Effects of Static-Field Penetration and Atomic Polarization on the Capacity of a Capacitor, Field Evaporation, and Field Ionization Processes*

Tien Tzou Tsong and Erwin W. Müller

Physics Department, The Pennsylvania State University, University Park, Pennsylvania 16802

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Both static-field penetration and atomic polarization at a metal surface change the effective work function of the surface in a high electric field. The former increases the effective work function, while the latter reduces it in a positive field. The change may amount to several electron volts at a field strength of 6×10^8 V/cm. These two effects should therefore be included in the calculation of the capacity in thin dielectric structures and in the theory of both field evaporation and field ionization.

INTRODUCTION

A REAL metal surface differs from an ideal surface as discussed in classical electrodynamics, where the electric field does not penetrate into the metal. Static-field penetration into a real metal surface was first investigated by Rice[1] in 1928. He used degenerate Fermi statistics to show that for a mercury electrode the diffuse space charge layer acted like a constant capacitance arising from plane-parallel electrodes separated by a fraction of an angstrom of vacuum. A similar problem has also arisen in adsorption studies,[2] where the effective distance between an adatom and the metal plane must be considered. This distance includes a fraction of an angstrom of field penetration into the metal surface. Mott and Watts-Tobin[3] assume an exponential decay of the electric field into the metal surface and point out that the field penetration adds about 0.5 Å to the metal plane distance but does not add a constant capacitance to the surface. On the other hand, Ku and Ullman[4] show that the capacitance of a parallel-plane capacitor is the series combination of the capacitances of the dielectric and the metal electrodes.

In field-ion microscopy, the fields range to the order of 6×10^8 V/cm, and field penetration as well as surface atomic polarization change considerably the binding energy of a surface atom.[5,6] As will be discussed in more detail in later sections, these effects have not been agreed upon by various investigators. In this paper, we will reexamine the effects of field penetration and atomic polarization on a metal surface. It will be shown that the effects can be best described in terms of a change of work function. The capacitance of a thin parallel-plate capacitor, the binding energy of a surface atom in a high electric field, as well as the field ionization process, will then be examined.

[1] O. K. Rice, Phys. Rev. **31**, 1051 (1928).
[2] J. R. MacDonald and C. A. Barlow, Jr., J. Chem. Phys. **36**, 3062 (1962); J. H. DeBoer, Advan. Catalysis **8**, 25 (1956).
[3] N. F. Mott and R. J. Watts-Tobin, Electrochim. Acta **4**, 79 (1961).
[4] H. Y. Ku and F. G. Ullman, J. Appl. Phys. **35**, 265 (1964).
[5] E. W. Müller, Advan. Electro. Electron. Phys. **13**, 83 (1960).
[6] R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, Mass., 1961).

FIELD PENETRATION AND ATOMIC POLARIZATION

In a neutral state, the bulk charge density in a metal is given by

$$\rho(\mathbf{r}) = \sum_l Ze\delta(\mathbf{r}-\mathbf{r}_l) - e\sum_\alpha |\psi_\alpha(\mathbf{r})|^2$$

$$- e\int_0^\infty N(E_\kappa,T,\mathbf{r})|\psi_\kappa|^2 dE_\kappa, \quad (1)$$

where $\mathbf{r}_l$ is a lattice vector, $\delta(\mathbf{r}-\mathbf{r}_l)$ is Dirac's δ function, α indicates summation over all bound states (ion core states), $N(E_\kappa,T,r)$ is the density of occupied conduction-band states, and Z is the atomic number of the metal atom. The first term represents a contribution of nuclear charges, the second term is due to bound-state electrons, and the last term is due to conduction-band electrons or free electrons. The electric field is assumed to have negligible effect on the nuclear charge. The static-field penetration effect arises from a depletion of the conduction-band electron cloud near the metal surface by an applied voltage, while the surface polarization results from a field-induced deformation of the bound-state electron orbitals. In metals, the former effect is directly connected with the electric field outside the metal through Gauss's law, and the latter effect merely produces an additional surface-charge double layer.

To find out how an electric field penetrates into a metal surface, we consider a simple free-electron model of the metal in which the ions are replaced by a smoothed-out uniform back-ground of positive charge. The net charge density is everywhere zero inside the metal. The potential energy of electrons inside the metal is schematically shown in Fig. 1(a). The reference metal plane ($z=0$) in this model is made to coincide with the reference metal plane of the image potential of an external charge. The actual location of the reference surface plane can only be determined experimentally and is not essential in our analysis. When a voltage is applied between the metal and an opposite electrode, static-field penetration changes the potential energy of electrons inside the metal by an amount $-eV(z)$, as shown in Fig. 1(b). Since energy states above the Fermi level ζ_0 are not occupied, the electronic charge

density will be changed near the surface. The positive charge density everywhere remains unchanged, because the ions are rigidly attached to the lattice. Therefore, a net charge density results. A change in the Fermi level ζ_0 occurs only when the thickness of the metal is comparable to the field penetration depth, which we assume to be not the case here. At low temperatures, the voltage inside the metal then satisfies the following one-dimensional Poisson equation:

$$\frac{d^2V}{dz^2}=4\pi n_0 e\left[\left(1+\frac{eV}{\zeta_0}\right)^{3/2}-1\right], \quad \text{for} \quad z\leq 0 \qquad (2)$$

where n_0 is the number of free electrons per unit volume. The solution is subject to the following boundary conditions:

$$\begin{aligned} -dV/dz=F_0, &\quad \text{at} \quad z=0 \\ V=0 \quad \text{and} \quad F=0, &\quad \text{at} \quad z=-\infty. \end{aligned} \qquad (3)$$

Equation (2) is readily integrated. The electric field inside the metal is then given by

$$F=-\frac{dV}{dz}=-\left\{8\pi n_0 e\left[\frac{2\zeta_0}{5e}\right.\right.$$

$$\left.\left.\times\left(1+\frac{eV}{\zeta_0}\right)^{5/2}-V\right]-\frac{16}{5}\pi n_0\zeta_0\right\}^{1/2}. \qquad (4)$$

Rewrite Eq. (4) in the following form:

$$\frac{dV}{dz}=\frac{V}{\lambda}\left(1+\frac{1}{6}\frac{eV}{\zeta_0}-\frac{1}{48}\frac{e^2V^2}{\zeta_0^2}+\cdots\right)^{1/2}, \qquad (5)$$

where

$$\lambda=(\zeta_0/6\pi n_0 e^2)^{1/2} \qquad (6)$$

is the well-known impurity screening distance in metals. Values of λ as given by Friedel[7] and Ku and Ullman[4] are listed in Table I. It is easy to see that the infinite series in the bracket of the left-hand side of Eq. (5) converges rapidly for all values of eV/ζ_0. At low fields, $|eV/\zeta_0|\ll 1$, and to a first-order approximation in V terms, Eq. (5) reduces to a linear differential equation

$$dV/dz=V/\lambda. \qquad (7)$$

The solution subject to boundary conditions (3) is

$$V(z)=-F_0\lambda e^{z/\lambda}, \quad \text{for} \quad z\leq 0. \qquad (8)$$

Values of λ as given in Table I range from 0.21 Å for nickel to 1.0 Å for thallium. In field-ion microscopy,

TABLE I. The impurity screening distance λ in various metals.

Metal	Cu[a]	Al[a]	Tl[a]	Fe[a]	Ni[a]	Ag[b]	Au[b]	Cs[b]
λ (Å)	0.89	0.71	1.0	0.31	0.21	0.51	0.51	0.68

[a] From Ref. 7.   [b] From Ref. 3.

[7] J. Friedel, Advan. Phys. **3**, 446 (1954).
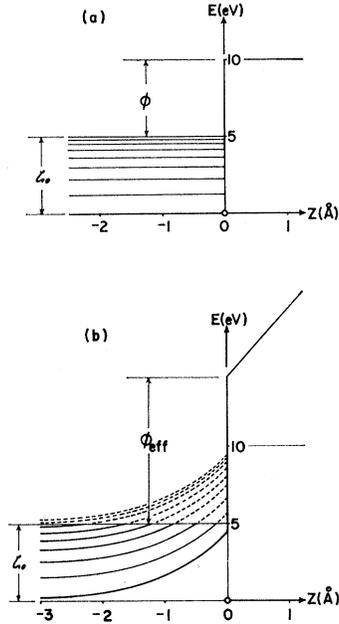
FIG. 1. (a) A simple model of a metal in the absence of an electric field. (b) In a positive electric field, the conduction-band energy levels are bent upward by field penetration. The electron density near the metal surface is reduced and the work function is effectively increased.

the field range of interest is between 2 and 6 V/Å. The condition $|eV/\zeta_0|\ll 1$ is therefore not fulfilled. The accuracy of Eq. (8) can be checked by solving Eq. (5) to include the second-order term in V.

$$\frac{dV}{dz}=\frac{V}{\lambda}\left(1+\frac{1}{12}\frac{eV}{\zeta_0}\right). \qquad (9)$$

Integrating Eq. (9), one gets

$$V/(1+\delta V)=ce^{z/\lambda}, \qquad (10)$$

where c is an integration constant and $\delta\equiv e/12\zeta_0$. Or,

$$V=ce^{z/\lambda}/(1-\delta ce^{z/\lambda}). \qquad (11)$$

Substituting boundary conditions,

$$-F_0=\frac{dV}{dz}\bigg|_{z=0}=\frac{c/\lambda}{(1-\delta c)^2}. \qquad (12)$$

Letting

$$a\equiv 1/c, \qquad (13)$$

one has

$$a^2-(2\delta-1/\lambda F_0)a+\delta^2=0, \qquad (14)$$

$$a=-(2\lambda F_0)^{-1}\left[(1-2\lambda F_0\delta)\mp(1-4\lambda F_0\delta)^{1/2}\right], \qquad (15)$$

and

$$c=-\lambda F_0\bigg/\frac{1}{2}\left[\left(1-\frac{eF_0\lambda}{6\zeta_0}\right)+\left(1-\frac{eF_0\lambda}{3\zeta_0}\right)^{1/2}\right]. \qquad (16)$$

The sign of the root term in the denominator is so chosen that as $\lambda F_0\delta\to 0$, c approaches $-\lambda F_0$. The solu-

tion of Eq. (9) is therefore

$$V(z) = -F_0\lambda e^{z/\lambda} \Big/ \frac{1}{2}\Big[\Big(1-\frac{eF_0\lambda}{6\zeta_0}\Big)+\Big(1-\frac{eF_0\lambda}{3\zeta_0}\Big)^{1/2}\Big]$$

$$\times\Big(1-\frac{ce}{12\zeta_0}e^{z/\lambda}\Big), \quad \text{for } z\le0. \quad (17)$$

Thus, at high electric fields, the penetration is even deeper inside the metal than that predicted by the simple exponential decay as expressed by Eq. (8). The difference between the two solutions is not negligible. For example, a metal with $\lambda=1.0$ Å and $\zeta_0=5$ eV in a field of $F_0=4.5$ V/Å, Eq. (8), gives $V(0)=-4.5$ V, while Eq. (17) gives $V(0)=-4.90$ V, as shown in Fig. 2. By examining Eq. (5), it is expected that Eq. (17) gives an accuracy within about 2% of the exact solution of Eq. (2) in the field range of interest, and for most practical purposes, the linear differential equation

$$d^2V/dz^2 = V/\lambda^2 \qquad (18)$$

suffices to describe the static-field penetration in this simple model of a metal to within about 10% accuracy.

As a result of the field penetration, the energy levels of electrons are bent upward by $-eV(z)$ and the electron density near the surface is reduced in a positive field, as schematically shown in Fig. 1(b). The work function of the metal surface in the field as given by

$$\phi(F) \equiv \lim_{d\to\infty}\Big[-eV(d)-e\int_0^d F(z)dz-\zeta_0\Big] \qquad (19)$$

changes by an amount

$$\Delta\phi_1 = -eV(0) = -e\int_{-\infty}^0 F(z)dz \qquad (20)$$

from the zero-field value

$$\phi(0) = \lim_{d\to\infty}[-eV(d)-\zeta_0]. \qquad (21)$$

Field-induced polarization of surface atoms produces a surface-charge double layer. The effective work function of the surface, therefore, changes[8] by an amount of

$$\Delta\phi_2 = -4\pi e\alpha_s(hkl,\lambda)F_0/s(hkl), \qquad (22)$$

where $\alpha_s(hkl,\lambda)$ is the polarizability of a surface atom at its site in a (hkl) plane and $s(hkl)$ is the surface area occupied by each atom. Kink-site atoms at low-index planes should be considered as surface atoms of very high index planes. The work function changes due to the two effects have opposite signs. Values of $\Delta\phi_1$, as given by Eqs. (20) and (17), may not be in very good quantitative agreement with experimental data because of the limitation of the Thomas-Fermi method, but the order of magnitude should be essentially

FIG. 2. Potential-energy change of an electron inside a metal with $\phi=5.0$ eV, $\zeta_0=5.0$ eV, $\lambda=1.0$ Å, and $F_0=4.5$ V/Å.

correct. Values of $\Delta\phi_2$ are, however, much more difficult to estimate. It is reasonable to assume that the value of α_s is even smaller than the ionic polarizability of a metal atom with the charge of the ion given by its valency, since the metal ion is embedded in a lattice site and is partially shielded from the field. One therefore expects $|\Delta\phi_1|\gg|\Delta\phi_2|$, and $\Delta\phi_2$ will be neglected in some of the following discussions.

APPLICATION TO A PARALLEL-PLATE CAPACITOR

The capacitance contribution from the field penetration effect in the metal electrodes of a parallel-plane capacitor has been discussed in detail by Ku and Ullman.[4] They solve the Poisson equation numerically and find that for reasonable electric fields in the dielectric ($<10^8$ V/cm) the lumped-series capacitance of the electrodes is practically constant and independent of applied voltage and dielectric thickness. The total capacitance is the series combination of the capacitances of the dielectric and the electrodes. The electrodes are effectively a capacitor with a thickness 2.3λ. Using Eqs. (8) and (17), an analytical form of the capacitance can be derived. First, we discuss the case of the vacuum capacitor. The work function and impurity screening distances of the two electrodes are denoted by ϕ_1,λ_1 and ϕ_2,λ_2, respectively. From the schematic potential diagram shown in Fig. 3, one has

$$V = \phi_1/e - V(0,\lambda_1) + F_0t - \phi_2/e - V(0,\lambda_2), \quad (23)$$

where t is the distance between the two electrodes and $V(0,\lambda_1)$ is given by Eq. (17), with $z=0$, and $\lambda=\lambda_1$. Since the net surface charge density is given by

$$\sigma = F_0/4\pi, \qquad (24)$$

the capacitance per unit area is

$$c = \frac{\sigma}{V} = \frac{1}{4\pi}\frac{1-(1/eV)(\phi_1-\phi_2)}{\{t-F_0^{-1}[V(0,\lambda_1)+V(0,\lambda_2)]\}}, \qquad (25)$$

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[8] The contribution of a surface-charge double layer to the work function of a clean metal as well as of a metal covered with an adsorption layer is a well-known fact; see, for example, C. Herring and M. Nichols, Rev. Mod. Phys. **21**, 185 (1948). The field-induced dipole moment of adatoms will therefore also affect the work function. A recent discussion is found in L. W. Swanson and R. Gomer, J. Chem. Phys. **39**, 2813 (1963).

which is slightly field-dependent even if $\phi_1=\phi_2$. When Eq. (8) is substituted for $V(0,\lambda)$ and the same metal is used for the two electrodes, one has

$$1/c=4\pi t+4\pi(2\lambda), \qquad (26)$$

which indeed represents the reciprocal capacitance of two capacitors in series with a constant capacitance of the electrodes separated by 2λ. When a dielectric of a dielectric constant ϵ is inserted in between the electrodes, the capacitance per unit area is given by

$$c=\frac{1}{4\pi}\frac{1-(1/eV)(\phi_1-\phi_2)}{\{t/\epsilon-F_0^{-1}[V(0,\lambda_1)+V(0,\lambda_2)]\}}, \qquad (27)$$

which again is slightly field-dependent. The field penetration effect can no longer be neglected when t/ϵ falls below about 50 Å. Thus our results, in general, support the arguments of Ku and Ullman[4] and are in disagreement with that of Mott and Watts-Tobin.[3]

APPLICATION TO FIELD EVAPORATION AND FIELD IONIZATION

The change in binding energy of an atom at a metal surface in an electric field due to atomic polarization and static-field penetration effects has been discussed by various investigators.[5,6,9–13] Müller[5] introduced a polarization energy term $\frac{1}{2}(\alpha_a-\alpha_i)F_0^2$ into the binding energy equation for the field evaporation process. Thus, the activation energy Q_n for n-fold charged ion in an image force theory[14] is given by

$$Q_n=\Lambda+\sum_n I_n-n\phi-(n^3e^3F_0)^{1/2}+\tfrac{1}{2}(\alpha_a-\alpha_i)F_0^2, \qquad (28)$$

where Λ is the sublimation energy, I_n is the nth ionization energy of the atom, α_a is the polarizability of the atom, and α_i is the polarizability of the n-fold charged ion. Müller also pointed out that due to a static-field penetration, the "electronic surface" is recessed, so that the distance between a surface atom and the reference metal plane is changed by an amount λ. Using this concept, Gomer and Swanson obtain in their theory of field desorption[10]

$$Q_n=\Lambda+\sum_n I_n-n\phi-n^2e^2/4(z_0+\lambda)$$
$$-neF_0(z_0+\lambda)+\tfrac{1}{2}(\alpha_a-\alpha_i)F_0^2 \qquad (29)$$

for an adatom held by localized bonds, where z_0 is the distance from the reference metal plane to the adatom in the absence of an external field. The derivation is based on the assumption that the metal plane is recessed by λ because of the field penetration effect.

[9] M. Drechsler, Z. Elektrochem. **61**, 48 (1957).
[10] R. Gomer and L. W. Swanson, J. Chem. Phys. **38**, 1613 (1963); L. W. Swanson and R. Gomer, *ibid.* **39**, 2813 (1963).
[11] E. W. Müller, Surface Sci. **2**, 484 (1964).
[12] D. G. Brandon, Surface Sci. **3**, 1 (1965).
[13] G. Ehrlich, Discussions Faraday Soc. **41**, 7 (1966); J. Chem. Phys. **48**, 1465 (1968).
[14] E. W. Müller, Phys. Rev. **102**, 618 (1956).

FIG. 3. Potential of an electron in a parallel-plate capacitor. The electron density at the surface of the positive electrode is reduced, while at the negative electrode the electron density is increased.

Müller[11] then tried to correlate the surface polarization energy with the field penetration depth, while Brandon[12] included both the atomic polarization and the field penetration effects by adding a $+neF_0\lambda$ term into Eq. (28). On the other hand, Ehrlich[13] suggested to write the last term in Eq. (28) in a form of αF_0^2 to include both effects, where α was considered to be an empirical correction factor. Here, we will reexamine the effect in terms of the simple physical model discussed in the preceding paragraphs.

The electronic surface is effectively recessed only when $\Delta\phi_1>\phi(0)$. When $\Delta\phi_1<\phi(0)$, only the electron density is reduced near the surface. Even if the electron surface is recessed, the image plane is essentially unchanged. As shown in Eq. (18), within about 10% accuracy, the Poisson equation governing free-electron distribution in a metal is linear, so that when V_1 and V_2 satisfy the Poisson equation, so does V_1+V_2. Superposition of two effects, e.g., image potential and applied voltage (external field), does not change the functional form of the charge distribution inside the metal; neither will it change the location of the reference metal plane. The image force potential is still represented by $n^2e^2/4z_0$, as in the case where no external field is applied. Since the work function of the metal surface in high electric fields is now changed by $\Delta\phi_1+\Delta\phi_2$, the binding energy of an atom is slightly modified to give

$$Q_n=\Lambda+\sum_n I_n-n\phi-neF_0\lambda+4\pi ne\alpha_s F_0/s$$
$$-(n^3e^3F_0)^{1/2}+\tfrac{1}{2}(\alpha_a-\alpha_i)F_0^2 \qquad (30)$$

and

$$Q_n=\Lambda+\sum_n I_n-n\phi-n^2e^2/4z_0-neF_0(z_0+\lambda)$$
$$-4\pi\alpha_s/s)+\tfrac{1}{2}(\alpha_a-\alpha_i)F_0^2. \qquad (31)$$

Although the Q_n, as given by Eqs. (31) and (29), differs only slightly, the Q_n given by Eqs. (30) and (28)

FIG. 4. Potential energy of an ion in a retarding potential analyzer, as discussed in Ref. 19.

differs considerably. Recent atom probe field-ion microscope work[15],[16] shows that tungsten field evaporates mostly as W^{3+} and partly as W^{4+} ions. Assuming an evaporation field of 6 V/Å and λ of 0.5 Å, the $neF_0\lambda$ term amounts to 9–12 eV, which is even larger than the

sublimation energy term. Neglecting the field penetration effect is therefore not realistic in the interpretation of binding energy measurements using the field desorption technique. It is also interesting to note that Eqs. (30) and (31) tend to predict slightly lower evaporation fields for higher charged ions than that predicted by Eqs. (28) and (29). This is not in contradiction to the atom probe measurements.

A change in the work function of the metal surface will also change the critical distance[5],[6] as well as the barrier penetration probability in the field ionization process. An increase in work function will greatly reduce the potential barrier outside the metal and increase the rate of ionization. In this case, however, the increase is limited by an additional potential barrier formed inside the metal. The critical distance for field ionization[5],[6] is slightly modified and is given by

$$z_c \approx (I - \phi - eF_0\lambda - \Delta\phi_2)/eF_0. \qquad (32)$$

Assuming the potential barrier outside the metal to be an equilateral triangle of base z_c and height $I - 2 \times \sqrt{(e^3F_0)}$ [6],[17] and the barrier inside the metal to be an exponentially decaying potential, the electron tunneling probability as calculated using the WKB method is

$$D(z_c) \approx \exp\left[-\left(\frac{8m}{\hbar^2}\right)^{1/2}\left\{\tfrac{2}{3}(I-2e^{3/2}F_0^{1/2})^{1/2}\frac{I-\phi-\Delta\phi_2}{eF_0} - \left[\tfrac{2}{3}\lambda(I-2e^{3/2}F_0^{1/2})^{1/2}-2\lambda(eF_0\lambda)^{1/2}\right]\right\}\right]. \qquad (33)$$

We therefore expect a slight difference in best image fields for various metals. In an alloy, different field ionization rates above each species as proposed by the authors,[18] can also be qualitatively explained in terms of a difference in field penetration depth for alloy species and consequently also the electric field above them. Quantitative calculation of the ionization rates above alloy species is meaningless at this moment in view of the qualitative nature of Eq. (33).

In principle, the combined effect $\Delta\phi_1+\Delta\phi_2$ can be determined from the onset voltage of field-ion energy distribution using the retarding potential technique, provided that at the critical distance of field ionization a simple image potential represents closely the potential energy of the ion. A potential-energy diagram of an ion in a retarding potential analyzer as originally given by the authors[19] is slightly modified and shown in Fig. 4. The onset voltage of field-ion energy distribution is given by

$$eV_{on} = I - \phi_{coll} + e^2/4z_c - e^2/4z_c', \qquad (34)$$

where ϕ_{coll} is the collector work function, z_c is the critical

distance of field ionization, and z_c' is the distance from the collector surface to the point where resonance or Auger neutralization of the ion takes place. Thus, by determining z_c from the onset voltage measurement, and substituting z_c into Eq. (32), $\Delta\phi_1+\Delta\phi_2$ can be obtained. However, this method involving determination of z_c through the image potential, which in turn is a small quantity, is rather critical in practice. $\Delta\phi_1+\Delta\phi_2$ so calculated by using data from Ref. 19 and $z_c'=5$ Å ranges from 7 to 10 eV for a tungsten emitter. This is much higher than expected from Eq. (17) because of the limited accuracy of the retarding potential data. A more reliable method for determining the work-function change in the presence of the very high field is yet to be conceived.

Note added in proof. We also like to point out that, as a result of the field penetration and polarization effects, the critical distance of field ionization is about 1 Å closer to the metal surface than that calculated by neglecting the two effects as can be seen from Eq. (32). Now it is more justified to consider the field ionization process as a charge rearrangement transition between $M+A$ and M^-+A^+ systems[20] (M represents the metal and A represents the atom) because the overlapping of the atomic electron wave function and the metallic electron wave function is sufficient to ensure the transition to occur.

[15] E. W. Müller, J. Panitz, and S. B. McLane, Rev. Sci. Instr. 39, 83 (1968).
[16] E. W. Müller, S. B. McLane, and J. A. Panitz, Proceedings of the Fourth European Regional Conference on Electron Microscopy, Rome, 1968 (unpublished).
[17] E. W. Müller and T. T. Tsong, Field Ion Microscopy (American Elsevier Co., New York, to be published).
[18] T. T. Tsong and E. W. Müller, Appl. Phys. Letters 9, 7 (1966); J. Appl. Phys. 38, 3531 (1967).
[19] T. T. Tsong and E. W. Müller, J. Chem. Phys. 41, 3279 (1964).

[20] D. S. Boudreaux and P. H. Cutler, Phys. Rev. 149, 170 (1966); Surface Sci. 5, 230 (1966).