to vanish at sufficiently high laser intensities, indicating that order has been lost in the probed surface layer. It is observed that as T_{bias} is raised, the peak laser intensity necessary to disorder the probed surface layers decreases from $\sim 4.3 \times 10^7$ W/cm² for $T_{bias} = 533$ K to $\sim 1.8 \times 10^7$ W/cm² for $T_{bias} = 590$ K. The peak surface temperature when the normalized RHEED streak intensity vanishes is obtained using the measured dependence of the RHEED intensity on temperature. In each of the sets of Fig. 5, the lowest peak laser intensity which corresponds to a vanishing RHEED streak intensity is converted to a temperature rise. When this is accomplished, we see that the peak surface temperature, $T_{bias} + \Delta T$, when order is lost in the probed layer is 607 K, 611 K, and 619 K for Figs. 5(a)-5(d), respectively. The average peak temperature at which order is lost is $\sim 615 \pm 20$ K. The peak temperature does not account for convolution effects. Including these effects in the analysis would lead to a somewhat greater peak surface temperature.

Fig. 5 Time-resolved RHEED measurement on Pb(100) show vanishing intensity at a temperature of $\sim T_m + 15$ K

These experiments show that residual order appears to be present on Pb(100) at a peak surface temperature of 615 ± 20 K. Convolution effects, due to the fact that the electron pulse width is about the same as for the laser, lower the experimentally measured peak surface temperature. Therefore, it is likely that residual order is present above T_m . At this high temperature, however, the surface most likely contains a high density of defects such as vacancies [Yang et. al., 1991]. The presence of vacancies would be expected to lower the degree of superheating by providing nucleation sites for melting. Indeed, compared with the results obtained in Pb(111), where superheating to ~ 720 K was observed [Herman and Elsayed-Ali, 1992], the results on Pb(100) show evidence of residual order at a significantly lower surface temperature. Finally, these experiments show that there exists a barrier for the growth of the disordered layer thickness on Pb(100) at temperatures above T_m . At temperatures greater than 615 ± 20 K, a second layering transition may occur that would result in a disordered layer thickness of $4\pi/k_1 \sim 5.7$ Å, a depth that exceeds the 5 Å probed by our RHEED gun.

VII. Annealing of Pb(111) by Laser Superheating

Motivated by our experiments on Pb(111), Häkkinen and Landman [1993] developed a molecular dynamics simulation of ultrafast laser heating of fcc metal. They modeled the structural evolution of the three low-index surfaces of copper after a laser pulse deposits its

energy into the electron system, which then couples that energy to the phonon system. The interaction among the Cu atoms was modeled based on many-body embedded atom potential, and Cu was chosen because of the availability of what is believed to be an accurate potential. Using the same potential and energy deposition conditions, the surfaces of Cu(110) and Cu(100) melted while Cu(111) superheated by as much as 40 K over the calculated bulk melting temperature. A very interesting observation is that even a highly damaged surface, with as much as 10% preexisting vacancies could also be superheated. This is surprising since it would be expected that, since melting is nucleated at defects, a highly defective surface will not superheat. However, the MD simulations showed that this large concentration of vacancies and adatoms anneal through a non-diffusional cooperative mechanism in which the adatoms settle in the top layer, while the cooperative atomic movement results in the filling of vacancies. This mechanism is attributed to the high vibrational amplitudes which atoms are forced into by the ultrafast superheating pulse in addition to the strain created by the islands and holes.

We are conducting experiments to investigate surface defect density after laser superheating of Pb(111). A highly ordered surface is used for these studies. This surface was produced by annealing near T_m for several days. By analyzing the diffraction streak profile, we can estimate terrace size. Relative density of vacancies can be obtained from the peak-to-background ratio for the out-of-phase condition. For the experimental results discussed below the sample was laser irradiated with different laser energies while it was kept at 573 K ($T_m = 600.7$ K). A RHEED pattern was acquired at room temperature after annealing before laser irradiation, and at 573 K after laser irradiation. The sample was then cooled to room temperature and a RHEED pattern was obtained. The next set of data is obtained by heating the sample to 573 K again, obtaining a RHEED pattern before and after laser irradiation. The sequence was repeated for different laser energies. The laser pulse width is ~ 100 ps, and for each datum the sample was irradiated by 500 laser pulses at a particular energy starting with the lower laser energies. The RHEED patterns are analyzed to obtain the average terrace width, which is directly related to the width of the diffraction streak in the out-of-phase condition after subtracting the instrumental response. The instrumental response is obtained from the width of the RHEED streak in the in-phase condition. Figure 6 shows a line scan through the 00 diffraction streak measured for the sample at 573 K, before and after laser irradiation. The laser fluence was such that to raise the surface temperature by 200 K. While for 200 ps pulses the maximum superheating without any surface melting was ~ 120 K, for 100 ps pulses is ~ 140 K. Therefore, for the data shown in Fig. 6, the surface superheats and then surface melting occurs. In fact, due to the energy spent in the latent heat of fusion, we do not expect that the melt will reach 200 K. From Fig. 6, two effects are observed; (1) a significant increase in the peak intensity-to-background ratio is observed; (2) some increase in the FWHM of the line scan through the RHEED streak is also observed.

Fig. 6 A line scan through the 00 streak of a RHEED pattern of Pb(111) before and after irradiation with 100 ps laser pulses

By analyzing this FWHM after subtracting the instrumental response we obtain the average terrace size. Figure 7 shows the average terrace width of monatomic steps on the surface of Pb(111) measured at 573 K before and after laser superheating. The solid line is a polynomial fit to guide the eye. We see a dramatic change in the terrace size starting at a pulse laser energy of ~10 mJ. Clearly the superheating pulse is reducing step density. This reduction in step density becomes larger when the maximum superheating is reached and surface melting occurs.

Fig. 7 Average terrace width of monatomic steps on the surface of Pb(111) measured at 573 K before and after laser superheating.

Step density reduction was not predicted in the model of Häkkinen and Landman. What was predicted is that the adatom and vacancy concentration is reduced by a superheating pulse. Evidence of this process is provided by the increase in RHEED streak intensity-to-background ratio after the superheating pulse. This is shown in Fig. 8, where the ratio of the background-to-peak minus background was obtained for the RHEED streak in the out-of-phase condition. LEED studies have shown that this ratio increases with vacancy density for the out-of-phase condition in which electrons scattered from the top layers undergo some destructive interference. A relation between the vacancy concentration and this ratio was derived [Yang et. al., 1991]. To obtain the relative vacancy concentration at different temperatures, it is necessary to obtain the mean vibrational amplitude perpendicular to the surface. Similar arguments can also apply to RHEED experiments [Lagally et. al.; Tang and Elsayed-Ali, 1994]. The trend we see is consistent with a reduction in surface vacancy concentration. We note, however, that step density reduction will also cause an increase in the RHEED streak intensity-to-background ratio. At the present time we are developing a methodology which we can use to separate the effects of step density reduction from vacancy annealing. We also point out that while the simulations were done on Cu(111), the potential used to model atomic interaction has the same form as that for Pb(111), both are fcc metals.

Fig. 8 Ratio of background-to-peak minus background for the RHEED streak in the out-of-phase condition versus laser pulse energy. The sample was laser was kept at 573 K. A laser energy of ~10 mJ corresponds to surface superheating by ~120 K.

VIII. Superheating of Pb Crystallites on Graphite

We have studied melting and solidification of Pb on graphite using reflection high-energy

8 ± 2 K above the bulk melting temperature. Upon lowering the temperature, supercooling of the Pb by 70 ± 2 K was also observed. Superheating of micron sized crystallites bounded by close packed facets, by few degrees above T_m , has been observed [Métois et. al., 1989; Spiller, 1982]. Métois et. al., deposited 3000 Å of Pb on a graphite substrate and the surface was annealed above the bulk melting temperature of Pb, and then cooled. This caused the formation of a large number of Pb crystallites. They were able to overheat sharp edged Pb crystallites with {111} facets by approximately 3 K. The facet shape was studied in detail using SEM [Heyraud et. al., 1983]. In the Pb/graphite system, some irregular particles were found to superheat by 2 K.

We investigated the melting characteristics of Pb on graphite. Multi-layers of Pb grown on pyrolytic graphite offer several advantages for the study of surface effects by RHEED. The interaction of Pb with the graphite is purely through Van der Waals forces, and complications due to chemical processes are not present.

Through analysis of the RHEED pattern profile width, the size of the deposited crystallites of Pb is found to be larger than the graphite texture, as the FWHM of the peak intensity profile of Pb spot is smaller than the graphite profile width. The Pb crystallites are approximately 1.6X larger than the graphite crystallites. The measured lattice is 5.72 Å, corresponding to the 6.06 Å diagonal length of the Pb(111) unit cell in the $(0\bar{1}\bar{1})$ direction. Similar to the graphite surface, when the crystal was rotated, the Pb./ rod is always observed in the pattern, indicating that the reciprocal lattice is circularly rotated about the [111] axis of Pb. The intensities also change with the azimuthal angle and has the maximum when Pb $(0\bar{1}\bar{1})$ is parallel to graphite [100]. This indicates that the Pb crystallites have a texture structure, similar to the graphite substrate such that the crystallites are rotated about the [111] axis with respect to each other. Therefore, we conclude that the Pb growth is such that the particles are oriented with the Pb(111) parallel to {0002} of graphite ($(111)_{Pb} // (0002)_{graphite}$), and $(0\bar{1}\bar{1})_{Pb} // [100]_{graphite}$. By using 14.9 eV for the inner potential of Pb, the incident angles corresponding to the Bragg condition is obtained [Jalochowski and Bauer, 1988].

For an electron energy of 12 keV and for the Bragg condition corresponding to $n = 3$, the incident angle for graphite and Pb is 2.21° , 2.68° respectively. Thus, the Bragg reflection spots are separated vertically on the screen. Therefore, measurement of Pb spot intensity is not affected by the graphite spot intensity. The specular beam obtained from 4 ML Pb was analyzed to investigate the temperature dependence of the spot intensity. Figure 9(a) shows the intensity of the 333 Bragg reflection spot of Pb for an incident angle of 2.57° (near 2.68°), as a function of temperature. The two curves corresponding to heating, and cooling are distinguished by two arrows in opposite directions. The temperature was raised from 343 K to 633 K, and then lowered to 373 K. Figure 9 (b) shows the intensity change at the higher temperature range extracted from Fig. 9 (a). The abrupt change in the diffraction spot intensity is due to melting/solidification phase transitions. As the temperature is increased from room temperature to 590 K the intensity decreases exponentially. In the temperature range between 601 K and 610 K, the intensity drops abruptly. This drop begins at 601 K, higher than the melting point of Pb as seen in Fig. 9 (b). During the cooling process, the intensity undergoes a large change over

the temperature interval 535 K to 530 K, a much lower temperature than the melting point. As the temperature falls below 530 K, the intensity increases exponentially. The Debye Waller factor is obtained from a least squares fit to the exponential part of the curve. The Debye temperature obtained is 79 ± 3 K, which is higher than the surface Debye temperature of 66 K for the Pb(111) surface, and lower than 88 K of bulk Pb.

Fig. 9 Intensity of the 333 Bragg reflection spot of Pb(111) as a function of temperature

When the sample is heated slightly above the melting temperature of Pb, the graphite diffraction spots appear, indicating the exposure of the substrate surface to the electron beam. We assume that the Pb layers condense into liquid droplets on the substrate after partial melting exposing the graphite. Subsequently when the sample temperature is lowered, Pb droplets are recrystallized. This occurs at 70 ± 2 K below the bulk melting temperature of Pb and is indicated by the reappearance of a clear diffraction pattern characteristic of Pb. Previous SEM investigation [Heyraud et. al., 1983] showed the formation of spherical Pb particles on the graphite after annealing. The Debye temperature we estimate for the 4 ML film is 79 ± 3 K, revealing surface Debye effects. For the 14 ML and 70 ML thick films we measured a surface Debye temperature of 91 ± 3 K and 86 ± 3 K, respectively. These values are in agreement with the known bulk Pb Debye temperature of 88 K, within the experimental uncertainties.

Our RHEED intensity measurements indicate 8 ± 2 K superheating of the deposited Pb films. In our work we did not pre-treat the film by annealing the sample after Pb was deposited. The Pb atoms, deposited at room temperature, were seen to grow as oriented crystals on the graphite substrate. These crystals when heated close to the melting temperature may form crystallites with {111} facets contributing to the superheating. SEM images we obtained of as-deposited Pb on graphite with mean thickness of ~ 400 Å, clearly show facets in the larger crystallites.

We also observed supercooling of the Pb film by 70 ± 2 K. This is attributed to a nucleation barrier for solidification which results from the competition between the decrease in

free energy upon solidification and the increase in free energy associated with the existence of a solid-liquid interface. The free energy of a solid droplet is related to its radius, r . At solid-liquid interfaces, a nucleation barrier for solidification exists for $r < r_0$, where r_0 is some critical radius determined by the surface characteristics of the substrate [Woodruff, 1973]. The droplets with radii, $r < r_0$, supercool. The critical radius estimated for Pb is approximately 40 Å, when the degree of supercooling is 70 K.

At the present time we are preparing to conduct picosecond time-resolved RHEED experiments in order to test for the amount of superheating of the Pb{111} crystallites with the much increased heating rate provided for by the picosecond laser. The proposed experiments are discussed in our renewal application.

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Appendix A
List of Publications Resulting From DOE Support

PUBLICATIONS RESULTING FROM DOE SUPPORT

PUBLICATIONS IN REFEREED JOURNALS

Z. H. Zhang, B. Lin, X. L. Zeng, and H. E. Elsayed-Ali, "Annealing of Pb(111) by Pulsed Laser Superheating," in preparation.

H. E. Elsayed-Ali and F. Ercolessi, "Surface Superheating," in preparation, to be submitted to Rev. Mod. Phys.

Z. H. Zhang, P. Kulatunga, and H. E. Elsayed-Ali, "Reflection High-Energy Electron Diffraction Study of Melting and Solidification Of Pb on Graphite," submitted to Phys. Rev. B.

H. E. Elsayed-Ali, "Temperature-Dependent Reflection High-Energy Electron Diffraction Study of Pb on Si(111)," submitted to Solid State Commun.

J. Cao, Y. Gao, C. A. Schmuttenmaer, R. J. D. Miller, H. E. Elsayed-Ali, and D. A. Mantell, "Anomalous Feature Observed in the Excited Electron Lifetime Measurements of Copper Surfaces," submitted to Phys. Rev. Lett. (Partial support)

H. E. Elsayed-Ali, "Measurement of the Surface Debye Temperature with Reflection High-Energy Electron Diffraction," scheduled to appear in J. Appl. Phys., 1 May 1996.

D. Tang, H. E. Elsayed-Ali, J. Wendelken, and J. Xu, "Scanning Tunneling Microscopy Study of Pb on Si(111)," Phys. Rev. B 52, 1481-1484 (1995).

M. Aeschlimann, C. A. Schmuttenmaer, H. E. Elsayed-Ali, R. J. D. Miller, J. Cao, Y. Gao, and D. A. Mantell, "Observation of Surface Enhanced Multiphoton Photoemission from Metal Surfaces in the Short Pulse Limit," J. Chem. Phys. 102, 8606-8613 (1995). (partial support)

M. Aeschlimann, E. Hull, C. A. Schmuttenmaer, J. Cao, L. G. Jahn, Y. Gao, H. E. Elsayed-Ali, D. A. Mantell, and M. Scheinfein, "A Picosecond Electron Gun for Surface Analysis," Rev. Sci. Instrum. 66, 1000-1009 (1995).

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BOOK CHAPTERS

H. E. Elsayed-Ali and P. M. Weber, "Time-Resolved Surface Electron Diffraction," in Time-Resolved Diffraction, edited by J. R. Helliwell and P. M. Rentzepis, World Scientific, in Press.

PUBLICATIONS IN CONFERENCE PROCEEDINGS

(INVITED): M. Aeschlimann, E. Hull, C. A. Schmuttenmaer, J. Cao, Y. Gao, D. A. Mantell, and H. E. Elsayed-Ali, "Time-Resolved Electron Diffraction to Study Photoinduced Molecular Dynamics at Single Crystal Surfaces," in Time Resolved Electron and X-Ray Diffraction, edited by P. M. Rentzepis, SPIE Proceedings Vol. 2521, SPIE's 40th Annual Meeting, pp. 103-112, San Diego, CA, 9-14 July 1995.

(INVITED): H. E. Elsayed-Ali, "Time-Resolved reflection High-Energy Electron Diffraction of Metal Surfaces," in Time Resolved Electron and X-Ray Diffraction, edited by P. M. Rentzepis, SPIE Proceedings Vol. 2521, SPIE's 40th Annual Meeting, pp. 92-102, San Diego, CA, 9-14 July 1995.

T. Juhasz, C. Suarez, W. E. Bron, and H. E. Elsayed-Ali, "Femtosecond Measurements of Ballistic and Interactive Transport of Nonequilibrium Electrons in Thin Gold Films," Ultrafast Phenomena, Ninth International Meeting, Optical Society of America, Dana Point, CA, 2-6 May 1994. (Partial support)

C. A. Schmittenmaer, M. A. Aeshelimann, J. Cao, H. E. Elsayed-Ali, R. J. D. Miller, D. A. Mantell, and Y. Gao, " Femtosecond Studies of Carrier Relaxation Processes at Single Crystal Metal Surfaces," Proc. SPIE 2125, 98 (1994). (partial support)

H. E. Elsayed-Ali and J. W. Herman, "Structural Properties of Metal Surfaces Subjected to Ultrafast Laser Heating," Int. Conf. on Lasers '93, V. J. Corcoran and T. A. Goldman (eds.) (STS Press, McLean, VA, 1994), pp. 42-49, Lake Tahoe, NV, December 1993.

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PUBLISHED ABSTRACTS

H. E. Elsayed-Ali, D. Tang, and H. Wang, " Temperature Dependent Reflection High Energy Electron Diffraction Study of Pb on Si(111)," 42nd National American Vacuum Society Symposium, Minneapolis, MI, 16-20 October 1995, P. 145.

J. Cao, R. J. D. Miller, Y. Gao, H. Elsayed-Ali, C. A. Schmittenmaer, and D. A. Mantell, "Time-Resolved Two-Photon Photoemission Studies of the Electron Dynamics of Au(111) Films," Amer. Phys. Soc. March Meeting, San Jose, CA, 20-24 March 1995. (Partial support)

Y. Gao, J. Cao, R. J. D. Miller, H. Elsayed-Ali, and D. A. Mantell, "Anomalous Long Electron Lifetime Observed on Alkali Metal Covered Cu Films," Amer. Phys. Soc. March Meeting, San Jose, CA, 20-24 March 1995. (Partial support)

D. Tang and H. E. Elsayed-Ali, "Temperature Dependent Properties of Pb(100) Studied Using Reflection High-Energy Electron Diffraction," 1994 Meeting of the Southeastern Section of the American Physical Society, Bull. Amer. Phys. Soc., Vol. 39, No. 8, p. 1817, Newport News, VA, 10-12 November 1994.

M. Aeschlimann, E. Hull, J. Cao, C. A. Schmittenmaer, L. G. Jahn, Y. Gao, H. E. Elsayed-Ali, D. A. Mantell, and M. R. Scheinfein, "Time-Resolved RHEED of Study Photoinduced Molecular Dynamics at Single Crystal Surfaces," 14th European Conference on Surface Science (ECOSS-14), Leipzig, Germany, 19-23 September 1994.

M. A. Aeschlimann, J. Cao, C. A. Schmittenmaer, H. E. Elsayed-Ali, Y. Gao, R. J.D. Miller, and D. A. Mantell, "Femtosecond Studies of Electron of Relaxation at Metal Surfaces," Lasers in Surface Science, Adriatico Research Conference, Trieste, Italy, 9-12 August 1994. (Partial support)

M. A. Aeschlimann, J. Cao, C. A. Schmuttenmaer, H. E. Elsayed-Ali, Y. Gao, R. J. D. Miller, and D. A. Mantell, "Dynamik an Festkoerperoberflaechen Mittels Femtosekunden 2-Photonen-Photoemission," Fruhjahrstagung der Deutschen Physikalischen Gesellschaft, Munster, Germany, 21-25 March 1994.(partial support)

C. A. Schmuttenmaer, J. Cao, M. A. Aeschlimann, H. E. Elsayed-Ali, Y. Gao, R. J. D. Miller, and D. A. Mantell, "Generation of Photoelectrons with Excess Kinetic Energy from Metal Surfaces," Laser Science (ILS-IX), Toronto, Canada, 3-8 October 1993. (Partial support)

C. A. Schmuttenmaer, J. Cao, M. A. Aeschlimann, H. E. Elsayed-Ali, Y. Gao, R. J.D. Miller, and D. A. Mantell, "Photoexited Charge Transfer to Adsorbates at Metal Surfaces," Laser Science (ILS-IX), Toronto, Canada, 3-8 October 1993. (Partial support)

T. Juhasz, H. E. Elsayed-Ali, G. O. Smith, C. Suarez and W. E. Bron, "Femtosecond Hot Electron Transport Measurements in Gold Films with Different Crystal Structures," Laser Science (ILS-IX), Toronto, Canada, 3-8 October 1993. (Partial support)

Appendix B
Theses Completed and Presently Conducted Under DOE Support

THESES COMPLETED UNDER DOE SUPPORT

J. W. Herman, "Time-Resolved Structural Studies of the Low-Index Faces of Lead," Ph.D. thesis, Department of Physics, University of Rochester, 1993.

E. A. Murphy, "Experimental Studies of Surface Melting and Time-Resolved Superheating of Metal Surfaces," Ph.D. thesis, Department of Physics, University of Rochester, 1993.

THESES PRESENTLY CONDUCTED UNDER DOE SUPPORT

P. Kulatunga, "Melting Dynamics of Metal Microcrystallites," tentative title, Ph.D. program, Department of Physics, Old Dominion University.

B. Lin, "Time-Resolved Electron Diffraction Studies of Temperature Induced Surface Disorder," tentative title, Ph.D. program, Department of Electrical and Computer Engineering, Old Dominion University.

T. Suliman, "Development of an Ultrafast Electron Diffraction and Microscopy System," tentative title, M.S. program, Department of Electrical and Computer Engineering, Old Dominion University.

X. Zeng, "Ultrafast Superheating of Low Index Metal Surfaces," tentative title, Ph.D. program, Department of Electrical and Computer Engineering, Old Dominion University.

Appendix C
Copies of Some of the Publications and Manuscripts Resulting from DOE Support

Reflection high-energy electron-diffraction study of surface disorder and anomalous expansion of Pb(100)

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(Received 2 June 1994; revised manuscript received 7 September 1994)

The temperature-dependent surface structural behavior of Pb(100) is studied using reflection high-energy electron diffraction. Anomalous surface expansion for temperatures between room temperature to about 500 K is observed. A high density of surface vacancies appears at temperatures above ~ 500 K.

Reflection high-energy electron diffraction (RHEED) is used to study the temperature-dependent structural properties of Pb(100). Compared to low-energy electron diffraction (LEED), estimating the lattice spacing by RHEED is more precise, since the specimen-to-screen distance can be greater, and the distance between RHEED streaks can usually be measured more accurately than distances between LEED spots. The surface sensitivity of RHEED is comparable to that of LEED with the advantage that the probed depth can be varied by changing the incidence angle of the electron beam on the surface rather than changing the primary electron energy, as for LEED.

Several structural studies have been previously performed on fcc(100) metal surfaces near its bulk melting temperature T_m .¹⁻⁷ A recent study on Pb(100) and its vicinal surfaces using medium-energy ion scattering showed that a limited amount of disorder began to form on Pb(100) at temperatures above 500 K, where T_m for Pb is 600.7 K.³ The disordered layer thickness on Pb(100) was observed to increase logarithmically up to 2–3 K below T_m and then saturates at about 1.3 ML's, measured up to $T_m - 0.05$ K. The maximum amount of disorder on the vicinal surfaces increased with the miscut angle from 1.9 to 3.5 ML's on the 5° and 10° miscut surfaces, respectively. This is in contrast to the divergence of the disordered layer thickness on Pb(110) as T_m is approached. This behavior, where the disordered layer thickness is finite as T_m is approached, is known as incomplete surface melting.³

Further experiments on Pb(100) with high-resolution low-energy electron diffraction (HRLEED) have shown a weak disordering at ≈ 570 K.⁵ This disordering is preceded by an anomalous surface expansion at $T \leq 480$ K and an abrupt generation of surface vacancies beginning at ≈ 510 K. An anomalous surface expansion was also observed on Ni(001) using LEED.⁴ An x-ray photoelectron diffraction study of Pb(100) showed evidence of a logarithmic growth of the disordered layer thickness beginning at 585 ± 5 K and up to the highest temperatures studied at $T_m - 2$ K.⁶

Recently, there have been several molecular-dynamics (MD) simulations modeling surface melting of fcc(100) surfaces.⁸⁻¹⁰ The simulations by Häkkinen and Manninen⁸ examine the (110), (100), and (111) surfaces of copper, from 0 K to T_m . This study, which uses

effective-medium theory, allows for the direct comparison of the three low-index faces using the same MD potential and identical cell sizes. The results show pronounced disordering of Cu(110), weak disordering of Cu(100) just below T_m , and superheating of Cu(111). In addition, the high-temperature behavior of vicinal surfaces of Au(100) was studied using the many-body "glue" potential.⁹ In these studies, structural modulation in the disordered film was evident on Cu(100) and the vicinal surfaces of Au(100).

In the present paper, we describe an experimental study of the high-temperature structural behavior of Pb(100) using reflection high-energy electron diffraction. The experiment was performed in a vacuum chamber with a base pressure in the low range of 10^{-10} torr. The sample was cut with a fine band saw to twice its final thickness, polished with silicon carbide grit paper, and finally chemically etched in a mixture of 80% glacial acetic acid and 20% hydrogen peroxide until a mirrorlike finish was obtained. The sample was clipped to a resistively heated molybdenum heater mounted on a three-axis manipulator, which also has polar and azimuthal rotation. Two thermocouples placed at different locations on the sample monitored its temperature.

The sample was cleaned with cycles of 30 min argon-ion bombardment at a temperature of 500 K followed by

FIG. 1. A schematic diagram of reflection high-energy electron diffraction RHEED. The electron beam is incident on the surface at an angle θ , probing the first few atomic layers. The RHEED pattern, which consists of streaks oriented perpendicular to the plane of the surface, is detected on a phosphor screen.

FIG. 2. A three-dimensional picture of a RHEED pattern intensity. The profiles are taken along the streaks. The height of the peak is proportional to intensity (in arbitrary units). From the front to back, the streaks are the 01, 00, and $0\bar{1}$, respectively.

5 min annealing at 550 K. The sample cleanliness was checked by Auger electron spectroscopy using a cylindrical mirror electron energy analyzer. The RHEED pattern is monitored by a phosphor screen located 23 cm away from the sample. The RHEED pattern is focused, using a camera lens, into a 512×512 charge-coupled-device (CCD) detector. The output of the CCD detector is digitized and stored in a computer for data analysis.

A schematic diagram of reflection high-energy diffraction is shown in Fig. 1. The electron beam is incident along the [011] direction at an angle of 2° – 5° with the surface of the sample. In Fig. 1, the central diffraction beam is the 00 streak. The 01 and $0\bar{1}$ streaks are on the two sides of 00 streak. A three-dimensional plot of a RHEED pattern is shown in Fig. 2. The profiles are taken along the RHEED streaks.

In Fig. 3 we display a set of RHEED profiles taken along the 01 RHEED streak at different temperatures.

FIG. 3. A set of normalized RHEED profile intensities for the 01 streak plotted at various temperatures. The electron beam is incident at an angle $\approx 2.7^\circ$ with the surface, which establishes the first in-phase condition. The electron beam energy is 14 keV.

The horizontal axis is the position along the RHEED streak. The vertical axis is the RHEED streak intensity. The peak intensity of each curve is normalized by dividing the intensity at each position by that at the peak. From this set of profiles, we find that the peak position of the streak shifts towards the shadow edge (left side of the figure) as temperature increases. These shifts represent a decrease in the electron momentum component perpendicular to the surface of the sample, k_1 , due to the surface expansion as will be described next. Shifts in RHEED streak peak position are related to shifts previously observed in HRLEED I - V curves with temperature.⁵

In our experiment, the probed depth is obtained by using an empirical relation between electron energy and inelastic mean-free path, along with the measured angle of incidence of the electron beam.¹¹ For an electron-beam energy of 14 keV and an angle of incidence of 3° from the surface, the probed depth is ≈ 4 Å, reaching about two layers for the Pb(100) surface. If the outgoing electron wave contained contributions from layers deep within the crystal, each reflected coherent wave front from different layers would interfere. The condition of constructive interference is called the in-phase condition, and it can be expressed as

$$k_1 = 2\pi m / b \quad (1)$$

where k_1 is the perpendicular component of the outgoing electron momentum, m is an integer, and b is the distance between two atomic layers in the [100] direction.

In the RHEED geometry, the Ewald sphere cuts the reciprocal-lattice rods at a grazing angle. Thus, the diffraction condition in the RHEED geometry results in streaks rather than spots as observed in LEED. It can be shown that

$$\Delta\alpha \approx \frac{\Delta G}{k \sin\alpha} \quad (2)$$

where α is the electron reflection angle with respect to

the surface, $\Delta\alpha$ is the angular spread of the reflected beam, ΔG represents the width of the reciprocal-lattice rod and k is the electron momentum. As a result of the small value of incidence angle relative to surface in the RHEED geometry, the position of the peak of the RHEED streak is sensitive to the perpendicular component of momentum transfer.

The angle of incidence of the electron beam on the sample, θ , was set such that the perpendicular component of the outgoing electron momentum, k_1 , equals $2\pi m/b$, where $b=2.48$ Å, the spacing between two atomic layers in the [100] direction. This corresponds to the in-phase condition.

When the surface thermally expands in the vertical direction from b to $b+\Delta b$, the in-phase condition changes to

$$k'_1 = 2\pi m / (b + \Delta b). \quad (3)$$

This changes the perpendicular component of the electron momentum. The change in k_1 is described by

$$\Delta k_1 = k'_1 - k_1 = 2\pi m [1/(b + \Delta b) - 1/b] \approx (-2\pi m \Delta b / b^2). \quad (4)$$

The thermal expansion of the top atomic layers, $\Delta b/b$, can be estimated from

$$\Delta b/b = -\Delta k_1 (b/2\pi m). \quad (5)$$

The change in the perpendicular component of momentum transfer, Δk_1 , can be found from the measured peak position shift along the streak,

$$\Delta k_1 = k \Delta d / L \quad (6)$$

where Δd is peak position shift, $k=2\pi/\lambda$ is the magnitude of the electron momentum, where λ is the electron wavelength, and L is the distance between the sample and the phosphor screen.

Following the analysis, we set the incidence angle, such that the RHEED pattern is in the first or the second in-phase condition, $k_1=2\pi/b$ and $4\pi/b$, respectively. A larger peak shift is expected for the second in-phase condition for the same temperature increase. Figure 4 is a

FIG. 4. A set of normalized RHEED profile intensities for the 01 streak are plotted at various temperatures. The electron beam is incident at an angle $\approx 5^\circ$ with the surface, which establishes the second in-phase condition. The electron beam energy is 15 keV.

set of profiles for the 01 streak on the second in-phase condition. The surface temperature is marked on the side of each profile. It is apparent that the shift is approximately double that of the first in-phase condition, shown in Fig. 3, which is consistent with the above simple model.

From Figs. 3 and 4 we calculate a surface expansion of about 4% in the temperature range from room temperature to 500 K. We observe an anomalous thermal expansion of 7–8 times larger than that for the bulk. This result shows agreement with that previously obtained using HRLEED,⁵ which is 3.4% expansion of the top atomic layer spacing in the range from 300 to 480 K. Further consideration of the observed shifts in Figs. 3 and 4 indicates that the rate of RHEED streak peak shift with temperature is larger at higher temperatures. Thus, it appears that the coefficient of thermal expansion normal to the surface increases with temperature, as observed by Cao and Conrad for the Ni(100) surface.⁴

For this simple model to be valid, the thermal expansion parallel to the surface must be much smaller than that perpendicular to it. Thermal expansion parallel to the surface can be monitored by measuring the distance between two adjacent streaks as a function of temperature. Moreover, this simplified analysis depends on the kinematic interpretation of the RHEED pattern and ignores multiple scattering. Therefore, we can only estimate the amount of anomalous expansion. The fact that this estimate is about the same if we use the first or the second in-phase condition is consistent with the assumption that multiple scattering effects have no significant effect on the RHEED peak streak shift.

A set of normalized RHEED streak profiles for the 00 streak at different temperatures is plotted in Fig. 5. A dramatic change in the profile shape is observed when the temperature is raised over 500 K. This implies that a certain structural change has occurred on the Pb(100) surface. A possible reason for that profile change is the generation of surface defects such as vacancies. These defects change the shape of the reciprocal-lattice rods. Generation of surface defects with temperature can be observed in Fig. 6, in which the ratio of background intensity to peak intensity, $I_{\text{back}}/(I_{\text{peak}} - I_{\text{back}})$, as a func-

FIG. 5. Normalized RHEED profile intensities taken along the 00 streak at various temperatures. The electron beam is incident at an angle $\approx 27^\circ$ with the surface, and the electron beam energy is 14 keV. The RHEED profile shape change with temperature is evident.

FIG. 6. The ratio of the background intensity to the peak intensity $I_{\text{back}}/I_{\text{peak}} - I_{\text{back}}$ plotted as a function of temperature. Our RHEED data are represented by solid circles. Open triangles and squares are HRLEED data for out-of-phase and in-phase conditions, respectively, taken from Ref. 5 (see text).

tion of temperature is plotted. Our data are represented by solid circles. The background level is the intensity measured at a location between the 00 and 01 streaks. Similar ratios taken from HRLEED measurement by Yang *et al.*⁵ are also plotted. The open triangles are ratios for the out-of-phase condition, empty squares are for the in-phase condition.

In the LEED data of Yang *et al.*⁵ the ratio $I_{\text{back}}/(I_{\text{peak}} - I_{\text{back}})$ for the in-phase condition is observed to remain very small below 540 K. This indicates that thermal diffuse scattering is not important at temperatures less than 540 K. Following the theoretical calculation of Pimbley and Lu,¹² a high ratio for an out-of-phase condition indicates generation of high density of vacancies beginning at $480 < T < 540$ K for the LEED data of

Yang *et al.*, and beginning at ~ 530 as shown in our RHEED data. The background intensity I_{back} , is proportional to $2n(1-n)[1 - \cos(k_1 b)]$, where n is the vacancy concentration at the surface. To describe the temperature dependence of that ratio, the above relation was modified by Yang *et al.*⁵ such that

$$I_{\text{back}} \propto 2n(1-n)[1 - \cos(k_1 b)](1 + k_1^2 \langle u_1^2 \rangle), \quad (7)$$

where $\langle u_1^2 \rangle$ is the mean-square vibrational amplitude perpendicular to the surface. When the in-phase condition is satisfied ($k_1 b = 2m\pi$, where m is an integer), there is no background intensity. However, the background intensity reaches maxima for the out-of-phase condition when high density of surface vacancies are present.⁵ Thus, results shown in Figs. 5 and 6 can be related to the generation of high density of surface vacancies when the temperature is raised over ~ 500 K. The data shown in Fig. 6 do not account for the difference in the probing depth of our RHEED experiment when compared with that for LEED. According to the conditions reported in Ref. 5, the probing depth in the LEED experiment is expected to be somewhat larger. Moreover, the RHEED background was taken without any energy filtering.

In conclusion, we have used a simple model to extract from RHEED profiles the surface expansion normal to the surface. Anomalous surface expansion of about 4% in the temperature range from room temperature to 500 K was observed. This is 7–8 times larger than that in the bulk. High density of surface vacancies appear at temperatures above 500 K.

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Scanning-tunneling-microscopy study of Pb on Si(111)

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Scanning-tunneling microscopy has been used to study temperature and coverage dependence of the structure of lead on the Si(111)- 7×7 surface. For low Pb coverage, the Pb atoms favored the faulted sites. The ratio between the number of Pb atoms on faulted to unfaulted sites increased after sample annealing. An energy difference of 0.05 eV associated with a Pb atom on these two sites is estimated. The mobility of Pb atoms on Si(111) was observed at a temperature as low as 260°C for a coverage of 0.1 and 1 ML.

Lead on silicon represents an attractive system to study metal-semiconductor interfaces. Phase diagrams do not show the presence of any chemical compounds at the Pb/Si interface. Only for such well-defined metal-semiconductor contacts will it be possible to relate their electronic properties directly to the crystal structure and chemical binding at the interface. Mutual solubilities of Pb in Si are negligibly small,¹ thus the interface is abrupt. These properties make the Pb/Si interface a good system for studying the basic interactions of metals on semiconductors.

Several studies have been done on the Pb/Si(111) interface.²⁻⁸ These studies have utilized a variety of surface analysis techniques including low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), low-energy ion-scattering spectroscopy, Auger-electron spectroscopy, reflection high-energy electron diffraction, photoemission spectroscopy, and thermal desorption. In contrast to the above-mentioned chemical simplicity of the Pb/Si interaction, a relatively complex surface structural behavior was observed. For example, three different $\sqrt{3}\times\sqrt{3}$ phases were reported by Le Lay *et al.*¹ In addition, the final Pb structure on the Si(111) depends on the annealing history³ as well as deposition rate and substrate temperature. Thus, more investigations are necessary for better understanding of the structural properties of the Pb/Si interface. Here we report on a temperature-dependent STM study of the Pb/Si(111) interface. At a coverage less than ~ 0.1 monolayer, the Pb atoms appear to favor the faulted sites on the Si(111)- 7×7 unit cell. We measured the ratio between the number of occupied faulted and unfaulted sites after proper annealing. Based on that measurement, we can calculate the energy difference associated with Pb atoms on the two different sites.

Our experiments were performed in an ultrahigh vacuum chamber, equipped with both STM and LEED facilities. The base pressure of the chamber was $\sim 1\times 10^{-10}$ torr. The Si(111) samples used in these measurements were cut from a *p*-type wafer with 1 Ω cm resistivity, and had a size of $10\times 3\times 0.2$ mm³. The samples were

clamped on a tantalum mounting stage. Lead was evaporated from a cell at 570°C. The silicon samples were heated resistively by directly passing current through them. Each new sample was outgassed by heating it overnight at 600°C. Samples were cleaned with several flashes up to 1250°C, followed by annealing at 900°C for 0.5 min. and then slow cooling at a rate of about 0.5°C/sec. The sample temperature was measured by two pyrometers, to cover a temperature range of 200–1250°C, and the sample cleanliness was monitored by observation of the sharp 7×7 LEED pattern as well as STM images. Figure 1 shows a typical STM image of a clean Si(111)- 7×7 surface structure. A single-atom step is also shown in the image.

Growth experiments were performed at room temperature for a coverage range of $0\leq\theta\leq 3$ ML where a monolayer is defined as 7.85×10^{14} atoms/cm². Figure 2 shows

FIG. 1. An STM image of a clean Si(111)- 7×7 with a step on it. The image size is 110×110 Å², obtained at sample bias of 2 V and 0.7 nA constant tunneling current.

FIG. 2. A $140 \times 140 \text{ \AA}^2$ STM image of 0.07 ML Pb on Si(111)- 7×7 at room temperature. Trios of Pb atoms are preferentially covering the faulted side of the 7×7 unit cell. The STM was operated at 0.2 nA constant tunneling current, with 0.4 V bias on the sample.

an STM image of 0.07 ML Pb on Si(111)- 7×7 . For this coverage, the Si(111)- 7×7 LEED pattern did not change significantly from its original shape. Our results show that the Pb atoms favored the faulted sites in the unit cell of the 7×7 structure and formed trios. This is consistent with a previous STM measurement.³ Similar behavior was found in the Ag/Si(111)- 7×7 (Refs. 9 and 10) and the Pd/Si(111)- 7×7 (Ref. 11) systems. For the Si(111)- 7×7 structure, the Si-atom-induced surface states are mainly derived from the interaction between the adatom P orbital and the dangling-bond orbital of the Si bilayer. Tunneling current spectroscopic images of these adatom dangling-bond states suggest a significantly higher state density for the adatom on the faulted site than on the unfaulted site of the unit cell.¹² In the dimer-adatom-stacking-fault model,¹³ the Si lattice on the unfaulted side has an atom in the second bilayer sitting directly in the middle of a ring of six atoms making up the first bilayer. This leads to a fairly closed structure. In contrast, on the faulted half, the first bilayer is rotated 180° to line up with the second bilayer. This openness may explain why faulted sites are preferred by the Pb atoms.¹¹

We next heated the sample and observed the distribution of Pb atoms in relation to the faulted and unfaulted Si(111)- 7×7 sites. After annealing at 260°C for 40 sec, more Pb atoms are observed on the faulted sites, causing the ratio R of Pb at faulted sites to that at unfaulted sites to increase. The high mobility of Pb atoms on the surface implies that Pb atoms overcome the relatively small energy barriers which inhibit Pb atoms from diffusion on the Si substrate. It is possible to estimate the energy difference ΔE associated with the Pb atoms at faulted and unfaulted sites, using the ratio R after annealing,

$$R = \frac{N_f}{N_u} = e^{(-\Delta E/KT)},$$

where N_f and N_u are numbers of faulted and unfaulted

FIG. 3. A $750 \times 800 \text{ \AA}^2$ STM image of 0.3 ML Pb on Si(111)- 7×7 at room temperature. The STM was operated at 0.2 nA constant tunneling current, with 1.5 V bias on the sample.

sites occupied by Pb atoms, respectively, K is Boltzmann's constant, and T is the surface temperature. This ratio R is about 2.5 in our case. An increase in R when annealing the sample was also observed for the Ag/Si(111)- 7×7 system.¹⁰

We believe that the mechanism for the increase of the ratio R with annealing is not solely due to the thermal statistics. There are 19 dangling bonds on every Si(111)- 7×7 unit, 18 of them in faulted and unfaulted sites, and none of them in the dimer walls. At low coverage, Pb atoms bond first at the dangling bonds; this can be seen from Fig. 3, which shows an STM image of 0.3 ML Pb on

FIG. 4. An $800 \times 600 \text{ \AA}^2$ STM image of 1 ML Pb deposited on Si(111)- 7×7 at room temperature deposition. No annealing was performed. The STM was operated at 0.2 nA constant tunneling current, with 0.5 V bias on the sample.

FIG. 5. A $360 \times 390 \text{ Å}^2$ STM image of 1 ML Pb deposited on Si(111)- 7×7 at room temperature then annealed at 260°C for 30 sec. The area is covered by 1×1 and $\sqrt{3} \times \sqrt{3}$ domains. The STM was operated at 0.2 nA constant tunneling current, with 1.5 V bias on the sample.

Si(111)- 7×7 ; the dimer walls are still clear at this coverage. This implies that the energy barriers on the dimer walls are higher than the energy difference between the faulted and unfaulted sites. Proper annealing makes Pb atoms gain enough energy to overcome the barrier; the resulting Pb atom distribution on faulted and unfaulted sites could reflect the energy difference. From the value of the ratio R , we estimate that this energy difference ΔE is $\sim 0.05 \text{ eV}$. It is likely that this energy difference is affected by the formation of the stacking fault in the Si(111)- 7×7 unit cell. The stacking fault introduces a new state with an energy of 0.1 eV on top of the valence band at Γ .¹⁴ In addition, theoretical calculations have found that the introduction of a stacking fault into the top layer raises the surface energy slightly, in the range 0.02–0.06 eV per 1×1 cell.¹⁵ This is similar to the energy cost of a stacking fault in the bulk, which has been calculated to be $\sim 0.04 \text{ eV}$ per 1×1 cell.¹⁶

We next consider higher coverage of Pb on the Si(111). Figure 4 shows an STM image of 1 ML of Pb deposited at room temperature. The growth of Pb on Si(111)- 7×7 was observed to follow the Stranski-Krastanov (layer-plus-island) growth mechanism; however, the intermediate layers have a different structure and formation process at different deposition temperatures. At room temperature, the intermediate layer was found to be a Pb(111) epitaxial layer with the Pb[110] direction parallel to the Si[110] direction. The intermediate Pb(111) layer,

FIG. 6. A $90 \times 75 \text{ Å}^2$ STM image of 1×1 structure in Fig. 5. The STM was operated at 0.3 nA constant tunneling current, with 1.5 V bias on the sample.

which is not observed by STM, is possibly shrunk by up to 5.3% for lattice matching.⁴ We also observed that the Pb atoms were mobile at a coverage of 1 ML after annealing the sample at 260°C for 40 sec. After such annealing, the LEED pattern was observed to change with new spots corresponding to the $\sqrt{3} \times \sqrt{3}$ structure, rotated 30° . Meanwhile, the STM image after annealing shows that the Pb atoms formed a mixture of islands with 1×1 and $\sqrt{3} \times \sqrt{3}$ structures appearing. Figure 5 is an example of this mixture of 1×1 and $\sqrt{3} \times \sqrt{3}$ $R 30^\circ$ structures. As in previous measurements, using the same sample voltage bias, we cannot distinguish atoms of 1×1 and $\sqrt{3} \times \sqrt{3}$ structures.³ In Fig. 6 we show the 1×1 structure in which atoms could not be distinguished in Fig. 5. This 1×1 structure is not a compressed Pb(111) overlayer after annealing, though its [110] direction is still parallel to the Si[110] direction. The spacing of the Pb atoms is $\sim 3.5 \text{ Å}$, which is equivalent to a coverage of 1.2 ML as defined before. Meanwhile, our $\sqrt{3} \times \sqrt{3}$ structure is equivalent to $\frac{1}{3}$ ML Pb coverage. This kind of 1×1 structure is different from that previously observed for Pb deposition done at 340°C , which undergoes a reversible phase transition below $\sim 300^\circ\text{C}$ to a type of $\sqrt{3} \times \sqrt{3}$ $R 30^\circ$.¹

In conclusion, we have observed that Pb atoms are mobile on the Si(111) surface at a temperature of 260°C . The energy difference between the Pb faulted and unfaulted sites is estimated to be 0.05 eV. This energy is close to the theoretical calculation of energy induced by a stacking fault in the bulk.

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Surface Debye temperature measurement with reflection high-energy electron diffraction

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Measurement of the surface mean-square atomic vibrational amplitude, or equivalently the surface Debye temperature, with reflection high-energy electron diffraction is discussed. Low-index surfaces of lead are used as examples. Particular details are given about the temperature-dependent diffraction pattern of Pb(100) in the Debye–Waller region. The use of reflection high-energy electron diffraction for measurement of the substrate surface temperature in thin-film deposition chambers is suggested. © 1996 American Institute of Physics. [S0021-8979(96)08209-8]

I. INTRODUCTION

Monitoring of substrate temperature during thin-film deposition is often important for controlling the properties of the grown thin film. This measurement, however, is not necessarily straightforward. For example, in molecular-beam epitaxy, *in situ* measurement of the substrate temperature is complicated by the fact that the rotating holder does not permit good thermal contact between holder and thermocouples. A discrepancy of more than 70 °C between thermocouple reading and actual surface temperature was estimated.¹ Pyrometers can be used, however, they are sensitive to viewpoint transparency. Previously, it has been proposed that a surface phase transformation with a known critical temperature can be used for temperature calibration, and reconstruction in GaAs has been used for that purpose.¹ Here we show that the intensity of reflection high-energy electron diffraction (RHEED) is sensitive to surface temperature due to the Debye–Waller effect. The use of the Debye–Waller effect on the RHEED intensity provides a general method of surface temperature measurement for surfaces with known Debye temperature. Alternatively, RHEED can be used to study the vibrational properties of surfaces and epitaxial thin films with submonolayer sensitivity.

An understanding of the vibrational properties of surface atoms is of both fundamental and technological importance. For example, vibrational entropy is thought to contribute to the nature of surface segregation in alloys.^{2,3} The surface atom vibrational properties are also known to affect surface phase transformations such as the case for surface melting.^{4–6} Moreover, the vibrational properties of thin layers deposited on substrate provide information on the nature of interaction at the interface. It is well known that a surface does not behave as a simple termination of the bulk. One way in which this is manifested is in the increased vibrational amplitude of surface atoms. This is related to the asymmetric bonding and the reduced number of nearest neighbors that characterize a surface atom as compared with an atom in the bulk. Measurements of the enhanced vibrational amplitude of surface atoms have been carried out using low-energy electron diffraction (LEED).^{7,8} In the LEED studies, the Debye–Waller effect, which shows as a decrease in the elastic diffraction intensity with temperature and an

increase in background intensity, was used to characterize the surface thermal vibrations and to determine an effective surface Debye temperature Φ_D . In many of these studies, Φ_D was observed to increase with increasing incident electron beam energy. This is explained by the fact that higher incident electron energies lead to larger probed depths of the electron beam which, for high enough energy, approach bulklike characteristics.

RHEED represents another technique with which to determine surface Debye temperatures. The probed depth of the 10–20 keV electrons in the RHEED geometry, where the angle of incidence of the electron beam is typically 1°–5° with respect to the plane of the surface, is comparable to that of low-energy electrons (50–1000 eV) at near-normal incidence. Therefore, LEED and RHEED have comparable surface sensitivities. However, RHEED is much more widely used in thin-film growth studies, both as a qualitative structural probe and for thickness measurement and control using the well-known RHEED intensity oscillation.^{9–12}

II. DEBYE–WALLER EFFECT

The sensitivity of the diffraction intensity to temperature arises from the increase in the atomic vibrational amplitude with temperature. This is observed as a decrease in the elastic diffraction intensity with increased temperature. In the Debye–Waller treatment, atomic vibrations are assumed to be harmonic and the influence of multiple scattering events is ignored. In general, the harmonic vibration assumption is most valid for temperatures below the Debye temperature, however, this assumption is justified at higher temperatures when considering the intensity of the elastic diffraction peaks. Accordingly, the intensity attenuation of an elastic diffraction peak is described by¹³

$$I_n(T) = I_n(0) \exp(-MT), \quad (1)$$

where $I_n(T)$ is the n th-order diffraction intensity at temperature T , $I_n(0)$ is the n th-order diffraction intensity for a hypothetical rigid lattice, and

$$-MT = -\langle [\Delta \mathbf{k} \cdot \mathbf{u}(T)]^2 \rangle = -|\Delta \mathbf{k}|^2 \langle u^2(T) \rangle \quad (2)$$

is the Debye–Waller factor. $\mathbf{u}(T)$ is the instantaneous displacement of an atom from its equilibrium position. The

FIG. 1. This illustration shows how the parameters necessary for the calculation of the surface Debye temperature are obtained in RHEED. The incident electron beam, specular beam, and first-order diffracted electron beams are labeled k_0 , k'_0 , and k'_1 , respectively. The momentum changes as corresponding to the 0th-order and the first-order diffraction are given by Δk_0 and Δk_1 , and the ratio of their magnitudes is equivalent to the ratio of the measured distances from the transmitted beam. The angle of incidence θ is calculated from the specular spot.

separation performed in the second step of Eq. (2) is valid under the assumption of an isotropic vibrational amplitude. While this assumption is valid for atoms in the bulk, for surface atoms, anisotropy in the Debye temperature has been previously reported.⁸ In general, the vibrational amplitude of surface atoms perpendicular to the surface is larger than that direction parallel to the surface. For the low-order streaks (e.g., 00 and 01), Δk in the RHEED geometry is almost perpendicular to the surface. Therefore, for the low-order streaks we mainly measure the mean-square atomic vibrational amplitude perpendicular to the surface. For the n th-order diffracted beam, the momentum change resulting from the elastic scattering is

$$\Delta k = \Delta k_n = k'_n - k_0, \quad (3)$$

where k_0 and k'_n are the momentums of incident and n th-order elastically diffracted beams, respectively. $\langle u^2(T) \rangle$ is the mean-square displacement of an atom from its equilibrium position. The slope M of $\ln[I(T)]$ vs T gives the surface Debye temperature and can be written as

$$M = \frac{|\Delta k_n|^2}{|\Delta k_0|^2} \frac{\langle u^2(T) \rangle}{T} = \frac{|\Delta k_n|^2}{|\Delta k_0|^2} \left(\frac{4\pi}{\lambda} \sin \theta \right)^2 \frac{3\hbar^2}{mk_B \Phi_D^2}. \quad (4)$$

For the specular spot, the momentum Δk is totally in a direction perpendicular to the crystal surface, while for $n > 0$ there is a parallel component of momentum transfer. The angle of incidence θ is defined from the plane of the surface, λ is the wavelength of the electrons, $\hbar$ is Planck's constant divided by 2π , m is the atomic mass, k_B is Boltzmann's constant, and Φ_D is the surface Debye temperature. The parameters $\Delta k_n/\Delta k_0$ and θ are obtained from the diffraction pattern as demonstrated in Fig. 1. The distances from the specular spot to the shadow edge d and from the sample to the image plane L allow us to calculate θ . Providing one obtains Δk_n , the effective surface Debye temperature, or

ing RHEED.

Face	E (keV)	θ (°)	D_λ (Å)
(110)	18.2	2.8	4.6
(100)	14.0	3.2	4.2
(111)	18.2	2.4	3.9

equivalently the component of $\langle u^2(T) \rangle$ in the direction of Δk can be obtained from a measurement of the ratio $I_n(T)/I_n(0)$.

III. EXPERIMENT

We next demonstrate the use of RHEED to measure the surface Debye temperature of Pb(111), Pb(100), and Pb(110) surfaces. By observing the intensity attenuation of the RHEED streak maxima as a function of temperature, the dependence of $\langle u^2(T) \rangle$, and hence Φ_D , on surface orientation is obtained. The surfaces were mechanically polished and chemically etched as discussed in previous publications.¹⁴ The experiments were performed in an ultrahigh-vacuum chamber with a base pressure in the low 10^{-10} Torr range. The samples were cleaned before each experimental run with cycles of Ar^+ bombardment for 30 min at 500 K followed by annealing for 5 min at 550 K. Auger electron spectroscopy was used to confirm the surface cleanliness of the samples. The samples were mounted on a resistively heated stage and the temperature was measured with two thermocouples mounted on the surface. Quantitative analysis of the RHEED streak intensity from the samples was carried out by imaging the phosphor screen detecting the RHEED pattern on an array detector interfaced to a personal computer.

The experimental conditions are given in Table I where E is the electron energy, θ is the angle of incidence of the electron beam measured from the surface of the sample, and D_λ is the depth probed by the electron beam. The probed

FIG. 2. RHEED intensity normalized to that at 407 K, $\ln[I(T=407\text{ K})/I(T)]$, is plotted vs temperature. The slope is used to obtain the surface Debye temperature of Pb(111). The dashed line corresponds to the slope expected for a surface Debye temperature of 88 K, which is the Debye temperature of bulk Pb. The larger slope associated with the Pb(111) surface demonstrates the increased thermal vibrations of surface atoms relative to those of the bulk.

FIG. 3. Three-dimensional plots of RHEED patterns of Pb(100) obtained at different temperatures. The height of the streak profile represents the intensity of the streak (in arbitrary units). (a)–(d) show intensity of RHEED pattern at 306, 415, 508, and 555 K, respectively. The arrows are drawn along the RHEED streaks, and show the direction of increased momentum transfer perpendicular to the surface. The electron beam was incident along the [011] direction.

depth is obtained using an empirical relation between the electron energy and the inelastic mean-free path along with the measured angle of incidence of the electron beam.¹⁵

IV. RESULTS AND DISCUSSIONS

An example of a RHEED streak intensity measurement for the Pb(111) surface is given in Fig. 2 where the intensity of the 01 streak measured at its peak is shown as a function of temperature. The data are plotted on a semilogarithmic scale and shows an exponential decrease in the RHEED

FIG. 4. RHEED intensity (in arbitrary units) along the 01 streak for Pb(100) is plotted for different temperatures varying from 307 to 493 K. Each location on the streak corresponds to different momentum transfer with respect to the incident beam, Δk . The two vertical lines give the range of locations along each RHEED streak which we use to obtain the Debye–Waller curves.

streak intensity with temperature for the studied range, which extends up to $T_m - 15$ K. For comparison, the expected Debye–Waller reduction in the elastic diffraction intensity assuming a bulk Debye temperature of 88 K is plotted on the same graph. The effective surface Debye temperature is obtained from Eq. (4) using the experimentally determined slope of the RHEED streak intensity, the angle of incidence of the electron beam, and the momentum transfer corresponding to the considered location on the diffraction pattern. Only single scattering events are considered in this analysis. Moreover, since no electron energy filtering of the RHEED pattern was performed, the background includes inelastically scattered electrons. From the RHEED patterns obtained at room temperature, the intensity of the inelastically scattered electrons is much smaller than the elastic peaks. At the higher temperatures, the ratio of the intensity of an elastic peak to the background increases. Background subtraction from the elastic peaks was accomplished by measuring the background intensity midway between two RHEED streaks for each temperature and subtracting it from the elastic peak intensity measured at the same temperature. The observed larger slope of the RHEED data as compared with the slope predicted assuming a bulk Debye temperature implies that the surface atoms experience an increased vibrational amplitude relative to bulk atoms. The Debye–Waller behavior of surface atoms on Pb(111) is consistent with other experiments showing that this surface does not exhibit anharmonic surface vibration, thought to be a precursor to surface melting. The (110) and (100) surfaces displayed Debye–Waller behavior up to 520 and 550 K, respectively. At higher temperatures, deviation from Debye–Waller behavior occurred

TABLE II. The surface Debye temperature for Pb(100) calculated at different positions along the 01 streak.

$\Delta k_x / \Delta k_0$	M (10^{-3} K)	Φ_D (K)
0.881	6.93	52.3
0.896	7.33	51.8
0.912	7.56	51.9
0.928	7.94	51.5
0.943	8.65	50.2
0.959	9.03	49.9
0.975	9.15	50.4
0.991	9.55	50.1
1.007	10.21	49.3
1.023	10.69	48.9
1.039	10.00	51.4

indicating the enhanced density of surface defects, anharmonicity in the atomic vibration,¹⁶ or enhanced inelastic processes which could dominate at higher temperatures.¹⁷ Anharmonicity and temperature generated surface defects would generally cause the Debye-Waller curve to bend downward, while enhanced inelastic scattering with temperature can cause the curve to bend upward. Thus, to obtain the surface Debye temperature it is important to conduct the measurement in a temperature range for which the simple kinematic Debye-Waller theory can apply.

Analysis of the exponential region of the data for Pb(110) and Pb(100) yields the effective surface Debye temperatures for these surfaces. A set of three-dimensional plots of RHEED patterns showing intensity changes with temperature for Pb(100) is shown in Fig. 3. The height of the profile is proportional to the RHEED intensity. The 00 order is in the center of the pattern. This set of plots shows the intensity of the RHEED pattern as a function of surface temperature, which is indicated on the side of each diffraction pattern. The attenuation at a particular location on the streaks depends on the transfer of momentum, Δk . In Fig. 4 the RHEED streak intensity along the 01 streak is plotted for different temperatures ranging from 307 to 493 K. The x axis represents the streak position as determined by the pixel number of the array detector observing the diffraction pattern. The y axis is the relative RHEED streak intensity. At higher temperatures, the temperature dependence of the streak intensity shows deviation from the exponential Debye-Waller behavior. In addition, anomalous surface expansion, which is to some degree occurring even at room temperature, starts to become significant enough to cause a noticeable shift in the peak of the streak location.¹⁸ These complications for this surface limits the Debye-Waller temperature region and makes it necessary to analyze only the lower-temperature data in order to extract from it the surface Debye temperature. Deviation from Debye-Waller behavior is even more noticeable in

FIG. 5. The temperature dependence of the RHEED streak intensity for Pb(100) at different locations on the 01 streak. The Debye temperature corresponding to each curve is calculated in Table II.

Pb(110) which is well known to undergo surface premelting at temperatures significantly below the bulk melting temperature.^{4,5}

The temperature dependence of the RHEED streak intensity at different locations on the streak is displayed in Fig. 5. The position at which each Debye-Waller curve is obtained is indicated on the figure by the pixel number which corresponds to that shown in Fig. 4. Clearly the slope of each exponential curve is dependent on its location on the RHEED streak which determines Δk . Analysis of Fig. 5 is given in Table II where the Debye temperature of Pb(100) is calculated using the temperature-dependent streak intensity at different locations along the 01 streak. In Table II, the amount of momentum transfer along the RHEED streak increases with the pixel number. ($\Delta k_x / \Delta k_0$ of 0.88 corresponds to pixel number 342, while that for $\Delta k_x / \Delta k_0$ of 1.039 corresponds to pixel number 402.) The value of the Debye temperature obtained from this set of data is 50.7 K. Analysis of the temperature dependent decay of the 00, 01, 0 $\bar{1}$ streaks obtained from three different sets of data indicates that the surface Debye temperature of Pb(100) is 49 ± 5 K.

Values of Φ_D for the three low-index faces of Pb are given in Table III along with values previously obtained from LEED.¹⁹ RHEED measurements reported here are for the temperature dependence of the 0th-order and the two first-order streaks. The momentum change for the n th-order streak $|\Delta k_n|$ has components both perpendicular and parallel to the surface plane. To separate these components, a more detailed study which probes multiple crystallographic directions is necessary. The experimental errors in the reported RHEED measurements are due to the spread in the slopes of the semilogarithmic plots obtained for these measurements and the uncertainty in the angle of incidence and momentum transfers as measured from the RHEED pattern.

TABLE III. The Debye temperature for the low-index surfaces of lead.

Technique	Pb(110)	Pb(100)	Pb(111)	Reference
LEED	$37 \pm 20\%$ K	...	$55 \pm 20\%$ K, $49 \pm 20\%$ K	19
RHEED	30 ± 5 K	49 ± 5 K	60 ± 8 K	14, present work

We have demonstrated that RHEED is a comparable technique to LEED in probing the thermal vibrations of surface atoms. RHEED is suitable for submonolayer detection, with up to 0.1 monolayer mean thickness detection capability reported.²⁰ In addition, from a practical point of view, RHEED is the principle structural diagnostic tool in molecular-beam epitaxy. Its grazing angle of incidence makes it compatible with real-time observation of the surface quality during thin-film growth. Oscillations in RHEED intensity, in particular in the specular spot, has been extensively used to monitor and control layer-by-layer growth.⁹⁻¹² Quantitative analysis of the Debye-Waller effect on the RHEED pattern provides the ability to monitor the effect of film thickness, with submonolayer accuracy, on the thermal vibrations of surface atoms. An understanding of the vibrational amplitude of surface atoms during film growth could be correlated with other technologically important parameters such as surface diffusion and substrate-adsorbate coupling. The simple analysis presented here, which ignores inelastic and dynamical scattering effects, is inadequate for a description of much of the temperature dependent vibrational behavior of the surface atoms. However, at some temperature range, the simple kinematic Debye-Waller analysis of the temperature dependence of the RHEED intensity seems to apply. We also point out that, for a surface with a known Debye temperature, the Debye-Waller reduction in the RHEED streak intensity with temperature can be used to obtain the substrate surface temperature in molecular-beam epitaxy or other high-vacuum thin-film deposition systems.

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Time-resolved structural studies of the low-index faces of lead

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Reflection high-energy electron diffraction with 200-ps time resolution is used to study the structural behavior of the three low-index faces of Pb. The surfaces are subjected to heating and cooling rates on the order of 10^{11} K/s. The open Pb(110) surface is seen to reversibly disorder below the bulk melting temperature, T_m . In contrast to Pb(110), the close-packed Pb(111) surface sustains superheating to $T_m + 120$ K. Pb(100), a surface with atomic packing intermediate to that of Pb(110) and Pb(111), shows evidence of residual order at a temperature above the bulk melting point.

I. INTRODUCTION

Although the phenomenon of melting has been studied extensively for many years, a complete understanding of the process remains elusive. It has long been speculated that melting is initiated at the surface, at a temperature below the bulk melting point, T_m .¹ A well-known relation suggests the tendency of a particular surface to melt:²

$$\gamma_{sv} > \gamma_{sl} + \gamma_{lv}, \quad (1)$$

where γ_{sv} , γ_{sl} , and γ_{lv} represent the interfacial free energies of the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively. This relation is valid for many surfaces at temperatures below T_m . The relation implies that, above a certain temperature, it is energetically favorable for the surface to form a thin disordered layer between the ordered solid and the vapor. This phenomenon, known as surface melting, offers an explanation for the lack of parity between supercooling and superheating.

The supercooling of melts of metals has been observed for many years.² Supercooling is attributed to a nucleation barrier to solidification that is a result of the competition between the decrease in free energy upon solidification and the increase in free energy that is associated with the formation of a solid-liquid interface. In the case of superheating, however, the presence of a thin disordered surface layer formed below T_m provides a vast two-dimensional site for the nucleation of melting into the bulk as T_m is approached. Therefore, for surfaces that disorder below T_m , there does not exist a nucleation barrier for melting, and this precludes substantial superheating. To form an understanding of bulk melting, extensive work has been performed examining the role of the surface in the process.³

One of the first conclusive experimental observations of surface melting was on Pb(110) using medium-energy ion scattering (MEIS).⁴ A reversible order-disorder transformation was observed on Pb(110), with disorder beginning in the temperature range of 450–560 K, where T_m for Pb is 600.7 K. The thickness d of the disordered layer increased logarithmically beginning at 560 K

($d \sim \ln[T_m/(T_m - T)]$). At temperatures above $T_m - 0.3$ K, the disordered layer thickness was observed to increase according to a power law ($d \sim [T_m - T]^{-1/3}$).⁵ The functional character of the growth laws is predicted from mean-field theory.⁶ Other techniques were used to study the surface melting of Pb(110).^{3(b)} These techniques are complementary, and provide a coherent picture of surface melting as a continuous phase transformation. X-ray photoelectron diffraction⁷ and low-energy electron diffraction (LEED) [Refs. 8(a) and 8(b)] yielded temperatures for the onset of surface disorder of 530 and 543 K, respectively. In addition, x-ray scattering,⁹ UV photoelectron spectroscopy,¹⁰ quasielastic atom scattering,¹¹ diffuse-light scattering,¹² and scanning tunneling microscopy¹³ studies have observed surface melting on Pb(110).

To determine the role of the crystal surface orientation in the melting process, further MEIS studies were performed.¹⁴ Pb surfaces were again studied, and the majority of the crystalline faces considered exhibited pronounced surface disordering with the exception of the vicinal surfaces within $\sim 17^\circ$ of the {111} plane, and $\sim 10^\circ$ of the {100} plane. The closed Pb(111) surface was observed to remain ordered up to $T_m - 0.5$ K. In the MEIS experiments, the number of disordered atoms per unit area at temperatures near T_m versus surface orientation was qualitatively consistent with predictions made from surface free-energy measurements on Pb crystallites.¹⁵ These measurements, made using electron microscopy, displayed minima in the normalized surface free energy at the {111} and {100} orientations.¹⁵ Compared with the results from MEIS, the electron microscopy experiments predicted a significantly smaller angular region about the {100} orientation, where pronounced disorder is absent. In addition to the experiments on Pb, the importance of surface orientation was demonstrated on Al surfaces with Al(110) displaying surface melting and Al(111) remaining ordered.¹⁶

A recent MEIS study of Pb(111) and vicinal surfaces revealed another interesting aspect of surface melting.¹⁷ These experiments showed that vicinals with miscut angles $\theta < 2^\circ$ remain ordered, while vicinals with $\theta > 13.9^\circ$ exhibited pronounced surface melting. Vicinal surfaces

with $2.0^\circ < \theta < 13.9^\circ$ exhibited the phenomenon of *surface-melting-induced faceting*, where the surface decomposes into "dry" and "melted" facets that coexist on the surface. In these experiments, the microscopic faceting was observed at a temperature of $T_m - 0.05$ K. In addition, the phenomenon of faceting has been observed on a macroscopic level with micrometer-sized Pb crystallites.^{18,19} A theoretical treatment based on a free-energy analysis predicted the faceting behavior in these experiments.²⁰

A recent MEIS study was performed on Pb(100) and its vicinal surfaces to clarify the high-temperature structural behavior of this surface, whose packing density is intermediate to that of Pb(110) and Pb(111).²¹ The experiments showed that a limited amount of disorder began to form on Pb(100) at $T > 500$ K, with the degree of disorder on the considered vicinal surfaces increasing with increasing miscut angle. A logarithmic increase of the disordered layer thickness was observed on Pb(100) up to $T_m - 2$ K, where the thickness saturated at ~ 1.3 monolayers, measured up to $T_m - 0.05$ K. For the vicinal surfaces, the maximum amount of disorder was ~ 1.9 and ~ 3.5 monolayers on the 5° and 10° miscuts, respectively. The saturation of disordered layer thickness is known as *incomplete surface melting*, and is in contrast to the divergence of the disordered layer thickness on Pb(110).

The mean-field theory used by Pluis, Frenkel, and van der Veen in their MEIS study of the orientation dependence of surface melting does not account for the non-divergence of the disordered layer thickness that occurs in incomplete surface melting.⁶ The role that the ordered substrate plays in the energetics of the disordered layer was recently addressed by Chernov and Mikheev.²² In their model, the solid substrate induces a periodic density modulation in the disordered layer. The modulation is in a direction parallel to the solid-disordered layer interface. In the so-called layering model, the free energy of the disordered layer has an oscillatory character with a period of $2\pi/k_1$, where k_1 is the wave number corresponding to the first maximum in the structure factor of the bulk liquid. (For Pb, $2\pi/k_1 = 2.86$ Å.²¹) As a consequence, it becomes energetically favorable at high temperatures for the surface to form a disordered layer, with a thickness being an integral multiple of the layering period. The thickness of the disordered layer that forms in incomplete melting does not diverge as T_m is approached. This is in contrast to the behavior of Pb(110) and Al(110), which experience complete surface melting. Experimental results on the surface disordering of Ge(111),²³ Pb(100),²¹ and the (100) face of the molecular crystal caprolactam²⁴ have been in qualitative agreement with the layering model.

Along with the experimental studies of surface melting, many molecular-dynamics (MD) studies of the structural behavior of surfaces have been conducted recently. With the development of many-body potentials, which realistically treat metallic bonding, MD studies are modeling surface-melting behavior with improved accuracy. Several fcc metals have been modeled including Al,²⁵⁻²⁷ Au,²⁸⁻³¹ Cu,³²⁻³⁷ Ni,^{38,39} and Pb.⁴⁰ The general trend suggests that the propensity of a surface to remain or-

dered up to T_m is influenced by surface orientation, in agreement with experimental studies. The studies that treated the open fcc(110) surfaces demonstrated the tendency of this surface to disorder below T_m .^{25,26,29,30,33-36,39} Some of these studies showed qualitative agreement with the logarithmic growth law that is evident from the experiments.^{29,30,33} The disorder on the (110) surface seems to be mediated by the formation of adatom-vacancy pairs.^{25,26,33-36,39} Indeed, the formation energy of a vacancy, E_v , obtained from simulations of various fcc crystalline faces, is a factor of 4 smaller for a (110) surface as compared with a (111) surface.²⁵ This demonstrates the tendency of the open surface to form defects. In the simulations that examined (111) surfaces, surface stability up to T_m was observed as well as superheating.^{28,30,36,37,40(b)}

Surface-melting-induced faceting has also been observed in molecular-dynamics simulations. Au(111) and vicinals^{31(a),31(b)} and vicinals of Pb(111) [Refs. 31(b) and 40(b)] have exhibited faceting. The study that examined Au(111) revealed that surface reconstruction plays an important role in faceting.^{31(b)} At low temperatures, Au(111) has a $(23 \times 3^{1/2})$ reconstructed unit cell. In the simulations, the (534) vicinal of Au(111) was observed to facet at $0.8T_m$ as a result of surface reconstruction. In contrast to this behavior, the same vicinal of Pb(111), a surface that does not exhibit reconstruction, was free of faceting at $0.8T_m$.^{31(b)}

The fcc(100) surface has been modeled less extensively.^{36,38} One study that treated the low-index faces of Cu showed disordering on Cu(100) just below T_m , behavior that is qualitatively intermediate to that observed on the (110) and (111) surfaces.³⁶ In this study, as well as in a MD study of the high-temperature structure of vicinal surfaces of Au(100),^{31(c)} stratification in the disordered layer was evident. Results of experiment and simulation suggest that the tendency of a surface to disorder below T_m depends on several factors. These include (i) the orientation-dependent surface-packing density (see Fig. 1), which influences the vibrational properties of surface atoms; (ii) the formation energy of surface defects such as adatoms and vacancies; and (iii) the ability of adatoms to diffuse on the surface.

In this study, we investigate the structural behavior of the three low-index faces of lead, using time-resolved reflection high-energy electron diffraction (RHEED). Our work is aimed at determining how the crystal surface influences the temporal dynamics of the melting process. Following a brief description of the experimental method

FIG. 1. The three low-index faces of a fcc metal displaying the orientation dependence of the surface packing density.

in Sec. II, we present in Sec. III results of our time-resolved structural studies of Pb(110), Pb(111), and Pb(100). The results are summarized in Sec. IV.

II. EXPERIMENT

The samples were cut from a single crystal rod aligned to within 0.75° of the appropriate orientation using Laue back reflection. The surfaces were mechanically polished prior to chemical etching in a solution of 80% glacial acetic acid and 20% hydrogen peroxide (30% in water). The samples were clipped to a resistively heated Mo stage. A thermocouple was placed between a retaining clip and the surface of the sample. The thermocouple was calibrated to the freezing and boiling points of water and to the melting point of Pb. The experiments were performed in an ultrahigh vacuum chamber with a base pressure in the low 10^{-10} range. The samples were cleaned before each experiment with cycles of Ar^+ bombardment followed by annealing. Surface cleanliness was checked using Auger-electron spectroscopy. An Auger spectrum of the clean Pb surface is shown in Fig. 2. Auger spectra were taken at an elevated temperature to ensure that no high-temperature surface impurity segregation was occurring.

The time-resolved RHEED technique will be described briefly here. It has been described in more detail elsewhere.⁴¹ A diagram of the experimental setup is shown in Fig. 3. A Nd:YAG (yttrium aluminum garnet) laser beam ($\lambda = 1.06 \mu\text{m}$, 200-ps pulsewidth) is split into two beams. The first is amplified, passes through an optical delay line, and strikes the surface of the sample at near-normal incidence. The second is frequency quadrupled and strikes the cathode of a photoactivated electron gun, producing electron pulses with a temporal width comparable to that of the fundamental beam. The electrons are collimated and accelerated to energies in the 15–20-keV range, and interact with the crystal in the glancing-incidence RHEED geometry, probing the first few atomic layers. Since the absorption depth of the laser into the

FIG. 3. Time-resolved reflection high-energy electron diffraction (RHEED). The laser pump and electron probe are synchronized on the surface of the sample. The electron beam is incident on the surface at an angle of 1° – 3° with an energy typically in the 15–20-keV range.

sample ($\sim 140 \text{ \AA}$ for Pb at $\lambda = 1.06 \mu\text{m}$) is much larger than the probed depth of the electrons (typically $< 5 \text{ \AA}$), we conclude that the probed layer is essentially isothermal. The optical delay line provides the means by which the laser heating pulse and the electron probe pulse are temporally synchronized on the surface. Since the heating pulse and electron pulse originate from the same source, the system is inherently free of the timing jitter that is typically associated with electronically synchronized experiments.

Static RHEED measurements are an important component of the experiment, as they yield equilibrium surface structural information and also serve as a means to convert the time-resolved diffraction intensity to a surface-temperature rise. In this mode of operation, a Hg lamp is used to excite the cathode of the photoactivated electron gun, producing a steady electron beam. The RHEED pattern from the surface is detected by a microchannel plate (MCP) proximately focused to a phosphor screen. The resulting image is lens coupled to a linear array detector for intensity analysis. For all of the experiments reported here, the intensity of the (10) diffraction streak was measured. Line scans were taken through the center of the streak.

III. RESULTS

A. Pb(110)

The first surface studied was Pb(110),⁴² which has been shown to readily disorder below T_m .³ As an initial step to characterize the structural dynamics of Pb(110), measurements of the RHEED streak intensity versus temperature were performed. The energy of the electrons was 18.2 keV, and the beam was incident along the $\langle 1\bar{1}2 \rangle$ azimuth at an angle of $\sim 2^\circ$, resulting in a probed depth of approximately two monolayers. Results of this measurement are given in Fig. 4, where the inset is a plot of the data on a semilogarithmic scale. The intensity is seen to decay exponentially from the lowest considered temperature 487 K up to a temperature of $\sim 520 \text{ K}$. This portion of the data is consistent with the Debye-Waller effect,

FIG. 2. Auger-electron spectrum of a clean Pb surface. The energy of the primary exciting electron beam is 3 keV. Pb peaks are labeled with the corresponding energies in electron volts. No surface impurities are detected.

FIG. 4. RHEED streak intensity from Pb(110) normalized to that at 487 K vs temperature. A curve fit is made to the data and is used with the heat-diffusion model to obtain the predicted time-resolved modulation of the RHEED streak intensity in Fig. 5. Inset: The data are plotted on a semilogarithmic scale. The line fit includes data points up to that which maximizes the linear correlation coefficient. Note the departure from exponential Debye-Waller behavior at ~ 520 K.

which predicts an exponential decay of elastic diffraction intensity with temperature. Above 520 K, the intensity is seen to deviate from Debye-Waller behavior. The initial deviation is most likely due to the anharmonic surface vibrations on Pb(110), which have been deduced from measurements of the surface expansion.⁴³ At higher temperatures, the deviation is attributed to surface disordering. Above $T \sim 540$ K, the RHEED signal decayed into the inelastically scattered background, leading us to conclude that the probed surface layer is disordered. We therefore identify $T_d \sim 540$ K as the disordering temperature of the probed layer. This behavior is qualitatively similar to that observed by Yang, Lu, and Wang on Pb(110) with high-resolution LEED.^{8(c)} In their experiment, the intensity of the (00) beam at the in-phase condition departed from Debye-Waller attenuation at ~ 520 K.

Next we performed time-resolved measurements on Pb(110). The RHEED streak intensity, normalized to that at the sample bias temperature of 487 K, was obtained for given delay times between the arrival of the laser heating pulse and the electron probe pulse. Results are given in Fig. 5, where the solid lines represent the conversion of the temperature obtained from a one-dimensional heat-diffusion model to a normalized diffraction intensity using the static calibration of Fig. 4. The heat-diffusion model is given by

$$C \frac{dT(z,t)}{dt} = K \frac{d^2T(z,t)}{dz^2} + I_p(1-R)\alpha \exp(-\alpha z)f(t), \quad (2)$$

where $T(z,t)$ is the temperature at a distance z normal to the surface ($z=0$), t is time, $C=1.58 \times 10^6$ J/m³K is the heat capacity per unit volume,⁴⁴ $K=32.2$ W/mK is the thermal conductivity,⁴⁴ $R=0.81$ is the reflectivity,⁴⁵ $\alpha=7.05 \times 10^7$ m⁻¹ is the absorption coefficient,⁴⁵ I_p is the peak laser intensity measured in W/cm², and $f(t)$ represents the temporal profile of the heating pulse, which is assumed to be Gaussian.

FIG. 5. Time-resolved RHEED streak intensity measurements on Pb(110). The pulse width of the laser is measured at full width at half maximum (FWHM). The corresponding surface temperature is obtained using the data of Fig. 4. (a) $I_p = 1.4 \times 10^7$ W/cm², 165 ps; (b) $I_p = 2.0 \times 10^7$ W/cm², 165 ps; (c) $I_p = 2.7 \times 10^7$ W/cm², 175 ps; and (d) $I_p = 3.6 \times 10^7$ W/cm², 170 ps. In (c) and (d) the normalized streak intensity is seen to vanish for some time, indicating that order is lost in the probed surface layer. The subsequent reappearance of the streak intensity indicates the reordering of the surface.

The error bars in Fig. 5 reflect the uncertainty in the RHEED streak intensity and are primarily due to MCP noise. Other sources of error in the time-resolved experiments include the spatial nonuniformity of the laser heating, which was measured to be $\pm 12\%$ across the width of the sample, and the stability of the laser. The long-term laser stability was monitored throughout the experiment, and was maintained constant to within 10%. All of the time-resolved measurements presented here are the result of the convolution of the electron probe pulse with the temporal temperature profile on the surface. These convolution effects are most prominent for the times near the normalized RHEED streak intensity minimum, where the rate of change of temperature with time is greatest. Including these effects in the analysis leads to a somewhat higher peak surface temperature than what is measured. The absolute timing between the electron probe pulse and the laser heating pulse was not determined experimentally. We set the temporal position of the model with respect to the experimental data by minimizing the mean-square difference between model and experimental data for the times between 1 and 2 ns in Figs. 5(a)–5(c), and between 1.3 and 3.3 ns for Fig. 5(d). In these time intervals, convolution effects are not expected to be significant.

We next discuss the time-resolved RHEED results of Pb(110) displayed in Fig. 5. In Figs. 5(a) and 5(b), I_p is low enough not to cause any surface disordering. The surface temperature was raised from 487 K to measured peak surface temperatures of ~ 515 and ~ 530 K in Figs. 5(a) and 5(b), respectively. These are in reasonable agreement with the values of 523 and 537 K predicted by the heat-diffusion model. In Figs. 5(c) and 5(d), the peak laser intensity was increased to facilitate surface heating to temperatures above the disordering temperature T_d . In these sets, the heat-diffusion model predicted peak sur-

face temperatures of 558 ($T_d + 18$ K) and 581 K ($T_d + 41$ K), respectively. In both cases, the normalized RHEED streak intensity is observed to vanish for some time, indicating that the probed surface layer is disordered. The time duration over which the diffraction intensity vanishes increases from ~ 200 ps for a peak predicted temperature of $T_d + 18$ K [Fig. 5(c)] to ~ 500 ps for a peak predicted temperature of $T_d + 41$ K [Fig. 5(d)]. We conclude that, with the heating rate of 10^{11} K/s available from the pulsed laser, surface disordering cannot be bypassed. Furthermore, from the time-resolved data we see that the temperature at which the surface disorders is not significantly altered from that measured statically.

Subsequent to disordering, the surface recrystallizes and cools as the heat is conducted to the bulk of the sample. This is evident from the recovery of the diffraction intensity. In Figs. 5(c) and 5(d), the experimentally measured surface temperature is in accord with the model in the times where the normalized RHEED streak intensity is nonvanishing, indicating agreement with the results from heat diffusion both prior and subsequent to surface disordering. This indicates that the nucleation and growth of the disordered layer, as well as the regrowth of crystalline order, occur on a time scale less than the 180-ps pulse width of the electron probe.

The conclusion that surface disordering is a reversible process is based on static experiments where the disordered layer thickness is shown to be a distinct function of temperature, a quality that distinguishes surface disordering from bulk melting. The reversibility of surface disordering has not been previously tested for extremely high heating and cooling rates. The time-resolved results in Fig. 5 that show the recovering elastic-diffraction intensity subsequent to surface disordering indicate that surface disordering is reversible even at extremely high heating and cooling rates.

The observations of the fast regrowth of crystalline order on the time scale of the present experiment are consistent with the time scales for atomic rearrangement on Pb(110) deduced from measurements of surface mobility using He scattering.¹¹ The results of this experiment were described well by the following expression for the temperature-dependent mobility of surface atoms on Pb(110):¹¹

$$D_s(T) = D_0 \exp(-Q_s/k_B T), \quad (3)$$

where $D_0 = 26 \text{ cm}^2/\text{s}$, the activation energy of diffusion is $Q_s = 0.65 \text{ eV}$, k_B is Boltzmann's constant, and T is temperature. The study concluded that for $T \geq 550$ K, the mobility of surface atoms exceeds that of the bulk liquid. The above expression yields a value of $\sim 0.23 \text{ \AA}^2/\text{ps}$ at $T_d \sim 540$ K, comparable to the mobility of liquid Pb close to T_m ($0.22 \text{ \AA}^2/\text{ps}$). At a temperature of T_d , over the 180-ps time scale of our electron probe, the disordered atoms diffuse over an area of $\sim 40 \text{ \AA}^2$. This area is sufficient to include all adjacent lattice sites that are potentially unoccupied. Therefore, over the time duration of the electron probe, atoms in the disordered layer have sufficient mobility to travel to adjacent lattice sites.

The time-resolved measurements on Pb(110) lead us to

conclude that for heating and cooling rates on the order of 10^{11} K/s, (i) surface disordering is not bypassed, therefore precluding the existence of a nucleation barrier to disordering for these conditions; (ii) the temperature at which the surface disorders is not altered significantly from that measured statically; (iii) the nucleation and growth of surface disorder occur on a time scale less than 180 ps even for relatively small departures above T_d ; and (iv) surface disordering is reversible upon cooling, even at the high rates achieved with pulsed laser heating.

B. Pb(111)

The next surface we studied was the close-packed, nonmelting Pb(111) surface, where experiments were performed to determine if the surface could be superheated.⁴⁶ The superheating of metals represents an experimental challenge and is not commonly observed. However, superheating of solids can be observed under some special conditions. Quartz and other solids that have highly viscous melts can readily be superheated.⁴⁷ This can be understood by considering the speed of propagation v of the solid-liquid interface.⁴⁸ In this treatment, v is proportional to D , the coefficient for self-diffusion in the liquid. By the Stokes-Einstein relation, D is inversely proportional to the viscosity η ; thus the velocity of the solid-liquid interface is proportional to $1/\eta$. Therefore, solids that melt into highly viscous liquids are associated with extremely slow motion of the solid-liquid interface, which allows the interior of the solid to be substantially superheated.⁴⁷ Typically, melts of metals have viscosities many orders of magnitude lower than that of the previously mentioned solids. Therefore, once the surface melts, the solid-liquid interface can propagate into the bulk with velocities up to the velocity of sound in the metal.⁴⁹ However, by bypassing the melting effects of the surface, modest superheating of metals has been achieved. Preferentially cooling the surface to prevent melting,⁵⁰ coating one solid with another of higher T_m ,⁵¹ and embedding precipitates in a host metal of higher T_m (Ref. 52) are some of the methods that have been used to superheat metals. An outstanding question has been whether a surface that does not experience surface melting can be superheated. Experiments performed on *free* surfaces showed that superheating of several degrees could be observed on small metal platelets with extensive close-packed, nonmelting surfaces.⁵³ The experiments presented here were performed to determine if the free Pb(111) surface could be superheated to a larger degree using fast laser heating.

As with Pb(110), we first measured the RHEED streak intensity versus temperature. The angle of incidence of the 18.2-keV electron beam was $\sim 2^\circ$, leading to a probed depth of two monolayers. The electron beam was incident along the $\langle 01\bar{1} \rangle$ azimuth. Results of this measurement are shown in Fig. 6, where the RHEED streak intensity is normalized to that at 407 K, and the inset is plotted on a semilogarithmic scale. It is apparent that the behavior of Pb(111) is qualitatively different from that of Pb(110) shown in Fig. 4, where deviation from Debye-Waller behavior occurred at $\sim T_m - 80$ K. With Pb(111),

FIG. 6. RHEED streak intensity of Pb(111), normalized to that at 407 K, vs sample temperature. An exponential curve fit has been made to the data. Inset: The data plotted on a semi-logarithmic scale showing Debye-Waller behavior up to $T_m - 15$ K.

the RHEED streak intensity is seen to decay exponentially in the considered temperature range extending to $T_m - 15$ K. This is consistent with the Debye-Waller effect, and agrees qualitatively with the results from MEIS, where Pb(111) was shown to remain ordered up to $T_m - 0.5$ K.¹⁴

In the next set of experiments, Pb(111) was subjected to laser pulses with $I_p \sim 3.3 \times 10^7$ W/cm², while the sample bias temperature T_{bias} was raised from 495 to 575 K. The RHEED streak intensity, normalized to that at T_{bias} , is shown in Fig. 7(a) for the time corresponding to the minimum of the diffraction intensity, t_0 . (The time t_0 is temporally close to the time corresponding to the peak of the surface-temperature rise. These times do not coincide due to the effects of convolution.) The diffraction intensity is observed to decrease linearly with T_{bias} . No sudden decrease in diffraction intensity is observed that would in-

dicate a phase transformation taking place on the surface. The diffraction intensity is converted to a temperature jump ΔT by utilizing the static RHEED measurement of Fig. 6. The result of this conversion is shown in Fig. 7(b), where for $T_{\text{bias}} \geq 530$ K, the peak surface temperature $T_{\text{bias}} + \Delta T$ exceeds T_m , and the surface is superheated. It is observed that ΔT increases linearly with T_{bias} . This reflects the changing optical and thermal properties of the sample in the temperature range considered. The change in surface reflectivity R with temperature is a significant factor in the increase of ΔT with T_{bias} since the absorption of laser energy at the surface is proportional to $1 - R$. The reflectivity of the surface at the heating laser wavelength was measured directly and found to decrease from 0.78 to 0.74 in the temperature range of Fig. 7. The results from a solution of the heat-diffusion model are shown in Fig. 7(b) as well. The larger ΔT predicted by the model is due to the above-mentioned convolution effects, which lead to a somewhat lower experimentally measured surface-temperature rise. In addition, the increase in ΔT with increasing T_{bias} was observed at delay times subsequent to t_0 ; these results are given in Fig. 8. For a given T_{bias} we observe a decrease in ΔT with increasing delay time. This reflects the cooling of the surface after the arrival of the heating laser pulse.

Further experiments were performed to determine the magnitude of superheating that could be sustained on Pb(111). The sample was biased at $T_{\text{bias}} = 586$ K ($T_m - 15$ K) and transiently heated with varying peak laser intensities. The RHEED streak intensity normalized to that at T_{bias} was obtained at given times throughout the laser-heating process. Such a set is shown in Fig. 9. This set was performed at the time t_0 . The inset of Fig. 9 is the data plotted on a semilogarithmic scale. Two regimes are evident: the first, where $I_p < 3.5 \times 10^7$ W/cm² shows an exponential decay of the diffraction intensity with I_p , consistent with Debye-Waller behavior; in the second regime, where $I_p \geq 3.5 \times 10^7$ W/cm², we observe a marked deviation from exponential behavior, indicating that melting is occurring on the surface.

FIG. 7. (a) Modulation of the normalized RHEED streak intensity for $I_p \sim 3.3 \times 10^7$ W/cm² and varying sample bias temperatures T_{bias} . This data set was obtained at the time corresponding to the temporal minimum of the normalized streak intensity, t_0 . (b) The streak intensity of (a) is converted to a peak surface-temperature rise ΔT , using the data of Fig. 6. Results from the heat-diffusion model are plotted as well. The higher ΔT predicted by the model is due to convolution effects that are most prominent at t_0 . For $T_{\text{bias}} \geq 530$ K, the peak surface temperature exceeds T_m .

FIG. 8. Surface-temperature rise vs T_{bias} for $I_p \sim 3.3 \times 10^7$ W/cm² performed at t_0 and subsequent delay times. The general trend of increasing ΔT with T_{bias} is attributed to the change in optical and thermal properties of the sample in the temperature range considered.

FIG. 9. RHEED streak intensity normalized to that at 586 K vs peak laser intensity. This data set was performed at t_0 . Inset: A plot of the data on a semilogarithmic scale showing deviation from Debye-Waller behavior at $I_p \sim 3.5 \times 10^7$ W/cm². The corresponding peak surface temperature is $\sim T_m + 120$ K.

We next estimate the temperature at which deviation from exponential, Debye-Waller behavior occurs, and identify this as the peak observed superheating temperature. To accomplish this, we consider diffraction intensity modulations for small I_p such that the corresponding temperature jumps ΔT lead to peak temperatures below T_m . In the Debye-Waller region, $\Delta T \propto I_p$; therefore, lower values of I_p can be used to make a correspondence between I_p and peak surface temperature. When this is done, we conclude that deviation from Debye-Waller behavior occurs at a temperature of ~ 720 K ($\sim T_m + 120$ K). Furthermore, the time-resolved diffraction data have a slope when plotted on a semilogarithmic scale that is equivalent to the slope from the static RHEED measurement of Fig. 6, within experimental error. This error can result from the fact that this experiment was performed at the time t_0 where convolution effects can be prominent. The exponential dependence of the normalized RHEED streak intensity up to $T_m + 120$ K indicates that the surface retains order above T_m , and behaves according to the Debye-Waller effect with mean-square vibrational amplitudes in excess of that at T_m .

The time-resolved measurements of the diffraction intensity versus I_p were carried out at other times relative to the time t_0 . Figure 10 shows measurements performed at $t_0 + 500$ ps and $t_0 + 4000$ ps. The insets are plotted on

a semilogarithmic scale. In both cases, for $I_p < 3.5 \times 10^7$ W/cm² we observe an exponential decrease in diffraction intensity with increasing I_p , as is evident from the linear behavior in the insets. A distinct break from exponential behavior occurs at $I_p \geq 3.5 \times 10^7$ W/cm², consistent with the value obtained at the time t_0 . We conclude that this deviation from Debye-Waller behavior is due to melting taking place on the surface. This deviation, at $I_p \geq 3.5 \times 10^7$ W/cm², is most likely not attributed to anharmonic vibrations due to the observed deviation from exponential behavior at $t_0 + 4000$ ps, an amount of time after t_0 where such vibrations should not be present due to the rapid decrease of the surface temperature rise.

Similar measurements were performed with the electron beam incident at an angle of $\sim 1^\circ$ with respect to the surface. This led to a probed depth of less than a monolayer. Plots of the RHEED streak intensity normalized to that at 586 K are shown in Fig. 11 for the times t_0 and $t_0 + 4000$ ps. A break from exponential Debye-Waller behavior is seen to occur at $I_p \sim 3\text{--}4 \times 10^7$ W/cm², consistent with what was observed for the previous data with an angle of incidence of $\sim 2^\circ$.

Time-resolved experiments examining the RHEED streak intensity throughout the heating process were carried out with $T_{\text{bias}} = 586$ K. The RHEED streak intensity, normalized to that at 586 K, was obtained at various delay times. Results for varying I_p are shown in Fig. 12. Figure 12(a) exhibits the qualities of classical heat diffusion: a rapid decrease in the normalized streak intensity followed by an increase as the heat is conducted to the bulk of the sample. The data set of Fig. 12(a) was normalized to sets taken at lower T_{bias} , which corresponded to peak temperatures below T_m . This comparison showed good agreement, indicating that the data of Fig. 12(a) are consistent with classical heat diffusion. Since the time-resolved RHEED streak intensity at $T_{\text{bias}} = 586$ K exhibited Debye-Waller behavior up to $I_p \sim 3.5 \times 10^7$ W/cm², the static RHEED calibration of Fig. 6 can be used to determine the peak ΔT of Fig. 12(a). When this is done, a peak surface temperature of $T_m + 110$ K is deduced.

In Figs. 12(b)–12(d), the surface was subjected to $I_p > 3.5 \times 10^7$ W/cm², the threshold for Debye-Waller behavior. We observe a clear deviation from classical heat diffusion in the tail after ~ 1.5 ns. The streak intensity, subsequent to an initial fast rise at t_0 , fails to recover

FIG. 10. RHEED streak intensity normalized to that at 586 K vs peak laser intensity. These sets were performed at times of $t_0 + 500$ ps and $t_0 + 4000$ ps. The insets are plotted on a semilogarithmic scale, and show the break from Debye-Waller behavior at $I_p \sim 3\text{--}4 \times 10^7$ W/cm², consistent with what was observed at the time t_0 .

FIG. 11. RHEED streak intensity normalized to that at 586 K vs peak laser intensity for an electron-beam angle of incidence of $\sim 1^\circ$ at the times t_0 and $t_0 + 4000$ ps. Insets show the departure from Debye-Waller behavior at $I_p \sim 3\text{--}4 \times 10^7$ W/cm 2 .

to what is expected from heat diffusion. The behavior at times after t_0 is also reflected in the data of Fig. 10. We attribute this to melting on part of the surface. In Figs. 12(b)–12(d), the value of the normalized streak intensity at times after t_0 depends on the ratio of the molten portion of the probed surface area to that which remains solid. This in turn is influenced by the spatial intensity profile of the laser pulse on the sample surface. In these experiments, the laser nonuniformity was measured to be $\pm 18\%$ across the width of the sample. This was accomplished by measuring the laser intensity passing through a small pinhole that was scanned through the beam. This measurement, however, does not preclude the existence of laser nonuniformities on a micrometer scale. Laser-intensity variations on this scale could influence the dynamics of the melting process.

We define the time τ to be the time interval between t_0 and the time at which the diffraction intensity deviates from behavior consistent with classical heat diffusion. To determine τ , a nonmelting superheated set was normalized to a given melting set and subtracted from it. The difference that resulted was fitted with a polynomial that

was differentiated to observe the break from nonmelting behavior. A plot of τ versus peak laser intensity is given in Fig. 13 for data sets biased at 586 K. The time τ is observed to decrease from 1200 to < 300 ps for $I_p \sim 3.8 \times 10^7$ W/cm 2 to $I_p \sim 6.0 \times 10^7$ W/cm 2 , respectively.

From the experiments on Pb(111), we conclude that this surface, which exhibits no surface melting, sustains superheating to $\sim T_m + 120$ K. This is evident from the exponential Debye-Waller behavior of the RHEED streak intensity in this temperature range. In the superheating regime, the excess surface temperature is manifested as lattice mean-square vibrational amplitudes exceeding that at T_m . Melting is apparently bypassed by the 10^{11} -K/s heating and cooling rates available with pulsed laser heating. At incident peak laser intensities greater than $\sim 3.5 \times 10^7$ W/cm 2 , the surface melts, as is evident from the pronounced deviation from Debye-Waller behavior. The larger heating rates available with lasers of shorter pulse width could conceivably lead to a larger degree of superheating.

As an interesting postscript to the experiments on Pb(111), recent molecular-dynamics simulations were performed by Häkkinen and Landman examining the dynamics of melting and superheating of Cu surfaces.³⁷ Motivated by the time-resolved laser heating experiments, they constructed a model that incorporated ener-

FIG. 12. Time-resolved normalized RHEED streak intensity of Pb(111) irradiated with laser pulses of varying peak intensity. Set (a) is consistent with classical heat diffusion and corresponds to a peak surface temperature of $T_m + 110$ K. In sets (b)–(d), where $I_p \geq 3.5 \times 10^7$ W/cm 2 , the surface begins to melt, as is evident from the pronounced deviation from classical heat diffusion.

FIG. 13. The time interval τ , from t_0 to the time at which deviation from classical heat diffusion occurs, is extracted from data sets as in Figs. 12(b) and 12(c). The time τ is seen to decrease with increasing peak laser intensity.

FIG. 14. RHEED streak intensity from Pb(100) normalized to that at 377 K vs temperature. The inset shows the data plotted on a semilogarithmic scale. The solid lines are polynomial fits to the data. The streak intensity is observed to deviate from Debye-Waller behavior for $T \geq 475$ K.

gy transfer from the electronic system to the lattice. The subsequent lattice dynamics were modeled with the many-body embedded-atom potential. They observed rapid and reversible disordering of the Cu(110) surface, in analogy to Pb(110). In contrast to this, Cu(111) was shown to sustain superheating of 40 K. Further simulations focused on the effects of defects in the superheating process.³⁷ Defects such as steps and vacancies are expected to be present on any metal surface in experimental situations. The simulations showed that even highly defect-ed Cu(111) surfaces, with up to a 10% initial surface vacancy concentration, sustained substantial superheating. A settling mechanism involving adatoms was observed in the annealing process that acted to fill existing vacancies and restore crystalline order. Processes such as this may be involved in the time-resolved experiments on Pb(111), where a large degree of superheating was sustained.

C. Pb(100)

The final surface considered was Pb(100),⁵⁴ which has been shown to experience incomplete surface melting. Using MEIS, it was observed that the disordered layer that forms on the surface does not nucleate further melting up to a temperature of $T_m - 0.05$ K.²¹ The aim of our time-resolved experiments on Pb(100) was to determine if the disordered layer that forms on the surface is stable at temperatures above T_m . The first experiment on Pb(100) measured the temperature dependence of the RHEED streak intensity. The 15-keV electron beam was incident along the $\langle 001 \rangle$ azimuth at an angle of 3° , resulting in a probed depth of ~ 5 Å. This corresponds to ~ 3 monolayers. A plot of the RHEED streak intensity normalized to that at 377 K is shown in Fig. 14. The inset is a plot of the data on a semilogarithmic scale. A nonexponential decrease in diffraction intensity with temperature is observed starting at a temperature of ~ 475 K. The data are qualitatively similar to that obtained on Pb(100) by Yang *et al.* using high-resolution LEED.⁵⁵ The deviation from Debye-Waller behavior may be related initially to the surface expansion that they observed between 300 and 470 K. In this temperature range, the surface undergoes an expansion exceeding that of the

bulk by a factor of 7. This surface expansion is directly related to the anharmonic nature of the surface interatomic potential. In addition, deviation from Debye-Waller behavior can be attributed to the abrupt increase in vacancy concentration observed beginning at 510 K.⁵⁵

To determine the peak temperature rise induced on the Pb(100) surface by the heating laser pulse, time-resolved measurements were performed at the time t_0 . For these experiments, the sample was biased at temperatures of 450 and 533 K. The RHEED streak intensity, normalized to that at 450 K, is shown in Fig. 15 for various peak laser intensities I_p . The normalized streak intensity is converted to a temperature rise ΔT , using the calibration of Fig. 14. The result of this conversion is shown in the inset of Fig. 15, where ΔT is plotted versus I_p . The temperature rise is observed to be directly proportional to I_p , which is consistent with classical heat diffusion. The maximum peak temperature in all of these sets is below T_m . These data do not account for the effect of convolution.

FIG. 15. RHEED streak intensity vs peak laser intensity on Pb(100) at the time t_0 . The sample was biased at 450 K. Inset: Peak surface temperature rise ΔT vs I_p . The inset is a result of the conversion of the streak intensity modulation to a ΔT using the data of Fig. 14. These data are used to determine ΔT for RHEED measurements with T_{bias} closer to T_m .

In the next set of experiments the RHEED streak intensity, normalized to that at a given T_{bias} , is obtained for various I_p . In these experiments, performed at t_0 , T_{bias} is raised close to T_m . Results are shown in Fig. 16, where the set in Fig. 16(d) is biased just 11 K below T_m . At sufficiently high I_p , the normalized streak intensity is observed to vanish, indicating that order has been lost in the probed surface layer. The value of I_p necessary to disorder the probed surface layer decreases from $\sim 4.3 \times 10^7$ W/cm² for $T_{\text{bias}} = 533$ K to $\sim 1.8 \times 10^7$ W/cm² for $T_{\text{bias}} = 590$ K. The data of Fig. 15 are used to determine the peak surface temperature at which the normalized RHEED streak intensity vanishes. In each of the sets of Fig. 16, the lowest I_p leading to a vanishing RHEED streak intensity is converted to a temperature rise using Fig. 15. From this conversion, we see that the peak surface temperature $T_{\text{bias}} + \Delta T$, when order is lost in the probed surface layer, is $\sim 615 \pm 20$ K. The error accounts for (i) the spread of the static RHEED data; (ii) the spread of the temperature-rise data of Fig. 15; and (iii) the nonuniformity of laser heating, which was measured to be $\pm 25\%$ over the entire width of the sample. Factors not accounted for in this peak temperature include convolution effects and the changes in the thermal and optical properties of the sample occurring over the considered temperature range. These effects lead to a somewhat greater peak surface temperature than what is experimentally observed.

The temporal behavior of the heating and disordering process on Pb(100) was examined using time-resolved RHEED. In Fig. 17, results are given for varying sample bias temperatures and incident peak laser intensities. In Figs. 17(a) and 17(b), the incident peak laser intensity was not sufficient to cause disorder in the probed layer. This is evident by the nonvanishing diffraction intensities in these sets. In Fig. 17(c), sufficient laser intensity was provided to disorder the probed surface layer. The disordering is evident from the vanishing streak intensity at time

FIG. 17. Time-resolved normalized RHEED streak intensity on Pb(100) at different bias temperatures, subjected to varying peak laser intensities. (a) $T_{\text{bias}} = 321$ K, $I_p = 4.4 \times 10^7$ W/cm²; (b) $T_{\text{bias}} = 570$ K, $I_p = 2.3 \times 10^7$ W/cm²; (c) $T_{\text{bias}} = 570$ K, $I_p = 3.4 \times 10^7$ W/cm²; and (d) $T_{\text{bias}} = 570$ K, $I_p = 5.1 \times 10^7$ W/cm².

~ 1 ns. Subsequent to disordering, the surface recrystallizes and cools, as is seen from the increasing streak intensity at later times. Finally, in Fig. 17(d), the streak intensity fails to recover for times ≥ 4 ns after the initial disordering, which is an indication of melting on the surface. In these experiments, no surface damage was visible upon recrystallization.

From our experiments on Pb(100) we conclude that residual order is present on Pb(100) at a peak surface temperature of 615 ± 20 K. Considering the previously mentioned convolution effects, it is likely that residual order is present above T_m . At this temperature the surface is most likely proliferated with defects such as vacancies.⁵⁵ The degree of superheating would undoubtedly be lowered by the presence of vacancies. Compared with Pb(111), where superheating to ~ 720 K was observed,⁴⁶ Pb(100) shows evidence of residual order at a much lower surface temperature. Our experiments show that the disordered layer that forms near T_m is stable in a narrow temperature range above T_m . Evidently, in this temperature range a second layering transition is not energetically favorable. Above the observed peak surface temperature, further disordering occurs and the residual order in the probed layer vanishes. At this temperature, a second layer transition may take place increasing the disordered layer thickness to $4\pi/k_1 \sim 5.7$ Å, exceeding the 5 Å probed by our electron beam.

IV. SUMMARY

From our experimental results on the low-index faces of Pb, we conclude that the time-resolved surface structural behavior of Pb has a pronounced orientation dependence. The open Pb(110) surface was seen to disorder rapidly and reversibly with the 10^{11} -K/s heating and cooling rates available from pulsed laser heating. It is likely that higher index planes, which were shown to exhibit surface disordering in the case of Pb,¹⁴ would exhibit

FIG. 16. Normalized RHEED streak intensity vs peak laser intensity for T_{bias} successively closer to T_m . The streak intensity vanishes for I_p above a certain threshold depending on T_{bias} . This threshold is used along with the data of Fig. 15 to determine the temperature at which order is lost in the probed layer.

it rapid disordering analogous to that observed on Pb(110). In contrast, the close-packed Pb(111) surface, which was shown not to experience surface melting,¹⁴ exhibited Debye-Waller behavior upon laser heating up to $\sim T_m + 120$ K. We are not aware of any larger superheating of a free metal surface; however, greater superheating may be possible with larger heating rates. In addition, the nonmelting (0001) face of Bi was shown to exhibit substantial superheating using time-resolved RHEED.⁵⁶ The last surface we studied was Pb(100), a surface that exhibits incomplete surface melting. Pb(100) showed residual order up to $\sim 615 \pm 20$ K, a result that differs from that obtained on Pb(111) in two respects. First, the diffraction intensity from Pb(100) deviated from Debye-Waller behavior at $T \sim 475$ K, unlike Pb(111), which upon laser heating showed Debye-Waller behavior up to $T \sim 720$ K.⁴⁶ It is likely that Pb(100) develops a

high concentration of surface defects at temperatures above 500 K.⁵⁵ Second, the temperature at which order is completely lost on Pb(100) is much lower than that of Pb(111). The disordered layer that forms on Pb(100) at elevated temperatures precludes substantial excursions above T_m . However, our time-resolved experiments show that residual order on Pb(100) is preserved for small excursions above T_m . This implies that there is a barrier for the growth of the disordered layer thickness on Pb(100) at temperatures above T_m .

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Time-resolved reflection high-energy electron diffraction is used to study the structural behavior of Pb(100) subjected to 200 ps laser pulses. Analysis of the electron diffraction intensity indicates that residual order is present on the surface at a temperature of 615 ± 20 K, where the bulk melting temperature of Pb is 600.7 K. This implies that the disordered film that forms on Pb(100) is stable up to the bulk melting temperature and above.

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Since the initial work of Frenken and co-workers on Pb(110) [1], there has been a great deal of work performed to characterize the phenomenon of surface melting [2]. Surface melting is the formation of a disordered "quasiliquid" layer with thickness on the order of several atomic layers at temperatures below the bulk melting point T_m . Relatively few structural studies have been performed on fcc(100) surfaces near T_m [3-7]. A recent study on Pb(100) and vicinal surfaces using medium energy ion scattering (MEIS) showed that a limited amount of disorder began to form on Pb(100) at temperatures above 500 K, where T_m for Pb is 600.7 K [4]. The disordered layer thickness on Pb(100) was observed to increase logarithmically up to 2-3 K below T_m and then saturate at 1.3 monolayers, measured up to $T_m - 0.05$ K. The maximum amount of disorder on the vicinal surfaces increased with miscut angle from 1.9 to 3.5 monolayers on the 5° and 10° miscut surfaces, respectively. This is in contrast to the divergence of the disordered layer thickness of Pb(110) as T_m is approached. This behavior, where the disordered layer thickness is finite as T_m is approached, is known as incomplete surface melting. Incomplete surface melting cannot be explained by the mean-field theory used by Pluis, Frenkel, and van der Veen in their MEIS study of Pb [3(b)]. A recent model has been developed that includes the effect of the substrate on the disordered layer [8]. In this model, the ordered substrate induces a periodic density modulation in the disordered layer in a direction parallel to the solid-disordered layer interface. This modulation makes it energetically favorable for the surface to form disordered films with the thickness being an integral multiple of $2\pi/k_1$, where k_1 is the wave number corresponding to the first maximum of the structure factor of the bulk liquid. For Pb, $2\pi/k_1$ is approximately 2.86 Å [4]. The disordered layer that forms is stable up to T_m and does not act as a nucleus for further melting. The so-called layering model has proven successful in describing the disordering of Ge(111) [9], Pb(100) [4], and the (100) face of caprolactam [10].

Further experiments on Pb(100) with high-resolution low-energy electron diffraction (HRLEED) have shown a weak disordering at ~ 570 K [5]. This disordering is pre-

ceded by an anomalous surface expansion at $T \leq 480$ K and an abrupt generation of surface vacancies beginning at ~ 510 K. An anomalous surface expansion was also observed on Ni(001) using LEED [6]. An x-ray photoelectron diffraction study on Pb(100) demonstrated evidence for logarithmic growth of the disordered layer beginning at 585 ± 5 K and up to the highest temperature studied, $T_m - 2$ K [7].

Recently, there have been several molecular dynamics (MD) simulations modeling surface melting of fcc(100) surfaces [11-13]. The simulations by Häkkinen and Manninen examine the (110), (100), and (111) surfaces of copper, from 0 K to T_m [11]. This study, which uses effective-medium theory, allows for the direct comparison of the three low-index faces using the same MD potential and identical cell sizes. The results show pronounced disordering of Cu(110), weak disordering of Cu(100) just below T_m , and superheating of Cu(111). In addition, the high-temperature behavior of vicinal surfaces of Au(100) was studied using the many-body "glue" potential [12]. In both the studies of Cu(100) and the vicinal surfaces of Au(100), structural modulation in the disordered film was evident.

In the present Letter, we describe an experimental study of the high temperature structural behavior of Pb(100) using time-resolved reflection high-energy electron diffraction (RHEED). This technique, which has been described in more detail elsewhere [14], involves splitting the fundamental beam of a Nd:YAG laser ($\lambda = 1.06 \mu\text{m}$, 200 ps) into two parts. The first beam is amplified and interacts with the surface at near normal incidence, providing a pulsed heating source. The second beam is frequency quadrupled to the ultraviolet ($\lambda = 0.266 \mu\text{m}$) and is incident on the cathode of a photoactivated electron gun, producing electron pulses with a temporal width comparable to that of the fundamental laser pulse. The resulting electron beam is incident on the surface of the sample in the glancing angle RHEED geometry and probes the first few atomic layers. The energy of the electrons in the experiments reported here is 15 keV. The heating laser beam and the electron probe are temporally synchronized on the surface of the sample. An optical delay line is used to set different delay times

between the heating laser pulse and the electron probe pulse. This allows RHEED patterns to be obtained throughout the pulsed heating process.

Our previous time-resolved RHEED experiments were performed on Pb(110) [15] and Pb(111) [16]. Pb(110) was seen to reversibly disorder below T_m , while Pb(111) sustained superheating to $\sim T_m + 120$ K. These experiments demonstrated the contrasting melting behavior of open and close-packed surfaces. Here we report on a study of the behavior of Pb(100), a surface that exhibits incomplete surface melting. The time-resolved RHEED measurements on Pb(100) that are presented here show that the residual surface order is lost at a temperature of 615 ± 20 K. The observation of residual order implies that the disordered layer that forms on Pb(100) does not nucleate further melting as T_m is approached and is stable at temperatures above T_m .

The Pb(100) sample was cut from a single-crystal rod aligned within 0.75° of the (100) orientation using Laue back reflection. The preparation of the surface is described elsewhere [16]. The experiments were performed in an ultrahigh vacuum chamber with a base pressure in the low 10^{-10} range. The sample was cleaned before each experiment with cycles of Ar^+ bombardment followed by annealing. Surface cleanliness was checked using Auger electron spectroscopy. Auger spectra were taken at elevated temperatures to insure that no high-temperature surface impurity segregation was occurring.

As an initial step in characterizing the structural behavior of Pb(100), measurements of the RHEED streak intensity were performed as a function of the surface temperature. A Hg arc lamp was used to excite the cathode of the photoactivated electron gun, producing a continuous electron beam. The 15 keV electron beam was incident along the (001) azimuth at an angle of 3° , resulting in a probed depth of ~ 5 Å, corresponding to ~ 3 monolayers. The diffracted electrons of the RHEED pattern were amplified by a microchannel plate which is proximity focused to a phosphor screen. The resulting RHEED pattern was lens imaged onto a linear-array camera for quantitative intensity analysis. In all of the experiments reported here the intensity of the (10) RHEED streak was examined. Line scans were taken through the center of the streak. A plot of the RHEED streak intensity normalized to that at 377 K is shown in Fig. 1. The inset is a plot of the data on a semilogarithmic scale. A qualitative difference is seen between these data and that obtained previously for Pb(111), which exhibited an exponential decrease in the diffraction intensity with temperature consistent with the Debye-Waller effect [16]. For Pb(100) we observe a nonexponential decrease in diffraction intensity from a temperature of ~ 475 K, over much of the temperature range in Fig. 1. The data are qualitatively very similar to that of Yang *et al.* obtained on Pb(100) using HRLEED [5]. This deviation from Debye-Waller behavior may initially be related to the anomalous surface expansion that they observed to

FIG. 1. RHEED streak intensity normalized to that at 377 K vs sample temperature. The orientation of the sample was the same as that for the time-resolved experiments. The inset is the data plotted on a semilogarithmic scale. In both plots, the solid line is a polynomial fit to the data. This RHEED intensity data are used to convert the normalized streak intensity of the time-resolved experiments to a surface temperature rise.

occur below 480 K in the HRLEED study, in addition to the abrupt increase in vacancy concentration that they observed beginning at 510 K.

In order to determine the temperature rise induced on the Pb(100) surface by the heating laser pulse, time-resolved measurements were performed at the experimentally determined time of the minimum of the RHEED streak intensity, t_0 , which is temporally close to the time of maximum surface-temperature rise. These two times do not coincide because of convolution effects that occur as a result of the finite pulse width of the electron probe. Such effects are most prominent near the temporal peak of the surface temperature profile where the rate of change of temperature with time is greatest. By examining solutions of a heat diffusion model for our experimental conditions and assuming an electron pulse width comparable to that of the fundamental laser pulse, we conclude that these effects can lower the experimentally measured peak surface temperature rise by approximately 20%. Measurements of the electron pulse width and space-charge broadening effects were previously performed on the photoactivated electron gun used in this study [14(b)]. For the initial experiments, the sample was biased at temperatures of 450 and 533 K, well below T_m . The angle of incidence of the electron beam on the surface and the azimuthal orientation of the sample were kept constant for all the RHEED streak intensity measurements. The RHEED streak intensity, normalized to that at 450 K is shown in Fig. 2 for various peak laser intensities. To convert the normalized streak intensity to a temperature rise, ΔT , the calibration of Fig. 1 is utilized. The inset of Fig. 2, where ΔT is plotted versus peak laser intensity, is the result of this conversion. A linear rela-

FIG. 2. Time-resolved RHEED streak intensity vs peak laser intensity on Pb(100) irradiated with Nd:YAG ($\lambda = 1.06 \mu\text{m}$, 200 ps) laser pulses. The sample was biased at a temperature of 450 K and the RHEED pattern was observed at the time of its intensity minimum. The inset is a plot of surface temperature rise, ΔT , vs peak laser intensity that is the result of converting the normalized streak intensity data to a ΔT using the calibration of Fig. 1. This is used to determine the surface temperature rise for data sets where the sample bias temperature is closer to T_m . The effect of convolution is not accounted for in these data.

tion between ΔT and peak laser intensity is observed which is consistent with classical heat diffusion. The maximum peak temperature in all of these sets is less than T_m . These sets give ΔT for a given peak laser intensity.

We next discuss experiments in which the RHEED streak intensity, normalized to that at a given bias temperature T_{bias} , was obtained for various peak laser intensities. Results are shown in Fig. 3 for four experiments representing bias temperatures successively closer to T_m , where the set in Fig. 3(d) is biased just 11 K below T_m . These sets were obtained at the time t_0 . In each of the sets, the normalized streak intensity is observed to vanish at sufficiently high laser intensities, indicating that order has been lost in the probed surface layer. It is observed that as T_{bias} is raised, the peak laser intensity necessary to disorder the probed surface layers decreases from $\sim 4.3 \times 10^7 \text{ W/cm}^2$ for $T_{\text{bias}} = 533 \text{ K}$ to $\sim 1.8 \times 10^7 \text{ W/cm}^2$ for $T_{\text{bias}} = 590 \text{ K}$. The peak surface temperature when the normalized RHEED streak intensity vanishes is obtained using the data of Fig. 2, which yields the surface temperature rise, ΔT , for a given peak laser intensity. In each of the sets of Fig. 3, the lowest peak laser intensity which corresponds to a vanishing RHEED streak intensity is converted to a temperature rise using the calibration of Fig. 2. When this is accomplished, we see that the peak surface temperature, $T_{\text{bias}} + \Delta T$, when order is lost in the probed layer is 607, 621, 611, and 619 K for Figs. 3(a)–3(d), respectively. The average peak temperature at which order is lost is $\sim 615 \pm 20 \text{ K}$. The error bar accounts for (i) the spread of the static RHEED data, (ii)

FIG. 3. RHEED streak intensity normalized to that at the sample bias temperature vs peak laser intensity. The streak intensity is observed to vanish for peak laser intensities above a certain threshold. This threshold is used along with the data of Fig. 2 to determine the surface temperature at which order is lost in the probed layers.

the spread of the temperature-rise data of Fig. 2, and (iii) the nonuniformity of laser heating, which is measured to be $\pm 25\%$ over the entire width of the sample. Our reported peak temperature does not account for convolution effects, which were mentioned earlier, and assumes that the thermal and optical properties of the sample do not change significantly over the considered temperature range. Including these effects in the analysis would lead to a somewhat greater peak surface temperature. In addition, since to a first approximation ΔT is proportional to peak laser intensity, the data of Fig. 3 suggest that the loss of residual order is not abrupt.

Further experiments were performed to examine the temporal behavior of the heating and disordering process. In these experiments, the normalized RHEED streak intensities were obtained at various delay times between the arrival of the heating laser pulse and the electron probe pulse at the surface of the sample. Results for varying sample bias temperatures and incident peak laser intensities are shown in Fig. 4. In Figs. 4(a) and 4(b), the sample was subjected to laser intensities sufficiently only to heat the surface but not cause disorder. These sets exhibit qualities consistent with laser heating with heating and cooling rates on the order of 10^{11} K/s : a rapid decrease in the streak intensity, as the surface temperature rises with the arrival of the heating laser pulse, followed by a rapid increase in streak intensity as the heat is conducted to the bulk of the crystal. In Fig. 4(c), sufficient laser intensity was provided to disorder the probed surface layer as is evident by the vanishing streak intensity near 1 ns. After disordering, the surface recrystallizes and cools as is seen from the increasing streak intensity for later times. Finally, in Fig. 4(d), the streak intensity remains suppressed for times $\geq 4 \text{ ns}$ after the initial disordering.

FIG. 4. Time-resolved normalized RHEED streak intensity on Pb(100) with different bias temperatures, T_{bias} , and peak laser intensities, I_p . (a) $T_{\text{bias}} = 321$ K, $I_p = 4.4 \times 10^7$ W/cm². (b) $T_{\text{bias}} = 570$ K, $I_p = 2.3 \times 10^7$ W/cm². (c) $T_{\text{bias}} = 570$ K, $I_p = 3.4 \times 10^7$ W/cm². (d) $T_{\text{bias}} = 570$ K, $I_p = 5.1 \times 10^7$ W/cm².

This is an indication of melting on the surface. In all of the experiments reported here, no surface damage was observed.

In conclusion, we have observed residual order to be present on Pb(100) at a peak surface temperature of 615 ± 20 K. Considering that the previously mentioned convolution effects lower the experimentally measured peak surface temperature, it is likely that residual order is present above T_m . At this high temperature, however, the surface most likely contains a high density of defects such as vacancies [5]. The presence of vacancies would be expected to lower the degree of superheating by providing nucleation sites for melting. Indeed, compared with the results obtained on Pb(111), where superheating to ~ 720 K was observed [16], the results on Pb(100) show evidence of residual order at a significantly lower surface temperature. Finally, these experiments show that there exists a barrier for the growth of the disordered layer thickness on Pb(100) at temperatures above T_m . At temperatures greater than our observed peak temperature, a second layering transition may occur that would result in a disordered layer thickness of $4\pi/k_1 \sim 5.7$ Å, a depth that exceeds the 5 Å probed by our electron beam.

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Superheating of Bi(0001)

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Superheating of Bi(0001) by about 90 K above the bulk melting temperature is observed using time-resolved reflection high-energy electron diffraction with ~ 200 -ps time resolution. Larger temperature excursions above the bulk melting temperature result in melting accompanied by irreversible laser damage to the surface. The rhombohedral structure of Bi leads to very different behavior of material parameters upon melting as compared with fcc metals. Therefore, our observation of the superheating of Bi(0001), together with the previously observed superheating of Pb(111), suggests the generality of the superheating phenomenon.

Undercooling of liquids is often observed; however, superheating of metals has only been observed under special conditions. The difficulty in superheating metals is attributed to the presence of nucleation sites for melting, such as crystal defects and free surfaces. For many metal surfaces, the formation of a surface-disordered layer below the bulk melting temperature provides a barrier to superheating. The role of the surface in the melting process can be suppressed by working with small crystallites with predominantly close-packed surfaces that are less susceptible to disorder. Small crystallites of exposed Pb(111) facets^{1,2} (0.01–0.5 μm in diameter) and Bi(0001) facets^{3,4} (0.07–0.15 μm in diameter) have been superheated by 2–3 and 7–10 K, respectively. Superheating has also been observed in cases where the nucleation of the melt at the free surface is suppressed. Superheating of Ag by at least 7.5 K has been observed for 120- to 160- μm -diam spheres of Ag coated uniformly with an 11- μm layer of Au.⁵ In other experiments, superheating by ~ 2 K was achieved by preferentially cooling the surface of Sn and Cu rods while internally heating the bulk.^{6,7} Superheating by tens to hundreds of degrees has been reported for metals and noble gases implanted in substrates with higher melting temperatures.^{8,9} More recently, superheating of the Pb(111) surface by ~ 120 K above the bulk melting temperature of 601 K has been observed using ~ 200 -ps time-resolved reflection high-energy electron diffraction (RHEED). In this case, melting of the free surface is bypassed by rapid heating and cooling of the surface with a pulsed laser.¹⁰ A similar time-resolved study on Pb(110) showed that surface melting could not be bypassed with laser heating at the heating and cooling rates used in the experiment.¹¹

Here we report on a superheating study of Bi(0001) us-

ing time-resolved RHEED with ~ 200 -ps time resolution. Bi was chosen because of its relatively low melting temperature ($T_m = 544$ K) and low vapor pressure ($\sim 2 \times 10^{-10}$ Torr) at the melting point, and the fact that previous slow-heating experiments have demonstrated superheating of Bi crystallites. Some of these Bi crystallites melted after a time delay of about 30 min when held at T_m and after about 10 min when held at $T_m + 5$ K.^{3,4} Using time-resolved RHEED with ~ 200 -ps resolution we are able to achieve heating rates of $\sim 10^{11}$ K/s, approximately 13 orders of magnitude larger than that used in the Bi crystallite experiments. In addition, because of the open pseudocubic crystal structure of Bi, liquid Bi is more dense than the solid, and it has been suggested that such unusual structural differences between a crystal and its melt may provide a barrier for rapid melting.¹²

We have observed superheating of Bi(0001) by about 90 K. Larger temperature excursions above T_m result in melting and irreversible laser damage to the surface. Scanning electron microscopy (SEM) images show the presence of a laser-induced periodic surface structure in the damaged region of the sample, the spacing of which is approximately the heating laser wavelength ($\lambda = 1.06$ μm). Significant and irreversible reduction in surface quality is observed, both as a decrease in RHEED streak intensity and as a visible dulling of the surface. We measure a decrease in the reflectivity of the surface at the laser wavelength as a result of the laser damage.

In our experiment a Nd:YAG laser pulse (where YAG denotes yttrium aluminum garnet) is split into two beams. The fundamental wavelength ($\lambda = 1.06$ μm) is amplified and used for heating of the surface at near-normal incidence while a small portion of the beam is frequency quadrupled ($\lambda = 0.266$ μm) and is incident on the

cathode of a photoactivated electron gun, generating a pulsed electron beam. The repetition rate of the laser is about 15 Hz and its pulse width is ~ 200 -ps full width at half maximum (FWHM). The electron energy is 15.0 keV and the width of the electron pulse is comparable to that of the fundamental laser pulse. The electron pulses interact with the sample at glancing incidence to generate the RHEED pattern. By optically delaying the heating laser pulse relative to the electron pulse the time evolution of surface heating can be studied. The diameter of the heating laser beam is ~ 1 cm, measured at FWHM, which is large enough to illuminate the entire sample. The RHEED pattern is lens coupled from a microchannel plate/phosphor-screen assembly to a linear-array detector. A RHEED streak is then monitored by a line scan perpendicular to the streak and through its peak intensity. A mechanical shutter is placed in the path of the heating laser beam allowing the averaging of line scans of heated and unheated streaks in separate memories. Shot-to-shot laser fluctuations as well as long-term fluctuations in the intensity of the electron beam are compensated for by normalizing the streak intensity associated with the heated surface to that associated with the unheated surface $I/I(T_{\text{bias}})$ and averaging over ~ 800 laser shots for each scan. Long-term heating laser fluctuations are controlled to within $\pm 10\%$. The spatial nonuniformity of the beam across the sample is determined to be $\pm 15\%$ using a two-dimensional array detector. Our time-resolved temperature measurements are a result of the convolution of the temporal profile of the electron pulse with that of the surface temperature. The convolution effects are more significant for times where the rate of change of temperature with time is largest. This effect is not accounted for in our analysis, and, as a result, the peak surface temperature induced by the laser is actually somewhat larger than what is reported here. The experimental technique is further described in Ref. 13.

Two Bi(0001) samples were used for these experiments. The single crystals were grown from bismuth of 99.999% purity. The samples were cut to within $\pm 1^\circ$ of the (0001) surface. The surface was then mechanically lapped to a $1\text{-}\mu\text{m}$ finish and chemically etched in 20% HNO_3 followed by 10% HCl . The angle of incidence was approximately 1° – 2° , corresponding to a probe depth of 1 – 3 Å. In both cases, the electron beam is incident along the $[10\bar{1}0]$ direction. Base pressure in the ultrahigh vacuum system is in the low 10^{-10} -Torr range. Surface cleanliness is checked with Auger electron spectroscopy. Before each experiment, the sample is cleaned with argon-ion bombardment and annealed to 523 K.

In order to relate a given decrease in RHEED streak intensity to a temperature rise ΔT , we obtain an intensity versus temperature calibration. The sample is mounted on a resistively heated Mo stage, and the temperature is monitored by a thermocouple mounted on the surface. The thermocouple was calibrated to the freezing and boiling temperatures of water and to the melting temperature of Pb under vacuum measured in a previous experiment,¹¹ and to the melting temperature of Bi under vacuum. For the RHEED streak intensity versus temperature

measurements, the electron gun is activated at a 1-kHz repetition rate with the frequency-quadrupled Nd:YAG laser. An example of an intensity versus temperature calibration is shown in Fig. 1. At least three calibrations were taken for each sample. The data are normalized to the streak intensity at the lowest temperature studied. The intensity of the diffraction pattern is consistent with Debye-Waller behavior up to the highest temperature studied, 523 K (i.e., the diffraction streak intensity attenuation is exponential with temperature indicating that no surface disordering occurs). The line fit of $\ln[I/I(T=300\text{ K})]$ versus T is forced through zero at the minimum temperature, and the best line fit is found by the method of least squares. The error bar is determined by the range of Debye temperatures calculated from all of the intensity calibration data. From the slope of the calibration a surface Debye temperature of 42 ± 9 K can be extracted, which is consistent with the previously reported value of $48\text{ K} \pm 20\%$ for Bi(0001) and Bi(0112) using low-energy electron diffraction.¹⁴

We next discuss the time-resolved RHEED experiments. To determine the maximum superheating temperature, we observe the behavior of $I/I(T_{\text{bias}})$ versus peak laser intensity I_p for $T_{\text{bias}} = 523$ K at four different time delays. Figures 2(a)–2(d) show $\ln[I/I(T_{\text{bias}})]$ versus I_p for $t = t_0$, $t = t_0 + 0.5$ ns, $t = t_0 + 1.0$ ns, and $t = t_0 + 4.0$ ns, respectively, where t_0 is defined as the time of maximum modulation of $I/I(T_{\text{bias}})$ due to heating. The linear regions in Figs. 2(a)–2(d) show exponential decay consistent with Debye-Waller behavior. Deviation from this linear behavior is due to melting. By relating I_p to ΔT using Figs. 1 and 2(a), we confirm that the linear behavior of $\ln[I/I(T=523\text{ K})]$ versus I_p at $t = t_0$ is a continuation of the Debye-Waller effect observed below T_m within the experimental error. The line fits to the linear regions are forced through $\ln[I/I(T_{\text{bias}})] = 0$ when $I_p = 0$. In Fig. 2(a), the value of $\ln[I/I(T_{\text{bias}})]$ corresponding to the maximum I_p before deviation from linear

FIG. 1. A calibration is obtained to determine the temperature rise induced by the laser. We measure the intensity attenuation of the RHEED streaks as a function of surface temperature. The behavior of $\ln[I/I(T=300\text{ K})]$ vs T is consistent with the Debye-Waller effect throughout the temperature range studied. We obtain a surface Debye temperature of 42 ± 9 K for the Bi(0001) surface.

FIG. 2. The logarithm of the ratio of the heated streak intensity to the intensity at $T_{\text{bias}} = 523$ K is plotted vs peak laser intensity and temperature for (a) $t = t_0$, (b) $t = t_0 + 0.5$ ns, (c) $t = t_0 + 1.0$ ns, and (d) $t = t_0 + 4.0$ ns. Deviation from Debye-Waller behavior is seen, which corresponds to the onset of melting. Superheating of Bi(0001) occurs up until the break from the line fit that occurs at $2.0 \pm 0.2 \times 10^7$ W/cm² corresponding to a superheating temperature of 90 ± 25 K.

behavior is extracted and converted to a peak temperature rise ΔT , using the calibration in Fig. 1. The temperature axis is also given in Fig. 2. We find that for $T_{\text{bias}} = 523$ K, observation of melting occurs for $I_p = 2.0 \pm 0.2 \times 10^7$ W/cm². This corresponds to $\Delta T = 110 \pm 25$ K or, equivalently, a superheating temperature of 90 ± 25 K, not accounting for convolution effects. Included in this error bar is the range of temperatures obtained from the values of I_p corresponding to the point of deviation from Debye-Waller behavior in Fig. 2 (± 15 K), the error in converting diffraction intensity to temperature from the calibration of Fig. 1 (± 9 K), and the temperature uncertainty introduced by the spatial nonuniformity of the laser (± 15 K).

Ultrafast surface heating to peak temperatures below and above T_m is studied by temperature biasing the sample between room temperature and $T_m - 21$ K while monitoring the modulation of the streak intensity before, during, and after the arrival of the heating pulse. Figure 3 shows $I/I(T_{\text{bias}})$ versus delay time t . For $T_{\text{bias}} = 300$ K and $I_p = 2.0 \times 10^7$ W/cm² [Fig. 3(a)], the change in surface temperature ΔT at $t = t_0$ is approximately 115 K. The surface temperature remains below T_m . In Fig. 3(b), $T_{\text{bias}} = 429$ K and $I_p = 2.0 \times 10^7$ W/cm². The laser heating raises the surface temperature to $\sim T_m$. For $T_{\text{bias}} = 512$ K and $I_p = 2.0 \times 10^7$ W/cm² [Fig. 3(c)], the surface is heated to $\sim T_m + 90$ K, approximately the maximum observed superheating temperature. When $I/I(T_{\text{bias}})$ is converted to temperature using the calibration of Fig. 1, the temporal evolution of surface temperature is qualitatively consistent with a one-dimensional heat-diffusion model for Figs. 2(a)–2(c).^{15,16} For

FIG. 3. The ratio of the heated streak intensity to the intensity at the bias temperature vs delay time is displayed for various bias temperatures. At temperatures below that of maximum superheating, the behavior is qualitatively consistent with a one-dimensional heat-diffusion model for laser heating both below and above T_m (a)–(c). Melting is evidenced in (d) as a deviation from this behavior.

$T_{\text{bias}} = 523$ K and $I_p = 2.4 \times 10^7$ W/cm² [Fig. 3(d)], the maximum superheating temperature is exceeded and melting occurs. This is indicated by a strong deviation from the behavior predicted by heat-diffusion model [i.e., difference in the behavior of Fig. 3(d) for large t when compared to Figs. 3(a)–3(c)] as well as visible laser damage to the surface. We monitor the sample visually to obtain a qualitative estimate of the threshold for laser damage and find that the earliest visual observations of damage coincide with the point at which $\ln[I/I(T_{\text{bias}})]$ versus I_p deviates from linear behavior.

After damage has occurred, the RHEED streaks are still visible but their intensities are diminished, indicating a reduction in the surface quality. We measure the reflectivity of the surface for $\lambda = 1.06$ μm at room temperature both before and after the occurrence of laser damage and find that the reflectivity has decreased from 0.67 to 0.49. SEM images of the laser-damaged surface indicate that the surface has melted. The SEM images show the formation of a periodic structure with periodicity about equal to the wavelength of the laser. This periodic structure forms in a hexagonal arrangement of melt puddles, which in some regions coalesce into parallel rows. The spacing between puddles and rows is approximately equal to the wavelength of the heating laser.

Previous pulsed-laser melting experiments on the (0001), $(\bar{1}010)$, and $(2\bar{1}\bar{1}0)$ surfaces of Bi with a ruby laser with a 30-ns pulse width have shown defect formation on the $(\bar{1}010)$ and $(2\bar{1}\bar{1}0)$ surfaces resulting from mechanical stress induced by slip planes parallel to the (0001) surface. In these experiments, the Bi(0001) surface regrew epitaxially from the liquid with no laser-induced periodic surface structure observed.¹⁷ The different behavior observed in our experiments may be related to the two-orders-of-magnitude difference in pulse width.

In the previous superheating experiments on Pb(111),¹⁰ surface damage was only induced by the laser for an I_p much larger than that which corresponded to maximum superheating. However, this damage could be removed by pulsed-laser melting above the superheating threshold. For Pb(111) the threshold for pulsed-laser melting is lower than the threshold for pulse-laser damage although for Bi(0001) these two thresholds appear to be comparable.

In conclusion, using time-resolved RHEED we have observed superheating of Bi(0001) by 90 ± 25 K. For laser heating corresponding to a larger ΔT , melting is observed as a deviation from Debye-Waller behavior. For these

larger heatings, irreversible laser damage resulting in a hexagonal periodic surface structure is also observed. Bi and Pb experience very different properties associated with bulk melting, such as volume change and change in electrical and thermal conductivities.¹⁸ Therefore, our observation of superheating of Bi(0001), coupled with the previously observed superheating of Pb(111),¹⁰ suggests the generality of the superheating phenomenon.

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Temperature-dependent x-ray photoelectron diffraction of Pb(100): Experimental results and the single-scattering cluster model

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An angle-resolved x-ray photoelectron diffraction study of the temperature-dependent surface structure of Pb(100) is performed. Below 550 ± 11 K, the decrease in forward-scattered intensity attenuation is exponential with temperature. The intensity attenuation of the forward-scattered peaks is much larger than predicted by both single-scattering and multiple-scattering x-ray photoelectron diffraction models for a bulklike lattice. Corrections for surface relaxation and thermal expansion in the single-scattering cluster model result in an increase in the predicted intensity attenuation; however, sufficient agreement between experiment and calculation is not achieved.

I. INTRODUCTION

X-ray photoelectron diffraction (XPD) is well established as a means to study the structure of surfaces and overlayers.¹⁻³ More recently, XPD has been used to study temperature-dependent surface effects, such as surface disordering below the bulk melting temperature.⁴⁻⁷ The relatively simple single-scattering cluster (SSC) method has been successful in predicting surface structure and relative peak heights in photoelectron diffraction; however, the peak intensities are generally overpredicted. Multiple scattering reduces the peak intensities and can be partially accounted for in the SSC model by reducing the mean-free path of electrons and the magnitude of the atomic-scattering factor. However, detailed multiple-scattering calculations are often necessary to achieve agreement with experiment.^{8,9} In general, SSC calculations underestimate the dependence of the forward-scattered peaks on temperature. This has been demonstrated in temperature-dependent XPD azimuthal-scan studies of Cu(001)⁶ and Ge(111).⁷ In the Cu(001) experiment, reasonable agreement with the SSC method was shown for forward-scattered peaks at large angles relative to the surface normal. For such large angles multiple scattering is not expected to be important. These previous SSC studies suggest that multiple-scattering calculations are required for improved accuracy of the model.

Here we report on the temperature-dependent structure of Pb(100) for $300 \text{ K} < T < 550 \text{ K}$ using XPD, and a comparison of our experimental results to the predictions made by XPD models. Our analysis points to the need for further theoretical development in interpreting and predicting such data so that XPD may become a more quantitative tool in the study of temperature-dependent surface behavior. Below ~ 550 K, we observe that the intensity attenua-

tion of the forward-scattered peaks is exponential with temperature. The intensity attenuation is much greater than that predicted by the SSC model for the forward-scattered peaks from a bulklike lattice. We include both surface relaxation and thermal expansion in the SSC model; however, the inclusion of such effects only results in slightly improved agreement between experiment and calculation. A slablike multiple-scattering calculation that assumes a bulklike lattice does not show significant improvement in the agreement with the experimental results.¹⁰ Experimental results on the temperature-dependent behavior for $T > 550$ K, where Pb(100) begins to experience surface disordering, were previously reported in Ref. 5.

This article is organized in the following manner: In Sec. II we describe the experimental conditions; in Sec. III the data analysis is explained. In Secs. IV and V the model is introduced and results are discussed, respectively. Concluding remarks are made in Sec. VI.

II. EXPERIMENT

The crystal was oriented to within 0.75° of the Pb(100) surface as confirmed by Laue back reflection. Polishing and chemical etching of the sample resulted in a mirrorlike finish. The sample is mounted on a resistively heated Mo stage. The sample temperature is monitored with thermocouples at the front and back surfaces of the sample. The maximum temperature difference between the front and back of the sample is 1 K and the temperature stability is better than ± 0.6 K.

Before data acquisition, the sample was cleaned with cycles of argon-ion bombardment and annealing to approximately 2 K below T_m until an atomically clean surface was obtained as indicated by x-ray photoelectron spectroscopy. A Mg K α x-ray source ($E = 1253.6$ eV) at 28.8° from

the surface normal provided the incident radiation. The binding energy of the Pb $4f_{7/2}$ core level is 136.6 eV; therefore, the photoelectrons have a kinetic energy of 1117.0 eV above the Fermi level. The scattered-electron intensity was measured with a hemispherical electron-energy analyzer mounted on a two-axis goniometer. The angular resolution of the analyzer as determined by low-energy electron diffraction is 1.6° full width at half-maximum. The base pressure of the ultrahigh vacuum system is 1×10^{-10} Torr. The actual pressure during data acquisition was in the 10^{-9} Torr range, due to the x-ray source and heating of the sample. Polar scans were taken at 1117.0 eV and at two off-peak energies (1133.6 and 1093.6 eV) simultaneously with angular steps of 1° . The scans at the off-peak energies were used to determine instrumental effects.

III. ANALYSIS

Analysis of the polar scans is accomplished in the following way: Background electrons are accounted for by fitting a polynomial to the highest-temperature scan after the remaining forward-scattered peaks are removed. At such high temperatures, approximately 1–2 K below T_m , the forward-scattered peaks are weak due to surface disordering. The instrumental response is determined from a polynomial fit to the scan at 1133.6 eV. The choice of the scan at 1133.6 eV over the one at 1093.6 eV is made to avoid the effects of the secondary tail of the Pb $4f_{7/2}$ peak, although this is found to be unnecessary since the scans have the same shape and therefore only differ by a multiplicative constant. The data correction is accomplished as follows:

$$I_{\text{corr}}(\theta, \phi, T) = \frac{I(\theta, \phi, T) - I_{\text{bkgd}}(\theta, \phi)}{I_{\text{ir}}(\theta)}, \quad (1)$$

where ϕ is fixed for the polar scans. $I(\theta, \phi, T)$, $I_{\text{bkgd}}(\theta, \phi)$, and $I_{\text{ir}}(\theta)$ are the as-acquired data, background, and instrumental response. $I_{\text{corr}}(\theta, \phi, T)$ is the corrected data. The method of data correction, as well as corrected polar scans of the [001] azimuth of Pb(100) for various temperatures, are shown in Figs. 1(a) and 1(b).

We next analyze the temperature dependence of the forward-scattered peaks. When $\ln[I_{\text{corr}}(\theta, \phi, T)]$ is plotted versus T , we see that the intensity attenuation is exponential up to 550 ± 11 K. Reported errors in excess of ± 0.6 K result from slight differences in the temperature of deviation from exponential behavior for the eight forward-scattered peaks. Above 550 ± 11 K, $\ln[I_{\text{corr}}(\theta, \phi, T)]$ versus T diverges rapidly from the exponential decay observed at lower temperatures. Figure 2 shows $\ln[I_{\text{corr}}(\theta, \phi, T)]$ versus T for $\theta = 0^\circ, 18^\circ, 45^\circ$, and 72° along the [001] azimuth for $T \leq 550$ K. The best line fit is achieved using the method of least squares. The highest temperature data included in the fit is chosen so as to maximize the statistical correlation coefficient between the line fit and the data. At temperatures above 550 ± 11 K the attenuation of the forward-scattered peaks shows evidence of surface disordering. This temperature region is discussed in detail in Ref. 5.

FIG. 1. (a) The method of data correction is shown for a polar scan of the [001] azimuth of Pb(100) at $T = 326 \pm 0.6$ K. (b) Corrected polar scans along the [001] azimuth of Pb(100) obtained from Eq. (1) are given for $T = 326 \pm 0.6$ K, 425 ± 0.6 K, 526 ± 0.6 K, and 597 ± 0.6 K.

IV. MODEL

We next discuss the SSC model and apply it to our experimental conditions. An electron that is forward scattered immediately after being emitted experiences no Debye-Waller effect since it experiences no momentum change. The electrons contributing to a forward-scattered peak are either forward scattered immediately after being

FIG. 2. The logarithm of the corrected forward-scattered intensity is plotted as a function of temperature for the experimental data for $\theta = 0^\circ, 18^\circ, 45^\circ$, and 72° along the [001] azimuth. The data show a trend of increasing slope with decreasing probe depth. The experimental data for $\theta = 0^\circ, 35^\circ$, and 55° along [011] have the corresponding slopes: $m(0^\circ) = -1.34 \times 10^{-3} \text{ K}^{-1}$, $m(19^\circ) = -1.39 \times 10^{-3} \text{ K}^{-1}$, $m(55^\circ) = -1.27 \times 10^{-3} \text{ K}^{-1}$, and $m(55^\circ) = -1.70 \times 10^{-3} \text{ K}^{-1}$.

emitted, or elastically scattered one or more times before being scattered in the forward direction. The probability for a scattering event preceding forward scattering is quite low for electrons with kinetic energies > 600 eV. This is due to the atomic-scattering factor, which is strongly peaked in the forward direction. This property is responsible for the general success of the SSC method in predicting the structure and relative peak heights observed in XPD experiments.

In XPD, the single-scattering diffraction intensity for unpolarized incident photons can be written as^{2,3}

$$I^{(n)}(\mathbf{k}) \propto \left| \exp\left(\frac{-L_n}{2\lambda}\right) + \sum_j \frac{|f_j(\theta_j)|}{\beta r_j} W_j \exp\left(-\frac{L_j+r_j}{2\lambda}\right) \right. \\ \times \exp\{i[|\mathbf{k}|r_j(1-\cos\theta_j) + \Psi_j(\theta_j)]\} \left. \right|^2 \\ + \sum_j \frac{|f_j(\theta_j)|^2}{\beta^2 r_j^2} \exp\left(-\frac{L_j+r_j}{\lambda}\right) (1-W_j^2), \quad (2)$$

for an emitter in the n th layer. $L_n = z_n/\cos\theta$ is the path of the unscattered and attenuated electron wave inside the solid, z_n is the distance between the n th layer and the surface, θ is the polar angle defined from the surface normal, λ is the mean free path of electrons in the solid, $f_j(\theta_j)$ is the atomic-scattering factor, θ_j is the scattering angle measured from the direction of forward scattering, $|\mathbf{k}|$ is the magnitude of the electron wave vector, r_j is the distance between the j th scatterer and the emitter, and $|\mathbf{k}|r_j(1-\cos\theta_j)$ and $\Psi_j(\theta_j)$ account for phase changes due to path-length differences and scattering, respectively. β is a correction factor, which partially accounts for the reduced forward-scattering amplitude that would result from spherical-wave calculations. This reduction is usually around 50%, which corresponds to $\beta=2$.^{2,3} W_j is the Debye-Waller factor, which accounts for the increased mean vibrational amplitudes of atoms with temperature and is given by

$$W_j \propto \exp[-|\Delta\mathbf{k}_j|^2 \langle u_j^2(T) \rangle] \\ = \exp[-2|\mathbf{k}|^2(1-\cos\theta_j) \langle u_j^2(T) \rangle],$$

where

$$\langle u_j^2(T) \rangle = \frac{3\hbar^2 T}{M k_B \theta_D^2}. \quad (3)$$

$|\Delta\mathbf{k}_j|$ is the magnitude of the momentum change resulting from scattering with the j th atom, $\langle u_j^2(T) \rangle$ is the mean-squared atomic displacement from equilibrium in the direction of $\Delta\mathbf{k}_j$ and is assumed to be isotropic, $\hbar$ is Planck's constant divided by 2π , M is the mass of the atom, k_B is Boltzmann's constant, and θ_D is the Debye temperature. The last term in Eq. (2) accounts for overcounting of lattice-vibration effects in the first term.

In our SSC calculations we make the small atom approximation, i.e., a plane-wave electron wave function is assumed. The cluster size is $9 \times 9 \times 15$ atoms, corresponding to a crystal with 81 atoms in each layer and 35 Å thick. The contribution of the bottom layer to the diffraction is

$< 5\%$ of the total intensity. The center atom of each layer is chosen as the emitter. Scattering factors based on free-atom scattering of incident plane waves are obtained from the literature.¹¹ Electrons with an energy of 1117.0 eV have an estimated inelastic mean-free path λ_{in} of 24 Å in lead.¹²⁻¹⁴ However, multiple scattering events effectively reduce λ_{in} and it was found that using $0.5 \lambda_{in} < \lambda_{eff} < 0.75 \lambda_{in}$ is more consistent with experimental results.^{2,6,15} (λ_{eff} is defined as the effective mean-free path.) For Pb, we choose $\theta_D = 62$ K [$\theta_D(\text{bulk})/\sqrt{2}$] and $\lambda = 12$ Å ($0.5 \lambda_{in}$). In addition, we choose $\beta=2$. The diffraction intensity is calculated for $300 \text{ K} < T < 600 \text{ K}$ in 50 K temperature intervals and 1° steps in θ .

V. RESULTS AND DISCUSSION

Our XPD experiments clearly show that for $T < 550 \pm 11$ K, the intensity attenuation of the forward-scattered peaks is exponential with temperature. The degree of attenuation is significantly in excess of that predicted by XPD models including the Debye-Waller factor. However, from Eq. (3) we see that the intensity attenuation with temperature depends on the value of θ_D . Experimentally, θ_D is a combination of surface and bulk effects.

We consider θ_D as a function of the thickness of the surface layer contributing to the diffraction. The surface-layer thickness is equal to the component of the electron mean-free path perpendicular to the surface, $\lambda_{eff} \cos\theta$. For a given azimuth, the transition from a bulklike to a surfacelike θ_D can be observed by monitoring how the slope of the linear region changes with decreasing surface-layer thickness. Figure 2 shows the logarithm of the corrected forward-scattered intensity as a function of temperature from which an obvious trend of increasing slope with increasing polar angle in θ_D can be observed as a function of surface-layer thickness for $\theta=0^\circ$, 18° , 45° , and 72° along the [001] azimuth of Pb(100). This trend is less obvious for the [011] azimuth, the slopes of which are given in the figure caption. The $\sim 12\%$ difference between the slopes for $\theta=0^\circ$ along [001] and [011] may be attributed to the relatively small number of data points that comprise each line fit or possibly to a slight tilt in the plane of crystal rotation relative to the electron-energy analyzer. However, the same trend in slopes for $\theta=0^\circ$ is observed in the SSC model. Comparing the experimental slopes corresponding to $\theta=0^\circ$ and $\theta=72^\circ$ for [001] (and $\theta=0^\circ$ and $\theta=55^\circ$ for [011]) we see that θ_D decreases with the surface-layer thickness, i.e., as less and less of the bulk is sampled. If we assume that the slope of the linear region in Fig. 2 is proportional to $1/\theta_D^2$ as in Eq. (3), we calculate that θ_D for a surface layer of ~ 2 monolayers ($\theta=72^\circ$) is approximately 70% of that obtained when ~ 5 – 7 monolayers are probed ($\theta=0^\circ$). For $\theta=0^\circ$, θ_D is a combination of both bulk and surface effects.

The SSC calculations described in Sec. IV are unsuccessful in providing reasonable agreement with the temperature dependence of the forward-scattered peaks that we observe for Pb(100). The slopes of $\ln[I(\theta, \phi, T)]$ versus T are underpredicted by the model by one to two orders of

magnitude. This leads us to investigate surface effects that have not yet been included in the model, such as surface relaxation and thermal expansion.

We include surface effects by accounting for the fact that Pb(100) is not accurately modeled by a bulk-terminated surface. In fact, unusually large surface relaxations have been observed on both Pb(100) and Pb(110) when compared to many other face-centered-cubic (fcc) (100) and fcc (110) metal surfaces. For example, the first interlayer contraction for Pb(100), Pb(110), Cu(001), and Ni(001) has been reported to be about 8%, 16%, 1%, and 3%, respectively.¹⁶⁻¹⁸ In addition, a large thermal expansion perpendicular to the surface has been observed for Pb(100) when $300 \text{ K} < T < 470 \text{ K}$. In this temperature range, the thermal-expansion coefficient is approximately $2 \times 10^{-4} \text{ K}^{-1}$, about seven times the bulk thermal expansion.¹⁹

Therefore, we apply the following corrections to our model: an 8.0% contraction to the first interlayer spacing, a 3.1% expansion to the second, and a 3.0% contraction to the third at 300 K.¹⁶ Next, a thermal expansion of $2 \times 10^{-4} \text{ K}^{-1}$ is included for the first interlayer spacing, and the SSC slopes are calculated for $300 \text{ K} < T < 470 \text{ K}$.¹⁹ The SSC slopes including these effects show an increased temperature dependence; however, the change does not satisfactorily account for the discrepancy between the model and experiment. Polar scans including these corrections are given with experimental scans in Fig. 3 for $T = 350 \text{ K}$ for the [001] and [011] azimuths. These plots show reasonable agreement with the experimental polar scans, especially for the first three peaks along [011]. However, the forward scattering along the nearest-neighbor direction, $\theta = 45^\circ$ along [001], is still significantly overemphasized since multiple-scattering events are not accounted for. The calculated slopes for several polar angles along [001] and [011] are obtained from plots of $\ln(I)$ versus T for the two azimuths in Fig. 4.

When comparing the data and the model in Figs. 2 and 4, it is important to note that the model does not take into account the fact that a surface atom may experience a larger thermal vibrational amplitude perpendicular to the surface than parallel to it, or even that the vibrations in the plane of the surface may not be isotropic. In addition it does not account for a layer-dependent Debye temperature. Therefore, it is not surprising that the trend of increasing temperature dependence with increasing polar angle observed in the data is not observed in the calculation.

The SSC method has previously been applied to the temperature-dependent behavior of forward-scattered peaks for azimuthal scans of Cu(001).⁶ The effect of the surface was accounted for by assigning θ_D (surface) to the first atomic layer and θ_D (bulk) to the remaining layers. Multiple-scattering effects were partially accounted for by adjusting β and λ . However, the authors saw a significant difference between the experimental slopes and those predicted by the model, especially for forward-scattered peaks at $\theta = 45^\circ$, where multiple scattering is expected to play an important role. This work involved the calculation of an average scattering angle $\bar{\theta}_j$ by inserting θ_D (bulk) and the

FIG. 3. Polar scans for the (a) [001] and (b) [011] azimuths of Pb(100) at $T = 350 \text{ K}$ are compared to the polar scans predicted by the SSC model when surface relaxation and thermal expansion are included. The scans are normalized to unity for the peaks at 0° . The solid and dashed lines represent the experimental data and the model, respectively.

slopes obtained from the model into Eq. (3). Using this $\bar{\theta}_j$ with the experimental slopes allowed for the calculation of an effective θ_D . A similar experiment on Ge(111) also showed a significant difference between the temperature dependence predicted by the SSC model and the data.⁷ As a check to our SSC model, we first calculate the intensity attenuation of the forward-scattered peaks for Cu(001) and obtain reasonable agreement with Ref. 6. Next, we perform a similar calculation of $\bar{\theta}_j$ using the slopes from

FIG. 4. The logarithm of the corrected forward-scattered intensity is plotted as a function of temperature for the SSC model including surface relaxation and thermal expansion for (a) $\theta = 0^\circ, 18^\circ$, and 45° along the [001] azimuth and (b) $\theta = 0^\circ, 19^\circ$, and 35° along the [011] azimuth. $\theta = 72^\circ$ and $\theta = 55^\circ$ along [001] and [011], respectively, are not included since the SSC model did not predict the existence of these peaks much above the background level.

our model and θ_D (bulk) = 88 K for $\theta = 0^\circ$, 18° , and 45° [001], and $\theta = 0^\circ$, 18° , and 35° along [011]. We find $3^\circ < \theta_f < 5^\circ$, which leads to θ_D (effective) = 24 K. This is consistent with the Cu(001) and Ge(111) calculations that reported $\theta_D(\text{bulk})/\theta_D(\text{effective}) \approx 4$. Our experimental and calculated slopes for Pb(100) are a little over one order of magnitude larger than those of Cu(001) and Ge(111) as a result of the significantly lower Debye temperature of Pb [$\theta_D(\text{Pb}) = 88$ K, compared to $\theta_D(\text{Cu}) = 343$ K and $\theta_D(\text{Ge}) = 374$ K]. A previous XPD experiment on Pb(110) showed experimental slopes of the same order of magnitude as we have observed in our experiment.⁴ A large thermal expansion has been observed for the Pb(110) surface as well.^{18,20}

Finally, we are led to inquire about multiple-scattering effects; however, the attenuation of the Pb(100) forward-scattered peaks cannot be explained by even a slab-type spherical-wave multiple-scattering calculation performed by Tong.¹⁰ In this model the sample was assumed to be 20 layers thick and to have a bulklike lattice spacing and bulk θ_D . Slight improvement is seen, but our experimental slopes still exceed the temperature dependence predicted by the multiple-scattering calculation by at least an order of magnitude. Therefore, the discrepancy between the temperature dependence of the experiment and the SSC calculation does not appear to be completely explained by multiple-scattering effects.

VI. CONCLUSIONS

We demonstrate that the SSC model, including the Debye-Waller factor, shows reasonable agreement with the angular position of most forward-scattered peaks in experimental XPD polar scans on Pb(100) but significantly underpredicts the temperature dependence of the forward-scattered peaks. This model also includes reductions in the mean-free path of electrons and the atomic scattering factor which partially account for multiple-scattering effects. This complements previous comparisons between experiment and the SSC model for azimuthal scans on Cu(001) and Ge(111).^{6,7} Our results show a much stronger temperature-dependent effect than is predicted by SSC calculations even when surface relaxation and thermal expansion are accounted for in the model. The experimental intensity attenuation is exponential with temperature. Larger lattice vibrations are observed on the surface relative to the bulk as an increase in the slope of $\ln[I(\theta, \phi, T)]$ versus T for decreasing surface-layer thickness. This suggests that the enhanced lattice vibrations near the surface are important in XPD. The increasing application of XPD to study temperature-dependent behavior of surface structure and the general inability of the SSC model to accurately predict the degree of experimen-

tally observed forward-scattered peak attenuation suggest a need for further theoretical consideration. Although our study suggests that multiple-scattering effects are not completely responsible for the discrepancy, it would be interesting to see how the inclusion of surface relaxation, thermal expansion, and a layer-dependent Debye temperature would affect multiple-scattering calculations. Other thermal effects not discussed here, such as thermally produced surface defects (for example, vacancies), may also play a role. Further theoretical investigations are needed so that XPD may be used as a quantitative technique for the study of temperature-dependent surface behavior.

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A picosecond electron gun for surface analysis

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Theoretical and experimental investigations for a new design of an ultrashort pulsed laser activated electron gun for time resolved surface analysis are described. In addition, a novel electron detection and image analysis system, as it applies specifically to time resolved reflection high-energy electron diffraction in the multiple-shot operation, are reviewed. Special attention is directed to minimize the photoelectron transit-time spread from the electron gun, in spite of an unusually long focal length and a small convergence angle of the pulsed electron beam. Both requirements are necessary to use the electron gun for diffraction techniques. The design value for the temporal resolution in the synchroscan operation is 1.3 ps. Based on a thorough theoretical investigation, a new electron gun has been designed, constructed, and tested. © 1995 American Institute of Physics.

I. INTRODUCTION

The ability to observe atom/surface dynamics is possible with the advent of electron-scattering techniques having picosecond and subpicosecond temporal resolution. Detailed studies of surface phase transformations and the dynamics of molecular interactions at surfaces are important in characterizing the initial stages of epitaxy during film growth, as well as the initial stages of surface melting/sublimation during the heating process. The reduced symmetry present at the surface often changes the energetics and time scales of important fundamental physical processes such as melting which emphasize the importance of understanding the role that the surface plays in initiating physical phenomena.

The combination of high temporal resolution light activated probes with surface sensitive analysis techniques provides a viable method for studying dynamics at surfaces with picosecond and even femtosecond temporal resolution. For example, time-resolved photoemission spectroscopy¹⁻³ utilizing the pump-probe method has already proven to be a very useful technique for studying the electronic properties of surfaces and interfaces into the femtosecond time scale. The vibrational relaxation of adsorbates has been investigated using time-resolved sum frequency generation⁴ and infrared reflection absorption spectroscopy.⁵ Time-resolved second-harmonic generation^{6,7} has been used to study the structural properties of laser heated surfaces.

Here, we describe our efforts at combining reflection high-energy electron diffraction (RHEED) with ultrashort pulsed lasers. Time-resolved RHEED can be used to effec-

tively monitor the surface structure and mean vibrational amplitude of atoms at the surface with picosecond time resolution.^{8,9} Specifically, we utilize a photoactivated RHEED electron gun excited by two picosecond laser pulses. The resulting electron-beam pulses are less than 5 ps wide, contain enough electrons, and can be sufficiently well focused to produce high quality electron-diffraction patterns. We describe the electron gun, the laser system, and the time-resolved diffraction system performance.

II. ELECTRON GUN DESIGN

A. Design methodology

The development of femtosecond lasers and their extensive use to study various physical phenomena have motivated the development of a subpicosecond temporal resolution streak camera. In a streak camera, an optical signal is converted into an electrical signal using a photocathode. Ideally, the resulting electron pulse should be an exact temporal and spatial replica of the optical excitation pulse. The electron pulse is rapidly scanned (streaked) across a two-dimensional observation plane, usually a phosphor screen/image intensifier¹⁰ or microchannel plates,¹¹ by a set of high-speed deflection plates.

Streak cameras operating in the subpicosecond time range have been successfully developed.^{10,12-18} The instruments attaining the high temporal resolution have optimized electron optical components. The achievement of high temporal resolution is the result of using a photocathode with an extremely narrow (photo)emission electron energy distribution. Narrow energy widths insure that initial electron velocities are nearly identical such that the adverse effects of chromatic aberrations can be minimized in the electron-beam forming optics. Photoemission electron energy widths as narrow as 0.1 eV can be achieved by selecting a photocathode material with a work function that is slightly less than the laser excitation photon energy, and employing a thin film which minimizes the redistribution of electron energies due to scattering during the process of emission and escape from the surface itself. The photocathode must be a conductor, or operated in a regime which guarantees charge balance to

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prevent the adverse effects of charging. Once a narrow temporal distribution of electrons has been produced with nearly the same kinetic energy, charged particle lenses must transport them to the target without temporally broadening the electron distribution. The primary causes of temporal redistribution in electron beams are path-length differences between the photocathode and target for different segments of the electron beam and space-charge (Boersch) effects. In order to minimize the effects of space-charge broadening, the electrons should be accelerated as quickly as possible once exiting the photocathode, and the number of (low-energy) beam crossovers should be minimized. In addition, the deflection plates used in streak cameras possess fringing field inhomogeneities which must be carefully controlled in order to reduce temporal dispersion. Further care must be taken in the design of the deflection plates to control capacitive effects which limit slew rates and switching speeds. Finally, the efficiency of the electron detector must be as high as possible. Single electron detection can be accomplished with phosphor screens and image intensifiers, or array detectors such as are used in a Vidicon.¹⁹

In order to minimize transit-time broadening due to path-length differences between electrons following different trajectories from the photocathode to the target, the initial electron spatial distribution must be small (much smaller than the inner diameter of the smaller electron focusing electrode). The use of long focal length lenses also decreases transit-time dispersion due to path-length differences. Space-charge broadening of the electron pulse near the photocathode can be minimized by using as large an extraction field as possible.

The large extraction field quickly accelerates the electron pulse, thereby minimizing the time when low-energy electrons in close proximity can exchange energy. The extraction field is limited, however, by the vacuum breakdown field and the presence of any asperities on the cathode surface which might begin to undergo field emission. Typically, maximum dc electric fields near the cathode are limited to 5 kV/mm even though vacuum breakdown occurs near 30 kV/mm. Space-charge broadening can also occur in the postcathode electron optical column near beam crossovers and in regions of space where the electrons are significantly decelerated for focusing. The effects of space-charge broadening in the electron optical transport column can be mitigated through careful electron optical design of electrostatic lens elements,^{11,12,14-18} or through the use of magnetic focusing lenses¹³ where the electron velocities are not changed. Both approaches have yielded picosecond temporal resolution, although the suitability of magnetic focusing systems to ultrahigh vacuums maintained for surface science remains problematic. Single-shot temporal resolution of 0.3 ps has been demonstrated.^{14,16,17} For multiple-shot operation, jitter represents a major source for loss of temporal resolution. Synchronscan operation of a Photochron IV streak tube has demonstrated 930 fs temporal resolution.¹⁸ Our goal was an electron gun similar to the Photochron IV streak tube, but with focusing conditions that provide a real image 500 mm from the photocathode, and a beam that is relatively collimated (convergence angle about 1 mrad). Both requirements are necessary to use the electron gun for diffraction techniques, i.e., in order to separate diffraction spots and lines in the diffraction pattern.

FIG. 1. Electrode configuration of the photoactivated electron gun together with the nominal operating voltages.

B. Electrode configuration

Primarily for design simplicity, and ultimately for UHV compatibility, we have selected an all electrostatic focusing system for our time-resolved RHEED gun. A schematic cross section of the photoactivated RHEED gun is shown in Fig. 1. The photocathode is held at potential V_0 . While the emitted electrons are spatially divergent, a pinhole is used to extract relatively collimated electrons. This extraction electrode is part of the first lens and is held at a potential V_1 such that the photoelectron extraction field is large. Electrodes with potentials V_1 , V_2 , and V_3 form the first extraction lens. This zoom lens configuration is selected for its robust performance at long focal lengths, and small intrinsic aberrations.²⁰ Electrodes with potentials V_3 , V_4 , and V_5 form a long focal length Einzel lens used for secondary focusing. Two lenses are necessary for focusing the electron beam at a distance of 0.5 m from the photocathode with a nominal spot diameter on the target of less than 300 μm with a nearly parallel beam. The requirement of a well focused and collimated electron beam is necessary for RHEED applications. In addition, no crossover points are located inside the electron lens column. These conditions are consistent with maintaining low electron density inside the electron lens column in order to minimize space-charge broadening in that region. Some compromise between these requirements and that of maximizing the electric field and potential throughout the photocathode-to-anode region is incorporated in the design. For example, a relatively long electron lens column was necessary in order to achieve good electron collimation over the relatively long distance of 0.5 m.

The photocathode is composed of a 40 nm thick Ag film deposited *ex situ* on a sapphire substrate. When excited by a frequency doubled dye laser with 4.0 eV photon energy, the photoelectrons have a narrow distribution of electron energies. Although the photon energy is less than the work function of Ag (4.3 eV), the photoemission current displayed a linear dependence on the incident radiation intensity, indicat-

ing that the emission process results from single photon processes. The lowering of work functions of thin metal films,²¹ thermal distribution of electron energies near the Fermi energy, or the presence of a thin layer of contamination on the surface may all play a role in initiating photoemission in this system with 4.0 eV photons. Since 40 nm of Ag is continuous and well conducting, surface charging of the photocathode cannot contribute to the reduction of the energy needed for photoemission. The spatial distribution of emitted electrons is defined primarily by the diameter of the illuminating radiation, and secondarily by the angle defining pinhole aperture in the extraction electrode V_1 . The nominal diameter of this aperture is 200 μm . The size of the optical pinhole image formed on the photocathode determines the size of the focused beam on the screen and therefore represents the physical source of the electron optical transport lenses. Since the cathode is held at -15 kV, and the extraction electrode is held at -8.75 kV, a planar extraction field of 3.125 kV/mm accelerates the photoemitted electrons. Characteristic of planar extraction fields is a linear magnification of nearly 1. The angular width of the source at the pinhole is 10 mrad assuming uniform emission at the photocathode into all directions. This is a conservative upper limit.

The inner diameter of all of the lens elements is 15 mm with the exception of the inner diameter in the focusing electrode V_2 which is 3 mm. The zoom lens forms a virtual image of the source which is in turn focused onto the phosphor screen by the Einzel lens.

C. Calculated electron trajectories and field distribution

The electron optical properties of the RHEED gun were computed numerically. The potential and field distribution were found by numerically solving Laplace's equation for given boundary conditions, using the boundary element method.²²⁻²⁵ The suitability of these techniques for the computation of paraxial properties and primary aberration coefficients for electron optical systems (in the absence of space charge) is widely accepted.^{23,25} Specifically, cylindrically symmetric electrode geometries were approximated by straight-line segments, or electrode subelements. The two-dimensional Green's function was integrated over the discretized electrode distribution, using pulse weighting functions for the charges, and either pulse-, or δ -function,²⁶ testing functions. The all orders electron trajectories were computed by integrating the equations of motion in time.²⁷ The integration routine was based on a modified Adams-Moulton-Bashforth (predictor-corrector) method.²⁸ In our implementation, both paraxial and all orders trajectories (where no approximations to the lens fields were made) were computed. Accurate calculations of third- and fifth-order geometric and first-order chromatic aberration coefficients were possible. The electron optical properties of each of the two lenses are summarized in Table I. The object f_o and image side f_i side focal lengths are given in millimeters. The object F_o and image F_i side focal points are referenced to the cathode ($z=0$ mm) and are also given in millimeters. The asymptotic projector aberration expansions for the spherical

TABLE I. Electron optical lens parameters.

V_0 (kV)	V_1 (kV)	Lens potentials			
		V_2 (kV)	V_3 (kV)	V_4 (kV)	V_5 (kV)
-15.00	-8.75	-1.50	-2.50	-9.375	0.00
First-order optical properties					
	f_o (mm)	f_i (mm)	F_o (mm)	F_i (mm)	
Zoom lens	39.92	56.48	-44.41	50.54	
Einzel lens	111.09	124.21	-114.66	119.78	
Spherical aberration coefficients					
	C_{s0} (mm)	C_{s1} (mm)	C_{s2} (mm)	C_{s3} (mm)	C_{s5} (mm)
Zoom lens	6850.0	-23100.0	23900.0	-16600.0	3510.0
Einzel lens	23800.0	-89900.0	128000.0	-81400.0	19500.0
Chromatic aberration coefficients					
	C_{c0} (mm)	C_{c1} (mm)	C_{c2} (mm)		
Zoom lens	62.8	-106.0	45.0		
Einzel lens	273.0	517.0	246.0		

C_s and chromatic C_c aberration coefficients²⁷ are given in millimeters, where

$$C_s(\text{object}) = C_{s0} + \frac{C_{s1}}{M} + \frac{C_{s2}}{M^2} + \frac{C_{s3}}{M^3} + \frac{C_{s4}}{M^4},$$

$$C_c(\text{object}) = C_{c0} + \frac{C_{c1}}{M} + \frac{C_{c2}}{M^2},$$

and M is the linear magnification of the lens. The performance of the entire electron optical transport system is given explicitly in Table II where each individual contribution to the final spot size is analyzed. Clearly, the spot size is dominated by the magnification of the source, implying that the RHEED spot on the target could be further reduced in size by using a smaller pinhole aperture (at the expense of current). Electron lenses possess focusing defects much in the same way that conventional optical lenses do. However, these focusing defects or aberrations are far more severe in

TABLE II. Electron optical column performance.

Linear magnification	1.68
Angular magnification	0.38
Spherical aberration coefficient	51859 mm
Chromatic aberration coefficient	21 mm
Astigmatism and field curvature	2671 mm
Coma	46 mm
Distortion	0.25 mm
Image radius (spherical aberration)	0.0229 mm
Image radius (chromatic aberration)	0.0001 mm
Image radius (magnified source)	0.1680 mm
Image radius (astigmatism)	0.0820 mm
Image radius (coma)	0.0492 mm
Image radius (distortion)	0.0066 mm
Image radius (diffraction)	0.0000 mm
Image diameter (0.2 mm aperture)	0.34 mm
Convergence angle (upper limit)	3.80 mrad
Convergence angle (half intensity)	1.30 mrad

charged particle optics lenses. Of the primary aberrations, perhaps the most important is spherical aberration. The spherical aberration results from off-axis fields being stronger than those on axis, resulting in a stronger focusing of far off-axis trajectories. It is impossible to eliminate spherical aberrations in conventional, axially symmetric lenses without introducing space charge on axis. The chromatic aberration results from the focus defect associated with finite-energy distributions within the electron beam itself. Since electron lenses essentially focus the momentum of the electrons, more energetic electrons are focused more weakly than lower energy electrons, resulting in a focusing error. Coma is a focus defect whereby off-axis rays entering the optical system with differing angles are not uniformly focused. Characteristic comma-shaped beam distributions are common in systems dominated by coma. The distortion aberration causes off-axis to be displaced. The most common manifestation of distortion is the mapping of a square array into a barrel-shaped or pincushion-shaped pattern in the image plane. The image is distorted (in shape) with respect to the object, and is most severe for extreme off-axis rays of little slope. Finally, astigmatism and field curvature are aberrations whereby different axes of the image are focused with different strengths as a result of off-axis illumination. The resulting defocus in the image results. We summarize these third-order aberrations for our electrostatic lenses in Table II.

The temporal resolution of this lens column was also computed from a knowledge of the all orders trajectories. The average transit time from photocathode to the scattering target is 7350.7 ps. The deviation in transit times weighted for all trajectories through the RHEED gun was computed to 1.26 ps, full width at half maximum. The choice of lens potentials shown in Table I indicates that the electron beam never has less than 5.625 keV of kinetic energy after the extraction pinhole in order to reduce the effects of space-charge broadening. This would have been impossible to achieve with a single electron lens column.

D. Electron gun construction

An electron gun has been constructed based on the above design. The outside diameter is 25 mm and the overall length is 330 mm. The lenses, anode, and diffraction plates are made out of aluminum and fabricated in our laboratory. Ceramic balls were used as spacers between the lenses. Deflection plates are incorporated at the end of the gun in order to steer the photoelectron beam towards the sample. The electron gun assembly is shielded with a μ -metal tube to avoid any distortion of the electron beam from stray magnetic fields (primarily the earth's field and the magnets of the ion-pump system). The photocathode is a 40 nm thick Ag film evaporated on a sapphire window. Metals are good candidate materials for laser-driven photocathodes because of the ease of preparation, high damage threshold, and large free-electron density. The main drawbacks of metals are low quantum efficiencies and the high work function (4–5 eV) which require UV photons for linear (one photon) photoemission. The photocathodes are processed by thermal evaporation in a separate chamber and were installed into the electron gun without further processing.

FIG. 2. Photocurrent as a function of the Ag film thickness in the transmission mode. The photocathodes are deposited by thermal evaporation on a sapphire substrate.

Figure 2 shows the photocurrent as a function of the Ag film thickness measured with a Faraday cup. As a light source we used an Hg(Xe) arc lamp and a bandpass filter in order to separate the same wavelength as that of our Nd:YLF laser system ($h\nu=4.2$ eV). Since the photocathode is used in the transmission mode, the photoelectron current is expected to be governed by the photon and the electron mean-free path. The measured value of the photon mean-free path (penetration depth) is 211 Å for $h\nu=4.2$ eV (Ref. 29) and the measured mean-free path for emission of these low-energy photoelectrons is about 10 Å.³⁰ The result of three different series of film preparation shows that the photoyield is indeed decreasing with increasing silver film thickness ($d>20$ nm). However, the actual behavior shows a very complex dependence of the photoelectron yield on film thickness with a second maximum at about 40 nm. Although the reason for this second maximum is not well understood, a change of the Ag film structure—such as the generation of colloidal silver features on the sapphire window—after a certain deposition thickness may account for this observation. Microscopic roughness of metal films—especially silver films—is known to enhance a variety of optical scattering processes at the surface and is well studied using different techniques such as surface enhanced Raman scattering.³¹ The major contribution to the enhancement is understood to originate from the coupling of photons into surface plasmons in regions of surface roughness. The decay of these nonradiative surface plasmons into one electron excitation can drastically increase the photoyield as first reported by Endrit and Spicer.³² The choice to use a 40 nm thick Ag film as a photocathode, instead of a 20 nm thick one was made in order to assure good electrical conductivity across the film and to increase its durability to withstand many months of operation.

III. LASER SYSTEM

The laser system used in the experiments consists of a cw pumped, mode-locked Nd:YLF (neodimium yttrium lithium fluoride) master oscillator, a Nd:YLF regenerative amplifier, and a dual jet, synchronously pumped dye laser with two amplification stages (Fig. 3).

In particular, the output of the master oscillator (15 W, 1053 nm, 60 ps FWHM at 76 MHz) is split using a half-

FIG. 3. A schematic diagram of the laser system.

wave plate and a polarizer. A small fraction is used to seed the Nd:YLF regenerative amplifier and the rest is focused into a heated KTP crystal for second-harmonic generation. The frequency doubled output from the nonlinear crystal at 527 nm (1 W) is used to synchronously pump a dual jet dye laser with Rhodamine 6G as the gain medium and DODCI as the saturable absorber. The dye laser output (0.1 W, 76 MHz, and 800 fs FWHM) is then amplified in two Rhodamine 610 amplification stages.

The dye amplification stages are pumped by the frequency doubled output of the regenerative amplifier. The amplifier is seeded with pulses from the main oscillator and a Faraday isolator is used to prevent feedback between the cavities. A lithium niobate Pockels cell (Medox E-O) is used to extract the amplified pulses from the regenerative amplifier cavity. The output (1 W, 1053 nm, 500 Hz) is frequency doubled in a BBO crystal to generate 0.5 W at 500 Hz (1 mJ) pulses at 527 nm. A dichroic beamsplitter is used to separate the fundamental from the second-harmonic output. The amplified pulses at 527 nm are then delayed and split with 8% of the power used in the first dye amplification stage and 92% in the second stage. A 27 cm focal length lens is used to focus the 527 nm pump pulses as well as the 590 nm pulses from the dye laser into the first amplification stage. The spot sizes at the first stage are 140 (dye laser) and 160 μm (pump), yielding an intensity of approximately 10^{10} W/cm^2 . A 10 cm focal length lens collimates the output of the first stage into the second stage where the dye laser spot size is 1 mm. The remaining 92% of the pump pulses is suitably delayed and focused into the second stage with a 1 m focal length lens. The amplification stages consist of 2 mm path-length cuvettes adapted to allow the flow of a solution of Rhodamine 610 in methanol. The concentration of Rhodamine 610 is adjusted to optimize the amplified power. The amplified dye laser output is 20 $\mu\text{J/pulse}$ at 500 Hz at 590 nm and 2 ps (FWHM).

The amplified dye laser pulses are then focused into a

FIG. 4. Profile of the electron beam at the phosphor screen, 0.5 m away from the cathode.

KDP crystal to generate the second harmonic at 295 nm, which are then focused onto the photocathode of the electron gun.

IV. ELECTRON GUN PERFORMANCE

The electron gun was tested first in a separate glass vacuum chamber with a base pressure of 10^{-7} Torr. The operating voltages are shown in Fig. 1. A sapphire window passed the slightly focused ($f=500 \text{ mm}$) UV beam into the vacuum system onto the Ag photocathode at normal incidence. Figure 4 shows the profile of the electron beam at the phosphor screen, 500 mm away from the cathode. This geometrical arrangement is identical to that used for RHEED. The pinhole following the cathode has a diameter of 200 μm . The measured full width at half maximum (FWHM) of the electron beam at the phosphor screen is 272 μm . If the photocathode aperture is the beam defining aperture, then the image profile should have been about 330 μm (see Table II: linear magnification = 1.68). The fact that the measured profile was less than this indicates that the spot was limited by the source (incident light beam profile) and not the cutoff aperture. The convergence of the electron beam is about 1 mrad as measured by scanning the beam with the edge of a razor blade. This relatively small value ensures that the beam size is below 1 mm at the phosphor screen as well as on the sample. Therefore the quality of the diffraction pattern is dominated by the smoothness of the sample surface and not by the convergence (collimation) of the electron beam.

The average photocurrent was measured with a Faraday cup connected to a Keithley picoammeter. The log-log plot in Fig. 5 shows the linearity of the average electron current (slope=1) as a function of the laser-pulse energy. The current was found to be directly proportional to the laser intensity up to a pulse energy of about 0.5 μJ , focused to a 300 μm spot. The measured average electron current at this pulse energy was 3.5 pA, which results in about 5×10^4 electrons per pulse at a repetition rate of 500 Hz. Thus the nonaveraged current within individual pulses is 1.3 mA. Space-charge effects at higher intensities limit the emission of electrons as seen in Fig. 5 for $I > 0.5 \mu\text{J}$. When the charge of the extracted photoelectrons reaches a certain value q_c , the amplitude of the

FIG. 5. Averaged electron current as a function of the laser pulse energy for a 40 nm thick Ag cathode.

electric field falls to zero and any additional photoelectrons cannot be emitted until part of the electron cloud has left the surface region. The time resolution is known to deteriorate quite rapidly above this region due to space-charge broadening. Therefore the electron pulse must be generated with minimum of space-charge dispersion in order to obtain the desired temporal resolution. The laser induced damage threshold of the photocathode is about $1 \mu\text{J}$ (1 mJ/cm^2) as evidenced by visible damage to the cathode.

In order to determine the temporal width of the electron pulse, we use a jitter-free streak camera device. An ultrashort voltage ramp pulse with a rise time of a few hundred ps on a pair of deflection plates is synchronized with the electron pulse and sweeps it across the phosphor screen. The duration of the electron beam is proportional to the calibrated length

of the streak. This sweep requires the electrical ramp pulse (5 kV) to be synchronized to the electron pulse with high accuracy. In the repetition mode, the streak length, and therefore the overall time resolution of the electron pulse measurement, is limited by the jitter between the high-voltage pulse for the deflection plate ramp and the electron pulse. Conventional electronics can at best offer a jitter of several ps for short times, in addition to long term delay drift. Instead, we use a laser activated photoconductive switch as developed by Mourou *et al.*^{33,34} A diagram of the experimental arrangement is shown in Fig. 6. The laser light is split into two beams. One beam is frequency quadrupled and used to generate a pulse of electrons at the photocathode of the electron

FIG. 6. Experimental configuration of a jitter-free streak camera device for the measurement of the electron pulse width, based on a laser activated photoconductive switch.

FIG. 7. A schematic diagram of RHEED showing the formation of the Laue rings on the phosphor screen.

gun. The other beam is suitably delayed and then used to strike a GaAs photoconductive switch which triggers a fast RC circuit to begin charging the pair of deflection plates to a potential of 5 kV. The switching is based on the photogeneration of carriers in a semiconductor bulk by the ultrashort laser pulse. The rise time of the switch is essentially determined by pulse duration and circuit bandwidth. The sweep time of the voltage ramp is given by the RC circuit, which includes R_c and the capacitance of the deflection plates C_{plates} .

We could not experimentally verify the limit of the temporal resolution because of the nonlinearities in the sweep speed of the GaAs switch. According to our preliminary results, an upper limit on the electron pulse width of $\tau_e < 5$ ps can be concluded. Further work is underway to calibrate the GaAs switch and the optical setup to overcome this problem.

V. TIME-RESOLVED ELECTRON DIFFRACTION

A. RHEED setup

Reflection high-energy electron diffraction (RHEED) is one of several diffraction techniques that have the capability of investigating surface order with great accuracy. In the RHEED technique, high-energy electrons (10–20 kV) are diffracted off an ordered surface at a glancing angle ($< 2^\circ$). For a flat single crystal, the RHEED pattern consists of a set of streaks oriented perpendicular to the sample surface (elastic two-dimensional Laue scattering) as shown schematically in Fig. 7.

The intensity of these diffraction patterns is temperature dependent, as in low-energy electron diffraction. As the temperature is raised, the atomic vibrational amplitude increases, which leads to a reduction of elastically scattered electrons and causes a reduction of the diffraction pattern intensity. This is known as the Debye–Waller effect.³⁵ Figure 8(a) shows scans through one of the RHEED streaks from a platinum single crystal taken at various temperatures, obtained during a static heating experiment. The measured decay of the peak height as a function of temperature is shown in Fig. 8(b). From the linearity of this semilogarithmic plot, it is

(a)

(b)

FIG. 8. (a) Scans through the diffraction patterns from a platinum single crystal taken at various probe temperatures. (b) Semilogarithmic plot of the measured decay of the peak heights as a function of the sample temperature.

evident that the RHEED streak intensity follows an exponential decay in accordance with the Debye-Waller theory.³⁵ These intensities give us an accurate calibration of the temperature of the surface, i.e., the temperature of the surface can be determined by comparing the pattern intensity with this calibration curve.

The use of time-resolved RHEED to study ultrafast dynamics at solid surfaces is a fairly recent development. It is explained in detail by Elsayed-Ali *et al.*⁸ and will be discussed here only briefly. The basic concept of this technique is the use of a photoactivated electron gun, which produces the electron probe pulse synchronized to a pump laser pulse to monitor a transient event. A schematic diagram of the experimental setup is illustrated in Fig. 9. The amplified dye laser light is split into two beams. One beam (pump) is used to transiently heat the sample surface. The other beam (probe) is frequency doubled and suitably delayed, and is used to generate a pulse of electrons at the photocathode of the electron gun. The electrons are then used to probe the structure and mean vibrational amplitude of the surface by measuring the intensity change of the streaks on a phosphor

FIG. 9. Experimental setup for time-resolved RHEED. This technique allows one to observe laser induced transient temperature and structural changes at the surface region with a time resolution given by the duration of the electron pulse.

screen as a function of the pump-probe delay. This enables the observation of laser induced transient temperature and structural changes at the surface region with a time resolution limited by the duration of the electron pulse.

B. Electron detection system

In order to obtain quantitative information of the diffraction intensity, time-resolved RHEED is signal limited when compared to conventional static RHEED systems. The electron signal has a pulse length of only a few ps and the number of electrons available in a single pulse is small ($\sim 10^4$ per pulse). Therefore it is essential to have an image detecting device with sensitivity to single electrons with a very low dark current. This requirement can be fulfilled with high gain microchannel plates (MCP) as an amplification stage followed by a phosphor screen. The signal obtained from the phosphor screen can then be recorded and analyzed. The spatial resolution is limited by the MCP channel diameter and their center-to-center spacing.

As shown in the schematic diagram of Fig. 10, we use a Chevron MCP detector with a 40 mm diameter P20 phosphor screen on a fiber-optic faceplate as the vacuum interface. The fiber-optic faceplate provides one-to-one imaging of the diffraction pattern, i.e., a recording film or an array detector with another fiber-optic window can be placed directly in

FIG. 10. Electron detection and data collection systems currently used in our time-resolved RHEED setup.

contact with it without requiring any further focusing. The MCP and phosphor screen are placed 170 mm from the sample where the electron beam is diffracted. This location allows the points and line patterns to be separated easily even for high-energy electrons and superstructures.

C. Image analysis system

As shown in Fig. 10, the data collection system is based on a CCD camera, a video frame grabber, and a 486 computer. Our system is similar to one previously reported by Clarke *et al.*³⁶ That system was used to measure RHEED signals as a function of time during MBE film growth. Our system is not configured for real time signal monitoring. Thus there are a number of choices that we made in our system configuration to achieve high performance as well as low cost. Our time resolution comes from the timing between laser and electron pulses (time when the laser beam impinged on the sample and the time when the electron beam arrived). Because the laser repetition rate is 500 Hz, no attempt is made to synchronize the laser to the video camera. Instead, multiple pulses (from 80 to 500) are averaged for each video frame. Further signal averaging is accomplished by adding data from multiple video frames.

For our CCD detector we use a Pulnix TM-745E camera. This was chosen because of its relatively low cost, high sensitivity, as well as its ability to integrate low light level images on the camera. Typically we would integrate each frame for 1 s. This is accomplished by using a logic signal from a Keithley PIO-12 board in the computer to turn on the image inhibit line to the camera. The only disadvantage of this camera is its inability to manually control the black level. In most cases this is not a serious problem since the background level is determined from video frames collected with the laser on and with the laser off. These are collected alternately by opening and closing a shutter in the path of the laser beam by using a logic signal from the Keithley board to a Uniblitz VS14S1w0 control unit and shutter.

We use an Imaging Technology VFG frame grabber. Though we had planned to use a feature of this frame grabber board that allowed the use of a higher performance non-standard video camera, we found that the Pulnix camera worked adequately for our application. The data collection cycle is designed to minimize deadtime. At the end of a camera integration cycle the whole video frame is grabbed. The shutter is opened or closed and the next camera integration cycle is started. During the time the camera is integrating the next frame, the data from the previous frame is processed. Thus it is crucial that all the data can be processed by the time the next video frame from the camera is ready to read. We found that for a 1 s integration time more than half of the video frame could be processed. A greater proportion of the frame could be handled either by increasing the integration time or by using a faster computer.

We organized the data collection into different regions on the CCD array. Usually one or more regions are used to collect the RHEED pattern, one to measure the overall background level, and a few to measure the intensity in individual streaks. The most time consuming portion of data processing

FIG. 11. RHEED pattern of a Ni(100) surface, [010] azimuth, with adsorbed oxygen $c(2 \times 2)$ structure, using ultrashort ($\tau < 5$ ps) electron pulses.

for the regions consists of transferring the data values from the frame grabber board memory into the computer memory. Then the data can be stored as an image.

Usually, the data in a region is compressed into line format by adding the data values by row and/or by column. This generates a line scan that is typically used to show the multiple peaks in a RHEED spectrum. Also, the total intensity in the region is computed and stored. Such data is analogous to RHEED oscillation data that is used in MBE growth. The total intensity is displayed on the computer screen primarily to allow the users to follow the data collection process, but it is also useful for measuring the background level and for calibration. The whole video image is also displayed on a separate TV monitor. In order to achieve adequate signal-to-noise ratio, multiple video frames are collected and averaged for each time delay. At the end of signal averaging for a given time delay (typically 2 min) the laser-on and laser-off data for each region is stored on the hard disk, the laser delay line is changed to a new time delay, the data arrays are reinitialized, and the process is restarted. By storing the laser-on and laser-off data separately, further data processing could be delayed until after the experiment is completed.

D. Performance

As mentioned above, the electron pulse is used for surface analysis, primarily for probing the surface temperature and order by utilizing the time-resolved RHEED technique. Figure 11 shows the two-dimensional diffraction pattern (RHEED streaks) of a Ni(100) surface with adsorbed oxygen $c(2 \times 2)$ structure, along [010] azimuth, using ultrashort ($\tau < 5$ ps) electron pulses. The image was recorded on a photographic film in contact with the fiber-optic faceplate. The electron gun was operated at 18 kV. The fine streak pattern (zero-order Laue ring L_0) and even some Kikuchi lines are clearly visible and demonstrate the excellent signal-to-noise ratio that we achieve with our short electron pulses. The first-order Laue ring L_1 does not appear in the picture because the L_1 radius for the incident electron-beam energy of 18 keV is larger than that of the RHEED screen. As previously observed by several authors,³⁷ adsorption of oxygen on clean Ni(100) at 400 K leads to the appearance of an ordered

(a)

(b)

FIG. 12. Line scan through the diffraction patterns of a Pt(111) surface. (a) The raw data after signal averaging for 60 frames at 1 s, (b) after subtracting the CCD background from the raw data.

overstructure. First, at low oxygen coverage ($\Theta \leq 1/4$ ML) the overstructure forms the $p(2 \times 2)$ structure and then, for longer exposure ($\Theta \leq 1/2$ ML), the $c(2 \times 2)$ structure forms. It should be emphasized that in spite of the low oxygen coverage and the small number of electrons produced by the ultrashort electron pulses (compared to the conventional cw RHEED technique) the additional diffraction pattern due to the ordered oxygen overstructure is clearly visible. This allows investigation of transient phenomena of the substrate and adsorbed species at the same time. For example, a thermal nonequilibrium in the adsorbate-metal complex after a laser heating pulse can be directly monitored in real time. Initial results will be discussed in a later paper.

Figure 12 shows a line scan through the diffraction pattern of a Pt(111) surface approximately perpendicular to the streaks. The data were obtained with the CCD camera and processed with the frame grabber as discussed above. The line scan is an integration of five rows (five pixels of the CCD camera) in order to average over fluctuation in the direction along the streaks. Figure 12(a) shows the raw data after signal averaging for 1 min (60 frames at 1 s). Immediately after the measurement, the CCD background of 60 frames was also measured and subtracted from the raw data. Figure 12(b) illustrates the same line scan after the background subtraction. No smoothing is necessary for further data processing.

As discussed above, the basic idea of the time-resolved

FIG. 13. Transient surface temperature rise and decay of a Pt(111) single-crystal surface after a 100 ps IR laser heating pulse.

RHEED experiment is to observe laser induced transient temperature and structural changes of the surface region. We measured the temperature change of the Pt(111) single-crystal surface after a 100 ps IR laser heating pulse. The reduced streak intensity due to the laser pulse was compared with a calibration curve obtained by a static heating measurement. Based on this calibration the heating IR laser pulse raised the surface temperature by 20 K (see Fig. 13). In order to minimize experimental error due to long term drift, a computer controlled shutter is placed in the path of the IR heating beam. The purpose of the shutter was to chop the IR beam with a frequency of 1 Hz which allows one to quickly alternate between a hot (shutter open) and a cold (shutter closed) measurement. The normalized difference between the hot and the cold measurement was averaged over 60 cycles. An exposure time for one point (delay time) of 2 min (includes on and off time) is needed for such a small temperature change to average out shot-to-shot laser fluctuations of the IR heating laser pulse, the electron probe pulse, and the gain of the MCP plates. Because of the glancing angle of incidence of the electron probe pulse and the perpendicular direction of the heating laser pulse, the temporal resolution is not only limited by the pulse width of the electron gun but also by the time difference between an electron scattered at the front edge of the sample to an electron scattered at the trailing edge of the sample. Therefore, in order to increase the overall temporal resolution of this technique below 15 ps, the sample has to have a width smaller than 1 mm.

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Reflection High-Energy Electron Diffraction Study of Melting and Solidification of Pb on Graphite

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Abstract

Melting, and solidification of Pb on graphite have been investigated using reflection high-energy electron diffraction. Pb films of thicknesses 4, 14, and 70 monolayers were observed to melt at 8 ± 2 K above the bulk melting temperature. Supercooling of Pb by 70 ± 2 K was also observed. Superheating is attributed to the formation of crystallites bounded by the nonmelting Pb{111} surfaces.

I. Introduction

It is well established, that the surface can begin to disorder at temperatures lower than the bulk melting temperature [1-3]. Pre-melting has been observed on the Pb(110) surface using medium-energy ion scattering (MEIS) [4]. A reversible order-disorder transformation was observed on the Pb(110) surface with disorder occurring in the temperature range of 450 - 560 K, which is much lower than the Pb melting point, $T_m = 600.7$ K [4]. The increase in the thickness, l , of the disordered layer (as determined from the analysis of the energy spectra of scattering protons) was seen to be logarithmic from 560 K ($l \sim \ln [T_m / (T_m - T)]$). At temperatures above $T_m - 0.3$ K, the disordered layer thickness was observed to increase as $l \sim (T_m - T)^{-1/3}$ [5]. A recent MEIS study on Pb(111), and vicinal surfaces has revealed that those with miscut angle $\theta < 2^\circ$ remain ordered up to T_m , while vicinal surfaces with $\theta > 13.9^\circ$ exhibit pronounced surface melting. Vicinal surfaces with $2^\circ < \theta < 13.9^\circ$ were observed to exhibit surface melting induced faceting, where the surface was seen to decompose into ordered, "dry" facets, and "melted" facets. These facets were seen to coexist on the surface at temperatures near T_m . MEIS experiments on Pb(111), and its vicinal surfaces were performed at temperatures up to $T_m - 0.05$ K. The surface melting induced faceting is thought to be responsible for the observed thermal step collapse on Pb(111) [13]. In addition, faceting has been observed to occur on a macroscopic level. Faceting of micron-sized Pb crystallites were observed using scanning electron microscopy (SEM) [14,15]. A theoretical treatment based on free energy analysis has predicted the faceting behavior in these experiments [16,17].

While supercooling of the melt is a readily observable phenomenon, under normal conditions superheating of solids above the bulk melting point, T_m is not easily observed. Apparently, there is no energetic barrier for the nucleation of melting. In pulsed laser heating of Pb(111), superheating was observed in time-resolved reflection high-energy electron diffraction (RHEED) experiments [18-21]. Also, superheating of micron sized crystallites bounded by close-packed facets by few degrees above T_m , has been observed by Métois et. al., Spiller, and Dáegas et. al. [22-24]. Métois et. al., deposited 3000 Å of Pb on a graphite substrate and the surface was annealed above the bulk melting temperature of Pb, and then cooled. This caused the formation of a large number of Pb crystallites. They were able to overheat sharp edged Pb crystallites with {111} facets by 3 K. The facet shape was studied in detail using SEM by Heyraud et. al. [25]. In the Pb/graphite system, some irregular particles were found to superheat by 2 K [23]. Recent theoretical calculation has successfully predicted superheating related to facets in connection to partial wetting angle of the surface, and the tilt angle of the melted regions in the vicinal surface undergoing non-melting induced faceting [26]. Superheating of coated clusters has also been theoretically investigated, and these simulations show a dependence of coating thickness on the degree of superheating [27].

We report on the melting characteristics of Pb on graphite. Multi-layers of Pb grown on graphite offer a relatively simple system to study melting of thin films. The interaction of Pb with the graphite is purely through Van der Waals forces, and complications due to chemical reactions are not present.

II. Experimental method

An ultrahigh vacuum chamber equipped with a RHEED system was used in this study. The residual gas pressure in the chamber was less than 8×10^{-10} Torr except during Pb deposition, at which time the vacuum was $\sim 6 \times 10^{-7}$ Torr. The electron beam energies used were 12 keV and 15 keV. A 12 mm $\times$ 12 mm $\times$ 2 mm pyrolytic graphite (0002) substrate was used. A clear RHEED pattern of the graphite surface was obtained by peeling off a few layers of carbon with the aid of an adhesive tape prior to loading the sample in the UHV chamber. Further cleaning of the substrate was not necessary due to the inertness of the graphite surface, however, the sample was heated at 450 °C for 6 hours prior to Pb deposition. Pb was deposited on the graphite substrate using a molybdenum basket, and the deposition rate was monitored with a quartz-crystal thickness monitor. The deposition rates varied from 0.2 Å/s to 4 Å/s. Pb deposited on the graphite can be evaporated by heating the sample for several minutes at 600 °C. This was verified by the clear RHEED pattern of the graphite surface.

The substrate was mounted on a resistively heated stage capable of reaching temperatures up to 1000 °C. The temperature was measured by a K-type, thermocouple which was clipped onto the substrate surface. The thermocouple was calibrated to the bulk melting temperature of Pb, and boiling point of distilled water. These results showed an uncertainty of ± 2 degrees near the Pb melting point and ± 1 degree near the boiling point of water.

RHEED peak intensity measurements are carried out by a charge-coupled detector (CCD) interfaced to a personal computer. The imaging system is used to monitor the RHEED intensity and the spot position on the screen. RHEED images at different temperatures are stored for further analysis. Several of the Pb films were removed from the UHV chamber for SEM observations. The Pb growth mode and crystal shape were investigated.

The graphite substrate used in the present experiment is a commercial pyrolytic monochromator type [28, 29]. Since naturally occurring graphite single-crystals are relatively small and difficult to obtain, the most widely studied form of graphite are these highly orientated pyrolytic graphite. This polycrystalline material with a hexagonal structure has a relatively large grain size (about 3-10 μm), and a good c^* -axis orientation (misorientation angle less than 2 degrees). Despite the relatively simple structure and ease of surface preparation, interpretation of the diffraction pattern of this graphite is not straightforward [30-33].

The most common structural form of graphite is hexagonal, for which the crystal structure is shown in Fig. 1(a) [33]. The Bravais unit cell of the crystal is shown by the highlighted outline. The coordinates of the four corner atoms are (0,0,0), (0,0,1/2), (1/3,2/3,1/2), and (2/3,1/3,0) respectively. The unit cell as viewed from the top is shown in Fig. 1(b). The crystal consists of layers having a honeycomb arrangement of carbon atoms, which are strongly bonded to one another. The nearest neighbor distance is 1.42 Å whereas the in-plane lattice constant is 2.46 Å. The layers are spaced 3.35 Å apart and are held together by weak van der Waals forces. Neighboring layers are shifted relative to each other leading to an ABABAB... stacking sequence and a c^* -axis lattice constant of 6.70 Å perpendicular to the

layers. This stacking sequence gives rise to two non-equivalent carbon atom sites within the two-dimensional surface unit cell. One carbon atom (A-site) has a neighboring carbon atom directly below in the next layer, whereas the other carbon atom (B-site) is located above the center (hollow site) of the six-fold carbon ring in the second layer.

III. Results

A. Graphite surface

Figure 2 is a RHEED pattern taken of the clean graphite (0002) surface with a 12 keV electron beam incident along the [100] direction. The incident angle of the electron beam was $\sim 3^\circ$, which corresponds to the Bragg condition of the graphite surface. In the pattern, the three dimensional diffraction spots of graphite can be clearly observed. The broad spots are arranged in a rod along the vertical direction in the order $0.l$, $1.l$, $2.l$ with periodically varying intensities along the [001] axis. The $0.l$ and $1.l$ rods are brighter than the $2.l$ rod, particularly the specular beam at the $0.l$ rod shows the maximum intensity due to the Bragg reflection condition being satisfied. Through the analysis of the specular spot profile, the size of the polycrystallites is approximated to be $2\pi/L$, where L is the FWHM of the peak intensity profile.

We calculated the reciprocal lattice structure of graphite using the atom positions (0,0,0), (0,0,1/2), (1/3,2/3,1/2), and (2/3,1/3,0) of the Bravais unit cell shown in Fig. 1 [34]. The reciprocal spot intensity is given by

$$I_{hkl} = f^2 [1 + \cos\pi l + \cos\pi(4/3h + 2/3k) + \cos\pi(2/3h + 4/3k + l)]^2 + f^2 [\sin\pi l + \sin\pi(4/3h + 2/3k) + \sin\pi(2/3h + 4/3k + l)]^2.$$

where h , k , and l are the Miller indices. Thus, the diffraction spots will disappear ($I_{hkl} = 0$) when the following conditions are satisfied:

- (1) $l = \text{odd integer}$, and either $4/3h + 2/3k = \text{odd}$, $2/3h + 4/3k + l = \text{even}$, or $4/3h + 2/3k = \text{even}$, and $2/3h + 4/3k + l = \text{odd}$.
- (2) $l = \text{even integer}$, $4/3h + 2/3k = \text{odd}$, and $2/3h + 4/3k + l = \text{odd}$.

Therefore, the 001, 003, 005, 111, 333, 555, 310, 113, $\bar{1}21$, $2\bar{1}1$... spots etc., will not be seen. Figure 3(a) shows the reciprocal lattice structure in which $0.l$, $1.l$, and $2.l$ rods intersect the Ewald sphere which correspond to the same rods in the RHEED pattern as shown in Fig. 2. For [100] incidence, it is clear from the reciprocal lattice that the $0.l$ and $1.l$ lines intersect the reciprocal spots as shown by the concentric black circles. The $2.l$ line does not intersect any of the spots, but in the pattern the $2.l$ rod can be clearly seen along with the $0.l$, and $1.l$ rods. When the crystal is rotated about the [001] axis, the rods remain observable in all azimuthal orientations, but their intensities change with the azimuthal angle. As shown in Fig. 2, when the electron beam is incident along the [100] direction, the $0.l$ and $1.l$ rods are relatively strong, for the beam incident along the [100] direction the intensity at $1.l$ ($l = 0$) has the maximum.

However when the crystal is turned 60° parallel to $[110]$ direction, the $2.l$ rod remains brighter than the $1.l$ rod. This shows that the reciprocal lattice of the pyrolytic graphite is rotated about the c^* -axis to produce smeared out rings of the reciprocal lattice points except along the c^* -axis direction itself. The rings shown in Fig. 3(a) represent cylinders concentric with the c^* -axis. This indicates that the surface of the graphite substrate consists of a collection of small crystals. These crystals have a c^* -axis texture structure. Even though the crystals are in general randomly oriented, there is a preferred crystal orientation.

The reciprocal (001) plane for $l = 0$ is shown in Fig. 3 (b). From the separation width between $0.l$ and $1.l$ rod the measured lattice constant is $4.24 \text{ \AA}$. This corresponds to the diagonal distance of $4.25 \text{ \AA}$ of the graphite unit cell in the $[100]$ direction.

The incident angle of the 15 keV electron beam was adjusted in order to trace the 002 , 004 , and 006 Bragg reflection spots. The inner potential (V_0) of the graphite (0002) surface was calculated by using the expression $V_0 = E(\sin^2\theta - \sin^2\theta_0)$ [35]. Here $\sin\theta_0$ is given by the Bragg condition as $2d\sin\theta_0 = n\lambda$, where d is the inter-planar distance perpendicular to the graphite (0002) surface. The V_0 thus obtained is 12.3 eV . Using the inner potential energy $V_0 = 12.3 \text{ eV}$, the Bragg condition for each order of diffraction spots at $E = 15 \text{ keV}$ is given in Table 1.

B. Growth of Pb on graphite and intensity measurement

Pb was deposited onto the clean graphite surface as described previously. Figure 4(a) shows the RHEED pattern after the deposition of approximately 4 ML of Pb. The 12 keV beam is incident along the $[100]$ direction of the graphite crystal. In the RHEED pattern, spots and rods (streaks) can be seen. The diffraction spots along the $0.l$ rod, and particularly the specular beam are seen to be sharper than for the graphite pattern shown in Fig. 2. Figure 4(b) shows the peak profile of the specular beam. The size of the deposited crystallites of Pb is found to be larger than the graphite as the FWHM of the peak intensity profile of Pb spot is smaller than the graphite profile width. The Pb crystallites are approximately a factor of 1.6 larger than the graphite crystallites. Also the intensity of the diffraction spots due to the graphite $0.k$ rod is diminished, and between the $0.l$ and $1.l$ rods of graphite the $Pb.l$ rod is seen. The measured lattice distance between $Pb.l$ and $0.l$ rods is $5.72 \text{ \AA}$, corresponding to the $6.06 \text{ \AA}$ diagonal length of the Pb (111) unit cell in the $[0\bar{1}\bar{1}]$ direction. Similar to the graphite surface, when the crystal was rotated, the $Pb.l$ rod is always observed in the pattern, indicating that the reciprocal lattice is circularly rotated about the $[111]$ axis of Pb. The intensities also change with the azimuthal angle and has the maximum when Pb $[0\bar{1}\bar{1}]$ is parallel to graphite $[100]$. This indicates that the Pb crystallites have a texture structure, similar to the graphite substrate such that the crystallites are rotated about the $[111]$ axis with respect to each other. Therefore, we conclude that the Pb growth is such that the particles are oriented with the $Pb\{111\}$ parallel to $\{0002\}$ of graphite $((111)_{Pb} // (0002)_{\text{graphite}})$, and $[0\bar{1}\bar{1}]_{Pb} // [100]_{\text{graphite}}$. By using 14.9 eV for the inner potential of Pb, the incident angles corresponding to the Bragg condition is given in Table 2 [36].

For an incident electron energy of 12 keV to obtain the Bragg condition corresponding to $n = 3$, the incident angle for graphite and Pb is calculated to be 2.21° and 2.68° , respectively.

This indicates that the Bragg reflection spots are separated vertically on the screen. Therefore, measurement of Pb spot intensity is not affected due to graphite spot intensity. The specular beam obtained from 4 ML Pb was analyzed to investigate the temperature dependence of the spot intensity. Figure 5(a) shows the intensity of the 333 Bragg reflection spot of Pb for an incident angle of 2.57° (near 2.68°), as a function of the substrate temperature. The small difference between the observed incident angle corresponding to $n = 3$ Bragg condition and that calculated is within the experimental error or might be due to dynamical effects. The two curves corresponding to heating and cooling are distinguished by two arrows in opposite directions. The temperature was raised from 343 K to 633 K, and then lowered to 373 K. Figure 5(b) shows the intensity change at the higher temperature range extracted from Fig. 5(a). The abrupt change in the diffraction spot intensity is due to melting/solidification phase transitions. As the temperature is increased from room temperature to 590 K the intensity decreases exponentially. This change is shown in Fig. 5(a). In the temperature range between 601 K and 610 K, the intensity drops abruptly. This drop begins at 601 K, higher than the melting point of Pb as seen in Fig. 5 (b). During the cooling process, the intensity undergoes a large change over the temperature interval 535 K to 530 K, a much lower temperature than the melting point. As the temperature falls below 530 K, the intensity increases exponentially. To calculate the Debye-Waller factor, the log of RHEED intensity at temperatures lower than 493 K (during the heating process) was plotted as shown in Fig. 6. The Debye Waller factor is obtained from a least squares fit to this curve. The obtained Debye temperature is 79 ± 3 K, which is higher than the surface Debye temperature of 66 K for Pb(111), and lower than 88 K of bulk Pb [37].

Figure 7(a) is a three-dimensional plot showing the RHEED intensity profile during heating and cooling. Figure 7(b) shows the RHEED intensity profile obtained, during heating, at 343 K, 568 K, and 630 K, and during the cooling at 624 K, 539 K, 525 K, and 373 K. As can be seen from Figs. 7(a) and (b), there are small peaks in the profile after the abrupt drop in intensity. On observing a series of RHEED patterns obtained at various temperatures, the intensity of the Pb reflection spots continue to diminish above 605 ± 2 K, while the weak graphite spots become prominent. This is due to the Pb crystallites forming droplets upon melting, exposing the graphite surface. When cooling the substrate below 530 K, the Pb spots are seen to reappear indicating recrystallization of Pb. Figure 8 is a three-dimensional plot of a RHEED pattern after the sample has cooled to 373 K. At this temperature, the diffraction spots due to Pb are clearly visible.

Figure 9 is a three-dimensional plot of a RHEED pattern of the graphite surface covered with 14 ML of Pb. In this case, the Pb reflection spots are brighter than those observed for the 4 ML of Pb (Fig. 4). The graphite spots are not as visible in this case as for the 4 ML case. This indicates that Pb on the graphite nearly covers the whole surface with the {111} plane. The sample was then heated to 633 K, then cooled to 423 K, and the intensity measurement is repeated. Figure 10(a) and 10(b) show RHEED spot intensity changes during the heating and cooling processes, similar to Fig. 5(a) and 5(b). The abrupt changes of the intensity due to the phase transformations (melting and solidification) are clearer than for the 4 ML case. Melting and solidification are observed between the temperature intervals of 600 K - 605 K, and 540 K - 547 K, respectively. Figure 11 is a semi-logarithmic plot of RHEED intensity as a function

of temperature during the heating process. A Debye temperature of 86 K is obtained from the plot. Similar to the 4 ML case, the graphite spots become more prominent at temperatures between the two steps in the intensity change where the Pb spots disappear from the RHEED pattern due to Pb melting.

We have also studied Pb film thicknesses of ~ 70 ML and ~ 150 ML. The intensity changes are similar to the 4 ML, and 14 ML cases. We summarize the measured temperature ranges over which the changes in the spot intensity occurred, and the Debye temperatures for each of the films in Table III. The average Pb superheating is measured to be 8 ± 2 K, and supercooling by 70 ± 2 K.

The sudden change in the spot intensity can be understood by considering the melting, and solidification of the Pb layer. Above the melting point, the Pb layer melts, and after the temperature decreases below the temperature of crystal nucleation, the Pb is recrystallized. This process corresponds to a first order phase transition in the Pb, which induces the abrupt change in the RHEED intensity, since this phase transition occurs discontinuously.

C. SEM observations

Figure 12(a) and 12(b) are SEM images taken after the depositing ~ 400 Å of Pb on the graphite. In Fig. 12(a), a large number of the Pb crystals can be seen, the average size of the crystals is approximately $1.3 \mu\text{m}$. Between the larger crystals, a number of small crystals are also visible. Closer observations by SEM shows a two-dimensional layer on the substrate. This indicates that larger Pb crystals form on the Pb layers. The growth seems to be Stranski-Krastanov growth mode. Figure 12(b) shows the profile of one crystal. Facets joined by smooth edges can be seen clearly.

IV. Discussion

The RHEED observations are in agreement with the previous SEM work of Heyraud et al., that the Pb layers are epitaxial on graphite with $(111)_{\text{Pb}} // (0002)_{\text{graphite}}$ [22]. For low coverage, both Pb spots and graphite spots are observed in the RHEED pattern. This indicates the formation of Pb crystallites without full coverage of the substrate surface. At high coverage, more than ~ 15 ML, the graphite spots completely disappear, and are replaced by Pb spots. This indicates near full coverage of the graphite surface with $\text{Pb}\{111\}$ crystals. Our SEM observations also showed the formation of a large number of Pb crystals on the substrate. These crystals grow epitaxially with the orientation $[0\bar{1}\bar{1}]_{\text{Pb}} // [100]_{\text{graphite}}$, and show $[111]$ texture structure.

When the sample is heated slightly above the melting temperature of Pb, the graphite diffraction spots appear, indicating the exposure of the substrate surface to the electron beam. We assume that the Pb layers condense into liquid droplets on the substrate after partial melting exposing the graphite. Subsequently, when the sample temperature is lowered, Pb droplets are recrystallized. This occurs at 70 ± 2 K below the bulk melting temperature of Pb and is indicated

by the reappearance of a clear diffraction pattern characteristic of Pb. Previous SEM investigation by Heyraud et. al., showed the formation of spherical Pb particles on the graphite after annealing [22]. The Debye temperature estimated for the 4 ML film is 79 ± 3 K, revealing surface Debye effects. For the 14 ML and 70 ML thick films we measured a surface Debye temperature of 91 ± 3 K and 86 ± 3 K, respectively. These values are in agreement with the known bulk Pb(111) Debye temperature of 88 K, within the experimental uncertainties.

Our RHEED intensity measurements indicate 8 ± 2 K superheating of the deposited Pb films. Superheating by 3 K was observed by Métois et. al., under *in situ* SEM experiment. Métois et. al., observed superheating of Pb crystallites formed upon annealing the Pb deposited on the graphite. They were able to obtain a large population of polyhedral crystallites of 0.2 - 0.5 μm in diameter. It was observed that sharp-edged crystallites with Pb{111} facets superheated by 3 K, whereas crystallites with different shapes melted at the bulk melting temperature of Pb. Recent theoretical calculations also predicted the possibility of facet induced superheating of Pb [18].

In our work we did not pre-treat the film by melting and recrystallizing the sample after Pb was deposited. The Pb atoms, deposited at room temperature, were seen to grow almost in crystals on the graphite substrate. These crystals when heated close to the melting temperature may form crystallites with {111} facets contributing to the superheating. Our SEM images of ~ 400 Å of Pb on graphite at room temperature, clearly show facets in the larger crystals. Stewart's calculation indicated that, in the melting temperature range, the {111} facet grows with temperature [38].

We also observed supercooling of the Pb by 70 ± 2 K. This is attributed to a nucleation barrier for solidification which results from the competition between the decrease in free energy upon solidification and the increase in free energy associated with the existence of a solid-liquid interface. The free energy of a solid droplet is related to its radius, r . At solid-liquid interfaces, a nucleation barrier for solidification exists for $r < r_0$, where r_0 is some critical radius determined by the surface characteristics of the substrate [1]. The droplets with radii, $r < r_0$, supercool. The critical radius estimated for Pb is approximately 40 Å, when the degree of supercooling is 70 K [37].

We have shown that Pb thin films on graphite superheat by 8 ± 2 K. Supercooling by 70 ± 2 K was also observed. Superheating is attributed to the formational crystallite bounded by the nonmelting Pb{111} surfaces.

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Table I

Angle of Incidence at Bragg Condition (graphite)

	n	1	2	3	4	5	6
15 keV	0	--	0.48°	1.97°	2.98°	3.94°	4.85°
12 keV	0	--	0.54°	2.21°	3.36°	4.42°	5.45°

Table II

Angle of Incidence at Bragg Condition (Pb)

	n	1	2	3	4	5	6
15 keV	0	--	0.86°	2.40°	3.57°	4.68°	5.74°
12 keV	0	--	0.96°	2.68°	4.00°	5.24°	6.43°

Table. III

Phase and Debye Temperature characteristics of Pb thin films on graphite.

Thickness (ML)	Melting point (K)	Solidification point (K)	Debye Temperature Θ (K)
4	601-606	530-535	79 ± 3
14	601-605	540-547	91 ± 3
70	608-613	529-533	86 ± 3
150	605-609	523-532	

Caption

- Fig. 1. (a) The most common structure of hexagonal graphite. The Bravais unit cell of the crystal is shown by the highlighted outline. The coordinates of the four corner atoms are $(0,0,0)$, $(0,0,1/2)$, $(1/3,2/3,1/2)$, and $(2/3,1/3,0)$ respectively. (b) The unit cell of the top view of (a). The nearest neighbor distance is $1.42 \text{ \AA}$ whereas the in-plane lattice constant is $2.46 \text{ \AA}$. The layers are spaced $3.35 \text{ \AA}$ apart. Neighboring layers are shifted relative to each other leading to an ABABAB... stacking sequence and a c^* -axis lattice constant of $6.70 \text{ \AA}$ perpendicular to the layers.
- Fig. 2. A RHEED pattern taken of the clean graphite (0002) surface with a 12 keV electron beam incident along the $[100]$ direction. The incident angle of the electron beam was $\sim 3^\circ$, corresponding to the Bragg condition of the graphite surface.
- Fig. 3. (a) The reciprocal lattice structure of graphite. The $0.l$, $l.l$, and $2.l$ rods intersect the Ewald sphere which correspond to the same rods in the RHEED pattern as shown in Fig. 2. (b) The reciprocal (001) plane for $l = 0$. From the separation width between $0.l$ and $l.l$ rod the measured lattice constant is $4.24 \text{ \AA}$. This corresponds to the diagonal distance of $4.25 \text{ \AA}$ of the graphite unit cell in the $[100]$ direction.
- Fig. 4. (a) The RHEED pattern after the deposition of approximately 4 ML of Pb. (b) The peak profile of the specular beam. The size of the deposited crystallites of Pb is found to be larger than the graphite as the FWHM of the peak intensity profile of Pb spot is smaller than the graphite profile width.
- Fig. 5. (a) The intensity of the 333 Bragg reflection spot of Pb for an incident angle of 2.57° , as a function of the substrate temperature. The two curves corresponding to heating, and cooling are distinguished by two arrows in opposite directions. The temperature was raised from 343 K to 633 K, and then lowered to 373 K. (b) The intensity change at the higher temperature range extracted from (a). The abrupt change in the diffraction spot intensity is due to melting/solidification phase transitions.
- Fig. 6. The log of RHEED intensity at temperatures lower than 493 K (during the heating process) is plotted. The Debye Waller factor is obtained from a least squares fit to this curve. The obtained Debye temperature is $79 \pm 3 \text{ K}$.
- Fig. 7. (a) A three-dimensional plot showing the RHEED intensity profile during heating and cooling. (b) The RHEED intensity profile obtained during heating, at 343 K, 568 K, and 630 K, and during the cooling at 539 K, 525 K, 463 K, and 373 K.
- Fig. 8. A three-dimensional plot of a RHEED pattern after the sample has cooled to 373 K. At this temperature, the diffraction spots due to Pb are clearly visible.

Fig. 9. A three-dimensional plot of a RHEED pattern of the graphite surface covered with 14 ML of Pb.

Fig. 10. RHEED spot intensity changes during the heating (a) and cooling (b) processes.

Fig. 11. A semi-logarithmic plot of RHEED intensity as a function of temperature during the heating process. A Debye temperature of 86 K is obtained from the plot.

Fig. 12. SEM images taken after the depositing $\sim 400 \text{ \AA}$ of Pb on the graphite. (a) A large number of the Pb crystals can be seen, the average size of the crystals is approximately $1.3 \text{ }\mu\text{m}$. (b) The profile of one crystal, and facets joined by smooth edges can be clearly seen.

Fig. 1 (a)

Fig. 1(b)

Fig. 2

Fig. 3 (a)

Fig. 3 (b)

Fig. 4(a)

Fig. 4(b)

Fig. 5 (a)

Fig. 5 (b)

Fig. 6

Fig. 7 (a)

Fig. 7(b)

Fig. 8

Fig. 9

Fig. 10 (a)

Fig. 10 (b)

Fig. 11

(a)

(b)

Fig. 12

TEMPERATURE DEPENDENT REFLECTION HIGH ENERGY ELECTRON DIFFRACTION STUDY OF Pb ON Si(111)

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ABSTRACT

The structures of Pb on Si(111)-7x7 has been studied using temperature dependent reflection high energy electron diffraction. Three different phases giving $\sqrt{3}\times\sqrt{3}$ -R30° Pb diffraction patterns are observed. These are the 1 ML incommensurate (IC) phase, the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase, and the 1/6 ML $\sqrt{3}\times\sqrt{3}$ -R30° mosaic phase. A phase transformation resulting in the disappearance of the $\sqrt{3}\times\sqrt{3}$ diffraction streaks into the background is observed at 300 °C and 570 °C for the 1 ML IC phase and the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase respectively. Through quantitative analysis of the temperature dependent diffraction streak intensity, the Debye temperature of the 1 ML IC phase is measured to be 55 ± 15 K, whereas that for the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase is 80 ± 10 K.

Keywords: A. Surfaces and interfaces, C. Surface electron diffraction (LEED, RHEED)

Lead on silicon represents an attractive system to study metal-semiconductor interfaces. Phase diagrams do not show the presence of any chemical compounds at the Pb/Si interface. Mutual solubilities of Pb in Si are negligibly small¹⁻², thus, the interface is abrupt. Such an unreactive system is of basic interest because it may provide a good medium to study two-dimensional (2D) behavior. In spite of the chemical simplicity of the Si/Pb interface, characterization of the structure of the adsorbed Pb layer is complicated by the different phases and phase transformations that Pb can have on Si.³⁻¹¹

The Pb/Si(111) interface has been studied for some time. The earliest study on this system was that by Estrup and Morrison.³ Using low energy electron diffraction (LEED) they proposed epitaxial growth of Pb on Si(111)-7x7 at room temperature. The growth mode was observed to follow a Stranski-Krastanov (SK, layer plus island) mechanism. After annealing, two $\sqrt{3}\times\sqrt{3}$ -R30° patterns were observed at a coverage of 1/3 monolayer (ML) and 4/3 ML. At ~ 300 °C, the 4/3 ML phase showed an order-disorder phase transformation. Heating above ~ 650 °C irreversibly transforms the 4/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase into the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase. Saitoh et. al.,⁴ using LEED and ion scattering spectroscopy confirmed the SK-mode of growth and the two $\sqrt{3}\times\sqrt{3}$ -R30° phases. Thermal desorption of the 4/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase was observed to follow zero-order kinetics and leaves the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase. Thermal desorption of the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase was observed to proceed with higher order kinetics. In a subsequent study, Le Lay et. al.,⁵ using LEED proposed three different $\sqrt{3}\times\sqrt{3}$ R-30° phases at 1, 2/3, and 1/3 ML. The phase transformation for the 1 ML phase, which was observed at ~ 280 °C, was attributed to an order-order transition to the 1x1 structure. The desorption kinetics observed by Le Lay et. al.,⁵ confirmed that of Saitoh et. al.⁴ Contrary to the proposed epitaxial

$\sqrt{3}\times\sqrt{3}$ R-30° 1 ML phase, Grey et. al.,^{6,7} using X-ray diffraction proposed 30° rotated, close-packed incommensurate (IC) phase at a saturation coverage of ~ 1.3 ML. This phase was obtained for room temperature deposition after annealing at 200 °C. Using reflection high energy electron diffraction (RHEED) and LEED, Weitering et. al.,⁸ supported the IC phase of Pb on Si(111). The most detailed picture of the structure of Pb on Si(111)-7x7, is that provided by the scanning tunnelling microscopy (STM) studies of Ganz et. al.,^{9,10} and Hwang et. al.,¹¹ In addition to the STM studies, Ganz et. al.,^{9,10} used thermal desorption, Rutherford backscattering, and LEED to study the structure and coverage of the different phases of Pb on Si(111)-7x7. For annealed surfaces their studies showed the presence of a 1 ML 30° rotated incommensurate layer (which was in some of the previous work mistakenly identified as a $\sqrt{3}\times\sqrt{3}$ -R30° phase), a 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase, and a mosaic 1/6 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase consisting of alternating chains of Pb and Si adatoms. Hwang et. al.,¹¹ showed that in the 1 ML IC phase, the Pb atoms are displaced laterally from ideal T_1 sites to form trimers centered on T_4 sites or H_3 sites. The single T_1 -site bond for the IC phase is relatively weak consistent with the observed zero-order desorption kinetics. For the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase, the Pb atoms are in the T_4 -site with three bonds to Si atoms. This stronger bonding configuration results in the higher order desorption kinetics for this phase. Here we use temperature-dependent RHEED to investigate the mean-square vibrational amplitudes of the different phases of Pb on Si, or equivalently the adatom Debye temperature. We show that the mean-square vibrational amplitude of the different Pb phases on Si(111) correlates with the strength of bonding. We also report on measurements of temperature-induced phase transformations for Pb on Si(111). In addition to the order-order

transformation previously observed for the 1 ML IC phase at 300 °C, we observe an order-disorder phase transformation for the 1/3 ML $\sqrt{3}\times\sqrt{3}$ -R30° phase at ~ 570 °C.

The experiments were performed in an ultrahigh vacuum chamber, equipped with a RHEED facility. The base pressure of the chamber was $\sim 2\times 10^{-10}$ torr. The Si(111) samples were cut from a p-type wafer with 15 Ω -cm resistivity, and had a size of 7 x 1.8 x 0.4 mm. The samples were clamped on a tantalum mounting stage. Lead (99.9995%) was evaporated from a cell located 5 cm away from the sample. The lead coverage was monitored by a crystal thickness monitor. The silicon sample was heated by directly passing current through it. Each new sample was outgassed by heating it overnight at 600 °C. Cleaning was performed by flashing the sample up to 1200 °C, followed by heating to 900 °C, then slow cooling at a rate of ~ 1 K s⁻¹. This process was repeated several times. The sample temperature was measured by a W-5%Rh and W-26%Rh type thermocouples pressed against the back side of the sample. An infrared pyrometer was used to double-check the higher temperature (> 300 °C) range. The RHEED pattern was monitored by a phosphor screen located 24 cm away from the sample and focused, using a camera lens, into a 512x512 charge-coupled-device (CCD) detector. The output of the CCD detector was digitized and stored in a computer for data analysis. The electron beam energy was 15 keV. Sample cleanliness was monitored by observation of the sharp 7x7 RHEED pattern.

For the experiments reported here, about 3 monolayer (ML), where a monolayer is defined as 7.85×10^{14} atoms/cm², were deposited on Si(111)-7x7 at room temperature. Film thickness measurement was performed with a crystal thickness monitor using the factory supplied calibration. When depositing Pb on clean Si(111) at room temperature, the 7x7 feature became faint at ~1 ML coverage. Further Pb deposition caused the 7x7 pattern to disappear, and

only weak 1×1 streaks with an increased background remained. The orientation of the 1×1 structure is parallel to the original Si(111)- 1×1 structure, whereas, the $\sqrt{3} \times \sqrt{3}$ was rotated 30° from 1×1 structure. It is difficult to distinguish the Pb(111)- 1×1 structure from that of the Si(111)- 1×1 in the RHEED pattern. However, if we set the incident electron beam parallel to the $\bar{1} \bar{1} 2$ azimuth of the Si lattice, the $\sqrt{3} \times \sqrt{3}$ - $R30^\circ$ structure could be easily detected. Annealing at $\sim 260^\circ\text{C}$ results in the appearance of the $\sqrt{3} \times \sqrt{3}$ diffraction pattern. Based on previous work,¹⁰ we attribute this to the 1 ML IC phase, with excess Pb atoms forming islands. Annealing at $\sim 360^\circ\text{C}$ results in a strong $\sqrt{3} \times \sqrt{3}$ diffraction pattern also superimposed on the 1×1 structure. We attribute this to be due to the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ - $R30^\circ$ phase formed by desorption of the 1 ML IC phase. Figure 1(a) is a three-dimensional plot of a RHEED pattern taken at this orientation with the Pb $\sqrt{3} \times \sqrt{3}$ - $R30^\circ$ superstructure clearly visible. A line profile taken perpendicular to the streaks of this RHEED pattern is shown in Fig. 1(b). For quantitative analysis, the streak intensity was taken as the peak intensity minus background. The background was obtained by averaging the intensity measured between streaks at both sides of the analyzed streak, as illustrated in Fig. 1(b). The electron angle of incidence was ~ 2 degrees from the surface, resulting in a probe depth of about 1-2 ML. At this angle of incidence, relatively strong $\sqrt{3} \times \sqrt{3}$ streaks were observed.

The sensitivity of the diffraction intensity to temperature arises from the increase in the atomic vibrational amplitude with temperature. This is observed as a decrease in the elastic diffraction intensity with increased temperature. If we only consider the increased thermal vibrations of the adsorbed Pb atoms with temperature, the intensity attenuation of a superstructure elastic diffraction peak is described by:¹²

$$I(T) = I(0)\exp(-MT) \quad (1)$$

where $I(T)$ is the diffraction intensity at temperature T , $I(0)$ is the diffraction intensity for a hypothetical rigid lattice, and:

$$-MT = -\langle(\Delta\mathbf{k} \cdot \mathbf{u}(T))^2\rangle = -|\Delta\mathbf{k}|^2\langle\mathbf{u}^2(T)\rangle \quad (2)$$

is the Debye-Waller factor. For the n th-order diffracted beam, the momentum change resulting from the elastic-scattering is:

$$\Delta\mathbf{k} = \Delta\mathbf{k}_n = \mathbf{k}'_n - \mathbf{k}_0 \quad (3)$$

where $\mathbf{k}_0$ and $\mathbf{k}'_n$ are the momentums of incident and n th-order elastically diffracted beams, respectively. $\langle\mathbf{u}^2(T)\rangle$ is the mean-square displacement of an atom from its equilibrium position. The slope M of $\ln[I(T)]$ versus T gives the surface Debye temperature and can be written as:

$$M = \frac{|\Delta\mathbf{k}_n|^2}{|\Delta\mathbf{k}_0|^2} \frac{\langle\mathbf{u}^2(T)\rangle}{T} = \frac{|\Delta\mathbf{k}_n|^2}{|\Delta\mathbf{k}_0|^2} \left(\frac{4\pi}{\lambda} \sin\theta\right)^2 \frac{3\hbar^2}{mk_B\Phi_D^2} \quad (4)$$

For the specular spot, the transfer of momentum, $\Delta\mathbf{k}$, is totally in a direction perpendicular to the crystal surface, while for $n > 0$ there is a parallel component of momentum transfer. The angle of incidence, θ , is defined from the plane of the surface, λ is the wavelength of the electrons, $\hbar$ is the Plank's constant divided by 2π , m is the atomic mass, k_B is Boltzmann's constant, and Φ_D is

the surface Debye temperature. The above analysis is valid for the high temperature limit ($T > \Phi_D$) and neglecting anharmonic lattice vibrations.

A RHEED study of the temperature dependence of the elastic diffraction intensity leads to a determination of the surface Debye temperature. The parameters $\Delta k_x/\Delta k_0$ and θ are obtained from the diffraction pattern. $\Delta k_x/\Delta k_0$ at some location on the n th-order streak is equal to the ratio of the distances from the transmitted beam to the specific location on the n th-order streak and distance from the transmitted beam to the specular spot. This analysis was conducted for the observed three phases of Pb on Si(111).

In Fig. 2 the intensity of a $\sqrt{3} \times \sqrt{3}$ streak of the 1 ML IC phase is plotted as a function of temperature. The $\sqrt{3} \times \sqrt{3}$ streaks disappeared to the background level at $\sim 300^\circ\text{C}$, consistent with previous observations of an order-order phase transformation to the 1×1 structure.⁵ The data show some deviation from the exponential Debye-Waller behavior. From the present results we cannot make a conclusion regarding if this deviation is real or it is due to errors in the data. We note that the intensity of the diffraction pattern for the 1 ML IC phase was significantly weaker than for the other two observed phases. It has been previously proposed that for an incommensurate adsorbate there is no true long-range order at temperatures above zero.¹³⁻¹⁵ The nature of order in such films is described as an extended short-range order. This is in contrast to a commensurate film which can have a true long-range order. For a commensurate film the intensity of the superstructure reflections can be described by an exponential Debye-Waller factor multiplied by a temperature dependent order parameter.^{16,17} For temperatures below that of a phase transformation, the order parameter can remain almost invariant and, thus, the intensity of the superstructure streaks can follow the exponential Debye-Waller behavior. For an

incommensurate film, where there is only an extended short-range order, theory predicts that a sharp diffraction pattern with intensity following the Debye-Waller behavior should exist at some temperature range.¹⁸ However, the diffraction intensity from incommensurate films are significantly lower compared to the commensurate case. This is due to the abundance of low-frequency oscillation modes which when excited weakens the diffraction pattern through the Debye-Waller effect.¹⁵ Deviation from Debye-Waller behavior can occur due to anharmonic effects, multiple-scattering (dynamic) effects on RHEED, and the presence of any temperature induced phase transformation. The exponential fit to the data gives a Debye temperature of 55 ± 15 K for the incommensurate 1 ML phase. The high temperature behavior of this phase above 412 K is not shown. The data above this temperature was scattered and depended on the annealing time. Several processes could have contributed to that. These include, changes in the ratio of the Pb incommensurate 1 ML phase to the 1×1 phase by annealing, thermal desorption reducing the surface density of the Pb atoms, and possibly phase transformations to other surface structures.

Annealing at ~ 360 °C results in strong $\sqrt{3} \times \sqrt{3}$ streaks also superimposed on the 1×1 streaks. We attribute this to the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ R-30° phase formed by desorption of the 1 ML IC phase. Figure 3 shows three-dimensional profiles of RHEED patterns for the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase obtained at three different temperatures. The general trend in decay of intensity along the RHEED streak depends on the momentum transfer, Δk , along the streak as expected from Debye-Waller behavior. Quantitative temperature dependence of the lowest order $\sqrt{3} \times \sqrt{3}$ RHEED streak intensity is shown in Fig. 4. The inset shows a semilogarithmic plot with an exponential fit to the data. As shown, the data follows the Debye-Waller behavior with a calculated Debye

temperature of 80 ± 10 K. In contrast to the 1 ML incommensurate phase which undergoes an order-order phase transformation at ~ 300 °C, the $\sqrt{3} \times \sqrt{3}$ streaks of the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase are observed up to ~ 570 °C, much higher than the Pb bulk melting point, $T_m = 600.7$ K. Above that temperature the $\sqrt{3} \times \sqrt{3}$ streaks disappears within the background. We point out that a $\sqrt{3} \times \sqrt{3}$ -R30° reconstruction of Si(111) was previously observed.¹⁹ However, our $\sqrt{3} \times \sqrt{3}$ -R30° phase cannot be due to this Si reconstruction because we can see the reversible transformation only in a certain amount time when the temperature is raised or lowered around 570 °C. After maintaining the sample near 570 °C for more than 10 seconds, the $\sqrt{3} \times \sqrt{3}$ pattern disappeared irreversibly due to thermal desorption. This transformation is probably an order-disorder phase transformation. The high temperature behavior of the $\sqrt{3} \times \sqrt{3}$ streak intensity for this phase was not shown in Fig. 4 due to the scatter in the data caused by further desorption, annealing, and/or a phase transformation.

After obtaining the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase and with further annealing at 400 °C for a few seconds, the $\sqrt{3} \times \sqrt{3}$ streaks became more intense than the original $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase. This ordered $\sqrt{3} \times \sqrt{3}$ structure remains above 450 °C. However, no specific transformation temperature was determined. This phase appears to be the $1/6$ ML $\sqrt{3} \times \sqrt{3}$ -R30° mosaic phase observed in the STM study of Ganz et. al.,¹⁰ and the study of Karlsson et. al.,²⁰ using angle-resolved photoelectron spectroscopy. This mosaic phase was proposed to consist of alternating chains of Pb and Si adatoms at T_4 sites, thus, forming 1:1 Pb to Si ratio. Temperature dependent RHEED indicates a Debye temperature for this phase almost the same as that for the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase, ~ 80 K.

In conclusion, we have observed three different phases of Pb on Si(111). The Debye temperature of the 1 ML incommensurate phase is measured to be 55 ± 15 K, while that for the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase is 80 ± 10 K. An order-disorder phase transformation for the $1/3$ ML $\sqrt{3} \times \sqrt{3}$ -R30° phase is observed at ~ 570 °C.

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FIGURE CAPTIONS

Figure 1

(a) A three-dimensional plot of RHEED pattern intensity profiles of Pb $\sqrt{3}\times\sqrt{3}$ -R30° structure on Si(111). The electron beam was incident along $\bar{1}\ \bar{1}\ 2$ azimuth of Si(111). (b) A line profile taken perpendicular to the streaks. One of the $\sqrt{3}\times\sqrt{3}$ streaks is used to show how background subtraction was performed.

Figure 2

$\sqrt{3}\times\sqrt{3}$ streak intensity of the 1 ML incommensurate phase plotted as a function of temperature. The inset is a semilogrithematic plot. An exponential fit to the data gives a Debye temperature of 55 ± 15 K.

Figure 3

A set of three-dimensional plots of RHEED intensity profiles for the Pb $1/3$ ML $\sqrt{3}\times\sqrt{3}$ -R30° phase at different temperatures. The middle two streaks are $\sqrt{3}\times\sqrt{3}$ streaks.

Figure 4

The intensity of the lowest order $\sqrt{3}\times\sqrt{3}$ streak of the $1/3$ ML $\sqrt{3}\times\sqrt{3}$ -R30° phase plotted as a function of temperature. The inset is a semilogrithematic plot. An exponential fit to the data gives a Debye temperature of 80 ± 10 K.

Fig. 1 (b)

Fig 2 (a)

Fig. 3(c)

Fig 3 (c)

Fig. 4

Time-resolved reflection high-energy electron diffraction of metal surfaces

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ABSTRACT

We review time-resolved reflection high-energy electron diffraction studies of 200-ps laser heated metal surfaces. The dynamic structural behavior is shown to be strongly dependent on surface orientation and is different from that observed under slow heating conditions. Single crystals of lead and bismuth are used as examples.

Keywords: electron diffraction, metal surfaces, melting, ultrafast phenomena

1. INTRODUCTION

Time-resolved reflection high-energy electron diffraction is used to study the structural behavior of the three low-index faces of Pb and that of Bi(0001). The surfaces are subjected to heating and cooling rates on the order of 10^{11} K/s. The open Pb(110) surface is seen to reversibly disorder below T_m .¹ This behavior is consistent with that well demonstrated by several groups using static heating conditions.^{2,6} In contrast to Pb(110), the close-packed Pb(111) surface superheats to T_m+120 K.⁷ Pb(100), a surface with atomic packing intermediate to that of Pb(110) and Pb(111), shows evidence of residual order at a temperature above that of bulk melting.⁸ For Bi, which is a semimetal, the close-packed Bi(0001) surface is shown to superheat by ~ 90 K.

2. TEMPERATURE DEPENDENT STRUCTURAL PROPERTIES OF SURFACES

In the past several years, it has become well established that the temperature dependent structural properties of the surface is different from that of the bulk.^{2,6} This is thought to be due to the asymmetric bonding at the surface atoms and the reduced number of nearest neighbors when compared with that of the bulk atoms. These properties of surface atoms manifest themselves as increased atomic mean vibrational amplitude at the surface (lower Debye temperature) and a reduced melting point for some surfaces. The reduction in the surface disorder temperature can be quite large as was observed for Pb(110).³ For Pb(110), a reversible order-disorder transformation was observed to begin at a temperature as low as 150 K below the bulk melting temperature $T_m=600.7$ K. The first atomic layer is fully disordered at ~ 50 K below T_m . The disordered state shows enhanced self diffusion similar to the liquid state and has liquid-like density and surface mobility. This order-disorder transformation is reversible and the thickness of the disordered layer increases with temperature. These observations were verified by several surface sensitive techniques.^{2,5}

The temperature dependent structural properties of lead crystals were found to be highly dependent on surface orientation.⁹ Fig. 1 shows a schematic of the three low-index faces of an fcc crystal, such as lead, and displays the orientation dependence of surface packing density. For an fcc metal, an atom on the {110}, {100}, and {111} surfaces has 7, 8, or 9 nearest neighbors, respectively compared to 12 nearest neighbors for bulk atoms. The least densely packed surfaces appear to have the highest propensity to disorder. A study of various Pb surfaces showed that the majority of crystalline faces exhibit surface disordering below T_m with exception of surfaces within $\sim 17^\circ$ of the {111} plans and $\sim 10^\circ$ of the {100} plans. The closed Pb(111) surface was observed to remain ordered up to the highest temperature studied, $T_m-0.05$ K, for a miscut angle $< 2^\circ$ from {111}.¹⁰

Pb(100), which has a packing density intermediate to Pb(110) and Pb(111), showed limited disorder for temperatures higher than 500 K. At $T_m - 2$ K a disordered surface of ~ 1.3 monolayer develop for the Pb(100) surface. This disordered surface layer remains stable up to the highest measured temperature, $T_m - 0.05$ K. The thickness of the disordered surface layer increases with the miscut angle and is ~ 3.5 monolayer for 10° miscut. The saturation of the surface disordered layer thickness is known as incomplete surface melting and is in contrast with the divergence of the disordered layer thickness on Pb(110) and the nonmelting of the Pb(111) surface.¹¹

While the phenomenon of surface melting and orientation dependent structural properties of surfaces have been thoroughly studied for Pb, experiments and modelling of other materials suggest the generality of these observations. For example, experiments on Al(110)¹² showed complete surface melting below its T_m similar to that observed for Pb(110). Surface disordering has also been observed in semiconductors such as Ge(111).¹³ Molecular dynamics modelling of fcc metals suggests that the propensity of a surface to remain ordered up to T_m depends on the surface orientation, in agreement with the experimental studies.¹⁴

We have been investigating the structural behavior of metals using time-resolved reflection high-energy electron diffraction (RHEED). Our work is aimed at determining how the crystal surface influences the temporal dynamics of melting during laser irradiation.

3. EXPERIMENTAL DETAILS

We use the technique of time-resolved reflection high-energy electron diffraction (RHEED) to study the structural behavior of metal surfaces upon ultrafast laser heating.¹⁵ A schematic diagram of the experimental setup is shown in Fig.2. A 200-ps (FWHM) Nd:YAG laser ($\lambda = 1.06 \mu\text{m}$) heats the sample while the electron probe pulse is generated by a photoactivated electron gun driven by the fourth harmonic of the Nd:YAG laser. The spacial delay line allows to vary the time between the fourth harmonic and the fundamental, thus, it is possible to obtain time-resolved RHEED patterns. The laser heating pulse and the electron probe pulse are synchronized to better than 1 ps. The diffraction patterns are acquired by a linear array detector with computer interface to capture line scans through the RHEED streaks. A mechanical shutter modulates the heating laser pulses while the RHEED patterns, obtained with the heating laser on or off, are sorted out in the computer and averaged in separate memories. This effectively compensates for shot-to-shot fluctuations in the laser.

The samples were cut from single-crystal rods aligned using Laue back reflection. All samples were grown from 99.999% pure metal. The surface was mechanically polished and then chemically etched. The samples were mounted on a resistively heated Mo base with a thermocouple placed between the retaining clip and the surface of the sample.

The time-resolved RHEED system was operated in ultrahigh vacuum (10^{-10} torr). The samples were cleaned *in situ* by cycles of Ar-ion bombardment followed by annealing within 15-20 K from T_m . A cylindrical mirror electron energy analyzer with an integral electron gun for Auger analysis is used to check for surface cleanliness that is maintained so as no detectable impurities are observed during data acquisition.

Electrons of 15 to 20 KeV in energy were used to obtain the RHEED patterns. The angle of incidence was ~ 1 to 2 degrees from the surface which results in a probed depth of < 5 Å. The skin depth of the $1.06 \mu\text{m}$ laser in lead and bismuth is ~ 150 Å. Therefore, the probed layer is essentially isothermal.

4. RESULTS

Time-resolved reflection high-energy electron diffraction is used to study the structural dynamics of surfaces as they are heated with ~ 200 -ps laser pulses. The procedure we follow in studying each surface is to first obtain RHEED pattern intensity as a function of temperature. In this case the sample is heated on a hot stage attached to the sample manipulator in the ultrahigh vacuum. The photoactivated electron gun is illuminated by ultraviolet light from an arc lamp which provides a stable source of light for photocathode activation. These measurements are conducted in order to provide information on (i) the temperature dependent structural properties of the studied surface under equilibrium, slow heating, conditions, (ii) the surface

atom mean vibrational amplitude, i.e. the surface Debye temperature, which shows as temperature dependence of the RHEED streak intensity. This temperature dependence of the RHEED streak intensity is used as a calibration curve for converting time-resolved RHEED intensity into surface temperature.¹⁶ An example for Pb(111) is shown in Fig. 3. In the inset the logarithm of the intensity of the RHEED streak, normalized to that at 407 K, at a particular location near its maximum intensity is displayed as a function of temperature. It shows exponential dependence as expected from Debye-Waller theory. This calibration curve is used to convert the time-resolved RHEED intensity obtained for the same conditions as for the static measurement. The temporal development of the surface temperature is displayed in Fig. 3. The solid line represents a solution of the heat diffusion equation for the experimental conditions used.

4.1 Pb(110)

Pb(110) is the least packed of the low-index faces of lead and its disordering properties below the bulk melting temperature is well established.³ In Fig. 4 the RHEED streak intensity observed near the maximum of the 01 streak is plotted as a function of temperature. The RHEED intensity is normalized to that at 487 K. The inset is a semilogarithmic plot. The intensity is seen to decay exponentially up to ~520 K. This is consistent with Debye-Waller behavior which describes the reduction in the number of elastically scattered electrons due to the increased mean atomic mean vibrational amplitude with temperature. Above 520 K deviation from the exponential behavior is observed. Above 540 K, the RHEED streak intensity decays into the inelastically scattered background as a result of the disordering of the probed surface layer. Thus, we identify the surface disorder temperature, T_d , to be 540 K.

We next discuss the time-resolved disordering of Pb(110).¹ In these experiments the sample base temperature was set at 487 K using the hot stage. The laser heating pulse raises the surface temperature from its initial base temperature to a temperature ranging from below to above the surface disorder temperature, T_d . The time-resolved intensity of the RHEED streaks is then obtained for given time delays between the laser heating pulse and the electron probe pulse.

The time-resolved modulation of the RHEED streak intensity for various laser intensities is shown in Fig. 5. This is to be compared with the solid line, which is the calculated intensity modulation obtained by converting the temperature obtained from the one-dimensional heat diffusion model to an intensity modulation using the calibration in Fig. 4. In Figs. 5(a) and 5(b), the laser heats the surface to temperatures less than the disorder temperature, T_d . A solution of the heat diffusion model for the experimental conditions used in Figs. 5(a) and 5(b) gives peak surface temperatures of 523 K and 537 K respectively. We then heated the surface with laser intensities sufficient to raise the surface temperature above T_d . For the case in Fig. 5(c), the model indicates that the surface temperature is raised to ~558 K, approximately 18 K above T_d . For the case of Fig. 5(d), a surface temperature rise of ~581 K is predicted, approximately 41 K above T_d . In both cases, there exists some time where we are unable to detect RHEED streaks, indicating that the probed surface region (~2 monolayer) is disordered. The time for which the streak vanishes depends on the level of heating above T_d and is ~200 ps for Fig. 5(c) and ~500 ps for Fig. 5(d). This is followed by reappearance of the RHEED streaks as the surface cools and reorders.

These results show that for Pb(110) subjected to heating and cooling rates of 10^{11} K/s, surface premelting is not bypassed and the disorder temperature appears to be unaltered from that under slow heating conditions. Moreover, the nucleation and growth of surface disorder occur on a time scale less than 180 ps even for ~18 K heating above T_d .

4.2 Pb(100)

We next discuss RHEED observations of Pb(100).⁸ For slow heating conditions, this surface was previously shown to experience incomplete surface melting. That is the disordered layer that forms on the surface remains stable in size up to $T_m - 0.05$ K. We first measure the temperature dependence of the RHEED streak intensity as shown in Fig. 6, in which the results were normalized to that at 377 K. A nonexponential decrease in diffraction intensity with temperature is observed starting at ~475 K. Similar deviation from Debye-Waller behavior was previously observed in high-resolution LEED experiments and is thought to be related to the surface thermal expansion which is about seven times that of the bulk in the temperature range of 300 to 470 K. Deviation from Debye-Waller behavior can also be attributed to an abrupt increase in vacancy concentration beginning at 510 K.¹⁷

To determine the peak temperature rise induced on the Pb(100) surface by the heating laser pulse, time-resolved measurements were performed at the delay time which gives maximum reduction in the RHEED streak intensity (time near maximum surface temperature rise). The RHEED streak intensity, normalized to that at 450 K, is plotted in Fig. 7, as a function of peak laser intensities, I_p . The normalized streak intensity is converted to a temperature rise, ΔT , using the calibration of Fig. 6, and the result is shown in the inset of Fig. 7. The temperature rise is observed to be directly proportional to I_p , as expected. The maximum peak temperature in all of these sets is below T_m . These data do not account for the effect of convolution due to the finite width of the electron probe pulse, which is comparable to that of the heating pulse. This finite pulse width of the electron probe tends to reduce the observed modulation to the streak intensity, and thus underestimates the temperature rise.

Similar time-resolved measurements were conducted for different sample initial temperatures and with laser intensities such that the surface was raised closer to T_m . Results are shown in Fig. 8. At sufficiently high I_p , the normalized streak intensity is observed to vanish, indicating that order has been lost in the probed surface layer. The data in Fig. 7 are used to determine the peak surface temperature at which the normalized RHEED streak intensity vanishes. This threshold intensity is converted to temperature rise using Fig. 6. Results show that the peak surface temperature when order is lost in the probed surface layer is 615 ± 20 K. The error bar indicated does not account for the convolution effects and changes in the thermal and optical properties of the sample. Accounting for these would lead to a somewhat greater peak surface temperature than what is reported. Thus, it is likely that residual order is present above T_m . At this temperature, the disordered layer appears to remain stable. Compared with results we will discuss for Pb(111), where superheating to ~ 720 K was observed, Pb(100) shows evidence of residual order at a much lower surface temperature.

4.3 Pb(111)

We next discuss laser heating experiments of Pb(111).⁷ The sample was biased at 586 K ($T = T_m - 15$ K) and transiently heated with varying peak laser intensities, I_p . The experiments were performed at the time corresponding to the minimum of the normalized streak intensity. We measured the RHEED streak intensity and normalized it to that at 586 K, as shown in Fig. 9. From the semilogarithmic plot in the inset of Fig. 9, two regimes are evident. First, where $I_p \leq 3.5 \times 10^7$ W/cm², the RHEED streak intensity follows an exponential decay with peak laser intensity, consistent with Debye-Waller behavior. Second, where $I_p > 3.5 \times 10^7$ W/cm², the RHEED streak intensity shows a deviation from exponential behavior indicating that the surface is experiencing disorder consistent with melting. The normalized streak intensity in the exponential region was transformed to a temperature jump, ΔT , by using the results of the static RHEED calibration. In the exponential Debye-Waller region, ΔT is proportional to the laser intensity, therefore, the lower values of the laser intensity and the corresponding temperature jumps can be used to relate the peak laser intensity with ΔT . When this is done, we observe the departure from Debye-Waller behavior to occur when the surface is heated to ~ 720 K. In addition, the temperature-dependent RHEED streak intensity has a slope, when plotted on a semilogarithmic scale, equivalent to that from the static RHEED measurements within the experimental error. This observation indicates that for peak a surface temperature less than 720 K, the surface remains ordered, cools below T_m , and exhibits Debye-Waller behavior. Thus, we conclude that Pb(111) can be superheated by ~ 120 K using ~ 180 -ps laser pulses. In this context, superheating refers to a lattice mean-square vibrational amplitude in excess of that at T_m which is still consistent with a Debye-Waller decrease in the elastic diffraction intensity. At higher temperatures melting occurs, resulting in a pronounced departure of the RHEED streak intensity from Debye-Waller behavior. The laser heating experiment with the sample biased at 586 K was also carried out at various times after the time of the minimum normalized RHEED streak intensity, ranging from 500 ps to 4000 ps. At all of the delay times examined, deviation from Debye-Waller behavior consistently occurred above a peak laser intensity of $\sim 3.5 \times 10^7$ W/cm² leading us to conclude that this deviation is due to melting on the surface.

The temporal evolution of the RHEED streak intensity was observed with the Pb(111) sample biased at 586 K. The normalized RHEED streak intensity was obtained at various delays between the arrival of the laser heating pulse and the pulsed electron probe. Results for a peak laser intensity of $I_p \approx 3.3 \times 10^7$ W/cm² are shown in Fig. 10(a). This data is consistent with classical heat diffusion, showing a fast decrease in the diffraction intensity as the laser pulse heats the surface and a rapid recovery as the heat is conducted to the bulk. In Figs. 10(b)-10(d) the surface was heated with $I_p > 3.5 \times 10^7$ W/cm², the threshold intensity for Debye-Waller behavior, as determined from Fig. 1. A qualitative difference between these

sets and Fig. 10(a) is evident. As I_p is increased, the diffraction intensity fails to recover to what is expected from classical heat diffusion. We attribute this to melting on part of the surface. In Figs. 10(b) and 10(c), the streak intensity exhibits an initially fast rise after the intensity minimum, similar to that seen in the nonmelting sets. In this time period the surface is most likely molten in some regions due to the nonuniformity of laser heating, which was measured by a scanning pinhole of 500 μm in diameter, to be $\pm 18\%$ across the surface, and is a superheated solid in the remainder of the probed area. The excess surface temperature diffuses for some time, τ , after which pronounced melting occurs, as reflected in the failure of the streak intensity to recover.

To extract τ we first compared the time-resolved RHEED intensity of the experiments that showed no melting and no superheating with those that were superheated but displayed no apparent anomalous behavior [see Fig. 10(a)]. This comparison showed good agreement indicating that the superheated sets that do not show melting display behavior consistent with classical heat diffusion. Having verified this, we then compared the time-resolved RHEED intensity of the experiments that showed melting with those that did not and looked for the time at which deviations occurred. A nonmelting, superheating set was normalized to a given melting set and subtracted from it. The resulting difference was then fitted with a polynomial and differentiated to observe the break from nonmelting behavior. The difference of this time and the time of the intensity minimum was identified as τ . The time τ was observed to decrease from ~ 1200 ps to < 300 ps for laser intensities corresponding to peak temperature rises of 130 K and 215 K, respectively. This demonstrates the decreasing time duration of superheating with increasing temperature.

4.4 Bi(0001)

We next report on a superheating study of Bi(0001) using time-resolved RHEED. Bi was chosen because, similar to Pb, it has a relatively low melting temperature and low vapor pressure at the melting point, and the fact that previous slow-heating experiments have demonstrated superheating of Bi crystallites. Some of these Bi crystallites melted after a time delay of about 30 min. when held at the bulk melting temperature, $T_m = 544$ K, and after about 10 min. when held at $T_m + 5$ K.^{18,19} Using time-resolved RHEED with ~ 200 -ps resolution we are able to achieve heating rates of $\sim 10^{11}$ K/s, approximately 13 orders of magnitude larger than that used in the Bi crystallite experiments. Because of the open pseudo-cubic crystal structure of Bi, liquid Bi is more dense than the solid, and it has been suggested that such unusual structural differences between a crystal and its melt may provide a barrier for rapid melting.²⁰ Upon melting, Bi experiences an increase in coordination number and in the electrical and thermal conductivities.²¹ This is in contrast to Pb, which, upon melting, experiences a positive volume change, maintains the same coordination number, and experiences a decrease in the electrical and thermal conductivities.²¹ We chose the close-packed (0001) surface for our superheating experiments since open surfaces are more likely to exhibit surface melting, providing a nucleation site for bulk melting at T_m .

The same experimental techniques were utilized as for Pb. Static RHEED measurements showed no surface disordering up to the highest temperature studied, 523 K ($T_m = 544$ K) and the RHEED streak intensity exhibited Debye-Waller behavior.

We next discuss our time-resolved RHEED measurements.²² Figure 11 shows the RHEED streak intensity normalized to that at 523 K at the time of minimum streak intensity and 4 ns later. For $I_p \leq 1.9 \times 10^7$ W/cm², the RHEED streak intensity is consistent with Debye-Waller behavior. For $I_p \geq 1.9 \times 10^7$ W/cm², deviation from the exponential Debye-Waller behavior is observed consistent with melting, and permanent laser damage on the surface. This damage could be visually observed and was accompanied by a reduction in the RHEED streak intensity. No such damage was observed in the case of Pb(111). This might be related to the negative volume change upon melting of Bi. When comparing the normalized RHEED streak intensity in Fig. 3 at $I_p = 1.9 \times 10^7$ W/cm² with the static calibration, we find that $\Delta T = 105 \pm 10$ K corresponding to a superheating of 90 ± 10 K. This superheating temperature, as well as that reported for Pb(111), does not account for convolution effects arising from the fact that the electron probe pulse width is comparable to the decay time of the surface temperature near its peak. Including this effect in the analysis would show a somewhat larger superheating.

5. CONCLUSION

The surface of lead crystals shows structural behavior that depends on the surface orientation when heated with 200-ps laser pulses. While the open Pb(110) surface disorders below the bulk melting temperature, it was possible to superheat the close-packed Pb(111) surface by up to 120 K. We have obtained similar superheating results for the Bi(0001) surface. We think that these general trends of the surface structural dependence on its orientation during pulsed laser heating can apply to other materials. In pulsed laser processing with sub-nanosecond lasers, this orientation dependence influence, to some extent, the threshold for surface melting and the resulting surface structure.

6. ACKNOWLEDGEMENT

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Fig.1 A schematic of the three low-index faces of a face centered crystal.

Fig.2 A schematic diagram of the time-resolved reflection high-energy electron diffraction system. Part of the laser pulse is frequency quadrupled and used to activate the photoactivated RHEED electron gun producing an electron pulse that is well synchronized with the laser heating pulse. Timing between the electron and laser heating pulses is set by the spacial delay line. The RHEED patterns are digitized and stored for further analysis.

Fig.3 RHEED streak intensity of Pb(111) normalized to that at 407 K obtained as a function of temperature. The inset is a semilogarithmic plot. The intensity was measured near the peak of the 01 streak. The reduction in RHEED streak intensity with temperature follows a Debye-Waller behavior with a Debye temperature of 61 ± 7 K.

Fig.4 RHEED intensity of Pb(110) normalized to that at 487 K versus temperature. The inset is a semilogarithmic plot.

Fig.5 Time-resolved RHEED streak intensity measurements on Pb(110) for different heating laser peak intensities. The heating laser pulse width measured at full-width at half-maximum is 170 ± 20 ps. (a) $I_p = 1.4 \times 10^7$ W/cm²; (b) $I_p = 2.0 \times 10^7$ W/cm²; (c) $I_p = 2.7 \times 10^7$ W/cm²; $I_p = 3.6 \times 10^7$ W/cm². The solid line is the calculated RHEED intensity.

Fig.6 RHEED intensity of Pb(100) normalized to that at 377 K versus temperature. The inset is a semilogarithmic plot.

Fig.7 RHEED streak intensity for Pb(100) at time of maximum modulation by the laser heating pulse. The sample base temperature was 450 K. The peak surface temperature ΔT versus peak laser intensity is shown in the inset.

Fig.8 Normalized RHEED streak intensity versus peak laser intensity for the Pb(100) sample at base temperatures successively closer to T_m .

Fig.9 RHEED streak intensity of Pb(111) normalized to that at 586 K versus peak heating laser intensity at the time corresponding to the minimum of the normalized streak intensity. The inset is a semilogarithmic plot that shows deviation from Debye-Waller behavior at $I_p \approx 3.5 \times 10^7 \text{ W/cm}^2$. The corresponding peak temperature is $\sim 720 \text{ K}$, approximately 120 K above T_m .

Fig.10 Time-resolved normalized RHEED streak intensity of Pb(111) irradiated with laser pulses of varying peak intensity. Set (a) is consistent with classical heat diffusion and corresponds to a superheating of $\sim 110 \text{ K}$. At higher peak laser intensities, the surface begins to melt and this is evident in the deviation of these sets from classical heat diffusion.

Fig.11 Time-resolved RHEED streak intensity of Bi(0001) normalized to that at 523 K versus peak heating laser intensity at the time corresponding to the minimum of the normalized streak intensity (a) and 4 ns later (b). Deviation from Debye-Waller behavior at $I_p = 1.9 \times 10^7 \text{ W/cm}^2$ is observed. The corresponding peak temperature is -630 K, approximately 90 K above T_m .

Time-resolved electron diffraction to study photoinduced molecular dynamics at single crystal surfaces

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ABSTRACT

We present a detailed description of ultrafast electron diffraction and its application to study photoinduced molecular dynamics at single crystal surfaces. Experimental investigations for a new design of an ultrashort pulsed laser activated electron gun ($\tau < 5$ ps) for time-resolved surface analysis are described. In addition, a novel electron detection and image analysis system, as it applies specifically to time-resolved reflection high-energy electron diffraction in the multiple-shot operation, are reviewed. The total experimental temporal resolution is discussed in terms of the electron pulse width and the time difference between an electron scattered at the front edge of the sample to an electron scattered at the trailing edge of the sample.

Keywords: time-resolved electron diffraction/ ultrafast spectroscopy/ surfaces science/ pulsed electron gun

1. INTRODUCTION

All time domain dynamical examination require a probe with comparable or shorter time resolution than the relaxation processes of the perturbed system, which for molecule-surface reactions are typically in the picosecond to femtosecond range. So far, all dynamical probe techniques are based on laser-light-surface reaction, because ultrashort laser pulses currently are the only means which fulfill the temporal requirements requisite for an initiating and monitoring transient events. However the complexity of molecule-surface dynamics may not be completely understood by laser probe techniques alone. Photon-activated probes with high temporal resolution combined with surface sensitive analysis techniques such as electron scattering techniques, provides a viable method for studying dynamics at surfaces with picosecond and even femtosecond temporal resolution. Electron diffraction has the advantage of revealing the surface structure and mean vibrational amplitude of molecules and atoms at the surface. Here, we describe our efforts at combining reflection high-energy electron diffraction (RHEED) with ultrashort pulsed lasers. In time-resolved RHEED the pump is a light pulse and the probe is a short pulse of high-energy electrons that is diffracted from the surface. This enables the observation of laser induced transient temperature and structural changes at the surface region with a time resolution limited by the duration of the electron pulse^{1,2} and the electron transit time across the sample. For example photoinduced charge transfer affects the bonding of adsorbates and can cause structural changes in both the adsorbate and the substrate. Using time-resolved RHEED, separate determination of the substrate-surface temperature and the adsorbate disorder (temperature) can be made simultaneously. In this way the prediction of nonequilibrium between the lattice (phonon) effective temperature and the adsorbate effective temperature after an ultrashort laser pulse can be directly tested.

In this paper we provide a full account of the technique and its application to adsorbate/metal systems. Specifically, we utilize a photoactivated RHEED electron gun excited by 2 picosecond laser pulses. The resulting electron beam pulses are less than 5ps wide, contain enough electrons and can be sufficiently well focused to produce high quality electron diffraction pattern. We describe the electron gun, the electron detection and data collection systems, and the time-resolved diffraction system performance.

2. TIME RESOLVED ELECTRON DIFFRACTION FOR SURFACE ANALYSIS

2.1 RHEED setup

Reflection high energy electron diffraction (RHEED) is one of several diffraction techniques that have the capability of investigating surface order with great accuracy. In the RHEED technique, high-energy electrons (10 - 20 keV)

Figure 1: a) A schematic diagram of RHEED showing the formation of the Laue rings on the phosphor screen. b) Semilogarithmic plot of the measured decay of the (01)-peak height as a function of the sample temperature.

are diffracted off an ordered surface at a glancing angle ($< 2^\circ$). For a flat single crystal, the RHEED pattern consists of a set of streaks oriented perpendicular to the sample surface (elastic two-dimensional Laue scattering) as shown schematically in Fig. 1a. The intensity of the diffraction pattern is temperature dependent, as in low energy electron diffraction (LEED). As the temperature is raised the atomic vibrational amplitude increases which leads to a reduction of elastically scattered electrons and causes a reduction of the diffraction pattern intensity. This is known as the Debye-Waller effect. Fig. 1b shows the measured peak height decay of one of the RHEED streaks as a function of temperature from a platinum single crystal, obtained during a static heating experiment. From the linearity of this semilogarithmic plot, it is evident that the RHEED streak intensity follows an exponential decay in accordance with the Debye-Waller theory. These intensities give us an accurate calibration of the temperature of the surface, i.e. the temperature of the surface can be determined by comparing the pattern intensity with this calibration curve.

Figure 2: Experimental setup for time-resolved RHEED. This technique allows to observe laser-induced transient temperature and structural changes at the surface region with a time resolution given by the duration of the electron pulse.

The use of time-resolved RHEED to study ultrafast dynamics at solid surfaces is a fairly recent development. It is explained in detail by Elsayed-Ali *et al.*¹ and will be discussed here only briefly. The basic concept of this technique is the use of a photo-activated electron-gun, which produces the electron probe pulse synchronized to a pump laser pulse to monitor a transient event. A schematic diagram of the experimental setup is illustrated in Fig. 2. The amplified dye-laser light is split

into two beams. One beam (pump) is used to transiently heat the sample surface. The other beam (probe) is frequency doubled and suitably delayed, and is used to generate a pulse of electrons at the photocathode of the electron-gun. The electrons are then used to probe the structure and mean vibrational amplitude of the surface by measuring the intensity change of the streaks on a phosphor screen as a function of the pump-probe delay. This enables the observation of laser-induced transient temperature and structural changes at the surface region with a time resolution limited by the duration of the electron pulse and transit time.

2.2 Picosecond electron gun

The development of femtosecond lasers and their extensive use to study various physical phenomena have motivated the development of subpicosecond temporal resolution streak cameras. In a streak camera, an optical signal is converted into an electrical signal using a photocathode. Ideally, the resulting electron pulse should be an exact temporal and spatial replica of the optical excitation pulse. The electron pulse is rapidly scanned (streaked) across a two dimensional observation plane, usually a phosphor screen/image intensifier⁴ or microchannel plates,⁵ by a set of high speed deflection plates.

Streak cameras operating in the subpicosecond time range have been successfully developed.^{4, 6-12} The instruments attaining the high temporal resolution have optimized electron optical components. The achievement of high temporal resolution is the result of using a photocathode with an extremely narrow photoemission electron energy distribution. Narrow energy widths insure that initial electron velocities are nearly identical such that the adverse effects of chromatic aberrations can be minimized in the electron beam forming optics. Photoemission electron energy widths as narrow as 0.1 eV can be achieved by selecting a photocathode material with a work function that is slightly less than the laser excitation photon energy, and employing a thin film which minimizes the redistribution of electron energies due to scattering during the process of emission and escape from the surface itself. The photocathode must be a conductor, or operated in a regime which guarantees charge balance to prevent the adverse effects of charging. Once a narrow temporal distribution of electrons has been produced with nearly the same kinetic energy, charged particle lenses must transport them to the target without temporally broadening the electron distribution. The primary causes of temporal redistribution in electron beams are path length differences between the photocathode and target for different segments of the electron beam and space-charge (Boersch) effects. In order to minimize the effects of space-charge broadening, the electrons should be accelerated as quickly as possible once exiting the photocathode, and the number of (low energy) beam cross-overs should be minimized. In addition, the deflection plates used in streak cameras possess fringing field inhomogeneities which must be carefully controlled in order to reduce temporal dispersion. Further care must be taken in the design of the deflection plates to control capacitive effects which limit slew rates and switching speeds. Finally, the efficiency of the electron detector must be as high as possible. Single electron detection can be accomplished with phosphor screens and image intensifiers, or array detectors such as that used in a Vidicon.¹³

In order to minimize transit time broadening due to path length differences between electrons following different trajectories from the photocathode to the target, the initial electron spatial distribution must be small (much smaller than the inner diameter of the smaller electron focusing electrode). The use of long focal length lenses also decreases transit time dispersion due to path length differences. Space charge broadening of the electron pulse near the photocathode can be minimized by using as large an extraction field as possible. The large extraction field quickly accelerates the electron pulse thereby minimizing the time when low energy electrons in close proximity can exchange energy. The extraction field is limited, however, by the vacuum breakdown field and the presense of any asperities on the cathode surface which might begin to undergo field emission. Typically, maximum d.c. electric fields near the cathode are limited to 5 kV/mm even though vacuum breakdown occurs near 30 kV/mm. Space-charge broadening can also occur in the post-cathode electron optical column near beam cross-overs and in regions of space where the electrons are significantly decelerated for focusing. The effects of space-charge broadening in the electron-optical transport column can be mitigated through careful electron optical design of the electrostatic lens elements,^{5, 6, 8-12} or through the use of magnetic focusing lenses⁷ where the electron velocities are not changed. Both approaches have yielded picosecond temporal resolution, although the suitability of magnetic focusing systems to ultrahigh vacuums maintained for surface science remains problematic. Single shot temporal resolution of 0.3 ps has been demonstrated.^{8, 10, 11} For multiple-shot operation, jitter represents a major source for loss of temporal resolution. Synchroscan operation of a Photochron IV streak tube has demonstrated 930 fs temporal resolution.¹² Our goal was an electron gun similar to the Photochrom IV streak tube, but with focussing conditions that provide a real image 500 mm from the photocathode, and a beam that is relatively collimated (convergence angle about 1 mrad). Both requirements are necessary to use the electron gun for diffraction techniques, i.e. in order to separate diffraction spots and lines in the diffraction pattern.

Figure 3: Electrode configuration of the photoactivated electron gun together with the nominal operating voltages.

Primarily for design simplicity, and ultimately for UHV compatibility, we have selected an all electrostatic focusing system for our time-resolved RHEED gun. A schematic cross section of the Photoactivated RHEED gun is shown in Fig. 3. The photocathode is held at potential V_0 . While the emitted electrons are spatially divergent, a pinhole is used to extract relatively collimated electrons. This extraction electrode is part of the first lens and is held at a potential V_1 such that the photoelectron extraction field is large. Electrodes with potentials V_1 , V_2 and V_3 form the first extraction lens. This zoom lens configuration is selected for its robust performance at long focal lengths, and small intrinsic aberrations.¹⁴ Electrodes with potentials V_3 , V_4 and V_5 form a long focal length Einzel lens used for secondary focusing. Two lenses are necessary for focusing the electron beam at a distance of 0.5 m from the photocathode with a nominal spot diameter on the target of less than 300 μm with a nearly parallel beam. The requirement of a well focussed and collimated electron beam is necessary for RHEED applications.

In addition, no crossover points are located inside the electron lens column. These conditions are consistent with maintaining low electron density inside the electron lens column in order to minimize space-charge broadening in that region. Some compromise between these requirements and that of maximizing the electric field and potential throughout the photocathode-to-anode region is incorporated in the design. For example, a relatively long electron lens column was necessary in order to achieve good electron collimation over the relatively long distance of 0.5 m.

The spatial distribution of emitted electrons is defined primarily by the diameter of the illuminating radiation, and secondarily by the angle defining pinhole aperture in the extraction electrode V_1 . The nominal diameter of this aperture is 200 μm . The size of the optical pinhole image formed on the photocathode determines the size of the focussed beam on the screen and represents, therefore, the physical source of the electron optical transport lenses. Since the cathode is held at -15 kV, and the extraction electrode is held at -8.75 kV, a planar extraction field of 3.125 kV/mm accelerates the photoemitted electrons. Characteristic of planar extraction fields is a linear magnification of nearly 1. The angular width of the source at the pinhole is 10 mrad assuming uniform emission at the photocathode into all directions. This is a conservative upper limit. The inner diameter of all of the lens elements is 15 mm with the exception of the inner diameter in the focusing electrode V_2 , which is 3 mm. The zoom lens forms a virtual image of the source which is in turn focussed onto the phosphor screen by the Einzel lens.

The electron optical properties of the RHEED gun were computed numerically, based on solving Laplace's equation for given boundary conditions, using the boundary element method.¹⁵⁻¹⁸ The performance of the entire electron optical transport system is given explicitly in Table I. The spot size is dominated by the magnification of the source, implying that the RHEED spot on the target could be further reduced in size by using a smaller pin-hole aperture (at the expense of current). Electron lenses possess focusing defects much in the same way that conventional optical lenses do. However, these focusing defects or aberrations are far more severe in charged particle optics lenses. Of the primary aberrations perhaps the most important is spherical aberration. The spherical aberration results from off-axis fields being stronger than those on axis, resulting in a stronger focusing of far off-axis trajectories. It is impossible to eliminate spherical aberrations in conventional,

axially symmetric lenses without introducing space-charge on axis. The chromatic aberration results from the focus defect associated with finite energy distributions within the electron beam itself. Since electron lenses essentially focus the momentum of the electrons, more energetic electrons are focused more weakly than lower energy electron resulting in a focusing error. Coma is a focus defect whereby off axis rays entering the optical system with differing angles are not uniformly focused. Characteristic comma-shaped beam distributions are common in systems dominated by coma. The distortion aberration causes off-axis rays to be displaced. The most common manifestation of distortion is the mapping of a square array into a barrel shaped or pin-cushion shaped pattern in the image plane. The image is distorted (in shape) with respect to the object, and is most severe for extreme off axis rays of little slope. Finally, astigmatism and field curvature are aberrations whereby different axes of the image are focused with different strength as a result of off-axis illumination. A defocused image will result if the above aberrations are not anticipated and corrected.

Table I: Electron Optical Column Performance

Linear magnification	1.68
Angular Magnification	0.38
Spherical Aberration Coefficient	51859 mm
Chromatic Aberration Coefficient	21 mm
Astigmatism and Field Curvature	2671 mm
Coma	46 mm
Distortion	0.25 mm
Image Radius (spherical aberration)	0.0229 mm
Image Radius (chromatic aberration)	0.0001 mm
Image Radius (magnified source)	0.1680 mm
Image Radius (astigmatism)	0.0820 mm
Image Radius (coma)	0.0492 mm
Image Radius (distortion)	0.0066 mm
Image Radius (diffraction)	0.0000 mm
Image Diameter (0.2 mm aperture)	0.34 mm
Convergence Angle (upper limit)	3.80 mrad
Convergence Angle (half intensity)	1.30 mrad

The temporal resolution of this lens column was also computed from a knowledge of the all orders trajectories. The average transit time from photocathode to the scattering target is calculated to be 7350.7 ps. The deviation in transit times weighted for all trajectories through the RHEED gun was computed to be 1.26 ps, full width at half maximum. The choice of lens potentials shown in Fig. 3 indicates that the electron beam never has less than 5.625 keV of kinetic energy after the extraction pinhole in order to reduce the effects of space-charge broadening. This would have been impossible to achieve with a single electron lens column.

An electron gun has been constructed based on the above design. The outside diameter is 25 mm and the overall length is 330 mm. The lenses, anode, and diffraction plates are made out of aluminium and fabricated in our laboratory. Ceramic balls were used as spacers between the lenses. Deflection plates are incorporated at the end of the gun in order to steer the photoelectron beam towards the sample. The electron gun assembly is shielded with a μ -metal tube to avoid any distortion of the electron beam from stray magnetic fields (primarily the earth's field and the magnets of the ion-pump system). The photocathode is a 40 nm thick Ag film evaporated on a sapphire window. Metals are good candidate materials for laser-driven photocathodes because of the ease of preparation, high damage threshold, and large free-electron density. The main drawbacks of metals are low quantum efficiencies and the high work function (4-5 eV) which requires UV photons for linear (one photon) photoemission. The photocathodes are processed by thermal evaporation in a separate chamber and were installed into the electron gun without further processing.

2.3 Laser system

The laser system used in the experiments consists of a cw pumped, mode-locked Nd:YLF (Neodimium Yttrium Lithium Fluoride) master oscillator, a Nd:YLF regenerative amplifier and a dual jet, synchronously pumped dye laser with 2 amplification stages. The amplified dye laser output is 20 μ J/pulse at 500 Hz at 590 nm. The amplified dye laser pulses ($\tau < 2$

ps) are then focused into a KDP crystal to generate the second harmonic at 295 nm, which is then focused onto the photocathode of the electron gun. A sapphire window passed the slightly focused ($f = 500$ mm) UV beam into the vacuum system onto the Ag-photocathode at normal incidence.

2.4 Electron gun performance

The electron gun was tested first for operating voltages as indicated in Fig. 3. The average photocurrent was measured with a Faraday cup connected to a picoammeter. The current was found to be directly proportional to the laser intensity up to a pulse energy of about $0.5 \mu\text{J}$, focused to a $300 \mu\text{m}$ spot diameter. The measured average electron current at this pulse energy was 3.5 pA , which results in about 5×10^4 electrons per pulse at a repetition rate of 500 Hz . Thus, the instantaneous current within individual pulses is 1.3 mA . Space-charge effects at higher intensities limit the emission of electrons for $I > 0.5 \mu\text{J}$. When the charge of the extracted photoelectrons reaches a certain value q_c , the amplitude of the electric field falls to zero and any additional photoelectrons cannot be emitted until part of the electron cloud has left the surface region. The temporal resolution is known to deteriorate quite rapidly above this region due to space-charge broadening. Therefore, the electron pulse must be generated with minimum of space-charge dispersion in order to obtain the desired temporal resolution. The laser induced damage threshold of the photocathode is about $1 \mu\text{J}$ ($1 \text{ mJ}/\text{cm}^2$) as evidenced by visible damage to the cathode. In order to determine the temporal width of the electron pulse, we use a jitter-free streak camera device as described in Ref.19. For laser pulse energies $< 0.5 \mu\text{J}$, the electron pulse was shorter than the temporal resolution of our streak camera ($< 5 \text{ ps}$). Therefore, an upper limit on the electron pulse width of $\tau_e < 5 \text{ ps}$ can be concluded.

2.5 Electron detection and image analysis system

Time-resolved RHEED is signal limited when compared to conventional static RHEED systems. The electron signal has a pulse length of only a few ps and the number of electrons available in a single pulse is small ($\sim 10^4$ per pulse). Therefore, in order to obtain quantitative information of the diffraction intensity, it is essential to have an image detecting device with single electron sensitivity and with a very low dark current. This requirement can be fulfilled with high gain microchannel plates (MCP) as an amplification stage followed by a phosphor screen. The signal obtained from the phosphor screen can then be recorded and analyzed. The spatial resolution is limited by the MCP channel diameter and their center-to-center spacing. As shown in the schematic diagram of Fig. 4, we use a chevron MCP detector with a 40 mm diameter P20 phosphor screen on a fiber optic faceplate as the vacuum interface. The fiber optic faceplate provides one-to-one imaging of the diffraction pattern, i.e., a recording film or an array detector with another fiber optic window can be placed directly in contact with it without requiring any further focusing. The MCP and phosphor screen are placed 170 mm from the sample where the electron beam is diffracted. This location allows the points and line patterns to be separated easily even for high-energy electrons and for observing superstructures.

Figure 4: Electron detection and data collection systems currently used in our time resolved RHEED setup.

As shown in Fig. 4, the data collection system is based on a CCD camera, a video frame grabber, and a 486 computer. Our image analysis system is similar to the one previously reported by Clarke *et al.*²⁰ That system was used to measure RHEED signals as a function of time during molecular beam epitaxy (MBE) film growth. Our system is not configured for real time signal monitoring. Thus, there are a number of choices that we made in our system configuration to

achieve high performance as well as low cost. Our temporal resolution comes from the timing between laser and electron pulses (time when the laser beam impinged on the sample and the time when the electron beam arrived). Because the laser repetition rate is 500 Hz, no attempt is made to synchronise the laser to the video camera. Instead, multiple pulses (from 80 to 500) are averaged for each video frame. Further signal averaging is accomplished by adding data from multiple video frames.

Our CCD detector is a Pulnix TM-745E camera. This was chosen because of its relatively low cost, high sensitivity, as well as its ability to integrate low light level images in the camera. Typically, we would integrate each frame for one second. This is accomplished by using a logic signal from a Keithley PIO-12 board in the computer to turn on the image inhibit line to the camera. The only disadvantage of this camera is its inability to manually control the black level. In most cases this is not a serious problem since the background level is determined from video frames collected with the laser on and with the laser off. These are collected alternately by opening and closing a shutter in the path of the laser beam by using a logic signal from the Keithley board to operate a Uniblitz VS14S1w0 control unit and shutter.

We use an Imaging Technology VFG frame grabber. Though we had planned to use a feature of this frame grabber board that allowed the use of a higher performance non-standard video camera, we found that the Pulnix camera worked adequately for our application. The data collection cycle is designed to minimize deadtime. At the end of a camera integration cycle the whole video frame is grabbed. The shutter is opened or closed and the next camera integration cycle is started. During the time the camera is integrating the next frame, the data from the previous frame is processed. Thus, it is crucial that all the data can be processed by the time the next video frame from the camera is ready to read. We found that for a 1 second integration time more than half of the video frame could be processed. A greater proportion of the frame could be handled either by increasing the integration time or by using a faster computer.

We organized the data collection into different regions on the CCD array. Usually, one or more regions are used to collect the RHEED pattern, one to measure the overall background level, and a few to measure the intensity in individual streaks. The most time consuming portion of data processing for the regions consists of transferring the data values from the frame grabber board memory into the computer memory. Then the data can be stored as an image. Usually, the data in a region is compressed into line format by adding the data values by row and/or by column. This generates a line scan that is typically used to show the multiple peaks in a RHEED pattern. Also, the total intensity in the region is computed and stored. Such data is analogous to RHEED oscillation data that is used in MBE growth. The total intensity is displayed on the computer screen primarily to allow the users to follow the data collection process, but it is also useful for measuring the background level and for calibration. The whole video image is also displayed on a separate TV monitor. In order to achieve adequate signal-to-noise ratio, multiple video frames are collected and averaged for each time delay. At the end of signal averaging for a given time delay (typically 2 minutes) the laser-on and laser-off data for each region is stored on the hard disk, the optical delay line is changed to a new time delay, the data arrays are reinitialized, and the process is restarted. By storing the laser-on and laser-off data separately, further data processing could be delayed until after the experiment is completed.

2.6 Transient surface temperature rise and fall

As mentioned above, the electron pulse is used for surface analysis; primarily for probing the surface temperature and order by utilizing the time-resolved RHEED technique. Fig. 5 shows the two-dimensional diffraction pattern (RHEED streaks) of a Ni(100) surface with adsorbed oxygen $c(2 \times 2)$ structure, along [010] azimuth, using ultrashort ($\tau < 5$ ps) electron pulses. The image was recorded on a photographic film in contact with the fiber optic faceplate. The electron gun was operated at 18 kV. The fine streak pattern (zero order Laue ring L_0) and even some Kikuchi lines are clearly visible and demonstrate the excellent signal-to-noise ratio that we achieve with our short electron pulses. The first order Laue ring L_1 does not appear in the picture because the L_1 -radius for the incident electron beam energy of 18 keV is larger than that of the RHEED screen.

As previously observed by several authors,²¹ adsorption of oxygen on clean Ni(100) at 400K leads to the appearance of an ordered overstructure. First, at low oxygen coverage ($\Theta \leq 1/4$ ML) the overstructure forms the $p(2 \times 2)$ structure and then, for longer exposure ($\Theta \leq 1/2$ ML), the $c(2 \times 2)$ structure forms. It should be emphasised that in spite of the low oxygen coverage and the small number of electrons produced by the ultrashort electron pulses (compared to the conventional cw RHEED technique) the additional diffraction pattern due to the ordered oxygen overstructure is clearly visible. This allows

Figure 5: RHEED pattern of a Ni(100) surface, [010] azimuth, with adsorbed oxygen c(2x2) structure, using ultrashort ($\tau < 5$ ps) electron pulses.

investigation of transient phenomena of the substrate and adsorbed species at the same time. For example, a thermal nonequilibrium in the adsorbate-metal complex after a laser heating pulse can be directly monitored in real time.

Fig. 6 shows a line scan through the diffraction pattern of a Pt(111) surface approximately perpendicular to the streaks through the maxima. The data were obtained with the CCD camera and processed with the frame grabber as discussed above. The line scan is an integration of 5 rows (5 pixels of the CCD camera) in order to average over fluctuations in the direction along the streaks. Fig. 6a shows the raw data after signal averaging for one minute (60 frames at one sec.). Immediately after the measurement, the CCD background of 60 frames was also measured and subtracted from the raw data. Fig. 6b illustrates the same line scan after the background subtraction. No smoothing is necessary for further data processing.

Figure 6: Line scan through the diffraction patterns of a Pt(111) surface. a) the raw data after signal averaging for 60 frames at 1 sec. b) after subtracting the CCD background from the raw data.

As discussed above, the basic idea of the time-resolved RHEED experiment is to observe laser induced transient temperature and structural changes of the surface region. As an initial experiment, we measured the temperature change of a clean Pt(111) single crystal surface after a 100 ps IR-laser (1.054 μ m) heating pulse. The reduced streak intensity due to the laser pulse was compared with a calibration curve obtained by a static heating measurement. Based on this calibration the heating laser pulse raised the surface temperature by 20° K (see Fig. 7). In order to minimize experimental error due to long-term drift, a computer-controlled shutter is placed in the path of the heating beam. The purpose of the shutter was to chop the heating beam at a frequency of 1 Hz which allows to quickly alternate between a hot (shutter open) and a cold (shutter closed) measurement. The normalized difference between the hot and the cold measurement was averaged over 60 cycles. An exposure time for one point (delay time) of 2 min. (includes both on and off time) is needed for such a small temperature change to average out shot-to-shot laser fluctuations of the heating laser pulse, the electron probe pulse, and the gain of the

MCP plates. Because of the glancing angle of incidence of the electron probe pulse and the perpendicular direction of the heating laser pulse, the temporal resolution is not only limited by the pulse width of the electron gun but also by the time difference between an electron scattered at the front edge of the sample to an electron scattered at the trailing edge of the sample. Therefore, in order to increase the overall temporal resolution of this technique below 15 ps, the sample must be smaller than 1 mm across.

Figure 7: Transient surface temperature rise and decay of a Pt(111) single crystal surface after a 100 ps laser heating pulse.

3. CONCLUSION

We described in this paper our efforts at combining reflection high energy electron diffraction (RHEED) with ultrashort pulsed lasers. Time-resolved RHEED enables the observation of laser-induced transient temperature and structural changes at the surface region on the time scale characteristic of the relaxation of vibrational motion and, therefore, allows investigation of transient phenomena of the substrate and adsorbed species. In this way the prediction of nonequilibrium between the lattice (phonon) effective temperature and the adsorbate effective temperature after an ultrashort laser pulse can be tested in real time.²²

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TIME-RESOLVED SURFACE ELECTRON DIFFRACTION

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I. INTRODUCTION

The study of the dynamics of surface phase transformations and reactions are of significant interest to understanding two dimensional behavior. Moreover, an understanding of surface reactions is important in many areas of technology which include thin film growth, surface processing, and surface catalyzed reactions. Many of the surface reactions and phase transformations occur in an ultrafast time scale. For example, the nucleation of melting could be in the picosecond time domain, or even faster depending on the experimental conditions [Schulz et. al., 1990]. Surface reconstruction and other diffusionless phase transformations can also occur in the picosecond time domain. Charge transfer between substrates and adsorbates could be virtually instantaneous (in the femtosecond time scale) [Pelak et. al., 1995]. A similar conclusion can also be made regarding photoinduced desorption. Surface vibrational states can have a relatively longer decay time which could extend to the nanosecond time domain. A better understanding of the dynamics of these surface processes has been the goal of many studies performed in the past several years. These studies have, to a large extent, utilized new ultrafast surface sensitive techniques based on the use of ultrafast lasers to initiate a surface reaction followed by probing of the electronic or structural properties of the surface using laser-based ultrafast surface probes. For example, time-resolved photoemission spectroscopy [Boker et. al, 1985; 1989; Schoenlein et. al., 1987; Schmittenmaer, et. al., 1994 ; Aeschlimann, et. al., 1995a] using a pump-probe arrangement have yielded important information on the electronic properties of surfaces and interfaces with femtosecond temporal resolution. The vibrational relaxation of adsorbates has been investigated using time-resolved sum frequency generation [Harris and Levinos, 1989; Harris et. al., 1990; Shane et. al., 1990] and infrared reflection absorption spectroscopy [Cavanagh et. al., 1992] . Time-resolved second-harmonic generation has been used to study the structural properties of laser heated surfaces [Hicks et. al., 1988; Tom et. al., 1988]. While surface electron diffraction has been used for many decades to characterize the atomic surface structure, surface diffraction techniques with high time resolution has only recently become available through the first demonstration of low energy electron diffraction (LEED) with

nanosecond time resolution [Becker et. al., 1984] and reflection high energy electron diffraction with ~ 100 picosecond time resolution [Elsayed-Ali and Mourou, 1988]. A time-resolved RHEED system with better than 5 ps temporal resolution has recently been developed [Aeschlimann et. al., 1995b]. Developments of a time-resolved LEED system with up to subpicosecond temporal resolution is underway [Weber et. al., 1995]. Here we review these developments and present results obtained on the dynamics of surface melting of the low index surfaces of Pb and of the close-packed Bi(0001) surface.

II. ELECTRON DIFFRACTION

A. Geometric Surface Electron Diffraction

Both LEED and RHEED are surface-sensitive probes for long-range order (~ 100 Å or more) which provides information on the atomic structure of surfaces. A diffraction pattern gives a statistical average of the structural arrangement of surface atoms over the entire probed region. In LEED, electrons with energies ranging from few tens of volts to several hundred volts are diffracted off the surface of a crystal. The angle of the electron incidence can widely vary, however, typically near normal incidence is used. For electron energies used for LEED, the electron mean escape depth is ~ 3 - 10 Å according to universal curves which are almost independent of the crystal material for electron energies up to ~ 200 eV [Riviere, 1973; Clarke, 1985; Zangwill, 1988]. LEED is therefore an intrinsically surface sensitive technique. Other advantages of LEED are that electrons may be directed to the surface at normal incidence, and that the two dimensional periodicity of the surface is displayed by a single diffraction pattern. The experimental techniques, the analysis of diffraction patterns, and implications regarding the structures of surfaces have been well reviewed [Lagally, 1985; Pendry, 1974; van Hove et. al., 1986]. A typical apparatus consists of an ultrahigh vacuum chamber, an electron gun featuring a thermionic electron emitter, and an electron detector. While two dimensional diffraction patterns are conveniently displayed by a phosphor screen, quantitative measurements of electron currents in individual diffraction spots are often performed with a Faraday cup.

In RHEED, fast electrons (10-50 keV) are incident on the surface at a glancing angle which is typically $< 3^\circ$. At these energies the penetration depth of the electrons can be quite large, in the range of several hundred Å. However, because of the glancing angle of the incident electrons in RHEED, the electrons only probe a few atomic layers into the surface. The RHEED geometry is particularly suitable for conditions when thin film growth is monitored since the detection screen can be located far from the sample.

Diffraction results when the Laue condition

$$(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R} = 2\pi m, \quad (1)$$

where $\mathbf{R} = n_1 \mathbf{a} + n_2 \mathbf{b}$

is satisfied. $\mathbf{k}$ and $\mathbf{k}'$ are the incident and scattered electron wavevectors. $\mathbf{R}$ is the Bravais lattice vector where $\mathbf{a}$ and $\mathbf{b}$ are the primitive lattice vectors for the surface, and m , n_1 and n_2 are integers [Lagally, 1985; Mahan et al., 1990]. The Laue condition can be satisfied for positive and negative values of m . The wave vectors give the direction and deBroglie wavelength of the electron beam such that

$$\mathbf{k} = \mathbf{p}/\hbar \quad (2)$$

with the magnitude of the $\mathbf{k}$ vector

$$|\mathbf{k}| = 2\pi/\lambda \quad (3)$$

where $\mathbf{p}$ is the electron momentum, $\hbar$ is Planck's constant divided by 2π , and λ is the electron wavelength, which can be obtained from the relativistic expression

$$\lambda = \frac{h}{\left\{ 2m_0 q V \left[1 + \frac{qV}{2m_0 c^2} \right] \right\}^{1/2}} \quad (4)$$

where h is Planck's constant, m_0 is the electron rest mass, q is the electron charge, V is the accelerating voltage, and c is the speed of light [Mahan, 1990].

The Laue diffraction condition can be illustrated by the Ewald sphere construction which represents a graphical method illustrating the conditions of constructive interference combined with single scattering to find the direction of the diffracted intensity maxima. When considering elastic scattering $\mathbf{k}-\mathbf{k}'$ defines a sphere of radius $2\pi/\lambda$, which is called the Ewald sphere. The origin of the $\mathbf{k}$ -space is at the point which the incident electron beam intersects the surface, which is the same point at which the diffracted beam emerges. The diffraction condition is given by the intersection of the Ewald sphere with the reciprocal lattice points [Lagally, 1985]. The reciprocal lattice vectors are obtained from the real lattice vectors by the transformation

$$\begin{aligned} \mathbf{a}^* &= \frac{2\pi \mathbf{b} \times \hat{\mathbf{n}}}{A} \\ \mathbf{b}^* &= \frac{2\pi \hat{\mathbf{n}} \times \mathbf{a}}{A} \end{aligned} \quad (5)$$

$$\text{where } A = \mathbf{a} \cdot \mathbf{b} \times \hat{\mathbf{n}} .$$

These are the two-dimensional analogs of the standard equations for calculating the reciprocal lattice. $\mathbf{a}$ and $\mathbf{b}$ are the primitive lattice vectors which generate the surface structure, $\mathbf{a}^*$ and $\mathbf{b}^*$

are the corresponding reciprocal lattice vectors, $\mathbf{n}$ is a unit vector normal to the surface, and A is the area of the two-dimensional primitive cell. Because of the two-dimensional nature of the surface, the reciprocal lattice net has a rod shape. The reciprocal lattice rods extend normal to the sample's surface [Pruyton, 1994; Mahan, 1990].

For LEED, where the electron energy could be 150 eV, the corresponding electron wavelength is $\lambda = 1 \text{ \AA}$. For RHEED, where for the results presented here the electrons are accelerated to 15 kV, which corresponds to $\lambda = 0.09 \text{ \AA}$. Thus, the radius of the Ewald sphere is much bigger in RHEED compared to LEED. Figure 1 is a schematic diagram illustrating the principles of LEED and RHEED. The intersection of the Ewald sphere with the reciprocal lattice rods is illustrated for both techniques. In the LEED geometry, Fig. 1(a), where electrons are usually incident normal to the surface, the Ewald sphere intersects a number of reciprocal lattice rods nearly parallel to the surface. Thus, a section through the reciprocal lattice can be imaged on the LEED screen. In RHEED, Fig. 1(b), the Ewald sphere cuts the reciprocal lattice rods at a grazing angle. Thus, the RHEED geometry provides only one section of the reciprocal lattice. LEED patterns provide a sharp spot pattern, whereas, RHEED patterns usually show some streaks or elongated spots which is sometimes referred to as rods. There are several common explanations for the observation of streaks (as opposed to spots) in RHEED. It is generally believed that under ideal experimental conditions a surface of high quality will generate a RHEED pattern consistent of spots. However, the frequently observed RHEED streaks can result from a high quality surface if we consider the instrumental response and thermal diffuse scattering due to surface atom vibrations [Holloway, 1979]. When considering the instrumental response, the finite width and the divergence of the electron beam results in the smearing of the origin of the k -space and hence the center of the Ewald sphere. A finite electron energy spread results in the Ewald sphere becoming a thin spherical shell with a thickness determined by the electron energy spread. The streaks are thought to result, or extend, due to the glancing angle of the incident electron beam, which results in an Ewald sphere intersecting the reciprocal lattice rods over an extended length. In most experimental cases, the observation of RHEED streaks is probably due to a combination of several effects, and can occur even from a high quality surface [Mahan, 1990].

In geometric RHEED, it is often found that the most important quantity measured is the spacing between the RHEED streaks. This is inversely proportional to the interatomic distance in the real lattice. The RHEED streak spacing is directly proportional to the spacing between the reciprocal lattice rods for a particular azimuthal orientation of the sample giving a symmetric pattern. The streak spacing observed on the phosphor screen of the RHEED system, W , is related to the reciprocal lattice spacing perpendicular to the direction of electron incidence, a^* , through the relation

$$\frac{W}{L} = \frac{a^*}{(2\pi/\lambda)}, \quad (6)$$

where L is the sample-to-screen distance and $2\pi/\lambda$ is the magnitude of the incident electron

thus, most of the laser energy is available to irradiate the sample. By spatially delaying the ultraviolet laser pulse from the fundamental, it is possible to obtain diffraction patterns of the studied sample from a few hundred picoseconds to up to tens of nanoseconds after laser irradiation. The spatial delay line allows to vary the time between the fourth harmonic and the fundamental. The laser heating pulse and the electron probe pulse are synchronized to better than 1 ps. We use the picosecond electron pulse to obtain a reflection high energy electron diffraction (RHEED) pattern of a clean surface.

The picosecond RHEED technique was used as a surface temperature probe and significant development was made to make it sensitive enough to detect the surface lattice temperature with a few degrees accuracy and ~ 100 -ps time resolution. This proved to be particularly challenging at high temperatures due to the increased background level in the RHEED patterns. These developments included: (i) The assembly of a 50-Hz, double-pass amplifier capable of delivering up to 30-mJ pulses with ~ 100 -ps pulse width to replace the 15-Hz system previously used. The increased repetition rate is very helpful in signal averaging, which enhances signal-to-noise ratio. (ii) Fast gating of the microchannel plates detecting the RHEED pattern (on several nanoseconds time scale) to minimize any dark noise and noise associated with leakage of ultraviolet light exciting the photocathode. (iii) The use of a gatable two-dimensional array detector with computer interface to capture the diffraction pattern. A computer-controlled shutter modulates the heating laser pulses while RHEED patterns, obtained with the heating laser on or off, are sorted out in the computer and averaged in separate memories. This method effectively compensates for shot-to-shot fluctuations in the laser and allows us to quantitatively analyze our time-resolved RHEED patterns. A RHEED pattern of the Pb(110) surface obtained by using picosecond electron pulses is shown in Fig. 5. The approximate location of the line scan across the image observed by the array detector is indicated.

The technique of picosecond time-resolved RHEED was used to probe the temperature (through the Debye-Waller effect) and the structure of the Pb(110) surface after picosecond laser heating. An example of the use of this technique to perform a time-resolved measurement of the temperature of the first few atomic layers subjected to picosecond laser heating is shown in Fig. 6. This technique, provides a tool to test molecular dynamics simulation of the melting transition by actually probing the dynamics of the surface disordering and regrowth of crystallinity.

The detection method used had a single electron sensitivity. For electron pulses of ~ 300 ps duration, the pulse contained about 10^5 electrons and it was possible to obtain a good RHEED pattern with one electron pulse. A RHEED pattern of Pb(110) obtained with a single pulse and after averaging 20 pulses is shown in Fig. 7. A RHEED system with a time resolution less than 5 ps have been constructed at the Center of Photoinduced Charge Transfer at Rochester. This system is activated by a femtosecond amplified dye laser or Ti:sapphire laser. Some details on this system were previously given [Aeschlimann et. al., 1995b].

The studied samples were cut from single-crystal rods aligned using x-ray Laue back reflection. All samples were grown from 99.999% pure metal. The surface was mechanically

polished and then chemically etched. The samples were mounted on a resistively heated Mo base with a thermocouple placed between the retaining clip and the surface of the sample.

The time-resolved RHEED system was operated in ultrahigh vacuum (10^{-10} torr). The samples were cleaned *in situ* by cycles of Ar-ion bombardment followed by annealing within 15-20 K from T_m . A cylindrical mirror electron energy analyzer with an integral electron gun for Auger analysis is used to check for surface cleanliness that is maintained so as no detectable impurities are observed during data acquisition.

Electrons of 15 to 20 KeV in energy were used to obtain the RHEED patterns. The angle of incidence was ~ 1 to 2 degrees from the surface which results in a probed depth of < 5 Å. The skin depth of the 1.06 μm laser in lead and bismuth is ~ 150 Å. Therefore, the probed layer is essentially isothermal.

B. Time-resolved LEED

The conventional LEED apparatus provides equilibrium structures of surfaces. To explore the time domain with low energy electron diffraction, additional features must be implemented into the experiment. First, the surface must be displaced out of equilibrium by a rapid (on the time scale of the process to be investigated) jump in a parameter that determines the equilibrium conditions. Secondly, the ensuing dynamical evolution of the LEED pattern must be followed in real time. Similar to the RHEED system, a short electron pulse is generated by ejecting electrons from a photocathode with a laser pulse. The electron pulse is accelerated to the target, and the diffraction pattern is observed with a position sensitive detector. The diffraction pattern yields the structure of the surface at the time when the electron pulse interacts with the surface. A second part of the laser pulse is used to displace the surface from the equilibrium. The time-dependence of the surface structure is probed by repeating the experiment with different time delays between the laser and the electron pulse. It is possible to keep the temperature jump small, on the order of 5 K, so that the time-dependent intensity is a nearly linear measure of the order parameter of the surface.

The methodology of time-resolved electron diffraction experiments is applicable to any dynamical process that exhibits a temperature dependent structure. While to date it has only been applied to study the dynamics of surface annealing [Becker et. al., 1984], one can equally envision investigations of the dynamics of adsorbed species, the desorption of adsorbates, or melting phenomena treated here in the context of the RHEED experiments. We illustrate the time-resolved LEED experiment using the example of surface reconstructions [Estrup, 1984; Willis, 1985; Thiel and Estrup, 1995]. Experiments without time resolution have well established that a surface may have a structure very different from that of a corresponding layer in the bulk. Now generally known as surface reconstruction, this phenomenon can dominate the physical and chemical properties of a surface. Based on the amount of motion required one can distinguish between mass-transport and displacive reconstructions. Mass-transport

reconstructions involve the motion of surface atoms over large distances; they do not conserve surface atom density. Displacive reconstructions require only small (less than a lattice parameter) displacements of surface atoms about their bulk truncation positions and conserve the surface atom density. Experiments have shown that mass-transport reconstructions proceed over time scales of microseconds to seconds, with a strong temperature dependence [Heinz, 1987]. Displacive phase transitions are expected to occur on a picosecond time scale, which to date has been out of reach of experimental methods. The picosecond time resolved LEED experiments discussed in this chapter are expected to measure the as of yet poorly characterized time scales of the displacive phase transitions. Such dynamical observations are expected to improve our understanding of the mechanism of surface reconstructions.

A particularly well analyzed reconstruction is that of the clean tungsten (001) surface [Felter et. al., 1977; Debe and King 1977; Evans-Lutterodt et. al., 1989; Robinson et. al., 1989]. When observed with conventional LEED, the reversible phase transition is revealed by superlattice diffraction spots that appear in the $(1/2, 1/2)$ positions, i.e. in the centers of the square reciprocal mesh of the (1×1) high-temperature phase, as the surface is cooled below room temperature. The appearance of the $(1/2, 1/2)$ spots reveals the change from a (1×1) to a $(\sqrt{2} \times \sqrt{2})R45^\circ$, or $c(2 \times 2)$, structure. The reconstruction involves only small ($0.24 \text{ \AA}$) displacements of tungsten atoms [Altman, 1988]. The W(001) surface reconstruction is a continuous phase transition [Evans-Lutterodt et. al., 1989; Robinson et. al., 1989], and the intensity of the superlattice diffraction spots associated with the low-temperature phase is reversible with temperature. The phase transition stretches over a temperature range of about 150 K.

Both the time-resolved LEED and RHEED experiments replace the conventional thermionic electron gun by a pulsed, laser driven gun. The time dependent dynamics is observed by scanning the temporal delay between a short laser pulse that heats the surface and the electron pulse that probes the structure of the surface. Figure 8 shows a schematic of a time-resolved LEED apparatus [Thompson et. al., 1995]. The diffraction experiment takes place in an ultrahigh vacuum environment ($P \sim 10^{-10}$ Torr) to maintain the cleanliness of the surface, since contaminants affect the structure [Estrup, 1984]. An argon-ion-laser pumped, mode-locked Titanium-Sapphire laser produces a train of 100 fs pulses in the 720-850 nm range with a repetition rate of 82 MHz. The beam is split into an infrared (IR) pump pulse and a probe pulse, which is frequency doubled into the near ultraviolet (UV) region in a BBO crystal. The IR pulse rapidly heats the surface and thereby induces a change in the temperature dependent surface structure. The near UV probe pulse irradiates a photocathode which emits a pulse of electrons with a time duration comparable to the optical pulse that produced it [Tsang et. al., 1991; Tsang, 1993]. The electron pulse is focused with electron optics designed to minimize the pulse broadening, and is then diffracted off the surface. The diffracted electrons are detected by a position-sensitive microchannel plate detector. By varying the delay time between the laser pump and the electron probe, a time profile of the diffraction intensity is obtained.

C. Experimental Considerations common to RHEED and LEED

1. Generation of electron pulses

Research on photocathode materials has a venerable tradition, dating back to the optimization of photomultipliers earlier this century [Sommer, 1968; Cardona and Ley, 1978]. The operating characteristics of a laser driven electron gun are, however, very different from the requirements of photomultipliers, motivating a renewed search for photocathode materials. Since many laser systems can now routinely deliver short pulses in the ultraviolet range of the spectrum, materials may be chosen with work functions higher than the ones of typical photomultipliers. Desirable characteristics of laser driven electron gun cathodes include a high quantum efficiency, fast response time, environmental stability, and resilience toward laser induced damage. Due to their very short electron-electron collision times, metals are expected to deliver the shortest electron pulses. Experiments [Tsang, et. al. 1993] have shown that no measurable temporal broadening is incurred by the transit time of electrons between the location of their excitation and the metal surface. A large number of metallic photocathodes have been tested, including lanthanum hexaboride [Oettinger, 1990], silver, copper and gold, [Aeschlimann et. al., 1995; Schmittenmaer et. al., 1995; Tsang et. al. 1991], magnesium, lithium [Thompson et. al., 1995], and cesium telluride [Kinross-Wright, 1994]. While the quantum yield of the alkali surfaces can reach 20 % [Kinross-Wright, 1994], their instability toward air is a distinct disadvantage. Progress has been reported in preparing environmentally stable alkali containing cathodes with excellent quantum yields by ion implantation [Girardeau-Montaut et. al., 1995].

The electrons ejected from the photocathodes exhibit an energy distribution with a width on the order of one electron volt. If the shortest electron pulses are desired it is important to minimize this width, because variations in the electron energies cause a temporal broadening of the pulse at the target. Classical work on photocathodes suggests that a laser photon energy close to the work function of the material would generate the smallest energy width [Sommer, 1968; Cardona and Ley, 1978]. However, recent work by a number of researchers in the field has convincingly demonstrated that at the large peak intensities of the ultrashort laser systems employed for electron guns the photoemission occurs via a multiphoton process [Schmittenmaer et. al., 1994; Weber et. al., 1995; Aeschlimann et. al.; 1995]. The electron pulse duration obtained at the target is therefore coupled to experimental parameters such as electron beam current, pulse repetition rate, the duration and energy of the laser pulses, and the spot size of the laser. The best operating conditions therefore depend sensitively on the system, and must be determined experimentally.

Using almost any of the cathode materials mentioned above, electron pulses with picosecond durations are straightforward to generate and use. Figure 9 shows a segment of a typical electron pulse train. It was recorded using a microchannel plate and time-resolved single particle counting electronics [Chang et. al., 1985]. The electron pulses were produced by irradiation of a thin film of Indium-Tin-Oxide by frequency-doubled Ti:sapphire laser pulses with a duration of 100 fs. The duration of the electron pulses shown in this figure, about 60 ps, is given solely by the temporal resolution of the timing electronics, indicating that the electron pulses are significantly shorter than that. Aeschlimann et. al. [1995] showed that the electron pulses

generated in their electron gun are even shorter than the 5 ps limit of a streak camera. The measurement of electron pulse durations in the femtosecond domain is still outstanding, and will require a technique to cross-correlate the electron pulse with the femtosecond laser pulse.

2. The surface temperature jump

The temperature jumps obtainable by exposing a surface to a short laser pulse can be varied over a very large range. Ultrashort laser pulses can be generated with pulse energies ranging from pico-Joules to Joules, and focal spot areas can be as small as 10^{-7} cm^2 . For all highly absorbing materials, such as the metals investigated with RHEED and LEED, the temperature jumps obtained with a single laser pulse can therefore heat the material beyond the melting point. When the most intense laser pulses are used a number of highly non-classical phenomena occur, such as thermionic emission of electrons out of an extremely hot electron gas [Riffe et. al., 1993]. For many of the experiments discussed in this chapter small temperature jumps are, however, preferable. In the surface reconstruction experiment the intensity of a half order diffraction spot depends on the temperature in a nonlinear fashion. The interpretation of the time-delayed data becomes simplified significantly if the temperature jumps are kept small, so that the intensity scales approximately linearly with the temperature. Temperature jumps on the order of a few Kelvin give rise to an intensity change in the half order diffraction spots of several percent only. The signal to noise ratio of the experiment must therefore be carefully optimized to allow a recording of the time-dependent diffraction intensity [Thompson et. al., 1995].

3. Limits on the temporal resolution

Some of the early time-resolved electron diffraction experiments were limited by the availability of short-pulsed laser systems. With the recent advent of commercial femtosecond lasers this limitation is effectively removed. There are, however, numerous effects that tend to reduce the time resolution available to laser-pump, electron-probe experiments. They are discussed in the present section.

In all experiments that use electron pulses as a probe it is important to carefully consider the temporal broadening effects arising from the velocity of the electron pulse as compared to the laser pulse that heats the target. In general one can reduce the temporal broadening arising from the overlap of laser with electron beams by reducing the diameters of both beams; there are, however, limitations imposed by considerations relating to the magnitude of the temperature jump, as outlined above, and relating to space-charge interactions. In diffraction experiments on surfaces it appears possible to improve the time resolution by tilting the wave front of the laser beam. In practice the beneficial aspects of that technique remain to be demonstrated, because to date other effects dominate the achievable time resolution.

Even if a femtosecond laser is employed to generate the electron pulse, the pulse duration at the target is usually in the picosecond domain. If metallic photocathodes are employed it can be

expected that memory effects during photoemission can be neglected [Tsang et. al., 1991; Tsang 1993]. However, electrons ejected from a metal by impact of a photon have a range of energies and angular distributions. The width of the energy distribution depends on the photon energy, the work function of the cathode and to some extent the temperature of the cathode. Even if the electrons are accelerated toward the target very rapidly the difference in electron velocities will cause significant temporal broadening for the short pulses considered here. The magnitude of the broadening depends on the initial and final kinetic energies of the electrons, as well as the distances traveled during acceleration and at constant potential. In general, all distances should be minimized, the electrons should be accelerated as quickly as possible to as high a voltage as possible, and the initial electron velocity should be minimized by choosing as small a laser photon energy as the photocathode material permits. A typical LEED gun can then produce electron pulses that are estimated to have a duration of less than 3 ps at the target surface.

Space charge interactions between electrons within a pulse lead to a swelling of the pulse in all spatial directions, implying a lengthening of the pulse duration. This space charge broadening is larger for slower pulse velocities, for two reasons: slower pulses have longer travel times during which the pulse may be broadened, and they also have higher electron densities for a given number of electrons per pulse [Thompson et. al., 1995]. Consider an electron pulse containing 1200 electrons, focused to a diameter of 250 μm with a duration of 2.5 ps. If this pulse travels with a kinetic energy of 200 eV, the electron density is 1.2×10^{-2} electrons/ μm^3 . This pulse is broadened by 10% of its original duration in 155 ps, corresponding to a travel distance of 1.3 mm. On the other hand, if this pulse is accelerated to 10 keV, it has a density of 1.7×10^{-4} electrons/ μm^3 ; this produces a 10% broadening in 370 ps, during which time the pulse travels 2.2 cm. It is clearly beneficial to operate the electron gun at the higher acceleration voltage. It may be possible to avoid the space charge problem altogether by generating electron beams with a high repetition rate laser system: with a laser pulse repetition rate of 80 MHz one obtains electron beam currents of 10^{-11} A even with one electron per pulse. This current may be sufficient for diffraction experiments that employ single electron counting schemes. The pulse spacing between the individual pulses of the mode-locked source is so large that space charge interactions arising from different pulses of the pulse train can be ignored.

Electrons in a short pulse are wavepackets of a finite coherence time, and are thus subject to a quantum mechanical spreading. The coherence time of the photoemitted electrons is not known. It can, however, be bracketed by considering the electron pulse duration and the energy bandwidth. Thus, the coherence time has as its lower limit the inverse of the energy spread of the electron beam. With $\Delta E = 0.3$ eV one finds a coherence time of at least 6 fs. The upper limit of the coherence time is given by the duration of the femtosecond laser pulse, which typically is about 100 fs. One can expect the quantum mechanical spreading to be very significant for the LEED experiment, but negligible for all but the highest time resolution RHEED experiments.

Ultrafast optical pump-probe spectroscopy is greatly aided by Fermat's principle,

$$\delta \int_{s_0}^{s_f} ds \frac{1}{c} n(s) = 0 \quad (9)$$

which states that if a perfect lens transfers a point source to an image point, all light rays travel for the same amount of time. Thus, if an ultrashort light pulse emerges from the point source, the pulse will have the same duration at the image point. Only dispersion effects lead to pulse broadening, and they are of course imposing the present 6 fs limit on optical pulses [Fork et. al., 1987]. Fermat's principle can be extended to electron optics, where it becomes [deWolf, 1990]

$$\delta \int_{s_0}^{s_f} ds \, m \, v(s) = 0 \quad (10)$$

In electron optics the electron momentum $mv(s)$ plays the role of the refractive index. There is however one important difference: the integral is not equal to the time it takes for an electron to move from point s_0 to s_f . Thus, electrons that emerge simultaneously from a point source do not arrive at the same time at the focal point of an electrostatic lens. Fermat's principle does not favor ultrashort electron pulses as it does ultrashort light pulses. In order to minimize the pulse broadening effects, the electron optics have to be as close as possible to the source, so that the radial deviation of the electrons from the axis is minimized. Furthermore, it may be beneficial to block off-axis electrons with an aperture.

To conclude this section we summarize the most important considerations for designing an electron gun that is capable of producing electron pulses of picosecond or subpicosecond durations. First it is necessary to operate the gun in a mode that ensures very few electrons per pulse in order to avoid spatial blooming by space charge interactions. For many experiments this necessitates a high repetition rate laser system. The cathode material must be matched to the laser wavelength and the laser peak intensity to produce electron pulses with a small energy spread. Alternatively, electron monochromatization may be advantageous. Electrons must be very rapidly accelerated to as high a velocity as possible, and the distance to the target must be minimized. Finally, the f-number of the electron optics should be very large in order to minimize the time lag between the axial and the marginal electrons of the beam.

Keeping all these aspects in mind it is quite feasible to construct electron guns that emit picosecond electron pulses [Aeschlimann et. al., 1995; Thompson et. al., 1995]. To achieve electron pulses with femtosecond duration Weber et. al. [1995] have suggested a reflectron electron gun. The basic idea is that an electron mirror can compensate for the temporal broadening that arises from the electron energy spread. Since the electron pulse is stretched for

most of the flight time to the target, the reflectron based electron gun is also expected to be very accommodating toward space charge effects, and may therefore allow more intense electron beams.

The time resolution of the surface experiments discussed in this chapter is ultimately limited by the electron-phonon relaxation time. The laser photon entering a metallic surface primarily excites electrons in the electron gas. Since the heat capacity of electrons is very small, the temperature rise is very large. Several experiments have demonstrated that the thermalization of the electron energy to the heat bath provided by lattice phonons proceeds on a time scale of hundreds of femtoseconds [Fujimoto et. al., 1984; Elsayed-Ali et. al., 1987; Elsayed-Ali et. al., 1991; Elsayed-Ali and Juhasz, 1993; Schoenlein et. al., 1987; Lin et. al., 1988; Bokor, 1989; Fann et. al., 1992a; 1992b; Sun et. al., 1993; Tas and Maris, 1994; Sun et. al., 1994]. While a comprehensive theoretical treatment is still outstanding, it can be speculated that processes such as melting and surface reconstruction depend on the phonon temperature, and are thus not immediately started with the absorption of the laser pulse. Femtosecond time-resolved experiments on surface structures are as of yet rare, and it can be anticipated that future work will provide intriguing new insights.

IV. THE HEAT DIFFUSION MODEL

Surface temperature profile

The time-dependent surface temperature is of fundamental importance for the time-resolved LEED and RHEED experiments since it provides the instrument's function required for the deconvolution of the data. To model the heat conduction it is convenient to assume a one-temperature system where the electrons and the lattice are considered to be in thermal equilibrium throughout the observation process. This assumption is reasonable, given that most current electron pulses have a duration on the order of 3 ps, and that the electron-phonon relaxation time in metals is typically less than 1 ps. Thus it is not necessary at this point to be concerned with either the initial nonthermal distribution of electrons [Sun et. al., 1993; Fann et. al., 1992a; 1992b] or the disequilibrium between the electron gas and the lattice. One shortcoming of the one-temperature calculation is that it ignores the well-known fact that more heat is transported into the bulk by the hot electrons generated in the initial photoexcitation than assumed by the lattice-temperature model [Brorson et. al., 1987; Juhasz et. al. 1993]. As a result, the actual peak surface temperature is expected to be lower, and the heat transport into the solid somewhat slower than the values obtained from the model calculations.

The classical heat diffusion model is based on the heat conduction equation:

$$\nabla^2 T(\mathbf{r}, t) = \frac{1}{\kappa} \frac{\partial(\mathbf{r}, t)}{\partial t} - \frac{1}{\kappa} g(\mathbf{r}, t) , \quad (11)$$

where κ is the thermal diffusivity of the solid, *i.e.* the thermal conductivity divided by the density specific heat, and $g(r,t)$ is the source function.

In order to obtain solutions to this equation the thermal radiation is neglected, and the sample is treated as a semi-infinite solid. The laser pulse profile is assumed to be hyperbolic-secant-squared in time and Gaussian in space, and the light intensity is assumed to decay exponentially into the solid. Thus the spatial and temporal profile of the heat source is

$$g(r,z,t) = \frac{0.88 I_m (1-R) \alpha \kappa}{K} e^{-(r/r_0)^2} e^{-\alpha z} \text{sech}^2(1.76t/\tau), \quad (12)$$

with I_m the peak laser intensity, R the reflectivity of the solid, r_0 the radial half width and τ the duration of the laser heating pulse. The absorption coefficient of the solid, α , is given by $\alpha = 4\pi k/\lambda$, with k the imaginary index of refraction and λ the wavelength of the laser radiation.

Given the above heat source profile, one can solve the heat conduction equation at the surface [Bechtel, 1975]:

$$\Delta T(r,z=0,t) = \frac{1.76 I_m (1-R) \alpha}{\rho c} e^{-(r/r_0)^2} \int_{-\infty}^t dt' \text{sech}^2(1.76 t'/\tau) \exp[\alpha^2 \kappa (t-t')] \text{erfc}[\sqrt{\alpha^2 \kappa (t-t')}] , \quad (13)$$

where $\text{erfc}(x)$ is the complementary error function. The result for the transient surface temperature at the spatial center of a Gaussian laser pulse, $\Delta T(0,0,t)$, is shown in Fig. 10 for the case of a 12 nJ pulse with a duration of 100 fs and a wavelength of 800 nm, which is focused to a spot diameter of 250 μm . The optical and thermal values of tungsten are used [Touloukian et. al., 1970; Touloukian and Buyco, 1970, Palik, 1985]. It is apparent that exposure of metallic surfaces to ultrashort laser pulses gives rise to a very rapid temperature jump that is a suitable instrument function for a picosecond time-resolved RHEED and LEED experiments. Due to the short duration of the laser pulses, it is possible to deconvolute the heating and cooling parts of the curve: the heating part is simply the integral over the incident sech^2 laser pulse, and the cooling part is the solution for instantaneous, exponentially decaying heat deposition into the solid.

The solutions for the transient surface temperature can be combined with the Debye-Waller formula for the integer-order spot intensity as a function of temperature to obtain the time-dependent spot intensity. Fig. 11 shows this expected intensity profile for an integer-order spot for a W(001) surface. By comparing those data with calculations of the intensities as a function of temperature and static intensity-vs.-temperature measurements, one obtains an experimental temporal temperature profile of the surface, which can be compared to the model presented in the previous section. The observation of the transient integer-order spot intensities furthermore finds application in the test of the one-temperature heat relaxation model, the verification of the electron pulse duration, and the evaluation of various electron pulse

broadening mechanisms discussed above.

With the transient temperature jump and the instrument function known one can extract the surface dynamics from the temperature-jump experiment. The fundamental quantity of interest is the time evolution $f(t)$ of the temperature dependent order parameter $s(T)$. In the LEED experiment the experimental observable is the intensity of half-order diffraction spots, which is related to the order parameter by

$$I_{1/2,1/2}(T) = a [s(T)]^2 + b \exp[-2M(T)] \quad (14)$$

with some proportionality constant a and the second term representing the thermal diffuse scattering which creates a uniform background. The temperature dependence of the order parameter is reflected in the T -dependence of the $W(001)$ half-order spots reproduced in Fig. 11. For an arbitrary temporal evolution function $f(t)$ of the order parameter the time-dependent change in the order parameter is given by the convolution integral

$$\Delta s(t) = \frac{1}{N} \int_{-\infty}^t F(t') f(t-t') dt' \quad (15)$$

where $F(t')$ is the forcing function and N the normalization integral. For small temperature jumps one can linearize the forcing function as

$$F(t') \approx \frac{ds}{dT} \Delta T(t') \quad (16)$$

with ds/dT the steady state temperature derivative of the order parameter, and $\Delta T(t)$ the instantaneous temperature calculated above. The transient jump of the half-order diffraction spot intensity can then be expressed as

$$\begin{aligned} \Delta I(t) &\approx \frac{dI}{ds} \Delta s(t) \\ &= \frac{dI(T)}{dT} \frac{1}{N} \int_{-\infty}^t \Delta T(t') f(t-t') dt' , \end{aligned} \quad (17)$$

where again only the linear term in the expansion of $I(t)$ is considered. Temperature jumps of a few Kelvin are easily obtained with mode-locked laser sources and ensure that the linearizations are valid approximations.

As a specific example we assume an exponential decay function $f(t-t') = e^{-(t-t')/\tau}$. Convolved

with the theoretical instrument function derived from (11), one obtains

$$\Delta I(t) = - \frac{1.76 I_m (1-R) \alpha}{\rho c} \left| \frac{dI(T)}{dT} \right| e^{-(t/\tau)^2} \frac{1}{N} \frac{e^{-t'/\tau_r}}{\tau_r} \times$$

$$\times \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \operatorname{sech}^2(1.76 t''/\tau) \exp[\alpha^2 \kappa(t' - t'')] \operatorname{erfc}[\sqrt{\alpha^2 \kappa(t' - t'')}] e^{t'/\tau_r} . \quad (18)$$

This result is entirely analogous to the one obtained for chemical relaxation methods that yield first order kinetics subsequent to temperature jumps independent of the actual order of the reaction [Eigen, 1954]. These methods enable a single time constant to be extracted from the data, yielding the time scale of interest, which is in the case treated here the reconstruction dynamics. The resulting decay curves are exhibited in Fig. 12 which shows the calculated superlattice peak intensity profiles for two reconstruction times of the W(001) system. Also shown is the instrument function for the reconstructed spots, which reflects the intensity assuming instantaneous reconstruction. It should be noted that the Debye-Waller effect is neglected in these calculations, since its contribution to the intensity change is much smaller than that of the reconstruction.

V. TIME-RESOLVED RHEED STUDIES OF METAL SURFACES

Time-resolved reflection high-energy electron diffraction was used to study the structural behavior of the three low-index faces of Pb and that of Bi(0001). The surfaces were subjected to heating and cooling rates on the order of 10^{11} K/s. The open Pb(110) surface was seen to reversibly disorder below T_m [Herman and Elsayed-Ali, 1992a]. This behavior is consistent with that well demonstrated by several groups using static heating conditions [van der Veen and Pluis, 1988; Frenken, 1989; Frenken and van der Veen, 1985; Frenken et. al., 1986; Prince et. al., 1988; Breuer et. al., 1990; Fuoss et. al., 1988; Thiry, et. al., 1987]. In contrast to Pb(110), the close-packed Pb(111) surface superheats to $T_m + 120$ K [Herman and Elsayed-Ali, 1992b]. Pb(100), a surface with atomic packing intermediate to that of Pb(110) and Pb(111), shows evidence of residual order at a temperature above that of bulk melting [Herman et. al., 1993]. For Bi, which is a semimetal, the close-packed Bi(0001) surface is shown to superheat by ~ 90 K. [Murphy et. al., 1993]

A. TEMPERATURE DEPENDENT STRUCTURAL PROPERTIES OF SURFACES

In the past several years, it has become well established that the temperature dependent structural properties of the surface is different from that of the bulk [van der Veen, et. al., 1988; Frenken, 1989; Frenken and van der Veen, 1985; Frenken and Maree, 1986; Prince et. al., 1988; Breuer et. al., 1990; Fuoss et. al., 1988; Thiry, 1987]. This is thought to be due to the asymmetric bonding at the surface atoms and the reduced number of nearest neighbors when compared with that of the bulk atoms. These properties of surface atoms manifest themselves as

increased atomic mean vibrational amplitude at the surface (lower Debye temperature) and a reduced melting point for some surfaces. The reduction in the surface disorder temperature can be quite large as was observed for Pb(110) [Frenken and van der Veen, 1985; Frenken et. al., 1986]. For Pb(110), a reversible order-disorder transformation was observed to begin at a temperature as low as 150 K below the bulk melting temperature $T_m=600.7$ K. The first atomic layer is fully disordered at ~ 50 K below T_m . The disordered state shows enhanced self diffusion similar to the liquid state and has liquid-like density and surface mobility. This order-disorder transformation is reversible and the thickness of the disordered layer increases with temperature. These observations were verified by several surface sensitive techniques.

The temperature dependent structural properties of lead crystals were found to be highly dependent on surface orientation [Pluis et. al., 1990]. Figure 13 shows a schematic of the three low-index faces of an fcc crystal, such as lead, and displays the orientation dependence of surface packing density. For an fcc metal, an atom on the {110}, {100}, and {111} surfaces has 7, 8, or 9 nearest neighbors, respectively compared to 12 nearest neighbors for bulk atoms. The least densely packed surfaces appear to have the highest propensity to disorder. A study of various Pb surfaces showed that the majority of crystalline faces exhibit surface disordering below T_m with exception of surfaces within $\sim 17^\circ$ of the {111} plans and $\sim 10^\circ$ of the {100} plans. The closed Pb(111) surface was observed to remain ordered up to the highest temperature studied, $T_m-0.05$ K, for a miscut angle $< 2^\circ$ from {111} [van Pinxteren and Frenken, 1993].

Pb(100), which has a packing density intermediate to Pb(110) and Pb(111), showed limited disorder for temperatures higher than 500 K. At T_m-2 K a disordered surface of ~ 1.3 monolayer develop for the Pb(100) surface. This disordered surface layer remains stable up to the highest measured temperature, $T_m-0.05$ K. The thickness of the disordered surface layer increases with the miscut angle and is ~ 3.5 monolayer for 10° miscut. The saturation of the surface disordered layer thickness is known as incomplete surface melting and is in contrast with the divergence of the disordered layer thickness on Pb(110) and the nonmelting of the Pb(111) surface [van Pinxteren and Frenken, 1992].

While the phenomenon of surface melting and orientation dependent structural properties of surfaces have been thoroughly studied for Pb, experiments and modelling of other materials suggest the generality of these observations. For example, experiments on Al(110) [Denier van der Gon et. al., 1990] showed complete surface melting below its T_m similar to that observed for Pb(110). Surface disordering has also been observed in semiconductors such as Ge(111) [Denier van der Gon et. al., 1990]. Molecular dynamics modelling of fcc metals suggests that the propensity of a surface to remain ordered up to T_m depends on the surface orientation, in agreement with the experimental studies [Häkkinen and M. Manninen, 1992; 1993].

The structural behavior of metals has been investigated using time-resolved reflection high-energy electron diffraction (RHEED). The aim of this work was to determine how the crystal surface influences the temporal dynamics of melting during laser irradiation.

Time-resolved reflection high-energy electron diffraction is used to study the structural dynamics of surfaces as they are heated with ~ 200 -ps laser pulses. The procedure followed in studying each surface is to first obtain RHEED pattern intensity as a function of temperature. In this case the sample is heated on a hot stage attached to the sample manipulator in the ultrahigh vacuum. The photoactivated electron gun is illuminated by ultraviolet light from an arc lamp which provides a stable source of light for photocathode activation. These measurements are conducted in order to provide information on (i) the temperature dependent structural properties of the studied surface under equilibrium, slow heating, conditions, (ii) the surface atom mean vibrational amplitude, i.e. the surface Debye temperature, which shows as temperature dependence of the RHEED streak intensity. This temperature dependence of the RHEED streak intensity is used as a calibration curve for converting time-resolved RHEED intensity into surface temperature. An example for Pb(111) is shown in Fig. 14. In the inset the logarithm of the intensity of the RHEED streak, normalized to that at 407 K, at a particular location near its maximum intensity is displayed as a function of temperature. It shows exponential dependence as expected from Debye-Waller theory. This calibration curve is used to convert the time-resolved RHEED intensity obtained for the same conditions as for the static measurement. The temporal development of the surface temperature is displayed in Fig. 14. The solid line represents a solution of the heat diffusion equation for the experimental conditions used.

B. SURFACE MELTING OF Pb(110)

Pb(110) is the least packed of the low-index faces of lead and its disordering properties below the bulk melting temperature is well established [van der Veen et. al., 1988; Frenken, 1989]. In Fig. 15 the RHEED streak intensity observed near the maximum of the 01 streak is plotted as a function of temperature. The RHEED intensity is normalized to that at 487 K. The inset is a semilogarithmic plot. The intensity is seen to decay exponentially up to ~ 520 K. This is consistent with Debye-Waller behavior which describes the reduction in the number of elastically scattered electrons due to the increased mean atomic mean vibrational amplitude with temperature. Above 520 K deviation from the exponential behavior is observed. Above 540 K, the RHEED streak intensity decays into the inelastically scattered background as a result of the disordering of the probed surface layer. Thus, we identify the surface disorder temperature, T_d , to be 540 K.

We next discuss the time-resolved disordering of Pb(110) [Herman and Elsayed-Ali, 1992a]. In these experiments the sample base temperature was set at 487 K using the hot stage. The laser heating pulse raises the surface temperature from its initial base temperature to a temperature ranging from below to above the surface disorder temperature, T_d . The time-resolved intensity of the RHEED streaks is then obtained for given time delays between the laser heating pulse and the electron probe pulse.

The time-resolved modulation of the RHEED streak intensity for various laser intensities is shown in Fig. 16. This is to be compared with the solid line, which is the calculated intensity modulation obtained by converting the temperature obtained from the one-dimensional heat

diffusion model to an intensity modulation using the calibration in Fig. 15. In Figs. 16(a) and 16(b), the laser heats the surface to temperatures less than the disorder temperature, T_d . A solution of the heat diffusion model for the experimental conditions used in Figs. 16(a) and 16(b) gives peak surface temperatures of 523 K and 537 K respectively. We then heated the surface with laser intensities sufficient to raise the surface temperature above T_d . For the case in Fig. 16(c), the model indicates that the surface temperature is raised to ~558 K, approximately 18 K above T_d . For the case of Fig. 16(d), a surface temperature rise of ~581 K is predicted, approximately 41 K above T_d . In both cases, there exists some time where we are unable to detect RHEED streaks, indicating that the probed surface region (~2 monolayer) is disordered. The time for which the streak vanishes depends on the level of heating above T_d and is ~200 ps for Fig. 16(c) and ~500 ps for Fig. 16(d). This is followed by reappearance of the RHEED streaks as the surface cools and reorders.

These results show that for Pb(110) subjected to heating and cooling rates of 10^{11} K/s, surface premelting is not bypassed and the disorder temperature appears to be unaltered from that under slow heating conditions. Moreover, the nucleation and growth of surface disorder occur on a time scale less than 180 ps even for ~18 K heating above T_d .

C. THE INCOMPLETE MELTING OF Pb(100)

We next discuss RHEED observations of Pb(100) [Herman et. al., 1993]. For slow heating conditions, this surface was previously shown to experience incomplete surface melting. That is the disordered layer that forms on the surface remains stable in size up to $T_m - 0.05$ K. We first measure the temperature dependence of the RHEED streak intensity as shown in Fig. 17, in which the results were normalized to that at 377 K. A nonexponential decrease in diffraction intensity with temperature is observed starting at ~475 K. Similar deviation from Debye-Waller behavior was previously observed in high-resolution LEED experiments and is thought to be related to the surface thermal expansion which is about seven times that of the bulk in the temperature range of 300 to 470 K. Deviation from Debye-Waller behavior can also be attributed to an abrupt increase in vacancy concentration beginning at 510 K [Yang et. al., 1991].

To determine the peak temperature rise induced on the Pb(100) surface by the heating laser pulse, time-resolved measurements were performed at the delay time which gives maximum reduction in the RHEED streak intensity (time near maximum surface temperature rise). The RHEED streak intensity, normalized to that at 450 K, is plotted in Fig. 18, as a function of peak laser intensities, I_p . The normalized streak intensity is converted to a temperature rise, ΔT , using the calibration of Fig. 17, and the result is shown in the inset of Fig. 18. The temperature rise is observed to be directly proportional to I_p , as expected. The maximum peak temperature in all of these sets is below T_m . These data do not account for the effect of convolution due to the finite width of the electron probe pulse, which is comparable to that of the heating pulse. This finite pulse width of the electron probe tends to reduce the observed modulation to the streak intensity, and thus underestimates the temperature rise.

Similar time-resolved measurements were conducted for different sample initial temperatures and with laser intensities such that the surface was raised closer to T_m . Results are shown in Fig. 19. At sufficiently high I_p , the normalized streak intensity is observed to vanish, indicating that order has been lost in the probed surface layer. The data in Fig. 19 are used to determine the peak surface temperature at which the normalized RHEED streak intensity vanishes. This threshold intensity is converted to temperature rise using Fig. 18. Results show that the peak surface temperature when order is lost in the probed surface layer is 615 ± 20 K. The error bar indicated does not account for the convolution effects and changes in the thermal and optical properties of the sample. Accounting for these would lead to a somewhat greater peak surface temperature than what is reported. Thus, it is likely that residual order is present above T_m . At this temperature, the disordered layer appears to remain stable. Compared with results we will discuss for Pb(111), where superheating to ~ 720 K was observed, Pb(100) shows evidence of residual order at a much lower surface temperature.

D. SUPERHEATING OF Pb(111)

We next discuss laser heating experiments of Pb(111) [Herman and Elsayed-Ali, 1992b]. The sample was biased at 586 K ($T \approx T_m - 15$ K) and transiently heated with varying peak laser intensities, I_p . The experiments were performed at the time corresponding to the minimum of the normalized streak intensity. We measured the RHEED streak intensity and normalized it to that at 586 K, as shown in Fig. 20. From the semilogarithmic plot in the inset of Fig. 20, two regimes are evident. First, where $I_p \approx 3.5 \times 10^7$ W/cm², the RHEED streak intensity follows an exponential decay with peak laser intensity, consistent with Debye-Waller behavior. Second, where $I_p > 3.5 \times 10^7$ W/cm², the RHEED streak intensity shows a deviation from exponential behavior indicating that the surface is experiencing disorder consistent with melting. The normalized streak intensity in the exponential region was transformed to a temperature jump, ΔT , by using the results of the static RHEED calibration. In the exponential Debye-Waller region, ΔT is proportional to the laser intensity, therefore, the lower values of the laser intensity and the corresponding temperature jumps can be used to relate the peak laser intensity with ΔT . When this is done, we observe the departure from Debye-Waller behavior to occur when the surface is heated to ~ 720 K. In addition, the temperature-dependent RHEED streak intensity has a slope, when plotted on a semilogarithmic scale, equivalent to that from the static RHEED measurements within the experimental error. This observation indicates that for peak a surface temperature less than 720 K, the surface remains ordered, cools below T_m , and exhibits Debye-Waller behavior. Thus, we conclude that Pb(111) can be superheated by ~ 120 K using ~ 180 -ps laser pulses. In this context, superheating refers to a lattice mean-square vibrational amplitude in excess of that at T_m which is still consistent with a Debye-Waller decrease in the elastic diffraction intensity. At higher temperatures melting occurs, resulting in a pronounced departure of the RHEED streak intensity from Debye-Waller behavior. The laser heating experiment with the sample biased at 586 K was also carried out at various times after the time of the minimum normalized RHEED streak intensity, ranging from 500 ps to 4000 ps. At all of the delay times examined, deviation from Debye-Waller behavior consistently occurred above a peak laser intensity of $\sim 3.5 \times 10^7$ W/cm² leading us to conclude that this deviation is due to melting on

the surface.

The temporal evolution of the RHEED streak intensity was observed with the Pb(111) sample biased at 586 K. The normalized RHEED streak intensity was obtained at various delays between the arrival of the laser heating pulse and the pulsed electron probe. Results for a peak laser intensity of $I_p \approx 3.3 \times 10^7 \text{ W/cm}^2$ are shown in Fig. 21(a). This data is consistent with classical heat diffusion, showing a fast decrease in the diffraction intensity as the laser pulse heats the surface and a rapid recovery as the heat is conducted to the bulk. In Figs. 21(b)-21(d) the surface was heated with $I_p > 3.5 \times 10^7 \text{ W/cm}^2$, the threshold intensity for Debye-Waller behavior, as determined from Fig. 13. A qualitative difference between these sets and Fig. 21(a) is evident. As I_p is increased, the diffraction intensity fails to recover to what is expected from classical heat diffusion. We attribute this to melting on part of the surface. In Figs. 21(b) and 21(c), the streak intensity exhibits an initially fast rise after the intensity minimum, similar to that seen in the nonmelting sets. In this time period the surface is most likely molten in some regions due to the nonuniformity of laser heating, which was measured by a scanning pinhole of 500 μm in diameter, to be $\sim 18\%$ across the surface, and is a superheated solid in the remainder of the probed area. The excess surface temperature diffuses for some time, τ , after which pronounced melting occurs, as reflected in the failure of the streak intensity to recover.

To extract τ we first compared the time-resolved RHEED intensity of the experiments that showed no melting and no superheating with those that were superheated but displayed no apparent anomalous behavior [see Fig. 21(a)]. This comparison showed good agreement indicating that the superheated sets that do not show melting display behavior consistent with classical heat diffusion. Having verified this, we then compared the time-resolved RHEED intensity of the experiments that showed melting with those that did not and looked for the time at which deviations occurred. A nonmelting, superheating set was normalized to a given melting set and subtracted from it. The resulting difference was then fitted with a polynomial and differentiated to observe the break from nonmelting behavior. The difference of this time and the time of the intensity minimum was identified as τ . The time τ was observed to decrease from $\sim 1200 \text{ ps}$ to $< 300 \text{ ps}$ for laser intensities corresponding to peak temperature rises of 130 K and 215 K, respectively. This demonstrates the decreasing time duration of superheating with increasing temperature.

E. SUPERHEATING OF Bi(0001)

We next report on a superheating study of Bi(0001) using time-resolved RHEED. Bi was chosen because, similar to Pb, it has a relatively low melting temperature and low vapor pressure at the melting point, and the fact that previous slow-heating experiments have demonstrated superheating of Bi crystallites. Some of these Bi crystallites melted after a time delay of about 30 min. when held at the bulk melting temperature, $T_m = 544 \text{ K}$, and after about 10 min. when held at $T_m + 5 \text{ K}$ [Peppiat, 1975; Blackman et. al., 1972]. Using time-resolved RHEED with $\sim 200\text{-ps}$ resolution we are able to achieve heating rates of $\sim 10^{11} \text{ K/s}$, approximately 13 orders of magnitude larger than that used in the Bi crystallite experiments. Because of the open

pseudo-cubic crystal structure of Bi, liquid Bi is more dense than the solid, and it has been suggested that such unusual structural differences between a crystal and its melt may provide a barrier for rapid melting [Mackenzie et. al. 1963]. Upon melting, Bi experiences an increase in coordination number and in the electrical and thermal conductivities [Frost, 1954]. This is in contrast to Pb, which, upon melting, experiences a positive volume change, maintains the same coordination number, and experiences a decrease in the electrical and thermal conductivities [Frost, 1954]. We chose the close-packed (0001) surface for our superheating experiments since open surfaces are more likely to exhibit surface melting, providing a nucleation site for bulk melting at T_m .

The same experimental techniques were utilized as for Pb. Static RHEED measurements showed no surface disordering up to the highest temperature studied, 523 K ($T_m = 544$ K) and the RHEED streak intensity exhibited Debye-Waller behavior.

We next discuss our time-resolved RHEED measurements [Murphy et. al., 1993]. Figure 22 shows the RHEED streak intensity normalized to that at 523 K at the time of minimum streak intensity and 4 ns later. For $I_p \leq 1.9 \times 10^7$ W/cm², the RHEED streak intensity is consistent with Debye-Waller behavior. For $I_p \geq 1.9 \times 10^7$ W/cm², deviation from the exponential Debye-Waller behavior is observed consistent with melting, and permanent laser damage on the surface. This damage could be visually observed and was accompanied by a reduction in the RHEED streak intensity. No such damage was observed in the case of Pb(111). This might be related to the negative volume change upon melting of Bi. When comparing the normalized RHEED streak intensity in Fig. 22 at $I_p = 1.9 \times 10^7$ W/cm² with the static calibration, we find that $\Delta T = 105 \pm 10$ K corresponding to a superheating of 90 ± 10 K. This superheating temperature, as well as that reported for Pb(111), does not account for convolution effects arising from the fact that the electron probe pulse width is comparable to the decay time of the surface temperature near its peak. Including this effect in the analysis would show a somewhat larger superheating.

VII. SUMMARY

In this chapter we attempted to present a brief review of the work performed in our laboratories in the area of time-resolved RHEED and LEED. This is clearly an area in its infancy and only a few laboratories are presently involved in these type of experiments. The work on surface melting and superheating has shown a great promise for this technique and demonstrated physical phenomena, such as the observed significant surface superheating, which would have not been readily observable by other time-resolved surface sensitive techniques. When pushing the temporal resolution to the few picosecond time domain, it is inevitable that the limitation on the number of electrons per pulse would limit this technique to reversible surface transformations or reactions. However, with a single ~ 300 ps electron pulse it is possible to obtain a good RHEED pattern [Elsayed-Ali and Herman, 1990]. The nucleation and growth of the various surface phase transformations can proceed on a time scale that can span many orders of magnitude. While desorption, for example, is recognized to occur on a femtosecond time scale,

diffusion-controlled surface phase transformations can occur over a much longer time scale. For the study of the dynamics of many surface reactions, the pump-probe arrangement might not be the most suitable one. Other arrangements include that of obtaining the temporal resolution by gating the microchannel plate detectors, or by streaking the diffracted electrons in a fashion similar to streak cameras. These modes of operation allow for operation of the time-resolved diffraction system to observe events on a time scale from the picosecond to the millisecond range. We finally note that a related area is that of fast electron microscopy. The status of transmission electron microscopy with nanosecond temporal resolution has been previously reviewed [Bostanjlo, 1989].

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Figures:

- Figure 1: A schematic diagram of the LEED and RHEED geometry showing how the Ewald sphere intersects the reciprocal lattice rods. In the LEED geometry the Ewald sphere intersects the reciprocal rods nearly parallel to the surface. However, in the RHEED geometry, because of the small angle of the incident beam with the surface and the much larger size of the Ewald sphere, RHEED patterns represents a cut through the reciprocal lattice perpendicular to the surface.
- Figure 2: The reciprocal lattice of Bi(0001) is determined using RHEED by obtaining diffraction patterns in two or more azimuthal directions.
- Figure 3: Integrated intensity of half-order beam in W(001) reconstruction versus temperature, using conventional LEED [Altman, 1989]. The incident electron energy was 212.7 eV.
- Figure 4: A schematic diagram of the time-resolved reflection high-energy electron diffraction system. A picosecond laser is used to heat the sample and activate an electron gun. The electron pulses are well synchronized with the heating laser. Timing between the arrival of the laser and electron pulses at the surface of the sample is adjusted by a mechanical delay line. An image analysis system is used to capture the diffraction pattern.
- Figure 5: A RHEED pattern of Pb(110) taken using picosecond electron pulses. One of the line scans is taken when the shutter is closed. A computer is used to sort out and average the line scans. The arrow indicates the approximate location of the line scan obtained by lens imaging this pattern onto the linear array detector.
- Figure 6: Transient surface temperature rise of Pb(110) irradiated with $3.2 \times 10^7 \text{ W/cm}^2$ peak intensity, $\sim 350 \text{ ps}$ FWHM, Nd:YAG ($\lambda = 1.06 \mu\text{m}$) laser pulses. Solid line was obtained from a heat diffusion model.
- Figure 7: A RHEED pattern of Pb(110) taken using the time-resolved RHEED apparatus (a) for a single shot, (b) after averaging 20 shots with lower microchannel plate gain. The electron pulse width was $\sim 300 \text{ ps}$ FWHM and electron energy 14 keV.
- Figure 8: Schematic of the Pump-Probe LEED experiment. BS = Beam Splitter; D = Delay Stage; BBO = β -Barium Borate; F = Filter; LC = Liquid Crystal; PD = Photodiode; PSD = Position Sensitive Detector; UHV = Ultrahigh Vacuum.

Figure 9: Measurement of the electron pulse train generated from the second harmonic of a pulsed Ti:Sapphire laser beam focused onto an Indium-Tin-Oxide photocathode. The measured FWHM of 63 ps is instrumentally limited. The time axis is calibrated to the 82-MHz repetition-rate of the laser pulses.

Figure 10: Calculated temperature profile based on the solution of the heat conduction equation at the center of a 250 μm diameter Ti:Sapphire laser spot for a W(001) surface initially at 250 K, heated by 12.2 nJ laser pulse at 800 nm with a duration of 100 fs. The inset shows the temperature rise due to the absorption of the laser pulse.

Figure 11: Calculated Debye-Waller intensity profile for an integer-order diffraction spot from a W(001) surface upon laser heating, given the surface temperature profile in Figure 10.

Figure 12: Calculated intensity profiles (solid lines) for the half-order diffraction spot in the W(001) reconstruction due to the laser-induced surface temperature profile shown in figure 11, for reconstruction times of (a) 5 ps, and (b) 100 ps. Also shown is the negative of the temperature profile (dashed lines), which is the instrument function for the half-order spot.

Figure 13: A schematic of the three low-index faces of a face centered crystal.

Figure 14: RHEED streak intensity of Pb(111) normalized to that at 407 K obtained as a function of temperature. The inset is a semilogarithmic plot. The intensity was measured near the peak of the 01 streak. The reduction in RHEED streak intensity with temperature follows a Debye-Waller behavior with a Debye temperature of 61 ± 7 K.

Figure 15: RHEED intensity of Pb(110) normalized to that at 487 K versus temperature. The inset is a semilogarithmic plot.

Figure 16: Time-resolved RHEED streak intensity measurements on Pb(110) for different heating laser peak intensities. The heating laser pulse width measured at full-width at half-maximum is 170 ± 20 ps. (a) $I_p = 1.4 \times 10^7 \text{ W/cm}^2$; (b) $I_p = 2.0 \times 10^7 \text{ W/cm}^2$; (c) $I_p = 2.7 \times 10^7 \text{ W/cm}^2$; $I_p = 3.6 \times 10^7 \text{ W/cm}^2$. The solid line is the calculated RHEED intensity.

Figure 17: RHEED intensity of Pb(100) normalized to that at 377 K versus temperature. The inset is a semilogarithmic plot.

Figure 18: RHEED streak intensity for Pb(100) at time of maximum modulation by the laser heating pulse. The sample base temperature was 450 K. The peak surface temperature ΔT versus peak laser intensity is shown in the inset.

Figure 19: Normalized RHEED streak intensity versus peak laser intensity for the Pb(100) sample at base temperatures successively closer to T_m .

Figure 20: RHEED streak intensity of Pb(111) normalized to that at 586 K versus peak heating laser intensity at the time corresponding to the minimum of the normalized streak intensity. The inset is a semilogarithmic plot that shows deviation from Debye-Waller behavior at $I_p \approx 3.5 \times 10^7 \text{ W/cm}^2$. The corresponding peak temperature is $\sim 720 \text{ K}$, approximately 120 K above T_m .

Figure 21: Time-resolved normalized RHEED streak intensity of Pb(111) irradiated with laser pulses of varying peak intensity. Set (a) is consistent with classical heat diffusion and corresponds to a superheating of $\sim 110 \text{ K}$. At higher peak laser intensities, the surface begins to melt and this is evident in the deviation of these sets from classical heat diffusion.

Figure 22: Time-resolved RHEED streak intensity of Bi(0001) normalized to that at 523 K versus peak heating laser intensity at the time corresponding to the minimum of the normalized streak intensity (a), 0.5, 1, and 4 ns later (b-d). Deviation from Debye-Waller behavior at $I_p = 1.9 \times 10^7 \text{ W/cm}^2$ is observed. The corresponding peak temperature is $\sim 630 \text{ K}$, approximately 90 K as above

Fig. 1(a)

Fig. 1 (b)

Z1432

Fig. 2

Fig. 3

A Picosecond Time-Resolved Surface Temperature Probe "Thermometer"

Fig. 4

Fig. 5

Decay of surface temperature rise

Fig. 6

Fig. 7

Pump-Probe LEED

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

(111)

(100)

(110)

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Fig. 20

Fig. 21

Figure 2

Fig. 22

Femtosecond time-resolved thermomodulation of thin gold films with different crystal structures

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A femtosecond laser is used to generate and probe hot electrons in polycrystalline and single-crystalline thin gold films. Transient thermorefectivity and thermotransmissivity for different heating-laser-pulse fluences are performed. Analysis of the transient thermotransmissivity and thermorefectivity signals allows us to resolve the modulation to the real and the imaginary parts of the dielectric constant. The latter is found to be dominant at our probe wavelength. The hot-electron energy-loss lifetime is shown to be 1–3 ps and increases with the laser fluence. For film thickness comparable to the optical skin depth, the transient decay time of the reflectivity and of the transmissivity are equal, with the polycrystalline films showing a slightly faster decay time. For thicker films, hot-electron transport to the bulk of the film gives a faster transient-reflectivity decay. Electron transport is slower in the polycrystalline films.

I. INTRODUCTION

The use of ultrafast lasers to generate nonequilibrium heating conditions in metals was suggested many years ago.¹ If a metal is subjected to pulsed-laser heating for which the pulse duration is less than or comparable to hot-electron energy-loss lifetime, then a transient inequality between the effective temperatures of the electrons and the lattice would occur. Nonequilibrium heating in metals is not limited to ultrafast laser heating. It is a general phenomenon that can occur when the electron gas in the metal is subjected to a transient event, such as picosecond or femtosecond laser heating, a fast electric current, or the slowing down of energetic charged particles. In fact, one of the earliest theoretical studies² of hot-electron generation and relaxation in metals was primarily concerned with the generation of these nonequilibrium conditions during the slowing down of energetic charged particles in metals.

Hot-electron energy-loss lifetime in metals, τ_{e-ph} , can vary greatly depending on the initial ambient temperature. At low temperatures, only low-energy acoustic phonons are available to interact with the hot electrons; and since the corresponding phonon density of states is small, the coupling of the electron gas to the phonons is weak. This results in an electron energy-loss lifetime on the order of 1 ns for copper at 25 mK.³ At higher temperatures, τ_{e-ph} is significantly reduced and at tens of degrees kelvin can be as short as a few picoseconds.^{4,5} Such extremely fast energy-loss lifetime have made the observation of nonequilibrium heating, in this region, inaccessible except with the use of ultrafast duration pulsed lasers. Moreover, the generation of a significant (up to a few thousand of degrees) difference between the effective electron and lattice temperatures is demonstrated only by the use of ultrafast lasers.^{5–10}

Nonequilibrium electron heating in metals has been ob-

served by ultrafast time-resolved thermomodulation reflectivity and transmissivity,^{4–8} thermally assisted multiphoton photoemission,⁹ and more recently single-photon photoemission.¹⁰ Femtosecond thermomodulation studies have demonstrated the fast nature of hot-electron relaxation by energy loss in geometrically confined films (with thickness comparable to the laser skin depth) and by energy loss and transport in thicker films. Subsequently, surface-plasmon resonance in thin silver films has been shown to provide a very sensitive probe of nonequilibrium heating.¹¹ A systematic study of electron-phonon coupling in different thin metal films was conducted.¹² In this later study, a very thin copper film deposited on the various metal films was used as a hot-electron probe, thus facilitating the study of hot-electron relaxation in different metals. Results were in agreement with a theoretical model of electron-phonon coupling.¹³ A thermomodulation study of electron-phonon relaxation in niobium was performed by observing the rate of lattice heating due to energy transfer from the hot electrons.¹⁴ An approach to measuring electron-phonon coupling in metals based on a comparison of the experimental damage threshold for different laser pulse widths with a heat transport model was previously proposed.¹⁵ However, some concerns regarding its implementation was subsequently commented on.¹⁶ In these studies the role of lattice imperfections on hot-electron energy loss and transport was not considered. Nonequilibrium heating by femtosecond lasers has also been shown to strongly affect the desorption kinetics of molecular adsorbates on metal substrates.¹⁷ In this case the desorption yield was described by that expected from coupling to the adsorbate of the substrate's nonequilibrium electrons, which are at a significantly higher temperature than that of the lattice.¹⁸

We have conducted a set of pump-probe experiments on thin (100–800 Å) single-crystalline and polycrystalline

gold films. An earlier account of our results was previously given.¹⁹ Here we detail our results and extend our analysis of the thermomodulation data. Both femtosecond time-resolved thermorefectivity and thermotransmissivity were observed. Reflectivity and transmissivity are complimentary in the sense that the reflectivity probes a depth comparable to the skin depth of the laser in gold (~ 150 Å), whereas the transmissivity probes the total thickness of the film. Moreover, for a uniformly heated film (when the thickness is less than or comparable to the laser skin depth), the combined transient reflectivity and transmissivity, along with the known thickness of the film and the index of refraction of the substrate, is sufficient to determine transient changes in the real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2 , respectively). Our results show that, for film thickness comparable to the skin depth, the decay time of the transient reflectivity is equal to that of the transmissivity. This occurs in both single-crystalline and polycrystalline films. For thicker films, hot-electron transport inside the film gives a faster transient reflectivity decay. Transient transmissivity decay time is less affected by the increased film thickness. Comparison of data using single-crystalline films to those using polycrystalline films indicates that electron transport is impeded by the predominantly elastic electron-grain boundary collisions.

II. EXPERIMENT

The polycrystalline gold films were deposited on a glass slide by conventional resistive evaporation techniques. The film thickness was determined by a crystal thickness monitor with an estimated accuracy of better than ± 50 Å for the 200-Å films. Electron diffraction patterns obtained from films deposited, under the same deposition conditions, on formvar supported on a standard copper electron microscope grid show a ring pattern. TEM images reveal a grain size on the order of a few hundred angstroms. Single-crystalline thin gold films were also fabricated by evaporation. For these films, however, we used a sodium chloride crystal as a substrate. To fabricate the single crystals, the substrate was heated to ~ 600 K then allowed to cool to ~ 450 K. A very thin layer (< 20 Å) of silver was initially deposited at a rate of ~ 1 Å/s. This serves to enhance the epitaxy of the subsequently deposited gold. After deposition of the gold film at ~ 450 K, at a rate of a few angstroms per second, the substrate was allowed to cool under vacuum then removed from the evaporator. The film was floated on distilled water, washed in sulphuric acid to remove the silver and any gold-silver alloy that might have formed in the interface, and then washed again in distilled water. Finally, the film was caught on a glass slide and allowed to dry.

Electron diffraction patterns obtained from the epitaxially grown films show a spot pattern consistent with a single crystal oriented in the (100) orientation. Transmission electron microscope images reveal oriented grains characteristic of epitaxially grown thin metal films. Electron diffraction patterns and electron micrographs of polycrystalline and single-crystalline 400-Å gold films are

shown in Fig. 1. A very high density ($> 10^{10}$ cm⁻²) of dislocations and twins are evident in the electron micrographs of the single-crystalline films. Such a high density of dislocations and twins is characteristic of these single-crystalline films.²⁰ From Fig. 1, the grain size for the polycrystalline samples can be estimated to be in the order of a few hundred angstroms. More quantitative surface grain size determination was accomplished using atomic force microscopy with an image analysis system. Images were obtained for both types of samples in air. The average grain size of a typical 200-Å polycrystalline film was determined to be 155 ± 10 Å. No systematic study of the dependence of the average grain size on film thickness was conducted. Atomic force microscope images of the 200-Å single-crystalline film showed oriented crystallites connected by bridges. Contrary to the polycrystalline films, obtaining atomic resolution on the single-crystalline film was possible. This seems to be consistent with the assumption of relative flatness of the epitaxially grown films, which has previously been concluded based on the observation of streaks in reflection high-energy electron diffraction patterns.²¹

The pump-probe experiments were performed with the use of a 76-MHz synchronously pumped linear-cavity femtosecond dye laser.²² Intracavity control of the group velocity dispersion is accomplished using Brewster-angle prisms. This system delivered ~ 150 fs (sech²) pulses at ~ 615 -nm wavelength (2-eV photon energy). A maximum pulse energy of ~ 0.6 nJ can be achieved. The laser is actively stabilized to achieve a stability of the frequency spectrum and pulse width for several hours. A conventional pump-probe setup was used. The probe beam was delayed from the pump using a stepper motor with 1- μ m resolution. Both pump and probe were incident on the sample at near normal incidence with their focal spot on the sample 5 ± 1 μ m as measured with a scanning blade. A 10 $\times$ microscope objective was used for focusing. The probe energy was fixed while the pump was varied using neutral density filters. The pump-to-probe energy was maintained higher than a factor of 17. The pump was modulated with either a mechanical chopper or an acousto-optic modulator and the thermomodulation signal was detected using a lock-in amplifier tuned to the pump chopping frequency.

FIG. 1. Transmission electron micrographs and electron diffraction patterns of polycrystalline and single-crystalline gold films.

III. FEMTOSECOND THERMOMODULATION

For metals, heating-induced modulation of their optical properties can result from many effects. Of particular importance to thermomodulation studies is the change in the occupancy of electronic states near the Fermi level.²³ The top of the *d* band to the Fermi level in Au is at ~ 2.4 eV.²⁴ Therefore, there are allowed transitions from the top of the *d* band to states near the Fermi level for a wavelength near that of the laser system used in the present study ($\lambda = 615$ nm). The electronic-heating-induced smearing of the Fermi distribution affects the complex dielectric constant (a function of wavelength) of the metal, thus modulating its optical properties. While our laser photon energy is lower than that of the interband edge, thermomodulation measurements,²⁵ and relativistic band calculations²⁶ of the optical properties of gold are in agreement on the existence of an absorption tail below the interband edge, which is due to band structure. This edge extends as low as 1.7 eV.²⁵ While the magnitude of the thermomodulation signal is significantly reduced at our laser wavelength compared to that near the interband edge, the signal we obtain is well within our detection limit.

Time-resolved thermotransmissivity signals of 200-Å single-crystalline gold film taken with two different laser heating fluences are shown in Fig. 2. The shape of these signals is very similar to those observed for thermoreflectivity for the 200-Å films. These signals consist of a fast initial modulation related to the heating laser pulse width, a transient fast decay occurring in a 1–3 ps time scale, and a subsequent long tail persisting for times that appear to be much longer than our probing time. The general shape of these signals is similar to those observed for other gold film thicknesses. The temporal evolution of the fast transient appears to be exponential for all laser fluences as shown by plotting it on a semilogarithmic plot. Both thermoreflectivity and thermotransmissivity ($\Delta R/R$ and $\Delta T/T$) are negative at the probe wavelength. The transient thermomodulation signal appears to be directly proportional to the heating laser fluence. For $\Delta T/T$, the maximum modulation ($\sim 4 \times 10^{-3}$ for a laser heating fluence of 4 mJ/cm²) was independent of film thickness for 200–800-Å films, to a

first-order approximation. On the contrary, for $\Delta R/R$ the maximum modulation decreased from $\sim 4 \times 10^{-3}$ to $\sim 1 \times 10^{-3}$ for the 800-Å films.

We next discuss the shape of the thermomodulation from a qualitative point of view. The heating laser pulse interacts initially with free and bound electrons in the metal. For gold the Fermi level is ~ 2.4 eV above the top of the *d* band. Since our pump-probe wavelength is 615 nm, which corresponds to an energy of ~ 2 eV, then our pump is mainly interacting with free electrons. As explained previously, there exists an absorption tail below the band edge that extends as low as 1.7 eV in gold. Thus, at our laser wavelength there is also some interband absorption. In fact, the overwhelming evidence that the thermomodulation signal observed with femtosecond laser systems is due to the smearing of the Fermi distribution,^{4,7} i.e., due to changes in the occupancy of states near the Fermi level as a result of electronic heating that modulates the dielectric constant. Consequently, the optical properties (as probed by transmissivity and reflectivity) is modulated. While the thermomodulation signals could result from other effects such as thermal expansion, enhanced electron-phonon interaction, and shifting of the Fermi level, these are thought to have only a relatively small contribution to the femtosecond thermomodulation signal. The magnitude of this contribution, however, is not well determined.

The initial fast thermomodulation signal is due to the electronic heating. Because of the low heat capacity of the electrons, they respond “instantaneously” to the laser field. During this fast heating of the electrons, the lattice remains very close to its initial temperature. The hot electrons generated by the laser field thermalize with each other by electron-electron collisions, transfer their energy to the lattice by electron-phonon collisions, and scatter at defects, impurities, and surfaces. The possibility of collective excitation of plasma oscillation is precluded since the plasma frequency corresponds to about the Fermi energy.²⁷ Thus, an electron-electron collision causes an excited electron to lose a large fraction of its energy. If we assume that electron-phonon collisions is the main mechanism by which the energy contained in the hot electrons is transferred to the lattice, then the fast transient signal decay time is related to the time needed

FIG. 2. Time-resolved thermomodulation transmissivity of 200-Å single-crystalline gold film taken with different heating laser fluences: (a) 1.4 mJ/cm², (b) 4.1 mJ/cm². The inset is a semilogarithmic plot of the fast transient decay.

for equilibrium to be established between the electrons and the phonons. The long tail, which persists in the thermomodulation signals for times that appear to be much longer than our probing time, can be explained by modulation of the optical properties as a result of simple heating of the metal as in conventional, i.e., slow thermomodulation spectroscopy.

While our experimentally measured quantities are those of the transient thermomodulation of the reflectivity and the transmissivity, these quantities are difficult to interpret in view of a change in the density of states near the Fermi level caused by electron heating. The measurement of the transient dielectric constant is more fundamental and lends itself to a clearer interpretation of nonequilibrium heating. The reflectivity and the transmissivity are related to the real and the imaginary parts of the dielectric constant through the Fresnel formula.²⁸ A derivation of this relation for an absorbing film deposited on a transparent substrate, and accounting for multiple reflection at the film-substrate interface was made by Abèles.²⁸ In thermomodulation, $\Delta R/R$ and $\Delta T/T$ result due to variations in ϵ_1 and ϵ_2 . For a small modulation, these are related by²⁹

$$\Delta R/R = \alpha_1 \Delta \epsilon_1 + \alpha_2 \Delta \epsilon_2, \quad (1)$$

$$\Delta T/T = \beta_1 \Delta \epsilon_1 + \beta_2 \Delta \epsilon_2, \quad (2)$$

where α_1 , α_2 , β_1 and β_2 are functions of ϵ_1 and ϵ_2 , and can be obtained from the relationships derived by Abèles, which is listed in the Appendix. Knowing $\Delta R/R$ and $\Delta T/T$, we can then solve for $\Delta \epsilon_1$ and $\Delta \epsilon_2$.

This type of analysis is valid only if the sample is heated uniformly across its thickness; that is, if the hot electrons are geometrically confined because the sample thickness is less than or comparable to the skin depth. An example of this analysis is shown in Fig. 3. Displayed in Figs. 3(a) and 3(b) are the transient thermorefectivity and thermotransmissivity for a 200-Å single-crystalline film. $\Delta R/R$ was obtained for a laser heating fluence of 3.33 mJ/cm², while $\Delta T/T$ was for a fluence of 2.96

mJ/cm². Since both $\Delta R/R$ and $\Delta T/T$ were directly proportional to the laser fluence, we have multiplied $\Delta T/T$ by a correction factor of 1.125 before performing the transformation to obtain the modulation in the dielectric constant. Solving for $\Delta \epsilon_1$ and $\Delta \epsilon_2$, we obtain the curves shown in Figs. 3(a) and 3(d). The following conclusions can be made regarding the transient modulation of the real and imaginary parts of the dielectric constant: (i) their temporal shape follows that of $\Delta R/R$ and $\Delta T/T$; (ii) the modulation in ϵ_2 is larger than that in ϵ_1 (peak $\Delta \epsilon_2/\epsilon_2 = 0.057$, while $\Delta \epsilon_1/\epsilon_1 = 0.017$); and (iii) $\Delta \epsilon_2$ is positive indicating an enhancement of absorption during transient heating. It is well recognized that modulation to ϵ_2 represents modulation to the sum of all electronic transitions at the probe wavelength originating in different areas of momentum space. A notable feature of modulation experiments on gold is a derivative peak centered at ~ 2.4 eV, which is attributed to transitions from the top of the *d* band to the Fermi level.^{23,24} Electronic heating results in reducing (increasing) the number of occupied states below (above) the Fermi level. Since our probe wavelength corresponds to an energy of 2 eV, the experimentally observed enhanced absorption is consistent with that expected, due to electronic heating.

We next decompose the transient modulation in the thermorefectivity and thermotransmissivity, each into two components related to the modulation of the real and the imaginary parts of the dielectric constant. The relative importance of these components is set by the magnitude of the coefficients α_1 , α_2 , β_1 , and β_2 at the probe wavelength. For $\Delta R/R$, these components are $\alpha_1 \Delta \epsilon_1$ and $\alpha_2 \Delta \epsilon_2$; and for $\Delta T/T$ these are $\beta_1 \Delta \epsilon_1$ and $\beta_2 \Delta \epsilon_2$. Such a decomposition of $\Delta R/R$ and $\Delta T/T$ is shown in Fig. 4, from which we can conclude the following: (i) the modulation of ϵ_2 is dominant at the probe wavelength, $\lambda = 615$ nm, and results in the negative sign for both $\Delta R/R$ and $\Delta T/T$, and (ii) the modulation of ϵ_1 results also in a negative sign for $\Delta R/R$, however, it results in a positive sign for $\Delta T/T$.

Inherent in the above analysis is the assumption of uniform heating across the thickness of the thin gold film. We justify this assumption by observing that the 200-Å films are comparable in thickness to the laser skin depth in gold at $\lambda = 615$ nm and that electron transport can further distribute electronic heating along the thickness of

FIG. 3. Transient (a) thermorefectivity $\Delta R/R$ and (b) thermotransmissivity $\Delta T/T$ of a 200-Å single-crystalline gold film. $\Delta R/R$ and $\Delta T/T$ are inverted to obtain the transient modulation to (c) the real, $\Delta \epsilon_1$, and (d) imaginary, $\Delta \epsilon_2$, parts of the dielectric constant.

FIG. 4. Transient (a) thermorefectivity $\Delta R/R$ and (b) thermotransmissivity $\Delta T/T$ after decomposing it into two components each related to the modulation of the real and imaginary parts of the dielectric constant.

the film. The degree by which this uniform heating assumption is violated depends on the film thickness and on the transport properties of the hot electrons.

IV. MODEL

The time evolution of the electron and the lattice effective temperatures, T_e and T_l , respectively, was previously described by a set of two coupled nonlinear partial differential equations:¹

$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla(\kappa \nabla T_e) - G(T_e - T_l) + P_0(r, t) \quad (3)$$

and

$$C_l \partial T_l / \partial t = G(T_e - T_l), \quad (4)$$

where the electronic heat capacity per unit volume $C_e(T_e)$ is assumed to be proportional to the electron temperature, C_l is the lattice heat capacity per unit volume, κ is the electronic thermal conductivity, G is the electron-phonon coupling parameter, which is assumed a constant, and $P_0(r, t)$ represents laser power deposited in the sample. These equations include several assumptions, which could be violated to some degree and can render their validity questionable. We next discuss these assumptions and elaborate on how they could affect the validity of the above simple model.

Local equilibrium is assumed among each of the electron and the phonon subsystems; that is, electron-electron (Coulomb) collisions are assumed to maintain the electron subsystem as a Fermi-Dirac distribution at temperature T_e , while phonon-phonon (anharmonic) collisions are assumed to maintain the phonon distribution as a Bose-Einstein distribution characterized by the temperature T_l . These assumptions are certainly violated over some time or even over all of our probing time. The validity of these assumptions was previously considered by Agranat, Anisimov, and Makshantsev.³⁰ Following their analysis, the thermalization time of the electron subsystem, τ_e , can be estimated from the relation

$$1/\tau_e \sim v_F k_F (\langle E \rangle / E_F)^2, \quad (5)$$

where v_F is the Fermi velocity, k_F is the Fermi wave vector, E_F is the Fermi energy, and $\langle E \rangle$ is the mean electron energy in the metal determined from the Fermi level. For gold, $v_F = 1.40 \times 10^8$ cm/s, $k_F = 1.21 \times 10^8$ cm⁻¹, and $E_F = 5.53$ eV. For a mean electron energy of 0.086 eV, which corresponds to 1000 K, the electron thermalization time, τ_e , is estimated to be ~ 250 fs. Since a mean electron temperature of 1000 K is readily obtained at the laser fluences reported here, electron thermalization is expected to occur on a time scale comparable to the heating-laser-pulse width, which is significantly less than the electron-phonon relaxation time. Under these conditions, assigning a temperature to the hot electrons can be justified when considering times longer than several hundred femtoseconds. To be precise, we refer to T_e as an effective electron temperature since significant deviations from local equilibrium conditions could be present during the femtosecond laser heating pulse, and perhaps some

deviation could be present afterwards.

A noteworthy experimental measurement of the hot-electron energy distribution is that of Fann *et al.*¹⁰ In their experiment, the electron energy distribution in a 400-fs laser-heated gold film was directly measured using time-resolved photoemission. The temporal resolution of this experiment was ~ 700 fs. Results showed that for all times above 800-fs delay between the heating pulse and the ultraviolet probe pulse, the measured hot-electron distribution can be well fitted to a Fermi-Dirac function. In these experiments, a laser heating fluence causing an effective peak electron temperature of several hundred degrees was used. While there was a reproducible deviation from a Fermi-Dirac function at early times, these represented only 10–50 % departure from the fit at delay times < 800 fs and were not present for longer delay times. Thus, our assumption of an effective electron temperature in the simplified model of Eqs. (3) and (4), does not seem to be in large error for the present experimental conditions.

We next consider the phonon subsystem. Phonon-phonon equilibration occurs through scattering described by the anharmonic potential. The thermalization time of the phonons, τ_{ph} , can be estimated by the relation^{30,31}

$$\tau_{ph} \sim l_{ph} / v_s, \quad (6)$$

where l_{ph} is the phonon mean free path, which depends on the phonon energy, and $v_s = 3.7 \times 10^3$ m/s is the speed of sound in gold. For equilibrium conditions at temperature T , $l_{ph} \sim M v_s^2 a / k T \gamma^2$, where $M = 329 \times 10^{-27}$ kg is the ionic mass, $a = 4 \times 10^{-10}$ m is a length of the order of the lattice constant, k is the Boltzmann constant, and $\gamma \sim 2$ is the Gruneisen constant. Evaluating τ_{ph} at $T = 300$ K provides an upper limit on the phonon thermalization time. Using these conditions, τ_{ph} is estimated to be of the order of 10^{-11} s, i.e., larger than the electron-phonon energy-loss lifetime. Thus, the phonon subsystem is expected to be out of equilibrium for times longer than τ_{e-ph} . The validity of the simple analysis of nonequilibrium heating represented by Eqs. (3) and (4) depends on the degree of departure from equilibrium conditions. For the experiments we are presently reporting on, the initial temperature of the gold film was ~ 300 K. The femtosecond heating pulse could not raise the lattice temperature by more than ~ 40 K. That is, during electron-phonon relaxation, the phonon population can be described by two components; a large component represented by a temperature of ~ 300 K, plus a small component of nonequilibrium phonons. Since the mean phonon temperature undergoes only a very small change by laser heating, it is reasonable to expect that, under these conditions, the deviation of the phonon subsystem from equilibrium would not significantly affect the electron-phonon decay and Eqs. (3) and (4) remain basically valid.

Another complication arises due to the nature of heat transport. In Eqs. (3) and (4), the electronic heat transport is assumed to be completely diffusive. The thermalized hot-electron population is assumed to diffuse to the bulk of the thin film due to the temperature gradient set between the laser-heated surface and the bulk of the sam-

ple. Femtosecond time-of-flight experiments have shown that hot-electron transport across 500–3000-Å gold films can proceed with a velocity approaching that of the Fermi velocity.⁸ These measurements provided significant evidence of a ballistic component to electronic heat transport. The question of the nature of hot-electron transport in femtosecond experiments is still not well answered and it is reasonable to expect that ballistic and diffusive transport are both occurring. The importance of each of these mechanisms depends on the considered depth inside the film and on the mean free path of the initial hot electrons.

Considering the geometry of the 200-Å films (film thickness slightly over the skin depth), hot electrons are geometrically confined and electron diffusion perpendicular to the surface is negligible; that is, the film is heated uniformly. This is due to the fact that the optical skin depth in gold is ~ 150 Å at $\lambda = 615$ nm and that hot-electron transport can effectively distribute the energy uniformly throughout the thickness of the film. In addition, radial diffusion of the hot electrons is negligible at time scales of interest (a few picoseconds after the heating laser pulse). Such radial diffusion is very slow since the heating laser beam diameter is much larger than the optical skin depth. Therefore, for the 200-Å films, the diffusion term could be dropped out of Eq. (3).

Electron-defect collisions are not explicitly included in Eqs. (3) and (4). Elastic electron-defect collisions modifies the diffusion term due to electron momentum change after such a collision. Electron collisions with defects are also known to modify electron-electron^{31–34} and electron-phonon coupling.^{34–40} These effects, however, will be neglected for now. Subsequently, we will show that the effect of electron-defect collisions on hot-electron energy loss can be empirically accounted for by modifying the electron-phonon coupling constant, G .

If we neglect diffusion and electron-defect collisions, then a solution of Eqs. (3) and (4) indicates that, initially, the electron temperature could be raised by more than 1000 K, while the lattice temperature remains basically unaltered as shown in Fig. 5. In this example, Eqs. (3) and (4) were solved for $C_e(T_e) = 66T_e$ J/m³ K, $C_l = 2.4 \times 10^6$ J/m³ K,⁴¹ a Gaussian heating laser pulse

FIG. 5. Temporal evolution of the effective electron and lattice temperatures, T_e and T_l , as predicted by the nonequilibrium heating model of Eqs. (3) and (4). The model was solved for a 200-Å film with a laser heating fluence of (a) 1 mJ/cm² and (b) 4 mJ/cm².

(150 fs full width at half maximum), 5% absorption, which was experimentally measured and assumed to be deposited uniformly across the thickness of the film, and neglecting electron transport. Comparison of Fig. 5(a) with Fig. 5(b) shows that τ_{e-ph} increases with the heating fluence. This is consistent with the thermomodulation results shown in Fig. 2. The physical reason for this increase in τ_{e-ph} is the linear dependence of the electronic heat capacity on the electron temperature. In the model shown in Fig. 5, we have assumed the electron-phonon coupling constant G to be 4×10^{16} W/m³ K. This value seems to best fit the decay time in the thermomodulation signal that we observed for the 200-Å polycrystalline films. The comparison of the transient thermomodulation decay time with the hot-electron energy-loss lifetime should be interpreted in view of several uncertainties. These include the pump laser fluence, which depends on the laser focal spot (5 ± 1 μ m), and in quantitatively relating the thermomodulation signal to hot-electron decay.

An important question associated with the femtosecond time-resolved thermomodulation experiments is how to quantitatively relate the thermomodulation signal to an electron effective temperature. One approach is to derive the transient modulation in the real and the imaginary parts of the dielectric constant using, for example, the measured transient modulation in reflectivity and transmissivity. Once the transient dielectric constant is known, it can be related to the band structure and the optical transitions in order to obtain an effective electron temperature. This, however, requires precise knowledge of all optical transitions at the probe wavelength and the manner in which the changes in the occupancy of states due to electronic heating affect their probability. Unfortunately, this information is not available, especially when considering that our probe laser wavelength is ~ 0.4 eV off resonance with the top of the d band to the Fermi-level transition.

Taking these difficulties into account, we have previously proposed an empirical method of analyzing transient thermorefectivity in order to obtain the transient effective electron temperature. Our proposed approach is based on deriving a differential thermomodulation "Fermi" function, which relates the electron-heating-induced thermomodulation to a unit electron temperature increase starting from a particular temperature. This differential Fermi function is obtained experimentally by performing transient thermomodulation at different ambient temperatures.⁵ Simply put, a constant electron temperature jump induces a thermomodulation signal that is dependent on the initial temperature of the electrons. For gold probed at $\lambda \sim 615$ nm, the differential Fermi function was experimentally shown to decrease towards zero as the ambient temperature is reduced below ~ 150 K. Asymptotic behavior appears to be reached near an ambient temperature of 300 K. Higher temperatures were not considered in Ref. 5. The decay time of the transient thermomodulation signal can resemble that of hot-electron decay time if the considered temperature region for the differential Fermi function is constant, which appears to be the case for the lower heating fluences. At the higher fluences, where the effective electron tempera-

ture is raised by many hundreds of degrees above the ambient 300 K, asymptotic behavior of the differential Fermi function might not persist. The extent for which the thermomodulation decay could deviate from the hot-electron decay is not known. This represents an uncertainty in the interpretation of the thermomodulation data. We could, however, conclude that there seems to be a qualitative agreement between the hot-electron decay time and the thermomodulation decay time based on the above-mentioned asymptotic behavior of the differential Fermi function. Moreover, it is interesting to note that the electron-phonon coupling parameter G derived from fitting the transient-thermoreflectivity decay with hot-electron decay as derived from Eqs. (3) and (4) shows remarkable agreement with that theoretically predicted for several metals.¹²

Another experimental effect on the transient thermomodulation signal is caused by the finite pulse width of our probe. Therefore, our thermomodulation signal is, in fact, the result of the convolution of the actual signal with the probe pulse. This only affects the shape of the signal near its peak, where the decay rate is fastest. Since the transient thermomodulation decay signals are about an order of magnitude larger than our probe pulse width, we do not expect that this effect would cause significant error. This convolution effect, however, appears to be visible in the semilogarithmic plots in the inset of Fig. 1, where early in the decay (≤ 0.5 ps) there appears to be a deviation from the simple exponential that is subsequently observed.

V. DEPENDENCE OF HOT-ELECTRON DECAY TIME ON CRYSTAL STRUCTURE

In order to investigate the role of defects on hot-electron energy-loss lifetime, τ_{e-ph} , we have conducted transient thermoreflectivity and thermotransmissivity on single-crystalline and polycrystalline 200-Å films. The decay time of the fast transient was measured as a function of the heating laser fluence. Results are shown in Fig. 6. Each datum is an average of 6–8 different mea-

FIG. 6. Decay time of the fast transient in the thermoreflectivity (solid symbols) and thermotransmissivity (open symbols) of 200-Å single-crystalline (diamond) and polycrystalline (squares) gold films as a function of heating laser fluence.

surements conducted using three sets of single-crystalline and polycrystalline films. The decay time is defined as the width of the transient signal at e^{-1} of the difference between the maximum transient and the slowly decaying tail following it. The standard deviation of the decay time measurements was less than 10% of the average value. Results clearly show a systematic, almost constant increase in the decay time for the single-crystalline films when compared with the polycrystalline films.

Several film properties could have caused this deviation. First, the film thickness could be different, which would cause a difference in power deposition between the polycrystalline and single-crystalline films. This is ruled out since both types of films were fabricated using the same conditions, except for the substrate type and temperature. Thus, errors in the relative thickness of the different films is very small (within several angstroms). As described previously, the fabrication of the single-crystalline gold films involves their deposition on a thin layer of silver deposited on a sodium chloride crystal. Some of the gold could alloy with the silver and this alloyed layer would then be acid etched along with the silver during removal of the gold film. The reduction in the gold film thickness by alloying and subsequent removal is minimized by maintaining a relatively low substrate temperature during gold film deposition, ~ 450 K, to minimize alloying without adversely affecting epitaxy. More importantly, the thickness of the silver layer when depositing the 200-Å film was only ~ 10 Å. Thus, alloying and subsequent removal of the gold film could not have reduced the film thickness by more than that.

Second, the removal process of the single-crystalline films could have introduced some unexpected changes in film properties that might have an effect on hot-electron decay. This hypothesis was tested by conducting the transient thermomodulation measurements on polycrystalline films deposited on a sodium chloride crystal at room temperature and subsequently removed using the same technique employed for the single-crystalline films. Results for these polycrystalline films were in agreement with those directly deposited on the glass slide. Thus, the film lift-off process could not have been responsible for the observed difference between the two types of films.

Third, the optical properties of the polycrystalline and single-crystalline films could differ in a way that causes the power deposition to vary for the same incident laser fluence. The film that absorbs more laser energy will subsequently have a longer transient decay time. This was a major concern especially since published data on the optical properties of thin films are known to differ among themselves and the absolute value of thin-film absorption cannot be easily measured with high precision. To check for the magnitude of the variation in power deposition between the polycrystalline and single-crystalline films, we have compared the magnitude of the maximum modulation in the transmissivity for the two kinds of films at different pump fluences. For this comparison, the transient thermomodulation measurements for the two types of films were conducted immediately, one after the other, to avoid changes in the laser heating fluence. Three independent measurements were made for each fluence

(four different fluences ranging from 0.7 to 4 mJ/cm² were considered). The peak thermomodulation transmissivity signal for the polycrystalline and single-crystalline films showed better than 5% agreement, with the modulation signal leaning towards being slightly higher for the polycrystalline films. This seems to preclude the possibility that the difference in the observed decay time between the polycrystalline and single-crystalline films is due to power deposition effects.

This leads us to the conclusion that the shorter transient thermomodulation decay time observed for the polycrystalline films is due to faster hot-electron energy loss (smaller τ_{e-ph}), which is promoted by an increased level of defects. Several theoretical studies have shown that defects can influence τ_{e-ph} by affecting the rate of energy transfer between electrons and phonons. Gold has a monatomic unit cell, therefore, there are no optical phonons. An increased level of defects promotes coupling between electrons and transverse acoustic phonons due to partial removal of crystal momentum conservation constraints by intermediate impurity scattering.³⁶ In contrast, ultrasonic attenuation experiments and theoretical calculations have shown that coupling between electrons and longitudinal phonons is reduced with increased level of defects.³⁸ This was explained by observing that the longitudinal vibrations, which the electrons fluctuate in phase with, set up regions of compressed electron gas with increased mean energy and others with dilated electron gas with reduced mean energy. Energy is dissipated from the longitudinal vibration by electron diffusion from the high-energy to the low-energy region. This diffusion is hindered by disorder, thus, electron-phonon coupling is reduced.³⁸ This effect, however, does not apply to our case, since it treats the case where the phonons are externally heated and subsequently come to equilibrium with the electrons (i.e., the inverse of our case). Therefore, the intermediate defect scattering is expected to reduce the hot-electron energy-loss lifetime.

We next briefly comment on the nature of electron-lattice defect collisions for the two different types of gold films used in our experiments. Each individual electron undergoes a collision with another electron or a phonon on the average within a mean free path. For a 2-eV hot electron, the mean free path for an electron-electron collision or an electron-phonon collision is about a few hundred angstroms. For the polycrystalline gold films used in the present experiments, microstructural examination revealed a large distribution of grain sizes with an estimated average of ~ 155 Å. Thus, the number of electron-grain boundary collisions is comparable to, or even larger than, that of electron-electron and electron-phonon collisions. Grain boundaries are known to be very efficient in scattering conduction electrons. For metals, the probability of an electron to pass a single grain boundary is theoretically estimated to be about 0.7.⁴² Given that each hot electron undergoes several collisions with grain boundaries prior to thermalization with the lattice, then grain boundaries could be responsible for the observed difference in the decay time between the polycrystalline and the single-crystalline films. Other defects such as dislocations or stacking faults, which are

present in the single-crystalline films, are known to be significantly less effective in scattering conduction electrons.⁴³ The scattering of conduction electrons by stacking faults in Cu was theoretically calculated.⁴⁴ At near all wave vectors, conduction electrons at the Fermi surface penetrate a stacking fault with a very small probability of scattering (10^{-3} – 10^{-4}). Thus, stacking faults represent a very weak perturbation to conduction electrons near the Fermi level.⁴⁴

For the 200-Å films, the average grain size is comparable to the film thickness and it is difficult to separate the role of lattice defects on hot-electron energy-loss lifetime from that of surfaces. Previous studies on the resistivity of thin films has indicated that the surface roughness of polycrystalline gold films causes the diffuse scattering of electrons at the surface. This is in contrast to the atomically smooth nature of the surface of single-crystalline gold films which specularly reflects the electrons.²¹ From a theoretical point of view, electron collisions with surfaces distort their momentum distribution in a manner that could depend on surface roughness.⁴⁵ Such surface effects were shown to penetrate into the interior a depth comparable to the mean free pass of the electrons⁴⁵ (i.e., throughout the thickness of the film). We have also conducted transient optical thermomodulation measurements on 100-Å polycrystalline and single-crystalline (epitaxially grown) films. For these films, electron microscopy showed the formation of separate islands that are interconnected by bridges with voids covering a significant area of the sample for both types of films. Similar trends were observed as for the 200-Å films.

We next compare the experimentally obtained transient decay time in Fig. 6 with the energy-loss lifetime, τ_{e-ph} , obtained from the simple model of Eqs. (3) and (4). In the experimental measurements, we define the decay time as the width of the transient signal at e^{-1} of the difference between the maximum transient and the slowly decaying tail following it. For the model we define the τ_{e-ph} as the width of the transient electron temperature at e^{-1} of the difference between the peak T_e and its final equilibrium value. These definitions are made here mainly to facilitate a comparison of the results for single-crystalline versus polycrystalline films. In Fig. 7, the

FIG. 7. Hot-electron energy-loss lifetime, τ_{e-ph} , obtained from Eqs. (3) and (4) for the experimental conditions of Fig. 6.

theoretical τ_{e-ph} is shown as a function of laser fluence for different values of the electron-phonon coupling parameter, G . Comparison of Fig. 6 with Fig. 7, shows that the model predicts well the experimentally observed increase in decay time with laser fluence. Moreover, the solution of the model for $G = 4 \times 10^{16} \text{ W/m}^3 \text{ K}$ shows agreement with the experimental transient decay time in the 200-Å polycrystalline films. For the single-crystalline films, comparison of the model with the experimental decay time indicates a small decrease in the electron-phonon coupling parameter from that for the polycrystalline film, $G \sim 3.5 \times 10^{16} \text{ W/m}^3 \text{ K}$.

VI. THE EFFECT OF CRYSTAL STRUCTURE ON ELECTRON TRANSPORT

The use of 200-Å films results in the geometric confinement of the hot electrons and thus allows the observation of the transient thermomodulation signal due to hot-electron energy loss without being affected by transport. For thicker films, hot-electron transport affects the thermomodulation signal. Therefore, the effect of lattice defects on hot-electron transport can be studied using thicker polycrystalline and single-crystalline films. We have conducted transient thermoreflectivity and thermotransmissivity on 400- and 800-Å polycrystalline and single-crystalline gold films. The decay time of the transient $\Delta R/R$ for single-crystalline films with different film thicknesses is shown in Fig. 8. We observe that as the film thickness is increased from 200 to 400 Å, there is a significant reduction (about a factor of 2) in the decay time. With the further increase in thickness to 800 Å, the reduction in the decay time is less. This shows that, for film thicknesses larger than the optical skin depth, the decay of the transient $\Delta R/R$ represents both hot-electron energy loss and electron transport inside the sample where it is not being probed by reflectivity.

We next consider the transient thermomodulation for the 800-Å single-crystalline and polycrystalline films. The results, displayed in Fig. 9, represent an average of 4–6 different measurements conducted on one set of films. The standard deviation in each decay time measurement is less 12% of the average value. Comparison

FIG. 8. Decay time of the fast transient in the thermoreflectivity as a function of laser heating fluence measured for film thicknesses of 200, 400, and 800 Å.

FIG. 9. Decay time of the fast transient in the thermoreflectivity (solid symbols) and thermotransmissivity (open symbols) of 800-Å single-crystalline (diamond) and polycrystalline (squares) gold films as a function of heating laser fluence.

of the results in Fig. 9 with that in Fig. 6 show that the transient decay time of $\Delta T/T$ is affected less by the increased film thickness than that of $\Delta R/R$ since reflectivity is influenced by each electron leaving the excited volume; whereas in a gross sense, transmissivity is influenced only by those electrons which leave (laterally) the volume associated with the probe beam path through the sample. This is a small effect since the diameter of the laser beam is much larger than both the optical skin depth and the film thickness.

For the 800-Å films, comparison of the transient thermoreflectivity for the polycrystalline films to those for the single-crystalline shows behavior opposite from that observed for the 200-Å films. The decay time of $\Delta R/R$ was faster for the single crystalline. We interpret these results by observing that, for the 800-Å films, hot-electron transport is impeded by grain boundaries. While grain boundaries increase electron-phonon coupling, this effect on transient $\Delta R/R$ decay time (which would cause it to decrease for the polycrystalline films) appears to be smaller than the opposite effect of impeding electron transport inside the film.

The thermal conductivity of metals is predominantly controlled by electron transport properties. The reduction of the thermal conductivity of metals by lattice defects is well demonstrated and is attributed to the reduction of electron mean free path. Previous transient thermomodulation studies have shown that the thermal diffusivity, defined as the ratio of the thermal conductivity to the heat capacity per unit volume, of evaporated and sputtered metal films can be significantly less than that of bulk materials. The thermal diffusivity of nickel thin films was reduced from its bulk value by a factor of 3 for an evaporated film and by a factor of 4 for a sputtered film.⁴⁶

In Fig. 9, an interesting sign reversal is observed in the difference between the decay time of the fast transient in $\Delta T/T$ for the polycrystalline and single-crystalline films as a function of laser fluence. This was also observed for 400-Å films. At this stage we can only offer the following qualitative explanation. We notice that $\Delta T/T$ is less affected by electron transport than $\Delta R/R$ and that hot-

electron transport competes with energy loss. For low laser fluences, where diffusion is less important, the increased electron-phonon coupling for the polycrystalline films results in a faster decay as observed for the 200-Å films. At the higher fluences diffusion becomes more important. This affects the spatial distribution of hot electrons across the film, causing it to be less uniform for the polycrystalline than for the single-crystalline films due to lower κ . Since the hot-electron energy-loss lifetime increases with the effective electron temperature, we would expect a slower transient decay time for the polycrystalline films. A quantitative analysis of electron transport would require a more extended treatment than that permitted by the diffusion term in Eq. (3). Among the factors which need to be considered are the possible role of ballistic hot-electron transport, the dependence of electron transport on T_e and T_l , and the nature of electron-lattice defects collisions.

We next make a brief comment on these factors and show that a much more complicated treatment is needed to model electron transport in the thicker films. The possibility of ballistic electron transport across the sample provides an uncertainty to Eqs. (3) and (4). In the femtosecond time-of-flight experiment of Ref. 8, heat transient time was clearly shown to scale linearly with sample thickness and to travel across the thickness of the sample with a velocity close to the Fermi velocity. This gives a strong evidence of a ballistic component to heat flow; however, as discussed in Ref. 8, femtosecond time-of-flight measurements by themselves do not provide a conclusive evidence of ballistic transport, since electron cooling and the dependence of the electronic thermal conductivity on temperature at large temperature excursions complicate the analysis. The relative magnitude of ballistic versus diffusive heat transport is not easily determined and requires further studies. A key parameter to better understanding this question is consideration of the available data on the range of hot electrons in gold. This represents a combined mean free path of electron-electron and electron-phonon scattering. The range of hot electrons in gold was previously measured as a function of hot-electron energy.²⁷ For 2-eV electrons, measured from the Fermi level, E_F , the range was 250 ± 30 Å. This increased to about 650 Å for 1-eV electrons. The electron-phonon mean free path slowly increases with electron energy, E , according to $l_{e-ph} \sim (E + E_F)^2$ and is inversely proportional to the lattice temperature.⁴⁷ For gold l_{e-ph} is about 200 Å for a 1–2-eV hot electron in a thermal phonon bath at 300 K.²⁷ For electrons close to the Fermi level, the electron-electron mean free path strongly depends on the electron energy according to $l_{e-e} \sim E^2$.⁴⁸ For 2-eV electrons, l_{e-e} is estimated to be several hundred angstroms.^{27,49} Since the 800-Å films are thicker than the range of a 2-eV hot electron, it is reasonable to expect that there is both a diffusive and a ballistic component to electron transport.

We next consider the dependence of the thermal conductivity on the effective electron and lattice temperatures. The thermal conduction of metals is dominated by electron transport. In the diffusive transport limit, the kinetic theory of gases indicates that the thermal conduc-

tivity is described by the relation

$$\kappa = \frac{1}{W} = \frac{1}{3} v C_v = \frac{1}{3} v^2 \tau C_v, \quad (7)$$

where W is the thermal resistance, C_v is the heat capacity per unit volume, which is directly proportional to the electron temperature, v is the average electron velocity, τ is the average time between collisions, and l is the mean free path between collisions. Electron-electron, electron-phonon, and electron-imperfection collisions determine l and τ , and consequently κ and W . For a conduction electron with a low-excitation energy above the Fermi level, the exclusion principle reduces the probability of an electron-electron collision, thus τ is predominantly limited by electron-phonon collisions. Under these conditions τ is inversely proportional to the lattice temperature, to a first-order approximation. Thus, the thermal resistivity due to electron-phonon collisions will have the dependence $W_{e-ph} \sim T_l/T_e$. However, in the present experiments lattice heating is only a small fraction of the initial sample temperature. Thus, the effect of electronic heating on the electron conductivity could be important. An excited electron with energy E above the Fermi level in a metal with an effective electronic temperature T_e has an electron-electron scattering rate $1/\tau_{e-e}$ of the form

$$1/\tau_{e-e} = aE^2 + b(k_B T_e)^2, \quad (8)$$

where k_B is the Boltzmann constant and a and b are independent of E and T_e .⁵⁰ If we assume that the electrons reach a state of quasiequilibrium among themselves, establishing an effective temperature $T_e \sim 1000$ K, then the scattering rate assumes the form $1/\tau_{e-e} \sim T_e^2$. Since the electronic heat capacity is directly proportional to the electron temperature, it follows that the electronic thermal resistivity due to electron-electron collisions, W_{e-e} , is proportional to T_e . Electron-defects collisions could also depend on T_e and T_l in a manner that is not presently understood and introduces an extra contribution to the thermal resistivity, W_{e-i} . If we assume that the collision rates due to the separate mechanisms can add up in accordance with the Matthiessen's rule, then the thermal resistivity, W , is the sum of W_{e-e} , W_{e-ph} , and W_{e-i} . While the dependence of W_{e-e} and W_{e-ph} on T_e and T_l is qualitatively understood, the quantitative contribution of each of these scattering mechanisms to W is not presently available for the case of nonequilibrium heating. Therefore, even if we assume the diffusive limit, it is difficult to proceed further with this type of analysis in order to quantitatively model hot-electron relaxation in the thicker films using Eqs. (3) and (4).

VII. CONCLUDING REMARKS

We have conducted femtosecond time-resolved thermorefectivity and thermotransmissivity on single-crystalline and polycrystalline thin gold films. The transient decay time for the reflectivity and the transmissivity are equal for film thicknesses comparable to the optical skin depth. For thicker films, a faster reflectivity decay time is observed due to hot-electron transport. Grain

boundaries, and perhaps surface roughness, in the polycrystalline films seem to slightly reduce the transient decay time, which is modeled by a small increase in the value of the electron-phonon coupling constant. Grain boundaries also appear to impede hot-electron transport which, for the thicker films, results in a slower decay time for the polycrystalline films.

We have shown that the technique of femtosecond transient thermotransmissivity and thermorefectivity can be used to study the effect of lattice defects on hot-electron energy loss and transport in metals. This technique provides a powerful tool to characterize the nature of electron interaction with various types of lattice defects. Using samples with controlled and well-characterized density of structural defects or impurities, it will be possible to study their effect on the strength of the electron-phonon coupling. Time-resolved thermomodulation also offers the possibility to probe how electron transport is affected by a particular type of defect or impurity. The time-of-flight experiment outlined in Ref. 8 provides a particularly attractive geometry for transport studies. Quantitative measurements on the strength of the thermomodulation signal and relating it to the number of electrons arriving at the back surface would provide significant information on the scattering strength of a particular lattice defect, such as grain boundaries. The initial hot-electron energy, measured from the Fermi level, could be varied using a tunable femtosecond pump laser. These types of experiments would provide the data needed to compare with present theoretical understanding on the probability of electron scattering at various types of defects.⁴¹⁻⁴⁴

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APPENDIX

The modulation of the real and the imaginary parts of the dielectric function, $\Delta\epsilon_1$ and $\Delta\epsilon_2$, is determined from the data on $\Delta R/R$ and $\Delta T/T$ as a function of time by considering the appropriate transformation. The complex index of refraction, $N=n+ik$, is related to the complex dielectric function by $N^2=\epsilon_1+i\epsilon_2$. We use the formulas derived by Abèles, which is a derivation of the Fresnel equations for an absorbing media on a transparent substrate. Multiple reflections at the metal-substrate

interface are accounted for. If we define $n_0=1$ and $n_s=1.5$ to be the index of refraction of air and glass, d is the gold film thickness, λ is laser wavelength, then the reflection and the transmission from the metal side are given by²⁸

$$R = \frac{abe^{2k\eta} + cde^{-2k\eta} + 2r \cos 2n\eta + 2s \sin 2n\eta}{bde^{2k\eta} + ace^{-2k\eta} + 2t \cos 2n\eta + 2u \sin 2n\eta},$$

$$T = \frac{16n_0n_s(n^2+k^2)}{bde^{2k\eta} + ace^{-2k\eta} + 2t \cos 2n\eta + 2u \sin 2n\eta},$$

where

$$\eta = 2\pi d/\lambda,$$

$$a = (n - n_0)^2 + k^2, \quad b = (n + n_s)^2 + k^2,$$

$$c = (n - n_s)^2 + k^2, \quad d = (n + n_0)^2 + k^2,$$

$$s = 2k(n_s - n_0)(n^2 + k^2 + n_0n_s),$$

$$u = 2k(n_s + n_0)(n^2 + k^2 - n_0n_s),$$

$$r = (n_0^2 + n_s^2)(n^2 + k^2) - (n^2 + k^2)^2 - n_0^2n_s^2 - 4n_0n_sk^2,$$

$$t = (n_0^2 + n_s^2)(n^2 + k^2) - (n^2 + k^2)^2 - n_0^2n_s^2 + 4n_0n_sk^2.$$

Starting from the values of n and κ , or equivalently ϵ_1 and ϵ_2 , it is possible to use the above equations to derive R and T . For our 200-Å gold films we measure $R=0.665\pm 0.02$, while $T=0.28\pm 0.02$. Since we can measure R and T for our samples, we can iterate through the above equations to obtain n and k . For example, for $n=0.19$ and $k=3.85$, we obtain $R=0.658$ and $T=0.273$, which is within our measurement accuracy. The published values of n and k are 0.21 and 3.272, respectively. We have found that our solutions for n and k are quite sensitive to the accuracy of the film thickness which is known only to ± 50 Å. This might contribute to the difference between our derived n and k and the previously published values. Moreover, the optical properties of thin films are known to depend on thickness and are sensitive to film preparation. Nevertheless, deviations in our derived values of n and k from the published data could only have a small effect on the calculated $\Delta\epsilon_1$ and $\Delta\epsilon_2$. In proceeding with the analysis, we used the published values of n and k .

In thermomodulation, $\Delta R/R$ and $\Delta T/T$ result due to modulations in ϵ_1 and ϵ_2 . These can be related by

$$\Delta R/R = \alpha_1 \Delta\epsilon_1 + \alpha_2 \Delta\epsilon_2,$$

$$\Delta T/T = \beta_1 \Delta\epsilon_1 + \beta_2 \Delta\epsilon_2,$$

where α_1 , α_2 , β_1 , and β_2 are obtained from the above relationships derived by Abèles. Knowing $\Delta R/R$ and $\Delta T/T$, we can then solve for $\Delta\epsilon_1$ and $\Delta\epsilon_2$.

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Observation of surface enhanced multiphoton photoemission from metal surfaces in the short pulse limit

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Photoelectrons with excess kinetic energy corresponding to several absorbed photons above the work function have been measured from atomically clean Cu(110) and Cu(100) surfaces under ultrahigh vacuum conditions. The power dependence of the photoemission yield does not follow a simple power law dependence corresponding to the number of photons absorbed. This behavior is reminiscent of other above threshold ionization (ATI) or tunnel ionization (TI) processes observed for atoms in the gas phase. The photoelectrons are generated with laser pulsewidths less than 100 fs in duration and peak powers as low as 100 MW/cm². These intensities are on the order of 10⁵ times lower than that required to observe similar phenomena in the gas phase. The relatively low intensities and correlation with surface roughness suggests a contribution from a surface enhancement mechanism. Thermal heating and space charge effects have been ruled out, and the possibility of electric field enhancement at the surface due to the coupling of photons into surface plasmons is discussed. The nonlinear yield and enhancement of the photoemission produced by short pulse excitation needs to be considered when discussing photoinduced hot electron reaction channels at metal surfaces. © 1995 American Institute of Physics.

INTRODUCTION

There exists a great body of research on the topic of above threshold ionization (ATI) of isolated atoms in the gas phase. Briefly, ATI is a multiphoton process in which an atom absorbs more photons than the minimum necessary for ionization.¹ With laser intensities in the 10¹³–10¹⁴ W/cm² range, as many as 40 peaks, have been reported in the electron energy distribution.² The number of review articles on this topic is evidence of the experimental and theoretical interest in this phenomenon.^{3,4} Despite the great amount of interest in gas phase ATI, comparatively little has been done to date concerning ATI at solid surfaces, often called above threshold photoemission (ATP).⁵

Our work is motivated by the desire to use current ATI theories to understand the more complicated behavior observed at a metal surface. Several new considerations arise as a result of the solid state medium. ATI spectra can show peaks due to resonances induced by the AC Stark shift arising from the enormous light field (excited bound states are shifted into resonance with an intermediate number of photons). In a metal, however, the continuum band structure prohibits any sharp features, and only AC Stark shifts into resonance with surface states and image states⁵ can produce

sharp features in the photoelectron spectrum. On the other hand, since the occupied density of states in a metal has a sharp cutoff at the Fermi energy, it is possible to measure a series of plateaus, rather than peaks, separated by the photon excitation energy. One intriguing possibility present during ATP that is not allowed in ATI is that there can be significant field enhancement at the surface caused by surface plasmons, image states, and/or adsorbate induced dipole fields.

A few recent studies in which the classic ATP behavior of multiple peaks or plateaus separated by the incident photon energy in their photoelectron spectrum from a metal surface have been reported.^{5–7} All these previous studies employ relatively high pulse energy (>100 μJ/cm²/pulse) or peak intensity (>10 GW/cm²) laser pulses. Together with the relatively long pulse durations involved, it is difficult to be sure that these results are not influenced by space charge effects, i.e., energy gained during the field-free Coulomb explosion of the electron cloud on the way from the sample to the detector.⁸

In this paper we present the first observation of ATP spectra from single crystal copper surfaces in the “very short” pulse regime, where very short refers to pulse durations less than ~500 fs (Ref. 3), and we also provide analogies with ATI and tunnel ionization (TI) experiments. Using pulse durations less than 100 fs, the electrons are produced with the kinetic energy possessed at the moment of photoemission, rather than the value that they would attain in a “long pulse” (pulse duration greater than ~0.5 ps) measurement, where the electrons can acquire significant amounts of the quiver energy back from the light field due to pondero-

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motive acceleration.⁴ Furthermore, we ensure that the average number of electrons emitted per pulse is on the order of one in order to avoid space charge effects as discussed by Petite *et al.*⁸ In the present study, electrons with as much as 7 eV kinetic energy have been measured. The present work is unique in that far lower laser pulse energy and peak intensity are used in this study than in previous work. This allows us to rule out several possible competing mechanisms, such as space charge acceleration, transient thermionic emission, and ponderomotive acceleration. Finally, it is necessary to find rough spots on the surface when using these low intensities, which indicates that surface roughness plays a critical role in this process.

Apart from the intrinsic interest in the surface-laser field interaction that leads to electrons with large excess energy, there are also important surface photochemical issues on which these observations may have an impact. Many photochemical processes at metal surfaces have been considered to be thermal in nature (i.e., simple laser heating of the lattice), especially when employing high intensity pulsed lasers.⁹ There has been an increasing amount of evidence that many of these processes are due to electronic excitations, however.⁹ Recently, a great deal of attention has been paid to nonthermal photoinduced reactions in which vibrationally and rotationally hot desorption products are observed. These have been observed for one-photon as well as multiphoton excitation. In either case, excited electrons are believed responsible for the reactions.¹⁰⁻¹²

These new observations of true surface photochemistry are generally interpreted as arising from subvacuum electrons within the metal that couple to excited states of adsorbates at the metal surface. The electronic reaction channel in multiphoton processes is separable from thermal mechanisms only when short pulses are utilized, that is, on time scales shorter than lattice heating from the photoexcited electrons. For one-photon processes, the electronic and thermal contributions can be separated by using very low intensity illumination,¹³ but for processes that have a superlinear fluence dependence, or when time resolved studies are carried out with short pulsewidths (<1 ps), it is necessary to have high intensity pulses, and the only way to separate thermal mechanisms from the electronic mechanisms is to use very short pulsewidths (<100 fs). This has been done successfully by several groups, and brings up the role of large amounts of sub-vacuum electrons. The production of potentially large numbers of highly reactive sub-vacuum and above-vacuum photoelectrons also needs to be considered in this problem because these electrons have been shown to efficiently interact with adsorbate molecules.^{9,12-17} The present work characterizes this aspect of the photophysical processes operating at the surface, which may also contribute to the surface photochemistry.

EXPERIMENT

The laser system used in these studies consists of a self-mode-locked Ti:Sapphire laser pumped by about 7.7 W from a cw Ar⁺ laser. This system produces pulses with energy of about 10 nJ/pulse, with a pulsewidth of 70–90 fs at a repetition rate of 82 MHz, and is tunable from 750 to 850 nm.

Pulse broadening due to the group velocity dispersion of the uncompensated pulse as it passes through focusing lenses and the chamber window leads to a pulse width of roughly 100 fs at the sample. Some of the results presented here required the use of a regenerative amplifier utilizing chirped pulse amplification.¹⁸ The amplifier is pumped by an intracavity doubled YLF laser operating at a repetition rate of 1 kHz that provides about 3 W of pump power. The output of the regenerative amplifier is about 400 μ J/pulse before recompression, and 180 μ J/pulse after recompression, and the pulse width is roughly 200 fs after recompression for the studies performed here.

The ultrahigh vacuum system uses standard techniques to achieve a base pressure of 2×10^{-10} Torr. Our Cu(110) and Cu(100) samples were cleaned by heating in oxygen to remove bulk carbon impurities and then further cleaned by repeated sputter-annealing cycles. We chose Cu because its electronic structure is relatively simple, and has been well studied. In addition, the laser photon energy of 1.6 eV is too small to excite either *d*-band electrons or image states by a one photon process, which might otherwise complicate the interpretation of the results. The work function of Cu(110) is 4.5 eV, and that for Cu(100) is 4.6 eV. In either case, at least three photons are required to produce photoemission since the photon energy is 1.6 eV. The Cu sample is mounted on a manipulator with five degrees of freedom that allows a variety of angles of incidence of the laser and detector angles to be investigated. The photoelectron spectra were measured with a 10 cm inner radius hemispherical energy analyzer with 1% relative energy resolution and a 10° acceptance angle. The data reported here, with the exception of the polarization dependence study, were obtained with the surface normal parallel to the axis of the detector entrance, and the laser beam making a 45° angle with the surface normal. The crystallographic [010] direction lies in the plane defined by the laser beam and the surface normal. Transmission energies of either 10 or 20 V were used, which leads to 100 or 200 meV resolution, respectively. A -3.0 to 6.0 V bias is applied to the sample to eliminate the effects of any stray electric fields. The applied bias voltage extends the range of *k* states being collected, but contributes less than 0.11 eV uncertainty to the energy resolution since the bias is small and copper exhibits nearly free electron behavior. The electron kinetic energies reported here have the kinetic energy due to the bias voltage subtracted, and correspond to the kinetic energy of the photoemitted electrons leaving the metal surface.

RESULTS

A schematic representation of the photoexcitation with the laser fundamental, second harmonic, and third harmonic is shown in Fig. 1. The measured spectra when using the three different photon energies are shown in Fig. 2. The lowest photon energy, shown as $h\nu_1$ corresponds to the fundamental laser wavelength at roughly 770 nm, or about 1.6 eV. Photon energies $h\nu_2$ and $h\nu_3$ are obtained by doubling and tripling the laser fundamental, respectively. Given the 4.5 eV work function of Cu(110), it is seen in Fig. 1 that photoemission requires three photons at the laser fundamental, or two doubled photons, or one tripled photon.

FIG. 1. Schematic representation of one-, two-, and multiphoton photoemission spectra from copper. The photon energy of the laser fundamental is $h\nu_1$, and that for the second and third harmonics is $h\nu_2$, and $h\nu_3$, respectively, and Φ is the work function.

The cases of one photon and two photon photoemission are in complete accordance with expectations, as seen in Figs. 2(a) and 2(b). That is, the width of the photoemission spectrum is given by the total photon energy minus the work function. The behavior is completely different in the case in which the laser fundamental is used. In particular, rather than dropping off at the point in energy where three photons have been absorbed, the kinetic energy of the photoelectrons extends 6–8 eV above the vacuum threshold. There are electrons being emitted whose kinetic energy would correspond to the absorption of over seven photons. Studies of the laser power dependence of the photoemission yield indicate that the yield as a function of electron kinetic energy does *not* follow a power law based on the number of photons that correspond to the kinetic energy of the emitted electron, as seen in Fig. 3(b).

As the sample is moved around normal to the direction of electron emission, hot spots are found at which the photoemission yield increases dramatically, on the order of a factor of 100–1000. These hot spots are much smaller than the laser beam waist at the sample. This was determined by translating the sample from side to side and measuring the distance from 10% of the maximum photoemission yield on one side of the maximum, through the maximum itself, and to 10% of the maximum on the other side. Given that the signal varies with the third power of the laser intensity, the 10% points occur at roughly 50% maximum laser intensity. We measured a distance of $96 \pm 15 \mu\text{m}$ as the distance be-

FIG. 2. One-photon, two-photon, and multiphoton photoemission spectra from Cu(110). (a), (b), and (c) are the spectra measured when using photon energies of $h\nu_3$, $h\nu_2$, and $h\nu_1$, respectively, as shown in Fig. 1. The peak laser intensities at $h\nu_3$, $h\nu_2$, and $h\nu_1$, are $1 \times 10^4 \text{ W/cm}^2$, $1 \times 10^7 \text{ W/cm}^2$, and $1 \times 10^9 \text{ W/cm}^2$.

tween a 10% photoemission yield on either side of the maximum. The beam waist (the diameter of the $1/e^2$ points) at the sample surface is measured to be about $100 \mu\text{m}$ through measurements with pinhole apertures which indicates a full width at half maximum (FWHM) of roughly $60 \mu\text{m}$, and yields an $85 \mu\text{m}$ projection on the surface since it is at a 45° angle relative to the laser beam. These measurements place an upper limit on the size of the hot spots and are consistent with roughness features that are far smaller than the laser beam spot size.

Polarization studies were carried out on the Cu(100) sample that support the interpretation of these results in terms of locally rough hot spots. Since *p*-polarized light is more strongly absorbed than *s*-polarized light, it is necessary to rotate the sample into an orientation normal to the laser beam in order to prevent the polarization-dependent absorptivity from affecting the polarization dependence studies. This causes the sample to be oriented at 45° relative to the detector entrance and slightly lowers the absolute intensity of the signal, but it does not affect the relative intensities of the spectra obtained. The polarization was rotated with a half-

FIG. 3. Typical spectra as a function of laser intensity. The intensity dependence shown in (a) and (b) are each obtained for about 50% of the hot spots. The laser intensities employed for the five curves are (i) 0.17 GW/cm², (ii) 0.28 GW/cm², (iii) 0.41 GW/cm², (iv) 0.68 GW/cm², (v) 0.89 GW/cm². The inset in b displays a log-log plot of the photoelectron yield vs the laser intensity taken while monitoring 0.8 eV electron kinetic energy (solid circles) and 2.5 eV electron kinetic energy (solid squares). The slope of the log-log plot at 0.8 eV is 2.8 and the slope at 2.5 eV is 3.2.

wave plate such that the position of the beam on the surface did not change. It is found that the signal has a twofold symmetry as a function of polarization rotation. That is, that maxima (and minima) are separated by 180° of polarization rotation, but the maxima and minima are not necessarily aligned with the crystallographic axes. Furthermore, if the crystallographic axes were significantly affecting the signal level, there would be horizontal and vertical maxima, where the fourfold symmetry reflect the underlying fcc lattice along the [100] direction. There are also secondary maxima and minima as a function of polarization rotation at more or less arbitrary polarization. Sometimes hot spots are found that have maxima with vertical polarization, sometimes with horizontal polarization, and sometimes at intermediate positions, all with equal probability. This indicates that the rough spots destroy the order at the near-surface region, and when

FIG. 4. The solid lines indicate the polarization dependence of three hot spots. A half-wave plate was rotated through 180° in order to rotate the laser polarization through 360°. The laser polarization is along the crystallographic [010] direction at 0°, 180°, and 360°. The dashed lines are the calculated polarization dependencies using Eq. (1) and the quantities in Table I.

the light couples into the hot spot it is not affected by the underlying crystallographic symmetry several tens of Å away. Figure 4 shows the polarization dependence of the photoelectron yield for three different hot spots. The solid lines are the measured data, and the dashed lines are the results of fitting the observed normalized yields to the following functional form:

$$Y = A_1 \cos^{2n}(\theta - \phi_1) + A_2 \cos^{2n}(\theta - \phi_2) + C, \quad (1)$$

the yield is given by Y . The coefficients A_1 and A_2 determine the maximum contribution from the $\cos^{2n}(\theta - \phi)$ terms. θ is the amount of rotation of the laser polarization, in degrees. ϕ_1 and ϕ_2 are the phases for each contribution, also in degrees. A constant offset is specified by C . The $\cos^{2n}(\theta - \phi)$ angular dependence was chosen to describe a dipole excitation mechanism with an intensity dependence that varies as the laser intensity taken to the n th power. The parameters for each of the curves in Fig. 4 are given in Table I. It is expected that n should be 3 if the yield depends on the laser intensity cubed, as is shown in the inset of Fig. 3(b). This, in fact, provides a reasonable fit in Figs. 4(a) and 4(b), but not Fig. 4(c). The purpose of plotting the polarization dependence is to demonstrate the varied responses for different

TABLE I. Parameters used to fit the curves in Fig. 4 to the functional form shown in Eq (1). The coefficients A_1 and A_2 were constrained to be equal in parts (a) and (b).

Curve	A_1	A_2	ϕ_1	ϕ_2	n	C
Figure 4(a)	0.58	0.58	36	134	3	0.41
Figure 4(b)	0.72	0.72	32	173	3	0.00
Figure 4(c)	0.28	---	6	---	1	0.68

roughness features rather than perform a detailed, quantitative analysis of the functional form that best describes the polarization dependence.

The twofold symmetry arises because the laser polarization has twofold symmetry and there is a strong, yet randomly oriented, polarization dependence for any given hot spot that is not related to the underlying crystal axes. The polarization dependence of a roughness feature arises from the fact that this is a nonlinear process, and if the light preferentially couples into a certain orientation on the roughness feature, then there will be a strong enhancement when the polarization is rotated into that particular orientation. The maxima at other angles and the offset from zero seen at some hot spots could be due to several roughness features with different orientations that are very close to each other, or a single roughness feature that happens to be able to efficiently absorb light of a variety of polarizations.

We find that the occurrence of hot spots is increased when the sample is not annealed after sputtering. It is known that sputtering roughens the surface on a nanometer scale,¹⁹ and this results in a higher probability of finding surface defects for better coupling of the laser field to the surface plasmons (see the following). There is a roughly tenfold increase in the number of hot spots per unit area, and the emission from the hot spots is slightly higher (about a factor of 2–5) when the sample is not annealed compared to when it is.

Semilogarithmic plots of the spectra as a function of laser intensity for two different spots are shown in Fig. 3. Two types of intensity dependent behavior are observed. Spectra similar to Fig. 3(a), where the slope changes as the laser intensity increases, are obtained about half the time, while the other half of the time the slope is constant as the laser intensity is increased, as shown in Fig. 3(b). The inset in Fig. 3(b) displays a log–log plot of the photoemission yield vs laser intensity at the two different electron kinetic energies indicated with the arrows. The fact that the slopes on the log–log plot are the same indicates the same power dependence at high kinetic energy as at low kinetic energy, even though an additional photons' worth of energy is absorbed. In the perturbative limit of multiphoton processes, the slope of a log–log plot of signal vs laser intensity will yield the number of photons involved in the process. Clearly, a perturbative description of the photoemission is incorrect, and this is exactly analogous to observations of ATI or TI in the gas phase.^{3,4}

FIG. 5. The effects of space charge are clearly seen as the laser intensity is increased from 1.0×10^9 (dotted line) to 2.6×10^{10} (dashed line) to 1.2×10^{11} W/cm² (solid line). As space charge effects become greater, a bulge develops in the high energy portion of the spectrum.

DISCUSSION

It is necessary to first rule out three possible mechanisms that might be thought to produce the observed spectra before discussing the underlying cause of these observations. First, the possibility of space charge effects needs to be ruled out. It is known that electrons that are confined to a small region in vacuum will all mutually repel each other due to the Coulombic repulsion, that is, space charge. We show that the space charge effect is not affecting our results. Petit and co-workers showed both theoretically and experimentally that if roughly 10 000 electrons are generated in a region the diameter of the laser beam (100 μ m) that is roughly 10 μ m thick, that they can reach kinetic energies on the order of 2–4 eV.⁸ We have measured roughly 1 pA of current drawn through the sample when using moderate laser intensity (1×10^8 W/cm²), which corresponds to less than 0.1 electron being emitted per laser pulse, and, therefore, completely eliminates the possibility of space charge effects from affecting our measurements. Furthermore, when employing the regenerative amplifier, we can increase the power per pulse by up to four orders of magnitude if desired. Figure 5 clearly shows the onset of space charge effects on the photoemission spectrum. The lower curve corresponds to that obtained at maximum intensity with the unamplified system, while the upper two curves demonstrate the measurable effects of space charge at one and two orders of magnitude higher intensity. At these higher laser intensities, the spectrum becomes distorted and develops a notable bump at higher kinetic energy. The fact that these distortions do not occur until a factor of 10 above the maximum intensity used in the studies with the unamplified laser provides further evidence that we do not need to consider space charge effects on the observed photoemission spectrum when not using the amplified laser system.

The enhanced yield of photoelectrons at higher laser intensity also needs to be considered. As seen from Fig. 5, for amplified laser conditions which approach the intensities of typical photodesorption experiments, the number of photoemitted electrons is significant enough to produce space charge effects. In this process, some electrons are accelerated toward the detector with higher energy, while an equal number are simultaneously accelerated back toward the surface and do not escape the surface region.²⁰ These latter electrons would be available for inducing desorption processes through well known electron induced desorption mechanisms, i.e., electron attachment leads to a large amount of vibrational energy in the adbond.^{12,13,15,17} The present study indicates such a process could be occurring under the intense laser excitation conditions typically employed. An important consideration is the relative contribution of photoemitted electron-induced desorption relative to other proposed mechanisms. This issue is an important one which needs to be resolved because photoemitted electrons offer an alternative, and to a certain extent, simple explanation for the non-linear yields of hot desorption products observed in femto-second laser studies of metal surfaces.

Next, the possibility of thermionic emission is ruled out. Thermionic emission results when the high energy tail of the Fermi-Dirac distribution of a hot, thermalized electron distribution extends above the vacuum level. For intense optical pulses of duration shorter than the electron-photon energy relaxation time (a few ps), a large thermal nonequilibrium between the electrons and phonons can be achieved due to the much smaller heat capacity of the electrons. If the photoelectron spectra measured here were to represent the high energy tail of a hot Fermi-Dirac distribution, the photoelectron yield would be proportional to $e^{-E/kT}$ and the slope of the semilogarithmic plots in Fig. 3(b) would yield the underlying electronic temperature. The slopes in Fig. 3(b) would then indicate an electronic temperature of about 7000 K, which is far too high, given our laser pulse energy of less than 100 nJ/cm²/pulse and the heat capacity of copper. A second method to rule out the possibility of thermionic emission is to perform a time resolved experiment using the pump-probe technique. We find that the photoelectron yield as a function of pump-probe delay is identical to the third order autocorrelation function of the laser pulse as shown in Fig. 6(a), i.e., the photoelectron yield is determined solely by the cube of the instantaneous laser intensity which is consistent with the slope of three in the inset of Fig. 3(b). If transient electronic heating was occurring, then the full width at half-maximum of this pump-probe experiment would be larger than the FWHM of the third order autocorrelation because the elevated electronic temperature persists for several hundred femtoseconds or longer, as measured by other workers using amplified femtosecond laser systems.^{21,22} Figure 6(b) presents the results of the calculated temperature rise²³ of the electron distribution for our experimental conditions. For simplicity, the electronic heat capacity was held fixed at 3.3×10^4 JK/m³, rather than letting it be linearly dependent on temperature, thus, the calculated electronic temperature rise will actually be overestimated. A thermal conductivity of 80 WK/m was used, and the peak laser intensity, pulse dura-

FIG. 6. (a) displays the photoemission yield as a function of delay time between two equal intensity pulses (solid circles) using the amplified laser with a 190 fs pulsewidth. The amplified laser was employed because a 2–3 mm beam diameter could be used, and it was not necessary to search for hot spots. The solid line is the calculated third order autocorrelation function for a Gaussian pulse with a 190 fs FWHM. (b) is the calculated electronic temperature rise of the sample when using the unamplified laser.

tion (FWHM), and spot size were 9×10^8 W/cm², 100 fs, and 100 μ m, respectively. The reflectivity and absorption coefficient were 0.5 and $79 \mu\text{m}^{-1}$, respectively. The electronic temperature and lattice temperature were not coupled to each other for this calculation because it is known that the timescale for energy relaxation from electronic excitation into the lattice takes place on a time scale of 1–3 ps,²⁴ which is much longer than the timescale of interest for this calculation. The results of this calculation show that the maximum temperature will be roughly 700 K, which is far lower than a temperature of 7000 K which would be required for a thermal distribution of electrons to produce the measured photoemission spectra (see the aforementioned). More importantly, if a thermal mechanism was responsible for the observed electronic distribution, the temperature would remain elevated for well over a picosecond, which clearly does not agree with the pump-probe measurements.

Finally, the possible effect of the laser field itself on the photoemitted electron energy spectrum needs to be considered. It is known that an electron that is in a very intense laser field will acquire kinetic energy as it is pushed out of the region of high laser intensity to low intensity. This effect is known as ponderomotive acceleration⁴ and arises from the Gaussian spatial distribution of the laser beam. The action of

the spatial intensity gradient is not instantaneous because the electrons must travel a distance on the order of the laser spot size to acquire kinetic energy due to acceleration from this gradient. For laser pulses shorter than one ps in duration, there is simply not enough time for the electron to gain a significant amount of kinetic energy before the laser pulse has ended.³ Therefore, this mechanism cannot account for the observed behavior of the photoelectrons.

As discussed in the Introduction, ATI or TI in the gas phase requires laser intensities on the order of 10^{14} W/cm², whereas the photoemission that we are measuring occurs at only 10^8 W/cm². The fact that the photoemission occurs at a metal surface, and that it depends on hot spots or surface roughness, reconciles these two seemingly contradictory observations. It is well known that a tremendous enhancement of the electric field at the roughened surface of a metal can be achieved through excitation of surface plasmons.²⁵ The excitation of surface plasmons by photons is forbidden at a smooth surface/vacuum interface, because it is not possible to simultaneously conserve energy and wave vector for both the photon and surface plasmon.²⁵ The most common way to overcome this obstacle is to deposit a thin metal film on a dielectric substrate, such as a quartz prism, and direct the light through the dielectric medium rather than through vacuum. This allows direct coupling of photons and surface plasmons, and is known as the attenuated total reflection (ATR) method.²⁵ A second method to couple photons and surface plasmons is to rule a grating on the surface. In this case, the photon wave vector and surface wave vector need not be equal; efficient coupling can be achieved whenever the difference between the photon and surface plasmon wave vectors are integral multiples of $2\pi/a$, where a is the grating constant. In the present study a randomly roughened surface is used, which can be described in terms of its Fourier components of a two-dimensional grating, and will thus be able to couple photons and surface plasmons over a wide range of difference in wave vectors.^{25,26} In addition to providing a coupling mechanism, surface roughness features can also serve to localize and further enhance the surface plasmons.^{25,26}

We deliberately roughened the surface to determine its effect on the photoemission yield. The sample was sputtered with Ar⁺ ions at kinetic energies from 1 to 3 kV, at 1×10^{-6} Torr background pressure for 20 min. Girard *et al.* have performed scanning tunneling microscope studies of a Cu(100) surface after sputtering with 0.6 kV Ar⁺ ions, and found roughness features on a 5–20 nm scale that are on the order of 1 nm deep.¹⁹ The higher energy Ar⁺ ions used in the present study will more effectively roughen the surface, leading to features that are the optimum size to maximize the localized surface plasmon fields.^{25,26} Studies of surface enhanced Raman spectroscopy, or SERS, found that the Raman yield could be increased by up to 6 orders of magnitude at a roughened silver surface.²⁶ Moskovits discusses SERS and reasons for the enhancement, and concludes that the largest contribution to the enhancement is due to coupling of the photons with surface plasmon modes via random surface roughness, as described earlier. In order to increase the SERS

yield by six orders of magnitude, the electric field would have to be enhanced by three orders of magnitude.

Based on these comparisons with previous work, the surface roughness encountered at the hot spots can increase the electric field enough to cause either ATP or TI. In atomic physics, the reason for the loss of the ATI structure at higher laser energies is tunneling. The electrons interact with the superposition of the Coulomb potential and the laser induced electromagnetic field. The maximum of this potential decreases steadily as the laser field increases. At a critical laser intensity, the electron can periodically tunnel into the vacuum as a result of the oscillating laser electric field. In the description of Corkum *et al.*,²⁷ the electron escapes with very little excess velocity and then behaves as a free particle in the laser field. The relevant quantity γ is proportional to the ratio of the laser frequency ω to the electromagnetic field strength E :

$$\gamma = \sqrt{\frac{I_p}{2U_p}} = \frac{\omega}{E} \cdot \frac{\sqrt{2mI_p}}{e}, \quad (2)$$

where I_p is the ionization potential of the atom, U_p is the ponderomotive potential, m is the electron mass, and e is the electron charge. This ratio is known as the adiabaticity, or Keldysh parameter and is essentially the ratio of the laser frequency ω to the tunneling frequency ω_t .⁴ The parameter γ is generally used to separate the multiphoton mechanism ($\gamma \gg 1$) from the tunneling ($\gamma \ll 1$) regime.

Using 110 ps long laser pulses with intensities up to 120 GW/cm², Toth *et al.* used photoyield measurements to show that a transition of pure multiphoton to optical tunneling may also occur at a gold surface.²⁸ However, that experiment was done in the long pulse regime ($t > 80$ ps) where ponderomotive acceleration and space charge broadening can influence the photoemission spectrum. In contrast to ATP, tunneling is not expected to lead to discrete steps characterized by a width equal to one photon energy. The electron kinetic energy distribution will instead be smeared out due to a spread in the initial time of tunneling, relative to both the phase of the laser field and the instantaneous intensity of the field at the time of emission.³ This view is supported by the recent measurement of Mevel *et al.*²⁹ who found strikingly similar behavior to this work for multiphoton ionization of noble gas atoms.

Optical tunneling from metals surfaces is more complicated than from single atoms. The Keldysh parameter γ depends critically on the local electromagnetic field strength, which in our case is significantly enhanced by the coupling of the laser light into surface plasmons. Tunnel emission studies performed with static fields show that roughly $5\text{--}10$ V/Å (10^{11} V/m) is required to allow electrons to tunnel into the vacuum, which would require a laser intensity of 1×10^{15} W/cm². The laser intensity used in the present studies is $10^7\text{--}10^9$ W/cm² which provides $10^7\text{--}10^8$ V/m.³⁰ Therefore, it is the surface roughness that provides the additional two to three orders of field enhancement with a concomitant four to six orders of magnitude intensity enhancement, which is consistent with previous SERS studies utilizing roughened surfaces.

SUMMARY

We have measured photoelectrons with far more kinetic energy than would be expected based on the work function of the sample and photon energy used. These results are unique in that they are obtained at lower intensity than similar gas phase studies and other above threshold photoemission studies from metals. The role of surface roughness, or defects, is seen to be critical in this process. It should be noted that the production of photoelectrons possessing large amounts of kinetic energy when employing photon energies well below the work function has important implications with respect to photodesorption studies carried out with intense laser pulses. One of the reasons that these results are important is that there are several groups investigating ultrafast desorption of adsorbates from metal surfaces driven by subvacuum hot electrons using high intensity femtosecond lasers.^{11,31-34} Furthermore, there are other groups that observe desorption driven by electrons photoemitted from a surface using ultraviolet light at very low intensities, indicating that it is the electron kinetic energy, not the number of excited electrons that drives many surface photoinduced processes.^{9,13,16,17}

The present study measures electrons with significant amounts of kinetic energy that are generated with photon energies well below the photoemission threshold using laser intensities at or below those used in many photodesorption experiments. Future studies will address whether multiphoton photoelectrons with excess kinetic energy or space charge effects at high fluence make a contribution to the photodesorption yield measured in the ultrafast photodesorption experiments.

The use of a high repetition rate, low pulse energy, ultrafast laser system has allowed data to be obtained that is free of ambiguities due to thermal heating of the sample (either electrons or lattice), space charge effects, or ponderomotive acceleration. Furthermore, the laser intensities used here are well below those required to produce above threshold phenomena in the gas phase, and the roughness of surface defects provides the requisite field enhancement at the surface. More important, however, is the fact that we have been able to measure photoelectrons with excess kinetic energy from copper surfaces with very low pulse energy, intensity, and duration, leading to a measurement that is free of contributions from competing processes that are present in earlier studies.

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Direct measurements of the transport of nonequilibrium electrons in gold films with different crystal structures

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The transport of femtosecond-laser-excited nonequilibrium electrons across polycrystalline and single-crystalline gold films has been investigated through time-of-flight measurements. The thicknesses of the films range from 25 to 400 nm. Ballistic electrons as well as electrons interacting with other electrons and/or with the lattice have been observed. The ballistic component dominates the transport in the thinner films, whereas the interactive transport mechanism is dominant at the upper end of the thickness range. A slower effective velocity of the interactive component is observed in the polycrystalline samples, and is assumed to arise from the presence of grain boundaries. The reflection coefficient of excited electrons at the grain boundaries is extracted from the experiment and is estimated to be $r \approx 0.12$. The experiment also suggests that thermal equilibrium among the excited electrons is not fully established in the first ~ 500 fs after excitation.

The dynamics of nonequilibrium electrons in solids has attracted considerable recent attention.¹ Nonequilibrium electrons in metals can be excited by laser pulses with durations less than, or comparable to, the excited-electron energy-loss lifetime (τ_e), such that a transient inequality between the effective electron and lattice temperatures (T_e and T_l) occurs. The excited electron population can be probed through measurements of the transient differential reflectivity (or transmissivity) of the sample. Loss of electron energy in the excited volume is attributed to energy transfer to the lattice through electron-phonon interactions plus electron transport out of the excited region. It has been shown that the relaxation of the nonequilibrium electrons is influenced by the crystal structure of the films, and by the consequent enhanced electron-phonon scattering in the polycrystalline films.² It has been established on experimental and theoretical grounds that electron-grain boundary interactions impede electron transport in polycrystalline films.^{3,4} Earlier experiments on this topic investigated electrons thermalized with the lattice through measurements of the temperature dependence of the resistivity of thin polycrystalline films.⁵ Unresolved, however, is the role of grain boundaries in the transport of nonequilibrium electrons in thin metal films. In the present experiment we investigate the transport of femtosecond-laser-generated nonequilibrium electrons in polycrystalline and single-crystalline gold films, through measurements of the time-of-flight across the film thickness which is made possible through an application of a thermorefectivity technique with femtosecond resolution.⁶

A synchronously pumped femtosecond dye laser⁷ with put pulses of ~ 150 fs duration at 2-eV photon energy and 76-MHz repetition rate is used to excite the electrons with $\sim 100\text{-}\mu\text{J}/\text{cm}^2$ fluence per pulse on the front surface

of the films. The beam is at near normal incidence and is focused to a diameter of $15 \pm 2\text{ }\mu\text{m}$. The skin depth $D \approx 15$ nm. Since an excitation gradient is generated between the skin depth and the rest of the sample, transport of the nonequilibrium electrons out of the excited volume occurs simultaneously with electron energy relaxation through electron-electron and electron-phonon interactions. Excited electrons which reach the back surface of the film introduce a change in the optical reflectivity which is probed with an appropriately delayed laser pulse. The probe beam is also at near normal incidence and is focused to the same diameter as the pump beam, but its intensity is always less than 10% of that of the pump beam. The intensity of the pump beam is modulated with an acousto-optic modulator and the differential reflectivity [$\Delta R/R(t)$] is detected with a lock-in amplifier tuned to the modulation frequency.

In transient thermorefectivity experiments the change of reflectivity is related to the change in the occupation number of electrons near the Fermi level.⁸ The occupation number is probed by monitoring the transition probability from the d band to near the Fermi level.⁸ Since the electron occupation number is not a linear function of the effective electron temperature, the change of the reflectivity is generally not proportional to the effective electron temperature at the surface.⁹ The nonlinearity becomes appreciable at lower ambient temperatures and large effective temperature excursions.⁹ Since the present experiment is performed at room temperature with relatively small pump laser irradiance, we assume a linear correspondence between the effective electron temperature and the transient change in $\Delta R/T(t)$. Effects other than changes in the effective electron temperature, such as shifting of the Fermi level, and thermal expansion of the lattice, can also cause reflectivity change, but they are

not significant on the femtosecond time scale.¹⁰ Following standard practices,^{1,2,6,8,9} corrections for the depth-dependent contribution to $\Delta R/R(t)$ (Refs 11 and 12) are ignored in the data analyses.

The gold films are fabricated by evaporation. The film thickness W is determined by a crystal thickness monitor with an estimated absolute accuracy of better than $\pm 20\%$. However the accuracy of the film thicknesses relative to each other is expected to be much better. Polycrystalline gold films are evaporated on ~ 1 -mm-thick sapphire substrates. Examination of films evaporated on an electron microscope grid adjacent to the sapphire substrate reveals a wide distribution of grain sizes with an average of $a_p = 16 \pm 2$ nm. Single-crystalline gold films are fabricated by epitaxial growth on a ~ 2 -nm silver layer grown on a heated NaCl crystal. The film is floated on distilled water, washed in sulfuric acid to remove silver and silver-gold alloy, then washed in distilled water. Finally the film is caught on a sapphire substrate. Electron diffraction obtained from these films shows a single crystal pattern in the (100) orientation. These films are known to possess high dislocation densities (10^{10} – $10^{11}/\text{cm}^3$) and twins.¹³

The transient thermorefectivity $[\Delta R/R(t)]$ normalized to its maximum value, and as measured on the back surface of the polycrystalline gold film samples, with thicknesses of 25, 100, 200, 300, and 400 nm, are displayed in Fig. 1. Similar results obtained on single-crystalline films are displayed in Fig. 2. As the thickness of the films is increased the traversal time of the electrons to cross the film, and therefore the delay in the transient $\Delta R/R(t)$, is increased. The short delay times which are observed indicate that energy is transported via electrons, which are out of equilibrium with the lattice.⁶ It is also important to note that the time to reach the maximum value of the transient $\Delta R/R(t)$, relative to its onset, also increases with increasing sample thickness of the polycrystalline samples. This effect is considerably smaller in the single-crystalline samples with thicknesses less than

FIG. 1. The normalized transient thermorefectivity signal $\Delta R/R(t)$ measured at the back surface of 25-, 100-, 200-, 300-, and 400-nm-thick polycrystalline gold films. The open circles represent the one-parameter fit of Eqs. (1a) and (1b) to data obtained in the 400-nm-thick films.

FIG. 2. The normalized transient thermorefectivity signal $\Delta R/R(t)$ measured at the back surface of 25-, 100-, 200-, 300-, and 400-nm-thick single-crystalline gold films. The open circles represent the one-parameter fit of Eqs. (1a) and (1b) to data obtained in the 400-nm-thick films.

400 nm. In order to measure the time required by the first wave of electrons to traverse the films, we measured the time to reach the signal onset of $\Delta R/R(t)$, relative to the excitation at $t=0$, for different sample thicknesses. For simplicity we assign the onset as 15% of the full signal level. The open symbols in Fig. 3 display the results. The circles and triangles represent the polycrystalline and single-crystalline samples, respectively. For each film thickness, the delay of the peak of $\Delta R/R(t)$ corresponds to the time required for the bulk of the excited electrons to reach the back surface. Measurements determining this delay (relative to $t=0$) in both polycrystalline and single-crystalline gold films are displayed by the filled symbols in Fig. 3.

As can be seen in Fig. 3, the time for the first wave of electrons to traverse the films is linear with sample thickness for both polycrystalline and single-crystalline films if the thickness is less than or equal to 300 nm. The linear dependence of the traversal time on the sample thickness is characteristic of ballistic transport, when the transport of the excited electrons occurs without any interactions among the electrons or between the electrons and the lattice. The velocity of the ballistic component is measured to be $\approx 10^6$ m/s in agreement with previously published values.⁶ In the case of the peak of $\Delta R/R(t)$ a linear dependence of the traversal times is observed for shorter thicknesses, namely, up to 100 nm in both types of the gold films. In the 400-nm-thick samples deviations from the linear dependence are observed for the onsets as well as for the peaks in both types of the gold films.

We interpret these results as follows. The transport of the excited electrons across the films with thicknesses less than or equal to 100 nm is mostly ballistic in both single-crystalline and polycrystalline materials. As the thickness of the film increases the fraction of the ballistic component decreases, and the excess energy is carried by electrons interacting with other electrons or/and with the lattice. The electrons undergo one or more scattering events, and we refer to them as the interactive component

FIG. 3. The delay of the onset of the back surface $\Delta R/R(t)$ as a function of the sample thickness measured at 15% of the full signal intensity (open symbols), and at the peak (filled symbols). The circles and triangles represent the data obtained in polycrystalline and single-crystalline films, respectively. Each data point is an average of four to six measurements, the error bars represent the standard deviations. Solid line, line fit for the first five experimental data points. Dashed line, parallel to the solid line for the benefit of the reader. Inset, the maximum of the back surface thermoreflectivity signal as a function of the sample thickness $\Delta R/R^{\max}(W)$ for polycrystalline and single-crystalline gold films. Solid line, the two-parameter fit of the $a \exp(-W/l)$ function to the data points.

of the transport. Interactive transport also includes the possibility of pure diffusion. Due to the scattering events the interactive electrons lose some of their excess energy during the transport. Since the interactive electrons arrive at the back surface of the sample later than the ballistic electrons, the appearance of the peak of the transient $\Delta R/R(t)$ signal is somewhat delayed. The effect is observed to be stronger in the polycrystalline samples,¹⁴ which indicates that the grain boundaries cause a slowing of the transport of the excited electrons. In samples with 400 nm thicknesses the ballistic component is diminished in both polycrystalline and single-crystalline samples.

We now turn to a quantitative analysis of the experimental results. The dynamics of the excited electrons can be modeled by a set of coupled differential equations, which are frequently referred to as "the two-temperatures model":¹⁵

$$C_e(T_e) \partial T_e / \partial t = \nabla(\kappa \nabla T_e) - G(T_e - T_l) + P(z, t), \quad (1a)$$

$$C_l \partial T_l / \partial t = G(T_e - T_l), \quad (1b)$$

where $C_e(T_e)$ is the electronic heat capacity (usually assumed to vary linearly with T_e), κ is the electronic thermal conductivity, G is the electron-phonon coupling parameter, $P(z, t)$ is the spatial and temporal evolution of the irradiance of the exciting laser pulse, and C_l is the heat capacity of the lattice. The use of Eqs. (1a) and (1b), however, requires the establishment of an electron temperature T_e . In several experiments which investigated the dynamics of laser excited hot electrons, it was generally assumed that the electron system thermalizes very

rapidly so that an electron temperature exists within the time resolution of the experiments which is ~ 100 fs.¹ On the other hand, it has also been suggested by several authors that the time scales for electron thermalization and for electron-phonon energy transfer may overlap, and therefore, the electron temperature may not be well defined.^{9,12,16} Recently Fann *et al.* have demonstrated that the thermalization of the hot electrons in gold can be as long as ~ 670 fs under special circumstances.^{17,18} An electron thermalization time of ~ 500 fs was measured in the case of weak excitations.¹⁹ The above results impact the interpretation of the present experiment in a number of ways. By definition, the ballistic electrons are not in thermal equilibrium. The presence of ballistic component is observed up to ~ 500 fs which means that thermal equilibrium among the electrons is not fully established during this time interval. On the other hand, as is mentioned above, the thermalization time of femtosecond laser excited nonequilibrium electrons has been independently observed to be about 500 fs.¹⁷⁻¹⁹ This is supported by our results that ballistic electrons were not observed in samples with thicknesses of 400 nm in which the traversal time of the electrons is ~ 500 fs or longer. In order to move the analysis beyond this point we assume a thermal equilibrium among the electrons arriving at the back surface of the 400-nm-thick films as well as a pure diffusive transport of these electrons. We numerically solve Eqs. (1a) and (1b) for the back surface T_e in the 400-nm-thick samples using the method described in Ref. 20. The electronic heat capacity $C_e(T_e) = 66 \text{ J/m}^3 \text{ K}^2 \times T_e$ for gold,²¹ and the electron-phonon coupling constant is $G = 3.5 \times 10^{16} \text{ W/m}^3 \text{ K}$ for single-crystalline films and $G = 4 \times 10^{16} \text{ W/m}^3 \text{ K}$ for polycrystalline films according to Ref. 2. The diffusion coefficient κ is treated as a parameter. The best agreement with the experimental data is found at $\kappa_s = 310 \text{ W/mK}$ in the case of single-crystalline films, while for polycrystalline films $\kappa_p = 180 \text{ W/mK}$ provided the best solution. The results of the calculations, $\Delta T_e = T_e(t) - T_{\text{ambient}}$, are displayed with open circles in Figs. 1 and 2. Since the calculations are limited to T_e at the back surface of the films, the agreement with the experiment decreases for delays larger than ~ 2 ps beyond which the influence of the effective lattice temperature on $\Delta R/R(t)$ is not negligible.

The difference in the transport of nonequilibrium electrons across single-crystalline and polycrystalline films is also demonstrated by measuring the intensity of the maximum of the transient thermoreflectivity at the back surface as the function of the film thickness. The results, $\Delta R/R^{\max}(W)$, for polycrystalline and single-crystalline samples are displayed in the inset of Fig. 3. An approximately exponential decay of the magnitude of the transient thermoreflectivity is observed in both samples. A somewhat stronger decrease in $\Delta R/R^{\max}(W)$ is observed in the polycrystalline versus the single-crystalline samples,¹⁴ supporting the results obtained by measuring the transversal time of the electrons. This observation is also consistent with previous experiments² in which an enhanced electron cooling rate was observed in polycrystalline films and, hence, the energy transported by the

electrons is expected to decrease.

Finally we discuss our experiment in the terms of the Mayadas-Shatzkes model of the electron transport in polycrystalline metals.³ In this model the grain boundaries are represented by parallel planes separated randomly with an average distance of d . The grain boundaries are assumed to partially reflect the electrons with a reflection coefficient r . It is also assumed that grain boundary scattering occurs simultaneously with an isotropic scattering background (due to electron-electron and electron-phonon interactions), and the interplanar spacing d can be identified as the average grain diameter a_p ($d = a_p$). Under these circumstances Tellier and co-workers^{22,23} have shown that transport in the polycrystalline films can be described by an effective mean free path l_p . We refer to this as the Mayadas-Shatzkes-Tellier (MST) model, and express the effective mean free path as

$$l_p/l_s = f(\alpha) = 1 - \frac{1}{2}\alpha + 3\alpha^2 - 3\alpha^2 \ln(1 + 1/\alpha), \quad (2)$$

where l_s is the bulk mean free path in the single-crystalline material and

$$\alpha = (l_s/a_p)[r/(1-r)]. \quad (3)$$

It follows from Eqs. (2) and (3) that the reflection coefficient of the electrons at the grain boundaries can be determined if l_p and l_s are known. The mean free path of the electrons could be calculated from the electronic thermal conductivity if an electronic temperature exists. Since this is not generally the case, we adopt an empirical approach described in Ref. 24. Specifically we fit a $\exp(-W/l)$ to the back surface $\Delta R/R^{\max}(W)$ signal displayed in the inset of Fig. 3, and define l as an average mean free path of the excited electrons. The method yields $l_p \approx 34$ nm and $l_s \approx 54$ nm for the polycrystalline and single-crystalline films, respectively. Substituting l_p and l_s into Eqs. (2) and (3), we obtain an estimate of $r \approx 0.12$ for the reflection coefficient of nonequilibrium electrons excited in the present experiment. At this point

it would be interesting to compare this value with that obtained with electrons thermalized with the lattice. However, to the best of our knowledge, there are no data available for gold. On the other hand, the grain boundary reflection coefficients in Al ($r=0.17$) and in Cu ($r=0.24$) obtained by electric current measurements^{3,25} appear to be higher.

In summary femtosecond time-of-flight experiments on thin gold films, with different crystal structures, have been carried out in order to investigate the transport of nonequilibrium electrons. The results indicate the presence of both ballistic and interactive components. The ballistic component dominates the transport in thin samples. The dominant role of the ballistic component decreases with increasing sample thickness. For samples thicker than 300 nm the transport is purely interactive. Additionally, the effective velocity of the interactive transport in the polycrystalline samples is observed to be somewhat slower than that in the single-crystalline samples. If one assumes that at the back surface of the thickest samples an electronic temperature and diffusive transport exist, it becomes possible to apply the "two-temperature model" and to determine the coefficient of the electronic thermal conductivity which appears to be larger for single-crystalline films as compared to the polycrystalline films. The difference can be explained by the reflection of the excited electrons at the grain boundaries. Analyzing the results in the terms of the MST model permits an estimate of the reflection coefficient (r) of the electrons at the grain boundaries to be ~ 0.12 . The coefficient is slightly smaller than the values of r in Al and Cu obtained with a different experiment technique.

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Time-resolved two-photon photoemission from Cu(100): Energy dependence of electron relaxation

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A time-domain measurement of the relaxation time of photoexcited electrons as a function of excitation energy at a single-crystal Cu(100) surface has been made with time-resolved two-photon photoemission. The relaxation lifetime of the excited electrons is found to decrease rapidly with the amount of excitation energy above the Fermi level, and we compare the measured lifetimes with a calculation based on Fermi-liquid theory. The results reveal a qualitative agreement with the theory, and indicate that effects due to transport of the electrons away from the surface and into the bulk are important.

In this paper, we report our recent measurements of excited-state lifetimes of photoexcited hot electrons in single-crystal Cu(100) using time-resolved two-photon photoemission. This study is a direct measurement of the excited electron lifetime as a function of excitation energy in a single-crystal sample. The single-crystal sample minimizes possible effects from defects or impurities, which allows us to focus on the fundamental electron-electron interaction. An important difference between the work presented here and previous studies is that the laser-pulse energy was kept very low (<0.5 nJ/pulse). Therefore, less than one electron per laser pulse is emitted, which avoids any problems due to distortion of the photoelectron spectrum from space-charge effects, and transient thermal heating of the lattice is also avoided. We find that the excited electrons relax in qualitative agreement with Fermi-liquid theory over a limited energy range, limited at higher energy by our finite temporal resolution, and at lower energy by transport effects.

Time-resolved two-photon photoelectron spectroscopy studies of metal and semiconductor surfaces provide valuable information regarding the electronic environment by revealing dynamical information as well as the energetics of the system. Furthermore, the energetics and dynamics of the unoccupied states as well as the occupied states are provided by the fact that it is a two-photon process, which is sensitive to the density and lifetime of the intermediate (unoccupied) states.^{1,2}

An important class of studies probes electron-lattice coupling in thin metal films where an intense laser pulse generates transient hot electrons.^{1,3-7} Using the technique of transient thermorefectivity and thermotransmissivity, several groups have investigated the electron-lattice and electron-electron coupling and found the electron relaxation time due to coupling with the lattice to be on the order of 1–3 ps,³⁻⁵ and that the rate of electron transport in thin films is on the order of the Fermi velocity, $10 \text{ \AA/fs}$.⁴

A more direct measure of the electron distribution is provided by two-photon photoemission since the energy of the photoemitted electrons is known precisely from their kinetic energy, the work function, and the photon energy used to emit them. There are several previous studies in which two-photon photoemission has been used to investigate the unoccupied states of clean metal and adsorbate-metal systems.⁸⁻¹⁵ Recently, the full power of time-resolved photoemission spectroscopy has been used by Fann *et al.* to characterize the time scale of the formation of an electronic equilibrium as well as the concurrent and subsequent electron-lattice relaxation after laser heating of a thin polycrystalline gold film by an intense laser pulse.¹

It is obvious that it will be impossible to determine the relaxation rate from frequency-domain measurements for the present case of excited electrons in a continuous band simply because no discrete spectral features exist. Even in cases where discrete features such as surface states do exist, the pitfalls of using linewidths to determine lifetimes have been clearly demonstrated in the case of a surface state of Cu(111), wherein the spectral width of the feature actually increased upon approaching the Fermi level.^{16,17} Time-domain measurements are therefore required to determine the lifetime in the presence of mechanisms that broaden spectral features. Furthermore, time-domain measurements of image states on Ag(100) have demonstrated the ability to determine lifetimes that cannot be accurately measured otherwise due to limitations of instrumental resolution.^{11,12}

Our experiment is designed to measure electron dynamics at metal surfaces. By using a low-pulse-energy and high-repetition-rate laser, as opposed to a low-repetition-rate and high-pulse-energy laser, we avoid ambiguities that might arise in a highly excited electron distribution or space-charge effects that can distort the measured photoelectron spectrum. We measure the relaxation of individual excited electronic states rather than the collective behavior of a transiently heated nonequilibrium distribution. This is an important dis-

The dependence of the width of the pump-probe scans as a function of intermediate-state energy can be understood in terms of an energy-dependent relaxation time for the excited electrons. A semiquantitative description of the properties of electrons in metals with several eV of excitation energy above the Fermi level is obtained by treating the excitation as a quasiparticle,²¹ and is referred to as Fermi-liquid theory. A quasiparticle refers to the excited electron as well as the distortion of surrounding particles brought on by the adiabatic interaction among particles.²¹ A critical parameter in this treatment is r_s , the radius of the sphere (in units of the Bohr radius, a_0) containing the effective volume of an electron. Alternatively, r_s is the ratio of the average potential energy relative to the average kinetic energy of the Fermi liquid.²¹ In metals, $1.8 \leq r_s \leq 5.6$, and for copper $r_s = 2.67$.²² Fermi-liquid theory has successfully described electron relaxation in previous time-resolved measurements,¹ and it

provides a fundamental description of electrons near the Fermi level. It is seen below, however, that some of the qualitative aspects of the measured energy dependence of the lifetimes are not in full agreement with the theory. Nonetheless, it provides an initial basis for comparison of the experimental results.

Using the approach taken by Quinn,²³ we can estimate the lifetime of the excited electrons by calculating the imaginary component of their energy, since the probability decays exponentially in time according to $e^{-t/\tau}$, with $\tau = \hbar/(2E_I)$. For low-energy excitations ($p/p_0 < 1.3$) the imaginary contribution to the energy is given by²³

$$E_I(p) \approx (e^2/2a_0) [\pi^{1/2}/32(\alpha r_s)^{3/2}] [\tan^{-1}(\pi/\alpha r_s)^{1/2} + (\alpha r_s/\pi)^{1/2}/(1 + \alpha r_s/\pi)] [(p/p_0)^2 - 1]^2/(p/p_0), \quad (1)$$

where $\alpha = [4/(9\pi)]^{1/3}$, p is the momentum of the excited electron, and p_0 is the momentum of the electrons at the Fermi level. Equation (1) can be evaluated with $r_s = 2.67$ and $e^2/(2a_0) = 13.6058$ eV to yield

$$E_I(p) \approx 0.66[(E_i - E_F)/E_F]^2 \text{ eV}, \quad (2)$$

$$\tau \approx 0.49[E_F/(E_i - E_F)]^2 \text{ fs},$$

where τ is the predicted lifetime, and p/p_0 in the denominator of Eq. (1) has been set equal to 1 since this treatment is only semiquantitative. The Fermi energy for copper, E_F , is 7.0 eV.²²

In order to compare the experimental results with Eq. (2), it is necessary to deconvolve the exponential component of the measured pump-probe scans from the underlying Gaussian contribution due to the autocorrelation of the laser pulse. First, the FWHM of the autocorrelation was obtained by averaging together the FWHM of the Gaussian fits of the nine pump-probe scans obtained between 4.4 and 4.8 eV. Then a nonlinear least-squares-fitting routine was used to deconvolve the exponential component of the pump-probe scans from this underlying instrument-response function. The most important aspect of Fig. 2(b) is the observed trend in lifetime vs energy; therefore, the difficulty in extracting time constants that are less than $\frac{1}{3}$ the pulse width (which would place a 16-fs lower limit on τ) does not adversely affect our analysis, since it is not the actual value of τ , but rather the trend that is important. These experimentally determined decays can then be compared to the results of Fermi-liquid theory. The solid line in Fig. 2(b) corresponds to the predicted lifetimes obtained from Eq. (2) after being scaled by a factor of 2.45. This comparison shows that the predicted lifetimes are reasonably close to the observations, but the energy dependence of the relaxation shows a systematic deviation.

There are a number of possible explanations for the observed discrepancy from Fermi-liquid theory. First, for real metals where $r_s > 1$, Fermi-liquid theory only provides a qualitative description. There are also two other factors that affect the measured dynamics that are not accounted for in Fermi-liquid theory. One is that the measured photoemission yield will decrease if the excited electrons move out of the region probed by the laser on a time scale faster than their relaxation time. At 395 nm, the light penetrates roughly 150

FIG. 2. Part (a) shows the FWHM of the pump-probe scans as a function of electron kinetic energy. The scans at different kinetic energies are not taken in order of increasing or decreasing kinetic energy to ensure that long-term drift does not affect the results. The error bars are one standard deviation uncertainty for the FWHM parameter obtained when fitting the scans to a Gaussian functional form. Typical pump-probe scans when monitoring electrons with 4.8- and 3.2-eV kinetic energy are indicated by filled triangles and open squares, respectively, in the inset. Part (b) is a comparison of calculated relaxation time constant τ with that deconvolved from the experimental data as a function of intermediate-state energy $E_i - E_F$, not kinetic energy of the emitted electron. The solid line is the result of Eq. (2) scaled by 2.45. The filled circles in part (b) are obtained by calculating the average of the deconvolved values of τ at each energy, and the error bars represent two standard deviations.

Å into the metal; therefore, electrons that have a chance to move that distance have a much lower probability of being measured, even though they are still excited. We are currently investigating further the issue of transport, both experimentally and theoretically. The other factor contributing to the disagreement of the measured lifetimes and those calculated from Fermi-liquid theory arises from the fact that only the $4s^1$ valence electrons are included in the calculation, and the $3d^{10}$ electrons that are 1.5–2.0 eV below the Fermi level are neglected. A treatment of the electron dynamics that includes the full band structure of copper will be necessary in order to make a quantitative comparison with the measured lifetimes.

Finally, a comparison with the related studies of Fann *et al.*¹ is in order. This earlier, pioneering work utilized a UV probe pulse to monitor the evolution and decay of a transiently heated electron distribution generated by an intense pump pulse in a polycrystalline, 300-Å-thick gold sample via photoemission. They modeled their results as a process in which the nascent (nonthermal) electron distribution thermalized and allowed the thermalized electron distribution to couple with the lattice. They found that Fermi-liquid theory qualitatively described (within a factor of 2.5) the relaxation of the nascent electron distribution to one with an elevated temperature. Thus, an emerging trend from these studies is that the relaxation time calculated from Fermi-liquid theory is somewhat too small, but the fact that both studies obtain 2.5 as the scale factor must be considered fortuitous.

There are two substantial differences between this paper and Ref. 1. First, this paper employs a single-crystal sample, whereas that in Ref. 1 is polycrystalline. It is known that the electron dynamics are different in single-crystal and polycrystalline thin films³ due to scattering from grain boundaries, and experiments performed with polycrystalline samples have an additional, uncharacterized, relaxation mechanism. The second, and more important, difference is that the present paper utilizes very-low-energy pulses, ~ 100 -nJ/cm² absorbed fluence, whereas the absorbed fluence is as high as ~ 300 μ J/cm² in Ref. 1. Therefore, in Ref. 1, the electronic temperature reaches peak values of roughly 1500 K, and electron-phonon coupling must be considered in addition to electron-electron scattering. That is, the electron

dynamics extracted from their model will depend on the parameter chosen for the electron-phonon coupling. Our experiment, on the other hand, has very low excitation levels, and the electronic temperature is not affected. At short times, on the order of 10–20 fs, before transport effects are significant, the measured relaxation time is only due to electron-electron scattering mechanisms. Therefore, a measure of the relaxation dynamics is obtained without having to invoke a model. While we do compare the measured dynamics with the results of Fermi-liquid theory, the actual measurement of the dynamics is independent of any model. The work in Ref. 1 and this paper are complementary to each other in many ways, and by considering the results of several experiments, a full description of electron relaxation dynamics will be obtained.

The results presented here demonstrate the feasibility of studying the relaxation of single electrons in metals directly in the time domain. It is seen that while Fermi-liquid theory is in qualitative agreement with these results, a more rigorous treatment will be necessary for quantitative comparisons since r_s for real metals is not within the range in which the random-phase approximation is expected to hold rigorously, and it will also be necessary to include the full band structure. Future work will address dynamical issues related to substrate-adsorbate hot electron transfer in the presence of the competing pathways of relaxation and transport into the bulk. Finally, the power of studies based on time-resolved laser spectroscopy is underscored by the statement made by Pines and Nozières:²¹ "... it [Landau's theory of quantum liquids] uses (and provides) far more information than any experiment will ever sample. For example, one never detects experimentally *one* quasiparticle; put another way, one never *measures* the quasiparticle distribution δn_p . What is observed experimentally is always an *average* property of the system, its charge, current, magnetization, etc." Clearly, experimental technology has made significant and unforeseen advances during the last 30 years, as it is now possible to directly measure the behavior of the quasiparticle distribution.

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tion because photoinduced surface chemistry employing conventional low-flux cw light sources such as arc lamps fall in the category of individually excited states.¹⁸ Several examples of surface-desorption and surface-dissociation processes are believed to be driven by subvacuum-level excited electrons. Dynamical information about the excited electrons such as that presented here will provide additional constraints regarding the extent and duration of interaction between the adsorbate molecules and the excited electrons.

The laser system used in these studies consists of a self-mode-locked Ti:sapphire laser pumped by about 7.7 W from a cw Ar⁺ laser producing about 9 nJ/pulse with a 50-fs pulse width at 82 MHz, with tunability from 750 to 850 nm. The second harmonic (2.92–3.31-eV photon energy) is generated without additional broadening by using a 250- μ m-thick Beta Barium Borate (BBO) doubling crystal, which achieves roughly 10–15 % conversion efficiency, and a pair of external prisms for group-velocity dispersion compensation of the frequency-doubled pulses is employed.¹⁹ Equal intensity pump and probe pulses are used.

The ultrahigh vacuum system uses standard techniques to achieve a base pressure of 1×10^{-10} torr. A clean and well-ordered surface is obtained by sputtering with argon ions and annealing at 700 °C. The Cu(100) sample is oriented at 45° relative to the laser beam. The sample is normal to the entrance axis of the energy analyzer, which is located 1.5 cm from the sample. A –3.0-V bias is applied to the sample to eliminate the effects of any stray electric fields. The applied bias voltage extends the range of *k* states being collected, but contributes less than 0.1-eV uncertainty to the energy resolution since the bias is small and copper exhibits nearly-free-electron behavior. The crystallographic [010] direction is horizontal (in the plane formed by the incident and reflected laser beam) when the azimuthal angle is 0°, and the azimuthal angle was held at 0° for the data presented here. As seen in Fig. 1(a), the energy of the intermediate state E_i above the Fermi energy E_F is given by $E_i - E_F = E_{KE} + \Phi - h\nu$, where E_{KE} is the electron kinetic energy at the sample surface with the energy due to the bias voltage subtracted, Φ is the work function for copper (4.6 eV), and $h\nu$ is the photon energy (3.14 eV). The energy analyzer used is a 10-cm inner-radius hemispherical energy analyzer with roughly 1% relative resolution and 10° acceptance angle. A transmission energy of 20 V is used, which leads to roughly 200-meV resolution.

A schematic diagram of the two-photon photoemission process being measured is shown in Fig. 1(a), and a typical photoemission spectrum, taken with one of the two laser beams blocked, is shown in Fig. 1(b). The signal intensity varies quadratically with laser power, as expected for a two-photon process. The pump-probe experiments are typically carried out by monitoring the number of electrons at a given kinetic energy as a function of delay between the pump and probe pulses. Scans obtained when monitoring electrons at 4.8 and 3.2 eV of kinetic energy (3.26 and 1.66 eV above the Fermi level, respectively) are shown in the inset of Fig. 2(a), and the 2:1 intensity ratio at the peak relative to the baseline indicates a sequential (noncoherent) two-photon process. Figure 2(a) presents the full width at half maximum (FWHM) of the pump-probe scans as a function of photoelectron kinetic energy when using a photon energy of 3.14

eV. The FWHM decreases as the photoelectron kinetic energy increases, which is to say that the FWHM decreases as the energy of the intermediate state above the Fermi level increases. While the present study was carried out solely with a 3.14-eV photon energy, it was found in previous work utilizing different photon energies that the dynamics are independent of photon energy, and are determined by the position of the intermediate level E_i above the Fermi level E_F .²⁰ As we are not able to autocorrelate the frequency doubled output of the laser (380–420 nm) with a doubling crystal to determine its FWHM, we must rely on the pump-probe spectra at the highest electron kinetic energies to determine the pulse width. As seen in Fig. 2(a), the relaxation dynamics at high kinetic energy are faster than the laser pulse width since the FWHM decreases to a nearly constant value that is consistent with the 50-fs pulse width of the laser fundamental.

The effects of laser polarization were investigated. This study was conducted to determine if simultaneous two-photon processes or sequential two-photon processes involving intermediate levels dominate the signal. If the two-photon photoemission measured here were a *simultaneous* process, then there should be a dramatic difference in the pump-probe spectrum depending on the relative polarizations of the pump and probe pulses. We find that the pump-probe FWHM is independent of the relative polarization of the pump and probe beams. That is, the same type of behavior as shown in Fig. 2(a) is obtained for either parallel- or crossed-polarized laser pulses. The FWHM for the Gaussian functions fitted to scans taken with *P-P*, *P-S*, and *S-S* polarizations at 3.2-eV photoelectron kinetic energy are 98 ± 5 , 104 ± 5 , and 98 ± 7 fs, respectively. This polarization independence of the dynamics indicates that the process we are measuring is a sequential two-photon process in which the electrons undergo elastic collisions between absorbing the two photons.

FIG. 1. Part (a) is a schematic representation of the two-photon process being measured. The shaded region indicates the density of occupied states. The photon energies used here access *s* electrons and the top of the *d* band. The work function Φ for Cu(100) is 4.6 eV, and the photon energy used in this study is 3.14 eV. Part (b) is the photoemission spectrum obtained with one beam blocked. The ~1.7-eV width of the spectrum (which is broadened to ~1.9 eV by the instrumental resolution of the energy analyzer) is obtained from the difference of the two-photon energy (6.3 eV) and the work function.