N71-17869

NASA TECHNICAL
MEMORANDUM

NASA TM X-2187

NASA TM X-2187

A LITERATURE SURVEY OF SOME SURFACE AND SUBSURFACE PROCESSES AFFECTING MATERIALS IN THERMIONIC DIODES

by Leonard K. Tower

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1971

1. Report No. NASA TM X-2187	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle A LITERATURE SURVEY OF SOME SURFACE AND SUBSURFACE PROCESSES AFFECTING MATERIALS IN THERMIONIC DIODES		5. Report Date March 1971 6. Performing Organization Code
7. Author(s) Leonard K. Tower		8. Performing Organization Report No. E-5987
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 120-27 11. Contract or Grant No. 13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

This report is a literature survey of surface and subsurface chemical and physical processes affecting materials in the thermionic diode. The processes considered were the evaporation and condensation of substrate materials, the bulk diffusion of metallic substrate materials, reactions between insulators and metals, and the surface self-diffusion and reconstruction of clean surfaces, faceting, and other surface reconstruction caused by contaminants or additives, solution, and oxidation.

17. Key Words (Suggested by Author(s)) Thermionic diodes Surface chemistry Surface physics	18. Distribution Statement Unclassified - unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 38	22. Price* $3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

A LITERATURE SURVEY OF SOME SURFACE AND SUBSURFACE PROCESSES AFFECTING MATERIALS IN THERMIONIC DIODES

by Leonard K. Tower

Lewis Research Center

SUMMARY

This report is a literature survey of surface and subsurface chemical and physical processes affecting materials in the thermionic diode. The processes considered were the evaporation and condensation of substrate materials, the bulk diffusion of metallic substrate materials, the reactions between insulators and metals, the surface self-diffusion and reconstruction of clean surfaces, faceting and other surface reconstruction caused by contaminants or additives, solution, and oxidation.

INTRODUCTION

The thermionic diode is a collection of interfaces or spaces between materials of unlike composition. Because of these inhomogeneities, processes result that can be lumped under the general heading of surface chemistry. There are interfaces between the solid conductors, insulators or containment walls and the gas or vacuum phases. There are contacts between insulators and metallic conductors. Also, there are contacts between unlike metals.

Figure 1 summarizes these contacts and some of the resulting physico-chemical processes which are surveyed herein. For the purpose of discussion in this report, two broad subdivisions of topics are made in the processes indicated in figure 1. In category I are placed those interfacial processes that can be expected in all diodes including the highly idealized vacuum diode: evaporation and condenstation of substrate materials, bulk diffusion of metallic substrate materials, reactions between insulators and metals, and surface self-diffusion and reconstruction of clean surfaces.

In practice, no true vacuum diode can be constructed. To the foregoing processes must be added those surface processes resulting from inevitable gaseous contaminants.

The inability to create perfect laboratory vacua gives rise to atmospheric contaminants. In addition, construction materials evolve gaseous contaminants either because of chemical decomposition, as in the case of insulator compounds, or because of impurities.

Although some gas phase contaminants are unavoidably present, additional contaminants may be deliberately introduced to affect the properties of the surface or the gas phase. Cesium, of course, is the most familiar example of such an additive. Cesium, barium, and other metallic additives will not be considered here since little chemical effect on substrate materials has been reported for them. However, the use of such electronegative additives as oxygen and fluorine in conjunction with metallic additives has been found beneficial to diode performance (refs. 1 to 3).

Processes involving the chemical interaction of these electronegative materials with substrate metals are placed in category II: chemisorption, faceting and other surface reconstruction caused by contaminants or additives, and solution and oxidation. Chemisorption, the initial stage in the chemical interaction of gases with substrates, is not considered as a separate topic.

A general survey of surface chemistry as related to thermionic diodes must encompass the following metals, which have been, or are being, considered for diode construction: hafnium (Hf), molybdenum (Mo), nickel (Ni), niobium (Nb), osmium (Os), rhenium (Re), tantalum (Ta), and tungsten (W).

Contaminants and potentially interesting additives that are likely to produce changes in the preceding substrates are carbon (C), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O), nitrogen (N), and the halogens.

DISCUSSION

CATEGORY I - SURFACE AND SUBSURFACE PROCESSES INVOLVING SUBSTRATE MATERIALS ONLY

Evaporation and Condensation of Substrate Materials

Large temperature differences between surfaces in the diode cause emitter material to be deposited on the collector. Similarly, emitter and collector metal may appear on insulators after a period of time.

Condensation of metals on insulators. - This effect is of concern in long-life diodes where conducting paths across insulators result in electrical shorts. The magnitude of the problem in any given situation can be expected to be related to a few obvious macroscopic variables: the lifetime desired; the amount of metallic area exposed to the insulator, which along with the metal temperature, determines the metal atom flux; and the degree of metal supersaturation at the insulator temperature. The degree of metal supersaturation is defined as the ratio of the vapor pressure required at the surface for the onset of condensation to the vapor pressure of the condensate above its own bulk phase at the same temperature.

Data concerning the nucleation of refractory metal thin films on insulators appears to be nonexistent as yet. Inasmuch as insulator shorting can be a failure mechanism, it may be encountered with growing frequency as converter life is extended. Much more experimental data will be required to assess the severity of the problem and to facilitate the design of converters that minimize it.

Available theories used for the analysis of experimental data of heterogeneous nucleation have been reviewed by Hirth and Pound (ref. 4), Rhodin and Walton (ref. 5), and Hruska, Hirth, and Pound (ref. 6). Three theories have been advanced, which differ in the degree of supersaturation to which they are applicable. These theories pertain to different ranges of size for the critical nucleus. The critical nucleus is that size of condensed particle whose free energy of formation from vapor atoms is a maximum. This free energy represents the thermodynamic barrier which the system must surmount in condensing spontaneously to form a bulk phase. The Hruska theory for critical nuclei containing more than 10^3 particles applies to a very low supersaturation. An important mechanism in the Hruska theory is the formation of critical nuclei by the impingement of mobile subcritical nuclei that are larger than the monomer.

For critical nuclei containing between 20 and 10^3 atoms, with a somewhat greater supersaturation, the theory of Pound, Simnad, and Yang (ref. 7) is applicable. The critical nuclei in this theory grow by addition of single particles (monomer) either from surface diffusion or direct impingement. The nuclei were considered to be cap shaped with properties of the bulk material ascribed to them. In a modification of the theory the nuclei are considered to be disk shaped. Experimental data consistent with either nuclei shape have been obtained.

For very large degrees of supersaturation pertaining to nuclei of less than five particles the theories of Hirth and Rhodin and Walton have been devised (ref. 5). The theory of Rhodin and Walton relates the shape and energy of some very small clusters (3 or 4 atoms) to the orientation and growth rate of thin films on the substrate.

Rhodin and Walton (ref. 5) and Hirth and Pound (ref. 4) also dealt with the rate of nucleation on imperfections. The theories predict that the rate of nucleation on cracks, holes, dislocations, and stepped planes of high Miller index number is far higher than on low index planes. These effects have been confirmed experimentally. Hirth and Pound questioned the effect of the thermal velocity of the condensate gas atoms in those cases such as molecular beams where the condensate source is at a different temperature than the substrate. Subsequently, Hruska and Pound (ref. 8) demonstrated for cadmium on glass that the beam source temperature has no effect. This suggests that the condensate equilibrates thermally with the substrate before nucleation and that arrival flux is a more important variable than source temperature.

Hirth and Pound (ref. 4) also discussed the possible effect of adsorbed impurities on the nucleation rate. Their conclusion was that contaminants will generally lower the condensation efficiency. Moreover, they pointed out that the validity of most nucleation experiments is thrown into question by the failure of investigators to insure clean surfaces.

Besides affecting the rate of nucleation the contaminant may alter the shape of the condensing nucleus by affecting the condensate-substrate interface energy. Thus, in thermionic converters, the rate at which nuclei coalesce to form conducting pathways on insulators may depend in part on the nucleus shape. If the nuclei wet the surface well, so as to remain thin, a continuous film may form rapidly. If surface wetting is poor, the nuclei may tend to be globular and thick, delaying the onset of a conducting film. Sundquist (ref. 9), in measuring surface energies of small metal particles, used the tendencies of some substrates to resist metallic wetting. He formed films of face centered cubic (fcc) metals (gold, silver, copper, nickel, and α and β iron) on beryllium oxide (BeO). When these films were suitably annealed they dispersed into tiny metal particles whose shapes, approximating those of free particles, could be observed. Sundquist chose BeO as a substrate because he expected it to resist wetting by metals more than other materials. The ability of insulators to resist wetting by condensing metals may be a significant factor in retarding electrical leakage.

In the thermionic diode cesium complicates this simple picture. Cesium, with its high vapor pressure relative to other metals, normally would not be expected on insulator surfaces which are above the cesium reservoir temperature. However, the nuclei of refractory metals present on insulators may encourage the cocondensation of cesium vapor on the refractory nuclei. In this event, the time to electrical breakdown may be reduced. Unfortunately, no data appear to exist on this problem of cocondensation on insulators.

Condensation of metals on metals. - The large temperature difference between emitter and collector assures that emitter material will in time be deposited on the collector in both vacuum and gas-filled diodes. Two concerns arise because of this process. One is the effect on converter life, the other is the effect on performance.

The mechanism of heterogeneous nucleation discussed previously may play a role in the condensation of emitter material on an unlike collector. However, the binding energies of emitter atoms to collector atoms should be of similar magnitude to the binding energy of emitter atoms among themselves. Since the equations for nucleation rate (ref. 4) depend exponentially on the binding energies, the nucleation rate may be very large indeed. The capability of forming at least a monolayer of emitter material on the collector then would seem to depend on (1) the rate of emitter evaporation and (2) the rate at which emitter material diffuses into the collector.

The net rate of loss of material from a metal surface can be estimated by the simple formula given in a review of evaporation by Hirth (ref. 10):

$$J = \alpha_V \frac{p_e - p}{\sqrt{2\pi mkT}} \tag{1}$$

where, with consistent units, α_V is the evaporation coefficient, p_e is the saturation pressure at T, p is the pressure of evaporating species adjacent to the surface, m is the mass of evaporating particle, k is the Boltzman constant, and T is the temperature of the surface.

Compilations of p_e for the elements are available (refs. 11 and 12).

Examination of an extensive review table of mass spectrometric results for the evaporation of inorganic materials by Drowart (ref. 13) reveals that the vapors of some metallic elements contain polymers. Equation (1) cannot be applied in a straightforward manner to these materials. Indeed, for such elements the vapor pressure data unadjusted for polymers (refs. 11 and 12) may be questionable. Fortunately, for the refractory metals of interest in converters no polymers have been observed.

Although emitter loss rates computed by equation (1) for some set of converter operating conditions may be negligible, evaporation cannot then be arbitrarily dismissed as a factor to be considered. For instance, preoperational processing may involve heating the components to temperatures considerably above the operating values. At the outset of converter life, emitter material may be present on the collector as found by Scott, Danko, and Chase (ref. 14). If the emitter and collector material differ, the performance which results may be attributed to the wrong materials.

On the other hand, Lawrence and Perdew (ref. 15) performed tests in which a thick layer of emitter tungsten was evaporated onto a nickel collector, with a resulting change in collector work function. After two weeks the collector work function returned to its value before the tungsten deposition although tungsten was still present on the collector. This was attributed to the masking effect of system contaminants.

Another fate which can befall emitter material deposited on the collector is diffusion into the collector lattice. Bulk diffusion will be considered in the next subsection.

Bulk Diffusion of Metallic Substrate Materials

The rate at which deposited emitter material diffuses into the collector, or the rate at which two metals at a cladding junction interdiffuse, is determined by equations for bulk diffusion in solids. These were reviewed by Shewmon (ref. 16).

A number of definitions have been established which are commonly employed in studies of metal diffusion. A discussion of experimental data requires clarification of these. The engineering definition of the diffusion coefficient D of two metals interdiffusing at a junction appears in the following differential equation for one-dimensional time-dependent diffusion:

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial N_1}{\partial x} \tag{2}$$

where N_1 is atom fraction of species 1 at coordinates x and time t. A similar equation applies to species 2. The origin of coordinate x is chosen at a great distance from the interface. Darken (ref. 17) showed that the chemical diffusion coefficient D is related to two other diffusion coefficients D_{12} and D_{21} thusly:

$$D = D_{12}N_2 + D_{21}N_1 \tag{3}$$

where N_1 and N_2 are mole fractions of species 1 and 2. Both D_{12} and D_{21} are functions of the local composition, thus, $D_{12} = D_{12}(N_1) = D_{12}(N_2)$, where $N_1 + N_2 = 1$. If the atom fraction of species 1 is made vanishingly small ($N_1 \rightarrow 0$, $N_2 \rightarrow 1$), the intrinsic diffusion coefficient D_{12}^* of species 1 in species 2 is observed:

$$D \equiv D_{12}^* \tag{4}$$

A common method of determining the intrinsic diffusion coefficient is by means of radioactive tracers. This technique has also been used to find self-diffusion coefficients. The assumption is made that the small difference in isotope mass is unimportant. The intrinsic diffusion coefficients D_{12}^* and D_{21}^* were shown to be related to D by Darken as follows:

$$\begin{aligned} D &= \left(N_2D_{12}^* + N_1D_{21}^*\right)\left(1 + N_2 \frac{d \ln \gamma_2}{dN_2}\right) \\ &= \left(N_2D_{12}^* + N_1D_{21}^*\right)\left(1 + N_1 \frac{d \ln \gamma_1}{dN_1}\right) \end{aligned} \tag{5}$$

where γ_1 and γ_2 are activity coefficients for species 1 and 2, defined in standard texts on chemical thermodynamics. For ideal solutions the γ are unity under all conditions.

Of course, the entire foregoing discussion is invalid as it stands if intermetallic compounds are formed.

A certain degree of regularity has been introduced into the study of metal diffusion coefficients as a result of the following empirical observations discussed by LeClaire (ref. 18) and Lazarus (ref. 19) concerning normal diffusional behavior:

(a) The temperature dependence of the intrinsic and the self-diffusion coefficients have the Arrhenius form

$$D = D_o \exp\left(\frac{-Q}{RT}\right) \tag{6}$$

where Q is an activation energy for diffusion, R is the universal gas constant, and T the absolute temperature.

(b) The energy Q for self-diffusion follows the approximation

$$\frac{Q}{R} \approx 17\ T_m$$

where T_m is the melting temperature in degrees K.

(c) The preexponential D_o falls in the range $0.05 \leq D_o \leq 5$ square centimeters per second.

Body centered cubic (bcc) metals have been observed (refs. 18 and 19) to fall into two classes. One class, comprising γ-uranium, β-titanium, β-zirconium and possibly vanadium, fails to satisfy one or more of the preceding criteria. The other class of body centered cubic metal, exhibiting so-called normal diffusional behavior, includes many of the refractory metals being considered for converters, namely, niobium, molybdenum, tantalum, and tungsten.

A complication arising in studies of metallic diffusion is the phenomenon of short circuiting. In polycrystalline materials, diffusion along grain boundaries can significantly increase the diffusion constant calculated from experimental data. Even in single crystals, diffusion along defects can greatly augment the transport process. Shewmon (ref. 16) reviewed the theory of high diffusivity briefly and cited some of the findings concerning this phenomenon: The coefficient for diffusion along grain boundaries must be about 10^4 times greater than the lattice diffusion coefficient to be detectable. The activation energy for grain boundary self-diffusion has been found to be 1/2 to 2/3 that of lattice diffusion for some common metals including silver, zinc, cadmium, and iron. As a result, grain boundary diffusion can be expected to predominate at low temperatures and lattice diffusion at high temperatures. Similarly, diffusion in single crystals along lattice dislocations can be expected to exceed the pure lattice diffusion coefficient at temperatures less than half the melting point.

The presence of these defect-caused diffusion processes can introduce difficulties in the taking or interpretation of meaningful bulk diffusion data. For example, Pawel and Lundy (ref. 20) stated that only in distances of less than 1000 Å from the interface is true bulk diffusion observed. Because of short circuiting in polycrystalline specimens, Hehemann and Leber (ref. 21) were unable to determine meaningful diffusional activation energies and preexponential for the columbium (now niobium) - tungsten system. Failure of other investigators to recognize the short-circuiting phenomenon may have resulted in the reporting of erroneous activation energies for some systems.

The experimental diffusion coefficients which follow are believed by the investigators to exclude the effect of short-circuiting. In real situations involving either polycrystalline materials or single crystals with defects, short circuiting will be present. Its importance in any given thermionic converter configuration may have to be determined experimentally.

For the diffusion of Nb^{95} in tantalum, Pawel and Lundy (ref. 22) found that

$$D(Nb^{95} \text{ in Ta}) = 0.23 \exp(-49\,700/T) \text{cm}^2/\text{sec} \tag{7}$$

within 20 percent. With the usual assumption that the isotope effect is small, this also represents the intrinsic coefficient for the diffusion of niobium in tantalum. The diffusion of Nb^{95} in tantalum was observed to be 85 percent faster than that of Ta^{182} in tantalum. Polycrystalline specimens were used above 1500° C. Below 1500° C, where short circuiting is a particular problem, single crystals were used.

For the diffusion of Ta^{182} in niobium, Lundy, Winslow, Pawel, and McHargue (ref. 23) found that

$$D(Ta^{182} \text{ in Nb}) = \left(1.0^{+0.9}_{-0.5}\right) \exp\left[(-50\,000 \pm 1200)/T\right] \text{cm}^2/\text{sec} \tag{8}$$

Both polycrystalline and single crystal specimens were used. They also found for the diffusion of Nb^{95} in niobium that

$$D(Nb^{95} \text{ in Nb}) = (1.1 \pm 0.2) \exp\left[(-48\,300 \pm 450)/T\right] \text{cm}^2/\text{sec} \tag{9}$$

Oxygen in atomic concentrations up to 450 ppm caused negligible effect. However, short circuiting was observed, and data showing evidence of it were not included in the foregoing determinations of D.

An interesting feature of the data of Lundy, Winslow, Pawel, and McHargue (ref. 23) is that the constants of equation (9) for the self-diffusion of niobium in niobium are remarkably similar to those of equation (8) for the diffusion of Ta in Nb. The actual coefficients are within a factor of about 2 of each other. This property has been observed for other refractory metal combinations (ref. 22). For combinations of metals with similar lattice constants, structure, and chemistry, where intrinsic diffusion coefficients are lacking, the use of self-diffusion coefficients may be justified as a first approximation.

To study the interdiffusion of niobium and molybdenum, Wyatt and Argent (ref. 24) welded niobium and molybdenum cylinders into diffusion couples. Over a wide range of alloy composition they found that the diffusion coefficient could be represented as

$$D = 1.5 \exp(-48\,000/T)\mathrm{cm}^2/\mathrm{sec} \tag{10}$$

Some scatter in the data prevented determination of the dependence on composition. Equation (10) thus represents both the intrinsic coefficient for diffusion of molybdenum into niobium, and the chemical diffusion coefficient (eq. (2)).

Hartley, Steedly, and Parsons (ref. 25) also studied niobium in molybdenum over a range of compositions. For molybdenum with a trace of niobium they determined the argument of the exponential to be -69 000/T and the preexponential to be 1000 square centimeters per second. Such a large preexponential is inconsistent with normal diffusional behavior (refs. 18 and 19).

The diffusion of Mo^{99} into molybdenum was found by Askill and Tomlin (ref. 26) to give self-diffusion coefficients for polycrystalline molybdenum of

$$D = 0.5 \exp(-48\,000/T)\mathrm{cm}^2/\mathrm{sec} \tag{11}$$

For single crystals they found

$$D = 0.1 \exp(-46\,400/T)\mathrm{cm}^2/\mathrm{sec} \tag{12}$$

Although the activation energy was lower for the single crystals, the diffusion coefficient for the polycrystalline specimens was about twice as large because of the larger preexponential.

Andelin, Knight, and Kahn (ref. 27) employed radioactive rhenium and tungsten tracers to study diffusion in tungsten. They found the intrinsic coefficient for diffusion of rhenium in tungsten to be

$$D(\mathrm{Re\ in\ W}) = (275\pm110)\exp\left[(-81\,900\pm1250)/T\right]\mathrm{cm}^2/\mathrm{sec} \tag{13}$$

The self-diffusion coefficient for tungsten was

$$D(W \text{ in } W) = (42.8 \pm 4.8)\exp\left[(-77\,000 \pm 300)/T\right] \mathrm{cm^2/sec} \tag{14}$$

The large preexponentials for tungsten tend to rank it with the other body centered cubic metals having anomalous diffusion behavior (refs. 18 and 19).

In monocrystalline nickel Ivantsov (ref. 28) found that the self-diffusion coefficient was

$$D = (2.59 \pm 0.08)\exp\left[(-35\,300 \pm 350)/T\right] \mathrm{cm^2/sec} \tag{15}$$

while in polycrystalline nickel,

$$D = (2.22 \pm 0.08)\exp\left[(-35\,000 \pm 350)/T\right] \mathrm{cm^2/sec} \tag{16}$$

Reactions between Metals and Insulators

Another phenomenon occurring at interfaces of dissimilar materials in converters is the chemical reaction between metals and insulators. From a practical standpoint these reactions can be divided into two groups. In some applications only support or physical contact is required, and chemical reactions are to be avoided or minimized. In other situations some degree of properly controlled interface reaction may be desirable. Seals are an example of this desirable situation.

The application of ceramic technology to the construction of satisfactory ceramic-metal seals has been facilitated by theoretical insight into the nature of interface bonding. Kingery (ref. 29) applied surface wetting and spreading theory to the prediction of ceramic-metal seal behavior. For example, ionic liquids are expected to wet solid metals without spreading, but liquid metals should not wet ionic solids. In some cases a change from an inert to an oxidizing sintering atmosphere promotes wetting by furnishing oxygen to the reaction at the interface. Adsorbed metallic fluxes such as titanium and zirconium can cause a lowering in interface energy which is beneficial to wetting, but ionic fluxes on oxide ceramics will tend to inhibit wetting. In some cases the effect of such flux additions are quite unexpected because of the number of variables which are changed by the additions.

A recent review of sealing problems (ref. 30) discussed some mechanisms of bonding. With some metal-insulator combinations, a glassy phase forms at the interface. In some cases the formation of this phase has been facilitated by an additive; for instance, manganese has been used in seals between Al_2O_3 and Mo to promote this layer. In another bonding mechanism a graded suboxide layer is formed between the metal and oxide by a reduction reaction in which titanium, zirconium, and niobium particles have been used. For some applications the use of a metal oxide flux aids the reduction reaction.

This effect was observed by Pincus (ref. 31), who applied MoO_3 powder to a seal between Mo and a ceramic composed mostly of Al_2O_3. The sintering temperatures required for a seal were far lower than when Mo powder was substituted for the MoO_3. Apparently a controlled oxidation of Mo metal occurs at the interface in each case. If MoO_3 is furnished, the oxygen required is evolved at a much lower temperature than it would be if the decomposition of Al_2O_3 is relied upon.

In the experiments of Armstrong, Chaklader, and Clarke (ref. 32), drops of molten nickel-titanium and nickel-chromium alloys were observed on flats of sapphire rods. The wetting angle between the drop and flat was used to compute the lowering of surface energy as a function of titanium or chromium concentration. The lowered surface energy resulted from the adsorption of an excess of these additives at the interface, as predicted by the Gibbs adsorption isotherm (ref. 33). Physical evidence of this segregation in the case of nickel-titanium alloys was given by X-ray diffraction which showed Ti_2O_3 at the boundary. No chromium compound was identified at the boundary for nickel-titanium alloys, but a change in sapphire color indicated chromium diffusion into the interface.

An earlier study by Allen and Kingery (ref. 34) involving nickel-titanium alloys on Al_2O_3 and tin-titanium alloys on Si_3N_4, $MoSi_2$, and SiC also suggested that titanium concentrates at the interface. The resulting decrease in interface energy appeared to be monotonic up to one monolayer of titanium.

Some new approaches to the construction of ceramic-metal seals have resulted from the advent of thermionic energy conversion. The necessity for simultaneous electrical isolation, good thermal conductivity, and tolerable thermal stress poses difficult problems. For thermionic applications graded seals appear promising. Gibson (ref. 35) investigated graded mixtures of niobium and Al_2O_3 powders, bonded by hot-gas isostatic pressing, with no brazing alloys to weaken the structure.

In another technique Kaufman, Tischler, and Breitweiser (ref. 36) employed niobium particles with an alumina coating of varying thickness. These particles were used to construct a seal of graded composition between niobium pieces. High shock resistance, thermal and electrical resistivity, and ease of fabrication are claimed for this seal.

In some diode applications a seal between the ceramic and the contacting metal is not required. Chemical reactions between the ceramic and metal may nontheless occur. If extensive condensed or gaseous reaction products are formed, these may prove very deleterious to the structure.

Grossman (ref. 37) surveyed reactions of tungsten, rhenium, molybdenum, tantalum, and niobium with Al_2O_3, BeO, ThO_2, Y_2O_3, and ZrO_2. From the thermochemistry of these materials he predicted that no solid oxides of the refractory metals would be formed by reaction with the ceramic oxides.

On the other hand, gaseous products are evolved from the contact of refractory metals and ceramic oxides. Chupka, Berkowitz, and Giese (ref. 38) observed the gaseous products resulting from the reaction of BeO and tungsten. Drowart, DeMaria, Burns, and Inghram (ref. 39) studied the gaseous species above Al_2O_3 in contact with tungsten and in contact with molybdenum. Figure 2 shows the total gas pressure (sum of the partial pressures) against $1/T$ for the systems studied in references 38 and 39.

Also shown are computations for the system $Nb\text{-}Al_2O_3$ from the data of Grossman (ref. 40). The enhanced total pressure for this system compared with $W\text{-}Al_2O_3$ and $Mo\text{-}Al_2O_3$ suggests that caution must be exercised in using $Nb\text{-}Al_2O_3$ contacts in thermionic systems at elevated temperatures.

Ackermann and Thorne (ref. 41) cited examples of several systems involving tantalum in which the metal interacts with the oxide ceramic to evolve substantial tantalum oxides. Among these systems are $Ta\text{-}Al_2O_3$, $Ta\text{-}ZrO_2$, and $Ta\text{-}ThO_2$. Therefore, the vaporization enhancement encountered with the $Nb\text{-}Al_2O_3$ systems may exist in these tantalum-containing systems also.

Surface Self-Diffusion and Reconstruction of Clean Surfaces

Clean surfaces, while not subjected to chemical attack, can undergo structural changes. The driving force for these changes is the effort of the surface to lower its free energy F. For a chemically clean system containing only a crystal and its vapor,

$$F = \int \gamma(\vec{\sigma})dA(\vec{\sigma}) \tag{17}$$

where $\gamma(\vec{\sigma})$ is the surface tension for a surface area element $dA(\vec{\sigma})$ whose orientation is described by the unit normal vector $\vec{\sigma}$.

Mullins (ref. 42) discussed the dependence of the equilibrium shapes of small particles of clean materials on the variation of γ with crystallographic orientation $\vec{\sigma}$. Conversely, the variation of γ with orientation has been studied by Sundquist (ref. 9) and Winterbottom (ref. 43) for small metal particles on a nonwetted BeO substrate.

Mullins also considered the conditions under which a clean, plane, monocrystalline surface of orientation $\vec{\sigma}$ might be expected to facet. While retaining this mean orientation, the surface may in principle be able to break up into facets of other orientation, reducing the free energy (eq. (17)) despite the increase in total area. Figure 3 illustrates the process.

As yet, no theoretical prohibition against such faceting has been presented. On the other hand, no evidence for faceting has been found under conditions where the surface is known to be absolutely free of contaminants.

Perfectly clean surfaces can undergo local rearrangement because of the presence of surface irregularities. For instance, the surface intersection of a grain boundary in a polycrystalline material with a surface protrusion or depression represents a thermodynamically unstable arrangement. As a result of such irregularities, a gradient in the chemical potential exists locally on the surface. This gradient provides the driving force for surface self-diffusion, described by the expression

$$\vec{J} = -\frac{N_0 D_s}{kT} \nabla \mu \tag{18}$$

where $\vec{J}$ is the vector for net flux of atoms along the surface, N_0 is the surface atom density, k is Planck's constant, and $\nabla \mu$ is the chemical potential gradient parallel to the surface. In general D_s, the surface self-diffusion coefficient, can be expected to be anisotropic, so that J and $\nabla \mu$ will not be parallel.

Gjostein (ref. 44) reviews experimental techniques by which the propagation of machined scratches and sinusoidal waves and thermal grain boundary grooves have been used to deduce the surface self-diffusion coefficient. While bulk self-diffusion, evaporation, and condensation participate in these processes, the principal contribution is usually from surface self-diffusion.

The methods of observing surface self-diffusion reviewed by Gjostein depend on mass transfer. On an atomic level surface self-diffusion has been studied by means of the field ion microscope. Bassett (refs. 45 and 46) evaporated clean tungsten tips by means of high fields. The tips were then annealed at successively higher temperatures with no field. At the beginning and end of each anneal the field ion patterns were examined for evidence of atom displacement between kink sites on the (110), (111), and (100) terraces. Activation energies for diffusion could be estimated from the temperature dependence of these displacements. The calculated energies were between 1.8 and 2.3 electron volts (174 000 and 222 000 J/mole). These energies were much lower than values computed using the assumption of pair bonding with an inverse sixth power attractive potential, and single-bond energies derived from the heat of sublimation. Probably the most interesting result here is the relatively low temperature (500 K) at which surface reconstruction was observed to begin.

Ehrlich and Hudda (ref. 47) studied the surface self-diffusion of tungsten atoms deposited on a field ion microscope tip from an evaporative source. Diffusion took place during a heating cycle with no field applied; observation of the field ion microscope patterns was at 20 K. Mobility as a function of surface orientation increased in the order (211) > (321) ~ (110) > (310) ~ (111). The coefficient for the (110) plane was D =

3×10^{-2} exp(-11 000/T) square centimeters per second. For the (321) surface, D = 1×10^{-3} exp(-10 000/T), and for (211), D = 2×10^{-7} exp(-6500/T).

Ehrlich and Hudda pointed out that the experimental differences in diffusion activation energy between the (321) and (211) planes are not predicted by simple pair interaction. Bassett (refs. 45 and 46) also found this concept inadequate. Ehrlich and Kirk (ref. 48), in an analysis using a Morse potential, incorporated the effect of fluctuations in lattice atom positions as the adsorbed atom moved. The energy of these displacements, when included in the potential barrier calculation, improved agreement between experimental and theoretical activation energies.

Such studies of self-diffusion on an atomic scale can shed much light on details of atom binding at the surface. Care must be taken, however, in extrapolating or relating the results to the mass transfer processes such as grain boundary thermal grooving which will actually be experienced in the diode. For example, Barbour, Charbonnier, Dolan, Dyke, Martin, and Trolan (ref. 49) studied diffusion of tungsten using field emitter tips. The rate of recession of a heated tip was observed by applying brief pulsed viewing voltages to minimize field effects. In the neighborhood of 2000 K the diffusion coefficient for surface self-diffusion was $D = 4 \exp\left[(-36\,000 \pm 9000)/T\right]$ square centimeters per second. The activation energy is about three or four times those observed by Ehrlich and Hudda (ref. 47).

The principal explanation for this difference is that Barbour, Charbonnier, Dolan, Dyke, Martin, and Trolan (ref. 49) were studying an overall surface self-diffusion process and Ehrlich and Hudda were observing only a portion of it. The following arguments of Gjostein and Hirth (ref. 50) may help to clarify the problem. The terrace-ledge-kink model (ref. 44) illustrated in figure 4 is commonly used as a description of the surface of a real metal. Diffusion in this model involves essentially movement of atoms from kink site to kink site via terrace sites. At terrace sites the surface atoms have the minimum number of nearest neighbors and are referred to as adsorbed atoms.

The diffusion of atoms confined to the terrace, observed by field ion microscopy or possibly by means of radioactive tracer atoms, can be described by the equation

$$J = -\frac{N_a D_a}{kT} \frac{\partial \mu}{\partial x} \tag{19}$$

where N_a is the concentration of adsorbed atoms on the terrace and D_a the coefficient for diffusion on the terrace. On the other hand, for overall diffusion, equation (18) evaluated in the direction of maximum J is

$$J = -\frac{N_0 D_s}{kT} \frac{\partial \mu}{\partial x} \tag{20}$$

where N_0 and D_s retain their previously assigned meanings.

Both D_s and D_a can be expressed as activated processes:

$$D_s = D_o \exp\left(-\frac{Q_s}{RT}\right) \tag{21}$$

and

$$D_a = D_{o,a} \exp\left(-\frac{\Delta H_a}{RT}\right) \tag{22}$$

where Q_s is the activation energy for mass transfer and ΔH_a is the activation energy for terrace diffusion. Gjostein and Hirth (ref. 50) demonstrated that for near-equilibrium processes

$$Q_s = \Delta H_a + \Delta H_{ka} \tag{23}$$

where ΔH_{ka} is the energy to move an atom from a kink site to a terrace site. Depending on the details of experiments involving the diffusion of distinguishable atoms or tracer atoms, the activation energy observed can vary between ΔH_a and Q_s, with an attendant variation in diffusion coefficient.

In reality the simple picture of surface self-diffusion developed by Gjostein and Hirth is complicated by additional mechanisms. Gjostein (ref. 51) discussed two basic diffusion mechanisms appearing in face centered cubic metals. For $T/T_m > 0.75$, where T_m is the melting temperature, diffusion appears to occur by the movement of surface vacancies. In equation (21) for D_s, $Q_s/R \cong 6.5\ T_m$ and $D_o \cong 0.014$ square centimeter per second. For $T/T_m > 0.75$, adatom diffusion predominates, with $Q_s/R \cong 15\ T_m$ and $D_o \cong 740$ square centimeters per second. In body centered cubic metals the predominant process is inferred to be vacancy diffusion, with $Q_s/R = 9.5\ T_m$ and $D_s = 3.6$ square centimeters per second. Gjostein also discussed the role of impurities in enhancing or suppressing surface self-diffusion.

Recent data for nickel can be compared with the foregoing empirical expressions for face centered cubic (fcc) metals. Nickel has a melting point of 1728 K (ref. 11). Melmed (ref. 52), using a field emission microscope, built up a treated emission tip with an electric field. The zero-field diffusion activation energy, determined by annealing the tip with the field off between 510 and 750 K, was 21 400±2100 calories per mole (89 500±8800 J/mole). Agreement with the low-temperature empirical rule $Q_s/R = 6.5\ T_m$ is excellent. Maiya and Blakely (ref. 53) observed the relaxation of sinusoidal grooves in the face of Ni single crystals between about 1200 and 1600 K. On the (100) face in the [110] direction Q_s was about 1.54 electron volts or 149 000 joules per mole, and D_0 was 2.6±1.6 square centimeters per second. On the (110) face in the [001] direction Q_s was 1.74 electron volts or 168 000 joules per mole, and D_0 was 12.8±4 square centimeters per second. On the (110) face in the $[1\bar{1}0]$ direction, Q_s was 1.85 electron volts or 178 000 joules per mole, and D_0 was 23.9±6.4 square centimeters per second. In these cases, both D_0 and Q_s fall between the low and high temperature empirical rules. This is possibly to be expected since some of the data were in the range $T < 0.75\ T_m$. The anisotropic character of the surface diffusion coefficient noted in the data for the (110) face requires that D_s in equation (18) be a tensor.

CATEGORY II - SURFACE AND SUBSURFACE EVENTS INVOLVING CONTAMINANTS OR ADDITIVES

The previous topics, under category I, represented real events to be expected in all thermionic diodes. However, a diode limited only to these processes would be idealized, since the role of the inevitable gaseous contaminants and beneficial additives was omitted. This portion will be devoted to a survey of these materials.

The classical view of the interaction of chemisorbed gases with the surface has been greatly altered in recent years. No longer can the adsorbate be considered as a layer limited to the surface and differentiated from a physisorbed layer only by difference in bonding strength and mechanism. Increasing amounts of evidence suggest that the adsorbate can profoundly alter the surface. In fact there appears to be a continuum of possible phenomena, commencing with surface alteration and ceasing only with the complete chemical alteration of the substrate.

This section will commence with consideration of processes whose major expression is at the surface or possibly an atom layer or so beneath. Following that, the penetration of additives deeper into the lattice will be surveyed.

Whether a phenomenon is to be regarded as pertaining to the surface and the subsurface or to the bulk is debatable in many cases. An effort will be made to sort the discussion into the two major groups, although the decision is often arbitrary.

Faceting and Other Surface Reconstruction Caused by Contaminants or Additives

The faceting of metals by reactive gases has been observed on a macroscopic scale. Moore (ref. 54) reviewed the results of experimental and theoretical research in this field. Theoretical interpretations of faceting due to the presence of adsorbed gases fall into two classes. In the thermodynamic approach faceting is regarded as a consequence of the attempt of the surface to lower its free energy in the presence of an adsorbed phase. The adsorption of gases alters the surface tension or specific surface free energy according to the Gibbs adsorption equation (ref. 33):

$$d\gamma + \Gamma \, d\mu = 0 \tag{24}$$

where μ is the chemical potential of the adsorbate and Γ is the amount of adsorbate per unit area. For an adsorbate which behaves ideally in the gas phase so that

$$d\mu = RT \, d \ln p$$

where p is the pressure, equation (24) becomes

$$\frac{1}{RT} \frac{d\gamma}{d \ln p} = -\Gamma \tag{25}$$

When adsorption occurs, the amount of change in γ may depend on crystallographic orientation. Therefore, some hitherto stable surfaces may be expected to decompose into facets of low index planes, alternating with more complex surface fragments, as discussed by Moore (ref. 54) and Winterbottom (ref. 55).

Although the surface energy hypothesis predicts correctly the possibility of facets of constant orientation, it is not considered proven. For one thing, measurements of γ are difficult. In particular, little data exist for body centered cubic metals (ref. 55). In the absence of overwhelming support, the existence of an alternative theory is to be expected. Thus, the kinetic theory of faceting proposes that faceting is an evaporation phenomenon. In this theory, the presence of adsorbate is presumed to suppress metal evaporation in degrees, depending on crystal orientation. This facilitates the bunching up of surface segments having complex orientations, with flat facets between, giving the observed step contours. A further conjecture can be made that even below the temperature of significant evaporation, the adsorbate may influence self-diffusion sufficiently to produce the observed faceting.

On the atomic scale the interpretation of some low energy electron diffraction (LEED) patterns as evidence of faceting appears to have gained wide acceptance. Indeed, the concept is sufficiently well accepted that observations made by other methods have been ascribed to faceting or other types of surface reconstruction. For instance Bell, Swanson, and Crouser (ref. 56) observed oxygen adsorption on the (110), (211), (111), and (100) planes of tungsten by field ion microscopy. In the temperature range of 1400 to 1800 K the peaks of the curves of preexponential in the Fowler-Nordheim equation against coverage were explained for the (100) and (111) planes in terms of faceting. Although faceting is well accepted, there has been some concern over details of observations. For instance Anderson and Danforth (ref. 57) observed the formation of {110} planes on a (100) surface of tungsten. Hayek, Farnsworth, and Park (ref. 58) observed no such effect on a (100) molybdenum surface, despite the chemical similarity of the metals.

Some of the doubts concerning the reconstruction hypothesis have been discussed by Germer (ref. 59). He suggested repeating certain LEED experiments that might be used to provide more support for reconstruction. However, Bauer (ref. 60), rebutting Germer, maintained that the experiments already performed, involving carbon on a (110) nickel plane, hydrogen on a (110) nickel plane, and oxygen on a (110) tungsten plane, were satisfactorily explained on the basis of unreconstructed surfaces. Interestingly, Ehrlich (ref. 61) in field ion microscope studies observed no reconstruction of the (110) tungsten plane by oxygen, nitrogen, or carbon monoxide. Bauer also questioned Germer's assumptions that diffraction patterns were produced by the top layer of atoms only, and that the adsorbates can shield the substrate atoms and yet have negligible cross section. Anderson and Estrup (ref. 62) in a LEED study of carbon monoxide adsorption on (100) tungsten argued against surface reconstruction because of the required high tungsten mobility and complicated mechanisms. Estrup and Anderson (ref. 63) stated that scattering from light adsorbate atoms is possible and that reconstruction for the (100) tungsten surface is less general than previously thought.

Those who object to surface reconstruction on the grounds insufficient surface mobility must contend with the fact of metal self-diffusion at relatively low temperatures, discussed earlier. Indeed many of the LEED patterns interpreted as evidence of reconstruction are developed by heating to temperatures appreciably above the onset of surface self-diffusion. For instance, the adsorption of oxygen on (100) tungsten at room temperature gives an increase in background, but a well ordered structure is seen only upon heating (ref. 57). May and Germer (ref. 64) adsorbed carbon monoxide on (110) tungsten and detected two states. LEED patterns corresponding to the more tightly bound state were detected only upon heating the crystal. Jackson and Hooker (ref. 65) found diffuse patterns when (110) molybdenum was exposed to carbon monoxide at room temperature. An ordered pattern developed upon heating to 1000^{0} C, a temperature well above the onset of surface self-diffusion. On the other hand, Chang and Germer (ref. 66) found a pattern when (112) tungsten was exposed to oxygen at room temperature. This was enhanced by a flash above 1000 K, which may have removed an amorphous layer of oxygen. Similarly, Park and Farnsworth (ref. 67) observed a sequence of structures by exposing nickel to increasing amounts of oxygen at room temperature. The intensity of these patterns was somewhat obscured by the inferred presence of some amorphous oxygen.

Observations leading to interpretations of adsorbate reconstruction at or within a very few atom layers of the surface have been made by other techniques. Brennan and Graham (ref. 68) used calorimetry to study the adsorption of oxygen on films of molybdenum, tungsten, cobalt, and nickel at 77 and 273 K. From their data they inferred that adsorption on molybdenum and tungsten essentially is limited to the surface. The data for cobalt and nickel suggested to them that adsorption at 77 K was at the surface and that at 273 K the oxygen was buried between the first and second metal atom layers. Subsequent adsorption on the surface atoms was then believed possible. However, caution must be exercised in extrapolating thin film results of this type to crystals. For instance, Alessandrini and Freedman (ref. 69) studied the oxidation of nickel thin films by electron diffraction. Low decomposition temperatures for the NiO were ascribed to the surface energy of the film.

Singleton (ref. 70) studied oxygen on polycrystalline tungsten ribbons at 300 to 850 K by flash techniques. He detected a process of activated adsorption on an already saturated surface which he ascribed to surface reconstruction.

Zingerman and Ishchuk made contact potential difference studies of oxygen on polycrystalline (refs. 71 and 72) and monocrystalline tungsten (refs. 73 to 76). Anomolies were encountered in curves of work function against oxygen exposure time for polycrystalline and (100) tungsten at surface temperatures above about 900 K. Curves of work function against electron stimulated desorption time also exhibited anomolies. These effects were postulated as being caused by limited penetration of oxygen into the lattice. However, the possibility of faceting was dismissed as an explanation (ref. 76).

Hopkins and Pender (ref. 77) studied the work function of (100) and (110) tungsten monocrystalline surfaces. An inflection, seen in curves of work function against inferred oxygen coverage for (100) tungsten and polycrystalline tungsten foil, was ascribed to faceting. Surprisingly, however, the curve for (110) tungsten shows a pronounced dip not seen by Zingerman and Ishchuk (ref. 74). Partial oxygen burial due to place exchange with tungsten atoms was advanced by Hopkins and Pender (ref. 77) as an explanation.

Holscher and Sachtler (ref. 78) studied the adsorption of carbon monoxide on tungsten by field ion microscope and field electron microscope methods. Various cycles of adsorption and readsorption were conducted at temperatures of 78 and 300 K. Field desorption of tungsten followed by field ion microscope examination was used to determine the subsurface condition after adsorption. Vacancies in the tungsten lattice were found for a few atom layers beneath the surface, even at 78 K. The authors concluded that adsorption weakened the intermetallic bond in a degree increasing with coverage. In a printed discussion of reference 78 this interpretation was controverted by Ehrlich and others (ref. 79). High viewing and desorbing fields and contamination were advanced as explanations for the observations. Indeed, Ehrlich criticized the concept of reconstruction in chemisorption, generally.

A similar earlier study by Müller (ref. 80) using a field ion microscope, revealed apparent corrosion of tungsten by oxygen. The corrosion penetrated two atom layers in a "few minutes" at 20 K and five layers at room temperature. Nakamura and Müller (ref. 81) studied the oxidation of tantalum by field electron microscopy. They found, below 450 K, corrosion of the first layer by oxygen with no penetration. Above 500 K the corrosion was observed to penetrate up to 55 atom layers.

Schissel and Trulson (ref. 82) studied the oxidation of tungsten by examining evolved gaseous products with a mass spectrometer. They explained the observed reactions by proposing a series of kinetic mechanisms, one of which involved a place change of oxygen and tungsten atoms.

In not all cases is the effect of oxygen at the surface limited to faceting or apparent surface reconstruction. Germer, Stern, and MacRae (ref. 83) conducted a LEED study of (111) nickel exposed to oxygen at a few hundred degrees centigrade. Some of the resulting patterns were interpreted as crystallites of NiO on the surface with inclined {111} facets. The crystallite lattice was found to have larger nickel atom separation than the substrate. Park and Farnsworth (ref. 84) did not observe these inclined planes.

Attention is invited to the great dependence of surface chemical effects upon the particular index plane of a given crystal being examined. Numerous instances of this specificity have appeared in this section.

Solution and Oxidation

As the interaction between contaminant and substrate becomes more extensive, a greater proportion of the contaminant will be found beneath the surface, either as a solute or as a compound with the metal.

The oxidation of nickel has been comprehensively studied. Quinn and Roberts (ref. 85) observed the chemisorption of oxygen on nickel at -195° C but found no evidence of incorporation into the lattice. J. Müller (ref. 86) ascribed a rapid initial uptake of oxygen on nickel powder at -78° and 22° C to chemisorption. The subsequent slow uptake was believed to be caused by lattice incorporation. Heating to 165° or 315° C caused no outgassing but regenerated the surface for fresh adsorption. Apparently the surface oxygen was incorporated into the lattice by the heating.

Roberts and Wells (ref. 87) found that the incorporation of oxygen into a nickel film was an activated process. Delchar and Tompkins (refs. 88 and 89) observed an activation energy of about 1 kilocalorie per mole (4000 J/mole). Despite the very low energy involved, the rate was found to be low. This they ascribed to a very small preexponential in the equation for the incorporation rate. They postulated that the oxygen, as a covalent atom, not an ion, passed into the lattice through a "gate" between four nickel atoms. The necessity for a coincident separation of the nickel atoms, creating an aperture of 1.28 Å (12.8 nm) diameter as shown in figure 5, resulted in the low transmission coefficient.

The initial stages in the oxidation of nickel result in an ordered nickel-oxygen structure at the surface. Farnsworth and Park in a series of publications (refs. 67, 84, 90, and 91) studied the oxidation of the (100), (110), and (111) surfaces. They found that, in the initial oxidation, the oxygen atoms replaced nickel atoms so as to form a structure with the chemical composition Ni_3O. Alternate (100) planes consisted of nickel atoms alone, and the other (100) planes consisted of half oxygen and half nickel. At smaller oxygen exposures than required for the Ni_3O structure, Park and Farnsworth (ref. 91) conjectured the formation of an Ni_7O structure. At higher exposures the NiO structure was observed. The surface of this structure appeared to be parallel with all orientations of the original nickel crystal face, since the nonparallel NiO faces described by Germer, Stern, and MacRae (ref. 83) were not seen.

Alessandrini and Freedman (ref. 69) studied the annealing of an Ni film containing NiO by electron diffraction. On annealing at 400° C to 650° C a structure was observed for which the composition Ni_8O can be inferred.

Boggio and Farnsworth (ref. 92) studied the interaction of oxygen with tantalum from room temperature to 300° C using LEED. The patterns seen were interpreted as a surface TaO structure, with the (111) face parallel to the (110) tantalum face.

Studies of tantalum oxidation at higher temperatures, from 300° C to 1800° C were made by Kofstad (refs. 93 to 95) and by Kofstad and Krudtaa (ref. 96). The formation of surface oxides was observed micrographically. The composition of the surface oxide, determined by X-ray diffraction, depended on temperature and oxygen pressure. Stages in the oxidation were believed to be adsorption, diffusion into the lattice, and then formation of the observed surface oxide. Chemisorption was believed to be rate-controlling in the initial stage. Using an elementary adsorption theory proposed by Ehrlich (ref. 97), Kofstad represented this stage of oxidation as

$$O_2 \text{ (gas)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 \text{ (physisorbed)} \tag{26}$$

$$2 \text{ sites} + O_2 \text{ (physisorbed)} \xrightarrow{k_2} 2\, O \text{ (chemisorbed)} \tag{27}$$

giving the rate expression

$$k = k_1 k_2 p_{O_2} \frac{(1 - \theta)^2}{k_{-1} + k_2(1 - \theta)^2} \tag{28}$$

where k_1 and k_{-1} are the rates for physical adsorption and desorption, respectively, k_2 is the rate of chemisorption from the physisorbed state, and θ is the fraction of chemisorption sites that are occupied. The difference between the energy of chemisorption E_2 and that of physical desorption E_{-1} was estimated to be 18 kilocalories per mole of O_2 (75 000 J/mole of O_2).

During the adsorption stage oxygen is diffusing into the metal, a process which continues until the solubility limit is reached. At this point precipitation of an oxide commences. Kofstad (ref. 95) summarized solubility limit data for oxygen in Ta from several sources. Typical values are 2 atom percent oxygen in Ta at 1000 K and 5 to 7 atom percent at 2000 K.

The solution of oxygen in tantalum is not ideal, since a tendency of oxygen atoms to associate was demonstrated by Powers and Doyle (ref. 98). A component of the relaxation of mechanical strain in tantalum filaments containing oxygen was ascribed to the association of oxygen atoms, $2O \rightleftarrows O_2$, with a free energy change of -2.5 kilocalories per mole of O_2 at 76 K (-10 500 J/mole of O_2). Nakamura and Müller (ref. 81) observed an apparent clustering of oxygen atoms in tantalum field ion microscope tips exposed to oxygen after a long anneal at 360 to 390 K.

The observations of Inouye (ref. 99) showed the oxidation of niobium to be quite similar to that of tantalum. He found four principal oxidation reactions: (1) Solution of oxygen, (2) internal oxidation, (3) oxide film formation, and (4) oxide-gas reaction. Internal oxidation describes the precipitation of an oxide below the apparent metal surface.

Taylor and Doyle (ref. 100) observed the solution of oxygen in niobium and alloys of niobium with hafnium, molybdenum, and tungsten. Rapid diffusion of oxygen to the center of Nb wires was found, with a solubility limit of 5.6 atom percent oxygen at 2158° C. Ultimately, the oxides NbO_2, Nb_2O_5, and NbO were observed at the surface. At 1500° C the oxide NbO was in equilibrium with O at a pressure of 10^{-11} torr:

$$NbO(s) \rightleftarrows Nb(s) + O(g)$$

Kofstad and Espevik (ref. 101) studied the low pressure oxidation of niobium at 1200° to 1700° C for pressures from 2×10^{-4} to 0.5 torr. They summarized the data from several sources for the solid solubility of oxygen in niobium as a function of temperature. Typical average values are 1 atom percent oxygen in niobium at 1000 K and 10 atom percent at 2500 K. Overall oxygen concentrations above these values resulted in the precipitation of oxides. They found the initial oxidation rate to be linear with oxygen pressure. This is in accord with the Ehrlich oxidation analysis (eqs. (26) to (28)) where adsorption is rate controlling. The difference between the energy of chemical adsorption E_2 and that of physical desorption E_{-1} was estimated to be 23 kilocalories per mole of O_2 (96 000 J/mole of O_2). Delgrosso, Carta, and Ricard (ref. 102) also found for this system that the initial oxidation was in accord with Ehrlich's analysis and that $E_2 - E_{-1}$ was 18.9 kilocalories per mole of O_2 (79 000 J/mole of O_2).

Pasternak and Evans (ref. 103) studied the time-varying interaction of oxygen with niobium ribbons at pressures in the range from 3×10^{-8} to 3×10^{-6} torr. The rate of adsorption was inferred from the sticking coefficient, and the change in electrical resistance indicated the amount of oxygen in solution. At room temperature adsorption was the rate controlling step, since solution was inferred to be so rapid that the surface and bulk concentrations were in equilibrium. Between 500 and 745 K a complex oxidation sequence appeared. There was evidence of an oxide buildup on the surface that lowered sticking coefficient and resisted diffusion to the interior. Subsequently the oxide film dissolved. At temperatures around 1500 K analysis of the data suggested that the oxygen was atomically adsorbed into one of two binding states. This detail is not accounted for in the Ehrlich analysis (refs. 97 and 101). No oxides were detected either on the surface or internally, since the solubility limit was not approached.

The materials niobium and tantalum, in addition to dissolving oxygen readily, have a capacity for nitrogen also. Nitrogen, because it desorbs from most metal surfaces at much lower temperatures than oxygen, is not normally viewed as a problem in thermionic converters. However, the use of niobium in graded seals and other components could conceivably introduce a puzzling contaminant into the diode. This might pose a particular problem in production model diodes disconnected from a vacuum source after construction. Cost and Wert (ref. 104) measured the metal-gas equilibrium in the niobium-nitrogen solid solution. They found that the equilibrium followed Sievert's law, implying the solution of nitrogen as atoms:

$$C_e = 6.2\times10^{-4} p^{1/2} \left[\exp(23\ 100/T)\right] \tag{29}$$

where C_e is the atom percent of nitrogen in niobium and p is the nitrogen pressure in torr.

Similar measurements were made by Pasternak, Evans, and Bergsnov-Hansen (ref. 105). Their expression for C_e is similar to that of Cost and Wert.

$$C_e = 1.2\times10^{-5} (p)^{1/2} \exp(26\ 900/T) \tag{30}$$

At 10^{-8} torr and 1500 K, C_e is 0.45 atom percent nitrogen. The investigators found that the extremely high diffusion rate of nitrogen in niobium kept the surface nearly free of adsorbate. As in the case of oxygen on niobium, surface adsorption became rate controlling. There was evidence that nitride phases do not segregate at the surface.

Griffiths and Pryde (ref. 106) measured the solubility of nitrogen in tantalum at pres-pressures of 10^{-8} to 10^{-3} torr and temperatures of 1600 to 2300 K. They found that

$$C_e = (4.4\pm0.4)\times10^{-4} p^{1/2} \exp(24\ 100+1000)/T$$

This expression pertains to very low concentrations of nitrogen in tantalum, up to 1 atom percent. At higher concentrations, evidence of ordering of the nitrogen has been found by other workers, resulting in the dependency $C_e \approx p^{1/2.4}$.

Less information is available concerning the solubility of common gases in other refractory metals. Sims (ref. 107) estimated the solubility of oxygen in rhenium at the melting point to be 12 ppm, a negligible amount. Few and Manning (ref. 108) found the solubility of oxygen in molybdenum to be 0.006 weight percent at 1600 K. Singleton (ref. 70) observed evidence of solution when oxygen was adsorbed on tungsten above 800 K.

The solution of gases in the refractories can cause difficulty in some studies of gas-surface interaction. Thus Nornes and Donaldson (ref. 109) observed the interaction of nitrogen at 300 K with a tungsten filament above 2000 K. An apparent solubility effect of nitrogen in tungsten, causing a perturbation in their measurements, was carefully eliminated. Stickney, Greaves, and Fehrs (ref. 110), measuring work functions of oxygen on various refractories, found that their results for tantalum were affected by solution. Haas, Jackson, and Hooker (ref. 111), in LEED studies of oxygen on niobium, tantalum, and vanadium surfaces, found that the dissolution of oxygen into the bulk made surface coverages ambiguous.

An added concern in all cases of substrate reaction with additive or contaminant gases is the nature of any gases evolved as products of reaction. These gases, if condensed on cold surfaces, can getter gaseous additives whose presence in the free state is beneficial to the diode. Although such evolution of gaseous reaction products can be harmful, there are cases where it can conceivably be used to advantage. Thus, halogens have been employed in a transport cycle to prevent the blackening of lightbulbs (ref. 112). A similar cycle has been proposed for the thermionic converter (ref. 113).

From material discussed earlier it is evident that the exposure of tantalum and niobium to low pressures of oxygen will not result in the appearance of a gaseous oxide phase. Stages of the oxidation process for these metals with increasing oxygen concentration appears to be first the solution then the precipitation of an oxide in equilibrium with the solution. At sufficiently high temperatures the oxygen will be evolved as an oxide. Taylor and Doyle (ref. 100) found that, if the temperature was above 2200° C and the oxygen pressure was around 10^{-6} torr, oxygen will desorb from niobium as an oxide. Pasternak and Evans (ref. 103) heated their oxygenated niobium ribbons to over 1800 K before any appreciable gas was evolved. At less than 1 atom percent oxygen in niobium, the principal evaporant was NbO. At higher concentrations, NbO_2 predominated. No gaseous O_2 was observed at any temperature, thus the adsorption of O_2 on niobium is essentially irreversible.

The most thoroughly investigated oxidation of a refractory metal involving the evolution of gaseous oxides is that of tungsten. Berkowitz-Mattuck, Buchler, Engelke, and

Goldstein (ref. 114) studied the oxidation of molybdenum and tungsten mass spectrometrically between 1500 and 2600 K and from 10^{-4} to 10^{-2} torr. The principal gaseous products from tungsten were WO_2(g) and WO_3(g). Smaller amounts of W_2O_6(g) and W_3O_9(g) were evolved at low temperatures. Analogous products were found for the molybdenum system. At about 1850 K and 10^{-3} torr approximately one oxygen surface collision out of 450 results in a gaseous molybdenum oxide molecule. This proportion is much less than would be predicted by thermodynamic equilibrium.

Similar studies for tungsten were made by Schissel and Trulson (ref. 82) at temperatures from 1400 to 3150 K and pressures up to 2×10^{-4} torr. The principal species evolved between 1400 and 2000 K were WO_2, WO_3, W_2O_6, and W_3O_9. Above 2000 K O predominated, with W and WO appearing above 2600 K. From their data Schissel and Trulson deduced a kinetic scheme for the surface reactions.

Singleton (ref. 115) observed the oxidation of tungsten at temperatures from 1300 to 2450 K. The oxygen pressure was from 10^{-8} to 10^{-5} torr, somewhat lower than pressures used by the other investigators. His results essentially confirmed those of references 114 and 115.

Ptushinskii and Chuikov (ref. 116) adsorbed oxygen on tungsten filaments at 10^{-7} torr and from 300 to 1500 K. The material evolved by flashing to 2500 K was observed by a mass spectroscope. Clearly, the experimental conditions were quite different from those of the previously described experiments, which were steady-state. Ptushinskii and Chuikov found that oxygen desorbed in two stages upon flashing. The low temperature stage evolved oxides; the high temperature stage atomic oxygen.

Singleton (ref. 70) also observed the material evolved by flashing a polycrystalline tungsten ribbon exposed to oxygen at 300 to 850 K. Flashes to temperatures below 1650 K evolved only tungsten oxides, but both oxides and oxygen were detected above. Adsorption on the clean ribbon was found to be affected by the type of surface preparation employed. Also the use of polycrystalline wire instead of ribbon increased the amount of oxygen desorbed, demonstrating the sensitivity of the flash process to surface structure.

Anderson and Danforth (ref. 57) flashed (100) tungsten surfaces used in LEED studies of oxygen adsorbed at 1250 K on tungsten. Heating to 1375 K destroyed facets that were created at high oxygen exposure. A LEED pattern associated with a lower oxygen exposure was thus recovered, which in turn was destroyed by flashing to 1525 K. The surface was cleaned at 1850 K. No large pressure pulses were seen upon flashing. The authors ascribed this to gettering of the oxygen on the walls and disputed the possibility of tungsten oxide desorption. This conclusion seems to contradict the finding of Ptushinskii and Chuikov (ref. 116) and Singleton (ref. 115).

SUMMARY REMARKS

This survey has been concerned with many types of chemical interactions at the interfaces present in the thermionic diode. As a result, a thorough treatment of each one has not been feasible. More importance has been attached to breadth than to depth. The references should provide much additional literature on the subjects in their respective fields.

The interfaces are the battleground where the inexorable, degrading forces of thermodynamics are countered by technology. Fortunately, the kinetic processes by which the deterioration occurs are subject to some degree of control by the designer. An understanding of the mechanisms may lead to choices of construction material and design which will delay the ravages of the hostile diode environment and give useful life.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 20, 1970,
120-27.

REFERENCES

1. Rasor, Ned S.; and Gammel, Gregor: Correlation of Emission Processes for Cesium-Additive Converters. Thermionic Conversion Specialist Conference, IEEE, 1967, pp. 110-119.
2. Rufeh, F.: Lieb, D.; and Fraim, F.: Recent Experimental Results on Electronegative Additives. Thermionic Conversion Specialist Conference, IEEE, 1967, pp. 25-28.
3. Aamodt, R. L.; Brown, L. J.; and Nichols, B. D.: Thermionic Emission from Molybdenum in Vapors of Cesium and Cesium Fluoride. J. Appl. Phys., vol. 33, no. 6, June 1962, pp. 2080-2085.
4. Hirth, J. P.; and Pound, G. M.: Condensation and Evaporation, Nucleation and Growth Kinetics. Macmillan Co., 1963.
5. Rhodin, T. N.; and Walton, Derek: Nucleation and Growth Processes on Solid Surfaces. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963, pp. 259-286.

6. Hruska, S. J.; Hirth J. P.; and Pound G. M.: Recent Developments in Heterogeneous Nucleation from the Vapor Phase. Surfaces and Interfaces. I – Chemical and Physical Characteristics. John J. Burke, Norman L. Reid and Volker Weiss, eds., Syracuse University Press, 1967.

7. Pound, G. M.; Simnad, M. T.; and Yang, Ling: Heterogeneous Nucleation of Crystals from Vapor. J. Chem. Phys., vol. 22, no. 7, July 1954, pp. 1215-1219.

8. Hruska, S. J.; and Pound, G. M.: Thermal-Beam Energy and Nucleation of Metal Crystals on Substrates. Trans. AIME, vol. 230, no. 6, Oct. 1964, pp. 1406-1413.

9. Sundquist, B. E.: A Direct Determination of the Anisotropy of the Surface Free Energy of Solid Gold, Silver, Copper, Nickel, and Alpha and Gamma Iron. Acta Met., vol. 12, no. 1, Jan. 1964, pp. 67-86.

10. Hirth, J. P.: Evaporation of Crystals. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963, pp. 199-219.

11. Stull, D. R.; and Sinke, G. C.: Thermodynamic Properties of the Elements. Advances in Chemistry Series. No. 18. American Chemical Society, 1956.

12. Nesmayanov, A. N.: Vapor Pressure of the Chemical Elements. Elsevier Publishing Co., 1963.

13. Drowart, J.: Mass-Spectrometric Studies of the Vaporization of Inorganic Substances at High Temperatures. Condensation and Evaporation of Solids. Emile Rutner, P. Goldfinger, and J. P. Hirth, eds., Gordon and Breach Science Publ., 1964, pp. 255-310.

14. Scott, J. M.; Danko, J. C.; and Chase, J. M.: Post-Test Examination and Analysis of a Cylindrical Thermionic Converter. Thermionic Conversion Specialist Conference. IEEE, 1967, pp. 304-311.

15. Lawrence, J.; and Perdew, J. P.: Effect on Thermionic Converter Performance of Emitter Material Evaporated on a Low Work Function Collector. Thermionic Conversion Specialist Conference. IEEE, 1965, pp. 289-296.

16. Shewmon, Paul G.: Diffusion in Solids. McGraw-Hill Book Co., Inc., 1963.

17. Darken, L. S.: Diffusion, Mobility and Their Interrelation Through Free Energy in Binary Metallic Systems. Trans. AIMME, vol. 175, 1948, pp. 184-201.

18. LeClaire, A. D.: Application of Diffusion Theory to the Body-Centered Cubic Structures. Diffusion in Body-Centered Cubic Metals. American Society for Metals, 1965, pp. 3-25.

19. Lazarus, David: Diffusion in Body-Centered Cubic Transition Metals - A Theoretical Critique. Diffusion in Body-Centered Cubic Metals. American Society for Metals, 1965, pp. 155-170.

20. Pawel, R. E.; and Lundy, T. S.: Diffusion of Nb^{95} into Tantalum Single Crystals. Acta Met., vol. 13, no. 3, Mar. 1965, pp. 345-351.

21. Hehemann, R. F.; and Leber, S.: Chemical Diffusion in the Columbium-Tungsten System. Trans. AIME, vol. 236, no. 7, July 1966, pp. 1040-1044.

22. Pawel, R. E.; and Lundy, T. S.: The Diffusion of Nb^{95} and Ta^{182} in Tantalum. J. Phys. Chem. Solids, vol. 26, 1965, pp. 937-942.

23. Lundy, T. S.; Winslow, F. R.; Pawel, R. E.; and McHargue, C. J.: Diffusion of Nb^{95} and Ta^{182} in Niobium. Trans. AIME, vol. 233, no. 8, Aug. 1965, pp. 1533-1539.

24. Wyatt, B. S.; and Argent, B. B.: The Interdiffusion of Niobium and Molybdenum. J. Less-Common Metals, vol. 11, no. 4, Oct. 1966, pp. 259-262.

25. Hartley, C. S.; Steedly, J. E., Jr.; and Parsons, L. D.: Binary Interdiffusion in Body-Centered Cubic Transition Metal Systems. Diffusion in Body-Centered Cubic Metals. American Society for Metals, 1965, pp. 51-75.

26. Askill, J.; and Tomlin, D. H.: Self-Diffusion in Molybdenum. Phil. Mag., vol. 8, no. 90, June 1963, pp. 997-1001.

27. Andelin, R. L.; Knight, J. D.; and Kahn, M.: Diffusion of Tungsten and Rhenium Tracers in Tungsten. Trans. AIME, vol. 233, no. 1, Jan. 1965, pp. 19-24.

28. Ivantsov, I. G.: Self-Diffusion in Monocrystalline Nickel. Phys. Metals Metallography, vol. 22, no. 5, 1966, pp. 77-81.

29. Kingery, W. D.: Role of Surface Energies and Wetting in Metal-Ceramic Sealing. Am. Ceram. Soc. Bull., vol. 35, Mar. 1956, pp. 108-112.

30. Levinson, David W.: Seal and Insulator Problems in Thermionic Converters. Rep. ARF2215-6, IIT Research Inst., Mar. 12, 1962. (Available from DDC as AD-273481.)

31. Pincus, A. G.: Mechanism of Ceramic-to-Metal Adherence. Ceramic Age, vol. 63, no. 3, Mar. 1954, pp. 16-20, 30-32.

32. Armstrong, W. M.; Chaklader, A. C. D.; and Clarke, J. F.: Interface Reactions between Metals and Ceramics: I. Sapphire-Nickel Alloys. J. Am. Ceram. Soc., vol. 45, no. 3, Mar. 1962, pp. 115-118.

33. Glasstone, Samuel: Thermodynamics for Chemists. D. Van Nostrand Co., Inc., 1947.

34. Allen, B. C.; and Kingery, W. D.: Surface Tension and Contact Angles in Some Liquid Metal-Solid Ceramic Systems at Elevated Temperatures. Trans. AIME, vol. 215, no. 1, Feb. 1959, pp. 30-37.

35. Gibson, H.: Fabrication and Evaluation of Graded Type Ceramic-to-Metal Seals. Thermionic Conversion Specialist Conference. IEEE, 1967, pp. 253-259.

36. Kaufman, Warner B.; Tischler, Richard F.; and Breitwieser, Roland: A High-Temperature, Electrically Insulating Cermet Seal Having High Strength and Thermal Conductance. Thermionic Conversion Specialist Conference. IEEE, 1967, pp. 260-270.

37. Grossman, L. N.: Electrical Insulators and Spacers for Nuclear Thermionic Devices. Rep. GEST-2022, General Electric Co., Feb. 10, 1964.

38. Chupka, William A.; Berkowitz, Joseph; and Giese, Clayton F.: Vaporization of Beryllium Oxide and Its Reaction with Tungsten. J. Chem. Phys., vol. 30, no. 3, Mar. 1959, pp. 827-834.

39. Drowart, J.; DeMaria, G.; Burns, R. P.; and Inghram, M. G.: Thermodynamic Study of Al_2O_3 Using a Mass Spectrometer. J. Chem. Phys., vol. 32, no. 5, May 1960, pp. 1366-1372.

40. Grossman, L. N.: Niobium - Al_2O_3 Reactions Yielding Condensed and Volatile Products. J. Chem. Phys., vol. 44, no. 11, 1 June 1966, pp. 4127-4131.

41. Ackermann, R. J.; and Thorne, R. J.: Vaporization of Oxides. Progress in Ceramic Science. Vol. 1. J. E. Burke, ed., Pergammon Press, 1961, pp. 39-88.

42. Mullins, W. W.: Solid Surface Morphologies Governed by Capillarity. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963.

43. Winterbottom, W. L.: Equilibrium Shape of a Small Particle in Contact with a Foreign Substrate. Acta Met., vol. 15, no. 2, Feb. 1967, pp. 303-310.

44. Gjostein, N. A.: Surface Self-Diffusion. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963, pp. 99-154.

45. Bassett, D. W.: Thermal Rearrangement of a Prefectly Ordered Tungsten Surface. Nature, vol. 198, May 4, 1963, pp. 468-469.

46. Bassett, D. W.: The Thermal Stability and Rearrangement of Field-Evaporated Tungsten Surfaces. Proc. Roy. Soc. (London), Ser. A, vol. 286, no. 1405, June 22, 1965, pp. 191-203.

47. Ehrlich, Gert; and Hudda, F. G.: Atomic View of Surface Self-Diffusion: Tungsten on Tungsten. J. Chem. Phys., vol. 44, no. 3, Feb. 1, 1966, pp. 1039-1049.

48. Ehrlich, Gert; and Kirk, C. F.: Binding and Field Desorption of Individual Tungsten Atoms. J. Chem. Phys., vol. 48, no. 4, Feb. 15, 1968, pp. 1465-1480.

49. Barbour, J. P.; Charbonnier, F. M.; Dolan, W. W.; Dyke, W. P.; Martin, E. E.; and Trolan, J. K.: Determination of the Surface Tension and Surface Migration Constants for Tungsten. Phys. Rev., vol. 117, no. 6, Mar. 15, 1960, pp. 1452-1459.

50. Gjostein, N. A.; and Hirth, J. P.: On the Surface Self-Diffusion Coefficient. Acta Met., vol. 13, no. 9, Sept. 1965, pp. 991-997.

51. Gjostein, N. A.: Surface Self-Diffusion in FCC and BCC Metals. A Comparison of Theory and Experiment. Surfaces and Interfaces I: Chemical and Physical Characteristics. John J. Burke, Norman L. Reed, Volker Weiss, eds., Syracuse University Press, 1967, pp. 271-304.

52. Melmed, Allan J.: Surface Self-Diffusion of Nickel and Platinum. J. Appl. Phys., vol. 38, no. 4, Mar. 15, 1967, pp. 1885-1892.

53. Maiya, P. S.; and Blakely, J. M.: Surface Self-Diffusion and Surface Energy of Nickel. J. Appl. Phys., vol. 38, no. 2, Feb. 1967, pp. 698-704.

54. Moore, A. J. W.: Thermal Faceting. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963, pp. 155-198.

55. Winterbottom, W. L.: Crystallographic Anisotrophy in the Surface Energy of Solids. Surfaces and Interfaces I. Chemical and Physical Characteristics. John J. Burke, Norman L. Reed and Volker Weiss, eds., Syracuse University Press, 1965.

56. Bell, A. E.; Swanson, L. W.; and Crouser, L. C.: A Field Emission Study of Oxygen Adsorption on the (110), (211), (111) and (100) Planes of Tungsten. Surface Sci., vol. 10, no. 2, May 1968, pp. 254-274.

57. Anderson, J.; and Danforth, W. E.: Low Energy Electron Diffraction Study of the Adsorption of Oxygen on a (100) Tungsten Surface. J. Franklin Inst., vol. 279, no. 3, Mar. 1965, pp. 160-168.

58. Hayek, K.; Farnsworth, H. E.; and Park, R. L.: Interaction of Oxygen, Carbon Monoxide and Nitrogen with (001) and (110) Faces of Molybdenum. Surface Sci., vol. 10, no. 3, June 1968, pp. 429-445.

59. Germer, L. H.: The Uncertainty Regarding Reconstructed Surfaces. Surface Sci., vol. 5, 1966, pp. 147-151.

60. Bauer, E.: Comments on "The Uncertainty Regarding Reconstructed Surfaces" by L. H. Germer. Surface Sci., vol. 5, 1966, pp. 152-154.

61. Ehrlich, Gert: Chemisorption on Single Crystal Planes. Disc. Faraday Soc., no. 41, 1966, pp. 7-13.

62. Anderson, J.; and Estrup, P. J.: Adsorption of CO on a Tungsten (100) Surface. J. Chem. Phys., vol. 46, no. 2, Jan. 15, 1967, pp. 563-567.

63. Estrup, P. J.; and Anderson, J.: Characterization of Chemisorption by LEED. Surface Sci., vol. 8, no. 1/2, July-Aug. 1967, pp. 101-114.

64. May, J. W.; and Germer, L. H.: Adsorption of Carbon Monoxide on a Tungsten (110) Surface. J. Chem. Phys., vol. 44, no. 8, Apr. 15, 1966, pp. 2895-2902.

65. Jackson, A. G.; and Hooker, M. P.: A LEED Study of CO and CO_2 Adsorption on Mo(110). Surface Sci., vol. 6, 1967, pp. 297-308.

66. Chang, C. C.; and Germer, L. H.: Oxidation of the (112) Face of Tungsten. Surface Sci., vol. 8, no. 1/2, July-Aug. 1967, pp. 115-129.

67. Park, Robert L.; and Farnsworth, H. E.: Interaction of Oxygen with (110) Nickel. J. Appl. Phys., vol. 35, no. 7, July 1964, pp. 2220-2226.

68. Brennan, D.; and Graham, M. J.: Heats of Adsorption of Oxygen on Evaporated Films of Molybdenum, Tungsten, Cobalt, and Nickel at 77, 90, and 273° K, and Nature of Adsorbed Layers. Disc. Faraday Soc., no. 41, 1966, pp. 95-101.

69. Alessandrini, E. I.; and Freedman, J. F.: The Observation by Electron Diffraction of a "Superlattice" in Annealed Nickel Single Crystal Films. Acta Cryst., vol. 16, 1963, pp. 54-57

70. Singleton, J. H.: Adsorption of Oxygen on Tungsten at Temperatures from 300° to 850° K. J. Chem. Phys., vol. 47, no. 1, July 1, 1967, pp. 73-82.

71. Zingerman, Ya. P.; and Ishchuk, V. A.: Role of the Surface Layer in the Interaction of Molecular Oxygen with a Tungsten Surface. Soviet Phys. - Solid State, vol. 6, no. 4, Oct. 1964, pp. 904-911.

72. Zingerman, Ya. P.; and Ishchuk, V. A.: Investigation of the Interaction of Oxygen with Tungsten by the Method of Electron - Stimulated Desorption. Soviet Phys. - Solid State, vol. 7, no. 1, July 1965, pp. 173-180.

73. Zingerman, Ya. P.; Ishchuk, V. A.; and Krutilina, T. A.: Some Characteristics of the Interaction of Oxygen with the Surface of a Tungsten Single Crystal. Soviet Phys. - Solid State, vol. 7, no. 8, Feb. 1966, pp. 2078-2079.

74. Zingerman, Ya. P.; and Ishchuk, V. A.: Adsorption of Oxygen on the (110) Face of a Tungsten Single Crystal. Soviet Phys. - Solid State, vol. 8, no. 3, Sept. 1966, pp. 728-733.

75. Zingerman, Ya. P.; and Ishchuk, V. A.: Mechanism of the Sorption of Oxygen on the (100) Face of a Tungsten Single Crystal. Soviet Phys. - Solid State, vol. 8, no. 10, Apr. 1967, pp. 2394-2397.

76. Zingerman, Ya. P.; and Ishchuk, V. A.: Investigation of the Process of Sorption of Oxygen on (100) and (110) Faces of a Tungsten Single Crystal Using the Electron-Stimulated Desorption Effect. Soviet Phys. - Solid State, vol. 9, no. 3, Sept. 1967, pp. 623-629.

77. Hopkins, B. J.; and Pender, K. R.: The Adsorption of Oxygen on the Surfaces of (110) and (100) Oriented Tungsten Single Crystals. Surface Sci., vol. 5, 1966, pp. 155-159.

78. Holscher, A. A.; and Sachtler, W. M. H.: Chemisorption and Surface Corrosion in the Tungsten + Carbon Monoxide System, as Studied by Field Emission and Field Ion Microscopy. Disc. Faraday Soc., no. 41, 1966, pp. 29-42.

79. Anon.: General Discussion. Disc. Faraday Soc., no. 41, 1966, pp. 54-74.

80. Müller, Erwin W.: Surface Corrosion of Interstitials, Vacancies and α-Irradiation Damage by Controlled Field Evaporation of Atomic Layers. Structure and Properties of Thin Films. C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea, eds., John Wiley & Sons, Inc., 1959, pp. 476-489.

81. Nakamura, Shogo; and Müller, Erwin, W.: Initial Oxidation of Tantalum Observed in a Field Ion Microscope. J. Appl. Phys., vol. 36, no. 11, Nov. 1965, pp. 3634-3641.

82. Schissel, P. O.; and Trulson, O. C.: Mass-Spectrometric Study of the Oxidation of Tungsten. J. Chem. Phys., vol. 43, no. 2, July 15, 1965, pp. 737-743.

83. Germer, L. H.; Stern, R. M.; and Mac Rae, A. U.: Beginning of the Oxidation of Metal Surfaces. Metal Surfaces: Structure, Energetics and Kinetics. American Society for Metals, 1963, pp. 287-303.

84. Park, Robert L.; and Farnsworth, H. E.: The Interaction of O_2 with a Clean (111) Nickel Surface. Appl. Phys. Letters, vol. 3, no. 9, Nov. 1, 1963, pp. 167-168.

85. Quinn, C. M.; and Roberts, M. W.: Chemisorption of Oxygen and Subsequent Processes on Metal Films: Work Function Measurements. Trans. Faraday Soc., vol. 60, 1964, pp. 899-912.

86. Müller, J.: A Study of the Oxygen Adsorption on Nickel. J. Catalysis, vol. 6, Aug. 1966, pp. 50-56.

87. Roberts, M. W.; and Wells, B. R.: Chemisorption and Incorporation of Oxygen by Nickel Films. Trans. Faraday Soc., vol. 62, no. 522, Pt. 6, June 1966, pp. 1608-1619.

88. Delchar, T.; and Tompkins, F. C.: Chemisorption of Oxygen and Hydrogen on Nickel Films - Reconstitution of the Adsorbate-Adsorbant Interface. Surface Sci., vol. 8, 1967, pp. 165-172.

89. Delchar, T. A.; and Tompkins, F. C.: Chemisorption and Incorporation of Oxygen at a Nickel Surface. Proc. Roy. Soc. (London), Ser. A, vol. 300, no. 1461, Aug. 29, 1967, pp. 141-158.

90. Farnsworth, H. E.: The Formation of the Ni_3O in Single Crystals. Appl. Phys. Letters, vol. 2, no. 10, May 15, 1963, pp. 199-200.

91. Park, Robert L.; and Farnsworth, H. E.: CO Adsorption and Interaction with Oxygen on (110) Nickel. J. Chem. Phys., vol. 40, no. 8, Apr. 15, 1964, pp. 2354-2357.

92. Boggio, J. E.; and Farnsworth, H. E.: Low Energy Electron Diffraction Study of the Formation of TaO(111) on Ta(110). Surface Sci., vol. 3, 1964, pp. 62-70.

93. Kofstad, Per: The Oxidation Behavior of Tantalum at 700^o-1000^o C. J. Electrochem. Soc., vol. 110, no. 6, June 1963, pp. 491-501.

94. Kofstad, Per: Studies of the Oxidation of Tantalum at 1000^o-1300^o C. J. Less-Common Metals, vol. 5, no. 2, Apr. 1963, pp. 158-170.

95. Kofstad, Per: Low-Pressure Oxidation of Tantalum at 1300^o-1800^o C. J. Less-Common Metals, vol. 7, no. 4, Oct. 1964, pp. 241-266.

96. Kofstad, P.; and Krudtaa, O. J.: High Temperature Metallographic Microscope Studies of the Initial Oxidation of Tantalum. J. Less-Common Metals, vol. 5, no. 6, Dec. 1963, pp. 477-492.

97. Ehrlich, Gert: On the Kinetics of Chemisorption. J. Phys. Chem., vol. 59, no. 5, May 1955, pp. 473-477.

98. Powers, R. W.; and Doyle, M. V.: The Association of Oxygen Atoms in Interstitial Solid Solution in Tantalum. Trans. AIME, vol. 215, no. 4, Aug. 1959, pp. 655-665.

99. Inouye, H.: The Oxidation of Columbium at Low Oxygen Pressures. Columbium Metallurgy. D. L. Douglas, and F. W. Kunz, eds., Interscience Publishers, 1961, pp. 649-664.

100. Taylor, A.; and Doyle, N. J.: The Solid-Solubility of Oxygen in Nb and Nb-rich, Nb-Hf, Nb-Mo, and Nb-W alloys. Part I: The Nb-O System. J. Less-Common Metals, vol. 13, no. 3, Sept. 1967, pp. 313-330.

101. Kofstad, Per; and Espevik, Svein: Low-Pressure Oxidation of Niobium at 1200° - 1700° C. J. Electrochem. Soc., vol. 112, no. 2, Feb. 1965, pp. 153-160.

102. Delgrosso, E. J.; Carta, J. S.; and Ricard, A.: The Low Pressure Oxidation of Pure Columbium. Rep. PWAC-460, Pratt & Whitney Aircraft, Sept. 1965.

103. Pasternak, R. A.; and Evans, B.: Adsorption, Absorption, and Degassing in the Oxygen-Niobium System at Very Low Pressure. J. Electrochem. Soc., vol. 114, no. 5, May 1967, pp. 452-457.

104. Cost, J. R.; and Wert, C. A.: Metal-Gas Equilibrium in the Niobium-Nitrogen Terminal Solid Solution. Acta Met., vol. 11, no. 4, 1963, pp. 231-242.

105. Pasternak, R. A.; Evans, B.; and Bergsnov-Hansen, B.: Absorption, Degassing, and Solution Equilibrium in the Nitrogen-Niobium System at Ultrahigh Vacuum and High Temperature. J. Electrochem. Soc., vol. 113, no. 7, July 1966, pp. 731-735.

106. Griffiths, R.; and Pyrde, J. A.: Solubility of Nitrogen in Tantalum. Trans. Faraday Soc., vol. 63, 1967, pp. 2599-2604.

107. Sims, Chester T.: Properties of Rhenium. Rhenium. B. W. Gonser, ed., Elsevier Publishing Co., 1962, pp. 23-35.

108. Few, W. E.; and Manning, G. K.: Solubility of Carbon and Oxygen in Molybdenum. Trans. AIME, vol. 194, 1952, pp. 271-274.

109. Nornes, Sherman B.; and Donaldson, E. E.: Adsorption of Thermally Activated Nitrogen. J. Chem. Phys., vol. 44, no. 8, Apr. 15, 1966, pp. 2968-2973.

110. Stickney, R. E.; Greaves, W.; and Fehrs, D. L.: Experimental Measurements of the Work Functions and Desorption Energies of the Systems. O-W, O-Mo, O-Re, O-Ta, and Cs-O-Ta. Thermionic Conversion Specialist Conference. IEEE, 1967, pp. 138-144.

111. Haas, T. W.; Jackson, A. G.; and Hooker, M. P.: Adsorption on Niobium (110), Tantalum (110), and Vanadium (110) Surfaces. J. Chem. Phys., vol. 46, no. 8, Apr. 15, 1967, pp. 3025-3033.

112. Zubler, E. G.; and Mosby, F. A.: An Iodine Incandescent Lamp with Virtually 100 Per Cent Lumen Maintenance. Illuminating Eng., vol. 54, no. 12, Dec. 1959, pp. 734-740.

113. Tower, Leonard K.: An Analytical Study of the Continuous Chemical Regeneration of Surfaces. NASA TN D-1194, 1962.

114. Berkowitz-Mattuck, Joan B.; Buchler, Alfred; Engelke, John L.; and Goldstein, Steven W.: Mass Spectrometric Investigation of the Oxidation of Molybdenum and Tungsten. J. Chem. Phys., vol. 39, no. 10, Nov. 15, 1963, pp. 2722-2730.

115. Singleton, J. H.: Interaction of Oxygen with Hot Tungsten. J. Chem. Phys., vol. 45, no. 8, Oct. 15, 1966, pp. 2819-2826.

116. Ptushinskii, Yu. G.; and Cuikov, B. A.: Mass Spectrometric Investigation of the Interaction of Oxygen with a Tungsten Surface. Surface Sci., vol. 6, 1967, pp. 42-56.

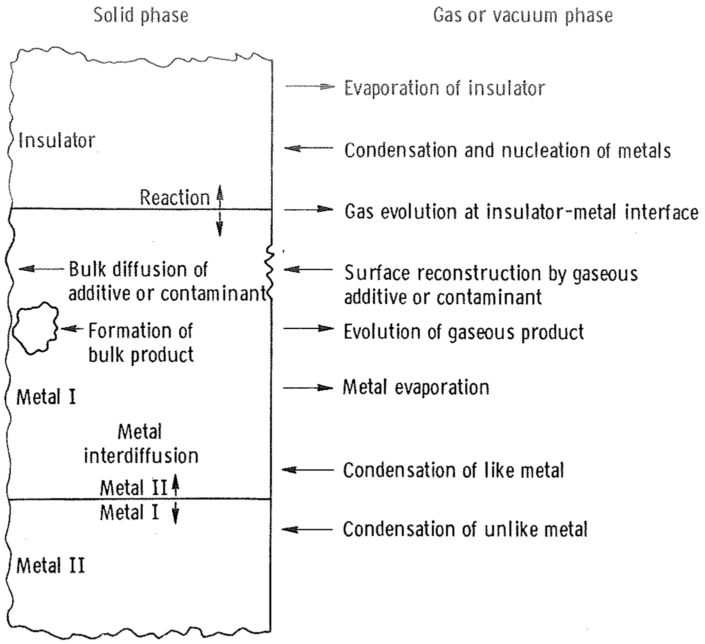

Figure 1. - Schematic diagram of some interface processes in thermionic diodes.

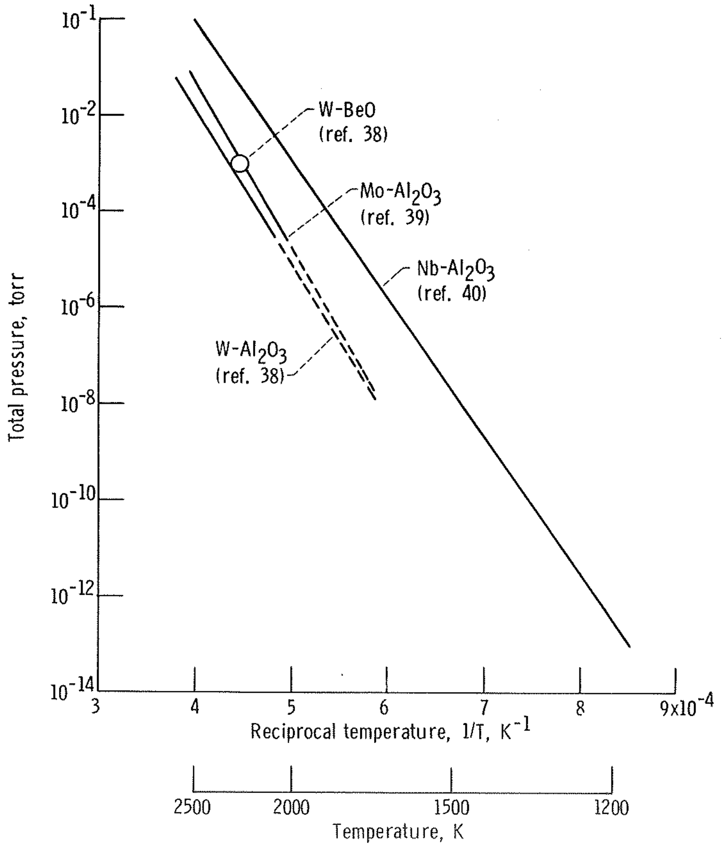

Figure 2. - Total gas pressure as function of temperature for some metal - ceramic oxide systems.

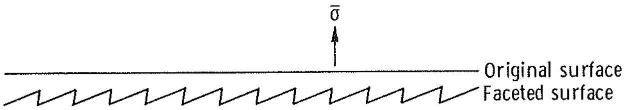

Figure 3. - Faceting of a plane, monocrystalline surface.

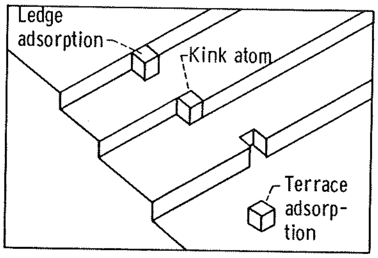

Figure 4. - Illustration of terrace-ledge-kink model.

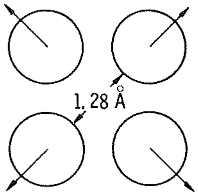

Figure 5. - Aperture in nickel surface postulated by Delchar and Tompkins (refs. 88 and 89). (1 Å = 10^{-10} m.)

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> — NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546