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EXPERIMENTAL STUDY OF THE SURFACE STRUCTURE
AND ELECTRONIC PROPERTIES OF SINGLE CRYSTAL
MOLYBDENUM AND TUNGSTEN RIBBONS

MASTER

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INTRODUCTION

This report contains a summary of the research conducted in the area of surface physics in our laboratory. Our original goal was to measure the surface defect structure, using low-energy electron diffraction (LEED) and to correlate these measurements with the thermionic emission constants, using a retarding potential technique, for single crystal tungsten and molybdenum ribbons. Techniques for making thin single crystals of W and Mo, for any desired crystal orientation, have been developed. 1, 2, 3

A number of LEED systems have been constructed with varying degrees of success. The final version is a versatile LEED system that also includes the capability of measuring the secondary electron emission energy distribution and Auger spectra. Some data, both LEED and Auger spectra has been obtained for both W and Mo single crystals.

A retarding potential experiment, similar to the arrangement used by Shelton,⁴ has been constructed. Considerable data has been obtained from this system. However, the data does not agree with the results that are predicted by theory. At the present time we have not been able to determine whether the difficulties are due to problems with the experimental arrangement. Because of the difficulties with the thermionic emission experiment, data has not been obtained that would allow for the correlation of surface defect structure and the thermionic emission constants.

CRYSTAL PREPARATION

Considerable effort has been expended during the contract period in obtaining suitable single crystal ribbon specimens for the LEED and thermionic emission experiments. Initially, single crystals were prepared from polycrystalline samples by the strain-anneal technique. This method did not yield reproducible results nor crystals of the desired orientation¹ and was abandoned in favor of the use of crystals cut from a single crystal boule.

The specification that was the most difficult to achieve in the crystal preparation was the requirement that the surface area should be large and the thickness of the crystals small. The large surface area, of the order of 1.0" x 0.25", is necessary if edge effects are not to invalidate the results. Thin crystals, 0.002" to 0.003", are required if excessive heating currents are to be avoided. In the samples actually used in the experiments, heating currents in the neighborhood of 20 A were sufficient to raise the temperature of the samples over 2000 K.

The single crystal boules were obtained from Materials Research Corporation, Orangeburg, New York and were MRC's MARZ grade crystals (triple-pass zone refined). Both the W and Mo boules had a symmetry axis along the (110) zone. The Mo boule was 0.5" in diameter and the W was 0.25" diameter.

Initially diamond sawing was used to cut the boules but EDM (Electric Discharge Machining) cutting was found to be superior and was used for most of the samples.

Following is a summary of the steps in the crystal preparation:

1. Orientation of the boule (Mo: 1.25 x 0.5 in. dia.; W: 1.25 x 0.25 in. dia.) by x-ray diffraction.
2. EDM slicing of the orientated boule (Mo: 1.1 x 0.5 x 0.030 in. slabs (110), (100), and (112) orientation; W: 1.1 x 0.25 x 0.030 in. slabs (110), (100), (112), and (111) orientation).
3. Orientation grinding of slabs using a Bridgeport vertical milling machine (with a goniometer transfer jig) as a surface grinder.
4. Backgrinding of the oriented slab to a uniform thickness of approximately 0.013 in. using the Bridgeport vertical milling machine as a surface grinder. Achievable uniformity 0.013 ± 0.0003 in.

5. Finish hand grinding of the orientated surface on 240, 320, 400, and 600 grit silicon carbide paper.
6. Diamond polishing of W crystals with 6 micron diamond suspension and 1/4 micron gamma alumina. Mo is not diamond polished.
7. Electropolishing of both surfaces of the slab to remove approximately 0.005 in. from each surface to a final ribbon thickness of approximately 0.002 in.

Some further comments of interest on the crystal preparation are:

1. Orientation to 1/2 degree is achieved regularly -- the limit of back reflection Laue techniques as well as our in-house processing.
2. Edging effects in electropolishing are eliminated by attaching the crystal to a polycrystalline Mo or W sheet, larger than the crystal, with Eastman 910 cement (a conductor). Removal of the crystal from the polycrystal sheet is achieved by soaking in dimethyl formamide.
3. Electropolishing of 0.005 in. from both faces of the ribbon was found to be necessary when obtaining 0.002 in. ribbons to avoid serious surface dislocation in the ribbon.
4. Final ribbon sizes are approximately the same as the original slab size, e.g., a 1.1 x 0.4 in. Mo ribbon is standard.
5. Electropolishing data: Mo electrolyte: 7 parts methyl alcohol, 1 part conc. sulfuric acid, current density: 16 A/in²;
W electrolyte: 20% (by weight) aqueous solution of NaOH, current density: 1.6 A/in².
6. Electropolish removal rate at specified current densities when used in a diode arrangement are Mo: 0.001 in./min.; W: 0.001 in./12-15 min.

The results of the above procedure yielded crystals that had smooth surfaces under 750X magnification. Electron microscope studies were initially used ^{1,2} in conjunction with the optical microscope studies. However, we decided that there was not enough additional data obtained from the electron microscope work to warrant its continued use.

A study of the effect of heating on the crystals ³ showed that the crystals retained their smooth surfaces if 0.005" or more material was removed during electropolishing. The amount of disorder introduced by heating could be controlled to some extent by removing less than 0.005" in the electropolishing step.

LEED STUDIES

LEED studies were initially proposed for obtaining information on the surface structure of the single crystals as a function of crystal heat treatment. The geometrical arrangement of the diffraction spots is a clear indication of the arrangement of the two-dimensional diffracting array on the surface of the crystal. Any changes in this array due to absorbed gases is easily detected in the shift of the diffracted beams ^{5,6}. It was hoped that structural changes in the crystal surface would lead either to a change in the geometry of the pattern or to a change in the intensity of a particular spot as a function of incident electron energy. The intensity data has not led to any fruitful results primarily because the theory of the interaction of the incident electron beam with the surface atoms has not been worked out in sufficient detail. At the present time, it does not appear that a detailed theory explaining the diffraction beam intensity variations with incident electron energy will be formulated in the near future.

The geometrical arrangement of the diffraction spots has not yielded the desired information on surface structure. The reason for this is the relatively large area of the incident electron beam. In our case, the beam diameter was approximately 0.1". The resulting diffraction pattern provides a good

indication of the average geometrical arrangement of the surface structure in an area equal to the beam area. However, the large beam prevents detailed information from being obtained on the short-range ($\sim 100 \text{ \AA}$) order-disorder structure of the surface. The size of the diffraction spot does indicate whether or not the area of the crystal being studied is predominantly ordered or disordered but it does not give a quantitative measure of the type or amount of the disorder.

In studying the energy distribution of secondary electrons emitted from a metal surface, Rudberg ⁷ found fine structure in the spectrum. This fine structure was found to be independent of the primary electron beam energy and characteristic of the target material. Lander ⁸ has shown that this fine structure is related to Auger transitions in the metal. A number of recent secondary emission studies ⁹⁻¹¹ have shown the versatility of the Auger spectrum studies in not only studying the target metal but also detecting small amounts of impurities on the crystal surface. Auger studies carried out in conjunction with LEED experiments have shown that the Auger spectrum is more sensitive to impurities and provides for identification of the impurity species. During the last year, our LEED system and associated circuitry were modified to include the capability of both Auger and LEED studies.

Experimental

Our first LEED system was constructed in an all glass vacuum chamber. Besides the usual difficulties of an all glass system, the orientation of the crystals and interchanging the crystals was excessively difficult and time-consuming. When metal vacuum systems became readily available with a variety of interchangeable components, we decided to use an all metal vacuum chamber.

The final version of the LEED apparatus is mounted in an Ultek stainless steel TNB bell jar. Two 50 l/sec ion pumps and a titanium sublimation pump bring the overall pumping speed to 3600 l/sec. A mechanical roughing pump

with a Zeolite cold trap is used for the initial pump-down. A copper pinch-off seal is used to isolate the system once the ion pumps have been started. Ultimate pressures in the 10^{-10} Torr range are readily achieved after outgassing and bakeout of the system.

The crystal mount can hold two crystals. This mount is attached to a rotary feedthrough mounted on a bellows. This arrangement provides three degrees of freedom for positioning the crystal in the electron beam. Flexible leads attached to the crystal mounting rods carry heating currents up to 25 A.

A three element electron gun provides the primary electron beam. The final electrode of the gun, the drift tube, has been reduced to a diameter of approximately 0.125". The cathode of the gun is a Phillip's L-cathode. Contamination from the cathode has not been observed. A small phosphor coated glass target is mounted on a rotary feedthrough and can be positioned in front of the crystal. This screen provides a convenient way for checking the electron gun focus. The two grid system originally used has been replaced by a three grid arrangement. The three grid system is more convenient for the Auger studies. The grids are chromium plated stainless steel hemispheres and the phosphor screen is a spun stainless steel hemisphere coated with zinc sulphide. The entire gun and grid assembly is mounted in a stainless steel shield. LEED patterns are observed through a 4" diameter glass port mounted on the bell jar.

A schematic diagram of the electronic circuitry used in the LEED experiment is shown in Fig. 1. The power supplies used to provide the electron gun voltages were regulated to 1/2% of the output voltage. Their combined ripple voltage was measured at 25 mV peak to peak. The 0 - 900 V battery supply provided a constant retarding voltage on the second grid to prevent inelastically scattered electrons from reaching the phosphor screen. The high voltage between the third grid and the screen provided the accelerating voltage for the electrons to excite the phosphor screen. A Photo Research Corp. spot photometer was used to

measure the brightness of the diffraction spots on the screen. The crystal could be maintained under field-free conditions with the last element of the gun, the first grid and the crystal at the same potential or the crystal could be biased slightly below ground potential to eliminate the possibility of space charge.¹² Although not shown in the diagram, the current to the crystal and to the various electrodes could be measured when necessary.

The electronic circuitry for the Auger measurements is more complicated and is shown in Fig. 2. The main feature is the addition of phase sensitive detection using an Electronics, Missiles and Communications Corp., Model RJB lock-in amplifier. The secondary electron current is modulated by a 105 Hz signal impressed on the second grid. This signal is also fed into the reference channel of the lock-in amplifier. One of the battery supplies provides a positive voltage for collecting the secondary electrons at the phosphor screen. The other battery supply is used as a retarding potential for retarding voltages up to 150 V. Above 150 V a Universal Electronics Model 1000-1 supply is used for the retarding potential and the battery supply bucks out part of the retarding voltage before it is applied to the X-input of the X-Y recorder. The Y-input of the recorder is taken from the output of the lock-in amplifier and is proportional to the secondary electron current at a particular retarding potential. The lock-in amplifier could be run in either the first or second derivative mode. The second derivative mode was usually used since this eliminated any unwanted 105 Hz pick-up. In addition, a small peak in the secondary electron spectrum will be considerably magnified in the second harmonic mode.

The maximum primary energy of the electron beam is 1000 V. Above 1000 V, some electrical breakdown occurred in the grid structure. During the Auger measurements, grid 1 is grounded to insure field-free conditions near the target and grid 3 is grounded to reduce capacitive coupling between grid 2 and the phosphor screen. The Auger spectra were scanned automatically by a motor-driven potentiometer.

Experimental Results

During the final phase of the contract period, most of the effort was concentrated on the Auger spectrum studies. LEED data was reported in a previous Progress Report.³ The LEED data showed that clean Mo crystals were obtained after heating to 1900 K for extended periods. The (100) surface of Mo required only 60 seconds at 1900 K to produce a clean surface. The Mo (110) surface required over 24 hours before the LEED pattern started to approach a clean pattern.

Preliminary results of the Auger studies have been obtained in two ranges, 1-3 eV and 7-35 eV for a ~~primary beam energy~~ of 950 eV. The large low energy peak near 5 eV due to true secondary electrons prevents observation of any Auger peaks that may be near 5 eV.

The spectrum in the 7-35 eV range for a W (110) crystal is shown in Fig. 3 and for a Mo (110) crystal is shown in Fig. 4. The peaks are broad but an estimate of the peak energy can be made. For W, the peaks occur at 14.6 eV and 21.5 eV while for Mo the peaks occur at 13.0 eV and 27.8 eV. These values are in good agreement with Harrower's¹³ results for polycrystalline Mo and Schiebner and Tharp's¹⁰ results for a (110) surface of W. However, Scheibner and Tharp found another peak for W at 18.0 eV which is not present in Fig. 3. This is most likely due to the rather large modulating voltage, 5 volts peak to peak, used in our experiment. Modulating voltages below 5 V were tried but noise problems prevented any results from being obtained. When the noise is eliminated, modulating voltages below 5 V will allow better resolution of the peaks and will reveal any peaks that have been missed.

The Auger peaks are partly attributed to surface dependent transitions and to bulk Auger transitions. The effect of surface conditions can be seen in Fig. 5 for the (110) Mo surface. The spectrum for the contaminated crystal was taken after the crystal was left unheated at an ambient pressure of 5×10^{-10}

Torr for 12 hours. The clean crystal spectrum could be obtained after heating the crystal for 2 seconds at 2050 K.

A sequence of spectra for a Mo (110) surface in the 1-3 eV range is shown in Figs. 6 and 7. Spectra A was taken 5 minutes after flashing the crystal to 2000 K for 5 min. The rest of the sequence was taken at various times after initial flashing with the crystal remaining unheated in an ambient pressure of 5×10^{-10} Torr. The time after flashing for the sequence of spectra are as follows: A-5 min., B-20 min., C-60 min., D-380 min., E-1380 min., and F-2670 min. Some evidence of a peak at 2 eV can be seen after 5 min. (A), and the peak becomes more pronounced as the crystal becomes further contaminated. After flashing the crystal to 2000 K for a few minutes, the peak disappears. The identification of the adsorbed species causing this peak is difficult since a number of elements could cause peaks near 4-5 eV. The curves shown in Figs. 6 and 7 have not been corrected for the contact potential between the crystal and the energy analyzer. This correction would shift the observed peak to 4 eV.

The results so far have shown the value of the Auger technique for determining the cleanliness of the crystal surface. Further work in the medium energy range, 7-100 eV, would provide positive identification of the adsorbed species. The combined Auger and LEED studies have shown that the Auger spectrum is sensitive to quantities of adsorbed gases that do not affect the LEED pattern.

THERMIONIC EMISSION MEASUREMENTS

The thermionic emission constants were measured by the retarding potential method used by Shelton⁴. Two planar crystals, separated by a shield containing a small aperture, are used as the emitter and collector. A magnetic field is used to collimate the electron beam. The following sections contain a detailed description of the experimental arrangement, pertinent theoretical equations

and their interpretation, data analysis and discussion of the experimental results.

Experimental Procedure

A schematic diagram of the diode structure is shown in Fig. 8. The emitted electrons passed through a small rectangular aperture, .00649" x .025", the long dimension of the aperture being perpendicular to the long dimension of the crystal. The aperture was cut in .0005" Ta foil and this foil was in turn attached to .005" Ta. The crystals were approximately 1.0" x .25" x .005" and were spot welded to .100" molybdenum rods. The distance between the crystals was .650" with the aperture midway between them. The aperture was constructed so that it could be moved parallel to the long dimensions of the crystal through a distance of .5". The diode arrangement was enclosed in a shield can constructed of .005" Ta, and the entire structure was mounted on a boron nitride insulating base.

In the original design the diode structure was mounted in a glass bell jar on a stainless steel base plate. This system had ceramic feedthroughs on the base plate that produced relatively large leakage currents. To eliminate these leakage currents, a new system was designed using glass feedthroughs with long insulating paths between the critical leads. A schematic diagram of the final version of the glass chamber is shown in Fig. 9. The diode structure was mounted in the constricted portion of the chamber in order that the crystals could be placed between the poles of a permanent magnet. A stainless steel bellows was used to move the aperture. The chamber was mounted on a stainless steel vacuum system.

The constricted portion of the glass chamber caused some difficulty because in making the constriction the glass became frosted in the region near the crystals. The frosted glass prevented accurate pyrometry of the crystals while mounted in the diode structure. Pyrometry data was taken with the

crystals mounted in separate evacuated tubes in which no shielding was used. A PYRO Micro-Optical Pyrometer¹ was used for the temperature measurements and the accuracy of these measurements was about ± 10 K. The temperature of the crystals for a particular heating current could be slightly higher when the crystals were in the shield can. As will be discussed below, this did not turn out to be a serious defect in the experiment.

The pumping system consisted of a 75 l/sec ion pump and a 3600 l/sec titanium sublimation pump. All seals were copper gasketed and bakeable to 450°C. The pumping procedure involved initial rough pumping with a mechanical forepump trapped by a zeolite trap cooled to -70°C. After the ion pump was started, the system was sealed-off from the forepump with a copper pinch-off seal. To obtain pressures in the 10^{-9} to 10^{-10} Torr range, three bakeouts to 400°C with outgassing of the metal parts in the tube between each bakeout were required. The ultimate vacuum attained was in the 10^{-10} Torr range and the pressure did not rise above 9×10^{-10} Torr when the crystals were raised to their operating temperature.

The magnetic field used to collimate the electron beam was provided by a 1.5 kilogauss permanent magnet with a 2.5" pole gap. The effect of the magnetic field on the energy distribution of emitted electrons has been studied by Greenburg¹⁴. The results of his experiment showed that applied fields up to 6 kilogauss had no effect on the thermionic emission current. The magnetic field also allows one to use the aperture area as the area of the emitting spot on the crystal. Fringing effects at the edge of the aperture due to the finite radius of the electron spiral cause an estimated reduction of less than 10% in the electron current. For the electron energy range used in this experiment, this reduction would be approximately constant and would not produce a measurable effect on the energy dependence of the current density.

Fig. 10 shows the schematic diagram of the measuring circuit. The Kepco KS8 supply was used as a constant current source for heating the crystals. This supply regulates the current to within $\pm .02\%$ for all line voltage and load resistance changes occurring in the experiment. The heating current was monitored by measuring the voltage developed across the .001 ohm precision resistor connected in series with the supply. Current through the crystal was reversed by means of the dpdt switch.

To prevent space-charge buildup between the emitter and aperture shield, a large accelerating potential, of the order of 100 volts was supplied by the Kay-Labs supply, Model 50B-100. The collector current was measured by either a Keithley 417 High-Speed picoammeter or by a Carey Vibrating Reed Electrometer. The Vibrating Reed Electrometer was used for measurements below 10^{-11} A. The Keithley Picoammeter was used for the higher current measurements because of its ease of operation and speed. The accuracy of the Keithley is $\pm 3\%$ and that of the Carey is $\pm .25\%$. The voltage drop across either electrometer was always less than 1 mV. The recorder output of the electrometer was measured by a Hewlett Packard 3440 Digital Voltmeter and digital recorder. This combination enabled all current measurements to be recorded directly and considerably reduced the time required for data acquisition. The retarding potential between the emitter and collector crystal was provided by a Princeton Applied Research Voltage/Current Reference Supply, Model TC-100.2BR. This supply has an accuracy of $\pm .005\%$ of the set voltage and a load and line regulation of $\pm .0001\%$. The 1000 ohm variable resistor in parallel with the emitter was used as a balancing resistor and allowed the emission current to be returned to the emitter at the same potential as the emission area on the emitter. This balancing resistor caused a great deal of trouble in this experiment and a complete discussion of the effect of this resistor on the data will be given in the data analysis section.

Theory

The theoretical current density from a metal at a temperature T and of work function $\bar{\phi}$ is given by the Richardson equation¹⁵

$$J_s = AT^2 (1 - \bar{r}) \exp(-e\bar{\phi}/kT) \quad (1)$$

where the emission constant $A = 120 \text{ amp/cm}^2\text{K}^2$ and $\bar{r}$ is an average reflection coefficient for the metal surface. In analyzing the experimental data, an empirical equation of the form

$$J_s = A_R T^2 \exp(-e\bar{\phi}_R/kT) \quad (2)$$

is used where A_R is the intercept and $\bar{\phi}_R$ the slope of a Richardson plot, $\ln J_s/T^2$ vs $1/T$. The empirical constants A_R and $\bar{\phi}_R$ can differ from the theoretical constants A and $\bar{\phi}$ because of patchiness of the surface, temperature dependence of the work function and reflection effects at the surface.

If the work function varies linearly with temperature, then

$\bar{\phi} = \bar{\phi}_R + \frac{d\bar{\phi}}{dT} T$ and the experimental value A_R can be written as $A_R = A \exp(-e \frac{d\bar{\phi}}{dT} / k)$. Thus, if one can measure $\frac{d\bar{\phi}}{dT}$, the true emission constants A and $\bar{\phi}$ can be obtained from the empirical constants. This is true as long as the emitting area of the crystal has a uniform work function.

To discuss the application of equation (2) to our experiment, it should be modified to allow for accelerating, zero and retarding fields. Since accelerating fields used in our experiment were not high enough to produce a measurable Schottky effect, the accelerating and zero field conditions yield the same current density, the saturation current density J_s . Fig. 11 shows a simplified energy diagram of the emitter and collector crystals under the three conditions: A-retarding field, B-zero field and C-accelerating field. Fig. 12 is a plot of the $\log J$ vs applied potential. Zero field conditions does not correspond to zero applied potential unless the emitter and collector work functions are the same. The location of point B, Fig. 12, is a measure of the contact potential between emitter and collector. If $\bar{\phi}_e$ is a function of

temperature, point B should shift to a different value of the applied potential and this shift can be used to determine $\frac{d\phi}{dT}$.

In the retarding region, A, the current density is given by

$$J = J_s \exp(-e\Delta V/kT) \quad (3)$$

where ΔV is the applied potential measured from the transition between the saturation and retarding region, point B. The slope of the $\log J$ vs ΔV curve can be used to determine the temperature of the emitter. A sharp break at point B, between the saturation and retarding regions, should occur if the emitter work function is constant over the emitting area and if there are no reflection effects.

In our experiment, a set of retarding potential curves were measured for various temperatures as indicated in Fig. 13. The transition potential from saturation to retarding region is represented by R_0 on these curves. Two Richardson plots are shown in Fig. 14. The one for the saturation region will have a slope and intercept proportional to ϕ_R and A_R respectively. The Richardson plot for the retarding region will have a slope proportional to $\phi_R + \Delta V$ but the intercept will be A ($120 \text{ A/cm}^2\text{K}^2$) instead of A_R because the total barrier the electrons see in the retarding region is independent of any changes of the emitter work function. Changes of collector work function could modify the intercept value. However, the collector is kept at constant temperature and work function changes due to contamination effects can be easily eliminated.

The intercept value in the retarding region is an important check on the theory and experimental procedure. Another important check is the sharpness of the break between the retarding and saturation region. To our knowledge, only one experiment⁴ has been reported in which the theoretical A value was obtained as well as the sharp transition between saturation and retarding regions. This experiment will be discussed further on in this report.

EXPERIMENTAL RESULTS

Effect of Balancing Resistor

The balancing resistor in parallel with the emitter crystal (Fig. 10) had some unexplainable effects on the resulting data and for this reason the use of this resistor will be explained in detail. The balancing resistor allows the collector current to be returned to the same potential as the emitting area. The procedure to set the correct point on the resistor is to apply a retarding potential and adjust the center tap of the resistor until there is no change in the collector current as the heating current direction is reversed by the dpdt switch. This technique has been used in all the previous planar geometry retarding potential experiments mentioned in this report.

If the collector current was returned to either end of the emitter crystal, there would be an additional voltage drop in series with the retarding potential due to the voltage drop along the emitter resulting from the heating current. In our experiment, the total voltage drop across the crystal due to heating current was in the range of 1 V to 2 V. If this drop across the emitter was linear with distance along the emitter and if the emitting area was in the center of the crystal, the voltage drop in series with the applied retarding potential would be from 500 mV to 1 V. Two serious problems with this voltage drop are that it would vary with different emitting areas on the emitter and it would be a function of temperature. For a fixed emitting area, the temperature effect would cause a shift in the transition point between the saturation and retarding potential regions. The transition point also shifts because of $\frac{d\bar{\alpha}}{dT}$ and the two effects could not be isolated. Determination of $\frac{d\bar{\alpha}}{dT}$ would be impossible under these conditions. Also, a Richardson plot using the retarding region as indicated in Fig. 12 could not be obtained since the set of points represented by A must all be taken at the same applied retarding potential. The retarding potential could not be determined because of the

unknown heating current drop.

Initially, a 20 Kohm, ten turn, potentiometer was used for the balancing resistor. An example of data using this resistor is shown in Fig. 15. The transition region extends over approximately 800 mV. Possible physical effects that could cause a wide "knee" region are a patchy emitting area, space charge, voltage drop across the emitting area or reflection effects.

The small emitting area ($1.047 \times 10^{-3} \text{ cm}^2$) and the fairly uniform surface as indicated by back-reflection Laue patterns and the electron microscopy studies would argue against a severe patch effect problem. The small emitting area would also indicate that the voltage drop across this area could not cause the knee rounding. A voltage drop of 1 V/in. would produce a 6.5 mV drop across the .00649" aperture width.

Space charge causes an effective shield around the emitter and tends to remove the low energy electrons from the collimated beam. An accelerating field between the emitter and aperture prevents space charge and aperture voltages as high as 150 V did not improve the knee region.

The investigation of reflection effects occurring at the collector was one of the objectives of this experiment. The rounding of the transition is so extreme that reflection effects alone do not offer a plausible explanation. A discussion of reported reflection effects is given below.

The width of the knee region could be improved considerably by changing the measuring circuit. If the collector current was returned to one end of the balancing resistor instead of the balance point, the knee region could be reduced to approximately 150 mV. This suggests that the collector current was producing a voltage drop across the balancing resistor. If the balance point were in the middle of the resistor, a collector current of 10^{-9} A would produce an IR drop of 10^{-2} mV . Compared to the 500 mV drop across half the emitter due to heating current and the 800 mV knee region, the collector current produces a negligible effect.

By changing to a 1 Kohm resistor, the knee region was reduced to 150 mV as shown in Fig. 15. This also indicates that the rounding of the knee region is at least partly due to the external circuitry. A full explanation of this result has not been discovered and until it can be explained, the validity of the retarding potential data is in doubt.

Results previously reported¹⁶⁻¹⁸ using planar geometry and a balancing resistor had rounded knee regions with the exception of Shelton's work. Webster¹⁶ attributed his 100 mV to 200 mV transition regions to a patchy surface. Kisliuk¹⁷ attributed a wide knee region to a thick aperture that intercepted part of the collimated electron beam. Luke¹⁸ used the Nottingham reflection factor¹⁹ to explain the 200 mV transition region in his data. This empirical reflection factor is $\exp(-V/0.191)$, where V (in volts) is the energy of the electrons above the vacuum level. This factor accounts for the loss of low energy electrons which would produce the rounding of the knee region. Hutson²⁰ verified Nottingham's results using a 180° magnetic analyzer to measure the energy distribution of the emitted electrons. Luke¹⁸, using a (110) Ta single crystal with planar geometry also obtained data that could be explained by this reflection factor. To our knowledge, Shelton's data⁴ on a (211) Ta single crystal with planar geometry is the only experiment that yielded a sharp transition region, less than 20 mV. In our work, it appears that the rounding of the knee is partly connected with an unexplainable effect due to the balancing resistor.

Data Analysis

An IBM 1130 computer was used to analyze the emission data and the following information was obtained:

1. Emitter temperatures from the pyrometry data and from the slope of the retarding potential curves.
2. $\frac{d\delta}{dT}$ from the slope of the R_0 vs T curve.

3. Richardson plots for the saturation region and for the retarding region.
4. Emission constants A_R , $\bar{E}_R$, and A from a least squares fit of the Richardson plots.

The computer program was checked by using artificial data taken from the Tables of Effective Work Function by Read²¹.

A typical set of retarding potential data (referred to as run 1) is shown in Fig. 16. The temperatures T_e , listed in Fig. 16 are from the slope of the retarding potential curves. The pyrometry temperatures, T_p and T_e for two separate runs are listed in Table I.

Table I
Comparison of Temperatures T_p and T_e

T_p (K)		T_e (K)	
Run 1	Run 2	Run 1	Run 2
1600	1598	1574	1552
1633	1628	1618	1577
1668	1663	1649	1643
1705	1695	1698	1692
1730	1726	1726	1729
	1754		1770
	1790		1818

For run 1, the two temperatures are in good agreement, within experimental error. However, T_p is consistently higher than T_e . In the second run, the two temperatures are not in good agreement. T_p is higher at the low temperatures and lower at the higher temperatures. We should expect T_p to be lower than T_e at all temperatures because T_p was measured without the shield. For the same heating current, the closed environment in the shield should have yielded higher temperatures. This discrepancy appeared in all the data and we do not have an adequate explanation for it. If points too close to the knee region or points near the noise level of the current readings were inadvertently included in the calculation of T_e , this would cause T_e to be higher than it actually was.

Richardson plots for the data of Fig. 16 are shown in Fig. 17. The T_e temperatures were used for these curves. The barrier height for the retarding region was 4.63 ± 0.17 eV and 4.61 ± 0.14 eV for the saturation region. The intercept of the Richardson plots yielded A values of $7.26 \text{ A/cm}^2\text{K}^2$ for the retarding region and $8.8 \text{ A/cm}^2\text{K}^2$ for the saturation region. As mentioned in the theoretical discussion, the intercept of the retarding region plot should give $A = 120 \text{ A/cm}^2\text{K}^2$. The $\frac{d\phi}{dT}$ obtained from this set of data was -2.0×10^{-5} volt per degree. This value was obtained from a first order least squares fit of R_0 , the potential at the knee, vs T . However, R_0 was not a linear function of T . In most cases, the slope of the R_0 vs T curve would be positive at the low temperatures and negative at the high temperatures. Over the temperature range used in the experiment, a single value of $\frac{d\phi}{dT}$ has little significance.

The same data was analyzed using T_p instead of T_e and the resulting barrier height was 5.52 eV (compared to 4.63 eV) and the A-value was $3039 \text{ A/cm}^2\text{K}^2$ (compared to $8.8 \text{ A/cm}^2\text{K}^2$). The higher barrier height is in better agreement with what one would expect for a clean (110) Mo surface even though the data using T_e temperatures should yield the correct results. The A-values are of no help in determining which temperatures should be used in the data analysis since neither calculation yields a correct A-value. Similar results were obtained for all runs taken during this experiment.

Since Shelton's data was available²², we decided to perform the same calculations on his data. Shelton was not able to obtain pyrometry data for his crystals but used the retarding potential curves by averaging the slope taking points about two decades apart. A comparison of his temperatures with temperatures calculated from a least squares fit of the data indicated differences as high as 70 K. He indicated that errors due to voltage drops across the electrometer would invalidate a least squares fit to his data. Using the temperatures reported by Shelton, we obtained for the saturation region an

A-value of $67 \text{ A/cm}^2\text{K}^2$ and a barrier height of 4.46 eV. The values reported by Shelton were $130 \pm 25 \text{ A/cm}^2\text{K}^2$ and $4.58 \pm 0.02 \text{ eV}$. For the saturation region our calculations yielded a result of $67 \text{ A/cm}^2\text{K}^2$ and 4.5 eV compared to his reported results of $950 \text{ A/cm}^2\text{K}^2$ and 4.74 eV. It is difficult to understand the large discrepancy in the A-values. Unless we have misinterpreted his data, it would appear that the Richardson equation has not been experimentally verified and its use in determining the true emission constants is still open to question. It is interesting to note that Shelton also was not completely free of the rounded knee problem. Although he obtained retarding potential curves with sharp breaks in them, less than 20 mV wide, the retarding potential curves he used for calculating the emission constants had knee regions extending over more than 100 mV. He attributed this to a misalignment effect which appeared at high aperture voltages, of the order of 130 V or more. We did not notice any dependence of the width of the knee region on aperture voltage.

CONCLUSIONS

During the course of this research techniques for producing thin single crystal ribbons of W and Mo have been developed. Single crystal ribbons as thin as 0.002" can be produced with all of the surface damage introduced during grinding removed. The crystals maintain an ordered surface after extensive heating in vacuum. Various amounts of disorder can be induced on the surface by varying the amount of material removed during electropolishing in the final fabrication of the crystals.

The original plan of correlating the surface structure with the electron emission constants by a combined experimental study using LEED and thermionic emission measurements has not been successful for two reasons. The first is that LEED data does not provide quantitative information on the short range order-disorder structure of the surface. The second reason was our unsuccessful attempts to obtain meaningful thermionic emission data. It now appears that

the attempt to obtain correlation between the surface structure and the emission constants should be abandoned and the research should be separated into two separate projects. One project would be the study of surface interactions using the combined LEED and Auger studies. The second project would be to investigate some of the difficulties turned up in our study of the thermionic emission experiment.

Systems recently became commercially available that have a complete LEED-Auger analyzer as well as a gas handling system. A small mass spectrometer can easily be added to these systems. In addition, work function changes can be measured using the contact potential difference method²³. These systems are powerful instruments for studying gas-surface interactions of almost unlimited variety.

Although work function changes can be measured in a combined Auger-LEED system, the absolute work function of the surface could not be measured unless one went to photoemission measurements. Photoelectric work function measurements, however, would not give information on the work function at high temperatures or the temperature dependence of the work function. The retarding potential method still appears to be the most feasible way of measuring work functions at elevated temperatures. As mentioned previously, we are no longer certain that the basic thermionic emission equation, the Richardson equation, has been verified experimentally. Although not of great practical importance, it is an interesting fundamental question as to whether or not the Richardson equation is valid. Further work using the method of Shelton should answer this question.

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Fig. 1 Schematic diagram of the LEED circuitry

Fig. 2 Schematic diagram of the Auger Circuitry.

Fig. 3 Auger Spectrum for a W (110) surface. Incident energy 950 eV.

Fig. 4 Auger Spectrum for a Mo (110) surface. Incident energy 950 eV.

Fig. 5 Effect of residual gases on Auger spectrum for a Mo (110) surface.

Fig. 6 Contamination sequence for a Mo (110) surface.

Fig. 7 Contamination sequence for a Mo (110) surface.

Fig. 8 Shield can and movable aperture for retarding potential measurements (A) Top view, (B) Lateral view.

Fig. 9 Flange and glass appendage for rotating potential measurements.

Figure 10 Measuring Circuit for Retarding Potential Exp.

Figure 11 Energy level diagram for emitter and collector.

Figure 12 Identification of the Retarding Potential Plot regions.

Figure 13. Procedure for obtaining a Richardson Plot from a set of Retarding Potential Plots.

Figure 14. A Richardson Plot for a retarding and a saturation potential.

Figure 15 Comparison of the Retarding Potential Plots using a 20 kohm and a 1 kohm balance potentiometer.

Figure 16 Retarding Potential Plots for Data Set 1.

Figure 17. Richardson Plot Using Data Set 1.