AD709985

FIELD ION MICROSCOPY

A Final Report to the

OFFICE OF NAVAL RESEARCH

Contract Nonr-N000 14-67-A-0385-0009

June 1, 1969 - May 31, 1970

Field Emission Laboratory
Department of Physics
The Pennsylvania State University
University Park, Pennsylvania

Erwin W. Mueller, Principal Investigator

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3 August 1970

Introduction

Work under this contract is an extension of investigations in field ion microscopy performed under the preceding contract[1] Nonr-656 (23) which had expired May 31, 1969. Although field ion microscopy as the only known means of viewing the atomic structure of a metal specimen is now a well established technique, not the least as a result of developments under the past contract, it has become quite clear through the present work that the two most basic effects employed, field ionization and field evaporation, are still incompletely understood. The new research is limited by the unexpected termination after one year when it was determined that this effort was not of relevance to the needs of the Navy. It has at least been possible to show in what direction advances can be made leading to a new understanding of the fundamental physical processes involved, as well as to a better foundation of image interpretation.

Summary of Scientific Accomplishments

Field ion microscopy depends upon field evaporation as the only means to prepare the specimen surface. Although the basic theory of the effect[2-4] sufficed as a guide for image interpretation, our discovery with the atom probe[5] of the high multiplicity of the charge of field evaporating metal ions proved

the inadequacy of the theory. Another unexpected result of our atom-probe work was the realization of an interaction of the imaging gas with the surface as seen by the adsorption of helium at temperatures up to above 80°K and the occurrence of metal-helium molecular ions as products of field evaporation[6]. Therefore, in the frame of the present contract, a new investigation of field evaporation rates of tungsten was undertaken by advancing both the phenomenological theory as well as by making refined measurements in a wide range of evaporation rates between 10^{-2} and 10^{7} atomic layers per second. The data yielded the location of the effective electronic mirror surface with respect to the evaporating kink site atom, the polarizability of the metal atom at the kink site, and the activation energy as well as the pre-exponential of the Arrhenius equation. In addition, the third and fourth ionization potential of tungsten has been obtained. This work has been disseminated[7] as Technical Report No. 1, dated Nov. 1969, and has subsequently been published in physica status solidi[8]. Specific aspects of this work have also been presented at the 16th Annual Field Emission Symposium[9].

An important result is the behavior of field evaporation in the presence of the imaging gas. While the reduction of the evaporation field by the gas has been known for a long time, Plummer and Rhodin[10] concluded that the gas effect disappears in pulse evaporation when times of less than 10^{-4} sec are used.

On this assumption their data of binding energies of single atoms of the transition elements on tungsten surfaces were derived, and detailed further conclusions were drawn about the contribution of the 5 d-electrons to the bond. Our field evaporation rate measurements together with results of the atom-probe work[11] clearly show that the reduction of the binding energy by the image gas already takes place at nanosecond pulse times. Thus the field evaporation data of Plummer and Rhodin, as well as their conclusions, are definitely not valid. An advanced theory of field evaporation in the presence of the image gas must be worked out if the desirable data for binding energies of single adatoms as measured by field ion microscopy be meaningful. With the attainment, for the first time, of a figure for the polarizability of a metal surface atom at a kink site we are now able to calculate the binding energy caused by dipole-dipole attraction of a polarized image gas atom to the polarized surface atom. The polarization binding energy is

$$H_f = \frac{1}{2}\,\alpha_A\,(f_A - 1)\,F_0^{\,2},$$

where f_A represents a short range enhancement factor.

$$f_A = \left(1 + \frac{2\alpha_M}{d^3}\right)^2 \Big/ \left(1 - \frac{4\alpha_M\alpha_A}{d^6}\right)^2,$$

Here α_A is the polarizability of the gas atom, F_0 the externally applied field strength, α_M the polarizability of the metal atom at its surface site, and d the distance between the centers of

the surface atom and the adsorbed gas atom. With the known polarizabilities and atomic radii of the noble gases, typical binding energies are 0.13 eV for He at F = 4.5 V/Å, 0.14 eV for Ne at 3.75 V/Å, and 0.15 eV for Ar at 2.2 V/Å. (The field strengths F are those of best imaging conditions, while field evaporation requires higher fields and provides stronger binding.) These binding energies are in agreement with the field and temperature ranges in which noble gas field adsorption is observed.

Adsorption by dipole-dipole forces implies the location of the gas atom at the apex of the surface atom, thus requiring the transition of the valence electron of the imaging gas atom to occur through the adsorbed gas atom. This novel picture of field ionization gives a well defined minimum distance of the ionizing atom from the surface, as determined by the diameter of the adatom. It explains the previously hard to understand extremely sharp location of the ionization zone, within a half width of 0.2 Å, which we derived earlier from our energy distribution measurements of field ions[12]. A more important implication is that field ionization always seems to require the adsorption of an image gas atom on top of the imaged surface metal atom. The effective adsorption, as measured by the time integral of site occupation is a function of the polarizability of the latter, and is temperature dependent. Thus, the field ion image represents a map of surface atoms having a strong induced dipole moment. In an alloy or otherwise inhomogenous surface, local image bright-

ness is now determined by the polarizabilities of the different surface entities. If this presently tentative mechanism of image formation could be supported by additional data of the polarizability of various surface atoms at their sites, field ion image interpretation would be considerably advanced.

We are therefore extending the evaporation rate measurements to other metals of interest. Preliminary data have been obtained for Ir, Pt, Ru, Hf and Mo using a Cober High Power Pulse Generator acquired from University funds. This precision pulse generator provides much better accuracy than the home-made pulser we had to use before. Similar to tungsten, all the metals studied so far show a large polarizability and a small atom-to-metal plane distance. Final analysis, however, could not be completed before the termination of the contract.

It has been pointed out[8] that all field desorption measurements yield only relative rates. There is no other conceivable technique, except an indirect determination from energy distribution measurement, to determine absolute field evaporation rates for lattice atoms. However, absolute field desorption rates can be determined straightforwardly for adatoms. A new bakeable UHV field ion microscope with a thermal deposition source has been built. Preliminary data on desorption rates has been obtained for tungsten adatoms on tungsten (110) planes.

A major shortcoming of field ion microscopy, particularly for its applications as a tool of metallography, is its very small field of view, the cap of a tip of typically 500 Å radius. We have attempted to extend the permissible specimen size by experimenting with FIM designs allowing for much larger tip radii. As the field F that must be applied for imaging is at least $4.5 \cdot 10^8$ V/cm, and for the necessarily preceding field evaporation even as high as $6.0 \cdot 10^8$ V/cm, the required operational voltages become very high. For the required tip geometry, $V \approx 5\ r_{tip} \cdot F$. So far the field ion microscopes used by other investigators were limited to a maximum voltage of 15 kV, while we have presented field ion micrographs[4,13] up to 27 kV. The problem is to prevent high voltage breakdown or spurious discharges in a gas-filled tube tc an extend that leakage currents remain below perhaps 1% of the total image current, the latter being in the 10^{-9} amps range. By reducing the volume of the cathode-cold finger cone surrounding the specimen tip and operating at a helium gas pressure below 10^{-4} Torr, we so far have been able to safely sustain peak voltages in excess of 45 kV. Specimens of W and Pt were photographed that had radii around 2000 Å, that means a 16 times larger area than a conventional tip. Numerous dislocations could be seen that probably would not have been stable in a tip of smaller radius. The 45 kV limit was in fact placed by atmospheric water condensation at the high voltage feed-through into the liquid-hydrogen-filled cold finger, and can be considerably exceeded by an improved

design of this section of the microscope. Because of the danger involved with the necessary liquid hydrogen cooling, such a microscope will eventually be constructed of metal rather than glass, and useful imaging of tips with up to 5000 Å radius and a resolution of 5 Å at 21°K and 3.3 Å at 4°K operating at 100 kV can be foreseen.

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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
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2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE

Field Ion Microscopy

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Report, June 1969 - May 1970

5. AUTHOR(S) *(First name, middle initial, last name)*

Erwin W. Mueller

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
3 August 1970	9	13

8a. CONTRACT OR GRANT NO.
N000 14-67-A-0385-0009

b. PROJECT NO.
NR 017-443

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Office of Naval Research

13. ABSTRACT

The basic physical effects used in field ion microscopy are not yet fully understood. Field evaporation rates of tungsten were measured in the range from 10^{-2} to 10^{7} atomic layers/sec, yielding the polarizability of a kink site surface atom, the activation energy and the pre-exponential of the field evaporation equation. Using the polarizability, the dipole-dipole binding energy of field-adsorbed noble gases has been calculated, and a modified mechanism of field ionization and image interpretation is proposed. A high-voltage field ion microscope has been operated at up to 45 kV, giving an increased field of view.

DD FORM 1 NOV 68 1473 (PAGE 1)

S/N 0101-807-6811

Unclassified

Security Classification

A-31408

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Field ion microscopy						
Field ionization						
Field evaporation						
Polarizability						