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**SURFACE THRESHOLD DISPLACEMENT ENERGY
MEASUREMENT OF SILICON**

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Abstract

A combination of low-energy electron-diffraction (LEED) techniques and Auger spectroscopy is used to examine the production of surface damage on silicon. Controlled damage of a Si(111) surface is produced and the extent of damage is monitored by the reduction of the integral-order LEED beams. Surface contamination is monitored by Auger spectroscopy before and after damage production to insure that the results apply to a clean silicon surface. The degradation caused by He^+ ion bombardment in the 10-80 eV range is measured and compared with

previous data of other workers on Ge (Ar^+ ion bombardment). Measured degradation data for the Si(111)-7 surface indicate that no sharp surface threshold displacement energy occurs. Degradation went to completion for each of the bombardments before a dose of 10^{16} ions/ cm^2 , in contrast to the Ge data. LEED beam-broadening measurements are used to distinguish between degradation due to lattice distortion and localized structural defects such as vacancies. Preliminary results indicate that the low-energy He^+ ion degradation is due to displacement damage.

Introduction

The exact nature of crystal structures and the interatomic forces holding them together has been a topic of scientific investigation for several centuries. The use of x-ray spectroscopy has enabled scientists to identify the bulk structures and propose binding schemes for these crystals. In 1927 Davisson and Germer¹ discovered experimentally that low-energy (200-eV) electrons striking a face of a nickel crystal actually are reflected in a manner that can most easily be interpreted as diffraction of plane waves by the regularly spaced atoms of the crystal. In an extensive set of experiments, they es-

tablished that the diffraction angle corresponds to a plane wave whose wavelength is given by de Broglie's formula. In 1928 Nishikawa and Kikuchi² succeeded in shooting a monoenergetic (68-keV) beam of electrons through a very thin sheet of mica onto a photographic plate. This diffraction pattern was in every way similar to an x-ray diffraction photograph using x rays of equal wavelength. Thus, these two experiments illustrated wave-particle duality and enabled electrons to be used for structure investigations.

Of fundamental importance is a knowledge of the strength of the forces holding

the atoms in their crystalline structure. In particular, much work has been done in studying the effects of radiation damage on semiconductor device operation. Also, the increasing employment of ion-implantation for fabricating devices has rekindled interest in damage studies. However, little work has been devoted to the study of the binding energies at crystalline surfaces. A real crystal must necessarily have a surface where the atoms readjust to form different binding schemes to compensate for missing atoms. The structures thus formed usually have different properties than the bulk because of their special binding schemes. Low-energy electrons bombarding a surface will penetrate only the outer surface layers of the crystal; thus by using low-energy electron-diffraction (LEED), the surface structure may be studied. LEED measurements are usually made with primary electron energies of less than 300 eV. This report will describe an investigation of the Si(111) surface in an attempt to determine a threshold energy for simple displacement damage.

Much improvement has been recently made in the measurement techniques of LEED, in the conditions under which the intensity measurements are made, and in the knowledge of the possible effects of various ion bombardments. Helium ion bombardment was used in this study instead of argon, the usual sputtering ion gas. Since the diffraction beam intensity goes as Z^2 , He atoms in the lattice in interstitial or substitutional sites should not contribute significantly to the primary Si diffraction beams. On the other hand, Ar has a Z of 18 which is even larger than the Z of 14 for Si; thus it might be expected

to degrade the Si diffraction when in the lattice. The purity of the ion beam was closely monitored by a residual gas analyzer (RGA), and cleanliness of the sample surface before and after irradiation was checked by Auger spectroscopy. Never before has Auger spectroscopy been used in connection with LEED studies of surface damage. Measurements of the diffraction spot intensities were made with a moveable Faraday cup, thus enabling the width and peak intensity of the beams to be accurately determined. Previous workers tended to use a spot photometer for intensity measurements.

Data for LEED beam degradation versus He ion dose must be determined in order to detect any surface threshold displacement energy. Thus bombardments must be performed over the energy range for which the maximum energy transfer relationship predicts a value near the expected threshold. Results of these degradation measurements may be compared to those of Ar bombardment of the Ge(111) surface already reported.³ Determination of the source of degradation, i.e., lattice distortion or vacancy production, may be made using LEED beam-broadening measurements pioneered by Park.⁴

It must be emphasized that this report is concerned with measurement of surface damage; thus our results are unique and may have no direct correlation to any bulk measurements. In this report a brief history of displacement energy predictions and measurements will be reviewed, LEED and Auger techniques will be explained, experimental conditions will be discussed, and the experimental results obtained will be reported and explained.

Survey of Bulk and Surface Threshold Energy Literature

BULK MEASUREMENTS

Several estimates have been made of the threshold energy necessary for bulk atomic displacement and subsequent experiments designed to detect this energy. Most have been reviewed by Corbett in his 1966 book⁵ on radiation damage; therefore only an outline of this work will be given here, along with more recent work.

The initial estimate was made by Seitz in 1948.⁶ He argued that the threshold displacement energy, E_D , should be about four times the sublimation energy of the material; thus he arrived at a value of ~ 25 eV for most materials.

The most satisfactory estimate of the threshold displacement energy for Si is given by Bauerlein.⁷ He views the formation of a Frenkel defect as proceeding in three stages:

1. The four valence bonds to the near neighbors are broken with an energy expenditure of $4 E_V$.

2. The lattice atom is displaced between its three nearest atoms at an expenditure of energy U .

3. The displaced atom has to push aside the neighbors of the interstitial site to make room for the interstitial atom, but he argues that there is ample room in the Si lattice so that there is no need to displace the atoms surrounding the interstitial site and hence no energy lost in this process. He estimates that the energy U is $\sim 1/10$ eV. In view of the high lattice binding energy, he ignores the energy U . He argues that the single bond energy E_V is one-half the total bond

energy E_B per atom so that the displacement energy is $\sim 2 E_B$. Then he sets the total bond energy equal to the heat of sublimation with a correction for the fact that the atoms probably sublime as atoms in the normal s^2p^2 configuration rather than the sp^3 configuration which occurs in the lattice. He uses the total bonding energy since he believes that the electron will not undergo the sp^3 transition during the time of the displacement. Thus he adds the sublimation energy (107 kcal/mole or ~ 4.6 eV) to the excitation energy to promote an electron from the s state to the p state (73 kcal/mole or ~ 3.2 eV), giving a bond energy of 7.8 eV and a displacement energy of ~ 15.7 eV.⁸

Kohn⁹ should be remembered for first discussing the anisotropic nature of the displacement process and proposing that the $\langle 111 \rangle$ direction would be the easiest for displacement.

The electrical conductivity/Hall measurement is the most common technique used in radiation defect studies because of the sensitivity of the conductivity to added donor or acceptor levels due to irradiation. Irradiation of the sample produces electron energy levels in the forbidden gap which are usually deeper than those due to dopants; therefore, the number of free carriers is reduced. Experiments designed to measure the threshold displacement energy both for Si and Ge tend to fall into two camps:

1. those obtaining an E_D of ~ 15 eV,
2. those obtaining an E_D of ~ 22 eV.

In addition, the effects of anisotropy have not been consistent among the various experimentalists, and "sub-threshold"

damage at energies below their reported threshold values was usually observed.

Haddad and Banbury¹⁰ have pioneered the recent bulk displacement energy measurements on Si which incorporate computer-aided models of the displacement process. They measured the carrier removal rate (determined from Hall coefficient and resistivity measurements) as a function of electron beam energy for the $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ directions, and found anisotropy in their results. In a continuation of this work, Hemment and Stevens¹¹ have completed additional measurements on Si, and have developed a computer program which predicts a displacement energy profile and effective threshold displacement energy in the $\langle 111 \rangle$ direction of 22 eV, consistent with their data. Again, however, there are "sub-threshold" displacement effects observed.

SURFACE MEASUREMENTS

The only attempt known to this author to measure the degradation of LEED beam intensities after irradiation and determine the minimum ion energy for damage was by Jacobson and Wehner in 1965.³ They studied argon ion-bombardment damage on a Ge(111) surface and plotted the degradation of the (10) beam as a function of dose. Their principal results from these measurements are reproduced in Fig. 1. Their intensity ratio plots of I/I_0 (I_0 is the pre-bombarded intensity) show no sharp threshold for damage, but between the 50-eV and 100-eV energy Ar^+ bombardments there is a difference in the ability to reach complete degradation. (It should

be noted that the curves shown have been corrected for background intensity, i. e., when $I/I_0 = 0$ it means that the spot intensities reached the background level.)

Thus we may wonder if the low-energy degradation is of the same type as the higher energy degradation and question the possible causes of the degradation. Their results indicated that the surface structure formed by the low-energy bombardment was different from the "clean" structure, whereas the structure after bombardment with the higher energy ions was similar to the "clean" structure. One proposal for a difference of this type would be that the low-energy structure was caused by lattice distortion due to Ar gas entrapment. Degradation due to lattice distortion has been well documented in later LEED studies.⁴ If a sharp surface threshold displacement energy of 20 eV is expected for Ge, the maximum energy transfer formula would predict an energy of 75 eV for Ar^+ ions necessary to exceed this threshold. This value of Ar ion would fall between the two types of data point curves shown above; thus it is possible that the type of degradation seen for ion

Fig. 1. Degradation of the (10) beam at 36-eV electron energy versus the number of Ar ions/cm² bombarding the surface.

energies above 50 eV is caused by surface displacement processes, while the degradation for energies of ≤ 50 eV is due to another process. They also state the need to distinguish between degradation due to Ar gas entrapment and displacement damage, and remark that they do have gas entrapment for their low-energy bombardments.

They then proceed to propose a model for their data, predicting an exponential decay of I/I_0 with dose, and indicate that "the minimum ion energy for damage is ~ 20 eV." In the usual sense of a well-defined threshold energy, this statement is quite speculative. Of greater concern is the fact that during the investigation,

they had no means of checking the surface cleanliness, such as Auger spectroscopy, so other contaminants could have caused degradation. In addition, their dose measurement did not have a means of suppressing the secondary electron produced; thus their dose values are up to a factor of four too high.¹² In summary, no distinction between degradation due to displacement processes and other processes such as lattice distortion was made in this work, and their experimental conditions did not allow for controlled monitoring of the surface cleanliness as related to foreign impurity contamination.

LEED and Auger Spectroscopy Surface Investigation

LEED

The LEED optics unit used in this investigation consists of the electron gun, fluorescent screen, and four control grids. The outer grid is usually at specimen (ground) potential, thereby creating a field-free region between the specimen and the grid, which allows the diffracted electrons to move out radially toward the phosphorescent screen. The center two grids are suppressor grids, providing excellent cut-off characteristics and permitting the examination of the energy distribution of the inelastically scattered electrons. Various types of inelastic events which may occur include phonon, plasmon, and single-atom interactions. LEED will be concerned with the elastic component of the secondary emission current. The cut-off of the suppressor grid is also used to determine the strength of

magnetic field present. Since the pattern should collapse symmetrically toward the center if no field is present, a deviation from this indicates a field which may then be cancelled by use of a trim magnet or Helmholtz coils, etc. A strong magnetic field will bend the electron beam both on its path toward the sample surface and after diffraction on its way to the display screen, producing nonsymmetric diffraction spots. Additionally, the individual spots tend to be diffuse and warped from their normal round shapes. Our investigation calls for measurement of the intensity and spread of the diffraction spots. If the spots were not symmetric measurements would vary, depending upon the spot chosen for investigation.

The beam voltage is controlled by the biasing of the anodes of the electron gun assembly. Since the wavelength of the electron is proportional to $1/\sqrt{E}$, changing

the beam energy varies the position and appearance of various order spots. At very low beam voltages, the wavelength of the incident electrons becomes greater than the smallest periodic lattice spacing of the surface layers; therefore no first-order diffraction is possible. On the other hand high beam voltages produce a reduction in the diffraction angle, creating the appearance of several-order spots where before only the integral-order beams appeared, plus the possible appearance of fractional-order beams. Fractional-order beams are produced by periodic surface structures having spacing larger than the normal bulk lattice spacing.

In regard to notation for surface structures, the following convention has been adopted: If the surface structure has a periodicity different from the substrate periodicity and it is $N\vec{a}$ times as large in one parallel surface direction and $M\vec{b}$ times as large in the other ($\vec{a}$ and $\vec{b}$ are bulk translation vectors), the notation for that surface would be Symbol (hkl)-MXN. For our case, we consider the Si(111)-7 structure which has a surface periodicity seven times as large as the bulk spacing in both $\vec{a}$ and $\vec{b}$ directions. It is believed that the average number of surface layers contributing to a 100-eV LEED pattern is on the order of three. LEED patterns therefore represent 2D structures in the sense that the translational periodicity is only weakly explored in the direction normal to the incident electron beam.

In x-ray diffraction the sample is examined for its periodicity in three dimensions, but LEED only samples in directions perpendicular to the normal at the surface. We may think of the diffraction

conditions for the 3-D case as being satisfied whenever a reciprocal lattice point intersects with the Ewald sphere. This condition requires that $\vec{G} = \vec{k}' - \vec{k}$ where $\vec{G}$ is the reciprocal lattice vector, $\vec{k}$ is the wavevector for the incident wave, and $\vec{k}'$ is the wavevector of the scattered wave. Thus every point in the reciprocal lattice corresponds to a possible reflection from the real lattice so diffraction gives us a map of the reciprocal lattice points, and from this we may reconstruct the crystal lattice. For x-ray diffraction, we have three simultaneous equations to solve for the diffraction condition, and any change in wavelength of the beam (change in sphere radius) or change in orientation will cause diffraction not to occur. However, removing the periodicity requirement in one of the three dimensions for LEED causes continuous diffraction for continuous change in beam wavelength or orientation.

We know that the intensity of a diffraction beam will have different values for each of the various-order reflections. Usually the first-order reflection will be the most intense, with the higher-order reflections decreasing in intensity. For a given surface, the plot of intensity versus energy of the primary beam will appear as a series of peaks. The intensity of an integral-order reflection for a Si (111) surface as determined in the laboratory is shown in Fig. 2.

SILICON SURFACE PATTERNS

Throughout the investigation of Si (111) surfaces by LEED, two dominant patterns have been observed which were thought to be characteristic of a clean surface. They

Fig. 2. Relative intensity versus beam voltage.

are the Si(111)-5 and Si(111)-7 patterns. The Si(111)-5 pattern is usually obtained with a low-temperature $\sim 500^\circ\text{C}$ anneal after chemical etching. Figure 3a is a photograph of the Si(111)-5 pattern showing the characteristic six symmetric spots around the integral-order beams. The use of Auger spectroscopy has recently demonstrated that the Si(111)-5 pattern is not characteristic of a clean surface. One report¹³ indicates that the significant difference in a Si(111)-5 and Si(111)-7 structure is the absence of carbon in the surface. By looking at the problem in the laboratory, I have found that metal atoms (Mo and Ta) on the surface also will change the Si(111)-7 pattern into a Si(111)-5 pattern. It can only be said that several contaminants may change the 7-pattern to the 5-pattern. In addition, other impurities on the sample may produce entirely different surface structures and patterns. Figure 3b shows a pattern found by having nitrogen on the surface, as verified by the characteristic 3d0-eV N Auger peak.

Further heating at about 1200°C usually will produce the Si(111)-7 pattern. It has seven fractional-order spots between the

integral-order spots. This pattern is believed to be the only clean surface structure for the Si(111) surface. The pattern is shown in Fig. 4.

AUGER ELECTRON SPECTROSCOPY

Initially, the identification of LEED patterns and the proposal of a surface structure had serious limitations since no means of detecting the presence of impurities was available. With the use of Auger spectroscopy, however, surface impurities may be detected and identified.

Fig. 3. Si(111) contaminated surface LEED patterns. (a) Silicon Si(111)-5 pattern observed with Mo contamination. (b) Silicon pattern with N contamination.

Fig. 4. Showing Si(111) LEED pattern at a primary electron beam voltage of 45 eV.

Suppose that we have an atom with one of its inner shell electrons missing, as can happen with high-energy electron bombardment. Of course, the atom will try to return to a less energetic state. We usually assume that a characteristic x-ray photon will be given off as a return to the lower energetic state, although another competing process occurs in which the excess energy is given to another electron of the atom, thereby ejecting it. This second electron is an Auger electron, and it will leave the atom with a discrete kinetic energy determined by the electron energies involved. Pierre Auger first discovered these electrons in 1925 while interpreting cloud chamber experiments involving the ionization of inert gases by x rays.¹⁴

If the ionized inner level is the K shell of the atom and this level is filled by an electron from the L_2 level with the subsequent ejection of an Auger electron from the L_3 level, this ejected electron is referred to as the KL_2L_3 Auger electron. The kinetic energy of this Auger electron is given by

$$E = E_K(Z) - E_{L_2}(Z) - E'_{L_3}(Z) \quad (1)$$

where $E_K(Z) - E_{L_2}(Z)$ is the difference in the ionization energies of the K and L_2 levels (equal to the characteristic energy $h\nu$ of the x-ray photon if that process occurs), and $E'_{L_3}(Z)$ is the ionization energy of the atom already ionized in an inner shell. If $E_{L_3}(Z)$ is the ionization energy of the L_3 level of the neutral atom, we may approximate $E'_{L_3}(Z)$ by

$$E'_{L_3}(Z) \approx E_{L_3}(Z + 1) \quad (2)$$

since with a vacancy in the inner shell, the outer electron will move in a field roughly equivalent to that corresponding to atomic number Z .¹⁵

In general, for initial ionizations of shells having energies < 2 keV or so, the x-ray yield is negligible in comparison with the Auger yield.¹⁶ For initial K-shell ionization of Si, there is a factor of about 20 greater probability of Auger production than x-ray production. For lower atomic number materials, this factor is increased. As determined by x-ray measurements, the inner shell energies for Si are:

K	—1839 eV
L_1	—149 eV
L_2	—100 eV
L_3	—99 eV

By using the x-ray data (or by measurement techniques to be described), the Auger electrons expected for a particular element can be predicted. The most recent graph measured by Webbing and Strausser of Varian¹⁷ is shown in Fig. 5.

Fig. 5. Varian chart of Auger electron energies.

Fig. 6. Schematic of equipment used for measurement and display of Auger electron spectrum.

From this graph, the allowed Auger transitions for most elements may be found. So if we measure Auger electrons of a certain energy set, these energy values may be compared to those allowed for each element in order to determine the impurity present.

Figure 6 shows a schematic of the equipment used for Auger analysis. The electron source produces a 2-keV beam. This gun may be supplied separately, thus striking the sample at a glancing angle, or by the LEED gun operating in a high-voltage mode. The sensitivity of the analysis is increased by using the glancing angle gun since the excitation is then concentrated near the surface, thus enhancing the escape of low-energy Auger electrons. The outer grid is grounded to produce a field-free region, allowing the Auger electrons produced to travel in radial paths toward the first grid. The next two grids have the retarding voltage

applied to them, thus preventing those electrons which have kinetic energy less than the retarding potential from passing the grids on their way to the collector. Two grids have been shown to increase the resolution and to improve the definition of the retarding potential. On top of the negative dc potential supplied to these grids, an ac modulation voltage is also provided through transformer coupling. Our collector is a fluorescent screen biased to a few hundred volts positive with respect to ground. The fourth grid is grounded and serves as a shield for reducing the capacitive coupling to the collector of the ac voltages applied to the retarding grids.

If the sample is excited by electrons of energy E_p and the current to the collector is recorded while the retarding field voltage is swept from ground potential to $-E_p/e$, a retarding field plot of $I(E)$ versus E is obtained. This plot is shown in Fig. 7a. We would expect the current to decrease with increasing E since we are allowing only those electrons with energy $E - E_p$ to reach the collector.

To show how the secondary-electron energy distribution $N(E)$ or its derivative $dN(E)/dE$ is obtained, we expand the collector current $I(E)$ in a Taylor series about the dc retarding potential E_0 :

$$\begin{aligned}
 I(E) = & I(E_0) + \left. \frac{dI(E)}{dE} \right|_{E=E_0} (E - E_0) \\
 & + \frac{1}{2!} \left. \frac{d^2I(E)}{dE^2} \right|_{E=E_0} (E - E_0)^2 \\
 & + \frac{1}{3!} \left. \frac{d^3I(E)}{dE^3} \right|_{E=E_0} (E - E_0)^3 + \dots \quad (3)
 \end{aligned}$$

Fig. 7. Graphical output obtained from Auger electron spectroscopy system. (a) Retarding field plot (dc current); (b) secondary electron energy distribution (fundamental); and (c) derivative of energy distribution (2nd harmonic).

Our potential $E - E_0$ is made to vary sinusoidally by use of an ac signal of $k \sin(\omega t)$ on the retarding potential E_0 , which is swept up to E_p to obtain our plots. The first derivative of $I(E)$ is just equal to the secondary electron energy distribution as shown in Fig. 7b. Replacing $dI(E)/dE$ with $N(E)$,

$$I(E) = I(E_0) + kN(E) \sin \omega t$$

$$+ \frac{k^2}{4} \frac{dN(E)}{dE} \bigg|_{E=E_0} (1 - \cos 2\omega t) + \dots (4)$$

We see that by tuning our lock-in amplifier to the fundamental frequency, the secondary-electron energy distribution may be obtained. The Auger peaks appear as bumps on the $N(E)$ curve; therefore the sensitivity of the analysis may be increased by taking the derivative of $N(E)$, making these peaks more pronounced. Electronically this derivative is proportional to the 2nd harmonic; thus tuning the lock-in amplifier to 2ω will allow the Auger peaks to be identified. These data are then plotted on an X-Y recorder as the dc retarding voltage is swept.

Experimental Procedure

SAMPLE SURFACE PREPARATION

Clean, smooth surfaces were prepared by mechanical lapping and chemical etching to remove the damaged layers. The lapping compound was SiC, progressing from rough to fine for the final lapping. Various etches have been used in attempt-

ing to clean the surfaces, but the best results were obtained using an etch containing by volume¹⁸

- 50 lactic acid,
- 60 nitric acid,
- 20 sulphuric acid,
- 40 hydrofluoric acid.

The etch was quenched in a saturated iodine-methanol solution which left an iodine film on the surface after the methanol evaporated. Iodine on the surface prevents reaction of the Si with O and other gases while it is being prepared for insertion into the high-vacuum environment. The iodine was then removed by heating the sample under vacuum, leaving behind a clean Si surface. Samples prepared by the chemical etching method tend to have carbon and oxygen as their major surface contaminants, and those can be removed by high-temperature annealing, although this procedure may produce metallic surface impurities.¹⁹ After heating the sample at 900°C for 1 min, the O Auger peak would be significantly reduced; however, the C peak remained until the sample had been heated at ~1100°C for 30 sec. The C then presumably either diffused further into the bulk and became undetectable or formed CO or CO₂ and was pumped away by the vacuum-ion pumps. The cleanliness of the surface as displayed by the Auger spectrum was continuously monitored, and the surface was removed and etched again if the contamination became appreciable. Bombardment using ~200-eV Ar ions has in the past been used to improve the surface cleanliness; however, the author found that high-temperature anneals were more effective in accomplishing this.

Once while a new sample was being cleaned a LEED pattern appeared which had the form of the Si(111)-5 pattern with its six less intense spots around the integral-order Si diffraction spots. Since the Auger spectrum indicated an appreciable

amount of Mo on the surface, we assume this pattern is due to lattice restructuring caused by the Mo on the surface. Other metals have been reported to produce the same Si(111)-5 pattern, and we have observed the pattern with Ta on the surface in this laboratory. The amount of contamination on the surface necessary to change from the Si(111)-7 to Si(111)-5 pattern has not been accurately measured, but it would seem that the Si(111)-7 pattern is still maintained with up to 20% Ta contamination. Molybdenum seemed to change the pattern with less atoms on the surface than did Ta. A representative spectrum containing both Mo and C contamination is shown in Fig. 8. Here we have the derivative of the number of electrons in the secondary electron spectrum of the sample as a function of the energy of the electrons. Peaks of this spectrum correspond to allowed Auger transitions of the surface under consideration, and thus the energy of these peaks can be used to determine the presence of impurities on the substrate. Although no absolute correlation can be made between the number of atoms of various types from the derivative of the number plot, an estimate of the relative density of various atoms may be made. We notice that the principal Auger peak of Si has shifted from the reported value of 91 eV for clean Si, due to the presence of Mo and C on the surface. Shifts of 10 eV²⁰ or more are seen in other surfaces upon contamination, so the shift is believed to be real. A clean surface as recorded for the surface preparation techniques reported here has the shape of Fig. 9.

Fig. 8. Silicon Auger spectrum with apparent Mo and C contamination.

Fig. 8. Silicon Auger spectrum.

There also seems to be a correlation between the temperature-annealing history of the sample and the type of pattern seen, which may be more of a factor in the type of pattern seen than the amount of contamination on the surface, as long as their total coverage is less than a monolayer. Lower temperature anneals gave Si(111)-5 patterns while the higher temperature anneals gave the Si(111)-7 pattern. Thus it was necessary to heat the sample to about 1100°C after each bombardment for it to return to a condition like that observed before bombardment.

IRRADIATION PRODUCTION AND MEASUREMENT

We wish to study the production of surface damage by a monoenergetic source of particles which will not produce appreciable lattice strain if they stop in interstitial positions, thereby causing LEED intensity degradation. We want particles with a very low effective atomic radius. A proton source would be ideal, but proton sources capable of operating in the 100-eV range cannot be practically built. Therefore, for this work, a sputter ion source was used, with He used as the ionized species. Consideration of the ionization cross sections for production of He^+ and He^{++} indicate that in our range of operation (<200 eV) the production of He^{++} is quite improbable, thus our source is essentially He^+ . High-purity He was used (>99%), and this purity was checked during each bombardment with a RGA to prevent leaks from other gas bottles in the line.

The ion bombardment gun consisted of an emission electron cathode, an acceler-

ating grid for the produced ions, and focusing einzel lenses. In this system, the electrons produced by the cathode are accelerated through a positively biased grid. On the average, the electrons may pass several times through the grid structure before being collected there. While in transit the electrons collide with the gas molecules present in the chamber, thereby ionizing them. Since the maximum ionization cross section for He occurs at 140 eV, it is beneficial to have a fixed potential for the grid with respect to the cathode. After the ions are produced, they are accelerated toward the target and then focused by the accelerating/decelerating einzel lens configuration. In order to produce a field-free region for the ions as they travel toward the semiconductor target, the last plate of the einzel lens is at ground potential. A schematic of the ion-bombardment gun and einzel lens is shown in Fig. 10. Since results were desired for intensity degradation versus ion dose, a calibration of the gun dose production for various energy bombardments was recorded. This was done by placing a specially built Faraday cup in the position of the sample during irradiation and then measuring the ion current incident upon the Faraday cup collector. The ion current at the sample was linearly dependent upon the emission current from the ionizing cathode and the partial pressure of the gas species being ionized in the operating range under consideration. If the emission or the gas pressure was slightly different from the standard operating values during the actual ion bombardment, a linear correction was made for the dose.

Fig. 10. Schematic of ion bombardment gun.

Discussion

ENERGY TRANSFER AND THRESHOLD ENERGY MODELING

Scattering and Energy Loss

A most crucial question to be considered in determining the displacement energy threshold is the relationship between the measurable quantity (energy of the bombarding particle) and the measurement of the desired displacement energy threshold. Two areas must be considered when discussing particle scattering: (1) cross-section and scattering potentials, and (2) energy loss mechanisms and energy transfer relationships.

The scattering cross section provides an estimate of the probability of the displacement event taking place. A proper choice of scattering potential model and

related cross section requires a knowledge of the distance of closest approach of the projectile to the target atom, as determined by the initial kinetic energy of the projectile. If the projectile has large kinetic energy it will penetrate the electron cloud; consequently the scattering will be coulombic with the nucleus. The Rutherford cross section would be applicable for this case, but if the projectile only partially penetrates the electron cloud the scattering is of the Thomas-Fermi screened-potential type. In the lower energy limit the projectile does not have enough energy to penetrate the electron cloud; thus it will see a neutral atom and experience a billiard-ball collision. The smallest scattering cross section is

the Rutherford one; therefore this cross section is the lower limit of the scattering probability for threshold displacement. Since we are using very low energy bombardment, our cross section for threshold displacement should be that for billiard-ball scattering. Thus the cross section should be given by πR^2 , where R is the effective nuclear radius of Si atoms on the surface.

The two major energy losses in an elastic collision with an atom are electronic and nuclear losses. The electronic losses are due to excitation or ejection processes, and the nuclear losses result in translatory motion of the target atom. The relative importance of the two processes changes rapidly with the energy E and Z , the atomic number of the bombarding particle. Nuclear stopping dominates for low E and high Z , whereas electronic stopping becomes dominant for high E and low Z . Neither of these approximations can be made for the displacement measurement performed here. Computer calculations of the losses due to these processes have been carried out.²¹ An example of this type of calculation is shown graphically in Fig. 11. Again we are operating in the extremely low energy range where this graph does not apply.

If we consider only elastic scattering, the energy transfer relationship may be found using simple billiard-ball considerations of energy and momentum conservation. Maximum energy transfer occurs for a head-on collision. For this case, the well known maximum energy transfer relationship may be written as

$$E_T = \frac{4M_1 M_2}{(M_1 + M_2)^2} \times E_P \quad (5)$$

where M_1 is the mass of the projectile, M_2 the mass of the target atom, E_P the initial kinetic energy of the projectile, and E_T the energy transferred to the target atom. This report will consider only the case of He^+ ion bombardment of a Si surface; therefore for this report the equation has the numerical relationship

$$E_T = 0.436 E_P.$$

We see from this result that He ions are able to transfer at most 0.436 times their initial kinetic energy to the Si atoms in a head-on collision. Thus if the expected threshold energy was around 22 eV, it would take He ions of ~50 eV for a head-on collision to produce a displacement of the Si atom from a normal lattice site.

Threshold Energy Modeling

A simple model for atomic displacement would propose that the atom is bound in the lattice in an isotropic square-well potential of the depth E_D , the threshold displacement energy. This model would suggest that any dose of irradiation transferring less than E_D to the lattice atom

Fig. 11. Theoretical nuclear and electronic stopping-power curves, expressed in terms of the reduced variables ρ and ϵ (based on Lindhard *et al.*²¹).

Fig. 12. Displacement probability function P for step-function model; E_D is threshold displacement energy.

would be ineffective in displacing the atom, while for energy transfer of more than E_D there is a unit probability for displacement. This is called the step-function displacement probability model (see Fig. 12). Of course, for a real crystal whose structure has a distinct anisotropic characteristic, the simple model above would have to be modified for directional character and the possibility of more than one equilibrium interstitial position in a given direction. Thus, there may be a different threshold energy for displacing an atom from a normal lattice site for each of the stable interstitial positions available.

What one desires to do is to produce controlled damage by a monoenergetic source of irradiation in a given direction while some quantity which is damage sensitive is being measured, thus enabling a displacement probability function to be deduced. Our method of analyzing the threshold for displacement production involves the detection of the reduction of LEED beam intensity as a function of He^+ ion energy for incidence upon a $\langle 111 \rangle$ surface of Si. Thus, what we are seeking is a value for the minimum energy necessary to produce a $\langle 111 \rangle$ direction displacement

at the Si surface. It is believed that the movement of only one-tenth of a monolayer is enough to detect a reduction in beam intensity. When this reduction is observed as a function of the bombarding ion energy a profile of the displacement probability may be obtained, and by using our maximum energy transfer relationship we then obtain an upper limit on the energy necessary to produce the displacement. If additional loss mechanisms are present, the true displacement energy is less than the amount thereby deduced from the degradation measurements.

SILICON INVESTIGATION

Measurements Performed

Measurements were made primarily of the intensity and width of the integral-order LEED beam diffractions from the Si(111)-7 surface. These measurements included the initial clean intensity reading I_0 and the intensity after irradiation I throughout the 10^{14} - 10^{16} ions/cm² dose range. Helium ion bombardment has been used in this threshold measurement because of the small volume and low Z of the He atom. Since diffraction beam intensity is proportional to Z^2 of the scatterer, imbedded He ions ($Z = 2$) will produce few destructive LEED beams in comparison to Ar ions ($Z = 18$). Furthermore, the small volume of the He ions creates little distortion due to their presence in the lattice.

Plots of beam width were also made. This plot can be made in either diffraction angle or primary beam energy since one is related to the other through the diffraction condition. Width measurements are most easily made by varying the primary beam energy while keeping the Faraday

cup collector at a fixed angle in the plane containing the incident electron beam and the diffraction beam under consideration.

Experimental Conditions

During these measurements, care was taken to insure that the Si surface was clean, the ion beam was pure, and the diffraction spot intensity measured was a maximum. Sample surface cleanliness was monitored by Auger spectroscopy before and after the ion bombardment to insure that the degradation seen was not due to surface contamination from any unforeseen sources. Only Mo or Ta (metals used for sample holder) contamination buildup was ever observed during this investigation, and this occurred only after heating the sample and sample holder to 1100°C for 5 min or longer. This buildup may be attributed to diffused Mo or Ta from the holder across the Si surface. The contamination level was never allowed to exceed 5% of the silicon, as given approximately by the relative Auger peaks of the $dN(E)/dE$ plot. Experience showed that annealing at 1100°C for only 30 sec could both return the surface to its pre-bombarded intensity value and not produce Mo or Ta contamination.

The purity of the He ion beam was recorded by a residual gas analyzer (RGA), which was able to measure the relative amounts of gases present through mass separation after ionization. Checks were made of the gas purity before and after each bombardment run. Impurity levels were never allowed to exceed 1% of the He content.

The LEED beam intensity measurements were made with a Faraday cup collector equipped with a parallel suppres-

sor grid to allow only the elastically scattered electrons (diffraction component) to be measured. This Faraday cup collector was swept in both the θ and ϕ directions to find the peak intensity of the integral-order beam.

The LEED measurements were made in a vacuum of at worst 2×10^{-9} Torr, and many times in the 10^{-10} Torr range. The chamber had to be let up to a partial pressure of 2×10^{-5} Torr during the actual He^+ bombardment, but the chamber pumped down into the 10^{-9} Torr range in less than a minute after bombardment stopped. This fast pumpdown was achieved by shutting the vacuum-ion pump off from the chamber during bombardment and then gradually opening the pump to the He atmosphere. By use of this method, fast pumpdown was achieved, and no contamination was produced by the vacuum-ion pump sputtering previously trapped impurity gases.

Results

Data for the degradation of the 45-eV integral-order LEED beam after bombardment with He^+ ions have been obtained. Helium ion bombardment with energies of 10, 30, 50, and 80 eV has been performed, and the intensity degradation ratio I/I_0 has been measured as a function of the surface dose. Higher energy bombardment always produced faster degradation, and all intensities reached the background level with sufficient dose. These data are plotted in Fig. 13. The plots seem to decay exponentially with dose in the same manner as Jacobson and Wehner derived³

$$I/I_0 = e^{-2aD} \quad (6)$$

where a is defined as the mean area of

Fig. 13. Degradation of LEED beam at 45-eV electron energy versus He ion surface dose.

Fig. 14. Clean Si(111)-7 LEED beam width.

surface damage per ion and D is the surface dose (ions/cm²). Bombardment at 140 and 200 eV produced even faster degradation with complete degradation for $<10^{15}$ ions/cm² dose.

Beam width measurements were made for the "clean" surface condition and after ion bombardment of 10 eV He⁺ ions for a dose in the 10^{15} ions/cm² range, producing 66% degradation from the I_0 value. These graphs are shown in Figs. 14 and 15 respectively. Within the limits of experimental error, we see that no significant beam spreading has occurred after the ion bombardment. The asymmetry of this plot can be traced primarily to the difference in background levels. A higher background intensity is measured for higher primary beam energy, thus shifting the intensity value upward. A more recent plot of the clean beam width spread is shown in Fig. 16.

Discussion of Measurements

Initially, it was expected that He ion energy bombardments of <50 eV would produce no significant degradation of the LEED beam intensity, since a threshold of 20 eV was expected for surface damage. However, degradation for 50-eV He⁺ bombardment was seen, beginning with a dose of about 10^{14} ions/cm², and complete degradation was seen for a dose of

Fig. 15. Si(111)-7 LEED beam width after 66% degradation of He⁺ at 10 eV.

Fig. 16. Improved, clean Si(111)-7 LEED beam width.

about 2×10^{15} ions/cm². Thus, lower energy bombardments were made in an attempt to detect a sharp threshold energy for displacement damage. A 15-eV threshold would correspond to a 34-eV bombardment, so a 30-eV bombardment was performed in hopes of detecting the 15-eV threshold. Again, degradation started at about a 10^{14} ions/cm² dose. Degradation was even seen for 10-eV bombardment at this dose. Thus, there appears to be no sharp threshold for surface displacement damage at a Si(111) surface.

An average monolayer of Si would correspond to 1.35×10^{14} atoms/cm²; thus we are seeing the degradation after a monolayer coverage by the He ion source. Degradation cannot be traced to any coverage by a gas present in the 10^{-9} Torr vacuum, as this measurement was performed with no degradation seen after 30 min and only 10% degradation after 1 hour. All of the I/I_0 data points were taken in less than 1 hour with a 10^{15} dose taking 16 min; therefore, this contribution cannot explain the complete degradation of the data seen.

The slopes of the degradation curves are about the same, indicating the same type of degradation mechanism for each curve. No difference in the ability to reach complete degradation was seen for any of the runs, in contrast to the data of Jacobson and Wehner for Ar⁺ bombardment of Ge.³ Any suggestion of degradation due to He contamination for the lower energy ion bombardments is not supported by the data shown.

Higher energy bombardment is expected to produce more degradation than low-energy bombardment at constant dose. While this was always true for the same initial pre-bombarded intensity of the LEED beam (contamination and surface structure periodicity condition), data comparing results from different I_0 values showed differences in the I/I_0 ratio of a given ion energy and dose. This is to be expected, since the degradation characteristics of damaged surfaces can be different than that of a well-ordered surface. As was seen from the I/I_0 curves, a saturation effect occurs for large disorder. However, experimentally only large differences in I_0 values of factors of three or more were seen to significantly affect the data, since the samples were always quite clean as determined by the Auger spectrum. As mentioned, only 5% of a monolayer contamination was allowed for these runs before the sample was cleaned by chemical etching. Of course, intensity degradation measurements in themselves do not indicate the source of degradation. In particular, we cannot tell if the degradation is due to lattice distortions resulting from the bombarding atoms imbedded in the lattice or localized structural defects such as vacancies. In looking for a displacement

energy threshold for vacancy production by measuring LEED beam intensity degradation, the chance of lattice distortion must therefore be kept to a minimum. Helium was chosen for this reason instead of argon, the typical sputtering ion source used by investigators of ion-bombardment effects on surfaces. A method of detecting degradation due to lattice distortion and distinguishing this degradation from that due to vacancy production was not known until the significant paper, in 1966, of Park⁴ who stated:

"Let us assume, for example, that the effect of bombardment is to produce a random distribution of point defects in an initially perfect plane surface. This reduces the effective scattering area of the surface and will result in a decrease in diffraction intensities. However, the undamaged portions of the surface are in register with one another and scatter cooperatively. Therefore, the beam width will not be appreciably affected."

Lattice strain, however, results in beam broadening. The maximum strain has been shown to be⁴

$$s = \Delta V_n / 4V_n \quad (7)$$

where ΔV_n is the spread of the n th diffracted beam under question and V_n is the

beam voltage at maximum intensity. So a measurement of beam width before and after bombardment can be used to determine the source of the degradation seen.

The initial data found for low-energy He bombardment (10 eV) does not indicate broadening that is not within the experimental error. Most beam broadening (ΔV_n) seen by Park is of the order of 10 V. Thus, our degradation seen for low-energy He bombardment seems to be due to displacement damage and not lattice distortion. Consequently, no sharp threshold for surface displacement exists for the Si(111)-7 surface for He bombardment in the range observed. Instead, continuous degradation curves are obtained which all reach the background level with enough dose and have faster degradation-versus-dose rates for the higher energy He⁺ ion bombardment. These results indicate a distinct difference in the binding energy of bulk and surface Si atoms. Whereas the minimum energy necessary to displace a bulk atom in the $\langle 111 \rangle$ direction is believed to be 22 eV, we have observed displacements with as low as 5-eV energy available for displacement. We are led to believe that a factor of at least 4 lower binding energy is present at a Si(111)-7 surface.

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