10th Annual

Field Emission Symposium

Baldwin-Wallace College
Berea, Ohio
Sept. 4-6, 1963
10th Annual
Field Emission Symposium

Sponsored by
Union Carbide Corporation
and the
Office of Naval Research

Baldwin-Wallace College
Berea, Ohio          Sept. 4-6, 1963
PROGRAM
10th Annual Field Emission Symposium
September 3-6, 1963
Baldwin Wallace College

Tuesday, September 3, 1963

7:30 - 10:30
Registration and Room Assignment to Dormitory Facility
(Light refreshments will be served from 8:30 to 10:30).

Wednesday, September 4, 1963

8:00 - 8:45
Breakfast, Final Registration

First Session
Field Emission Microscopy: Theory and Innovations
R. Gomer, Chairman

9:00 "Current-Voltage Characteristics of the Helium Field Ion
Microscope," by E. W. Müller and F. I. Mann.


9:35 "The Theoretical Basis for the Current-Voltage Characteristics
of the Field-Ion Microscope," by M. J. Southon and D. G. Brandon.

10:00 "Image Intensification and Efficient Information Collection in
Field Ion Microscopy," by D. G. Brandon, D. S. Whitmell and
S. Ranganathan.

10:30 Coffee Break

10:45 "Image Intensifier Field-Ion Microscopy," by S. B. McLane, Jr.
and E. W. Müller.

11:10 "Field Ion Microscopy with Neon," by O. Nishikawa and E. W.
Müller.
Second Session
Field Ion Microscopy
W. P. Dyke, Chairman

1:30  "The FIM as a Possible Biological Tool: Feasibility Study of Shadowing Technique," by T. Gurney, F. Hutchinson and R. D. Young.

1:45  "Field Induced Surface Defects in Ion Microscope Patterns," by E. W. Müller.

2:10  "Ion Microscopic Examination of Surfaces," by G. Ehrlich and F. G. Hudda.


3:10  Coffee Break


5:00  Transportation to Parma Research Center - Tour

6:30 - 7:30  Cocktail Party - Parma Research Center - sponsored by Union Carbide Corporation.

7:30 - 10:30  Banquet - Parma Research Center
Thursday, September 5, 1963

8:00 - 8:45
Breakfast

Third Session
Field Ion Mass Spectrometry
E. W. Müller, Chairman


10:20 Coffee Break

10:35 "Field Impulse Desorption; Rate Determination of Cyclohexane Chemisorption on Platinum," by J. H. Block.


12:15 - 1:00
Lunch

Fourth Session
Field Electron Microscopy of Metals, Part I.
G. Ehrlich, Chairman

1:30  "The Simultaneous Determination of the Work Function and the Field Strength at the Surface of a Field Emitter," by A. van Oostrom.
2:00 "Field Emission Microscope Study of Niobium," by W. R. Savage.
3:00 Coffee Break
6:30 Dinner

Friday, September 6, 1963

8:00 - 8:45
Breakfast

Fifth Session
Chemisorption
R. Young, Chairman

9:00 "Desorption by Low Energy Electron Impact," by D. Menzel, R. Gomer and the University of Chicago, Department of Chemistry.
9:30 "Co-Adsorption of Hydrogen and Potassium on Tungsten," by L. Schmidt, R. Gomer and the University of Chicago, Department of Chemistry.
10:00 "FEM Observations with Molecular and Atomic Hydrogen Beams," by R. Klein.
10:30 Coffee Break


12:15 - 1:00 Lunch

Sixth Session
Chemisorption - Study of Metals, Part II
D. Brandon, Chairman

1:00 "Field Emission from Silicon," by G. Busch and T. Fischer.


2:30 "The Adsorption of Copper on Tungsten," by J. S. Anderson and J. P. Jones.

3:00 Coffee Break


Current - Voltage Characteristics of the
Helium Field Ion Microscope*

by

E. W. Muller and F. I. Mann
Pennsylvania State University

Stimulated by the work of Southon and Brandon\(^1\) we have re-examined
the supply function in the helium field ion microscope by measuring current-
voltage-temperature characteristics. We could not confirm their simple \(F^3\)
dependence in the full ionization range, but found the exponent varying for
different tips between about 2.5 and 5.5, increasing with decreasing cone angle.
The temperature dependence of ion current was also re-measured, with screen,
accelerating electrode and tip isothermal, to follow approximately a \(T^{-3/2}\) law.

The formerly used concept of a sphere of capture is unrealistic for the
interpretation of the results. Retaining the trapping condition \(1/2 \alpha F^2 > 3/2\)
kT\(_{\text{gas}}\), we can show from electrolytic trough measurements of field distribution
that the surface of capture forms a sleeve extending at 21 K more than 50 tip
radii up the shank. The experimental current and temperature dependence can
be quantitatively calculated assuming that all gas molecules arriving at the
surface of capture will eventually drift to the tip and be ionized.

\(^{1}\)M. J. Southon and D. G. Brandon, 9th Field Emission Symposium, also
Phil. Mag. 8, 579, 1963.

*Supported by the Office of Naval Research
The Gas Supply to a Field-Ion Emitter

by

M. J. Southon
Department of Metallurgy
University of Cambridge

Gas is attracted to the surface of a field-ion emitter by polarization forces. Expressions are derived for the supply of non-polar gas to spherical and cylindrical emitters, and corresponding results are given for polar gases. It is found that the supply of non-polar gas to a spherical emitter exceeds the zero-field supply by a factor \((\pi \alpha F^2 / 2kT)^{1/2}\) at high fields, where \(\alpha\) is the atomic polarizability and \(F\) is the field at the emitter surface. The discrepancy between this factor and the previously accepted value \((1 + \frac{1/2\alpha F^2}{kT})\) is explained by a consideration of the trajectories of gas atoms approaching the emitter.
A Theoretical Basis for the Current-Voltage
Characteristics of the Field-Ion Microscope

by

M. J. Southon and D. G. Brandon
Department of Metallurgy
University of Cambridge

The current-voltage characteristic of the low-temperature helium-ion microscope consists of two distinct stages, as previously reported. In the first stage the ion current increases with about the 30th power of the applied field, and in the second stage the current varies approximately as the cube of the field.

It is suggested that, in the first stage, the rate of arrival of image gas at the emitter tends to exceed the rate of ionization; in the steady state there is a large concentration of gas near the emitter and the ion current depends on the lifetime for ionization, which is a sensitive function of the applied field. In the second stage it is thought that the rate of ionization tends to exceed the rate of arrival of gas: the gas concentration at the emitter is small, and the ion current is limited by the gas supply to the emitter.

The supply of gas to the emitter is expected to vary approximately linearly with applied field, and a detailed consideration of the gas-surface interaction is introduced to account for the observed $F^3$-dependence of the ion current. An incoming gas atom will only be ionized if it remains near the emitter surface for a time comparable with the ionization lifetime. It is shown that only a small fraction of the kinetic energy of a gas atom is lost at each collision with the surface, and that sufficient energy may be retained to permit escape from the emitter after only one or two impacts. A calculation is given of the emitted ion current, which is proportional to the fraction of the gas supply which is captured by the emitter, the supply to the emitting point from the shank also being taken into consideration.

The calculated current-field characteristics, and their variation with temperature and emitter radius, agree well with experimental observations.
Image Intensification and Efficient

Information Collection in Field Ion Microscopy

by

D. G. Brandon, D. S. Whitmell and S. Ranganathan
Department of Metallurgy
University of Cambridge

Müller has emphasized the need for good, high resolution, image intensification in the field-ion microscope and recent commercial developments have for the first time made suitable high gain intensifiers available. Preliminary results with a five stage dynode system operated with optical coupling are extremely promising and good images have been obtained with neon at 1μ and 10 kv using an f. 3.5 lens and 2 second exposure times.

However, while the gain is extremely good, there is considerable information lost in this type of instrument, both due to the low photocathode efficiency (approximately 4% when operated with Willemite phosphors) and to the relatively small collection efficiency of the optical lens system (approximately 2.5% in the Cambridge system). In order to ensure that each ion contributing to the primary image also contributes to the final image on the photographic record, it is necessary to obtain of the order of 10^3 photons per ion. Since the maximum obtainable phosphor efficiencies are of the order of 10% for helium, this implies a primary ion energy of the order of 25 kv for 100% efficiency and hence suggests post-acceleration of the ions as a suitable technique.

This has been tried using a 70% transmission copper mesh with 350 squares per linear inch, and the photographic exposure times have been reduced to less than 5 minutes when using an f. 1 lens and Gevaert Scopic G film, even at very low kv without subsequent image intensification.

For neon-and argon-ion microscopy post-acceleration prior to image intensification cannot give satisfactory overall efficiencies at reasonable accelerating voltages and another technique is necessary. Preliminary experiments using a fine-mesh grid image converter have been very promising. The secondary electrons produced by ion impact at the oxide coated top surface of the grid are accelerated through the holes and magnetically focussed onto a fluorescent screen. When the image converter is operated at 10 kv, comparable intensities are obtained with neon at 1μ, argon at 2 x 10^-4 torr and helium at 3μ on the same tungsten specimen, while the image is in all three cases of similar intensity to that obtained by post-accelerating the helium image to 30 kv.
Image Intensifier Field Ion Microscopy*

by

S. B. McLane, Jr. and E. W. Müller
Pennsylvania State University

In field ion microscopy the non-refractory materials field evaporate at best image voltage, prohibiting direct photography with its long exposure times. Observation and recording under dynamic conditions is possible by electric image amplification.

Ion-electron image conversion by using secondary electrons from a $10^6$ holes per square inch mesh as originally used by von Ardenne has been tried and showed gains of the order of 10, but the loss of resolution due to the necessary grid-screen spacing is undesirable for our highly detailed ion images.

Much better results were obtained using a commercial (RCA) three stage image intensifier tube with photo cathodes. The system has an overall gain exceeding 2500 at a low noise level. Motion pictures have been made both in real time and slow motion. Synchronized pulses allow motion picture photography of field evaporation of the refractory metals where the field evaporation occurs at higher than best image voltages. Motion pictures will be shown using both helium and neon as imaging gases, and showing field evaporation of nickel, molybdenum, and iron whiskers. Single shot photographs have been made as fast as $1/1000$ sec.

The 1-1/2" image intensifier screen is capable of resolving 400,000 image points, and with proper matching of optical magnification and field of view there is no difficulty in resolving closely packed planes.

The noise in the system is observed as random scintillation on the output screen. The noise level drops with time of operation and after one hour of operation is hardly noticeable. The noise spots are easily distinguished from the atoms both by their short persistence and because their size on the screen is much smaller than the spot which depicts an atom.

*Supported by Office of Naval Research
Field Ion Microscopy With Neon *

by

O. Nishikawa and E. W. Müller
Pennsylvania State University

The resolution and general quality of the neon ion image has been reported at the ninth Field Emission Symposium. Our further investigations concerned onset voltages of field evaporation of metals in vacuum as well as in helium and neon, which are found not to be the same. In order to measure these differences a series of photographs taken at 50-volt increments were studied using our color comparison technique to visualize even a single atom evaporation. Dependence of field evaporation on gas pressure was also observed. Tungsten field evaporation voltages in helium and in neon are lower than that in vacuum by about 1% and 3% respectively, 1% and 6% for molybdenum and 1% and 4% for platinum. This reduction is caused by energy transfer to the surface atom from the incoming non-ionized gas molecule which has the energy \( E_i = \frac{3}{2} kT + \frac{1}{2} a F^2 \). The fraction of energy transfer is \( \Delta E_i = aE_i \), where \( a \) is the accommodation coefficient. Then the equation for the desorption field will be

\[
F_D = n^{-3} e^{-3} (\Lambda + V_I - \Phi - \Delta E_i)^2
\]

neglecting the temperature dependent term. Numerically calculated desorption field reductions agree with observed values.

At the evaporation field an incoming neon atom has enough probability to penetrate as a neutral the ionization zone above the high work function regions of the tungsten crystal. Collision with surface atoms knocks them off, thereby changing the local tip radius and building up a new field evaporation end form with highly protruding \([110]\) zone lines. A few surface vacancies inside closely packed net planes, disappearance of the \([100]\) -zone line and of high index net planes were observed and can be explained by neutral gas atom collision. The progress of field evaporation of tungsten in helium-neon mixed gas and the transition of the neon evaporation end form to the helium evaporation end form are shown in a motion picture taken with the image intensifier and the pulse technique.

* Supported by Aeronautical Systems Division, USAF, and Office of Naval Research
Heating and Cooling of Thin Wires by Field Emission

by

M. Drechsler and G. Jähnig
Fritz-Haber-Institut
Berlin-Dahlem

The heating of field electron cathodes, predicted by Nottingham in 1941 and recently found with special temperature measurement methods\(^1\),\(^2\), initiated the study of elementary emission heats.

Thin wires of some \(10^{-4}\) cm diameter are used instead of tips. With W and Pt wires average field emission heats per electron could be determined with a resistance measurement method and a temperature compensation method. An increase of emission heat with field strength and a decrease with temperature was found.

In the T-F-region the emission cooling effect was found and some cooling energies determined. The heating-cooling-boundary was observed, its temperature increases with field strength.

Using Nottingham's basic ideas and the energy distributions of Young and E. W. Müller and other authors, some emission energies were roughly calculated. Where a comparison between theory and experiments is possible now, qualitative and partly quantitative agreement is found.

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\(^1\)By measuring field emission depending on temperature, Drechsler, Field Emission Symposium 1961.

\(^2\)By measuring work function changes of adsorption layers depending on temperature. F. M. Charbonnier and co-workers, Field Emission Symposium 1962.
The FIM as a Possible Biological Tool:

Feasibility Study of Shadowing Technique

by

T. Gurney* and F. Hutchinson
Yale University

and

R. D. Young
National Bureau of Standards

The potential advantages of employing the field ion microscope for biological studies are obvious. Preliminary experiments have been carried out to study the feasibility of using a shadowing technique which involves the evaporation of tungsten onto its own substrate. When the substrate is at 21°K and 77°K no epitaxy was observed. Tungsten atoms appear to be deposited in a very open structure (a Swiss cheese or lacy structure). Successive desorptions were used to reveal the internal structure of the deposit.

*Guest worker, National Bureau of Standards
Field Induced Surface Defects in Ion Microscope Patterns*

by

E. W. Müller
Pennsylvania State University

Most metals, with the exception of W, Re, Ta, Ir, Rh and Pt cannot stand their evaporation field stress without developing surface defects. In some cases the defects are limited to certain crystallographic regions. Examples are Mo and Fe, which develop dense dislocation loops or an amorphous structure in the 111 region, or Pd and Ni, where the long range order is destroyed in the wide region around 012. Consideration of the bulk modulus shows that the volume expansion under field stress equals approximately the volume expansion to or beyond the melting point under ordinary conditions. The formation of shallow lying dislocation loops is aided by the shear component due to the inhomogenous field distribution. With very small tip radii the misfit is too small to form dislocations, so that the lattice remains perfect.

Other surface defects are due to the shift of lattice sites, which may account for the distinctly different patterns of b.c.c. W, Ta, Mo and Nb. Interstitial carbon in W becomes visible by field-induced lattice deformation.

Progress in field ion microscopy of lower melting metals depends then on the development of a field evaporation or field reaction process at reduced fields more than on image intensity amplification.

*Supported by Office of Scientific Research, USAF
Ion Microscopic Examination of Surfaces*

by

Gert Ehrlich and F. G. Hudda
General Electric Research Laboratory

The direct examination of adatoms in the ion microscope often results in a strong perturbation of the adsorbed layer. Despite this, significant information about surface events can be obtained in the ion microscope, even for very weakly held systems. This will be demonstrated by discussion of three related topics:

1. The Limiting Factor in the Direct Observation of Adatoms
2. Surface Motion of Metal Atoms
3. Physical Adsorption on Atomically Smooth Surfaces.

*Supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.
The Corrosion of Tungsten in Oxygen
by
S. S. Brenner
Edgar C. Bain Laboratory
United States Steel Corporation
Research Center
Monroeville, Pennsylvania

The field ion microscope has been used to study the initial stages of oxidation of tungsten at temperatures up to 1060°K. It was found that a critical oxygen pressure had to be exceeded to observe any definite signs of oxidation aside from the 2-5 Å deep surface rearrangement that occurred even in the absence of oxygen. At temperatures of 860-1060°K the critical oxygen pressure for 10 minute heating was about $10^{-4}$ Torr. Oxidation occurred with the formation of pits or holes 15 to 20 Å deep which presumably were filled with oxide and which field-evaporated at voltages below the image voltage. At temperatures below 860°K the critical pressure for oxidation increased. At 500°K after 19 hours exposure to $2 \times 10^{-2}$ Torr oxygen there was little evidence for any oxidation. Once initiated, the oxidation proceeded rapidly and large changes in the radius of curvature of the tungsten tip could be observed.
Order - Disorder in the Cobalt Platinum System

by

B. Ralph and D. G. Brandon
Department of Metallurgy
University of Cambridge

Equiatomic cobalt-platinum undergoes a transformation from a disordered face centered cubic structure to an ordered face centered tetragonal structure of the Au-Cu type. This alloy is of commercial importance since in the partially ordered state it exhibits excellent permanent magnetic properties.

Field-ion micrographs have been taken from the disordered alloy and from alloys which have been heat treated in the bulk to various degrees of order. The majority of the micrographs have been taken using helium gas but better images have recently been obtained using neon as the image gas.

The disordered alloy seems to exhibit some short range crystallographic regularity and the ordering process is envisaged as a growth and rearrangement process in these regions, rather than a nucleation and growth of perfectly ordered anti-phase domains. In the optimum magnetic state the alloy exhibits small regions of good order surrounded by relatively disordered material. This structure shows a density of lattice defects comparable with that of a heavily work hardened metal, an observation which is in agreement with the known mechanical properties.

As reported by Müller, the fully ordered alloy develops high index planes on field evaporation, similar to the structures obtained from a pure metal, but large numbers of dislocations, vacancies and other defects are still present.

The alloy investigated contains 52 atomic per cent platinum and hence was non-stoichiometric. Thus large numbers of vacancies might have been introduced at the ordering temperature (as in the case of Ni-Al), which, together with the change in lattice parameter on ordering could give rise to the high density of defects observed. However some of the apparent vacant lattice sites could also result from the preferential field evaporation of atoms on the wrong sites in the ordered lattice.
The Structure of Grain Boundaries and Segregation

Effects in Tungsten and Tungsten - 5% Rhenium

by

S. Ranganathan, B. Ralph and D. G. Brandon
Department of Metallurgy
University of Cambridge

The structure of grain boundaries and segregation and migration effects at boundaries can all be studied in detail with the field-ion microscope. This paper reports some detailed observations of the atomic configuration of grain boundaries in tungsten and tungsten-rhenium alloys.

Most boundaries had an axis of misorientation close to <110> and the degree of fit across a boundary was found to be a function of the angle of misorientation. This is in agreement with the Kronberg and Wilson model for high angle boundaries. Field evaporation leads to flattened regions near low angle boundaries, which can be explained on the basis of the distribution of strain energy in this region.

Segregation at grain boundaries cannot be detected by present methods for distinguishing between atomic species but rhenium segregation has been detected from the subsidiary effect of oxygen trapping.

Preliminary migration studies have also been carried out but results are of doubtful value as the driving force for migration is unknown.
Analysis of Atomic Species and the
Structure of Tungsten-Rhenium Alloys

by

B. Ralph and D. G. Brandon
Department of Metallurgy
University of Cambridge

Three tungsten-rhenium alloys containing 5%, 26% and 34% rhenium have been studied with the field-ion microscope. The first two of these alloys are solid solutions while the third is a two phase alloy with particles of $\sigma$ phase in a $\beta$ phase matrix. The effect of increasing solute concentration on the field-ion micrographs will be indicated and a method for distinguishing between atomic species presented. Explanations will be put forward to account for the micrographs obtained.

Additions of rhenium to tungsten have been shown to improve ductility up to about 30% rhenium. The following explanations have been put forward to account for this increase in ductility:

1. Grain boundary oxygen, is scavenged by the rhenium to give particles of a complex oxide.

2. Twinning becomes easier, and is a further mode of plastic deformation.

3. The concentration of interstitial oxygen is reduced.

Grain boundaries studied in tungsten 5% rhenium show strong segregation effects in the as-received alloy while micrographs from deformed specimens show streaking of image spots which is associated with the presence of stacking faults in the b.c.c. lattice.
Angular Distribution of Atoms and Molecules Field Ionized at Tips, and the Ion Emission Properties of Thin Wires

by

H. D. Beckey, J. Dahmen and P. Schülze
Institut für Physikalische Chemie der Universität Bonn
Germany

The angular distribution of atoms and molecules field ionized at tips was measured by means of an apparatus containing 10 concentric rings forming a hemisphere with the tip in its center. It could be shown that two strongly different types of angular distribution occur, depending on the nature of the gas and the temperature. The gases could be grouped into (a) permanent gases and, (b) vapors forming multimolecular adsorption layers on the tip. The former lead to an intensity distribution decreasing continuously with increasing emission angle; the latter, however, lead to a maximum of ion intensity at an angle between 30° and 40° from the tip center. An interpretation of the kinetics of processes causing this maximum is given.

Another series of experiments was concerned with measurement of the ion emission properties of thin wires. The application of thin wires instead of tips to field ion production in F. I. mass spectrometers is possible because the majority of substances to be investigated has ionization potentials much below that of gases used for F. I. microscopy. Field strengths of 2-5,10^7 V/cm are sufficient for field ionization of most of organic molecules and easily obtainable by wires of about 2/μ diameter. The advantages of using wires instead of tips are the following:

The emitter area is larger by a factor of about 10^4. This leads to a decrease of short time statistical ion current fluctuations from about ±5 per cent to ±0.7 per cent. The long time reproducibility of mass spectra is also much better than with tips. The effective increase of ion intensity is about of a factor 100 which enables the use of a simple Faraday cup detector instead of a secondary electron multiplier. The fragment to parent ion ratio is reduced as compared with that obtained with tips.

A new field ion source equipped with a wire emitter and its application to problems of analytical chemistry are described.
Field Ionization and Field Dissociation of Organic Molecules

by

H. D. Beckey

Institut für Physikalische Chemie der Universität Bonn
Germany

The existence of a pure field-effect dissociation of molecules immediately after field ionization has been shown by different experiments using a field ion mass spectrometer. Fragment ions from surface reactions, which occur in certain systems, could be excluded with the systems under investigation.

The large variety of field dissociation processes observed in field ion mass spectrometer required more systematic treatment. This was done by assuming a basic model underlying the effect of field dissociation. The rules derived from the model could be confirmed experimentally by the F. I. mass spectra of homologous series of organic substances. (Contributions have been made by H. Knoppel, P. Schulze and G. Wagner of our group).

After derivation of the basic model it will be shown that field dissociation of organic ions is dependent of mainly four factors:

1. Interaction of the positively charged parts of the molecule with the external electric field.

2. Charge distribution in the molecule influenced by the electric field.

3. Internal interaction of the field dissociating parts of the molecule.

4. Orientation of the atomic groups next to the dissociating bond.

Each of these four main factors in turn is dependent on further factors which will be discussed, the most important ones being the mass to charge ratio and the electronic structure of both the field ionized molecule and the charged respectively uncharged fragments.

Finally, the kinetics of the process of field dissociation will be discussed. It can be shown that field dissociation is a completely "nonstatistical" process occurring during a period of one molecular vibration after field ionization. In addition to this process a "statistical" (metastable) decomposition of field ionized molecules is possible and observable if it occurs within a time between $10^{-8}$ and $10^{-5}$ sec. In this case vibrational energy is transferred to the ion by transitions of the Franck-Condon type. It could be shown experimentally that by raising the temperature a continuous transition from the nonstatistical to the statistical process is possible with molecules showing strong charge redistribution after fragmentation.
Field Condensation and Field Corrosion

Observed by Mass Spectrometry

by

J. H. Block
Union Carbide European Research Associates, Brussels

The interaction of formic acid dipoles with a metal surface (W, Mo, Ni, Au and Pt) in an electric field (10⁷ to 10⁸ V/cm) causes field corrosion. For metals such as W, Mo and Ni this occurs at 20°C. Other metals like Au and Pt require high temperatures.

Dielectric layer formation and surface roughness created by field corrosion change the mass spectrum of formic acid as regards both the observed mass distribution and the signal shapes.

1. On rough surfaces protected by dielectric layers the ionization zone is no longer an equipotential surface. Mass signals of a single focusing spectrometer are therefore broadened.

2. Field condensation of formic acid is connected with the appearance of associates: HCOOH•H⁺, HCOOH₂H₂O⁺, (HCOOH)₂•H⁺, etc.

3. The dependence of intensities on temperature is not always reversible.

Other experimental observations are less understood. Thus the preionization easily observed with hydrocarbons such as benzene does not occur with formic acid under comparable conditions. The thermal decomposition of formic acid is normally a dehydrogenation on metal surfaces but the application of an electric field tends to favor dehydration. Energetic estimations of field effects may lead to an interpretation of this behavior.
Field Impulse Desorption; Rate Determination
of Cyclohexane Chemisorption on Platinum

by

J. H. Block
Union Carbide European Research Associates, Brussels

The adsorption and chemisorption of cyclohexane on platinum has been investigated by field-ion mass spectrometry. The field dependence of parent and fragment signals, as well as the mass spectrum under conditions of preionization, indicate that some fragments (mainly C₆H₁₁⁺) are formed by interaction with the metal. Surface structures such as Pt-C₆H₁₁ etc. have to be regarded as chemisorption layers, Pt-C₆H₁₂ is the adsorption layer. By field impulse desorption surface layers have been analyzed.

Experimentally variable pulse lengths (10⁻⁷ to 10⁻⁴ sec) and variable signal repetition rates (between 10³ and 10 per sec) have been used. By variation of pulse repetitions adsorption and chemisorption times between 0.1 sec and 100µ sec can be measured.

Chemisorption and adsorption isotherms are different for stationary and pulsed fields. Higher molecular attraction and lower chemisorption saturation at stationary fields explain the difference qualitatively.

The rate of chemisorption of cyclohexane gives evidence for an energetic heterogeneity of the platinum surface. Rates decrease with increasing chemisorption time or saturation. By comparison of times necessary for adsorption and for chemisorption, it has been found that part of the chemisorption layer is formed via an adsorption layer. Absolute rate constants of chemisorption may be calculated if the process is regarded as completely irreversible.

At higher temperatures new chemisorption products are formed and indicate the beginning of a catalytic dehydrogenation of cyclohexane.
Mass Spectrometric Investigations of the Field Ionization of Water Vapor on Tungsten, Platinum and Iridium Tips.

By

Werner Schmidt
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

In earlier investigations Inghram and Gomer and especially Beckey investigated the field emitted ions of water vapor as they formed on tungsten tips. These measurements were supplemented in several ways and furthermore extended to the systems Pt/H₂O and Ir/H₂O. The ion currents start very sharply immediately with large intensities at well defined field strengths. The latter are characteristic for each system (W/H₂O: 20 MV/cm, Ir/H₂O: 51 MV/cm, Pt/H₂O: 61 MV/cm).

The dependence of the relative abundances of the different ion species on the field strength was studied systematically. In the system W/H₂O except the well known ions H₃O⁺, (H₂O)⁺, n = 0, 1, 2, 3 many ions in the higher mass range were detected. Analysis of the latter showed that these are tungsten oxide ions in different states of oxidation and ionization with or without water molecules associated. In this way the etching effect of water, described first by Müller and Mulson, was demonstrated directly. At the field strength ions appear first, in the system Pt/H₂O and Ir/H₂O only H₂O⁺, (H₂O)⁺, n = 0, 1, 2 were detected. Higher field strength produced O⁺ and H₂O⁺. However on these tips no "etching effect" was observed between 60 and 120 MV/cm.

An explanation will be given for the sudden rise of the ion current at a characteristic field strength, and the dependence of the latter on the character of the metal. A rough estimate shows that already at these field strengths the ionization probability of H₂O is close to one.

The mechanism of the reactions initiated by the field ionization of H₂O on tungsten, platinum and iridium tips will be discussed.
Field Emission Spectroscopy*

by

Allan M. Russell
Department of Physics
University of California, Riverside

Measurements of the energies of electrons obtained from a semiconductor by field emission show promise of contributing information on the details of electron energy levels at the surface of the solid. Although theoretical work by Harrison\(^1\) indicates that the density of states cannot be determined by measuring the energies of electrons obtained from metals, the location of energy levels in semiconductors can be measured directly.

Recently, Callaway\(^2\) has published some calculations of the effects of high electric fields on the optical absorption of semiconducting compounds. A Stark-like splitting of electron energies into Landau levels is expected to be detectable in absorption measurements. It is believed that these may also be observable in field emission.

Results of measurements made on silicon and preliminary efforts to detect Landau levels in CdS by photostimulated emission will be described.

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*Supported, in part, by the Office of Naval Research
The Simultaneous Determination of the Work Function
and the Field Strength at the Surface of a Field Emitter

by

A. van Oostrom
N. V. Philips' Gloeilampenfabrieken

The size and shape of a field emitter tip can be determined from an
electron micrograph. Unfortunately the field strength across the tip surface
cannot be found in this way with a very high accuracy. Several methods to
overcome this problem will be briefly discussed.

A field emission analyzer is described which measures the total energy
distribution of electrons emitted from single crystal planes. The electrons
coming from a plane, selected by magnetic deflection, pass through an aperture
in the anode and are subsequently focussed in the center of a metal half-sphere
which serves as the collector. The properties of the lens have been studied
with a resistance network and an analog computer. Good agreement has been
found between results obtained with the network and the actual field emission
tube. The resolution of the analyzer is about 10 mV.

The total energy distribution has been calculated and a simple relation
between the half-width and the temperature has been found to exist over a wide
range of values of current density.

From the measured half-width of the energy distribution and the Fowler-
Nordheim plot the work function of single crystal planes of tungsten have been
determined with an accuracy of about 2%. For such good emitting planes as
f.i. (421) the work function derived from the slope of the Fowler-Nordheim
plot in the ordinary way falls within the experimental error of the energy distri-
bution measurements. Among other results to be discussed, will be the (110)
plane of tungsten and the system carbon on tungsten.
Field Emission Microscope Study of Niobium

by

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Experimental patterns have been obtained on contaminated and clean niobium surfaces. It is concluded that the equilibrium thermal end form consists of flat regions of low index crystallographic directions smoothly joined by curved transition regions to give an approximately spheroidal shape. Some evidence of faceting is seen in high magnification electron microscope shadowgraphs of some of the emitters. The surface film left by etching is removed with difficulty by flash heating in the FEM. Gases sorbed from the residual vacuum are easily removed and the clean pattern restored. The patterns obtained for niobium are strikingly similar to those observed by others for tantalum.
Surface Diffusion in Nucleation on Field-Emitter Substrates

by

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It has been realized for some time that surface diffusion kinetics in adsorption on field-emitter surfaces can be quantitatively described by measuring the rate of migration of a boundary across the surface. This method, however, implicitly assumes that a sufficient work function change in adsorption occurs so that a boundary can be detected. In this work, aimed at clarifying the nature of nucleation on substrates in deposition of metal from vapor, it was found that adatom diffusion rates could be measured under conditions where a migrating boundary was not observed. In these experiments the conditions required for an appreciable nucleation rate of silver, nickel, cadmium, and zinc on tungsten field-emitter surfaces was determined over the temperature range 75 to 350K. Since these metals have large adatom desorption energies in adsorption on tungsten, the critical adsorbed concentration for nucleation was given directly by the product of impinging flux and deposition time. However, at high substrate temperatures it was found that this relation was not obeyed even though desorption of adatoms was inappreciable. If the adatom concentration diffusing to the back side of the emitter is taken into account one can predict that nucleation kinetics should be described by plots of reciprocal nucleation time vs. impinging flux at a constant substrate temperature. These plots fit the experimental data and imply that the activational free energy for surface migration is about 0.4 eV in the observed cases.
The Desorption and Migration of Strontium on Tungsten*

by

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A study of the kinetics of the thermal desorption and migration of Sr on W has been performed in which the field electron microscope was used to identify the state of the adsorbate-substrate system. The activation energy for the thermal desorption of Sr from W was found to decrease with increasing Sr coverage, falling from a value of $97 \pm 5$ kcal/mole at zero coverage to $41 \pm 3$ kcal/mole at "monolayer" coverage. This latter value approaches the heat of sublimation of bulk Sr, 39 kcal/mole. The desorption energies found using field emission techniques deviated markedly from the extrapolated thermionic results of Moore and Allison\(^1\) near $\theta = 0$ and for $\theta > 0.5$. A linear relationship was found to exist between the activation energy for desorption and the logarithm of the pre-exponential factor in the rate equation, $k \frac{kT}{h} e^{\Delta S^*/R}$.

The surface diffusion of an initial Sr deposit less than one atomic layer was observed using a pulsed viewing voltage and was found to proceed with an activation energy of $36 \pm 5$ kcal/mole. The rate controlling process for this type of surface migration was considered to be diffusion from site to site on the W surface.

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Magnesium on Tungsten System

by
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U. S. Department of Commerce
National Bureau of Standards

The deposition, migration and desorption of magnesium on tungsten have been studied with a view to a later study of the oxidation of the magnesium layer. Second layer migration of the magnesium shows considerable anisotropy with an average $E_a$ of about 13 kcal/mole. The migration is easiest on the 110 and 111 planes, more difficult on the 211 and most difficult on the 100. Desorption is rapid at 225°C leaving a clean tip even when the deposit has had slight exposure to oxygen. Preliminary oxidation experiments show no signs of "island nuclei".
Oxidation of Tungsten and Tantalum

by

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Initial stages in the oxidation of tungsten and tantalum have been studied in the field electron emission microscope. Clean substrates at temperatures above 30°C have been exposed to oxygen pressures of $10^{-4}$ to $10^{-8}$ mm Hg. The emission patterns exhibit highly localized discontinuities in emission intensity after exposure to relatively high temperatures and pressures. Interpreting these discontinuities as being the result of first-order phase transformations, the course of reaction may be described as follows.

Below 400°C, the tungsten oxygen reaction is characterized by stable adsorbed states with no noticeable tendency for oxide formation. At temperatures between 400°C and 1000°C the adsorbed state is followed by the simultaneous nucleation of many oxide crystallites in preferred regions of the substrate. In contrast, the nucleation of oxide on tantalum at temperatures between 800°C and 1100°C occurs at random sites on the surface, is characterized by an increase in the number of crystallites with increasing reaction time (at constant temperature and pressure), and exhibits no grain boundary preference. The crystallites formed at 800°C have been identified as $\beta$-Ta$_2$O$_5$ by electron diffraction. Sub-oxides have not been observed.
Desorption by Low Energy Electron Impact

by

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and

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The effect of low energy electron impact (energies up to 150 ev) on adsorbed layers of hydrogen, oxygen and carbon monoxide on tungsten has been studied using the field emission microscope. No change in the adsorbed layer could be detected within the limits of experiment for hydrogen; for oxygen and CO there are effects under certain conditions of coverage. Cross sections and upper limits for cross sections in the cases without effect are estimated. A brief account of possible mechanisms is given.
Co-Adsorption of Hydrogen and Potassium on Tungsten

by

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The adsorption of potassium on tungsten, and the co-adsorption of hydrogen and potassium on tungsten and the adsorption of hydrogen on potassium have been investigated by means of field emission, employing liquid helium cooling of the apparatus for the maintenance of high vacuum. The behavior of K on W is qualitatively similar to that observed for Ba or Cs, with respect to work function vs. coverage, and surface diffusion behavior. Adsorption of molecular hydrogen on heavy potassium deposits or the co-adsorption of hydrogen and potassium on tungsten lead to no work function of pattern changes below 300 K where rearrangements and some work function decreases are observed. This is tentatively interpreted as a surface reaction between potassium and hydrogen, the tungsten surface acting as catalyst. Further evidence for this interpretation comes from the increased activation energy for potassium diffusion on a tungsten tip on which hydrogen has been preadsorbed. This system is discussed as an example of possible catalytic studies on simple systems by means of field emission techniques.
FEM Observations with Molecular and Atomic Hydrogen Beams

by

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National Bureau of Standards

The use of molecular and atomic beams with the field emission microscope is instructive because of the highly controlled deposition that is possible. The experiments to be described were done with a completely bakeable system in which the initial pressure was in the $10^{-10}$ torr region. The field emission tube was operated at 4.2°K with axis of the tungsten emitter perpendicular to the beam in one set of experiments and parallel to it in another. The deposition process, the relationship between work function and coverage, and the formation of a monolayer will be discussed. The variables in these experiments were the temperature of the tip, the density of the beam, the time of deposition, the beam temperature, and the composition of the beam in terms of molecular and atomic hydrogen.
Investigation of the Thermal Desorption and
Surface Diffusion of Cesium on
Tungsten, Molybdenum and Rhenium*

by

L. W. Swanson, R. W. Strayer and F. M. Charbonnier
Field Emission Corporation

Thermal desorption and surface diffusion of cesium on tungsten, molybdenum and rhenium substrates have been investigated by pulsed field emission microscopy. Rates of desorption, surface diffusion and corresponding activation energies have been measured over a coverage range of 0 to 1 monolayer. Certain similarities in the low coverage surface diffusion of cesium on the \{100\} regions of the body-centered-cubic structures (i.e. tungsten and molybdenum) and the \{10\overline{1}\} regions of the hexagonal close-packed structures of rhenium were observed and attributed to the atomic scale similarities between these crystallographic regions. The variation in the zero coverage desorption energy of neutral atoms (2.4, 3.0 and 3.8 ev for molybdenum, tungsten and rhenium respectively) is proportional to the average work function of the substrates. In each case, the desorption energy decreases with increasing cesium coverage. For each substrate investigated the work function was found to decrease linearly with increasing cesium coverage to a minimum work function of about 1.50 ev and to increase at higher coverages to a work function approaching that of bulk cesium.

It also was observed for each substrate investigated that the coverage $\sigma_m$ corresponding to the work function minimum also coincided with a minimum in the surface diffusion rates and a reversal in the emission distribution. It can be shown that the occurrence of a two-dimensional phase change at $\sigma_m$ from a dilute phase involving predominately repulsive interactions to a condensed phase involving attractive interactions can explain most of the experimental observations.

* Supported by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio.
Investigation of the Thermal Desorption and Surface Diffusion of Cesium on Tungsten with Varying Amounts of Oxygen

by

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Field Emission Corporation

The thermal desorption and surface diffusion of cesium on tungsten with varying amounts of oxygen have been investigated by pulsed field emission microscopy. The presence of oxygen has been found to markedly affect the rates of both desorption and surface diffusion and also the emission distribution. A preliminary investigation of the variation of these processes with increasing amounts of oxygen has been performed and has led to the following conclusions:

1. The adsorption and desorption of cesium on oxygen-covered tungsten appears to be reversible until the onset of incipient oxide formation and/or thermal desorption of the chemisorbed oxygen. The shape of the work function versus coverage curves are similar to that observed to cesium adsorption on clean substrates and presumably is controlled by a similar mechanism in both cases.

2. A decrease in the minimum work function from 1.5 to 1.15 ev and a decrease in the amount of cesium required to reach the minimum work function occurs with increasing oxygen coverage and can be attributed, at least partially, to an increase in the initial depole moment of the adsorbate.

3. As in the case of clean tungsten, a minimum in the diffusion coefficient and a corresponding reversal in the emission distribution at the cesium coverage corresponding to the minimum work function suggests the occurrence of a two-dimensional phase change as noted previously.**

4. An increase in both the activation energy for thermal desorption and surface diffusion with increasing oxygen coverage is evidence that oxygen induces a stronger bond between the adsorbed cesium and substrate.

* Supported by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio.

** Preceding Abstract
The Chemisorption of Gases on Tungsten

by

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The previously reported results on the significance of surface order in chemisorption have been extended in several directions. These include the study of surface stability as a function of temperature to set an upper limit on the useful experimental temperature range, the inclusion of samples containing grain boundaries and dislocations in the adsorption studies, and the sequential adsorption of reactive gases. Effects observed included a polarity sensitive, field induced surface mobility; relative surface disordering due to the chemisorption of different gases; and surface reactions. None of these showed any observable sensitivity to the degree of surface order or the presence of grain boundaries and dislocations.
Field Emission from Silicon

by

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and

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Field evaporation of silicon surfaces was rendered possible through the use of suitable preliminary treatment. One thereby obtains an atomically clean surface with unchanged doping of the material. The experimental results of field emission from silicon do not agree with theoretical predictions. There is a correlation between the Fermi-level in the bulk and the apparent work function: the latter is high when the Fermi-level is near the conduction band, and lower when the Fermi-level approaches the valence band. This behavior may be explained qualitatively through quantisation of the electron states in the space-charge region. Surfaces subjected to field evaporation have less than $5 \times 10^{12}$ acceptor surface states/cm² in the energy gap. The experiment provides no information about surface donors.
Field Emission From Germanium

by

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Studies of electron field emission have been made on germanium crystals cleaned entirely by field evaporation. In contrast to the emission from n-type samples, the emission from p-type germanium showed considerable light and temperature sensitivity and demonstrated pronounced deviations from the Fowler-Nordheim equation. Heating above 250°C caused a gradual disappearance of the unusual behavior, presumably by permitting inward diffusion of doping impurities along the shank of the tip.

From the results of measurements of spectral dependence, response to chopped light and energy distribution of the emitted electrons, it is believed that this behavior is due to inversion of the surface by the external field. Current flow across the resulting depletion layer between the p-type bulk and n-type surface region can produce very large internal fields (>10^4 V/cm) before breakdown occurs. Evidence for carrier multiplication and heating by the internal field has been obtained.

The energy distribution of electrons emitted from germanium has shown no band structure and appears indicative of emission from a degenerate surface region for all dopings.
Adsortion, Diffusion, and Epitaxial Growth of Cu/W

by

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The adsorption of Cu/W was examined over the temperature range 78 - 1100°K for a limited range of Cu flux density. Activation energies were measured for surface diffusion of one, two, and three atomic layers of Cu, for successive diffusion of one layer upon another up to four layers and for thermal desorption of Cu from W. The negative D.C. electric field used (~40 x 10⁶ V/cm) was found to decrease the activation energies by about 30%, and the controlled addition of oxygen or nitrogen increased the activation energy.

Epitaxial growth of large single-crystal layers of Cu occurred in the approximate temperature range 570 - 1100°K., at least. Nucleation occurred in patches at {011} step sites rather than homogeneously and was sensitive to small amounts of surface contamination. Details of the epitaxial relationship will be given and the role of surface diffusion will be discussed.
The Adsorption of Copper on Tungsten

by

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Although field emission microscopy has been used to study the deposition of metals in the form of whiskers (e.g. Melmed and Gomer 1961) and in thick films (e.g. Ashworth 1951, Melmed 1963), the conditions controlling condensation and evaporation of deposits of few atom layers thick are little known.

This paper reports experiments on the behavior of copper (f. c. c.; atomic radius 2.55 Å) on clean, flashed (2300°K) tungsten (b. c. c.; atomic radius 2.73 Å); measured deposits, giving coverages up to about 10 atom layers were used. Localized thick deposits, formed by condensation, spread by diffusion at or above 400°C to give uniform coverage. Depending on the coverage after spreading, the apparent work function derived from the Fowler-Nordheim relation shows three successive and reproducible stages of change:

1. An initial rise from 4.52 ev. to a maximum of 4.8 ev. for a dose N equivalent to about 3 monolayers incident;

2. A decrease to a minimum of 4.2 ev. as the dose N is increased from ca. 3 to ca. 9 monolayers;

3. A small subsequent rise for N>9 towards the value (4.3 ev.) typical of a thick copper deposit.

At temperatures above 1000 - 1100°C, copper evaporates and the changes in φ are reversed. The kinetic characteristics can be correlated with the φ-N relations summarized above, and reflect differences in the binding of copper atoms on layers of progressively decreasing mean thickness. Starting with deposits for which N>9, (stage 1) φ remains constant with time (e.g. at 1100°C) and then drops abruptly to its minimum value (4.2 ev.). In this "induction period", desorption rate is independent of coverage and the desorption energy Ed(1) = 64 ± 3 kcal mole⁻¹. In stage 2, N decreases from ca. 9 to about 3 monolayers coverage; φ rises progressively, according to a first-order rate law, to a maximum limiting value which remains unchanged for long times of heating at 1100°C; desorption energy Ed(2) = 70 ± 7 kcal mole⁻¹. Stage 3 is achieved at higher temperatures (> 1200°C). The last 3 atom layers are desorbed and φ returns to the value for clean tungsten. Ed(3) = 95 ± 6 kcal mole⁻¹. Stages 1 and 2 correspond to the desorption of copper from a copper surface; stage 3 to a stronger, thin-layer interaction of copper with tungsten.

The processes are related to changes in field emission patterns accompanying condensation, spreading and desorption, and are discussed in terms of the microtopography of the thermally annealed tungsten surface as revealed by field ion microscopy.
Investigation of Oxygen Chemisorption on Copper Whiskers

by

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Copper whiskers have been grown in situ by vapor deposition on tungsten and platinum substrates in an FEM tube at background pressures of less than $1 \times 10^{-9}$ torr. FEM patterns will be presented which are unusual for a face centered cubic metal. The patterns are stable up to the melting point and are dependent on the substrate material.

Possible causes of the anomalous patterns will be discussed and the behavior of the patterns when exposed to small amounts of oxygen will be illustrated. The oxygen is initially adsorbed on the \{110\} planes. After further exposure spreading occurs to the \{100\} planes. Emission from the \{111\} planes is relatively unchanged by the oxygen.

The above results are independent of temperature although the partial pressure of oxygen required for initiation of a change in the FEM pattern is lower for lower temperatures.

Fowler-Nordheim data have been obtained and estimates of the change in work function due to oxygen chemisorption determined.
Thermal Rearrangement of Iridium Surfaces

by

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The rearrangement of iridium surfaces heated at temperatures of 260 to 980°C was studied in the field ion microscope. Discontinuous heating of the iridium wire resulted first in the breakup of the high-index facets of the field-evaporated surface and then in the growth of the low-index planes. The growth of the (001) plane was followed at four different temperatures. It was concluded that the kinetics of the surface migration were influenced by traces of impurities in the residual gas.

In the presence of 10⁻³ Torr oxygen, migration occurred more readily and was observed at temperatures as low as 260°C. The (001) layers near the apex of the tip became square, bounded by edges of low kink density. The steps separating the (001) layers agglomerated to form steps several atomic units high. On the {113} and {110} planes the migration was anisotropic being faster in the close packed <110> directions. Many of the atoms migrating from the {113} and {110} planes redeposited at the {012}-{023} regions. At the lower temperatures the deposition occurred with the formation of many defects.
A Research for Germanium Film on Tungsten Surface

by

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Behavior of semiconducting material on tungsten surface has been studied observing the images of field emission microscope (FEM) in ultra-high-vacuum.

Germanium atoms can migrate easily on the tungsten surface at certain elevated temperature and make relatively uniform layer, and then cause to reduce field emission current by a factor of ten or so.

The contribution to reduction of current seems to be largest at a certain quantity of the adsorbed Ge layer which is thinner than the saturated layer at nearly room temperature.

Desorption energy is determined at three different coverages; at relatively high coverage, ad-atoms are desorbed at \( \sim 1140^\circ K \), at about one atomic layer coverage, \( \sim 1580^\circ K \), and at very low coverage, \( \sim 2400^\circ K \). Desorption energy at these coverages is 1.6 eV, 3.3 eV, 4.2 eV respectively.

The anisotropy of surface migration of germanium atoms is observed in three different types:

1. The heavily deposited layer migrates nearly uniformly on tungsten surface, showing front sharp boundary of dark region.

2. The film of few atomic layers migrates with the following typical mode, that is, over the \([110]\) zone, the migration is easier and faster than that toward the \{100\} planes. In this case, the diffusion energy on the \{110\} plane, \{111\} planes, and toward \{100\} planes are measured respectively 0.6 eV, 1.0 eV, 1.3 eV.

3. When the deposited quantity of Ge correspond to one layer or less, dim boundary migration is observed. The migration energy of this process is 1.38 \( \sim \) 1.40 eV. The migration of the secondary deposited layer is similar to that of the first one.

These results are correlated with the surface structure of crystal and adsorbate atoms.
A Research of Tantalum-Oxide Thin Film

by Field Emission Microscope

by

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At first we will explain the methods of getting the field emission microscope image of clean Ta surface.

Raising the temperature of Ta tip from room temperature to 1100°~1350°K, and applying the superposed d.c. 8 kV and a.c. 13 kV voltage between tip and screen, we have got many interesting patterns showing change of crystal structure of tip by electric field evaporation. By recording 16 mm. moving picture, the evaporation process becomes very clear.

When oxygen is introduced into the interior of microscope and its pressure is raised to $3 \times 10^{-7}$ Torr from $2 \times 10^{-10}$ Torr at room temperature, oxygen atoms are absorbed and field emission pattern changes. If the tip is heated, oxidation of Ta occurs and field emission pattern changes.

Process of field desorption of this Tantalum-oxide is observed by raising temperature to 1450°K. If the thickness of the oxide layer is changed, the field emission patterns change very clearly. By counting numbers of the disappearing step rings of crystal from the central part of tip, we measured the rate of desorption. From this rate, we got that the activation energy of clean Ta is 0.95 eV and of Tantalum-oxide is 3.3 eV.
Energy Distribution of Field-Emitted Electrons

From Tungsten Covered by Thin Germanium Films

by

I. L. Sokolskaya and N. W. Mileshkina

Field emission from thin films of germanium on tungsten has been investigated recently by the authors\textsuperscript{1}. Germanium deposition lowers the field emission from tungsten. At a temperature of about 500\textdegree{}K germanium migrates over the emitter tip surface with a sharp boundary (Fig. 1a, 1b). This diffusion process is similar to the low-temperature diffusion of oxygen, hydrogen and nitrogen on tungsten\textsuperscript{2,3,4}. The first germanium layer lowers the field emission current by a factor of about 25 with respect to clean tungsten. If additional germanium is deposited on one side of the tungsten tip, the second layer moves over the surface with a sharp boundary (Fig. 1c). When the second layer has covered the entire surface, the current decreases by a factor of about 45 with respect to clean tungsten. The slope of the Fowler-Nordheim plots for tungsten fully covered with Ge in the low-voltage region is the same as it is for clean tungsten, which means that the average work function is unchanged. However, the Fowler-Nordheim plots in the high-voltage region have a higher slope as shown in Fig. 2. The corresponding work function is estimated to be 5.2 eV.

The energy distribution was studied in an experimental tube of the type described by Young and Müller\textsuperscript{5}. Typical energy distribution curves of field-emitted electrons for clean tungsten are shown in Fig. 3a. The half-widths of the most of experimental curves measured in different tubes are 0.23 - 0.37 eV. Fig. 3b demonstrates energy distribution curves for tungsten tips covered by germanium films. It exhibits two well-defined peaks. The first of them coincides with the peak of the clean tungsten, while the second is displaced to the low-energy region. The distance between the two peaks is 0.8 - 1.0 eV for different tubes. When the thickness of the film is increased the height of the first peak decreases, while that of the second one increases (Fig. 4).

When the germanium film is removed the second peak disappears, while the first peak remains unchanged in shape. It had to be noted that metal coverage such as Ti film does not change the shape of the clean tungsten energy distribution curve.

Germanium films, which lower the field-emission current from the tungsten emitters, are unusually stable with respect to the residual gas contaminations; under usually vacuum conditions of about 10\textsuperscript{-9} mm, Hg the field current from this "dark" film remains unchanged during several days.
Discussion of the Results

We proposed to interprete these results by semiconducting properties of the thin germanium films. The following mechanism seems to explain the results satisfactorily. Deposited germanium forms a chemisorbed film of germanium after heating at about 500°K and spreading with a sharp boundary over the entire surface. The adatoms of this film are bound by covalent bonds and form a semiconducting layer in contact with the metal substrate. The thickness of the film is much less than the Debye length and therefore the work function of the film does not differ from that of the substrate. The first peak of the energy distribution curve is due to the electrons from the metal, which can tunnel through the semiconducting film representing an additional potential barrier for such electrons (Fig. 5). The second peak can be attributed to electrons tunneling from the valence band of the germanium layer. An increase of the field-emission current, which leads to an increase in the slope of the Fowler-Nordheim plot in the high-voltage region (Fig. 2) can be ascribed to the additional emission from the valence band of the germanium film.

Recent results of Russell show a similar shape of energy distribution curves of field-emitted electrons from silicon.

References
