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

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INTRODUCTION

Surface structure studies by optical and electron microscopy have resulted in improved sample preparation techniques. Mo (110) single crystals can be produced that maintain a highly ordered surface after heating to 2000°K in ultra-high vacuum. Crystals with varying degrees of surface disorder can now be produced.

Work function measurements on a (110) Mo single crystal have been completed. The resulting work function of 5.08 eV is believed to be characteristic of a disordered surface, not of a smooth (110) face. Design of a new retarding potential system has been finished and construction of the system is nearing completion.

Low energy electron diffraction (LEED) patterns for a Mo (100) surface have been obtained. The resulting pattern is in good agreement with the predicted pattern for a Mo (110) surface. A new LEED system mounted in a stainless steel bell jar is in operation.

SAMPLE PREPARATION

An evaluation of machining and polishing techniques for Mo single crystals has been made. Surface structure changes induced by AC resistive heating of the crystals in ultra-high vacuum have been studied by optical and electron microscopy. Electropolishing procedures for attaining smooth surfaces have been established.

Experimental. Mo single crystals with (110) orientations have been obtained from 0.375 in. diameter single crystal boules purchased from Materials Research Corporation. The detailed cutting, grinding and polishing procedures are outlined in a previous report.¹ Slabs 0.20 in. thick were cut from the boule. The final thickness of 0.003 in. was obtained by grinding and polishing.

¹O. R. Morgan and W. E. Blass, "Experimental Study of the Surface Structure and Electronic Properties of Single Crystal Mo and W Ribbons", Progress Report No. C00-1417-1, AEC Contract No. AT-(11-1)-1417.

Cleaning of the crystals prior to heating in ultra-high vacuum consisted of degreasing in acetone, boiling in a 20% KOH solution for 5 minutes, rinsing in boiling H₂O and a final rinse in methanol. The crystals were then mounted in a stainless steel bell jar system. After a pressure of 10^{-8} Torr was attained, the crystals were heated by AC resistive heating. The temperature of the crystals was measured by a Micro Optical pyrometer. After heating the surface of the crystals was studied using optical and electron microscopy. The electron micrographs were obtained from carbon-coilidoin replicas with germanium shadowing.

Results. Figure 1 shows the smooth surface obtained before heat treatment. For this sample, designated Mo17, mechanical grinding and polishing removed 0.015 in. from the original 0.020 in. thick slab. Electropolishing removed approximately 0.002 in. Figure 2 shows an optical micrograph, 50X, of the surface after heating to 2000°K for one hour. Figure 3 shows the same surface under 600X magnification and Figure 4 shows an electron micrograph of the surface. Although initially smooth, this crystal cannot be characterized as a perfect (110) face after heating to 2000°K. The bulk properties of the crystal probably have not changed since the X-ray pattern of Figure 5 indicates a nearly strain free perfect crystal. This X-ray pattern was taken after the 2000°K heat treatment and is similar to the X-ray pattern obtained before annealing.

A second sample, Mo18, was prepared following the same procedures used in preparing Mo17 except for the final electropolishing step. In the case of Mo18, 0.005 in. were removed in the final electropolishing step compared to 0.002 in. for Mo17. Figure 6 shows the surface of Mo18 before heating. The surface appears essentially the same as Mo17, Figure 1, at the same stage. After heating for 1 hour at 2000°K, the surface of Mo18 still appears smooth under 50X magnification, Figure 7. Under higher magnification, Figure 8, surface disorder induced by heating is evident. However, the amount of disorder has been greatly reduced.

These results indicate that more than 0.005 in. of the sample must be removed by electropolishing if a smooth surface is to be maintained after heating. If 0.005 in. or less of the surface is removed by electropolishing, any measurements sensitive to surface structure should not be characteristic of a perfect (110) plane. Besides showing the procedure for attaining smooth surfaces, these results indicate a procedure for attaining surfaces of varying degrees of disorder. By varying the amount of electropolishing, samples of different surface disorder can be obtained for thermionic and LEED measurements. These measurements will allow us to ascertain the effect of surface disorder on the work function and diffraction patterns.

During the remainder of the present contract period, (110) oriented samples of W and Mo will be prepared. Twenty W and Mo crystals have been cut from the single crystal boules and are presently being prepared. These samples will be annealed in the LEED system so that LEED patterns can be monitored during the annealing process. These samples will then be placed in the retarding potential system for measurement of the thermionic emission constants. The electropolishing procedure will be improved by the construction of a motor driven wheel as described by Steele.²

RETARDING POTENTIAL MEASUREMENTS

During the present contract period, thermionic emission measurements have been made on a (110) Mo single crystal. During the course of these measurements a number of difficulties with the present retarding potential system have been encountered. A new system has been designed and construction of the system is nearing completion.

²H. Steele, "Preparation of Large Single Crystals for Work Function Measurements" Proc. of M.I.T. Physical Electronics Conference, 123 (1963).

Experimental. The vacuum system and arrangement of components for the emission experiments was described in a previous report.¹ The measuring circuit is shown in Figure 9. The current to the collector crystal was measured by a Carey Vibrating Reed Electrometer, Model 31V. The retarding potential was initially obtained from a 6-volt battery and voltage divider. To provide greater stability and ease of measurement, the battery was replaced by a Leeds and Northrup Volt Potentiometer. The X-Y recorder was used to monitor the collected current over long periods of time in order to determine any changes in the current due to contamination or circuit instability. The retarding potential was applied to the emitter through a 20K ohm resistor. This zeroing resistor allowed the retarding potential to be applied at the same potential as the emitting area on the crystal. Difficulty arose in the use of this resistor and most of the measurements have been taken with the retarding potential applied to one end of the crystal. The voltage drop across the crystal from one end to the emission area due to the heating current is added to the measured retarding potential. This voltage drop varies with the heating current and thus the temperature of the crystal. Using the circuit in this manner, information on the shift of the retarding potential knee due to the temperature dependence of the work function is unattainable. Although the difficulty with the zeroing resistor has been eliminated, the results reported below do not include information on the temperature dependence of the work function.

The difficulties with the present system include a stationary aperture, high leakage currents, inconvenient sample replacement and excessively long pump down time. A new system has been designed to eliminate these problems. The system will use a Varian stainless steel bell jar system with a 75 liter/sec Vac-Ion pump. The retarding potential diode will be mounted in a glass appendage attached to a 4 in. port on the bell jar. Figure 10 shows a diagram of the glass appendage and

flange. Figure 11 shows the diode structure and details of the movable aperture. The aperture motion will be controlled externally by means of the metal bellows. All current and potential leads will be introduced through glass press leads which will provide a long leakage path between the emitter and collector leads. The insulator on the base of the shield will be of boron nitride. A metal shield between the crystals and the base will prevent evaporation onto the base and heating of the base through radiation. In the first system, ceramic to metal seals were used for the leads. These leads introduced leakage currents of the order of 10^{-12} amps. The base in the first system was not shielded and this resulted in a temperature dependent contribution to the leakage currents. Since all electrical connections in the new system are in the glass appendage, sample changing and aligning of the crystals can easily be done by removing the glass appendage from the bell jar.

Results. The work function of a (110) Mo crystal has been obtained by measuring the emission current as a function of retarding voltage at different temperatures. Figure 12 shows a typical Richardson plot for this crystal. The work function of 5.08 eV is in good agreement with work function measurements on single crystal wires which yielded a value of 5.4 ± 0.2 eV.³ Because of the difficulty with the zeroing resistor, the A/R value is not corrected for the temperature dependence of the work function. The work function is probably not characteristic of a perfect (110) face because the crystal was electropolished for only a short time with less than 0.002 in. removed during electropolishing. As mentioned in the section on sample preparation, heating of the crystal probably resulted in a highly disordered surface and the resulting work function would be lower than for a perfect crystal. After looking at the crystal with the optical microscope, it will be studied in the LEED system.

³E. A. Coomes and F. E. Girouard, "The Influence of Patches on the Average Thermionic Constants of W and Mo Emitters", Thermionic Conversion Specialist Conference, Cleveland, Ohio, 47(1964).

During the remainder of the present contract period, the improved retarding potential system will be completed. Measurements of the work function and temperature dependence of the work function of (110) oriented W and Mo crystals will be completed.

LOW ENERGY ELECTRON DIFFRACTION (LEED) STUDIES

Experimental. The glass LEED systems were abandoned in favor of a more versatile stainless steel bell jar system. The LEED system capabilities for complementary measurements such as secondary electron emission and contact potential difference has been improved by the change to a stainless steel bell jar system. The single aspect of crystal manipulation and replacement makes the change invaluable to the project. The vacuum system is a modified Ultek TNB system using all copper seals. Pressures below 10^{-9} Torr have been attained without bakeout.

Figure 13a shows a closeup of the bell jar and associated Helmholtz coils needed for cancellation of the earth's field. Figure 13b shows a view of the LEED system and associated circuitry. The crystal is mounted on the bellows flange shown at the top of the bell jar. The bellows allow motion for orienting and scanning the crystal. The system contains two ion pumps rated at 50 liters/sec and a titanium sublimation pump which brings the overall pumping speed to 3600 liters/sec.

A versatile control system has been constructed which allows for straight forward operation of the LEED system for pattern viewing as well as allowing any element to be specially controlled or monitored for a variety of different measurements.

Results. After AC heating a Mo (110) crystal to 2000°K at a pressure of 1×10^{-9} Torr a clean Mo (110) pattern was observed from 100 eV to 600 eV. The observed pattern agrees with the calculated pattern based on the (110) Mo unit cell. Figure 14 shows a calculated pattern for 529 eV and observed patterns at

490, 520 and 565 eV. Because of the rapid intensity variation on the (110) surface of Mo, the complete pattern is observed at only a few wave lengths. The maximum colatitude acceptance angle of the phosphor screen is approximately 30° . The indexing of the pattern follows from the two dimensional grating equations for the (110) unit cell. If ζ is the azimuth angle and φ the colatitude the diffraction conditions for the (110) unit cell of Mo are

$$\sin \varphi = (1/a) (75/V)^{\frac{1}{2}} (3m^2 - 8mn + 8n^2)^{\frac{1}{2}}$$

$$\tan \zeta = (dx/dy) (n/m - \frac{1}{2})$$

Where a is the Mo lattice parameter and d_x and d_y the repeat distances of the unit cell. Our diffraction beams are indexed as (m,n) .

The particular crystal sample used in this study had less than 0.002 in. of material removed by electropolishing. From the results described in the section on sample preparation we would expect this sample to be highly disordered. Evidence of this is seen in the LEED patterns of Figure 14. One would expect large diffuse diffraction spots and high background intensity from a disordered surface. For a highly ordered surface, the diffraction spots are much sharper than those of Figure 14 and the display outside of the spots should be black.

Current study is underway to verify the absence of carbon contamination on the crystals. Haas and Jackson⁴ observed carbon contamination on Mo with a Varian LEED system. Their source of Mo crystals was the same as ours and there is a possibility that carbon contamination is present in the single crystal boules. We are presently mounting a second crystal from the same boule used for the first crystal and will check for carbon contamination by observing 1) pattern geometry, 2) diffracted beam intensity and 3) reflection coefficient. These measurements will be taken after heating to 2000°K in vacuum and also after heating in an oxygen atmosphere. We also plan to observe oxygen adsorption on (110) Mo and compare our results with Haas and Jackson.

⁴T. W. Haas and A. G. Jackson, J. Chem. Phys., 44 2921(1966).

Preliminary intensity measurements have been taken using a Photo Research Spot Photometer and X-Y recorder. Further refinement in the reproducibility of these results is needed before a meaningful interpretation can be made.

Fig. 1 Mo 17 after electropolishing. (130X)

Fig. 2 Mo 17 after heating at 2000°K for 1 hour. (50X)

Fig. 3 Mo 17 after heating at 2000 °K for 1 hour. (600X)

Fig. 4 Mo 17 electron micrograph after heating at
2000 °K for 1 hour. (6000X)

Fig. 5 Mo 17 Laue pattern following 2000°K heating, 5 cm.

Fig. 6 Mo 18 surface before heating. (50X)

Fig. 7 Mo 18 after heating at 2000°K for 1 hour. (50X)

Fig. 8 Mo 18 after heating at 2000°K for 1 hour. (600X)

Fig. 9 Circuit for retarding potential measurements.

Fig. 10 Flange and glass appendage for retarding potential measurements.

Fig. 11 Shield can and movable aperture for retarding potential measurements. (A) Top view; (B) Lateral view.

Fig. 12 Richardson plot for Mo (110) surface

(A)

(B)

Fig. 13 LEED System : (A) Bell jar system and Helmholtz coils; (B) Associated circuitry.