

한국부식학회지  
Journal of Corrosion Society of Korea  
Vol. 10, No. 3, Sept. 1981

〈研究論文〉

# The Observations of Surface Diffusion in Tungsten and Rhenium in FIM\*

K. K. Orr\*\* and T. T. Tsong

Department of Physics, The Pennsylvania State University, University Park,  
PA 16802 U. S. A.

## Abstract

Using a field ion microscope (FIM) the inter-atomic interaction between tungsten and tungsten, and tungsten and rhenium was investigated.

## 초 록

FIM 을 사용하여 tungsten 표면에서의 ion 상태로 된 tungsten 그리고 rhenium 원자들의 확산현상 반응에 대해서 고찰했다.

## I. Introduction

Since Müller had invented field ion microscope (FIM) and showed the image of individual atoms of the surface of solid in 1951, the FIM turned out to be one of the most important tool to characterize the surface of solids including atomic vacancies and interstitials, impurity atoms, dislocation cores, slip bands, etc. The purpose for this investigation is to observe the interactions (field evaporation and surface diffusion) of vaporized tungsten and rhenium atoms on the surface of tungsten solid using FIM.

## II. Literature Survey

### A. Historic background of FIM

In 1928 Oppenheimer suggested that hydrogen in an electric field is possibly ionized by tunneling process. Fowler and Nordheim reported the barrier penetration of electrons. In 1936 Müller established experimentally the theory resulted in field emission microscope. Based

on the emission microscope in 1951 Müller introduced the image of the individual atomic crystal lattice from the emitter surface with positive hydrogen ions instead of electrons which is known as Field Ion Microscope (FIM) (1).

### B. Field evaporation

At cryogenic temperatures the surface of metals can be evaporated in the form of ions in applying a positive field even an order of several volts per angstroms in depth of the surface of metal (1). Since the evaporation can occur at cryogenic temperatures, the energy of an adatom on the surface is purely considered to be the binding energy atoms (1, 2). The binding energy which is related to the activation energy can be measured by the thermal desorption or field desorption techniques. The models to calculate the activation energy in the field evaporation process were presented by Müller (1) and Gomer (3).

Müller indicated that the activation energy is given by

$$Q_0 = A + \sum_n I_n - n\phi$$

Where  $Q_0$ : activation energy without applied field

$A$ : binding energy

$I_n$ : ionization potential

$\phi$ : work function

\*When work done the authors were a graduate student and associate professor, respectively, at Dept. of Physics, Penn. State University.

\*\*Present address: Department of Inorganic Materials Engineering, Hanyang University, Seoul Korea

$n$  : number of electrons

When an ion is sufficiently far from the specimen surface, its potential in one dimension can be written

$$V(x) = -\left(nFe^2x + \frac{n^2e^2}{4x}\right)$$

Differentiation of the above equation results in the expressions for the location and magnitude of the potential energy maximum

$$x_{max} = \left(\frac{ne}{4F}\right)^{\frac{1}{2}}$$

and 
$$V(x_{max}) = -(n^3e^3F)^{1/2}$$

The maximum in  $V(x)$  is the "Schottky hump." The energy barrier to be overcome is therefore  $Q = Q_0 - (n^3e^3F)^{1/2}$  as shown in fig. 1. Müller assumed that the barrier was overcome by thermal activation (1, 2).

Taking field evaporation to be a thermally activated process, the evaporation rate  $K_e$  is given by an Arrhenius eq.

$$K_e = \nu \exp\left(-\frac{Q}{kT}\right)$$

where

$\nu$  : vibrational frequency of the surface atom

$k$  : Boltzman const.

$T$  : emitter temperature

$Q$  : activation energy ( $Q = Q_0 - (n^3e^3F)^{\frac{1}{2}}$ )

Gomer and Swanson (1963) attempted a quantum

mechanical treatment of field evaporation by considering the transitions from the atomic to the ionic state (3).

### C. Surface diffusion

The occurrence of an atomic migration over its own lattice particularly at the surface is one of the most fundamental interatomic interactions. The diffusing particle proves the potential variations over the surface along its path. A study of surface diffusion will lead to deeper insights into the interatomic forces at the surface, and provide a basic knowledge for further understanding of crystal surface equilibrium and crystal growth, etc.

To determine the surface diffusion coefficient ( $D$ ) Smoluchowski (4), and Ehrlich and Hudda (5) discussed. In Smoluchowski's method, the fluctuations in the number of atoms contained in a given geometrical area are measured in the fixed intervals of time. Ehrlich and Hudda mentioned that Smoluchowski's method are not readily satisfied in the FIM.

Müller (1) and Ehrlich and Hudda (5) employed the probability theory of random work in the mean square displacement during a time interval sufficient for a large number of jumps. The mean square displacement is given by

$$\langle r^2 \rangle = Nl^2 = \tau \nu l^2 = 2D\tau$$

where  $\langle r^2 \rangle$ : mean square displacement

$\nu$  : frequency of the atomic jumps

$l^2$  : the average of the squares of the individual distances spanned by each of the  $N$  jumps

$\tau$  : time interval

$N$  : number of jumps

Ehrlich (6) reported a theory of the effect of the boundary on the surface diffusion which indicates that the mean square displacement in the limit ( $a/l^2 > 10N$ ) in one dimension is given by.

$$\langle r^2 \rangle \approx 2D\tau \left[ 1 - \frac{8}{3a} \left( \frac{D\tau}{\pi} \right)^{1/2} \right]$$

where  $a$ : length of line segment in the uniform initial distribution of the adatoms

The diffusion coefficient  $D$  can now be deduced from the experimentally observed mean square displacements, as followed by (5)

$$\nu = \frac{2D}{l^2} = \nu_0 \exp\left(-\frac{\Delta S}{R}\right) \exp\left(-\frac{Q_d}{RT}\right)$$

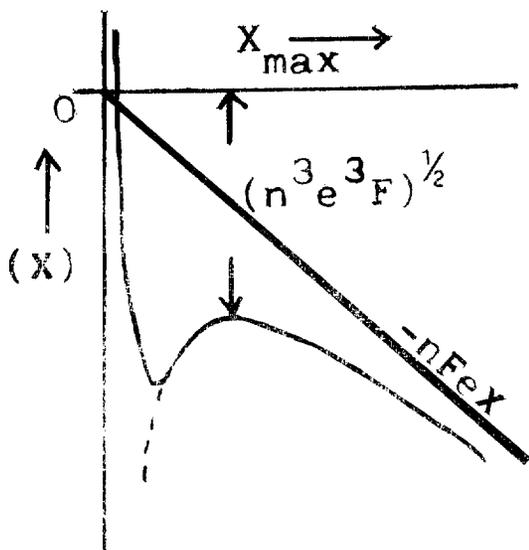


Fig. 1 Schematic diagram of the energy hump to be overcome by an ion before field evaporation can occur.

where  $\nu$  : jumping frequency

$\nu_0$ : frequency factor

$Q_d$ : enthalpy of activation energy

$\Delta S$ : entropy

$R$ : gas const.

$l$  : nearest neighbor atom distance in its lattice.

Ehrlich and Hudda (5) used their mean square displacement model to investigate the interaction tungsten atoms on the tungsten surface in the various crystallographic planes. Bassett and Parsley (7, 8, 9) have studied the cluster structures.

Ehrlich (10) investigated the chemisorption of  $N_2$  and CO on clean tungsten surfaces in FIM.

### III. Experiments

#### A. Basic features of FIM

The basic features of FIM is shown in fig. 2.

The specimen is a sharply polished wire of which radius is approximately 100-1000Å. It is kept at a high positive potential to produce a field of the order of magnitude of  $500 \frac{Mv}{cm}$ . The tip has another duty which is thermal contact with the coolant. The bottom of the microscope is coated with a fluorescent screen grounded. The microscope chamber is evacuated to a background pressure of less than  $10^{-6}$  Torr, and a gas such as helium is leaked into the chamber to a pressure of up to  $5 \times 10^{-3}$  Torr. The image information is carried from the tip surface to the screen by radially projected

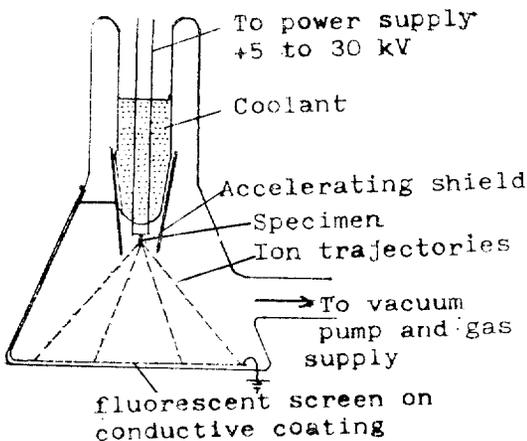


Fig. 2 Schematic diagram of a field ion microscope (FIM).

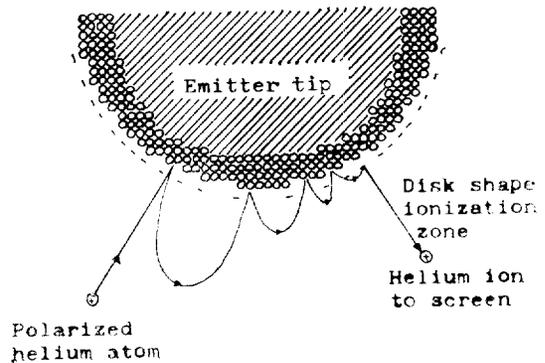


Fig. 3 Schematic diagram showing the field ion image formation.

positive ions (1).

When the electric field applied the the specimen is above the critical value, the gas is ionized near the specimen surface and the ions are projected on initially radial trajectories towards the fluorescent screen. Most ions leave the specimen tip from the points of highest field which usually occur above protruding atoms. A pencil beam of ions therefore travels from such atom to excite a spot of light on the screen, as shown fig. 3.

The image contains a bright spot for each prominent site on the specimen surface. The magnification is up to several million diameters, and the resolution is often between 2 and 3 Å (1, 2).

#### B. FIM for surface diffusion

The features and operations of the microscope for study of atomic interaction on the metal surfaces is basically same, but due to the measurement of sequent interaction it is modified as installed with a resistively heated tungsten source as shown in fig. 4 (5).

In the operation of the microscope, after obtaining atomically smooth emitter surface, the imaging gas is pumped out and the applied voltage is turned off. Tungsten atoms are deposited on the emitter by heating a filament source for the interaction of tungsten atoms on the solid surface of tungsten, and rhenium are heated to vaporize rhenium atom on the tungsten surface. The new atoms are then observed in the ion image, and their movement over the surface is explored by raising the temperature of the emitter to a predetermined

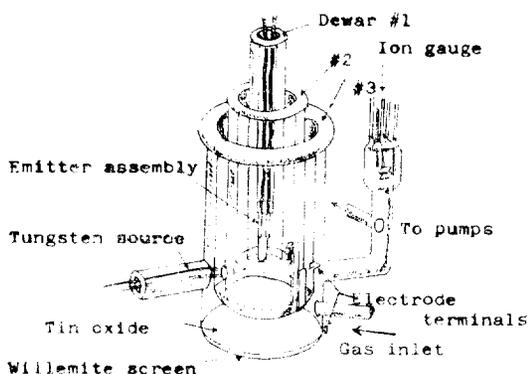


Fig. 4 Field-ion microscope for observation of surface diffusion. In operation, tube is attached to bakeable ultrahigh-vacuum system and gas supply.

value for a period of time when the voltage is off. Changes in the position of the atoms are recorded in a subsequent ion image upon cooling to 21°K (1, 2, 3).

#### C. Vacuum techniques

In order to prevent contamination of the specimen, a conventional field ion microscope operated with helium as the image gas requires a background pressure approximately  $10^{-6}$  Torr. Helium ionizes appreciably at a field about 4.5V/A which is significantly greater than the field required to ionize all impurities (2).

The vacuum system widely used in the FIM is the standard diffusion pumps which is connected with liquid nitrogen trap. The pumping-out process in the beginning of the operation can be controlled with a thermocouple gauge and an ionization gauge.

A fore vacuum storage bulb is also used to prevent vibration of the emitter tip.

#### D. Photography

The location of adatoms deposited on the metal surfaces and their displacements after each heating cycle can be determined by Müller's color superposition technique as shown in fig. 5.

Before heating, a photographic positive of the ion image is illuminated with a green light. After heating the coincident photograph is projected by a red light.

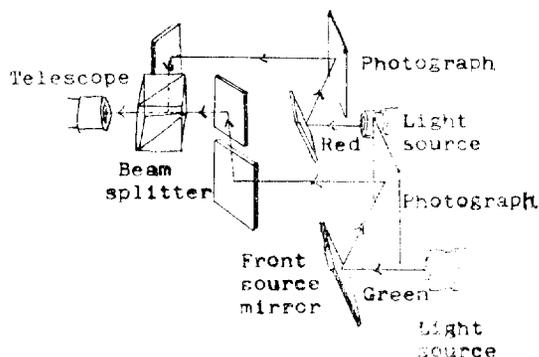


Fig. 5 Optical comparator for quantitative determination of atomic displacements.

Unchanged atoms appear orange which new atoms or vacancies appear red or green. The net distance travelled can be measured with a micrometer eyepiece inserted into the viewing telescope (1, 5).

### IV. Results and Discussion

#### A. Tungsten on Tungsten

Ehrlich and Hudda (5) quantitatively investigated in the interaction tungsten atoms on tungsten surface in FIM using their mean square displacement model as mentioned. The results indicated that the motion is random walks with two reflecting boundaries, and is established to be discrete with a jumping distance of 2.74 Å nearest neighbor. The activation energies  $Q_d$  calculated using the mean square displacement model does not agree to those calculated from the pairwise interaction theory, as shown in Table 1. Therefore, the study indicates that interaction between tungsten adatoms and tungsten are not pairwise.

In this study, however, the interactions of tungsten atoms on tungsten surface was observed as pair-wise additives.

Table 1. Diffusion Parameters (Tungsten Adatom on Tungsten)

Plane	$D$ ( $\text{cm}^2/\text{sec}$ )	$\Delta S$ (eu)	$Q_d$ (kcal/mole)	
			Experiment	Theory
(110)	$3 \times 10^{-2}$	$4 \pm 4$	22	31
(321)	$1 \times 10^{-3}$	$-3 \pm 3$	20	43
(211)	$2 \times 10^{-7}$	$-20 \pm 10$	13	41

### B. Rhenium on tungsten

Bassett et al (7) reported that Re did not form dimers, although larger clusters were observed. The present study indicated that surface diffusion occurred as Re adatom on W. In the diffusion of Re atoms on tungsten (123) planes, the motion is generally random walks with two reflecting boundaries, and is discrete with a jumping distance of 2.74 Å as W on W. The experimental potential barriers were observed for the diffusion on (110) planes. The exact statistical analysis of the one dimensional diffusion will be described elsewhere by authors.

### C. Rhenium-Rhenium interactions

No stable cluster of any form has been observed in 320–390°K range due to an existence of a repulsive potential between two Re atoms. Above 390°K, the potential barrier can be overcome and clusters can be formed. Clusters with more than 3 atoms are found to be stable with respect to re-orientation and surface diffusion. Diatomic clusters of bond length 2.74 Å are observed but are not stable, suggesting a bond strength of less than 1 eV. Below 320°K, very loosely bond diatomic clusters of bond length 7 Å.

### D. Tungsten-Rhenium interactions

Only preliminary data are available for tungsten-rhenium interactions. On tungsten (112) planes, they are quite similar to tungsten-tungsten interactions. When a Re and a W are in the same channel, they combine easily to form a cluster of bond length 2.74 Å. On the (110) plane, similar to two rhenium atoms, no stable W-Re cluster is observed below 332 K.

### E. Potential traps on surfaces.

At lower temperatures the diffusion atom was often trapped in a surface site and could no longer move at the original heating temperature. The traps are probably caused by some lattice defects or impurities on or the diffusion planes. The additional binding energy of the traps will be discussed elsewhere by authors.

### F. Cluster structure

With a resolution for 3 Å of the FIM, it is difficult to determine the exact structure of clusters without some degree of speculation. The assumption was made as the clusters have definite structures which are closely

related to the substrate atomic arrangements. Equilibrium cluster structures are so sensitive to the surface temperature. The surface atomic rearrangement was observed due to the thermal effect alone.

## V. Summary

1. The study of interatomic interaction is possible using a FIM.

2. Surface migration of a single to tungsten or rhenium atom on tungsten (123) planes is discrete jumps of 2.74 Å. Surface diffusion on tungsten (110) planes is along surface channels by overcoming two potential barrier.

3. Interatomic potentials between surface atoms depend on the substrate plane structure.

4. The equilibrium cluster structures are found to be related to substrate structures and also are found to be very sensitive to surface temperature.

5. Tungsten-rhenium interaction is only preliminary, but the possibility of studying initial stages of alloying using the FIM has been demonstrated.

## References

1. Müller, E. W. and Tsong, T. T., *Field Ion Microscopy Principles and Applications*, American Elsevier Company, Inc., New York (1969).
2. Bowkett, K. M. and Smith, D. A., *Field-Ion Microscopy*, North-Holland Publishing Co., American Elsevier Publishing Co., Inc. (1970).
3. Gomer, R., *Field Emission and Field Ionization* (Harvard Univ. Press, Cambridge, Mass.).
4. Smoluchowski, M. V., Sitzber. Akad. Wiss. Wien Math. Natur W. Kl. 123, 2381 (1914); *Kolloid Z.* **18**, 48 (1916).
5. Ehrlich, G. and Hudda, F. G., *J. Chem. Phys.* **44**, 1039 (1966).
6. Ehrlich, G., *J. Chem. Phys.* **44**, 1039 (1966).
7. Bassett, D. W. and M. J. Parsley, *Nature* **221**, 1046 (1969).
8. Bassett, D. W., *J. Phys. E* **3**, 417 (1970).
9. Bassett, D. W., *Surface Sci.* **21**, 181 (1970).
10. Ehrlich, G., *J. Chem. Phys.* **36**, 1171 (1962).