SPECIAL ASPECTS OF DIFFUSION IN THIN FILMS

R. W. Balluffi and J. M. Blakely

Department of Materials Science and Engineering
and the
Materials Science Center
Cornell University
Ithaca, New York 14850

August 1974

Cornell University
Ithaca, New York 14850

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Report #2287

Issued by

The Materials Science Center

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SPECIAL ASPECTS OF DIFFUSION IN THIN FILMS

R. W. Balluffi and J. M. Blakely
Department of Materials Science and Engineering
and the
Materials Science Center
Cornell University
Ithaca, New York 14850

ABSTRACT

We have attempted to identify and describe a number of factors which may cause diffusion in thin films to differ from the ordinary diffusion which occurs in bulk specimens at elevated temperatures. Diffusion in thin films may be expected to have special characteristics for a number of reasons. These factors are enumerated and discussed in turn with reference to experiment wherever possible.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PL

I. INTRODUCTION

In the present paper we attempt to identify and describe a number of factors which may cause diffusion in thin films to differ from the ordinary diffusion which occurs in bulk specimens at elevated temperatures. Diffusion in thin films may be expected to have special characteristics for a number of reasons which include the following:

- (1) thin films are invariably diffused at relatively low temperatures because of their poor thermal stability.
- (2) all volume elements are in close proximity to either a free surface or an interphase boundary of some kind.
- (3) films generally contain high densities of low temperature short circuits for diffusion such as grain boundaries and dislocations.
- (4) large biaxial stresses in the plane of the film are often present.
- (5) relatively high concentrations of uncontrolled impurities may be present as a result of special fabrication or diffusion conditions.
- (6) disordered or metastable structures may be present.
- (7) diffusion often occurs over short distances under the influence of large concentration or electrostatic potential gradients.
- (8) steep chemical gradients and low temperatures may affect the possible maintenance of local equilibrium at phase boundaries during multiphase diffusion.

These factors are discussed individually in the following sections. Selected experimental results are used wherever possible as examples.

II. EFFECTS DUE TO NEARBY SURFACES OR INTERFACES

The fact that every volume element in a thin film diffusion specimen is in close proximity to either a free surface or a phase boundary of same type may have a strong influence on the diffusion.

II.1 Space Charge Effects

In a metal the effects of electron surface states due to defects or impurities should be negligible because of the effective screening by the conduction electrons.

However, the situation may be different in the case of ionic materials or semiconductors where the free charge densities are small and screening distances large. The electrostatic potentials and point defect distributions near dislocations and interfaces in simple ionic solids have been the subject of considerable theoretical work, and there is now some experimental data confirming the existence of extensive space charge regions. Electronic space charge regions due to localized electronic states have significant effects in surface and thin film electronic conductance; they probably play an important role in the diffusion of ionized impurities near semiconductor surfaces. The effects of electrostatic fields on the diffusion of ionized impurities into semiconductors have, in fact, been reviewed by Hu.¹ A problem of considerable practical interest is the diffusion of one impurity in a region with an established concentration and electrostatic potential gradient produced by another impurity.

The idea that space charge regions will generally be associated with dislocations and interfaces in ionic crystals was initially suggested by Frenkel², and there have been a number of extensions

of his work aimed at calculating the details of the point defect densities near dislocations³ and planar interfaces.⁴⁻⁹ The defect is assumed to possess a localized charge with an adjacent balancing space charge region in which the charge density falls off approximately exponentially with distance. The characteristic decay distance (Debye length) will depend on the dielectric properties of the crystal, temperature and impurity levels but may be of the order of 10^2 - 10^3 Å. Thus, with such ionic systems, the diffusion characteristics of thin films are likely to be significantly different from bulk material.

A simple model explaining the existence of equilibrium charged defect clouds near dislocations and interfaces has been developed^{9,10} based to some extent on an analogy with electronic space charge layers in semiconductors. In Fig. 1 we show schematically a "one ion" free energy level scheme for the cations in a simple monovalent ionic solid possessing Frenkel disorder on the cation lattice.* The electrochemical potential of the cations may be evaluated^{9,10} from the bulk properties of the crystal. A dislocation or interface is assumed to provide an additional array of binding sites for the cations; these could, for example, correspond to dislocation jogs or surface kinks. At these sites the cation binding energy will be different from that in the normal lattice. Occupancy of these special sites, and hence the local charge of the dislocation or interface, will be determined by their position relative to the cation electrochemical potential μ_+ . If the surface sites lie below μ_+ (Fig. 1), the surface will acquire a net positive charge and a

*The model can be extended to crystals such as NaCl with Schottky disorder⁹. Space charge effects in the silver halides with cation Frenkel disorder have been studied most extensively.

balancing negative space charge region will develop consisting of a vacancy excess; if the surface site lie above μ_+ , a positive space charge region will develop with an enhancement of the interstitial density. Within the context of the model the parameters which determine the charge distribution are the number of active surface or dislocation sites and their energies; these in turn are the quantities which may be derived from experiments which measure the space charge characteristics. Multivalent impurities will also play an important role in determining the charge configuration.⁵⁻¹⁰ Even if the impurities remain homogeneously distributed they will affect the dislocation or interface potential through their influence on the cation electrochemical potential. The introduction of a divalent cation impurity into a monovalent crystal may result in the formation of a cation vacancy which, due to Coulomb attraction, will be associated with the impurity ion at low temperatures. The form of the variation with temperature of the cation electrochemical potential is shown schematically¹⁰ in Fig. 2 for a divalently doped crystal in which the binding (free) energy between the vacancy and impurity is B: curve b is for a higher doping level than a. At high temperature the behavior approaches that of an intrinsic crystal. The potential difference, ϕ , across the space charge region near the interface or dislocation is the difference between the electrochemical potential and the binding energy at the interface or dislocation sites.* It is clear that in passing through some particular temperature (T_a or T_b) the potential difference will change sign; this is the so-called isoelectric temperature. If,

* This will be a good approximation so long as the occupancy of the sites at the dislocation core or surface does not approach saturation.

for example, the space charge has an excess of vacancies (and deficiency of interstitials) below the isoelectric temperature it will have an excess of interstitials above it; clearly this will be of importance in determining the way in which ionic transport processes near the surface (or along dislocations) vary with temperature.

There have been a number of experimental studies of the charge configurations associated with dislocations, grain boundaries and free surfaces in ionic crystals. There are some conflicting results due to impurity effects and departures from equilibrium conditions, but there is good evidence to support the existence of defect space charges. The experiments have included the study of the motion of individual dislocation¹¹ and grain boundaries¹² under applied electric fields, internal friction due to dislocation damping¹³ and the variation of surface ionic conductance^{14,15,16} and electrostatic potential^{17,18,19} with temperature and surface orientation.

The effect of surface space charge regions on diffusion in thin films of ionic crystals may be discussed with reference to Fig. 3. This depicts a situation in which the space charge has an excess of vacancies and a deficiency of interstitials for two cases, viz (i) when the thickness of the film W is much greater than the Debye length λ (Fig. 3a,b) and, (ii) when W is comparable to λ (Fig. 3c,d). Detailed calculations for the second case have in fact been made for the silver halides by Tan and Høyen.²⁰ Cation diffusion parallel to the surface will be affected by the surface space charge regions in both cases; if cation vacancies are more mobile than interstitials an enhancement of the diffusion rate will

occur, whereas if interstitials are the more mobile defect the space charge region will be one of low diffusion rate. In case (ii) the self-diffusion rate by an interstitial mechanism parallel to the film surface would be significantly reduced below the value characteristic of bulk material. Diffusion normal to the plane of the film would be affected in a somewhat different way since the space charge regions are to be regarded as being in series with the bulk for this mode. For example, for interstitial self-diffusion the space charge region will act as a blocking layer in case (i).

In practice the ionic crystal film may be bounded on at least one side by a metallic layer as in Fig. 4. In this case the potential profile will not in general be symmetrical about the center of the film, (Fig. 4). If the metal-ionic crystal junction is reversible with respect to the exchange of metallic ions and there is a negligible concentration of conduction electrons in the film the total potential difference between film and metal will be determined by the equality of cation electrochemical potential. (This junction potential has been treated in some detail^{21,22} for the case of the silver halide-silver reversible contact.) The defect distribution near the metal surface will be described by the same Debye length as at the vapor interface although the potential differences across the two regions may differ in magnitude and even in sign. The effect of the dipolar layer at the metal contact on the diffusion properties of the film will be qualitatively the same as discussed in the previous paragraph.

It should be emphasized that so far we have been discussing equilibrium interface/dislocation space charge regions. Significant electrostatic potential gradients across thin films may also be

developed under non-equilibrium conditions such as exist during oxide formation at free surfaces. The origin of such potential gradients may be the difference in mobilities of diffusing metal and oxygen ions, the difference in electron Fermi levels (relative to vacuum) in the metal and oxide or a combination of both effects. The analysis of oxide film growth including these effects is thoroughly reviewed in a recent article by Lawless.²³

II.2 Other Surface Effects

Other effects due to nearby surfaces may occur under special circumstances.

Dzhafarov and Kulikov²⁴ report that the concentration profile after annealing of Ag¹¹⁰ deposited initially on flat surfaces of GaAs depends upon whether the surface is (111) or ($\bar{1}\bar{1}\bar{1}$). In this case the sphalerite structure causes one surface to consist of a layer of Ga atoms whereas the other surface consists of a layer of As atoms. The difference in behavior was attributed to the different natures of the interaction of the deposited silver with the Ga and As surfaces; the silver was believed to form a volatile compound with the Ga-rich surface and not with the As-rich surface. We note that the effect must be due to the influence of the surface since bulk diffusion must be isotropic in the cubic sphalerite structure.

When P is diffused into a Si crystal from a surface anomalous diffusion penetration curves are observed.²⁵ Yoshida, et al.²⁵ offer the following explanation for this phenomenon. The P atoms diffuse by a vacancy mechanism. However, when a P atom enters the Si lattice at the surface it does so by forming a bound P-vacancy pair. These pairs diffuse into the lattice where they become super-saturated and eventually dissociate. The surface therefore acts as

an effective source for excess vacancies which exert a strong effect on the diffusion in the nearby lattice.

III. SHORT CIRCUIT DIFFUSION ALONG DISLOCATIONS AND GRAIN BOUNDARIES

It is well established that dislocations and grain boundaries act as rapid diffusion short circuits in both metals²⁶⁻²⁸ and also in many non-metals^{27,29,30} such as ionic materials and semiconductors. In general, short circuit diffusion proceeds with a lower activation energy than lattice diffusion, and short circuiting therefore tends to become particularly important at relatively low temperatures. Since thin films are usually diffused at relatively low temperatures, and since thin films often contain unusually high densities of short circuiting paths, there are many situations where grain boundary or dislocation short circuit diffusion should become the dominant transport mechanism. We note that thin films may contain dislocation densities as high as 10^{10} - 10^{11} cm⁻² and have grain sizes smaller than 10^2 Å.^{31,32}

In analysing short circuit diffusion along grain boundaries it is customary to take the grain boundary as a homogeneous slab of width w_b which possesses a uniform diffusivity D_b .³³ Similarly, a dislocation is taken as a homogeneous cylinder (pipe) of area A_d and uniform diffusivity D_d .³⁴ The total mass transport along the short circuit path may then be described by using the product parameter $w_b D_b$ or $A_d D_d$. In reality both D_b and D_d are expected to fall off continuously with distance from the center of the short circuit region.²⁸ However, little is known at present about the detailed aspects of such behavior, and the homogeneous model is

therefore employed as a useful approximation. In the case of metals it is believed that the short circuiting region is narrow (of the order of few atomic distances), and such an approximation is therefore quite satisfactory. However, there is some speculation²⁹ that the short-circuiting region is orders-of-magnitude wider in ionic materials where space charge effects are important. This case is discussed in some detail below.

III.1 Single Phase Diffusion

Metals

The relative importance of short circuiting fluxes during diffusion in a thin film of a FCC metal consisting of a single phase may be demonstrated using the following diffusion parameters proposed recently by Gjostein:²⁸

$$w_b D_b (\text{cm}^3 \text{sec}^{-1}) \approx 1.5 \times 10^{-8} \cdot \exp[-8.9(T_m/T)] \quad (1)$$

$$A_d D_d (\text{cm}^4 \text{sec}^{-1}) \approx 5.3 \times 10^{-15} \cdot \exp\{-12.5(T_m/T)\} \quad (2)$$

$$D_l (\text{cm}^2 \text{sec}^{-1}) \approx 0.5 \exp[-17.0(T_m/T)] \quad (3)$$

Here, D_b is the diffusivity for an average high angle boundary, D_d is the average diffusivity for a dissociated dislocation with Burgers vector $a/2\langle 110 \rangle$, and D_l is the lattice diffusivity. These expressions represent average data for a variety of FCC metals normalized to a common reduced temperature T/T_m where T_m is the melting temperature. In order to obtain an estimate of the fluxes J_b , J_d and J_l which would be transported along boundaries, dislocations and through the lattice in a given thin-film diffusion situation consider a film containing rectangular grains of edge

dimension L running through the entire thickness and a density, ρ_d , of uniformly distributed dislocations also running through the film in a direction perpendicular to the surface. Consider the simple case where the concentrations on the front and back surfaces of the film are maintained constant, and a steady state has been reached where all gradients parallel to the plane of the film are eliminated. The diffusion fluxes through the film per unit area of surface are then related by

$$J_b/J_\ell = \frac{2w_b D_b}{D_\ell} \quad (4)$$

$$J_d/J_\ell = \frac{\rho_d A_d D_d}{D_\ell} \quad (5)$$

The regimes of grain size (L) and dislocation density (ρ_d) over which the different fluxes dominate are readily calculated from the above equations as a function of reduced temperature and are indicated in the maps shown in Fig. 5. As expected, lattice diffusion tends to be replaced as a dominant mechanism by both grain boundary and dislocation short circuiting as T decreases. Furthermore, dislocation diffusion tends to be replaced by grain boundary diffusion. Reasonable values of L and ρ_d which might occur in practice lie within the dashed rectangles. The results suggest that grain boundary short circuiting should dominate in polycrystals with $L < 10^{-2}$ cm at all temperatures indicated. For single crystal films dislocation short circuiting should dominate when $\rho_d > 10^{11} \text{ cm}^{-2}$ at $T/T_m = 0.6$ and when $\rho_d > 10^8 \text{ cm}^{-2}$ at $T/T_m = 0.3$. These results clearly indicate that we should expect short circuiting to be overwhelmingly dominant under many thin film diffusion conditions.

The geometry of diffusion in thin films when short circuiting is important is generally much more complicated, of course, than in the simple example used above. Highly complicated iso-concentration contours and diffusion flux patterns may develop depending upon factors such as:

- (i) the geometry of the short circuiting network
- (ii) the relative magnitudes of D_b , D_d and D_l
- (iii) the elapsed time of diffusion

Harrison³⁵ has pointed out that there are three characteristic short circuiting situations which might be expected when a species is diffused into a large bulk specimen.

Using his notation, a Type C situation exists when rapid diffusion occurs along the short circuit paths and lattice diffusion is sufficiently negligible that any leakage from the short circuits into the adjoining lattice is small enough to have caused a negligible perturbation of the concentration in the short circuits. As Harrison indicates, for self-diffusion such a condition requires that

$$D_l t \ll w_b^2 \quad (6)$$

for grain boundaries, or,

$$D_l t \ll A_d \quad (7)$$

for dislocations. These conditions could correspond to times which are very short depending upon the magnitude of the lattice diffusion coefficient. This type of diffusion is characterized by a highly selective penetration of the diffusing species along the short circuit network.

A Type A situation exists when every diffusing atom has diffused a sufficient distance in the lattice so that it has sampled at least

several short circuit paths. In this case each atom may be described by the same effective diffusion coefficient given by

$$\bar{D} = D_{\ell} + \frac{2w_b D_b}{L} \quad (8)$$

for grain boundary short circuiting, or

$$\bar{D} = D_{\ell} + A_d \rho_d D_d \quad (9)$$

for dislocation short circuiting; the concentration in the lattice and in the short circuits is uniform in any plane perpendicular to the diffusion direction. Such a condition should obtain when the lattice diffusion distance is considerably larger than the distance between grain boundaries or dislocations, i.e., when

$$D_{\ell} t \gg L^2 \quad (10)$$

or,

$$D_{\ell} t \gg 1/\rho_d. \quad (11)$$

This condition corresponds generally to a late stage of diffusion after considerable lattice diffusion has occurred.

Type B diffusion is intermediate between Types A and C. This type of diffusion is characterized by an initial rapid penetration along the short circuit network which quickly slows down as atoms leak out of the network into the adjacent lattice by lateral lattice diffusion. The geometry of the resulting diffusion distribution is therefore highly complex and consists of regions of preferential penetration in the lattice adjacent to elements of the short circuiting network.

It seems likely that all of these types of short circuiting diffusion could occur in single phase thin films under appropriate

conditions. Due to the small diffusion distances involved and the low temperatures which are generally employed we would expect Type B and C diffusion to be especially common. An essential condition for achieving Type A diffusion is that the spacing between the short-circuiting paths must be small compared to the film thickness. It seems likely that this condition could be found in films of moderate thickness containing unusually high densities of grain boundaries or dislocations. If this condition is not met the final diffusion distribution could be achieved as a result of Type B diffusion before all the diffusing atoms had a chance to visit short circuiting paths. It is also possible, of course, that short circuiting is almost negligible in certain situations. Turner³⁶ has reviewed investigations in which low temperature diffusion in thin films apparently occurred by lattice diffusion. He notes that in nearly all such cases the diffusion distance was small compared to the average spacing between short circuits.

No analytical treatments of these difficult diffusion situations in thin films have been carried out. In general, Type B kinetics present the most formidable difficulties. Unnam, et al.³⁷ have analysed such a problem using numerical methods for a two-component system consisting of a polycrystalline thin film deposited on a thick substrate. The analysis of even more complicated situations will require further elaborate computer modeling techniques.

Ionic Solids

As noted earlier the extent of the region of enhanced (or diminished) diffusivity associated with grain boundaries and dislocations in ionic materials may be much greater than in metals so that significant overlap of short circuiting zones will occur at

lower dislocation densities and larger grain sizes. For example, with a Debye length of 10^{30} Å the equilibrium space charge regions of adjacent dislocations will overlap considerably when their density reaches $\sim 10^{10} \text{ cm}^{-2}$; with such a concentration of dislocations (or grain sizes $\sim 10^{30}$ Å) we anticipate that the material will have no regions with bulk diffusion characteristics. For ionic materials it is convenient to distinguish two regions near the grain boundary (or dislocation) in which the diffusivity departs from its bulk value, (Fig. 6) viz, the core region of atomic dimensions in which the diffusivity is probably enhanced from its bulk value and a diffuse layer (space charge region) in which the diffusivity is either enhanced or suppressed depending on the mode of diffusion and the sign of the space charge. Since for the equilibrium situation explicit expressions can be derived for the defect densities in the space charge region it is possible, by assuming constant defect mobilities, to compute the excess current that would travel along this region when a given electro-chemical potential gradient is maintained across the film. For example for cation self diffusion by an interstitial mechanism the excess current in the space charge regions near a grain boundary would be

$$(D_I/kT) \int_0^{\infty} [\eta_I(x) - \eta_I(\text{bulk})] dx \text{ grad } \mu_+ \quad (12)$$

where the integration is performed over the space charge region, and where D_I and $\eta_I(x)$ are the cation interstitial diffusivity and concentration respectively with x the distance normal to the boundary, and $\eta_I(\text{bulk})$ the normal bulk interstitial concentration. The excess flux is thus proportional to the integrated cation interstitial excess in the space charge region. For AgBr for which

η (bulk) $\sim 10^{18} \text{ cm}^{-3}$ at 400°K, the excess number of interstitials has been found from experiment to be $\sim 10^{13}$ per cm^2 of interface¹⁴ and hence the flux through a film which columnar grains of dimensions $\sim 1000\text{\AA}$ would be enhanced by a factor of ~ 2 from the space charge regions alone. The core contribution would probably further increase the efficiency of the grain boundaries as short circuits.

As noted in a previous section the temperature dependence of the excess boundary flux is likely to be rather complicated when impurities are present. In passing through the isoelectric point for the boundary the space charge contribution will change sign while the core contribution may be expected to vary as discussed above for grain boundaries in metal films.

Data on grain boundary diffusion in ceramics has recently been collected by Mistler and Coble.^{38*} Since parameters of the space charge regions are not known for the materials in which diffusion has been studied it is not yet possible to make a quantitative comparison with predictions from the space charge theory.

* In their recent article Mistler and Coble³⁸ attempt to derive "effective grain boundary widths" from a combination of grain boundary diffusion and grain boundary migration data for metals and ceramics. Their estimates are based on the assumption that the boundary may be regarded as a uniform slab with isotropic diffusion characteristics. Diffusion parallel to the boundary is considered to occur at the same rate as diffusion normal to it. Clearly this is a totally unreasonable assumption for both metals and ceramics and their conclusions on boundary widths should not be considered as being even approximately correct. In a dislocation model of a grain boundary in a metal, atom motion parallel to the boundary along the cores is likely to be quite different from motion across the boundary. In an ionic material a grain boundary space charge region depleted in the mobile defect would act as a blocking layer and diffusion normal to the boundary would be slow whereas the core may still act as an efficient short circuit for parallel diffusion. We may also note that estimates of the quantity A_d (p. 9) associated with dislocations are usually obtained by making the assumption that diffusion within the core region is isotropic and that exchange between the core and surrounding matrix is not rate controlling (see, e.g., Mimkes, this volume).

III.2 Multiphase Diffusion

Exceedingly complex diffusion zones may be produced in multiphase diffusion zones where intermediate phases form and where short-circuiting occurs along rather widely spaced grain boundaries (as shown, for example, in Fig. 7 from the work of Tisone and Drobek³⁹). In such cases the intermediate phases do not form as thin layers of uniform thickness lying parallel to the plane of the thin film diffusion sandwich as would be expected for pure lattice diffusion.^{40,41} Instead, more rapid diffusion occurs at the grain boundaries, and the new phases form and grow preferentially in the grain boundary regions. Such conditions should be fairly common, since the grain size is often expected to be about equal to the thickness of the intermediate phase. Of course, when the average spacing of the short circuits is decreased more uniform layer structures should form even in the presence of strong short circuiting.

It is interesting to point out, however, that it seems possible for relatively planar layers of intermediate phases to grow in multiphase diffusion even in the presence of rather widely spaced short circuits. Consider, for example, the case illustrated in Fig. 8. Here an intermediate β phase is growing between α and γ phases, mainly as a result of rapid short circuiting along the grain boundaries and interphase boundaries. An atomic flux generated at the migrating α/β interface short circuits along the α/β interface and the β phase grain boundaries and is then deposited at the migrating β/γ interface via further short circuiting along the β/γ interface. Evidence that rapid diffusion can indeed occur along interphase boundaries has been presented by Aaron and Weinberg.⁴² For such boundaries it appears that the diffusivity increases as the

coherency of the boundary decreases. Furthermore, the thickness of the β layer, w , will increase approximately parabolically with time ($w \propto t^{1/2}$) if the reactions at the interphase interfaces are rapid enough to maintain approximate local equilibrium. The kinetics of the layer growth could therefore resemble those in a system where the layer thickness increases purely by lattice diffusion.^{40,41} Under these conditions a quasi-steady state will exist in the short circuits, and

$$\frac{dw}{dt} \propto \frac{(C_{\alpha\beta} - C_{\beta\gamma})D_b}{w} \quad (13)$$

where $C_{\alpha\beta}$ and $C_{\beta\gamma}$ are the constant concentrations maintained in the grain boundaries at the phase boundaries. Integration of eqn. (13) then leads to $w \propto t^{1/2}$. We note that approximately parabolic layer growth kinetics could also be obtained in the grain boundary short circuiting configuration in Fig. 8b, if diffusion along the phase boundaries were rapid enough.

Baird⁴⁰ has considered the growth kinetics of a layer of intermediate phase in an idealized case where short circuiting occurs only along the boundaries of columnar grains running perpendicular to the plane of the layer; i.e., no lateral short circuiting along phase boundaries of the type suggested previously in Fig. 8 is present. He presents a rather crude semi-quantitative analytical argument which suggests that in this situation the layer thickness should vary with time as $w \propto t^{1/n}$ where $2 < n < 4$ rather than $w \propto t^{1/2}$ as in the cases of the simple diffusion controlled situations discussed previously.

It is also possible, of course, that the reactions at the interface may not be rapid enough to maintain approximate local equilibrium as is discussed later in Section VIII. The kinetics of layer

growth would then be controlled by the rate of interface reaction. Under such conditions the tendency of grain boundary short circuiting to promote the preferential formation of intermediate phases along grain boundaries would be reduced, and there would be a strong tendency towards the formation of planar phase boundaries.

No attempt has yet been made to treat these complicated multiphase diffusion situations on a rigorous analytical basis. The mathematical difficulties appear to be overwhelming. Computer modeling therefore appears more promising, and work along these lines would be of interest.

III.3 Experimental Observations

The previous conclusions regarding the potential importance of short circuiting in many thin film diffusion situations are supported by numerous experimental results. In fact, under normal conditions transport in polycrystalline films at low temperatures appears to be dominated by transport along the short circuits as predicted above. In recent years relatively sophisticated techniques have become available for measuring the kinetics of diffusion in thin films and also for characterizing their defect structures, and the effects of short circuiting have therefore become clearly evident.

The results of a number of recent experiments demonstrating short circuiting in mainly metal films in the temperature range $0.3 \leq T/T_m \leq 0.6$ are listed in Table I. Most of these experiments indicate strong short circuiting along grain boundaries. However, the experiments of at least Thomas and Haas⁴⁸ and van Gurp⁴⁹ and possibly others indicate strong dislocation contributions.

We note that various types of short circuiting conditions were

evidently achieved in these experiments. For example, Type C kinetics were approached in the work of Tu and Rosenberg⁴⁷ where Pd atoms diffused exclusively along the grain boundaries of polycrystalline Ag films. On the other hand, Unnam, et al.³⁷ found Type B kinetics during the diffusion of Cu into Ni. In this experiment Cu diffused into the Ni via a grain boundary network and produced a situation where each Ni grain consisted of a Ni-rich core surrounded by a Cu-rich envelope.

In the case of multiphase diffusion, preferential diffusion and phase formation and growth in grain boundaries has been observed as indicated by the example in Fig. 7. Further examples of such behavior have been cited (or proposed) by other workers including Richards and McCann⁴⁴ Borders⁵² and Ziegler, et al.⁵⁴

The great complexity of Type B short circuiting kinetics has made both the experimental observation and the analysis of such kinetics extremely difficult. Most of the techniques for observing diffusion in thin films tend to average over relatively large lateral distances in the diffusion zone, and therefore detailed information about the actual distributions of diffusing matter in the non-uniform regions adjacent to the short circuiting paths is generally lacking. There is a clear need for higher resolution studies of these complex diffusion zones. The analysis of these complex short circuiting experiments is in a corresponding primitive state, and, as noted above, it appears that computer modeling would be helpful.

Considerable evidence has also been found for diffusional short circuiting along grain boundaries during the growth of oxide films. Work in this area has been reviewed recently by Lawless²³

who also points out that dislocation short circuiting may be of importance. However, the contributions of these latter short circuits are not so well established.

IV. EFFECTS OF STRESSES

Relatively large biaxial stresses are often present in thin films, and explanations of their origin have been reviewed in several places.^{55,56} Stresses in the range 10^9 - 10^{10} dynes cm^{-2} are commonly found.⁵⁵⁻⁵⁷ Stresses of this magnitude might be expected to exert significant effects upon thin film diffusion processes.

Consider first the simplest case of self-diffusion, and for preliminary purposes let us review the straightforward case of the effect of a hydrostatic compressive stress, p , on the diffusion rate in a solid. If the diffusion occurs by a point defect mechanism, the stress alters the equilibrium concentration of point defects (e.g., vacancies) and also influences the rate of exchange between the defects and the diffusing atoms. In the case of hydrostatic stress the equilibrium point defect concentration $x(p)$ is the same everywhere in the specimen and is given by

$$x(p) = x(0) \cdot \exp (-pV_f/kT), \quad (14)$$

where V_f is the volume expansion of the crystal on forming the defect. Also, the diffusivity of the defect in the presence of the stress is given approximately by

$$D_d(p) = D_d(0) \cdot \exp (-pV_m/kT), \quad (15)$$

where V_m is the volume expansion when the migrating defect is in the saddle point for exchange with an atom. Therefore, since the lattice diffusivity, D_L , is proportional to both D_d and x , we have

the simple result

$$D_L(p) = D_L(0) \exp\left(\frac{-V_m p}{kT}\right) \cdot \exp\left(\frac{-V_f p}{kT}\right). \quad (16)$$

We note that we have neglected minor effects of stress on pre-exponential factors in the above (see, for example, Shewmon⁵⁸).

Unfortunately, under conditions of biaxial stress, σ , the situation is considerably more complex. The concentration of point defects is no longer uniform throughout the volume; instead, each source or sink (i.e., surface, grain boundary or dislocation) tends to maintain the defects in local equilibrium in its immediate vicinity. Furthermore, the local equilibrium concentration depends in each case upon the orientation of the source (or sink) with respect to the stress axis. For example, in cases where the formation of a defect at a source causes the crystal to expand in the direction of an applied tensile stress the energy of defect formation is decreased by the work done by the stress, and the equilibrium defect concentration is correspondingly increased. Under these conditions defect currents tend to flow between the different sources and sinks producing Nabarro-Herring type diffusional creep⁵⁹ which acts in a direction to reduce the biaxial stress. An example of such a situation in a thin film is shown schematically in Fig. 9 where transverse grain boundaries are present, and where the equilibrium vacancy concentration is increased in their vicinities due to the biaxial tensile stress. In this situation vacancies tend to flow from these regions of high concentration to the specimen surface thereby establishing mass currents which tend to elongate the specimen in the direction of the biaxial stress.

The analysis of self-diffusion under such conditions is

obviously extremely complicated and depends upon the source and sink geometry, the extent to which point defect equilibrium is maintained at the sources and sinks, etc. If we take the case illustrated in Fig. 9, where we assume that tracer atoms diffuse into the film from a layer on the surface, we can identify several effects due to the stress. The average vacancy concentration is increased in the diffusion zone, the vacancy jump frequency is also increased, and many localized mass currents which are composed of both normal atoms and tracer atoms are present.

The average vacancy concentration in the diffusion zone in this case may be crudely estimated as

$$\bar{x}(\sigma) \approx 1/2 \cdot x(0) \cdot [\exp(\Omega\sigma/kT)+1]$$

where Ω = atomic volume, and we have neglected any lattice relaxation around the point defects. In the presence of the non-hydrostatic stress the defect diffusivity is actually a stress dependent tensor, since the activation energy required for a jump depends upon the angle between the jump direction and the principle axes of the stress field.^{60,61} In the present example, where we are mainly interested in the diffusivity in a direction perpendicular to the surface, we may approximate the average defect diffusivity as

$$\bar{D}_d(\sigma) \sim D_d(0) \exp\left(\frac{2}{3} \frac{V_m \sigma}{kT}\right) \quad (17)$$

where the factor 2/3 has been introduced in order to allow for the biaxial nature of the stress field. Therefore, the average atom lattice diffusivity is given approximately by

$$\bar{D}_l(\sigma) = \bar{D}_d(\sigma) \cdot \bar{x}(\sigma) \sim D_l(0) \exp\left(\frac{2V_m \sigma}{3kT}\right) \cdot \left[\frac{\exp(\Omega\sigma/kT)+1}{2}\right]. \quad (18)$$

The quantity V_m is expected to be relatively small compared to Ω .⁶² Taking $\sigma = 2 \times 10^9$ dynes cm^{-2} , $V_m = 0.2\Omega$ and $T = 250^\circ\text{C}$, we find $D_\ell(\sigma)/D_\ell(0) \sim 1.24$. The effect of stresses at this level would therefore be relatively small. However, it appears that larger stresses ranging up to 10^{10} dynes cm^{-2} would affect $\bar{D}_\ell$ by factors as large as 3-5. The small mass currents between the sources and sinks illustrated in Fig. 9 also act to increase the average rate of inward penetration of the tracer atoms. A portion of these currents is made up of tracer atoms, and the net effect is therefore an inward shift of the center of mass of the distribution of tracer atoms.

In considering these effects it should be emphasized that the mass currents shown in Fig. 9 provide stress relief and that they would therefore undoubtedly vary with time. In addition, we have assumed that the sources and sinks operate with a high enough efficiency to maintain local equilibrium and have considered the case where the stress is positive. In certain cases a negative stress may be present; this would merely reverse the effects discussed above.

In the case of solute atom diffusion the situation is further complicated by the fact that the local stress-motivated defect currents tend to exert a "sweeping" effect on the solute atoms. Since there is generally a binding energy between defects and solute atoms, and since the defect jumping rates are generally altered in the vicinity of solute atoms, a defect current is expected to cause a redistribution of the solute atoms relative to the host atoms. Anthony⁶³ and Dobson⁶⁴ have discussed this problem for a simple system consisting of solute atoms, host atoms and vacancies.

However, the problem is exceedingly complex, and no solutions in the presence of such complicated vacancy currents as those illustrated in Fig. 9 have been obtained.

It is important to point out that biaxial stresses should also affect the diffusivities in grain boundaries and dislocations. Since the diffusion in these short-circuiting paths is often dominant in thin film diffusion zones (Section III), this effect must be considered. There is a considerable body of information available which indicates that both grain boundary and dislocation diffusion occurs by a defect (e.g., vacancy) mechanism.^{26,28,65} In such a case we would again expect both the defect concentrations and their jump frequencies in the grain boundaries and dislocations to be affected by the biaxial stress. In the case of hydrostatic compression, Martin, et al.⁶⁶ found a decrease in the self-diffusion rate along grain boundaries in Ag corresponding to an activation volume $V_f + V_m = 1.1\Omega$. The behavior is quite comparable to the effect of pressure on lattice diffusion in Ag where diffusion occurs by a vacancy mechanism and where $V_f + V_m = 0.93\Omega$. An analysis similar to that carried out above for the effects of biaxial stress on lattice diffusion would therefore predict that the short circuiting diffusion in transverse grain boundaries and edge dislocations would be affected by factors of the same order of magnitude. In this respect we note that the effects of the biaxial stress should be largest in the transverse grain boundaries and edge dislocations (such as in Fig. 9), which are the defects which make the main short circuiting contributions in the important case where the average direction of diffusion is perpendicular to the film.

Stress motivated defect currents will also exist along the short circuiting paths if they act as highly efficient sources and

sinks and this will lead to so-called Coble-type creep⁶⁷ when grain boundary short circuiting dominates. In the case of solute diffusional short circuiting we should therefore expect "sweeping" effects due to the action of the stress motivated defect currents which are similar to those mentioned above for lattice diffusion. No analysis of this complex problem has been attempted. Gangulee⁶⁸ has presented some evidence for the accelerated penetration of Be solute atoms along transverse grain boundaries in Al thin films due to biaxial stress. However, the magnitudes of the stresses were not reported.

Stresses may exert further effects on diffusion in thin films in cases where more than one phase is formed. The effect of hydrostatic compression on diffusion in multiphase diffusion zones in bulk specimen has been investigated, and it has been pointed out⁶⁹⁻⁷¹ that the stress may not only influence diffusion rates within each phase but it may also influence the chemical compositions of the phases at the interphase boundaries and thereby influence the overall kinetics. However, an analysis by Castleman⁷⁰ shows that this latter effect should be relatively small under normal conditions. For thin films under biaxial stress conditions this effect should be even smaller and can almost certainly be ignored. We note that stress may also influence the rate of nucleation of a new phase in a diffusion zone if the volume of the new phase differs from that of the matrix. However, again this effect is reduced under biaxial stress conditions, since free expansion is possible in a direction normal to the surface.

Finally, we mention the effect of biaxial stress on the production of fissures, pores, spalling, etc. in multiphase diffusion

zones. As emphasized recently by Dearnaley and Hartley,⁷² many intermediate phases formed in such zones are characterized by considerable hardness and brittleness and are particularly susceptible to fracture. Furthermore, the partial molar volumes in many of these phases vary appreciably from those of other phases in the diffusion zone thereby producing large stresses. As Dearnaley and Hartley⁷² mention, observations of stress effects and blistering in oxide films^{73,74} are paralleled by those in metal and semiconductor silicide thin films produced by interdiffusion.^{54,75,76} Such effects may markedly affect the diffusion conditions by altering the geometry, introducing open diffusion circuits, creating short circuits along internal surfaces, etc. These effects have been well recognized in oxide film growth. However, less attention has been paid to such processes in thin film interdiffusion involving metals and semiconductors, and correspondingly little information regarding them is available. Many investigations of thin film multiphase diffusion zones have involved techniques which merely average over large lateral distances parallel to the film surface. There is therefore an urgent need for high resolution experiments which will yield detailed information regarding the fine structure and composition of the diffusion zone.

V. EFFECTS OF IMPURITIES

Relatively high concentrations of uncontrolled impurities may be present during thin film diffusion as a result of the particular fabrication or diffusion conditions which are employed. Two ways in which impurities may affect the diffusion may be distinguished:

i) Impurities may be incorporated in the bulk of the film during initial fabrication and thereby exert an effect on the subsequent diffusion.

ii) Impurities in the specimen environment (i.e., either the atmosphere or the specimen surface or substrate) may diffuse into the film, or else produce reactions at the film surface, during diffusion in a manner to perturb the diffusion in the nearby specimen volume. Such "near-surface" effects could be especially important in thin films, since all volume elements are close to the surface.

V.1 Bulk Impurity Effects

Let us consider possibility (i) first. It is well known that appreciable residual concentrations of impurities may be incorporated in the bulk of thin films during the growth process. In particular, atoms may become incorporated from the atmosphere or the source during evaporation or sputtering, and impurities may also diffuse into the film from the substrate. In general, the analysis of impurities in thin films has been difficult because of the small amount of material available. Reliable and quantitative data regarding impurity concentrations are therefore relatively scarce. Recently, Thomas and Haas⁴⁸ used Auger spectroscopy on evaporated Cr films and found appreciable S contamination even when nominally 99.999% pure Cr was used as a source. Also, C was detected under certain conditions when an Ir substrate was employed. Ziegler, et al.⁵⁴ found ~2.5 at.% argon in Hf films as a result of deposition from an argon glow discharge. Pliskin and Zanin⁷⁷ and Maissel⁷⁸ cite numerous other examples of gaseous impurity contamination during fabrication.

Bulk contamination by most impurity species at concentration levels less than 0.1 at.% may be expected to produce only a relative small effect on lattice diffusion in metal films. In many cases the solvent lattice self-diffusivity D_ℓ varies with the impurity atom fraction, x_i , according to

$$D_\ell(x_i) = D_\ell(0) [1 + bx_i] \quad (19)$$

where b is a constant which is typically in the range ± 10 -100.⁷⁹ An impurity concentration of $x_i = 10^{-3}$ would therefore only change D_ℓ by $\sim 10\%$, when $b=100$. However, it is interesting to speculate that impurities might exert larger effects in metal films in cases where grain boundary or dislocation short circuiting is dominant. There is considerable evidence that impurities may exert a strong influence on the diffusion rate of solvent atoms in grain boundaries.⁸⁰⁻⁸³ For example, it appears that Cu atoms can segregate to grain boundaries in Al and decrease the rate of grain boundary diffusion of Al atoms by a factor as large as 80.⁸³ Therefore, we might expect that the overall diffusion rate could be strongly affected, particularly at the relatively low temperatures characteristic of thin film diffusion where impurity segregation to grain boundaries would tend to be severe.⁸⁴ Similar effects can also be expected when dislocation short circuiting is dominant. We note that Thomas and Haas⁴⁸ found that S contamination enhanced the diffusion rate of Cr in Au by an order of magnitude, or more. Since they concluded that the dominant mechanism was dislocation short circuiting (Table I), it is tempting to attribute the result to the effect of S contamination on diffusion along dislocations.

Lattice diffusion rates in ionic thin films may be more strongly affected by impurities. For example, in the well known case of

NaCl the introduction of a divalent cation impurity such as Cd^{++} induces cation vacancies which causes a large diffusion enhancement in the low temperature "extrinsic" regime characteristic of thin film diffusion conditions.⁸⁵ In addition, short circuiting diffusion rates in ionic materials are also sensitive to impurity effects as pointed out by Kingery.²⁹ The effect of impurities on the nature of space charge regions near dislocations and grain boundaries in ionic crystals has been discussed in Sections II and III.

V.2 Near-Surface Effects

Consider now possibility (ii) mentioned at the beginning of this section. Feit, et al.⁸⁶ point out that small concentrations of unwanted impurity atoms initially present on the surface of an ionic material may diffuse into the specimen along with tracer atoms. If the impurities are heterovalent Feit, et al. show that the lattice self-diffusion rate may be strongly perturbed, since each impurity atom may introduce one or more extrinsic vacancies to maintain charge neutrality. Since it is difficult to eliminate all surface impurities, such effects may be quite large in thin films with large surface to volume ratios.

There is a whole class of surface phenomena in which oxidation reactions occur at the surface in a manner to perturb the diffusion in the lattice in the vicinity of the surface. In such cases we may regard the oxygen as the impurity species. Dobson⁶⁴ considers the case where a solute, which is more noble than the solvent, diffuses into a solvent on which an oxide layer is growing in an oxidizing atmosphere. In certain cases the oxide growth occurs at the oxide-solvent interface under conditions where solvent atoms

must be removed in the vicinity of the interface so that the growing oxide can be accommodated. These solvent atoms are removed by a vacancy flux to the interface which originates in the bulk of the solvent. Dobson then shows that this vacancy flux exerts a large perturbation on the solute diffusion.

A reversed situation in which the solute atoms are less noble than the solvent atoms, and the solute oxide is therefore stable relative to the solvent oxide, has been analysed by Reimann and Stark.⁸⁷ In this case the solute is initially present on the surface of the solvent as an oxide in an oxidizing atmosphere. The oxide gradually decomposes allowing the solute to diffuse into the solvent. An analysis of the kinetics shows that the inward diffusion of the solute is again perturbed. The theory seems able to explain some "near-surface effect" anomalies which occur when certain oxidizable elements are diffused into more noble solvents. In a later paper Teller and Stark⁸⁸ analyze an even more complicated situation where the oxidizable solute is only partially oxidized at the surface.

Finally, we mention another case somewhat similar to that considered by Dobson⁶⁴ (see above) where a solute, which is more noble than the solvent, diffuses into a solvent on which an oxide layer is growing in an oxidizing atmosphere. However, in this case the oxide layer grows at its free surface as a result of cation diffusion through the oxide, and vacancies are left behind at the oxide-solvent interface. This reaction requires that the growing oxide layer act as a source of extra vacancies which then diffuse into the solvent. The inward diffusion of solute atoms in the presence of these vacancies has been analysed by Hales,⁸⁹ and it is

shown that the diffusion is significantly perturbed. He shows that several observed "near-surface effect" anomalies seem explicable in terms of this model. We note that the vacancy behavior in this case is just the opposite of that in the situation analysed by Dobson⁶⁴ where the oxide/solvent interface acted as a vacancy sink.

As mentioned in Section II the diffusion of an impurity into a semiconductor containing an inhomogeneous distribution of another impurity is of interest in semiconductor devices. Of special interest is the influence of the electrostatic potential distribution produced by the background impurity on the diffusion rate. Both enhancement and suppressed of the penetration rate has been reported as discussed, for example, by Hu.¹

VI. DISORDERED OR METASTABLE STRUCTURES

Since thin films are often produced under highly non-equilibrium conditions at relatively low temperatures, they often possess non-equilibrium structures. Disordered or even amorphous structures are often obtained as well as non-equilibrium metastable polymorphs which possess crystal structures which differ from those of the expected equilibrium structures. Extensive reviews of these phenomena have been given by Khan⁹⁰ and Chopra.⁹¹ Also, in many cases of multiphase diffusion certain possible equilibrium phases are simply missing, or else appear (or disappear) at a later stage of diffusion. These phenomena can strongly affect diffusion processes, and are therefore discussed below.

Mukherjee and Evans⁹² studied the diffusion rate of B through SiO_2 films which were deposited on Si by the decomposition of tetra-ethoxysilane in an r.f. discharge. They then compared their

results with the diffusion rate of B measured in sputtered SiO_2 by Anand⁹³ and in thermally grown SiO_2 by Horiuchi and Yamaguchi.⁹⁴ The diffusion rate in the r.f. discharge films was found to be about two orders-of-magnitude larger than in the thermally grown films and about one order-of-magnitude larger than in the sputtered films. Furthermore, the diffusion rate in the r.f. films was larger when a lower oxygen concentration was used during preparation. Other work showed that there were differences in the Si-O-Si vibrational bands from spectra of the thermally grown and r.f. discharge films which could be interpreted on the basis of differences in specimen strain and density. Other absorption spectrum data indicated that the lower oxygen r.f. discharge film was oxygen-deficient, and that the higher diffusivity was therefore probably due to non-stoichiometry. In another investigation Hasegawa⁹⁵ measured the diffusion of Cu in boat-grown bulk GaAs and in epitaxial GaAs prepared using the $\text{AsCl}_3/\text{Ga}/\text{H}_2$ vapor transport method.⁹⁶ Large differences in the diffusion behavior were found, and the diffused copper concentration in the epitaxial GaAs was lower than in the bulk GaAs by more than an order-of-magnitude. These differences were interpreted on the basis of differences in defect concentrations (probably Ga vacancies) in the two materials. In the case of metals, Weaver and Brown⁹⁷ found rapid initial diffusion in evaporated Ag/Al thin film diffusion couples which they attributed to a high initial concentration of vacancies.

The above investigations illustrate effects due to structural disorder. We consider next the presence of metastable phases. Thomas and Haas⁴⁸ found that Cr which is normally BCC deposits on the Ir(111) face as a FCC phase, and that the FCC phase for thin-

film Au/Cu alloys is maintained for Cr concentrations larger than expected from the phase diagram. It has been found that Ta films consisting of either normal BCC Ta or else metastable β -Ta can be produced by appropriate sputtering techniques.⁵³ Tisone and Lau⁵³ studied interdiffusion in Au/BCC Ta and Au/ β -Ta films and found considerable differences in behavior which could be attributed to differences in crystal structures and/or microstructure. Francombe, et al.⁹⁸ studied diffusion in Au/Al films and reported the presence of a metastable FCC Au-rich phase during the early stages of diffusion which transformed mainly into AuAl_2 on further reaction with Al. Further discussion of the metastability of phases present in Au/Al films has been given by Weaver and Parkinson.⁹⁹

Finally, we mention examples of cases where possible equilibrium phases were missing or else appeared (or disappeared) at a later stage of diffusion. When a thin film diffusion couple is prepared from two pure metals it is generally expected that all of the intermediate phases between those metals on the equilibrium phase diagram may appear in order across the diffusion zone. Under actual conditions, however, some of these phases may either never form at all, or else be present in the form of such thin layers that they remain undetected during the entire diffusion process. In order to form at all each phase must be nucleated in the diffusion zone, and this process may either not occur or else occur slowly under the prevailing conditions. Furthermore, each phase, once nucleated, must grow to sufficient width in the diffusion zone to be detected. The growth of each phase depends upon the magnitudes of the atomic fluxes entering and leaving the phase at its boundaries. These fluxes in turn depend upon either the diffusion rates in the specimen

if the phase growth is diffusion controlled or else upon the interface reaction rates if the growth is reaction rate controlled (see Section VIII). Under certain conditions the width may remain extremely narrow.

Difficulty in nucleation may cause the late appearance of certain phases. For example, the nucleation of a given phase may depend, upon the pre-existence of another phase. Also, the late formation of a new phase may unbalance the diffusion fluxes in the diffusion zone and cause the disappearance of an already existing phase. Finally, the phases which may be present depend upon the overall boundary conditions on the thin film diffusion specimen. If the specimen consists initially of pure materials at the extremes of the diffusion zone, eventual depletion will occur. The total range of concentration available for the formation of various phases is therefore reduced, and the magnitudes of the various fluxes are altered. Certain phases may therefore disappear (or appear) in the diffusion zone.

Weaver¹⁰⁰ reports that in thin film Au/Al couples neither the Au_4Al nor the $AuAl$ phases, which are known¹⁰¹ to be equilibrium intermediate phases, have been found. On the other hand, both the $AuAl_2$ and Au_2Al phases have been detected. However, the $AuAl_2$ phase formed only after the formation of the Au_2Al . Also, no evidence has been found¹⁰⁰ for the Au_2Pb and Ag_3Al phases in Au/Pb and Ag/Al films respectively. Tu and Berry¹⁰² found no evidence for the CuAu phase in Cu/Au films at early times. However, this phase formed at longer times after Cu_3Au and $CuAu_3$ were already present. Borders⁵² has suggested that the CuAu forms from $CuAu_3$. Tisone and Drobek³⁹ studied the phases formed in thin film Au/Ti and Pt/Ti

couples. At least four stable intermetallic compounds have been identified¹⁰¹ in the Au/Ti system: i.e., Au_4Ti , Au_2Ti , AuTi and AuTi_3 . In the thin-film diffusion couples Au_2Ti formed first, and when the Au was depleted, AuTi formed between the Ti and the Au_2Ti . As diffusion proceeded further the Au_2Ti disappeared, and AuTi_3 began to form. It is also possible that Au_4Ti formed initially in the early stages of diffusion and was not detected. In the Pt/Ti system at least four stable compounds have been identified,¹⁰¹ i.e., Pt_3Ti , PtTi , PtTi_2 and PtTi_3 . In this case only the PtTi and PtTi_3 phases were found during thin film diffusion.³⁹ In diffused Cu/Sn films Tu¹⁰³ found the Cu_6Sn_5 phase at all temperatures between -2 and 100°C but did not find the Cu_3Sn phase below 60°C. Ziegler, et al.⁵⁴ found HfSi in Hf/Si thin films in the temperature range 550-650°C. At higher temperatures above 750°, HfSi_2 formed throughout the HfSi phase, and these workers suggest that HfSi_2 nucleated and grew at the grain boundaries of the HfSi . Poate and Tisone⁷⁶ report the presence of only Pt_2Si and PtSi in Pt/Si films even though Pt_5Si_2 is a stable intermediate phase.¹⁰¹ Furthermore, the Pt_2Si forms first. The PtSi then forms later at the Si/ Pt_2Si interface and quickly over-runs the Pt_2Si causing it to disappear.

VII. EFFECTS OF LARGE CONCENTRATION OR ELECTROSTATIC POTENTIAL GRADIENTS

Cahn and Hilliard¹⁰⁴ have shown that the expression for the free energy of a small volume element in a solid solution contains an extra "gradient energy" term when it lies in a compositional gradient. This effect exists even when the atomic volumes of the constituents are equal. When the atomic volumes vary with composition, and the mismatch is taken up by elastic strains rather than by misfit dislocations, an additional "coherency strain energy" term

is present as shown by Cahn.¹⁰⁵

These additional free energy terms contribute to the driving force for diffusion, and Cahn¹⁰⁵ has shown that to first order the basic diffusion equation may then be expressed in the form

$$\frac{\partial c}{\partial t} = M \left[\frac{\partial^2 f(c)}{\partial c^2} + \frac{2\eta^2 E}{1-\nu} \right] \nabla^2 c - 2M\kappa \nabla^4 c. \quad (20)$$

Here, M is the mobility measured in the absence of gradient and coherency effects, $f(c)$ is the free energy per unit volume of homogeneous material of composition c , η is the linear expansion of the material per unit composition change, E = Young's Modulus, ν = Poissons' ratio, and κ = the gradient energy coefficient. The term proportional to κ is due to the gradient energy and the term proportional to η^2 is due to the coherency strain energy.

In the case of thin film diffusion steep compositional gradients are often present during a major portion of the diffusion anneal, and it is therefore necessary to consider the possible effects of such gradients on the diffusion kinetics. A prior discussion of these effects has been given by Weaver in his review of 1971.¹⁰⁰

The effect of the gradient energy term in eqn. (20) has been investigated in the Au/Ag system by Cook and Hilliard.¹⁰⁶ In this system the effects of coherency strains are small, i.e., η^2 in eqn. (20) is essentially zero, and can be neglected. Sandwich specimens consisting of large numbers of thin alternate layers of Au and Ag were prepared by the successive deposition of Au and Ag from the vapor. Upon subsequent heating interdiffusion occurred, and the concentration profile in a direction normal to the plane of the

sandwich quickly became almost sinusoidal with a wavelength Λ given by the sum of the Au layer thickness and Ag layer thickness. The decay of the amplitude of this periodic composition modulation was then measured by means of x-ray diffraction. Specimens with wavelength Λ in the range 7-35 $\text{\AA}$ were studied. The effective diffusivity describing the decay of the modulation was then determined as a function of Λ . It was found that the effective diffusivity for Λ near 7 $\text{\AA}$ was almost 50% lower than for $\Lambda \rightarrow \infty$. However, the effect of the gradient energy died out quickly as Λ increased and was essentially negligible in specimens with $\Lambda > 20\text{\AA}$.

In a subsequent paper Philofsky and Hilliard¹⁰⁷ studied the effects of the coherency strain energy as well as the gradient energy, in the Cu/Pd system where there is an appreciable difference between the atomic volumes of the two constituents, i.e., $\sim 7\%$. Similar sandwich type specimens were used. In this case the specimens remained coherent when $\Lambda < 28\text{\AA}$. Over the range $28 < \Lambda < 38\text{\AA}$ there was a progressive loss in coherency (i.e., coherency strain energy), and this was accompanied by a factor of 2 decrease in the effective diffusivity. There was also an approximately 70% drop in effective diffusivity with decreasing wavelength in the range $10 \leq \Lambda < 28$ interpreted as due to the effect of the gradient energy term. As in the Au/Ag system, the effects of the gradient energy became relatively small for Λ greater than a few tens of angstroms.

We may therefore conclude that the gradient energy can exert a significant effect on thin film diffusion kinetics when the diffusion distance is of the order of $\sim 30\text{\AA}$, or less. Furthermore, the coherency strain energy may also markedly affect the kinetics when appreciable differences in atomic volumes exist. We note that the

effect of the coherence strains is independent of wavelength, and simply depends upon the degree of mismatch. However, coherency is generally lost when the diffusion distance increases sufficiently, and significant effects from coherency strain energy are therefore expected only when the diffusion distance is small.

Large electrostatic fields associated with space charge regions near thin film surfaces in semiconductor and ionic crystals may also lead to nonlinear diffusional behavior. From the usual rate theory arguments the flux of a species of charge q in a field of magnitude E is proportional to $\sinh(\frac{qEa_0}{kT})$ where a_0 is the distance between adjacent potential minima. Under normal circumstances $qEa_0 \ll kT$ and hence the hyperbolic function can be replaced by its argument. Since fields of order 10^8 V/m could exist immediately at the surface of a highly doped semiconductor, for example, we have for a singly charged diffusing species, $qEa_0 \approx 0.02\text{eV}$ which is comparable to kT . In this case the flux is no longer simply proportional to E but would contain terms proportional to E^3 , etc. It should be noted however that this effect would only be of significance in regions of exceptionally high local field.

For a polarizable ion diffusing in a strong electrostatic field the potential energy contains a term $\frac{1}{2}\alpha E^2$, where α is the polarizability. [This is somewhat analogous to the gradient energy term discussed above.] Rate theory would then lead to a flux proportional to $\sinh\{\frac{a_0}{kT}[qE - \alpha\frac{\partial E}{\partial x}]\}$; for a space charge potential varying approximately as $V_0 \exp(-x/\lambda)$ this becomes $\sinh\{\frac{a_0}{kT} \cdot \frac{V_0}{\lambda} e^{-x/\lambda} [q - \frac{\alpha}{\lambda}]\}$. Taking $\alpha \approx 10^{-40} \text{ f-m}^2$ shows that the polarization term will be completely negligible for all reasonable values of the Debye length λ . Also for the migration of an ionized species with a permanent dipole

moment ρ the flux $\propto \sinh\left[\frac{a_0}{kT} \cdot \frac{V_0}{\lambda} e^{-x/\lambda} [q-\rho/\lambda]\right]$; even taking $\rho=1$ Debye, a rather large moment, shows that the second term will be completely negligible in comparison with the first. The second term may however be of importance in the diffusion of an electrically neutral species possessing a permanent moment as, e.g., in the case of a bound ion-vacancy complex.

VIII. ON THE QUESTION OF DIFFUSION-CONTROLLED OR INTERFACE REACTION CONTROLLED KINETICS AT MIGRATING PHASE BOUNDARIES

If near equilibrium conditions are achieved in multiphase diffusion zones the intermediate phases which appear in the equilibrium phase diagram between the terminal phases in the diffusion couple should be formed in the diffusion zone, and the compositions of the various phases at the phase boundaries should be maintained at values very close to those called for by the equilibrium diagram. Under these conditions the diffusion is particularly simple and the rate at which the phase boundaries migrate is "diffusion-controlled" i.e., the rate is determined by how rapidly the diffusing species are able to diffuse both to and away from the boundary. However, in certain cases the kinetics of local reactions at the boundaries are too slow to maintain equilibrium conditions. The rate of interface migration then becomes "interface reaction-controlled". Several discussions of these aspects of multiphase diffusion behavior in ordinary bulk specimens have been given elsewhere.^{40,41,108}

It is readily seen that there may be a greater tendency for interface reaction-controlled kinetics in thin film multiphase systems than in corresponding bulk specimens. In thin film

specimens the thicknesses of the various phases are necessarily exceedingly thin, so that relatively large chemical potential gradients may exist. As a result the diffusion fluxes either into or out of the phase boundaries will be large compared to those in bulk specimens, and it becomes more difficult for the interface reactions to maintain local equilibrium at the boundaries. However, since thin films are usually diffused at relatively low temperatures another factor is present which must be considered. We generally expect the temperature dependence of the interface reactions to differ from the temperature dependence of the diffusion process. Therefore, the rate of diffusion could increase relative to the rate of interface reaction as the temperature is lowered, or vice versa.

These factors are well illustrated by the work of Guy and Oikawa¹⁰⁸ who analysed diffusion in a multiphase diffusion zone using a simple model which takes into account the kinetics of the reactions at the phase boundary. These workers assumed one dimensional diffusion in a two phase α/β diffusion zone in which lattice diffusion dominates. The α/β phase boundary was therefore planar and the concentrations in the α and β phases at the boundary were taken as variables, i.e., were not assumed to be maintained in local equilibrium. The net rate at which atoms of a given species jump out of a phase at the interface was plausibly assumed to be proportional to their local concentration. The net rate at which species i joins the β phase at the interface then takes the simple form

$$R_i = k_i \left[C_i^\alpha - \frac{C_i^{\alpha\alpha}}{C_i^{\alpha\beta}} C_i^\beta \right] \quad (21)$$

where k_i is the interface rate constant, C_i^{α} and C_i^{β} are the concentrations of component i actually present in the α and β phases respectively at the phase boundary, and $C_i^{o\alpha}$ and $C_i^{o\beta}$ are the corresponding equilibrium concentrations. Guy and Oikawa¹⁰⁸ then used numerical methods to determine the overall kinetics, taking into account both the diffusion rates in the two phases and the reactions at the interface. Some results are shown in Fig. 10 where the flux of species 2 crossing the phase boundary is shown as a function of time for different values of the interface rate constant. Under diffusion-controlled conditions this flux should fall off parabolically with time, i.e., as $t^{-1/2}$ (dashed line in Fig. 10). However, at the shorter diffusion times there is a tendency for the kinetics to be slowed down because the reactions at the interface then become rate limiting. Furthermore, it is seen that the deviations from diffusion-controlled behavior increase as the rate of the interface reaction becomes relatively slower as would be expected. In the regime where interface reaction-control dominates the flux is seen to be approximately constant. The velocity of the boundary v_b is proportional to the flux and is therefore constant in the interface reaction controlled region and varies as $t^{-1/2}$ in the diffusion controlled region.

We suggest that the steep gradients present during thin film diffusion (corresponding to the short diffusion times in Fig. 10) may tend to produce interface reaction-controlled kinetics. However, the effects due to the relatively low temperatures of thin film diffusion are difficult to assess, since we have essentially no information about the relative temperature dependence of the interface rate constants and the diffusion coefficients.

The problem of assessing the importance of these factors in thin films diffusion experiments is further complicated by possible effects due to short circuiting. We have pointed out in Section III.2 that intermediate phases may appear in the form of reasonably planar layers as a result of lattice diffusion or short circuit diffusion under certain special conditions, and that parabolic growth should then occur when the growth is diffusion-controlled. However, under other short circuit diffusion conditions preferential growth of intermediate phases in and along grain boundaries may occur (see Section III.2) leading to complex non-parabolic kinetics even under diffusion-controlled conditions. On the other hand, when the rate of migration of the interphase boundary is controlled by boundary reactions, the phase should tend to grow as a planar layer, and the growth will generally not be parabolic. Therefore, the observation of parabolic growth kinetics generally implies diffusion-controlled conditions, whereas the observation of apparent non-parabolic kinetics does not necessarily imply an interface reaction-controlled situation.

It is difficult to determine the conditions which prevailed in many experiments because of a lack of sufficiently detailed and reliable information. For example, Tu and Berry¹⁰² studied interdiffusion in the Cu/Au system by x-rays and metallographic observation and claimed that a layered structure of the type Cu/Cu₃Au/CuAu₃/Au with sharp steps in composition between the different phases formed. In addition, the layer thicknesses appeared to increase linearly with time suggesting an interface reaction-controlled situation. On the other hand, in more recent work, Borders⁵² has analysed interdiffusion in this system using ion backscattering

and concludes that the intermediate phases formed preferentially in the grain boundaries, and that there was no evidence for the formation of planar layers of CuAu_3 or Cu_3Au . In the case of the Al/Ag system Weaver and Brown⁹⁷ measured reflectivity changes at the specimen surface and interpreted their results on the basis of the diffusion-controlled parabolic growth of a Ag_2Al layer from the original Al/Ag boundary. More recently Westmoreland and Weisenberger¹⁰⁹ studied this system using helium backscattering and concluded that the interdiffusion of Ag and Al, without significant compound formation, plays a significant role at least in the initial changes in reflectivity. Furthermore, they conclude that further work would be required to determine if the apparent diffusion observed by backscattering is actually an average over intermetallic phases present in different lateral positions of the sample. They speculate whether growth of the Ag_2Al phase in some laterally non-uniform manner could explain all of the results. Finally, most recently Picraux¹¹⁰ has studied this system again by helium backscattering and concludes that Ag_2Al grows parabolically in the form of a layer.

Clearly, reliable detailed conclusions regarding the kinetics of the growth of intermediate phases cannot be drawn unless the geometry of the intermediate phases is known unambiguously, and the rate of migration of the interfaces is measured by some relatively direct means.

There are a considerable number of studies where the growth of intermediate phases has been observed with varying degrees of reliability and accuracy. A listing of some recent results is given in Table II. It may be seen that both apparent parabolic

and non-parabolic kinetics have been observed.

Finally, we mention a slightly different situation in which the growth rate of a new phase is apparently interface reaction-controlled. Hiraki, et al.¹¹⁴ covered a single crystal Si substrate with an evaporated Au layer and heated the specimen in an oxidizing atmosphere. A layer of SiO_2 was then found to grow on top of the Au layer. They attributed this result to the diffusion of Si atoms through the Au layer at a rate controlled by the release of Si atoms at the interface between the Si and Au.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Atomic Energy Commission under Contract AT(30-1)3504 and by the National Science Foundation under Grant #GH33233X. Additional support was received through the use of the technical facilities of the Materials Science Center at Cornell University.

TABLE I

Selected Recent Data Indicating Short Circuiting in Thin Film Diffusion

Diffusion Process	Observation	$\frac{T(^{\circ}\text{K})}{T_m(^{\circ}\text{K})}$	L (Å)	ρ_d (cm^{-2})	Ref
Cr in Au	preferential grain boundary penetration observed	0.3	20,000	-	43 (1968)
Au $\leftrightarrow$ Ni	diffusion rate increased as L decreased	0.5-0.6	300-1500	-	44 (1969)
Au in Cu	activation energy lower than that for D_ℓ	0.3-0.5	~ 100	-	45 (1969)
Cr in Au	preferential grain boundary diffusion observed; activation energy lower than that for D_ℓ	0.3-0.4	-	-	46 (1971)
Au in Ag	diffusion observed in polycrystalline specimens but not in single crystals.	0.4	350	10^9	47 (1972)
Ti in Pt	preferential grain boundary penetration observed	0.4	1,000	-	39 (1972)
Cr in Au	activation energy lower than that for D_ℓ	0.3-0.4	∞	-	48 (1972)
Si in Al	activation energy lower than that for D_ℓ	0.3-0.4	-	10^{10}	49 (1973)
Ni in Au	activation energy lower than that for D_ℓ	0.4	-	-	50 (1973)
Cu in Au	diffusion rate increased as L decreased	0.3	300	-	51 (1973)
Cu in Ni	evidence for preferential grain boundary penetration	0.6	10,000	-	37 (1973)
Cu $\leftrightarrow$ Au	evidence for preferential grain boundary penetration	0.4-0.5	-	-	52 (1973)
Ta in Au	evidence for preferential grain boundary penetration	0.3	1,000	-	53 (1974)

TABLE II

Recent Observations of the Growth Kinetics of
Intermediate Phases in Thin Film Diffusion Zones

System	Phase	Reported Growth Kinetics	Ref
Ti/Pt	Ti_3Pt	non-parabolic	39 (1972)
Pt/Si	$\text{PtSi}, \text{Pt}_2\text{Si}$	parabolic	111 (1972)
Pd/Si	Pd_2Si	parabolic	112 (1972)
Ti/Si	TiSi_2	parabolic	112 (1972)
Cr/Si	CrSi_2	non-parabolic	112 (1972)
Mo/Si	MoSi_2	non-parabolic	112 (1972)
Al/Ti	TiAl_3	parabolic	113 (1973)
Hf/Si	HfSi	parabolic	54 (1973)
Ta/Au	TaAu	parabolic	53 (1974)
Pt/Si	PtSi	parabolic	76 (1974)
Al/Ag	Ag_2Al	parabolic	110 (1974)

REFERENCES

1. S.M. Hu in D. Shaw (Ed.), Atomic Diffusion in Semiconductors, Plenum, New York, 1973, p. 217.
2. J. Frenkel, Kinetic Theory of Liquids, Oxford Univ. Press, London, 1946.
3. J.D. Eshelby, C.W.A. Newey, P.L. Pratt and A.B. Lidiard, Phil. Mag., 3 (1958) 76.
4. K. Lehovec, J. Chem. Phys., 21 (1953) 1123.
5. K.L. Kliewer, J. Phys. Chem. Solids, 27 (1966) 76.
6. K.L. Kliewer and J.S. Koehler, Phys. Rev., 140A (1965) A1226.
7. K.L. Kliewer and J.S. Koehler, Phys. Rev., 157 (1967) 685.
8. A.R. Allnatt, J. Chem. Phys., 68 (1964) 1763.
9. R.B. Poeppel and J.M. Blakely, Surface Science, 15 (1969) 507.
10. J.M. Blakely and S. Danyluk, Surface Science, 40 (1973) 37.
11. R. Davidge, Phys. Stat. Sol., 3 (1963) 1851.
12. C. Elbaum, Brown University, (Private communication).
13. a) J.S. Kim, Ph.D. Thesis, University of North Carolina, (1967).
b) L. Slifkin, W. McGowan, A. Fukai and J.S. Kim, Photog. Science and Eng., 11 (1967) 79.
14. R.C. Baetzold and J.F. Hamilton, Surface Science, 33 (1973) 461.
15. R.C. Baetzold, J. Phys. Chem. Solids, XX, (1973)
16. F. Trautweiler, L.E. Brady, J.W. Castle and J.F. Hamilton, in G.A. Somorjai (Ed.), Structure and Chemistry of Solid Surfaces, Wiley, New York, 1969, p. 83-1.
17. S. Danyluk and J.M. Blakely, Surface Science, 41 (1974) 359.
18. H. Wakabayashi, J. Phys. Soc. Japan, 15 (1960) 2000.
19. S. Sonoike and H. Wakabayashi, J. Phys. Soc. Japan, 14 (1959) 1664.
20. Y.T. Tan and H.A. Høyen, Surface Sci., 36 (1973) 42.
21. T.B. Grimley and J.F. Mott, Disc. Faraday Soc., 1 (1947) 3.

22. T.B. Grimley, Proc. Roy. Soc., A201 (1950) 40.
23. K.R. Lawless, Reports Prog. Phys., 37 (1974) 231.
24. T.D. Dzhaferov and G.S. Kulikov, Soviet Physics - Solid State, 12 (1970) 1237.
25. M. Yoshida, E. Arai, H. Nakamura and Y. Terunuma, J. Appl. Phys., 45 (1974) 1498.
26. R.W. Balluffi, Phys. Stat. Sol., 42 (1970) 11.
27. R.W. Balluffi and A.V. Granato (to be published).
28. N.A. Gjostein, Technical Report SR-73-29, Scientific Research Staff, Ford Motor Co., 1973.
29. W.D. Kingery, J. Amer. Cer. Soc., 57 (1974) 1, 74.
30. D. Shaw, in D. Shaw (Ed.), Atomic Diffusion in Semiconductors, Plenum Press, New York, 1973, p. 1.
31. K.L. Chopra, Thin Film Phenomena, McGraw-Hill, New York, 1969, p. 182 et. seq.
32. C.A. Neugebauer, in L.I. Maissel and R. Glang (Eds.), Handbook of Thin Film Technology, McGraw-Hill, New York, 1970, p. 8-3.
33. J.C. Fisher, J. Appl. Phys., 22 (1951) 74.
34. D. Turnbull and R.E. Hoffman, Acta Met., 2 (1954) 419.
35. L.G. Harrison, Trans. Faraday Sec., 57 (1951) 1191.
36. P.A. Turner, J. Vac. Sci. and Tech., 9 (1972) 262.
37. J. Unnam, J.A. Carpenter and C.R. Houska, J. Appl. Phys., 44 (1973) 1957.
38. R.E. Mistler and R.L. Coble, J. Appl. Phys., 45 (1974) 1507.
39. T.C. Tisone and J. Drobek, J. Vac. Sci and Tech., 9 (1972) 271.
40. J.D. Baird, J. Nucl. Energy, Part A, 11 (1960) 81.
41. G.V. Kidson, J. Nucl. Mat., 3 (1961) 21.
42. H.B. Aaron and F. Weinberg, Acta Met., 20 (1972) 339.
43. P.S. Kenrick, Nature, 217 (1968) 1249.
44. J.L. Richards and W.H. McCann, J. Vac. Sci. and Tech., 6 (1969) 644.
45. E.I. Alessandrini and J.D. Kuptsis, J. Vac. Sci. and Tech., 6 (1969) 647.

46. J.R. Rairden, C.A. Neugebauer and R.A. Sigsbee, *Metall. Trans.*, 2 (1971) 719.
47. K.T. Tu and R. Rosenberg, *Thin Solid Films*, 13 (1972) 163.
48. R.E. Thomas and G.A. Haas, *J. Appl. Phys.*, 43 (1972) 4900.
49. G.J. van Gorp, *J. Appl. Phys.*, 44 (1973) 2040.
50. M.M. Judy and K.M. Koliwad, *J. Electronic Mat.*, 2 (1973) 331.
51. S.U. Campisano, G. Foti, F. Grasso and E. Rimini, *Thin Solid Films*, 19 (1973) 339.
52. J.A. Borders, *Thin Solid Films*, 19 (1973) 359.
53. T.C. Tisone and S.S. Lau, *J. Appl. Phys.*, 45 (1974) 1667.
54. J.F. Ziegler, J.W. Mayer, C.J. Kircher and K.N. Tu, *J. Appl. Phys.*, 44 (1973) 3851.
55. K.L. Chopra, *Thin Film Phenomena*, McGraw-Hill, New York, 1969, p. 266.
56. D.S. Campbell, in L.I. Maissel and R. Glang (Eds.), *Handbook of Thin Film Technology*, McGraw-Hill, New York, 1970, p. 12-3.
57. A. Gangulee, *Acta Met.*, 22 (1974) 177.
58. P.G. Shewmon, *Diffusion in Solids*, McGraw-Hill, New York, 1963, p. 81.
59. F.R.N. Nabarro, *Theory of Crystal Dislocations*, Oxford Press, London, 1967, p. 355.
60. J.S. Koehler, *Phys. Rev.*, 181 (1969) 1015.
61. C.P. Flynn, *Point Defects and Diffusion*, Oxford Press, London, 1972, p. 413.
62. H.K. Birnbaum, B.L. Eyre and W. Drotning, *Phil. Mag.*, 23 (1971) 847.
63. T.R. Anthony, *Acta Met.*, 18 (1970) 307.
64. P.S. Dobson, *Phil. Mag.*, 24 (1971) 567.
65. J.T. Robinson and N.L. Peterson, *Surf. Sci.*, 31 (1972) 586.
66. G. Martin, D.A. Blackburn and Y. Adda, *Phys. Stat. Sol.*, 23 (1967) 223.
67. M.F. Ashby, *Acta Met.*, 20 (1972) 887.
68. A. Gangulee, *Phil. Mag.*, 22 (1970) 865.

69. L.S. Castleman and L.L. Seigel, Trans. A.I.M.E., 212 (1958) 589.
70. L.S. Castleman, Acta. Met., 8 (1960) 137.
71. H.A. Froot and L.S. Castleman, Trans. A.I.M.E., 227 (1963) 838.
72. G. Dearnaley and N.E.W. Hartley, Phys. Letters, 46A (1974) 345.
73. O. Kubaschewski and B.E. Hopkins, Oxidation of Metals and Alloys, Butterworth's, London, 1962, p. 64.
74. D.L. Douglas in Oxidation of Metals and Alloys, American Society for Metals, Metals Park, Ohio, 1971, p. 137.
75. J.A. Borders, private communication quoted by Dearnaley and Hartley in reference 72.
76. J.M. Poate and T.C. Tisone, Appl. Phys. Lett., 24 (1974) 391.
77. W.A. Pliskin and S.J. Zanin, in L.I. Maissel and R. Glang (Eds.), Handbook of Thin Film Technology, McGraw-Hill, New York, 1970, p. 11-1.
78. L.I. Maissel in L.I. Maissel and R. Glang (Eds.), Handbook of Thin Film Technology, McGraw-Hill, New York, 1970, p. 4-1.
79. R.E. Howard and J.R. Manning, Phys. Rev., 154 (1967) 561.
80. G. Barreau, G. Brunel, G. Cizeron and P. Lacombe, C.R. Acad. Sci. C(France), 270 (1970) 516.
81. H. Gleiter and B. Chalmers, High Angle Grain Boundaries, Pergamon Press, New York, 1972, p. 94.
82. R. Rosenberg, J. Vac. Sci. and Tech., 9 (1972) 263.
83. F.M. d'Heurle and A. Gangulee, in H. Hu (Ed.), The Nature and Behavior of Grain Boundaries, Plenum Press, New York, 1972, p. 339.
84. M.P. Seah and E.D. Hondros, Scripta Met., 7 (1973) 735.
85. P.G. Shewmon, Diffusion in Solids, McGraw-Hill, New York, 1963, p. 145.
86. M.D. Feit, J.L. Mitchell and D. Lazarus, Phys. Rev., B8 (1973) 1715.
87. D.K. Reimann and J.P. Stark, Acta Met., 18 (1970) 63.
88. C.M. Teller and J.P. Stark, Acta Met., 20 (1972) 1077.
89. R. Hales, J. Phys. Chem. Solids, 32 (1971) 1417.

90. I.H. Khan, in L.I. Maissel and R. Glang (Eds.), Handbook of Thin Film Technology, McGraw-Hill, New York, 1970, p. 10-1.
91. K.L. Chopra, Thin Film Phenomena, McGraw-Hill, New York, 1969, p. 189.
92. S.P. Mukherjee and P.E. Evans, Thin Solid Films, 14 (1972) 299.
93. K.V. Anand, Ph.D. Thesis, University of Manchester, 1968.
94. S. Horiuchi and J. Yamaguchi, Jap. J. Appl. Phys., 1 (1964) 315.
95. F. Hasegawa, J. Appl. Phys., 45 (1974) 1944.
96. M. Maruyama, S. Kikuchi and O. Mizuno, J. Electrochem. Soc., 116 (1969) 413.
97. C. Weaver and L.C. Brown, Phil. Mag., 17 (1968) 881.
98. M.H. Francombe, A.J. Noreika and W.J. Takei, Thin Solid Films, 1 (1967/68) 353.
99. C. Weaver and D.T. Parkinson, Phil. Mag., 22 (1970) 377.
100. C. Weaver, Physics of Thin Films, 6 (1971) 301.
101. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 1958; R.P. Elliott, Constitution of Binary Alloys, 1st Supplement, McGraw-Hill, New York, 1965; F.A. Shunk, Constitution of Binary Alloys, 2nd Supplement, McGraw-Hill, New York, 1969.
102. K.N. Tu and B.S. Berry, J. Appl. Phys., 43 (1972) 3283.
103. K.N. Tu, Acta Met., 21 (1973) 347.
104. J.W. Cahn and J.E. Hilliard, J. Chem. Phys., 28 (1958) 258.
105. J.W. Cahn, Acta Met., 9 (1961) 795.
106. H.E. Cook and J.E. Hilliard, J. Appl. Phys., 40 (1969) 2191.
107. E.M. Philofsky and J.E. Hilliard, J. Appl. Phys., 40 (1969) 2198.
108. A.G. Guy and H. Oikawa, Trans. A.I.M.E., 245 (1969) 2293.
109. J.E. Westmoreland and W.H. Weisenberger, Thin Solid Films, 19 (1973) 349.
110. S.T. Picraux, paper presented at 6th International Vacuum Conference, Kyoto, Japan, March 25-29, 1974: accepted for publication in Supplement to Japanese J. Appl. Phys.

- 111. H. Muta and D. Shinoda, J. Appl. Phys., 43 (1972) 2913.
- 112. R.W. Bower and J.W. Mayer, Appl. Phys. Lett., 20 (1972) 359.
- 113. R.W. Bower, Appl. Phys. Lett., 23 (1973) 99.
- 114. A. Hiraki, E. Lugujo and J.W. Mayer, J. Appl. Phys., 43 (1972) 3643.

FIGURE CAPTIONS

- 1 - (a) Schematic free energy level diagram for cations at various sites in an intrinsic monovalent ionic crystal. The chemical potential is indicated by a dashed line. Note that the various levels will be temperature dependent due to entropy contributions. (b) Equilibrium situation; the interface site has a positive charge associated with it and there is a potential gradient into the crystal.
- 2 - Plot of variation of cation electrochemical potential μ_+ versus temperature in a monovalent ionic crystal containing a divalent cation impurity where the vacancy-impurity binding free energy is $-B$. Curve b is for a higher divalent impurity level than a. The potential difference between the interface and the bulk, ϕ , is the difference between μ_+ and the free energy at the interface site.
- 3 - Potential variation and defect concentration across a thin film when the thickness W is much greater than the Debye length λ , ((a) and (b)). In (c), (d), where $W \sim \lambda$, the space charge region extends across the entire film. n_v and n_i are the numbers of vacancies and interstitials per unit volume respectively.
- 4 - Schematic potential variation across an ionic insulator crystal film bounded by a metal layer on one side to which the film makes a contact reversible with respect to cations. The potential difference ϕ between film and metal will appear mostly in the insulator.
- 5 - Regimes of grain size (L) and dislocation density (ρ_d) over which lattice diffusion (a), grain boundary short circuit diffusion (b) or dislocation short circuit diffusion (d) is dominant during steady state diffusion through a thin film specimen of a FCC metal. Each map corresponds to diffusion at a temperature, T , which is a fixed fraction of the absolute melting temperature, T_m .
- 6 - Possible form of the diffusivity as a function of position near a grain boundary (or dislocation) in an ionic solid. Two regions are distinguished; viz, the core and space charge

regions. In the latter the diffusivity parallel to the boundary may be enhanced (dashed curve) or suppressed (solid curve).

- 7 - Schematic representation of multiphase diffusion zone in a Pt/Ti thin film diffusion specimen showing preferential penetration along grain boundaries (after Tisone and Drobek³⁹).
- 8 - Growth of a relatively planar layer of intermediate β phase of thickness w by short circuit diffusion in a multiphase diffusion zone. Short circuiting occurs along grain boundaries and interphase boundaries.
- 9 - Stress-induced atomic currents flowing between surface sources and grain boundary sinks near surface of thin film subjected to a biaxial stress, σ .
- 10 - Flux of species 2 crossing the α/β phase boundary as a function of time during one dimensional lattice diffusion in a diffusion zone consisting of an α and a β phase. k_2 is the interface rate constant for component 2 and the figure applies to the special case $k_1/k_2=0.14$. (After Guy and Oikawa¹⁰⁸.)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10