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Field Desorption*

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Field desorption of barium, thorium, oxygen, and some other adsorbates is studied in a field emission microscope with reversed polarity as a function of field strength, temperature and degree of coverage. The desorption occurs in the 100, 200, and 500 million volts/cm range, for the three substances, respectively. At the highest fields the tungsten substrate itself evaporates at room temperature. The quantitative interpretation of the measurements suggests that field desorption be considered as an evaporation of ions in which the energy hump is reduced by the Schottky effect.

1. EXPERIMENTS

A. Desorption of Barium from Tungsten

THE emitter of a field emission microscope is most suitable for studying the behavior of metal surfaces at extremely strong electric fields. For a negative point the field strength is limited to some 50 to 70 Mv/cm, beyond which the current density of electron emission becomes excessively large. Much stronger fields, however, up to 570 Mv/cm for tungsten, can be applied to a positive metal surface. The drastic changes that occur under such extreme conditions can easily be observed in the electron image, when the microscope is operated again with a negative emitter.

The first observations of this kind have been made with barium on tungsten.[1,2] A barium film is deposited on the emitter tip and the average work function ϕ is measured from the slope of the Fowler-Nordheim characteristic, which is closely proportional to $\phi^{3/2}$ (Haefer,[3] Müller[4]). The average degree of coverage θ is then obtained from Becker's[5] thermionically determined relation between ϕ and θ. For a given emitter, the field factor relating the applied voltage to the field at the tip apex can be calculated from the voltage at which the clean tungsten surface emits a certain electron current. One uses the theoretical current densities of the Fowler-Nordheim theory, as handily presented in Dolan's[6] tables, and a reasonable assumption about the emitter geometry, e.g., according to Drechsler and Henkel's[7] method of superimposing a spherical and a hyperboloidal field.

If, for instance, a barium film with $\theta=0.35$ has been exposed for some seconds to a positive field of 90 Mv/cm at room temperature, one does not notice any change in the field emission pattern. However, after an exposure to 92 Mv/cm, the barium film is stripped off the 011 vicinity. The stripped area extends more and more as the field is increased. After an exposure to 110 Mv/cm the barium film remains only in the 111 and 001 region, at 125 Mv/cm field desorption occurs also at 111, and at about 150 Mv/cm the desorption is completed over the entire emitter cap, except for the shank where the field is much weaker. A similar sequence is shown in Figs. 1(a)–1(d). Figure 2 gives the desorption field that is required in the vicinity of 011 as a function of degree of coverage and with the temperature as parameter. At room temperature the desorption field at other crystallographic planes is much higher. However, at elevated temperatures, as soon as surface migration sets in, the whole film is torn off in the instant when field desorption starts around 011. No measured points are given in Fig. 2, since for one tip they do not scatter by more than 2% in the field strength. The absolute values of field strength are uncertain by about 15% because of present limitations in the determination of tip geometry.[8]

The data in Fig. 2 have been taken with the desorption field applied for about 3 seconds. If the exposure is extended to 300 sec, the fields required at room temperature are about 2% lower. On the other hand, with single microsecond pulses, the desorption field is about 5% higher, as measured by a Tektronix cathode-ray oscilloscope.

B. Desorption of Thorium from Tungsten

Field desorption of thorium from tungsten[9] requires much stronger fields. (See Fig. 3.) It begins in the vicinity of 011 at 235 Mv/cm, if the tip is at room temperature and the degree of coverage is small. The increase of the desorption field with θ is less than in the case of barium. When surface migration is possible, above 800°K, the entire thorium film desorbs. In the low-temperature range, other crystal planes, particularly 111 and 116, require much higher fields. If one starts with $\theta=0.85$, the thorium film remains as single islands on these planes after an exposure to about 350 Mv/cm. By careful adjustment of the field one can produce just two islands on the 111 planes alone, each

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* This research was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[1] E. W. Müller, Naturwiss. **29**, 533 (1941).

[2] E. W. Müller, Ergeb. exak. Naturw. **27**, 290 (1953).

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[4] E. W. Müller, J. Appl. Phys. **26**, 732 (1955).

[5] J. A. Becker, Trans. Faraday Soc. **28**, 149 (1932).

[6] W. Dolan, Phys. Rev. **91**, 510 (1953).

[7] M. Drechsler and E. Henkel, Z. angew. Phys. **6**, 341 (1954).

[8] W. P. Dyke and J. K. Trolan, Phys. Rev. **89**, 799 (1953).

[9] D. W. Feldman, Master's thesis, Physics Department, Pennsylvania State University, 1954 (unpublished).

having a diameter of only 100 A, and a work function of 3.0 ev, while the surrounding bare tungsten surface has about 4.5-ev work function. Field electron emission of such an emitter comes predominantly from the 111 spots, and dc current densities beyond 10^8 amp/cm^2 can be obtained easily before the thorium film spreads out by heat effects or space charge limits the current density.

C. Desorption of Oxygen and Some Other Adsorbates from Tungsten

Field desorption is not restricted to electropositive adsorption layers. Exploratory experiments have been made with oxygen.[10] A practically saturated film as obtained by admitting 10^{-6} mm O_2 for some minutes shows a slightly grainy structure due to irregular adsorption of molecular oxygen on top of the chemisorbed layer in direct contact with the substrate. The effective over-all work function of such a surface is 6.6 ev. Only after at least 310 Mv/cm have been applied, a slight decrease by one-tenth of an ev indicates the onset of desorption. The grainy structure of the second layer disappears above 420 Mv/cm. The chemisorbed layer in close contact with the surface is removed from the 011 vicinity at 480 Mv/cm, and only at 500 Mv/cm is the desorption almost completed. However, as will be discussed later, under this extreme condition the field evaporation of the tungsten substrate itself becomes noticeable. In a second experiment the oxygen covered emitter was initially heated to 1300°K in order to remove the second adsorption layer from the whole emitter structure. The remaining chemisorbed film was then desorbed from the cap by applying 500 Mv/cm at room temperature. Afterwards, by gradual heating of the tip without an applied field one can allow the oxygen which still covers the shank of the emitter to migrate towards its apex. At temperatures between 510 and 780°K, diffusion times from 660 to 7 sec were required for redistributing the oxygen over the whole cap. This corresponds to a heat of activation of 0.61 ev for the surface migration of chemisorbed oxygen on tungsten. Gomer[11] found about twice as much for the heat of activation when a previously clean tungsten surface was covered with oxygen. This discrepancy suggests that in the present experiments field desorption of oxygen was not complete. Probably some oxygen atoms remained on the more recessed sites with larger binding energy, and the subsequent migration occurred over the lower energy barriers which separate the more shallow adsorption sites.

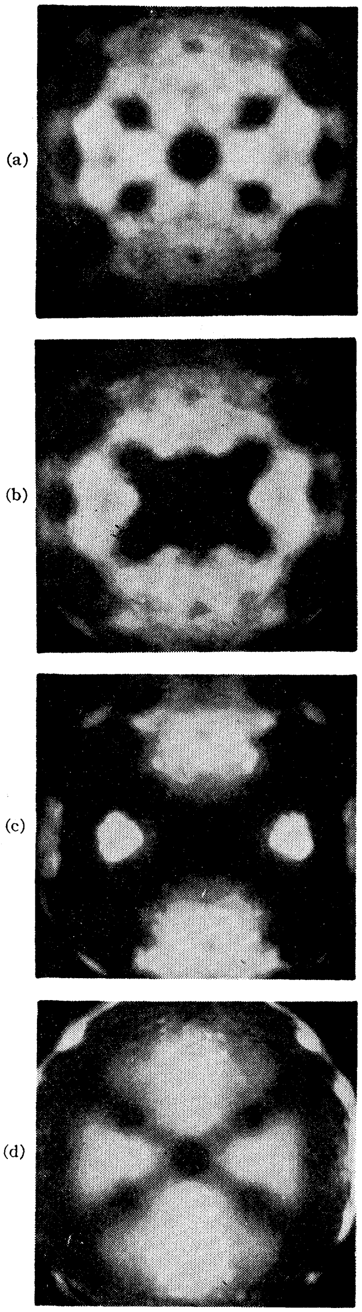

FIG. 1. (a) Field emission microscope pattern of a tungsten tip covered with barium, $\theta = 0.20$. Dark plane in center is 011, the four slightly smaller dark areas around are the 112 planes. The fine dark spots in the vertical axis below and above the center are the cube planes. (b) Same pattern after 88 Mv/cm positive field has been applied for 3 sec. Barium is desorbed in the vicinity of 011. (c) After an exposure to 115 Mv/cm, barium remains only on 111 and around the cube planes. (d) After application of 150 Mv/cm the bare tungsten surface shows up. Only at the rim of the pattern is some barium left over, because of the lower field at the shank of the emitter tip.

Very preliminary experiments were made with field desorption of Li, Na, Te, N_2, and phthalocyanine molecules[12] from a tungsten surface. The alkali metals are easy to desorb with fields in the 60 to 80 Mv/cm range. However, the data are not very reproducible because of the almost inevitable contaminations with gaseous matter. Te and N_2 were chosen as substances that might undergo a change from the state of physical adsorption to chemisorption by the influence of the high field, before desorption takes place. However, this effect, which has been proposed by Kirchner,[13] could not be detected. Field desorption of a Te film begins at about 280 Mv/cm, while N_2 requires 350 Mv/cm for

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[10] E. W. Müller, Z. Elektrochem. **59**, 372 (1955).

[11] R. Gomer and R. Wortman, J. Chem. Phys. **23**, 1741 (1955), and private communication.

[12] E. W. Müller, Z. Naturforsch. **5a**, 473 (1950).

[13] F. Kirchner, Naturwiss. **41**, 136 (1954).

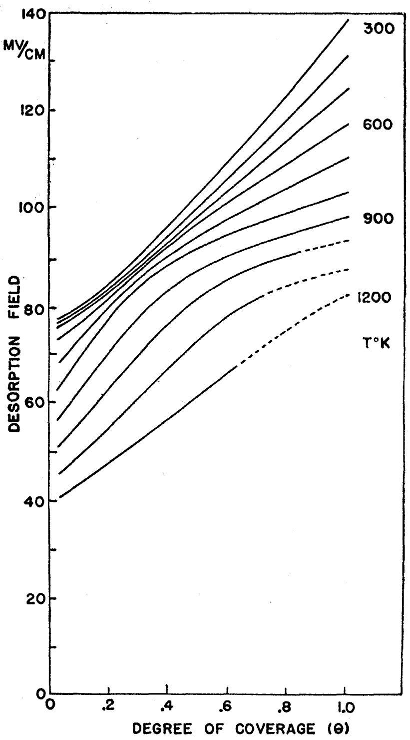

FIG. 2. Field strength for desorption of a barium film from the vicinity of the 011 plane of tungsten, as a function of degree of coverage ($\theta=1$ defined as a film with minimum work function), and with the temperature of the tungsten surface as parameter.

removal of the second layer, and probably 500 Mv/cm for the chemisorbed film, which is not so clearly visible as the oxygen film. The quadruplet patterns of phthalocyanine molecules were found to disappear at about 150 Mv/cm. For these exploratory observations the ac method[1] was found to be convenient. The field emission microscope is operated on 60-cycle ac high voltage, which is slowly increased during observation. The positive phase produces the high field of desorption, while in the negative phase the electron image of the surface appears on the screen. The electron peak current can be kept at any desired value by limiting the negative voltage peak at the tube by a resistor or by dc bias. Moving pictures for detailed studies of field desorption progressing over the different crystal planes have been obtained this way.

It may be noted that no experiments have yet been made to establish that all the desorbed particles actually come off as positive ions. However, from the interpretation given in the second part of the paper this is highly probable. With the usual small tip radii, the desorption of a monolayer yields only a current pulse of some 10^{-14} coulomb. An extremely small continuous ion current can be obtained for some minutes when the emitter is heated, so that ions torn off near the apex are being replaced by surface migration of atoms from the shank.

D. Field Evaporation of Tungsten

The question arises as to what might be the highest field strength a bare tungsten surface can stand. One calculates easily[2] that the mechanical force per unit area of the field $K=F^2/8\pi$ is large enough to stress the hemispherical emitter point up to the technical tensile strength of 575 000 lb/square inch at a field of 300 Mv/cm. Fortunately, the tip consists actually of a quite perfect single crystal, so that more than 510 Mv/cm could be applied at room temperature without rupture, and 570 Mv/cm, corresponding to a stress of 2 million lb/square inch, at the temperature of liquid hydrogen. However, at such fields the surface dissolves quite rapidly. The present experiments are not yet very accurate since the removal of a surface layer of tungsten from its own lattice does not show up so clearly as the desorption of a barium or a thorium film. So far, two different kinds of experiments of a merely exploratory nature have been made. In the first one a clean tungsten tip of, for instance, 700 A radius was exposed for 10 minutes to a voltage of 25 kv at room temperature. This increased the tip radius to 780 A. With reasonable assumptions about the tip shape, which have proved to be applicable to the study of surface migration of tungsten on its own lattice,[14] one can conclude that the field evaporation was somewhere between 1.7 and 4×10^{14} atoms per sec per cm^2 at an average field of 500 Mv/cm. A similar experiment with the tip heated to 900°K gave a rate of 5×10^{15} atoms per sec per cm^2 at an average field of 400 Mv/cm.

A more accurate determination of the evaporation rate can be made with a helium-operated field ion microscope.[15,16] The individual lattice steps around the 011 and 012 planes begin to decrease in diameter when the field is raised sufficiently. The edges of the planes move in concentric, almost elliptic polygons and in slightly discontinuous steps towards the center, where they collapse. For one typical experiment the data are as follows: Field electron emission of 10^{-8} amp at 1110 volts, 10^{-5} amp at 1650 volts, corresponding to a tip radius of 510 A and a field factor $F/V=28\,000$ cm^{-1}. In the field ion microscope the rings collapse in the center of 011 with a rate of 0.1 per second at 17 700 volts, 1 per second at 18 000 volts and 5 per second at 18 200 volts. With the assumption of a homogeneous field evaporation over the entire cap, one can say that one surface layer is removed each time one ring collapses. The measured desorption time is then 10 sec at 498 Mv/cm, 1 sec at 505 Mv/cm and $\frac{1}{5}$ sec at 510 Mv/cm. These data show that the lifetime of a tip at fields above 500 Mv/cm is quite short, for instance when used as an ion source. This kind of field evaporation can be used in field ion microscopy to clean and smooth an emitter surface without the application of heat. This is particularly valuable if one wants to produce extremely fine tips with radii in the 100 to 500 A range. Such tips, easily made by proper etching methods, by cathode

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[14] E. W. Müller, Z. Physik **126**, 642 (1949).

[15] E. W. Müller, Z. Physik **136**, 131 (1951).

[16] E. W. Müller and K. Bahadur, following paper [Phys. Rev. **101**, 624 (1956)].

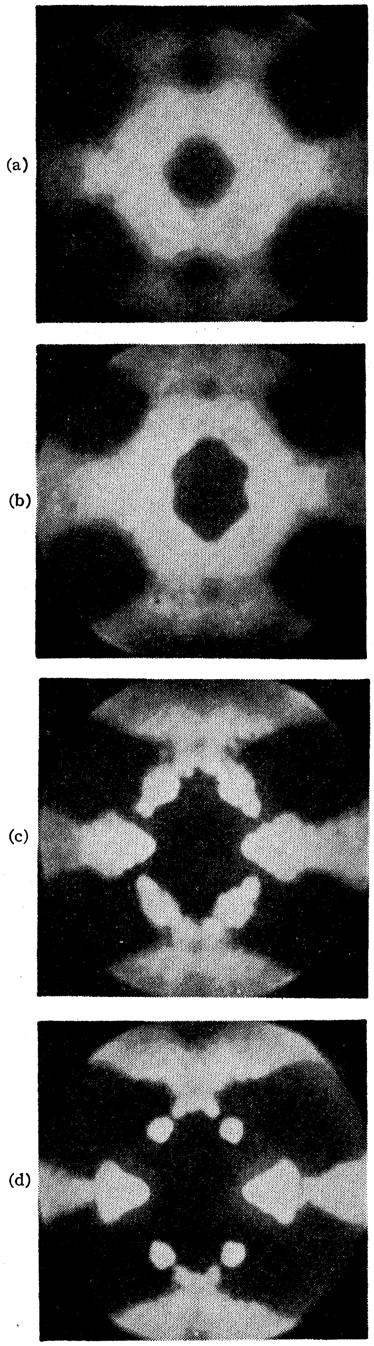

FIG. 3. (a) Field emission microscope pattern of a tungsten tip covered with thorium, $\theta=0.66$. Crystallographic orientation of the tip same as in Fig. 1. (b) Thorium desorbed from the vicinity of 011 by a positive field of 272 Mv/cm. (c) Thorium desorbed by a field of 314 Mv/cm. (d) After exposure to a field of 338 Mv/cm. Thorium film remains on triangular shaped 111 planes, on the 116 planes and around the cube planes.

sputtering[17] or oxide evaporation,[18] cannot be cleaned by heating, since surface migration would increase the radius considerably before the contaminations were evaporated. The geometrical shape of emitters that were exposed to field evaporation is quite different from the dynamic equilibrium form obtained by annealing the tip without an applied field. The edges of 011 and 112 net planes form very regular and smooth ellipses. A more detailed study of the topography of such surfaces as obtained from observations with a helium-ion microscope at low temperatures[19] shall be given in two forthcoming papers.

2. INTERPRETATION OF FIELD DESORPTION EXPERIMENTS

Barium on tungsten has been chosen for the first experiments because this adsorption system is relatively well-known from thermionic experiments. De Boer[20] has suggested that at low degrees of coverage barium is adsorbed in the form of doubly charged ions and is bound mainly by the image force. Although this picture, which gives satisfactory values for the binding energy, might not be entirely correct at the conditions prevailing in thermionic experiments, we assume that at the instant of field desorption barium does come off as a doubly charged ion. It is then possible that one metal electron tunnels into the ion after it has moved to some A units away from the surface, so that mass spectroscopical analysis would indicate only singly charged ions. We calculate the binding energy Q_0 of the ion by the thermionic cycle[21]

$$Q_0=\Lambda+V_I-2\phi, \tag{1}$$

where Λ is the heat of evaporation of the atom, V_I the ionization energy and ϕ the work function of the tungsten substrate. Λ for θ almost zero is not well known. While Dobretznow and Morozow[22] find, under not too good vacuum conditions, the heat of evaporation of barium atoms from tungsten to be 6.5 ev, Moore and Allison[23] give $\Lambda=3.7$ ev for $\theta>0.3$ and note a poor fit already between $\theta=0.2$ and 0.3. Lacking more reliable data, the following calculations are made with the median of the two figures, $\Lambda=5.1$ ev. The energy for double ionization of Ba is $V_I=15.2$ ev. The work function at the edge of the 011 plane of tungsten, where the desorption data of Fig. 2 were taken, may be estimated to $\phi=5.0$ ev.[4] This results in the binding energy $Q_0=10.3$ ev. Since the large mass of the ion excludes wave-mechanical tunneling, we consider field desorption simply as an evaporation over an energy hump Q which is reduced by the Schottky effect.

$$Q=Q_0-(n^3e^3F)^{\frac{1}{2}}, \tag{2}$$

where ne is the charge of the ion. The time required to overcome an energy hump Q by thermal agitation is

$$\tau=\tau_0 e^{Q/kT}, \tag{3}$$

τ_0 being the vibration time of the adsorbed particle, assumed to be in all our considerations 10^{-13} sec. The

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[17] E. W. Müller, Z. Physik **106**, 132 (1937).

[18] E. W. Müller, Z. Physik **108**, 668 (1938).

[19] E. W. Müller, Z. Naturforsch. **11a**, 89 (1956); J. Appl. Phys. **27**, 474 (1956).

[20] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Cambridge, 1935).

[21] L. P. Smith, Phys. Rev. **35**, 381 (1930).

[22] L. M. Dobretzow and G. A. Morozow, Physik. Z. Sowjetunion **9**, 352 (1936).

[23] G. E. Moore and H. W. Allison, J. Chem. Phys. **23**, 1609 (1955).

desorption field is then

$$F^{+}=n^{-3}e^{-3}[Q_0-kT\ln(\tau/\tau_0)]^2. \quad (4)$$

This formula describes very well the observed desorption fields for small θ including the dependence upon temperature and time. The measurements in Fig. 2 have been taken with the field applied for $\tau=3$ sec. Equation (4) gives then $F^{+}=78$ Mv/cm at 300°K and $F^{+}=44$ Mv/cm at 1200°K. For evaporation times of $\tau=300$ sec and $\tau=10^{-6}$ sec, one finds at room temperature the desorption field $F^{+}_{300\text{ sec}}=76.5$ Mv/cm and $F^{+}_{10^{-6}\text{ sec}}=85$ Mv/cm, respectively. Kirchner and Kirchner[24] apply also an image force consideration to the previously published experimental data of the present author,[2] assuming singly charged barium ions. However, this would require the heat of evaporation of the neutral atom to be $\Lambda=1.6$ ev only.

The close numerical fit of Eq. (4) when applied to barium might be partly accidental, since one cannot expect such a good agreement for the absolute values of field strength from the simple image-force model. This becomes more evident in the case of thorium, where the fields are about three times higher. The binding energy Q_0 is less accurately known. Although $\Lambda=7.7$ ev[25] might be correct, no data have been found in the literature for the ionization energy. If we assume the not entirely impossible value of $V_I=5.0$ ev, we obtain $Q_0=6.7$ ev for adsorption of a single charged Th ion on the 011 plane of tungsten, where ϕ is 6.0 ev.[4] This makes $F^{+}=243$ Mv/cm at room temperature and $F^{+}=100$ Mv/cm at $T=1090$°K, which is again in very good agreement with the measurements as shown in Fig. 4. If one takes $\phi=5.0$ ev for the work function of the vicinity of the 011 plane, the calculated desorption field is 1.38 times higher. This may still be considered as good an agreement as can be expected from the simple image force model. The time dependence has been measured by Feldman for two temperatures (Fig. 5). The points check with the theoretical curve as calculated from Eq. (4). The trailing off at $\tau>200$ sec may be due to surface migration.

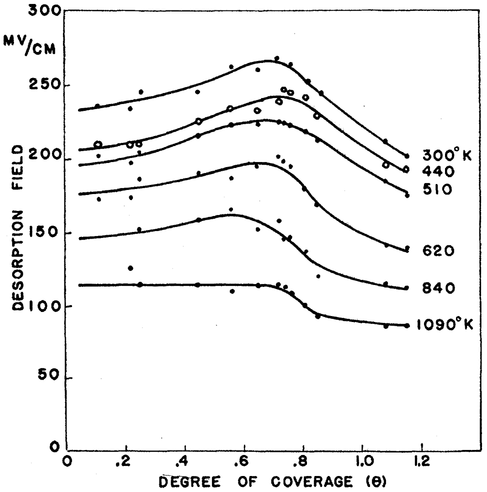

FIG. 4. Field strength for desorption of a thorium film from the vicinity of the 011 plane of tungsten, as a function of degree of coverage and with the temperature as parameter.

The data of Figs. 2 and 4 have been taken for desorption from the vicinity of 011, where closely packed 011 planes form wide terraces. At the other planes the desorption fields are considerably higher, in the same sequence 011, 112, 001, 111, and 116 in which the work function decreases.[4] Calculating Q_0 with $\phi_{116}=4.30$ ev from the thermionic cycle gives $F^{+}_{116}=390$ Mv/cm at room temperature, while $F^{+}=350$ Mv/cm was actually measured. The above sequence of the crystal planes is also the one of less and less closely packed surface atoms, and the image force model should not hold too well here because of the poor definition of the mirror plane.

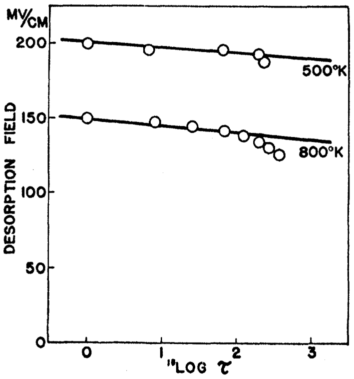

FIG. 5. Desorption of thorium from the 011 vicinity of tungsten. The required field is calculated from Eq. (4) as a function of time ($\log\tau_{\text{sec}}$) for two temperatures. The circles give experimental field strengths as measured by Feldman.

At a given crystal plane the desorption field increases also with the degree of coverage θ (for thorium only as long as $\theta<0.7$). The applied field must additionally balance the opposite field which is produced at the ion under consideration by its neighbors. The neighboring ions with their images form dipoles, the field of which can be easily computed by summing up the contributions of a square array of dipoles with moments μ and a lattice constant $a\theta^{-\frac{1}{2}}$.

$$F_{\text{dip}}=9.05\mu\theta^{\frac{3}{2}}/a^3. \quad (5)$$

The dipole moment μ of a single adsorbed particle as a function of θ can be found from the experimental determination of the corresponding decrease of thermionic work function $\Delta\phi$. Measurements of Becker[5] and others[20] can be approximated by the empirical formula

$$\Delta\phi=B\theta^{\frac{3}{4}}, \quad (6)$$

with $B=2.9$ ev for barium and 1.9 ev for thorium on tungsten ($\theta<0.7$). A sheet of θa^{-2} dipoles per cm^2 reduces the work function by

$$\Delta\phi=2\pi\mu e\theta a^{-2}. \quad (7)$$

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[24] F. Kirchner und H. Kirchner, Z. Naturforsch. **10a**, 394 (1955).
[25] I. Langmuir, J. Franklin Inst. **217**, 543 (1934).

Only one-half of the dipole moment effective in producing the dipole field contributes to $\Delta\phi$. This gives the desorption field as a function of θ:

$$F^{+}=F^{+}_{\theta=0}+\frac{9.05B\theta^{5/4}}{2\pi ae}. \tag{8}$$

The number of barium or thorium atoms per cm^2 at minimum work function ($\theta=1$) is not known accurately. We assume in both cases $N=a^{-2}=2.5\times10^{14}$ per cm^2, which makes the calculated desorption fields

$$F^{+}_{\mathrm{Ba}}=\ 78+66\theta^{5/4}\ \mathrm{Mv/cm},$$
$$F^{+}_{\mathrm{Th}}=243+43\theta^{5/4}\ \mathrm{Mv/cm}$$

match perfectly with the 300°K curves in Figs. 2 and 4 up to $\theta=0.7$. An interpretation of the experimental curves at larger coverages and at higher temperatures would require a more elaborate discussion involving consideration of the polarizability and the surface migration of the adsorbates.

While there is no doubt that field desorption of electropositive particles can be described properly as evaporation over the image force hump, field desorption of adsorbates with a high ionization potential V_I is probably determined by the necessity of lifting the ground level of the adsorbed atom above the Fermi level.

$$V_I-\phi=xF+e/4x. \tag{9}$$

The last term takes care of the electron and the ion image contribution to the potential. Eliminating x by finding the minimum potential on the right side of Eq. (9) gives under neglection of temperature effects the desorption field

$$F^{+}=(V_I-\phi)^2/300e\ \mathrm{v/cm}. \tag{10}$$

With $V_I=13.6$ volts for oxygen and a work function of $\phi=5.0$ ev for the edge of the 011 plane, where the observation was made, one obtains $F_0^{+}=513$ Mv/cm. However, it is felt that in the 500 Mv/cm range, the simple image-force model can be applied only very cautiously, and the good agreement with the experiments may be largely accidental. A more detailed consideration would have to take into account at least the fact that the ground level of the adsorbed atom is broadened by the proximity of the substrate metal, and that the "electronic surface" which produces the mirror image is slightly pushed into the interior of the metal by the high positive field. One can estimate that a fraction of the first atom layer of thickness $\Delta x=dF/4\pi Ne$ must be depleted of electrons in order to produce the surface charge (N= number of atoms/cm^2, d= thickness of first atom layer). On a 011 tungsten plane at 500 Mv/cm the electronic surface is recessed by 0.54 A.

Lacking a better method we finally apply Eq. (4) tentatively to field desorption of tungsten from its own lattice. With $\Lambda=8.78$ ev[26] and $V_I=7.98$ ev[27] we obtain $Q_0=10.76$ ev, and the field for desorbing one monolayer within one second at room temperature becomes $F_{\mathrm{w}}^{+}=693$ Mv/cm. This is about 1.38 times higher than the observed field, and the explanation lies probably in the inadequacy of the image force model at these extremely high fields. One might also assume that the charge of the ion at the instant of passing the hump is slightly larger than one. At the very close distance to the surface the ion might still share one electron with the substrate. An effective charge of $1.1e$ would be sufficient to match the experimental data (which might be wrong themselves by 20% on account of the very small tip radii used here) with Eq. (4), if Q_0 remains unchanged. This assumption has been tentatively made for the calculation of the time and temperature dependence of F_{w}^{+} in Fig. 6 in order to check the few experimental points with the proposed mechanism of field evaporation. The temperature dependence is so large that the lifetime of a tip at 500 Mv/cm is extremely short when the temperature is raised by only a few hundred degrees. An accurate check at 900°K is difficult because the tip builds up sharp edges by surface migration, so that the actual field is not well known any more.

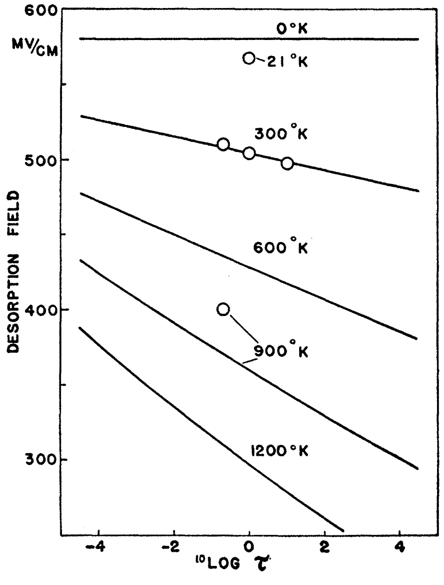

Fig. 6. Calculated field strengths which have to be applied for τ sec to evaporate one monolayer of tungsten from a tungsten surface. The circles represent measurements at room temperature, at liquid hydrogen temperature, and at 900°K, respectively.

Concluding, we can say that an interpretation of field desorption as evaporation of ions under consideration of the Schottky effect describes the experimental facts well enough to justify an application of this

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[26] *Landolt-Börnstein Physikalisch-Chemische Tabellen* (Verlag Julius Springer, Berlin, 1936), fifth edition, Vol. 3, p. 2711.

[27] W. Finkelnburg und W. Humbach, Naturwiss. **42**, 35 (1935).

method for predicting yields of field desorption ion sources, to compute binding energies on individual crystal planes from measured desorption fields and to prepare the operation of a microsecond pulsed ion desorption microscope promising sufficient resolution to resolve the lattice structure of the emitting surface.

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Field Ionization of Gases at a Metal Surface and the Resolution of the Field Ion Microscope*

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The mechanism of field emission of positive ions is considered as depending upon the supply of molecules and their ionization probability in a field up to 500 million volts/cm. Experimental current-field characteristics match the theoretical curves. The velocity distribution, measured in a retarding potential tube, shows that the ions originate some 5 to 100 A above the surface, depending upon the field. A simple mass spectrometer is described which uses the field emitter as a point ion source. The resolution of the field ion microscope is found to depend upon tip radius, polarizability and ionization potential of the gas, and possibly upon the accommodation coefficient and the temperature. Helium seems to give the best resolution of about 4 A. The possibility of operating a field desorption microscope with sufficient resolution to show the lattice structure of the surface is discussed.

1. INTRODUCTION

A SUFFICIENTLY strong electric field applied to a metal surface in such a direction as to make the metal positive gives an emission of positive ions. If the ions originate in an adsorbed layer or are provided by the emitter material itself, the ion source will be weak and rapidly exhausted.[1] A steady ion current up to the microampere range can be obtained when the matter to be ionized is supplied from the gaseous phase. This kind of emission was first used in the field ion microscope,[2] which is a conventional field emission microscope[3] operated with reversed polarity and filled with a gas at a pressure of several microns. The field ion microscope promises to become a useful tool for the study of the structure and behavior of metal surfaces on an atomic scale.[4] However, so far only a few experiments with gases, other than the originally proposed hydrogen and helium, have been reported,[5] as well as the application of the hydrogen-ion microscope for the visualization of surface structures that were interpreted to be screw dislocations.[6] A suggestion about the mechanism of field desorption has been made by Kirchner.[7] An important advance was made by Inghram and Gomer[8] when they introduced mass spectroscopical analysis of the field ions. Most of the results of the present paper were reported a year ago by one of the authors,[9] and a brief account of the subject is given in the *Encyclopedia of Physics*.[10]

2. THE SUPPLY FUNCTION FOR A POINT EMITTER

The ion current is the product of the number of gas molecules arriving at the emitter per unit of time, which we may call the supply function Z, and the efficiency of surface ionization. The number of molecules Z striking the tip is largely determined by the attraction of the molecules through the dipoles induced by the inhomogeneous field. We define a sphere of capture with radius r_c extending as far as the point where the dipole attraction is larger than or equal to the centrifugal force of a tangentially approaching molecule of polarizability α:

$$-\alpha F dF/dr = mv^2/r_c. \qquad (1)$$

We set $mv^2/2=kT$ and describe the field in the neighborhood of the tip by the semiempirical formula

$$F=7.75Vr_0^{2/3}/r^{4/3}, \qquad (2)$$

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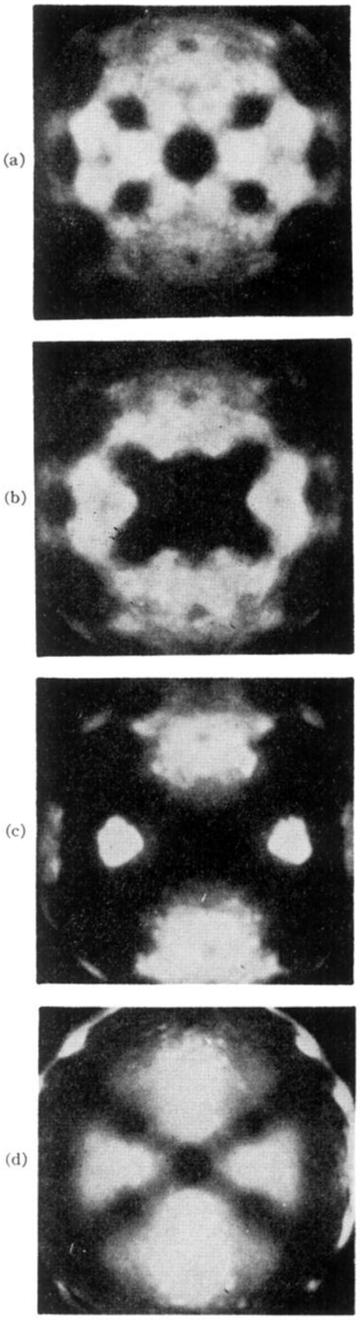

FIG. 1. (a) Field emission microscope pattern of a tungsten tip covered with barium, $\theta=0.20$. Dark plane in center is 011, the four slightly smaller dark areas around are the 112 planes. The fine dark spots in the vertical axis below and above the center are the cube planes. (b) Same pattern after 88 Mv/cm positive field has been applied for 3 sec. Barium is desorbed in the vicinity of 011. (c) After an exposure to 115 Mv/cm, barium remains only on 111 and around the cube planes. (d) After application of 150 Mv/cm the bare tungsten surface shows up. Only at the rim of the pattern is some barium left over, because of the lower field at the shank of the emitter tip.

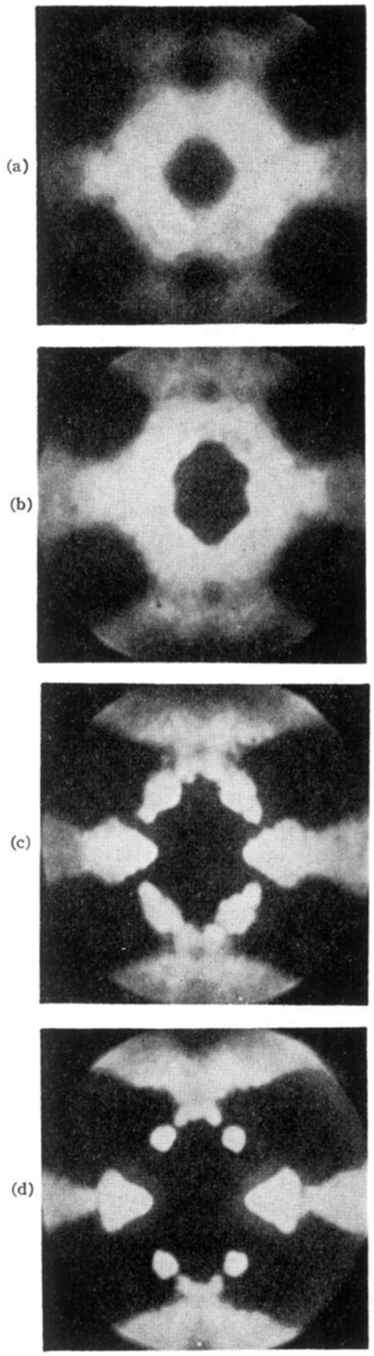

FIG. 3. (a) Field emission microscope pattern of a tungsten tip covered with thorium, $\theta=0.66$. Crystallographic orientation of the tip same as in Fig. 1. (b) Thorium desorbed from the vicinity of 011 by a positive field of 272 Mv/cm. (c) Thorium desorbed by a field of 314 Mv/cm. (d) After exposure to a field of 338 Mv/cm. Thorium film remains on triangular shaped 111 planes, on the 116 planes and around the cube planes.