Atomic transport in amorphous alloys: An introduction

Robert W. Cahn[a)]
Keck Laboratory for Engineering Materials, California Institute of Technology, Pasadena, California 91125

(Received 11 April 1986; accepted 24 April 1986)

The measurement of the diffusivities of metallic and metalloid species in amorphous alloys has necessitated the development of techniques capable of a resolution of a few nanometers over a total penetration depth of less than a micron. Various profiling techniques employing ion beams and the ultrasensitive multilayer technique are outlined. Generalities concerning the diffusion of different solutes in the same amorphous alloy or family of alloys, and the diffusion of the same solute in different amorphous alloys are presented, and the effect of solute concentration discussed. The role of amorphous alloys as diffusion barriers in microelectronic circuitry is outlined with emphasis on recent results. The influence of the nature of the substrate and metallic overlayer receives special attention. Barrier layers effective up to 700 °C have recently been made.

I. INTRODUCTION

Metallic glasses or, to use a more general designation, amorphous alloys, are strange materials that were first studied in depth in Southern California. The late Pol Duwez at the California Institute of Technology discovered in 1959 that an Au–Si melt, when frozen very fast, became a solid with a liquidlike configuration—a metallic glass. Similar materials are still being studied at Caltech, and in hundreds of laboratories all over the world, but such studies are no longer restricted to fast-quenched melts. Amorphous alloys are made by coevaporation or cosputtering[1,2] (this is the oldest approach); ion implantation[3]; ion-mixing of bilayers and multilayers[4,5]; electron or ion irradiation of crystalline solid solutions[6]; transient melting of an alloy surface layer by a moving or pulsed laser beam[7]; chemical or electroplating[8]; or by means of a solid-state (diffusive) amorphization reaction (SSAR).[9,10] The cited publications give specific instances or overviews of these various techniques.

Since this outline is presented in connection with a conference on coatings and my specific concern here is with barrier layers for use in high-temperature microelectronic circuits, I shall restrict myself to phases made by two techniques only—deposition by coevaporation or cosputtering, and rapid melt-quench—since the former is the only technique which has been used for making barrier layers and, together with the second, has also been used to prepare samples for diffusion studies. It should however be noted in passing that SSAR (also discovered at Caltech) has distinct potential as a future method of fabricating barrier layers. For instance, a layer of amorphous Ni–Nb could in principle be prepared *in situ* on a circuit by evaporating a series of ultrathin layers of Ni and Nb and then interdiffusing them before adding any needed metallic overlayers.

The variety of amorphous alloys which has been made is by now very large; certainly more than 100 distinct combinations have been described in literature since 1959, this information probably now exceeding 10 000 papers. For brevity and omitting semiconductor phases such as amorphous silicon, they can be divided into two large families: alloys of metals (most commonly early transition metals) with one or more metalloids, usually boron, phosphorus, and silicon; and alloys of pairs of metals, one or both of which are commonly transition metals. Materials in the first group have been made almost exclusively by melt-quenching; those in the second have been made by all the methods listed.

Readers who desire a general overview of the preparation, composition, structure, and properties of amorphous alloys have available extensive materials: there have been dozens of books, monographs, and review articles in the past ten years. Some of the most recent publications include Luborsky[11] (the most comprehensive single source), Chen,[12] Cahn,[13] and Herman.[14]

In what follows, I shall make no distinctions in terms of mode of preparation: to date, on the few occasions when a physical property of an amorphous alloy has been measured in samples made by two or more different techniques, no significant differences have as a rule been observed.

II. DIFFUSION—EXPERIMENTAL TECHNIQUES

Atomic transport, or diffusion, in an amorphous alloy is linked, in one way or another, with many of its most important properties. Self-diffusion, i.e., the transport of species initially present in the solid, is linked to viscosity, creep under applied stress, instability of ferromagnetic properties and electrical resistivity, internal friction, and the rate of crystallization. Chemical diffusion, i.e., the transport of an externally supplied species, determines the kinetics of oxidation, compound formation, and breakdown of a barrier layer by reaction with substrate or overlay; it can also modify crystallization kinetics.

Plainly then, a knowledge of diffusion characteristics in amorphous alloys is as important as corresponding information is for crystalline alloys; yet, apart from just two studies in the 1970's, measurements only began in earnest 6 yr ago, whereas diffusion in crystalline alloys has been studied for the past 60 yr. Why then was there a delay of nearly two decades between the discovery of amorphous alloys and the sustained study of diffusion in them?

The reason lies in the great experimental difficulties encountered in the task. When, say, the diffusivity of gold in crystalline copper is to be examined, gold (possibly radioactive) is electroplated on a polished copper surface, an anneal which may last for weeks follows, and the gold diffuses a

 © 1986 American Vacuum Society

distance of a millimeter or more; successive layers are then removed by turning in a watchmaker's lathe, and chemically analyzed or gamma counted. This is the simplest of a number of straightforward methods. None of them is applicable to the case of self- or chemical diffusion in an amorphous alloy, because the penetration depths are necessarily so small.

The difference stems from the fact that an amorphous alloy is in a metastable condition, and when heated high and long enough, it will crystallize. Even incipient crystallization must be avoided if one wants to measure diffusivities in an amorphous phase, and this restriction limits the depth to which a component, initially placed at the surface, can diffuse in. For all diffusing components except hydrogen, the smaller metalloid species (B,C), and the smallest metal atom (Li), the limiting diffusive penetration before crystallization that begins is considerably less than 1 μm: 0.1 μm is a safe limit. This imposes the need to use very special methods of measurement. It is in fact only the recent flowering of novel experimental techniques apposite to the study of phenomena in thin films which has permitted diffusion in amorphous alloys to be systematically investigated.

The methods which have been used have mostly involved ion beams in one capacity or another. In the earliest study of silver (chemical) diffusion in a $Pd_{81}Si_{19}$ glass,[15] radioactive ^{110}Ag was implanted just below the glass surface, and following a diffusion–anneal the surface was progressively eroded by argon ion bombardment. The silver concentration profile was deduced by measuring the radioactivity of the sputtered material. Valenta *et al.* some years later[16,17] used ^{59}Fe and ^{32}P to study Fe and P self-diffusivity in a-$Fe_{40}Ni_{40}P_{14}B_6$. Cahn *et al.*[18] used a different analytical technique, secondary ion mass spectrometry (SIMS), to measure the self-diffusivity of the stable isotope ^{10}B in a-$Fe_{40}Ni_{40}B_{20}$: Ion erosion was still needed, but the use of radioactive isotopes was abandoned and has not recently been much in evidence. It should be noted that in any measurement of a *self*-diffusivity, it is essential to use a labeled diffusant, be it radioactive or a stable isotope.

In a much-cited paper, Chen *et al.*[19] studied the chemical diffusion of Au in a-$Pd_{77.5}Cu_6Si_{16.5}$ (an alloy having the beneficial feature that the critical quenching rate from the melt needed to prevent crystallization is only about 100 deg/s). Chen *et al.* abandoned ion erosion altogether, and instead used Rutherford backscattering (RBS) of He^+ ions to assess the profile of the gold after diffusion. Since then, the use of nondestructive profiling methods has progressively taken over from the various approaches exploiting ion erosion. Thus Akhtar *et al.*[20,21] used RBS to compare gold diffusivities in a range of different glasses, and of several solutes in one glass ($Ni_{33}Zr_{67}$). This was, in fact, the first comparative study of the diffusivities of one solute in different amorphous solids (melt-quenched glasses in this instance) and of several solutes in one glass.

A particularly sophisticated and sensitive nondestructive approach, where it is applicable, is to exploit a nuclear reaction between the diffusing species and an ion probe. This has been done by Kijek *et al.*[22,23] to measure the chemical diffusivity of B in a-$Ni_{60}Nb_{40}$ utilizing the $^{11}B(p,\alpha)^8Be$ reaction. For this method to work well it is desirable (though not absolutely necessary) to have a strong resonance in the reaction cross section at a particular energy of the probe ion: in this instance, the peak comes at a convenient proton energy of 163 keV. As a result, the sensitivity is unusually high and it was possible to determine diffusivities over a range of 300 K (Fig. 1) which is double the temperature range usually accessible for a single diffusing system. Two features should be noted in Fig. 1: the random error ranged from a factor of less than 2 at the highest temperatures to one order of magnitude at the lowest temperatures (the larger of these errors is typical of many other investigations) and the Arrhenius plot (log D vs $1/T$) is not linear for the glass in its unrelaxed condition. This nonlinearity, surprisingly, is the exception rather than the rule in studies of diffusion in amorphous alloys.

There is a whole series of *indirect* ways of measuring diffusion in amorphous alloys: what these have in common is that no direct measurement of concentration profiles is involved. The earliest to be used was the study of crystallization kinetics[24] in glasses where the first-formed crystals have a different composition from the glass, so that long-range diffusion governs the kinetics. It is, however, impossible to be sure which species is the rate-determining diffusant. Other methods include internal friction governed by solute migration (used for measuring hydrogen diffusivities), motional narrowing of NMR lines, and in particular, x-ray diffraction from multilayer sandwiches. Such multilayers, consisting of successive ultrathin layers for instance, of two amorphous alloys of distinct compositions (some physicists unaware of long-standing metallurgical usage have miscalled such as-

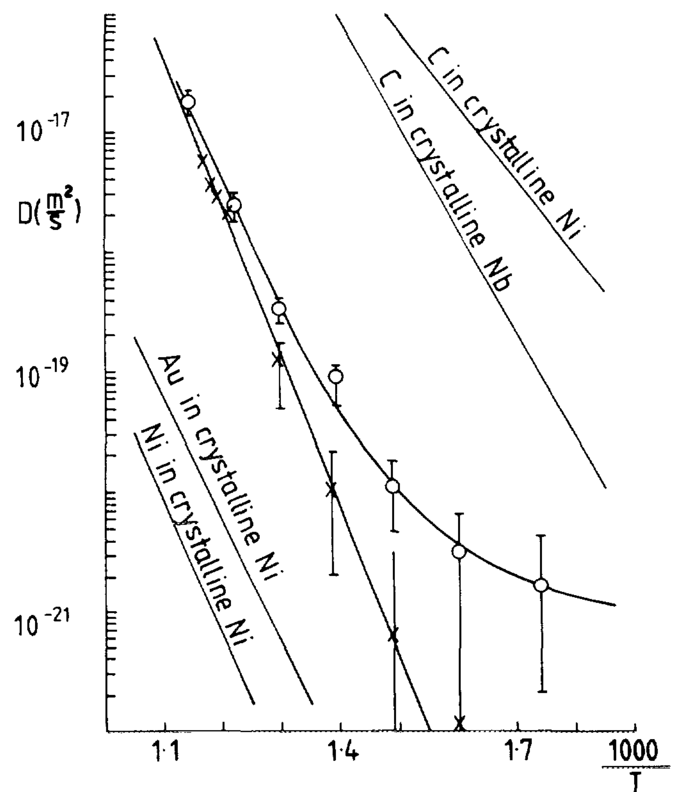

FIG. 1. Diffusion coefficients of ^{11}B in $Ni_{60}Nb_{40}$ glass. O unrelaxed; × relaxed 420 s at 878 K. (After Kijek *et al.*, Ref. 23.)

semblies "superlattices") can be heated so that the layers interdiffuse: then the x-ray diffraction satellites found within a few degrees of the direct beam progressively weaken as the contrast in electron density in successive layers attenuates. This approach has a venerable history in its application to crystalline alloys going back to DuMond and Youtz in 1935, but it was not until 1980 that it was first applied by Rosenblum *et al.*[25] to the study of amorphous alloys: here one determines the interdiffusion constant, $\tilde{D}$, which is a weighted mean of the individual self-diffusivities of the constituents. If very thin layers (a few nanometers) are used, then this is an extraordinarily sensitive technique, much more so than any of the others cited. Figure 2, from Greer and Spaepen's very recent review,[26] maps out the useful sensitivity ranges of the various techniques available for measuring diffusivities. (In this figure, "anodic oxidation" refers to a profiling method in which successive thin layers are anodically oxidized, dissolved off, and analyzed: cf a study of Ga diffusion in GaAs.[27]) A further forthcoming review which deals rather fully with the application of multilayers to diffusion, with special attention paid to amorphous alloys and to *a*-Si–Ge, is by Greer.[28]

III. SOME GENERAL FEATURES OF DIFFUSION IN AMORPHOUS ALLOYS

During the 11 yr that have passed since the first diffusion measurements in an amorphous alloy,[15] the total number of research publications on this theme has not yet reached 100. Nevertheless, a clear view has by now emerged of the main features of the process, and a very concise summary will be attempted. Substantial overviews of the subject have been published by Cantor and Cahn[29] and by Limoge *et al.*[30] and a very up-to-date survey by Cantor is in press.[31]

Generally, over the narrow temperature ranges imposed by the need to avoid crystallizing samples during diffusion experiments, log D vs $1/T$ plots are approximately linear. The upper curve in Fig. 1 is an exception. Many measurements have been made of both chemical and self-diffusivities in metal–metalloid glasses such as $Fe_{40}Ni_{40}B_{20}$ and Fig. 3 shows a recent compilation.[31] It can be seen that smaller atoms diffuse faster. (H diffusivities are many orders of magnitude higher still than B values; C diffusion has not been measured yet.) It should be noted that Fig. 3 uses as an abscissa a normalized temperature, T_g/T, where T_g is the glass transition temperature (the temperature below which diffusion is too slow for configurational equilibrium to be maintained). This way of plotting results for different amorphous alloys side by side is found to yield more regular relationships, and is now generally used. The point here is that at T_g, each glass has the same viscosity (a quantity which is inversely proportional to self-diffusivity).

Another plot using the T_g/T basis is seen in Fig. 4. Here four different metal–metalloid glasses are compared in respect of a single diffusant, Au, and it is seen that the results cluster close together. This implies that, at a given absolute temperature, gold diffuses more slowly in a glass with a higher T_g. A higher T_g implies, of course, a greater thermal stability; thus, a more stable glass is more resistant to diffusion at a given temperature.

This same characteristic can be looked at in another way. Modeling of the diffusion process in a glass/amorphous alloy has proved very difficult. The first attempts at a random walk analysis of the diffusion of an interstitial (small) atom through an idealized amorphous structure were made by Ahmadzadeh and Cantor[32] and, very recently, by Lançon *et al.*[33] The latter, in particular, simplifies the problem by applying percolation concepts, and a straight Arrhenius plot is predicted (in spite of the fact that there cannot be, unlike in a crystal, a single constant activation energy for atomic jumps from one potential well to its neighbor). Both these treatments are based on the idea that interstitial diffusion takes place between adjacent voids in the Bernal dense random packing structure. Cantor[31] discusses in statistical mechanical terms how these voids are modified as the temperature rises. Where the diffusion of larger atoms is concerned, especially in a metal/metal glass (the kind of process which in a crystalline material is termed "substitutional diffusion"), it is generally assumed that the largest voids in the glass structure are involved in diffusion and act as a sort of protovacancy (they are usually termed "holes"). The acceptability of the concept of well-defined holes of reasonably constant size and formation energy in an amorphous structure is much debated, but at the least, a self-consistent theory can be based on this notion.[13,34] Buschow[35] has published a correlation of the crystallization temperature, T_x (always very close to T_g), of a number of bimetallic glasses as a function of the calculated enthalpy ΔH_h of formation of holes in each glass (Fig. 5). (The basis of calculation of ΔH_h, derived

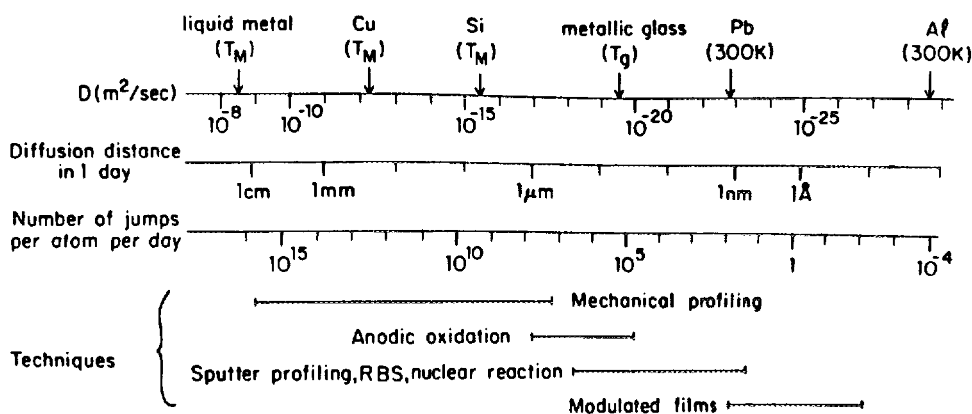

FIG. 2. Comparison of sensitivities of various techniques for measuring diffusivities. (After Greer and Spaepen, Ref. 25).

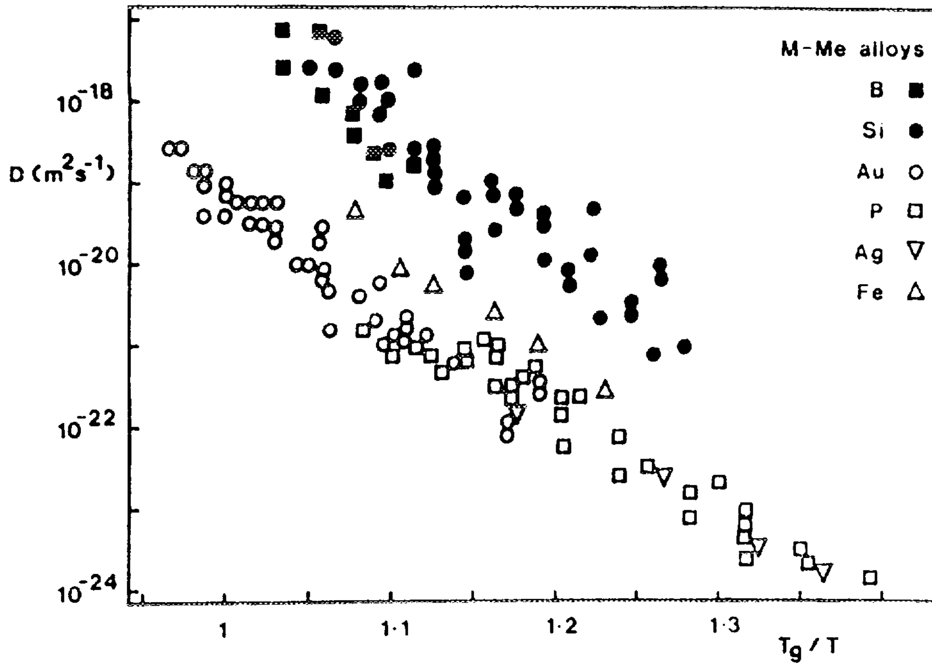

FIG. 3. Comparison of different diffusing species in metal–metalloid glasses. (After Cantor, Ref. 31).

from thermochemical data, can be found in Buschow's paper; it leans on the very influential theoretical methods of Miedema.)

Figure 5 implies that, comparing different glasses, the higher the formation energy of holes in a glass (i.e., the smaller their equilibrium concentration at a given temperature), the higher will be T_g and, according to plots such as Figs. 3 and 4, the lower will be the diffusivity of any particular solute species. Figure 5 could serve as a useful predictor of diffusion resistance (and therefore for diffusion barriers), though very recently Saris[36] has shown that too uncritical an application of the correlation of Fig. 5 can lead to errors.

The counterpart of the D/T_g correlation for a given solute is the correlation between the diffusivities of different metallic solutes in the same glass, and the melting temperatures of the various solutes. This correlation appears to be stronger than any correlation with atomic radius of the solute. (It thus appears that different regularities apply to the diffusion of small interstitial atoms, where size is important, and metal atoms.) Akhtar *et al.*[20] have compared the diffusivities of Pb, Pt and Au in a $Ni_{33}Zr_{67}$ glass and, more recently, Akhtar and Misra[37] compared the diffusivities of Pb, Ag and Al in a $Ni_{60}Nb_{40}$ glass. Diffusivities decrease in the first series of the order cited, which is also the order of the melting points of these metals in pure crystalline form, but not in the order of the atomic radius. (In the second series, Al is "out of order".) In an unavoidably hand waving sense, one could suggest that in general, atoms capable of higher cohesion when in their own crystal are also more strongly tied to a glass structure and thus find it harder to migrate. Whatever the merit of this formulation, Akhtar's observations provide a useful rule-of-thumb for roughly predicting the behavior of different solutes.

In crystalline alloys, chemical diffusivities are often found to be a function of solute concentration: the effect can be quite pronounced, especially for interstitial solutes, such as C in α-Fe. In amorphous alloys, this kind of dependence has

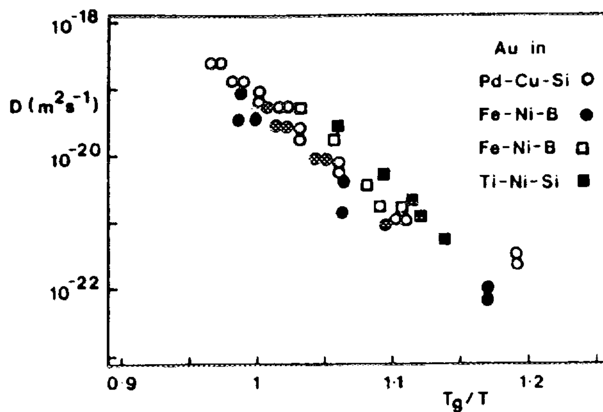

FIG. 4. Diffusivity of gold in metal–metalloid glasses. (After Cantor, Ref. 31).

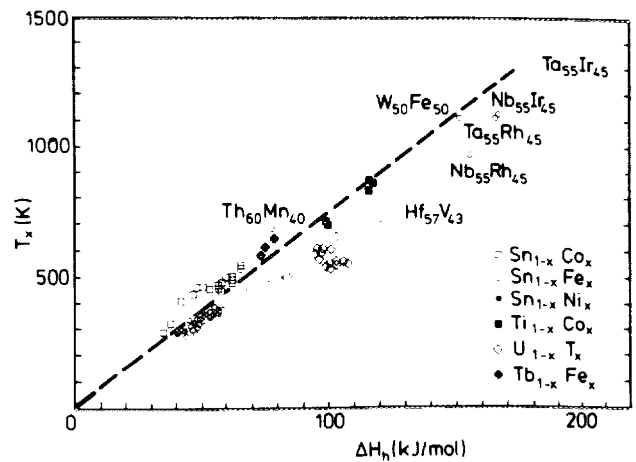

FIG. 5. Dependence of the measured crystallization temperature, T_x, of various binary metallic glasses on the formation enthalpy of a hole the size of the smaller of the constituent atoms, as calculated from thermochemical data. (After Buschow, Ref. 35).

hitherto only been found for hydrogen diffusion[38,39] (Fig. 6). Kirchheim *et al.*[38] were able to interpret this quantitatively in terms of the hypothesis that the first solute atoms, at low concentrations, are firmly held in deep potential traps (large holes?); subsequent atoms are less firmly held and so need less activation energy to make jumps. Farkas[40] has further elaborated on this trap model and was able to interpret experimental data for the diffusion of C in (crystalline) γ-iron.

The widespread observation that diffusion in an amorphous solid is slower than in the same material after it has crystallized must be reconsidered, as a universally valid generalization, in the presence of hydrogen [Fig. 6(b)]. In dilute solutions of H in Pd–Si glasses, this is true: but as the H concentration goes up, H becomes less firmly trapped in the glass than in the crystalline silicide (where presumably all hydrogen sites are energetically equivalent), and the situation is reversed.

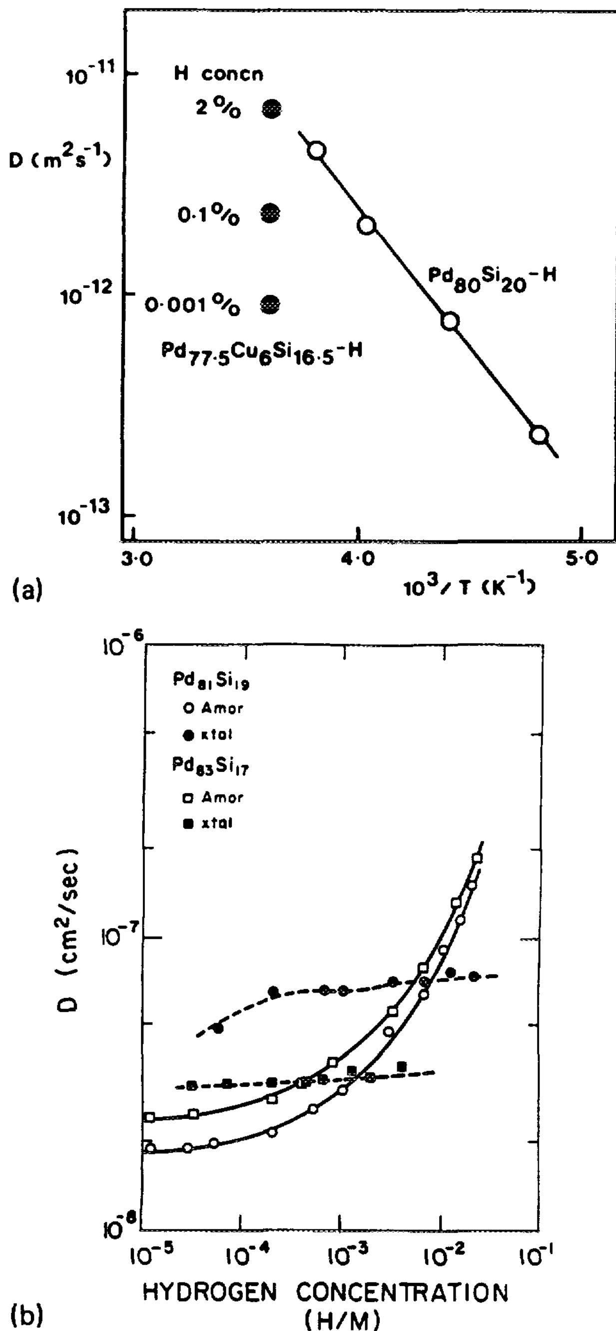

FIG. 6. (a) Arrhenius plot of hydrogen diffusivities in amorphous Pd–Si or Pd–Si–Cu in relation to hydrogen concentration, Ref. 29. (b) Comparison of hydrogen diffusivity at 292 K between amorphous and crystalline Pd–Si alloys. (After Lee and Stevenson, Ref. 39.)

Reference has already been made to the effect of relaxation anneals prior to a diffusion experiment on subsequently measured diffusivities, and Fig. 1 shows an example of such an effect. It should be noted that the effect is substantial only at low diffusion temperatures, and therefore for low diffusivities. Relaxation densifies the amorphous structure and reduces the amount of free volume (or, alternatively, the concentration of holes[13]), and this must be the basis of the reduction of diffusivities by relaxation.

A number of investigators have failed to find any relaxation effects on diffusion, and various interpretations have been advanced; for instance, a glass quenched in a relatively slow way from the melt will have more time to relax during the quench than a brutally quenched one, and so will be less liable to relax on subsequent annealing.[29,31] The experiments reported by Greer[28] by use of the multilayer technique, which allows extremely small diffusivities to be accurately measured, appear to have settled these arguments. At the low temperatures at which the multilayer diffusivities were measured, relaxation is very slow and thus will not saturate in the early stages of a diffusion experiment; a strong influence of relaxation on measured diffusivities is thus always observed. In the older experiments using profiling methods, higher temperatures had to be used and so relaxation must have gone far before a diffusivity can be measured; relaxation effects are therefore found to be weak.

Amorphous alloys used for barrier layers must *ipso facto* have low diffusivities at the temperatures of interest, and moreover they are made by vapor-deposition methods in which the effective quenching rate is much higher than in quenching from the melt (so that there should be negligible relaxation during fabrication). Amorphous barrier layers are therefore expected to show substantial relaxation effects on diffusivity, and several instances of this have been reported in the literature. To conclude this survey, we now turn to the matter of amorphous barrier layers.

IV. AMORPHOUS BARRIER LAYERS FOR MICROELECTRONICS

Diffusion barrier layers in microcircuits are essentially electrically conducting layers inserted between a semiconductor surface and a metallic conductor which would otherwise be in direct contact with the semiconductor, e.g., Si and Al. The barrier's function is to prevent deleterious compound formation between the semiconductor and the metal during periods when the circuit is at high temperature. This can be either during circuit fabrication or, more critically, in service if the microcircuit is to be used in a high-temperature environment. The great variety of crystalline compounds which have been proposed as barrier materials have been well reviewed by Nicolet.[41,42] The first suggestion that amorphous alloy films be used as barriers was presented by Wiley *et al.* at the first High-Temperature Electronics Conference

in 1981, and published in the Proceedings and elsewhere.[43] This suggestion may well have seemed akin to the proposal made at about the same time to use a-Ni–Nb as a first wall coating for a thermonuclear reactor because of its resistance to radiation damage! In each of these proposed applications, the idea of using a highly metastable material in or close to a high-temperature zone must have seemed distinctly eccentric. Yet at least where microelectronics is concerned the idea has quickly become familiar and accepted. By 1983, Nicolet *et al.* were again discussing possible barrier layers, this time in terms of a variety of amorphous alloys, including compositions in the Ni-Nb, Ni-Mo, Ni-W, Fe–W, Ta–Ir, W-Si, Mo–Si, and some ternary systems. Nicolet *et al.* had systematically studied the properties of a-$Fe_{37}W_{63}$ layers.[45] These 100 nm films on Si did not react to an unacceptable degree with the subjacent silicon till about 650 °C; on SiO_2, stability was achieved up to ~700 °C. The degree of stability of the barrier in the presence of a metallic overlay (Al, Cu, Ni, or Pt) depended somewhat on the nature of that metal film and also on its thickness (because that determines the supply of metal). This was probably the first recognition that the efficacy of a barrier layer depends in a complex way on both the substrate and the overlay.

Before surveying later work, it is important to explain just why a metastable phase can be more effective as a barrier than a polycrystalline film of a thermodynamically stable phase. The reason is simply that, in the temperature range of interest (400–700 °C), the crystalline films (typically silicides), which had previously been standard undergo diffusion preferentially at grain boundaries, which act as short circuits (as do individual dislocation lines). Amorphous phases are entirely homogeneous and contain neither grain boundaries nor dislocations. This is the basis of their efficacy. Indeed, Wiley *et al.*[43] observed that a-W–Si films retained their barrier efficiency even after crystallization had begun, so long as the crystallites were discrete and separated by stretches of amorphous material.

Doyle *et al.*[46,47] systematically studied the effect, on a-$Ni_{55}Nb_{45}$ films (40–1000 nm thick) with a gold overlayer, of different substrates, Si, GaAs, GaP, and they also compared Au diffusivity in a-$Ni_{55}Nb_{45}$ and a crystallized film of the same composition.[46] Figure 7 shows this comparison.[46] The difference of gold diffusivities at 400 °C is more than five orders of magnitude, and constitutes an impressive demonstration of the potential of amorphous barrier layers. Indeed, this figure made considerable impact at the time. As with other barrier layers, GaAs and GaP had lower useful temperature limits with this barrier layer than did Si.

A very recent study by Thomas *et al.*[48] examined the effect of Al overlayers on a-$W_{72}Si_{28}$ films; the effect of Al was to lower the effective crystallization temperature by at least 150 °C relative to the bare amorphous film. Perepezko and Wiley[49] examined diffusion of Ta or a-Ni–Ta into a-$Ni_{55}Nb_{45}$ and found that Ta, being a highly refractory solute, diffuses much more slowly than does Au. This is in accord with the general rule mentioned in the preceding section. It is also consistent with the observation by Kelly *et al.*,[50] who found that Ta–Ir barrier layers showed superior performance, evincing no interdiffusion after 24 h at 600 °C in a 50

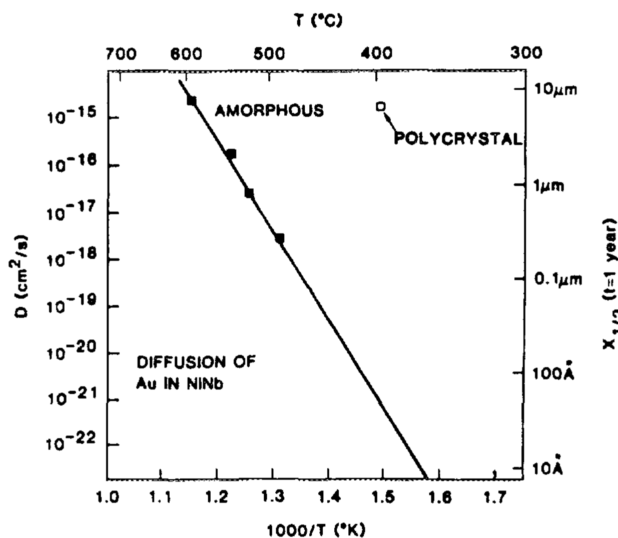

FIG. 7. The diffusivity of gold in amorphous and polycrystalline $Ni_{55}Nb_{45}$. The right-hand scale shows the diffusion distance for a period of one year. (After Doyle *et al.*, Ref. 46).

nm thick barrier in an Au/Ta–Ir/GaAs configuration. Very recently, Hunt *et al.*[51] have made detailed measurements of silicon diffusion in sputtered a-Ta–Ir films ranging from 39 to 59 at.%Ir. Interdiffusion was found to be negligible below 700 °C, as can be deduced from the experimental profiles in Fig. 8. At 900 °C, a silicide forms and the rapid diffusion at 900 and 950 °C takes place in a predominantly crystalline film. (The crystallization temperatures observed were somewhat lower than the value used in Fig. 5.)

Many of the desirable properties of amorphous barrier layers of diverse compositions, together with specifications for rf sputtering of the layers, are brought together in a recent patent specification by Perepezko and Wiley.[52] From this, and the many other recent publications, it is clear that with Si substrates and also with the more difficult GaAs, stability at 500 °C should be no problem, certainly with gold metallization. It seems that, in general, interdiffusion of overlay and substrate materials to generate undesired phases, rather than simple crystallization of the barrier layer, constitutes the limiting factor, but plainly, the higher the

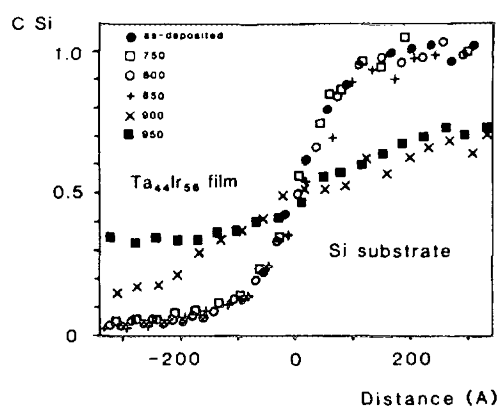

FIG. 8. Si concentration profiles from films of $Ta_{45}Ir_{55}$, as deposited on Si and after annealing for 1 h at a range of temperatures. (After Hunt *et al.*, Ref. 51).

crystallization temperature, the slower is diffusion in the layer at a given temperature.

By going to amorphous barrier layers made with highly refractory components, of which Ta–Ir is the prototype, safe temperatures as high as 700 °C promise to be routinely feasible. The information in Fig. 5 can be used to suggest promising new compositions, aided by a comprehensive tabulation of compositions and measured crystallization temperatures, such as that published for about 400 binary metal–metal glasses by Wang.[53] Preparation by rf sputtering should not prove a limiting factor, and there is plainly much worthwhile research still to do.

ACKNOWLEDGMENTS

I am grateful to the President and Provost of the California Institute of Technology for the award of a Fairchild Scholarship during the tenure of which this review was written. Thanks are due to Dr. B. Cantor, Dr. A. L. Greer, and Professor J. H. Perepezko for kindly providing preprints and reprints of recent work. I am happy to acknowledge that I have learned much from Professor M.-A. Nicolet and Professor W. L. Johnson.

[a] Present affiliation: Department of Materials Science and Metallurgy, Cambridge University, Pembroke Street, Cambridge CB2 3QZ, England.

[1] S. D. Dahlgren, in *Proceedings of the 3rd International Conference on Rapidly Quenched Metals*, Brighton, England, 1978, edited by B. Cantor (The Metals Society, London, 1978), Vol. 2, p. 36.
[2] W. Buckel and R. Hilsch, Z. Phys. **146**, 27 (1956).
[3] B. Rauschenbach and K. Hohmuth, Phys. Status Solidi A **72**, 667 (1982).
[4] B. Y. Tsaur, S. S. Lau, C. S. Hung, and J. W. Mayer, Nucl. Instrum. Methods **182/183**, 67 (1981).
[5] B.-X. Liu, M.-A. Nicolet, and S. S. Lau, Thin Solid Films **73**, 183 (1982).
[6] K. C. Russell, in *Proceedings of the International Seminar on Solute–Defect Interaction and Phase Transformations*, Kingston, Ontario, August 1985 (Pergamon, Oxford, England, 1986), in press.
[7] B. H. Kear, J. N. Mayer, J. M. Poate, and P. R. Strutt, *Metallurgical Treatises*, edited by J. K. Tien and J. F. Elliott (The Metallurgical Society of AIME, Warrendale, PA, 1981), p. 321.
[8] G. Dietz, J. Magn. Magn. Mater. **6**, 47 (1977).
[9] M. van Rossum, M.-A. Nicolet, and W. L. Johnson, Phys. Rev. B **29**, 5498 (1984).
[10] W. L. Johnson, in *Proceedings of the Conference on Liquids and Glasses*, (New York Academy of Sciences, New York, in press).
[11] *Amorphous Metallic Alloys*, edited by F. E. Luborsky (Butterworths, London, 1983).
[12] H. S. Chen, Rev. Mod. Phys. **43**, 353 (1980).
[13] R. W. Cahn, *Physical Metallurgy*, 3rd ed., edited by R. W. Cahn and P. Haasen (North-Holland, Amsterdam, 1983), p. 1780.
[14] *Ultrarapid Quenching of Liquid Alloys*, Treatise of Materials Science and Technology, edited by H. Herman (Academic, New York, 1981), Vol. 20.
[15] D. Gupta, K. N. Tu, and K. W. Asai, Phys. Rev. Lett. **35**, 796 (1975).
[16] P. Valenta, K. Maier, H. Kronmüller, and K. Freitag, Phys. Status Solidi **105**, 537 (1981).
[17] P. Valenta, K. Maier, H. Kronmüller, and K. Freitag, Phys. Status Solidi **106**, 129 (1981).
[18] R. W. Cahn, J. E. Evetts, J. Patterson, R. E. Somekh, and C. Kenway-Jackson, J. Mater. Sci. **15**, 702 (1980).
[19] H. S. Chen, L. C. Kimerling, J. M. Poate, and W. L. Brown, Appl. Phys. Lett. **32**, 461 (1978).
[20] D. Akhtar, B. Cantor, and R. W. Cahn, Scr. Metall. **16**, 417 (1982).
[21] D. Akhtar, B. Cantor, and R. W. Cahn, Acta Metall. **30**, 1571 (1982).
[22] M. M. Kijek, D. Akhtar, B. Cantor, and R. W. Cahn, in *Proceedings of the 4th International Conference on Rapidly Quenched Metals*, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1982), p. 561.
[23] M. M. Kijek, D. W. Palmer, and B. Cantor, Acta Metall. **34**, 1455 (1986).
[24] U. Köster and U. Herold, in *Glassy Metals I: Ionic Structure, Electronic Transport, and Crystallization*, edited by H.-J. Güntherodt and H. Beck (Springer, Berlin, 1981), p. 225.
[25] M. P. Rosenblum, F. Spaepen, and D. Turnbull, Appl. Phys. Lett. **37**, 184 (1980).
[26] A. L. Greer and F. Spaepen, in *Synthetic Modulated Structure Materials*, edited by L. Chang and B. C. Giessen, *Treatise on Materials Science and Technology*, edited by H. Herman (Academic, New York, 1985), p. 419.
[27] H. D. Palfrey, M. Brown, and A. F. W. Willoughby, J. Electrochem. Soc. **128**, 2224 (1981).
[28] A. L. Greer, in *Diffusion Phenomena in Thin Films*, edited by D. Gupta and H. S. Ho (Noyes, Park Ridge, NJ, in press).
[29] B. Cantor and R. W. Cahn, Ref. 11, p. 487.
[30] Y. Limoge, G. Brébec, and Y. Adda, in *Proceedings of the Conference on Diffusion in Metals and Alloys (DIMETA 82)*, Tihany, Hungary, September 1982 (Hungarian Academy of Sciences, Budapest, 1982).
[31] B. Cantor, in *Electric Power Research Institute/Acta Metallurgica Workshop on Amorphous Metals*, San Diego, May 1985, edited by R. I. Jaffee and P. Haasen (Pergamon, Oxford, 1986).
[32] M. Ahmadzadeh and B. Cantor, J. Non-Cryst. Solids **43**, 189 (1981).
[33] F. Lancon, L. Billard, W. Chambron, and A. Chamberod, J. Phys. F **15**, 1485 (1985).
[34] P. Ramachandrarao, B. Cantor, and R. W. Cahn, J. Mater. Sci. **12**, 2488 (1977).
[35] K. H. J. Buschow, Solid State Commun. **43**, 171 (1982).
[36] F. Saris, in *Proceedings of the Symposium on Beam–Solid Interactions and Phase Transformations* (Materials Research Society, Pittsburgh, PA, 1986), Vol. 51.
[37] D. Akhtar and R. D. K. Misra, Scr. Metall. **19**, 603 (1985).
[38] R. Kirchheim, F. Sommer, and G. Schluckebier, Acta Metall. **30**, 1054 (1982).
[39] Y. S. Lee and D. A. Stevenson, J. Non-Cryst. Solids **72**, 249 (1985).
[40] D. Farkas, Scr. Metall. **19**, 245 (1985).
[41] M.-A. Nicolet, Thin Solid Films **52**, 415 (1978).
[42] M.-A. Nicolet and M. Bartur, J. Vac. Sci. Technol. **19**, 786 (1981).
[43] J. D. Wiley, J. H. Perepezko, J. E. Nordman, and K.-J. Guo, IEEE Trans. Ind. Electron. **29**, 154 (1982).
[44] M.-A. Nicolet, I. Suni, and M. Finetti, Solid State Technol. 129 (1983).
[45] I. Suni, M.-A. Nicolet, C. S. Pai, and S. S. Lau, Thin Solid Films **107**, 73 (1983).
[46] B. L. Doyle, P. S. Peercy, J. D. Wiley, J. H. Perepezko, and J. E. Nordman, J. Appl. Phys. **53**, 6168 (1982).
[47] B. L. Doyle, P. S. Peercy, R. E. Thomas, J. H. Perepezko, and J. D. Wiley, Thin Solid Films **104**, 69 (1983).
[48] R. E. Thomas, J. H. Perepezko, and J. D. Wiley, in *Proceedings of the Symposium on Thin Films—Interfaces and Phenomena* (Materials Research Society, Pittsburgh, PA, 1986), Vol. 54, p. 127.
[49] E. A. Dolisz, B. L. Doyle, J. H. Perepezko, J. D. Wiley, and P. S. Peercy, in *Proceedings of the Symposium on Layered Structures, Epitaxy, and Interfaces* (Materials Research Society, Pittsburgh, PA, 1986), Vol. 37.
[50] M. J. Kelly, A. G. Todd, M. J. Sisson, and D. K. Wichenden, Electron. Lett. **19**, 474 (1983).
[51] A. J. Hunt, B. Cantor, and M. M. Kijek, in *First International Conference on Rapidly Solidified Materials*, San Diego, February 1985 (American Society Metals, Metals Park, Ohio, in press).
[52] J. H. Perepezko and J. D. Wiley, U. S. Patent 4 494 136, January 1985.
[53] R. Wang, Bull. Alloy Phase Diagrams **2**, 269 (1981).