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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

During the present contract period, further improvements in crystal preparation techniques have been carried out. Cutting of the crystals by electric discharge machining and refinement of the grinding and polishing procedures has considerably improved the size and quality of the crystals.

The low energy electron diffraction (LEED) system is now working consistently with a range of electron energies from 20 eV to 750 eV available. The crystal mounting in the LEED system has been modified to allow three degrees of freedom in positioning the crystal. Preliminary data on crystal cleaning of Mo (110) and (100) surfaces indicate significant differences in the rate of contamination of these two faces.

The retarding potential measurements have been beset with a number of difficulties which has required a complete modification of the vacuum chamber used for these measurements. The vacuum chamber has been modified and the internal structure for these experiments completed. The system has been assembled and vacuum processed.

Crystal Preparation

The preparation of suitable single crystal ribbons of Mo and W has been a continuing major effort. The thermionic emission experiment requires an oriented single crystal ribbon $1 \times 0.20 \times 0.002$ inch. From previous studies in our laboratory using optical and electron microscope techniques, it has appeared that at least 0.003 to 0.005 in. must be removed by electropolishing as a final step in crystal preparation if a reasonable surface dislocation density is to be achieved. Such major stock removal by electropolishing presented considerable difficulty due to edge losses and a resulting loss of crystal surface area. A number of techniques were tried in order to remove 0.005 inch by electropolishing and recently a successful method has been developed. At the present time we are able to remove 0.005 inch from a crystal face with negligible loss in ribbon surface area.

The crystals were obtained from Materials Research Corporation, Orangeburg, New York, and are MRC's MARZ grade crystals (triple pass zone refined). Both Mo and W boules with symmetry axes along a (110) zone were obtained. The Mo was 0.5 in. in diameter and the W was 0.25 in. in diameter.

Diamond sawing of the crystals was abandoned in favor of EDM (Electric Discharge Machine) cutting of 0.003 in. orientated slabs.¹

The crystal preparation, in summary, follows:

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 ± 0.0005 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.

The following comments are to be noted:

1. Orientation to 1/2 degree is achieved regularly -- the limit of back

¹John Dow and J. W. Blass of Honeywell, Inc. Minneapolis, Minnesota, performed some exploratory EDM cutting of Mo free of charge. The production slicing of the Mo and W boules was carried out by Twin City Manufacturing, Minneapolis, Minnesota.

reflection Lane 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 amp/in.²; W electrolyte: 20% (by weight) aqueous solution of NaOH, current density: 1.6 amp/in.²
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..

Figure 1 is a typical micrograph² of finished Mo and W crystals at approximately 750 X magnification. Figure 2 is a typical 5 cm back reflection pattern of an orientated Mo crystal.

LEED Studies

The LEED system was modified by an improved set of Helmholtz coils which reduce the earth's magnetic field in the diffraction chamber to 10^{-3} gauss so that low voltage electrons are now essentially undeflected in the chamber. The crystal manipulation system was modified to include rotation of the crystal along an axis

²The small dots on Figs. 1 and 5 are due to a pitted microscope mirror which we were unable to replace before the preparation of this report.

providing the manipulation system with a full three degrees of freedom. In addition, a gas admission system has just been added, but is not yet operative. The gas system will allow the admission of oxygen for crystal cleaning studies in an oxygen atmosphere. The LEED system is now completely operative and useable routinely over a range of electron energies from 20 eV to 750 eV.

During the past year, studies of crystal cleaning have been carried out on a (110) Mo crystal ribbon and a (100) Mo ribbon. Figure 3 is a typical 375 eV (110) pattern. Figure 4 is a crystal cleaning and contamination sequence. Figure 4a is a 285 eV pattern taken 30 hours after the conclusion of a 24 hour flashing (AC heating) at 1900° C. Figures 4b and 4c follow in sequence after a 1900° C flashing for 20 minutes, and Figures 4d, e, and f were taken 45 seconds, 4 minutes, and 20 minutes following a one minute 1900° C flashing. Some information relative to contamination can be deduced from the sequence. However, only a comparison with flashing at 1900° C in an oxygen atmosphere would yield significant information. Figure 5 is a 750 X photograph of the same Mo (110) crystal following crystal fracture during resistive heating at 2000° C. The crystal shown in Figure 5 has been heated above 1800° C for more than 300 hours using AC.

At this point it is possible to make a few remarks concerning the cleaning of Mo ribbons by resistive heating. We have looked at several (110) Mo ribbons in the past three years while the LEED system was in various stages of development. We have recently begun studies on a (100) Mo crystal as well as a mechanically polished (no electropolishing) (110) Mo crystal.

The following conclusions seem to be indicated:

1. LEED patterns are obtainable from non-electropolished Mo crystals.

However, there is some evidence for carbon contamination of the non-electropolished crystals while no evidence of carbon contamination on either the (110) or (100) electropolished Mo crystals is apparent.

2. The (110) surface of Mo appears to be highly stable relative to contamination since at pressures of approximately 5×10^{-10} Torr, patterns remain for several hundred hours after 1900° C cleanings while the (100) surface of Mo will only sustain a LEED pattern for approximately 15 hours after 1900° C cleanings. Increasing contamination is of course visible with increasing time in both cases.

It is also true that (100) crystal surfaces are easier to clean up than (110) surfaces. We have obtained a relatively satisfactory (100) surface following 1900° C cleanup for 60 seconds whereas the (110) surface following 24 hours at 1900° C is not really satisfactory. The effect of oxygen clean up has not been assessed as yet.

At the present time it appears that the electron energy range from 20 eV to 750 eV is more than adequate for obtaining information on crystal cleanliness. The modification of the LEED system to provide rotation of the crystal will allow intensity data to be obtained as a function of the electron beam angle of incidence. Since the use of the LEED system for contamination studies and determination of surface structure through intensity measurements will require full time use of this system, we decided that the proposed modifications to the system could not be justified. The improvement of the electron optics and the purchase of a new electron gun is not necessary as evidenced by the data already obtained on the system. Changing to AC modulation and detection of the beam was proposed for accurate measurements of contact potentials, reflection coefficients, and secondary emission yields. However we now believe that contamination studies and intensity measurements are more important and that there will not be adequate time on the LEED system to carry out the electron emission studies in the foreseeable future.

RETARDING POTENTIAL MEASUREMENTS

During the present contract period, some difficulty has been experienced with the vacuum system used for the retarding potential experiment. The main effort during this period has been concentrated on modifying the vacuum system and improving the experimental arrangement for the retarding potential measurements.

Horizontal mounting of the glass appendage, as originally planned, has been found somewhat inconvenient and hazardous in terms of breakage of the appendage. To eliminate these hazards, the bell jar has been modified to allow vertical mounting of the glass appendage. To increase the versatility of this system, an Ultek ten port ring has been added to the system. The pumping speed of the system has been improved by the addition of an Ultek four filament sublimation pump. The sublimation pump has considerably reduced initial pumpdown and bakeout time.

The internal structure for the retarding potential diode has been completed and vacuum processed. Although the moveable aperture is completed, it has not been connected to the bellows. Initially, we plan to take measurements without using the moveable aperture. If no further difficulties are encountered, the bellows will be connected to the system.

The vacuum system with all components for the retarding potential experiment, except the two crystals, has been assembled and vacuum processed. The system has attained an ultimate pressure of less than 10^{-9} Torr after one bakeout and there appears to be little difficulty in attaining lower pressures consistently.

Two Mo (110) crystals have been prepared by techniques described in the beginning of this report. These crystals are presently being vacuum processed and temperature vs heating current curves are being prepared using an optical pyrometer.

The crystal used for measurements described in a previous report³ has been

³D. R. Morgan and W. E. Blass, "Experimental Study of the Surface Structure and Electronic Properties of Single Crystal W and Mo Ribbons," Progress Report No. COO-1417-2, AEC Contract No. AT-(11-1)-1417.

studied by an optical microscope. The surface of the crystal appears similar to that shown in Figure 5. The measured work function of 5.08 eV is in good agreement with recently published data^{4,5} on the Mo (110) surface. This is somewhat surprising in light of the obvious departure of our sample from a uniform, smooth surface. One possible explanation for this agreement is that the crystal used in our experiments had some oxygen contamination remaining on the surface during the work function measurements. Oxygen contamination would raise the work function from that of the clean surface. The LEED data indicates, however, that the Mo (110) surface is highly stable relative to contamination. Another explanation is that the work functions measured in thermionic emission experiments and reported in the literature are actually measurements on surfaces with a large amount of surface disorder. This may indicate that the high work function values (7 - 8 eV) found in field emission experiments⁶ are closer to the true work function for a perfect surface while the thermionic values are more representative of a highly disordered surface. Further thermionic measurements on Mo and W crystals with subsequent study of the surfaces using LEED techniques and optical microscopy should help to clarify this point.

⁴U. V. Azizov *et al.*, Soviet Phys.-Solid State 7, 2232 (1966).

⁵O. D. Protopopov *et al.*, Soviet Phys.-Solid State 8, 909 (1966).

⁶R. D. Young and H. E. Clark, Phys. Rev. Letters 17, 351 (1966).

(110) Mo

(110) W

Fig. 1. Typical Microphotographs (747X) of Electropolished Crystals.

Fig. 2. Typical 5 cm Back Reflection Laue Pattern from an Electropolished Mo Crystal.

Fig. 3. 375 Volt LEED Pattern for (110) Mo Crystal.

Fig. 4. Crystal Contamination Sequence for (110) Mo Crystal.

Fig. 5. (110) Mo Microphotograph.

50 Volts

100 Volts

310 Volts

407 Volts

Fig. 6. LEED Patterns for (100) Mo Crystal.