DIFFUSION BARRIERS IN THIN FILMS

M.-A. NICOLET

California Institute of Technology, Pasadena, Calif. 91125 (U.S.A.)

(Received December 8, 1977; accepted March 3, 1978)

Some of the conditions which thin film diffusion barriers should satisfy are enumerated. Various ways to try to meet these conditions are illustrated by means of examples. It is shown that metal films chosen for their mutual immiscibility with the adjoining metals (passive barriers) usually fail as barriers (*i.e.* are non-barriers) because extended structural defects in the metal film constitute fast diffusion paths. Single-crystal barriers of such metals are effective but not practical. Barriers which are thermodynamically partially stable (partially stable barriers) and those which are fully stable (stable barriers) are discussed. Metal compounds of particular interest for such barriers are suggested. The concept of the sacrificial barrier, which is based on an irreversible loss of barrier material by interfacial reactions with the adjoining metals, is introduced and successful applications are presented. The stabilizing effect of impurities on an otherwise unstable barrier (stuffed barriers), the importance of mechanical stress and the critical influence of the fabrication process of a thin film barrier on its actual performance are described by practical examples. Values of the electrical resistivity for borides, carbides, nitrides and silicides of the early transition metals and values of the coefficient of linear thermal expansion of silicides are compiled for reference purposes.

1. INTRODUCTION

Diffusion barriers in thin films are almost synonymous with reliable contacts and metallization schemes. The present treatment of diffusion barriers in thin film systems is therefore largely inspired by the problems which have been confronted (or solved) in integrated circuit technology, and the problems of the electrical contact to the device in particular. No attempt has been made to be exhaustive or detailed. Rather, the aim of this review is to consider the important aspects of the subject, to illustrate them by examples, to classify thin film barriers and to show the difficulties encountered in arriving at an acceptable solution to and an adequate understanding of diffusion barriers.

2. DEFINING THE PROBLEM

We consider the simplest case as it presents itself in a typical solid state device.

An object, which may be a thin film itself or of a more bulky configuration and which consists of a material B, is to be provided with an electrical contact in the form of a thin metal film A, as shown in Fig. 1(a). The choice of the materials A and B is typically prescribed. In a silicon gate field-effect transistor (FET), for example, the gate material B is necessarily silicon, polycrystalline in structure and doped to meet specific device requirements. The metal A is aluminum or perhaps gold, and is chosen on the basis of the manufacturer's existing equipment, expertise or preference. Polycrystalline silicon in contact with a film of aluminum is a configuration which is not in equilibrium and is therefore a state with poor stability. The aluminum can diffuse into the silicon, irreversibly altering the electrical characteristics of the polysilicon gate. Given enough time, even the crystalline structure of the silicon gate will change (see Section 5.2). The ideal diffusion barrier separates A and B physically by interposing a barrier layer of a material X chosen so that under the same external conditions (ambient, time, temperature, stress etc.) the undesirable intermixing of A and B will be suppressed (Fig. 1(b)). The stability of the contact is thereby enhanced, but a number of assumptions have to be met if the introduction of the diffusion barrier is really to improve the situation. Ideally, the following conditions should be met:

(1), (2) the transport rate of A across X and of B across X should be small;
(3), (4) the loss rate of X into A and of X into B should be small;
(5), (6) X should be thermodynamically stable against A and against B;
(7), (8) there should be strong adhesion of X with A and with B;
(9), (10) the specific contact resistance of A to X and of X to B should be small;
(11), (12) X should be laterally uniform in thickness and structure;
(13) X should be resistant to mechanical stress;
(14) X should be resistant to thermal stress;
(15) X should be highly thermally conducting;
(16) X should be highly electrically conducting.

Clearly all these conditions cannot be fulfilled at once. It is therefore necessary to compromise.

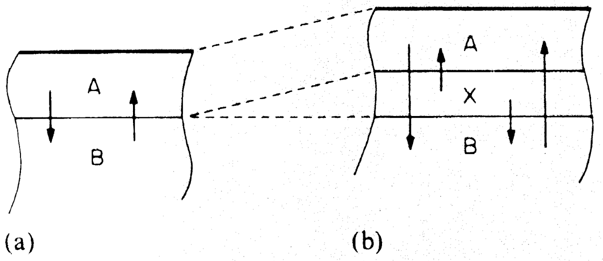


Fig. 1. A diffusion barrier X is inserted between a thin film A and a substrate (or another thin film) B to prevent intermixing of A and B. Some of the conditions which the barrier X has to meet are listed in the text.

In practice, a number of additional conditions must be imposed. For instance, it is important that the barrier be compatible with other steps employed in the fabrication of the device (such as selective chemical etching through photoresist masks) or that the barrier can be deposited reproducibly with existing equipment. Such constraints may differ from one device to another or between manufacturers. Ultimately, the usefulness of a barrier depends on economic considerations. This is the reason why it is often simpler to specify how diffusion barriers should not be made rather than to give rules about how they should be made. The body of knowledge of thin film phenomena and processes has grown much in the recent past, as witnessed by the number of books on the subject[1-9], but our understanding of atomic migration and reactions in thin films remains largely empirical. Certain facts of major importance for thin film diffusion barriers are well established, however.

3. THE NEED FOR DIFFUSION BARRIERS WITH THIN FILMS

In 1935 DuMond and Youtz[10] wanted to produce an artificial grating to determine X-ray wavelengths absolutely. They deposited many thin layers of gold and copper because they thought that two isomorphous metals would tend to form uniform films rather than to coalesce into islands. DuMond and Youtz discovered that the gratings they produced lost their ability to diffract X-rays after 2–3 d owing to the interdiffusion of gold and copper. They realized that, even though atomic diffusion in the solid phase is a relatively slow process, this action was nevertheless capable of degrading their gratings because of the extremely small thickness of the individual layers involved (about 100 Å for one copper and gold sequence). DuMond and Youtz turned their unstable gratings into objects which allowed them to measure the diffusivities of atoms in the solid phase. Four years later, they wrote a paper in which they gave the diffusion constant for gold through copper as about 5×10^{-20} cm^2 s^{-1} at room temperature[11].

DuMond and Youtz's paper contains two fundamental points. The first is that diffusion in the solid phase is a rapid process over small distances, even at room temperature. In a diffusion-limited process the root mean square of the distance covered increases as $(Dt)^{1/2}$ where D is the diffusivity and t the time. As the distance is reduced, the duration required to cover the distance by diffusion decreases rapidly. The second point is one which DuMond and Youtz did not mention and probably did not appreciate. If the bulk diffusion of gold in copper is measured at high temperatures and is extrapolated to room temperature, values of the order of 10^{-36} cm^2 s^{-1} [12] are predicted. The diffusion of gold through copper observed by DuMond and Youtz is faster by many orders of magnitude.

This is a result of great significance for diffusion barriers in thin films. Bulk diffusion is associated with a larger activation energy than grain boundary diffusion so that a cross-over from one diffusion process to the other is expected as the temperature changes. There is a rule of thumb which states that this cross-over temperature, which is known as the Tammann temperature, is at one-half or two-thirds of the melting temperature T_m (in kelvins) of a solid. Below the Tammann temperature atomic diffusion is no longer determined by regular bulk processes but is controlled by grain boundaries and other defects in the material. Grain boundaries and extended defects offer paths which enhance atomic mobility. In thin films, these paths can carry atoms rapidly across the films even at room temperature, thereby dominating the atomic traffic. Defects and grain boundaries are therefore of primary significance for barriers because, even if the bulk material of a chosen barrier film were to meet all the specifications of a diffusion barrier, the presence of grain boundaries and other extended structural defects in the thin film could entirely negate its usefulness as a barrier. In Section 4 we give some examples.

A rapid interdiffusion of atoms in thin films is not desirable because it generally means that the device characteristics will change with time. The changes are often injurious. Diffusion barriers are an attempt to retard this degradation by interposing a layer which will suppress, or at least strongly reduce, this undesirable transport of atoms.

4. ELEMENTAL BARRIERS

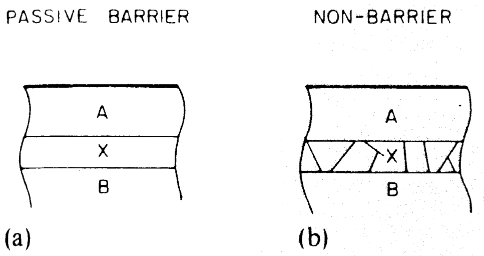
We shall assume first that the barrier material X is a pure metal. For simplicity, we shall also assume that the materials A and B are elemental. Choosing a metal as the barrier is the obvious response to the usual demand for high electrical conductivity in the barrier layer.

4.1. *Effect of structural defects (passive barriers and non-barriers)*

One obvious choice for the material of the barrier X is a metal which does not react chemically with A and B and which has negligible mutual solubility with both A and B (passive barrier, see Fig. 2(a)). Of course, there is no assurance that such a metal can be found but, even if it exists, the chances are that the metal will not behave as a diffusion barrier in the form of a thin film if grain boundaries or other extended defects are present (Fig. 2(b)).

Campisano *et al.*[13] have demonstrated the nature of the problem in a study of bilayer films of copper and lead. The two metals are immiscible in their solid bulk phases, do not form compounds and can thus be viewed as the two top layers (A and X) in Fig. 2. The films in the couple were 300–2000 Å thick and were vacuum deposited sequentially onto an inert substrate without breaking vacuum. Transmission electron microscopy (TEM) showed that, in the as-deposited state, the copper film was polycrystalline with an average grain size of the order of 100 Å while the lead film was polycrystalline with a much larger average grain size (about 2000 Å). After annealing under a flow of pure argon, the samples were re-analyzed by TEM for grain size and by backscattering spectrometry for atomic migration. It was found that lead had penetrated throughout the copper film but that copper in the lead film remained below the limit of detection. The average size of the copper grains increased to about 2000 Å through recrystallization and grain growth. No appreciable grain growth was noted in the lead film (see Fig. 3(a)).

The predominant motion of lead into copper is due to the much larger number of grain boundaries in the copper than in the lead film. Since the bulk solubilities are nil, the intermixing must come from structural defects such as grain boundaries. The point was proved by a second experiment in which a bulky polycrystalline copper substrate was pre-annealed at 800 °C for several hours. The average grain size of the copper was then about 30 μm. A lead film was deposited on this copper substrate as before, so that the average grain size (about 2000 Å) of the lead film was small compared with that of the copper substrate. After annealing, copper was found in the lead film but the level of lead in the copper was below the limit of detection (Fig. 3(b)). By inverting the ratio of the average grain size, the predominant moving species was changed from lead to copper. The



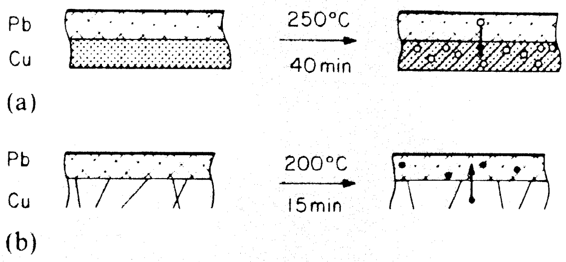


Fig. 2. A film of a metal X which is mutually immiscible with both A and B could theoretically be a good diffusion barrier (passive barrier) were it not for extended structural defects, such as grain boundaries, which constitute fast diffusion paths and short-circuit the barrier effect (non-barrier).

Fig. 3. In a thin film couple of mutually immiscible metals such as lead and copper, the relative grain size will determine the dominant moving species[13].

amount of copper found in the lead film was smaller than the amount of lead observed in the copper in the first experiment. This can be attributed to the smaller number of grain boundaries in the as-deposited film of lead compared with the copper film.

The grain size of a polycrystalline film is thus of primary significance in determining the atomic transport properties. The size of the grains, other structural characteristics such as defects, the texture and the stress generally depend on the method of fabrication of the film. For diffusion barriers, this means that the procedures applied in the fabrication process can be a critical factor in the success or failure of a barrier. For thin metal films deposited on substrates kept at relatively low temperatures, the rule is that, the higher the melting point of the deposited metal, the smaller is the grain size of the film[14]. The example of Fig. 3(a) conforms to this rule: the melting point of copper is 954 °C while that of lead is only 326 °C. When deposited on a substrate at room temperature, the copper film will have the smaller grain size of the two films. This difference results in the preferential diffusion of lead into copper. A further statement of the rule is that, during annealing, the small grains of the high melting point metal (in this case copper) grow fastest. This is also observed. As a consequence, the ability of lead to permeate the copper film decreases with annealing time, a result which Campisano *et al.* have also established. Furthermore, such an increase in grain size has been observed by Baglin and d'Heurle[15] who investigated Cr/Cu and Bi/Cu thin film couples. These two pairs of metals have very low mutual solid solubilities. Intermixing is nevertheless observed after heat treatment, as expected.

Another example of this kind is found in the Ti/Mo/Au metallization system[16]. The solid solubility of molybdenum in bulk gold is less than 1 at.% below 800 °C. The solid solubility of gold in bulk molybdenum is exceedingly small and the two metals do not form an intermediate phase[17]. It is found that in a thin film Mo/Au couple the molybdenum film contains approximately 2–3 at.% gold. Since the melting point of molybdenum (2620 °C) is much higher than that of gold (1063 °C), the molybdenum film is the finer grained of the two, so that gold will preferentially diffuse into the molybdenum film. The concentration of 2–3 at.% is typical of grain boundary decoration. For a hypothetical polycrystalline material with cubic grains of side 50 Å and a monolayer of foreign atoms on all grain boundaries, the apparent volume concentration of foreign atoms is of the order of 10 at.%. Grains are rarely as small as 50 Å in metal films and the decoration of the boundaries is not necessarily complete, so that concentration values of a few atomic per cent are typical. Thus a thin film of molybdenum does not constitute a diffusion barrier to gold. This fact has been confirmed again quite recently by Nowicki and Wang[18]. On this basis we would expect that adequate separation of gold cannot be achieved with molybdenum. A possible reason for the success of the molybdenum is discussed in Section 7.1.

A number of other thin film couples of this type have been studied. In magnetic bubble memories a thin film of a magnetic material is covered with strips etched from an overlying conducting layer. One scheme which has been considered is a film of Permalloy (80% Ni–20% Fe) with a gold film on top. Ziegler *et al.*[19] have investigated the stability of this thin film couple and of gold on nickel and iron films. After heat treatment at 350 °C, they observed gold concentrations in the range 1–10% in all three cases, although the solubility of gold in nickel is only about 0.1 at.% and the solubility of gold in iron is even less (about 0.01 at.%). The diffusion of iron and nickel into the gold is also observed. These findings are all consistent with dominant grain boundary effects.

The last example is that of gold and rhodium. The melting point of rhodium is 1966 °C, which is some 900 °C above that of gold. Films of rhodium deposited on room temperature substrates will have much smaller grains than films of gold. Gold thus diffuses into rhodium; DeBonte *et al.*[20] find that typically it is present in the rhodium immediately after deposition of the gold onto the rhodium film.

It will be useful to be able to refer to the various barrier types by simple names. We shall call the immiscible metal films discussed here non-barriers in view of the fact that these layers do not act as barriers in the typical polycrystalline form in which they are obtained by conventional deposition techniques.

4.2. *Single-crystal barriers*

The way to eliminate fast diffusion paths such as grain boundaries and dislocations is to use single-crystal films. This solution is not practical for applications but investigations have been carried out which show that, in principle, such films do indeed constitute effective passive diffusion barriers.

Tu and Rosenberg[21] produced thin film couples of 2000 Å palladium and 700 Å gold separated by an intermediate silver layer about 3000 Å thick. In one specimen the silver layer was single crystalline and so was the underlying gold film, both having been grown epitaxially on a single-crystal substrate of cleaved NaCl (Fig. 4(a)). In the other specimen the silver barrier layer and the gold layer underneath were both polycrystalline and had an average grain size of about 350 Å (Fig. 4(b)). This combination of metals is different in kind from those discussed so far. Gold forms solid solutions with silver and forms compounds with lead but silver and lead do not react and have low mutual solubility. Regardless of this, Tu and Rosenberg found that, after vacuum annealing for 48 h at 200 °C, the single-crystal layer of silver was essentially impermeable to gold and lead within the sensitivity of their measurements. In contrast, the polycrystalline silver layer did not prevent the formation of PbAu at the Pb–Au interface after only 24 h at 200 °C.

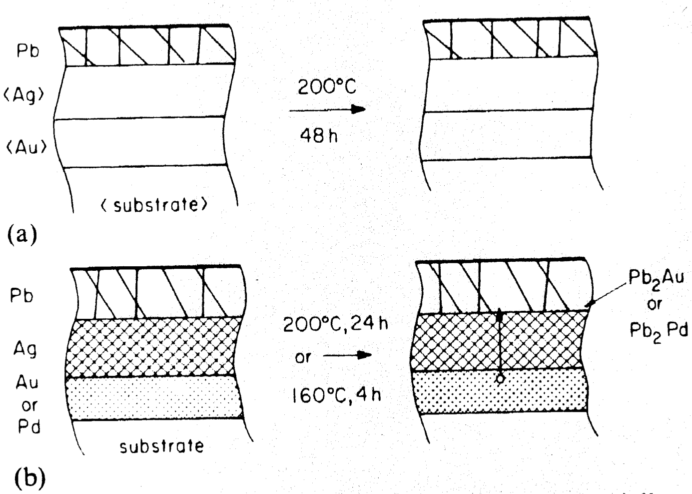
A second experiment with a polycrystalline silver layer was performed with palladium instead of gold. Metallurgically, palladium and gold behave similarly with respect to silver and lead but palladium and silver are sufficiently dissimilar for palladium to alter the lattice parameter of silver noticeably if a significant amount of the diffusing palladium goes into solid solution with the silver grains. The lattice parameter of silver was found to be unchanged even when the amount of palladium transported was substantial compared with the amount of the silver layer. This result indicates conclusively that palladium is confined to the grain boundaries and does not penetrate the grains. This observation is of interest in the light of the next example.

Kirsch *et al.*[22] also investigated the interdiffusion of Au/Ag thin film couples in the single-crystal and the polycrystalline state. In contrast to the previous experiment, their thin film couples were self-supporting and the lead layer was absent. The absence of the substrate is an unimportant difference, but the absence of the lead film is significant. When the single-crystal couple was vacuum annealed at 150 °C for 40 min the films underwent no detectable change (Fig. 5(a)). This result agrees with that shown in Fig. 4(a). When the polycrystalline film was similarly treated, gold was seen to diffuse into the silver layer and silver also diffused into the gold layer (Fig. 5(b)). This is in contrast with the result of Fig. 4(b), where the movement of gold was dominant. Kirsch *et al.* found that the distribution of gold and silver atoms in the host films was roughly uniform and that the volume concentration increased with the duration of annealing. After several months of storage at room temperature, the gold concentration in the silver layer was about 2 at.%, presumably because of the absorption of gold atoms on grain boundaries. After several hours at 150 °C, the concentration approached 10 at.%. Above 400 °C, the film couple rapidly approached the final state of a single uniform layer. At any given temperature the monotonic rise of the atomic concentration with time goes through distinct regimes, but the interpretation of this behavior is conjectural. At room temperature the grain boundary diffusion coefficient is estimated to be about 10^{-14} cm^2 s^{-1}. In comparison, the high temperature value of the bulk diffusion coefficient extrapolated to room temperature is about 10^{-32} cm^2 s^{-1}[23]. The factor of 10^{18} again shows the insignificance of bulk diffusion compared with grain boundary and other defect processes at room temperature. Another comparison of thin film pairs of polycrystalline and epitaxial (near single-crystal) structure is reported by Baglin *et al.*[24] on film couples of chromium and copper. In contrast with silver and gold, chromium and copper are immiscible in the solid phase. The results, however, were much the same: the single-crystalline couple was much more stable than the polycrystalline one.

4.3. *Driving force of a sink*

In the experiment of Kirsch *et al.*[22], the final state of the thin film reaction is a solid solution with an Au/Ag ratio given by the initial amounts of each species. Grain boundary decoration is the first step towards this final state but as time progresses the diffusion of gold into the silver grains and of silver into the gold grains will set in and will eventually convert both layers to the same solid solution.

Such a penetration of gold into the silver grains did not occur in the experiment of Tu and Rosenberg (Fig. 4(b)). We can explain this by observing that, when a lead layer is present, the migrating gold atoms are eventually absorbed by the formation of Pb_2Au. Evidently this reaction removes gold atoms from the grain boundaries at a much faster rate than does the process of diffusion into the silver grains. It is the presence of this efficient gold sink which prevents diffusion into the grains. This argument cannot explain why silver should not diffuse into the gold or palladium layer too. There is a possibility that this movement may have gone undetected in Tu and Rosenberg's measurements. They used X-ray diffraction, which has no depth resolution over the layer thickness, as their main investigative tool. Kirsch *et al.* relied mainly on backscattering spectrometry, which can resolve atomic distribution in depth to within 150–200 Å.



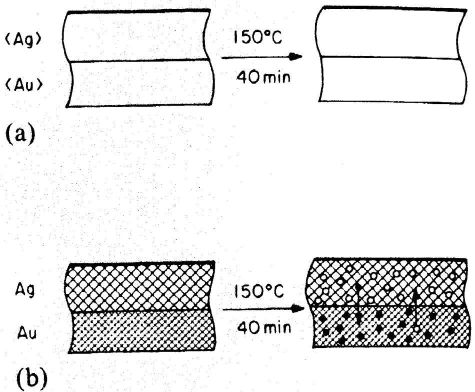


Fig. 4. (a) A single-crystal film of silver (grown epitaxially on a single-crystal film of gold) prevents the reaction of gold with lead during heat treatment and is a diffusion barrier in this case. (b) The same combination of thin metal films in a polycrystalline configuration does intermix; structural defects have ruined the barrier effect of the silver layer (non-barrier). The presence of the lead acts as a sink for gold (or palladium) atoms, and the gold (or palladium) does not alloy with the silver[21].

Fig. 5. (a) A single-crystalline bilayer of gold and silver resists intermixing during heat treatment at 150 °C for 40 min in spite of the fact that gold and silver form a solid solution. (b) The same bilayer in polycrystalline configuration intermixes during the same heat treatment and mutual dissolution of gold and silver sets in. Compare this final state with that shown in Fig. 4(b), where the presence of a sink suppresses mutual dissolution[22].

The presence of a sink at the boundary of a film which contains rapidly diffusing impurity atoms constitutes a strong driving force in thin film couples. A vivid demonstration of this is provided by thin evaporated films of gold or silver on silicon single-crystal substrates (Fig. 6)[25–27]. In the solid phase (*i.e.* below the eutectic temperature of 370 °C) silicon and gold are practically mutually insoluble. Because the substrate is single crystalline but the gold film is polycrystalline, no significant diffusion of gold into the silicon substrate will occur but a fast diffusion of silicon is expected along grain boundaries of the gold film on annealing below the eutectic temperature. This is indeed observed. In an oxidizing atmosphere (O_2, air, steam) SiO_2 will grow rapidly on top of the gold film at temperatures as low as 100 °C (Fig. 6(b)). Without an oxidizing atmosphere (as for example in vacuum or forming gas) insignificant amounts of SiO_2 are formed on the sample at temperatures as high as 300 °C (Fig. 6(a)). The rate of SiO_2 formation depends on the orientation of the substrate: the rate is about five times faster on ⟨110⟩-oriented substrates than on ⟨111⟩-oriented substrates. It is also found that the initial rate of SiO_2 growth is roughly the same regardless of the gold layer thickness. Apparently, the grain boundary transport is initially faster than the processes of injection and extraction of silicon at the boundaries of the gold film. Eventually the growth of SiO_2 comes to a halt. This effect has been attributed to a deterioration of the interface between the gold film and the silicon substrate and to changes in the bulk of the film. Roughly, the growth ceases when the amount of silicon transported across the gold is commensurate with the amount of gold in the film. The rapidity of the reaction at the Si–Au interface has been explained by postulating a change in the electronic state of the silicon atoms at the interface from a covalent to a metallic type of bonding as a result of the tendency of the metal atoms to penetrate the silicon lattice at the interface[28, 29].

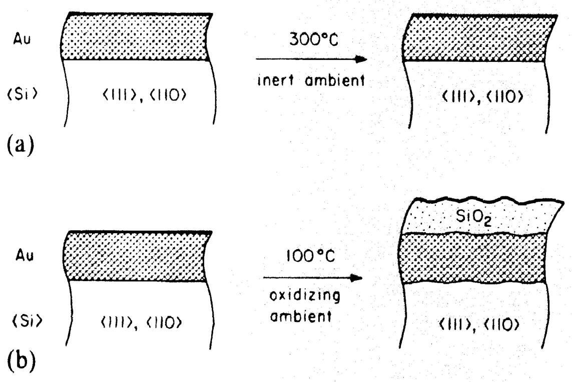


Fig. 6. The presence of a sink can affect the stability of thin films and can determine the outcome of an experiment: (a) a thin film of gold deposited on a silicon wafer is quite a stable system for annealing in an inert ambient but (b) it does not withstand only moderate annealing in an oxidizing ambient[25–27].

Generalizing from the results discussed so far, we conclude that immiscibility of the elements A and B with the metal X does not lead to successful barriers unless the barrier is a defect-free single-crystalline film, which is not an attractive solution for practical applications. Pairs of metals which form solid solutions, such as gold and silver, are then excluded as well because, in addition to the inadequacies of structural origin in the film, there is the added problem of bulk interdiffusion which must eventually lead to an overall modification of the barrier material. The only alternative is to resort to barriers involving compounds.

Another vivid demonstration of the effect a sink can have on the behavior of thin metal layers is offered by the Au/Ge/Ni system[30]. Bulk gold and germanium form a single eutectic, gold and nickel form a solid solution and germanium and nickel form compounds[17]. If the germanium layer and the nickel layer are separated by a layer of gold, all the germanium diffuses through the gold layer and combines with the nickel during heat treatment. The same final state is found if the germanium is initially dissolved in the gold. Gold and nickel do not interact much during this process. The condition which must be satisfied is that the atomic percentage of nickel exceeds that of germanium. This guarantees that all the germanium can be bound in the form of NiGe (the most Ge-rich compound of nickel). Under these conditions, the outcome is the same for annealing either above or below the Au–Ge eutectic temperature of 356 °C. If there is not sufficient nickel to bind all the germanium, all three elements become mixed in a laterally non-uniform aggregate. The results are quite similar if platinum is substituted for nickel[31].

5. COMPOUND BARRIERS

The advantages offered by compounds are their very large number and their varied properties, but the problem of choice is correspondingly magnified. In principle, a systematic application of the conditions listed in Section 2 should lead to the identification of promising compounds. In practice, the solutions adopted have been arrived at empirically because most of the information needed to make decisions on logical grounds is not available. One reason is that the values of the parameters derived from measurements on bulk material generally do not apply to thin films where the conditions of stress and structure differ from those of bulk material. There is also the possibility that undetected chemical impurities alter the film properties. This subject will be discussed further in Section 7.2. Here, we consider some solutions which rely on compounds for the barriers.

5.1. *Barriers which are thermodynamically partially stable* (*partially stable barriers*)

An attractive feature of the compound diffusion barrier is that it can be thermodynamically stable, *i.e.* with the barrier X in a state of lower free energy with respect to a reaction with A and B. Although this stability does not ensure a low diffusivity of A and B in the barrier, it does ensure that the barrier itself will not react with A and B.

An example of this kind has been investigated by Tu and Chance[32]. As shown in Fig. 4(b), a polycrystalline layer of silver does not prevent the diffusion of gold atoms and the subsequent formation of Pb_2Au. Let us assume that the gold alloys with silver rather than reacting with lead. The molar free energy of gold is thereby reduced with respect to its pure state since the alloy has a negative free energy of formation. The next step is to bind the gold chemically (*i.e.* to lower the molar free energy) so that the reaction with lead becomes energetically unfavorable. By calculation and experiment, Tu and Chance show that lead ceases to react with gold if the Au–Ag solid solution contains more than 70 at.% silver (Fig. 7). For palladium this limit is in the vicinity of 99 at.%.

This stability condition still leaves out of consideration the second interface of the barrier layer against the gold film (see Fig. 4(b)). As long as such a layer is present, the gold (or palladium) concentration in the compound layer cannot be maintained at a fixed value but will necessarily increase with time. To ensure the complete chemical stability of a compound barrier layer, it is therefore necessary in general to reach a state of stability against both A and B simultaneously. An Ag–Au (or Ag–Pd) alloy will not accomplish this in the case shown in Fig. 4.

Another thin film couple which is claimed to be stable is Ti_xW_{1-x}/Au. This metallization system has been introduced by Cunningham *et al.*[33] because of its desirable corrosion resistance and good stability. Tungsten is immiscible in titanium but titanium has a finite solubility in tungsten (about 10 at.% at 600 °C). If a little more titanium than is soluble in tungsten is introduced during the deposition of the film, the excess titanium is not actually dissolved in the tungsten but can impart desirable characteristics to the film. The corrosion resistance is attributed to the formation of the very stable TiO_2 on open surfaces; the good adhesion to silica or glass is ascribed to strong Ti–O bonds; the good electrical contact characteristics to gold are attributed to the presence of interfacial compounds formed between titanium and gold. The films are usually sputtered to avoid fractionation of the excess titanium during the deposition process. The result is a "pseudo-alloy" with a microscopically distributed excess of titanium embedded in it.

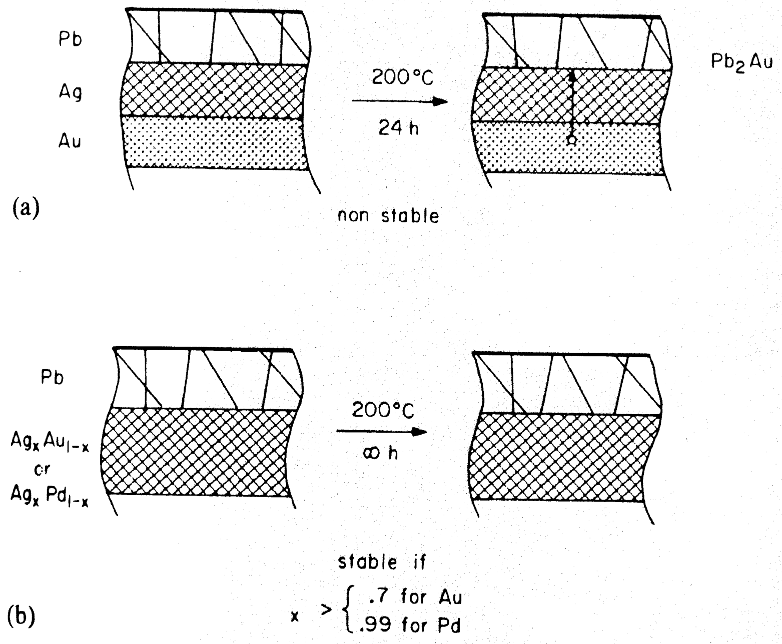
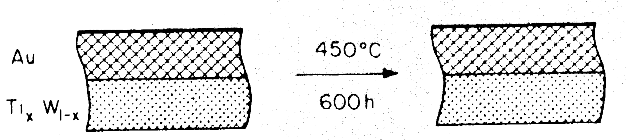


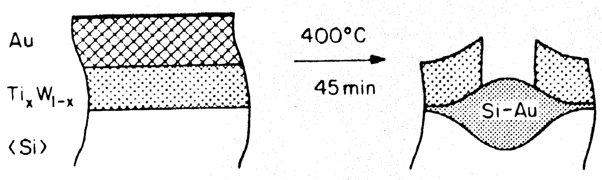
Fig. 7. (a) Gold is not stable against lead and reacts to form Pb_2Au even in the presence of an interposed polycrystalline silver film. (b) Gold dissolved in silver is thermodynamically stable against lead if the solid solution contains at least 70 at.% silver. For palladium this limit is in the vicinity of 99 at.% silver[32].

The stability of the Ti_xW_{1-x} layer against Au has been deduced from electrical measurements after annealing of the thin film couple at 450 °C for 600 h (Fig. 8(a)). A thermodynamic calculation to support the claim has apparently never been given. However, Harris *et al.*[34] have shown experimentally that a Ti_xW_{1-x} film is not stable against silicon but forms a ternary compound with it. The reaction with silicon sets in with measurable speed only at elevated temperatures (about 4.5 eV). At lower temperatures the pseudo-alloy is thus metastable against silicon, but it should nevertheless serve as an acceptable barrier between gold and silicon if neither are fast diffusers through the Ti_xW_{1-x} layer.

In fact, the atomic transport properties of this pseudo-alloy depend critically on the process of sputter deposition. Under certain deposition conditions the barrier rapidly cracks during annealing with a gold overlay. Massive transport of gold takes place through the fissures, and the gold alloys with the silicon substrate (Fig. 8(b)). This phenomenon is most pronounced at annealing temperatures above the Si–Au eutectic temperature of 370 °C and is less apparent below about 350 °C. The indications are that residual stress in the Ti_xW_{1-x} film plays a major role in the phenomenon, which apparently occurs even below the Si–Au eutectic temperature. The association with the eutectic temperature could mean that the diffusivity of gold (or silicon) in the pseudo-alloy is more significant than was originally believed. Without an atomic exchange of some sort across the barrier layer, it is difficult to explain why the Si–Au eutectic temperature has a particular significance in the process. The example demonstrates the very real significance of the requirement that the barrier layer should be mechanically stable against thermal or mechanical stress. The Ti_xW_{1-x} pseudo-alloy barrier has been used extensively in industry. It has also been considered[35] as a metallization scheme for GaAs.



(a) $Ti_{0.3}W_{0.7}$ stable against Au



(b) $Ti_{0.3}W_{0.7}$ not a barrier for Au against Si

Fig. 8. (a) $Ti_{0.3}W_{0.7}$ on an inert substrate is stable against gold at 400°C according to electrical measurements[33] but (b) the presence of mechanical stress can lead to catastrophic failure when $Ti_{0.3}W_{0.7}$ is used as a diffusion barrier between gold and single-crystal silicon.

A general kind of partially stable barrier is provided by silicide contacts. PtSi and Pd_2Si are used as the first contacting material because they make good low resistance contacts to silicon. Usually this first layer is then covered by another metal such as titanium. Titanium can also form silicides. The free energy of the whole system can thus be lowered if titanium reacts with the silicon. Whether PtSi is dissociated in the process and re-forms elsewhere or whether the titanium silicide is directly formed by diffusion of titanium or silicon across the Pd_2Si is a question of kinetics. At the temperatures and times usually involved, titanium reacts slowly with PtSi (perhaps because of the presence of impurities, see Section 7); this is the reason why the system can be applied successfully in practice. Basically, however, the combination of a silicide-forming metal layer with a silicide film on a silicon substrate is an unstable system.

5.2. *Thermodynamically stable barriers* (*stable barriers*)

A stable barrier layer must have a positive free energy of reaction with the material of the films on both sides of the barrier. The solution is to seek a material with a large negative energy of formation. Chemical compounds such as oxides and nitrides come to mind first, but transition metal carbides, borides and silicides are also strongly bonded compounds.

Nelson[36] has pointed out that the borides and mononitrides of titanium, zirconium, hafnium and vanadium have higher electrical conductivities than the pure metals. These compounds are inert with respect to copper, silver and gold. The mononitrides of these metals are quite stable, have very high melting points and offer an intriguing alternative to the standard barrier systems at present in use. An application of this idea has been described by Fournier[37] for the gate metallization of insulated gate field-effect transistors (IGFETs) where TiN is used as a barrier between titanium and platinum layers (Fig. 9). A layer of TiN only 100 Å thick provides adequate protection against the diffusion of platinum into the titanium during a heat treatment for 30 min at 450 °C. The diffusivity of platinum in the barrier is evidently quite low. In terms of their combined high stability, good electrical conductivity and low diffusivities, nitrides, borides and carbides are attractive alternatives for thin film barrier design. The possibility of meeting several important conditions for thin film diffusion barriers simultaneously by means of these metal compounds seems to have been largely overlooked. They offer a promising field for further study. The resistivities of the borides, carbides, nitrides and silicides of the nine early transition metals are given in Tables I–III. Figure 10 gives the linear thermal expansion coefficients of magnesium, the transition metals, silicon and germanium, and of some silicides of the metals.

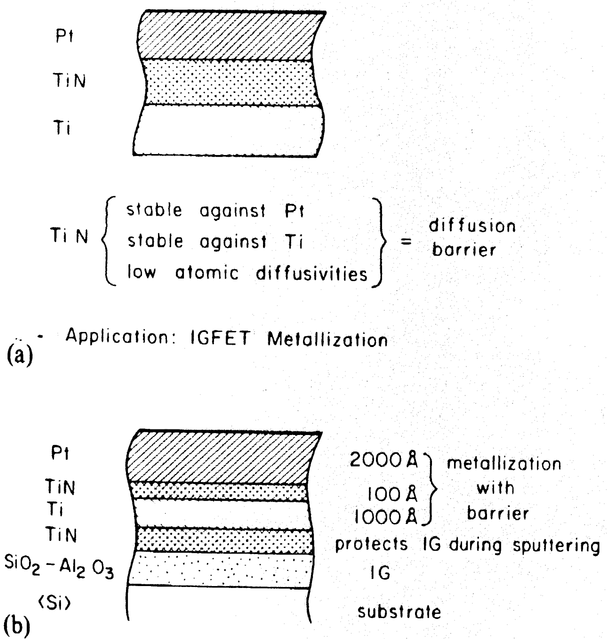


Fig. 9. (a) TiN is thermodynamically stable against titanium and also against platinum[36]. Its low diffusivities make it a good barrier for platinum and nickel. An application[37] to the gate metallization system of an IGFET is shown in (b).

Oxides are typically insulators. On this basis their value as diffusion barriers for electrical contacts is apparently nil. However, electrical current can pass through an insulator provided that the layer is thin enough and electrons can tunnel from one side of the insulator to the other. This is possible only for very thin barriers. Figure 11 shows the specific contact resistance expected for tunneling across a layer of SiO_2 of variable thickness with gold or aluminum contacts on either side. The calculations are based on the theory of Stratton[70]. Good ohmic contacts require values of specific contact resistance of the order of 10^{-6} Ω cm^2 or less. For the two cases considered, this condition requires thicknesses of less than 10 Å.

The question is whether such ultra-thin oxide layers will act as reliable diffusion barriers, even if the problems of pinholes, reproducibility and uniformity can be overcome. The question must be answered experimentally. For example, it

TABLE I

THE RESISTIVITY OF TITANIUM, VANADIUM AND CHROMIUM AND OF BORIDES, CARBIDES, NITRIDES AND SILICIDES OF THESE METALS

Titanium				*Vanadium*				*Chromium*			
	ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*
Ti	48.0		38	V	26.0		38	Cr	18.9		38
	55.0		39		26.0		39		15.3		39
	68.2		40		26.6		52		14.4		55
	48.0		41		26.6		53		18.9	Room temp.	56
TiB_2	14.4		38	VB_2	16.0		38	CrB_2	21.0		38
	14.1		39		16.0		39		≈25		39
	9.0	300 K	42		16.0		43		21.0		43
	15.0		43						84± 5		56
	20.0	25 °C	44	VB	35.0		47		21.0		47
	28.4		45		30.0		43	CrB	64.0		47
	15.2	Room temp.	46						69 ± 1	Room temp.	56
	15.0		47						64.0		43
TiB	40.0		47					Cr_2B	52 ± 2	Room temp.	56
	40.0		43								
TiC	52.5		38	VC	156?		38	Cr_3C_2	75.0		38
	59.5		39		156?		39				
	180.0		43		150		47				
	≈90	400 °C	48								
	90.0	Room temp.	46								
	180.0		47								
TiN	25.0		38	VN	85.0		38	Cr_2N	≈81		55
	85.5		39		85.9?		39		84 ± 5	Room temp.	56
	130.0		43		200.0		43				
	22.0	Room temp.	46		200.0		47	CrN	640 ± 40	Room temp.	56
	130.0		47						2500	270–295 K	57
									640 ± 40		55
$TiSi_2$	16.7	20 °C	49	VSi_2	13.3	20 °C	49	$CrSi_2$	1420.0	20 °C	49
	123.0		43		9.5		43, 47		200.0		43
	16.9		50		66.5		50		91.4		50
	123.0		51		66.5		52		1470.0		58
	19.9		41		64.0		51		≈500	300 K	59
	123.0		47		66.5		53		200.0	?	47
					66.5		41				
TiSi	39.3	20 °C	49								
				V_5Si_3	114.5		53				
Ti_5Si_3	350	20 °C	49		114.5		52				
				V_3Si	203.5		53				
					4.3	Low temp.	54				
					203.5		52				

The list is based on references in the data bank of the Electronic Properties Information Center (EPIC) of the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue University.

has been observed that layers of SiO_2 between 200 and 2000 Å thick, grown thermally on single-crystal silicon wafers, are permeable to gold[71]. When such oxide films are covered with dots of evaporated gold some 500 Å thick and are

TABLE II

THE RESISTIVITY OF ZIRCONIUM, NIOBIUM AND MOLYBDENUM AND OF BORIDES, CARBIDES, NITRIDES AND SILICIDES OF THESE METALS

Zirconium				*Niobium*				*Molybdenum*			
	ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*
Zr	41.0		38	Nb	16.0		38	Mo	5.2		38
	41.0		39		13.1		39		5.2		39
	63.4		40		14.6	298 K	61		5.2	Room temp.	46
					14.1	Room temp.	46				
ZrB_2	16.6		38	NbB_2	34.0		38	Mo_2B_5	25.0		38
	10.4		39		42.7		39		25.0		63
	7.0	300 K	42		32.0		43				
	9.0		43		32.0		47	MoB_2	45.0		63
	9–16	25 °C	44		32.0	25 °C	44		22.0		47
	38.8		45								
	9.2	Room temp.	46	NbB	64.0		47	MoB	45.0		39
	9.0		47		64.0		43		50.0		46
ZrB	30.0		43						45.0		63
									25.0		63
									50.0		47
								Mo_2B	40.0		63
ZrC	50.0		38	NbC	51.1		38	Mo_xC_y	133.0		39
	56.6		39		60.2		39				
	75.0		43		40.0	400 °C	48	Mo_2C	71.0		38
	≈60	400 °C	48		147.0		47		≈120	400 °C	48
	75.0		47						97.0		47
ZrN	21.1		38	NbN	60.0		38	MoN	1200 Ω kV^{-1} 1 μm layer		64
	13.6		39		200.0		39				
	14.0	Room temp.	46		200.0		43				
	56.0	1200 K	60		200.0	25 °C	62				
					200.0		47				
$ZrSi_2$	106.2	200 °C	49	$NbSi_2$	6.3		43	$MoSi_2$	26.4	25–160 °C	65
	161.0		43		50.4		50		21.8	20 °C	49
	75.8		50		6.3		58		21.6		50
	161.0		58		6.3		47		21.5		58
	161.0		47		52.0		51		≈21		66
ZrSi	49.4	20 °C	49						21.0		51
								MoSi	21.5		47
									21.5		43
								Mo_5Si_3	46.7		50
								Mo_3Si	21.6		50

The list is based on references in the data bank of the Electronic Properties Information Center (EPIC) of the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue University.

heated in the 500–700 °C temperature range for 4–36 h in a dynamic (continuously pumped) vacuum of about 10^{-6} Torr, a deterioration is observed at localized points on the gold dots and at their periphery. At these points gold seeps through the oxide and forms slowly spreading patches of Au–Si eutectic along the SiO_2–Si interface. The phenomenon does not occur in other atmospheres such as air,

TABLE III

THE RESISTIVITY OF HAFNIUM, TANTALUM AND TUNGSTEN AND OF BORIDES, CARBIDES, NITRIDES AND SILICIDES OF THESE METALS

Hafnium				*Tantalum*				*Tungsten*			
	ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*		ρ(μΩ cm)		*Ref.*
Hf	30.0		38	Ta	14.7		38	W	5.5		38
	30.0		39		12.4		39		5.03		39
					13.7	298 K	61		5.5		46
					13.5	Room temp.	46				
								W_2	81.0	Room temp.	40
				α-Ta	20.0		67				
				β-Ta	150.0		67				
HfB_2	12.0		38	TaB_2	37.4		38	W_xB_y	41.4		39
	12.0		39		41.4		39				
	15.0	300 K	42		68.0		43	W_2B_5	21.0		40
	10.0		43		68.0	25 C	44		43.0		38
	12.0	25 C	44		68.0	Room temp.	46				
	10.0		47		68.0		47				
				TaB	100.0		47				
					100.0		43				
HfC	109.0		38	TaC	42.1		38	W_xC_y	40.6		39
	109.0		43		40.6		39				
	≈60	400 C	48		30 170	298 K	61	WC	19.6		38
	109.0	Room temp.	46		≈60	400 C	48		54.0	Room temp.	46
	109.0		47		30.0	Room temp.	46				
								W_2C	≈70	400 C	48
									80.0		47
HfN	56.5	1200 K	60	Ta_4N_5	>800		67	W_xN_y	1650		39
				Ta_5N_6	≈500		67	WN	1900 Ω kV^{-1}		64
				TaN	200?		38				
					1650		39				
					≈250		68				
					245	298 K	61				
					≈400		69				
					135	25 C	62				
					≈250		67				
				Ta_2N	186		67				
					245	298 K	61				
					≈250		68				
				$TaSi_2$	38.0	20 C	49	WSi_2	38.2	20 C	49
					8.5		43		33.0		43
					46.1		50		33.4		58
					8.5		58		16.0		51
					8.5		47				
					41.0		51				

The list is based on references in the data bank of the Electronic Properties Information Center (EPIC) of the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue University.

helium or encapsulated vacuum, but it depends on the partial pressure of oxygen in the vacuum. The chemical reaction of gold with SiO_2 is not understood[72]. It is possible that films of other metals on ultra-thin SiO_2 layers are stable or that insulating layers other than SiO_2 may be useful as ultra-thin barriers. The stability of any such system has to be established by careful experiments; the outcome may depend on details of the fabrication techniques for the films.

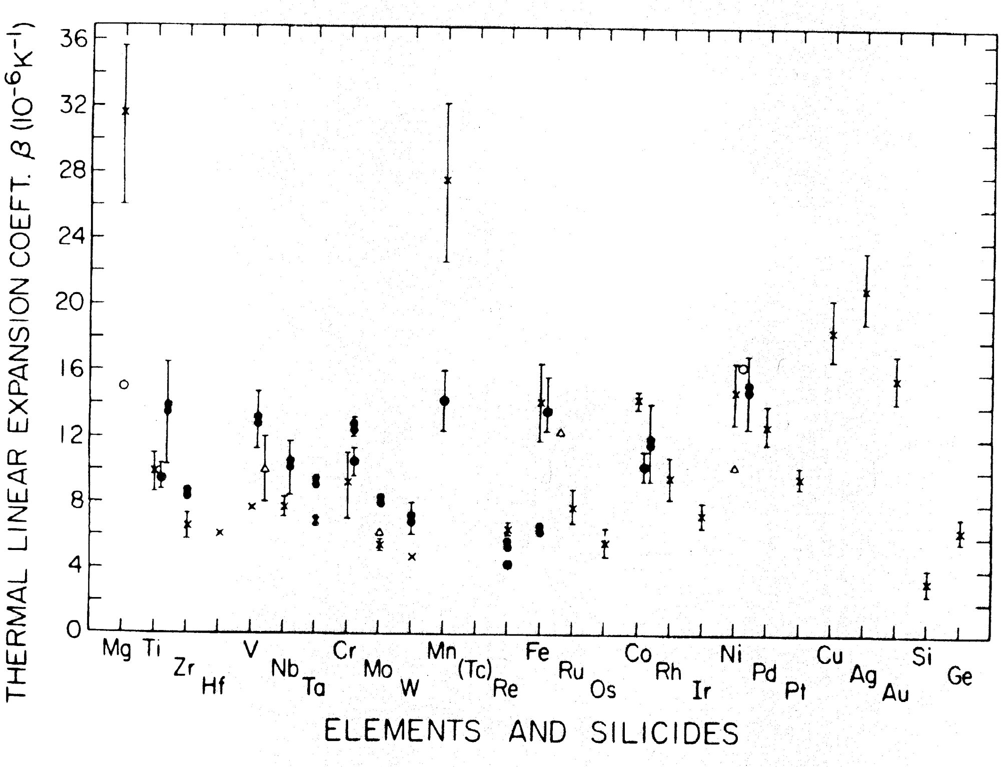


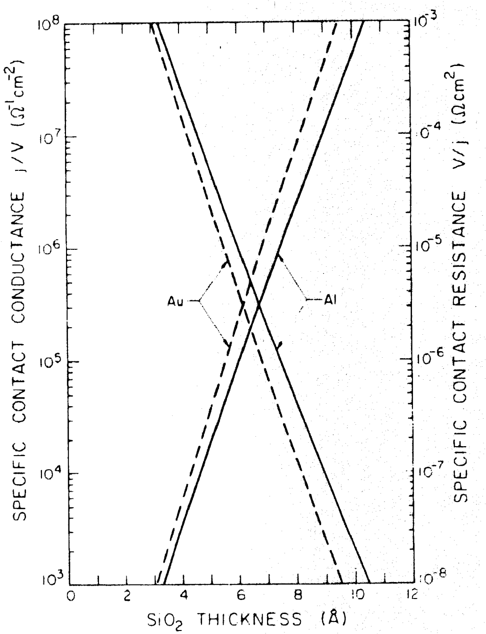
Fig. 10. The linear thermal expansion coefficient of magnesium, the transition metals, silicon and germanium and of some silicides of the metals: ×, M; △, M_3Si; ○, M_2Si; ●, MSi; ●●, MSi_2.

When electrical conduction across the barrier is not required, oxides offer attractive properties as diffusion barriers and are also used extensively for that purpose, as for example in multilayer metallizations of large-scale integrated circuits.

6. MULTILAYER SYSTEMS

The traditional engineering approach attempts to solve one difficulty at a time, rather than all of them at once. This thinking has dominated the practical solutions to diffusion barrier problems in the semiconductor industry. It is therefore no surprise that practical metallization schemes have a number of metal layers in which each layer is intended to serve some function. As an example, Fig. 12 shows the solid logic technology (SLT) used in the IBM 360 computer line to bond flip chips to the module substrate[73].

In this approach, the initial problem is the adhesion of the first metallization layer to the substrate. There is no serious adhesion problem with the silicon in the window of the field oxide, where electrical contact has to be made to the device. Many metals adhere well to silicon. However, the best electrical conductors (silver, copper, gold) do not stick to SiO_2 (Fig. 13(a)). The solution resorted to almost universally is first to apply a thin layer of "glue" for which titanium is the most popular choice (Fig. 13(b)). (The flip chip technology of Fig. 12 uses chromium instead.) The reason for the excellent adhesion of titanium to SiO_2 is that titanium has a negative heat of reaction with SiO_2 and breaks down SiO_2 to form titanium oxide. This explanation had been offered previously[36, 74]. Recent systematic experiments have confirmed it and have demonstrated that only the most reactive of the transition metals (*e.g.* titanium, zirconium, hafnium, vanadium, niobium) can be expected to adhere to SiO_2 on this basis[75].



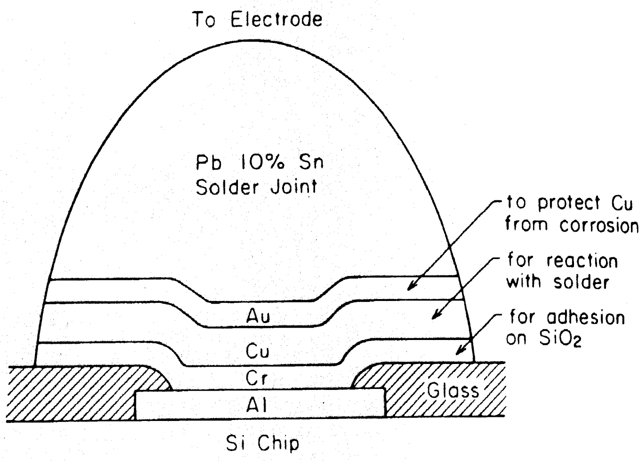


Fig. 11. Specific contact resistance and contact conductance for tunneling currents at low biases as a function of the thickness of the SiO_2 layer across which the electrons tunnel. The calculations are based on the theory of Stratton[70] assuming barrier heights of 4.1 eV for gold electrodes and 3.2 eV for aluminum electrodes on SiO_2. Other metals used for metallizations typically fall between these extremes. Good ohmic contacts require specific contact resistances of the order of 10^{-6} Ω cm² or less.

Fig. 12. The SLT used by IBM to bond flip chips to the module substrate. Each film is introduced to fulfil a specific function, as described[73].

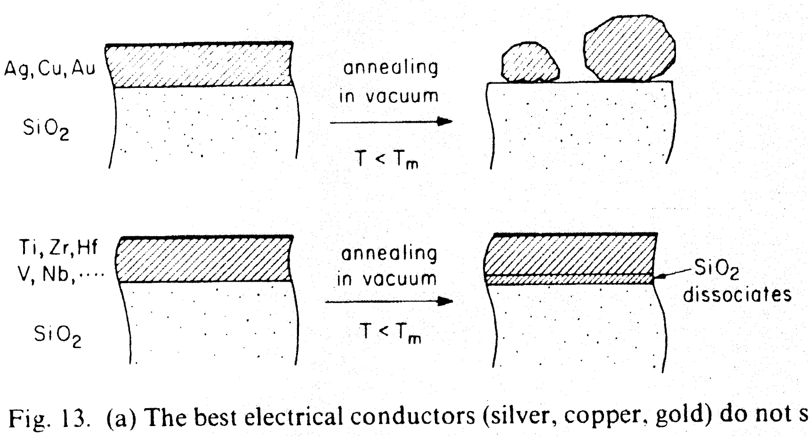


Fig. 13. (a) The best electrical conductors (silver, copper, gold) do not stick to SiO_2 and tend to ball up during a heat treatment even when the temperature never reaches the melting point T_m of the metal. (b) The early transition metals adhere very well to SiO_2 because they can dissociate the substrate and form a strong mechanical bond during a heat treatment in which external oxygen sources are absent (*e.g.* high vacuum)[36, 75].

The application of a "glue" solves the problem of adhesion but creates a new difficulty: the glue metal will also tend to react with the following layer of the metallization. If a gold film is deposited directly onto the titanium layer, the sheet resistivity of the thin film couple increases prohibitively in annealing tests and the corrosion resistance falls[33]. The engineering approach to the metallization problem thus leads unavoidably to the question of how thin film couples behave when the two metals involved can form compounds. This is the third of the three possible metal–metal combinations involving only solid phases (the other two being mutually immiscible metals and metals forming solid solutions*). It is therefore necessary to discuss the behavior of thin film couples of compound-forming metals.

6.1. *Compound-forming thin films*

Knowledge of reactions in compound-forming thin films has increased rapidly in recent years. This progress has been driven both by the advent of suitable analytical tools and by the critical importance of the subject in solid state device technology. We limit ourselves here to brief summaries of the major questions raised by thin film reactions in compound-forming binary systems. These questions are as follows.

(i) Which compounds form? The equilibrium state towards which two metal films must drive is given by the binary phase diagram of the two elements and the initial atomic ratio of the two films. How this state is reached is a kinetic question. The experimental fact is that some of the possible compounds never form in detectable amounts. For thin metal films on bulk silicon and germanium, Walser and Bené[76] have given a rule which specifies the compound which nucleates first at the metal–semiconductor interface. The rule is not infallible, but it has also been found to be correct in cases where the semiconductor is a thin film rather than a bulk wafer. Which other compounds (if any) will form later in the reaction is little understood.

(ii) When do compounds form? Here also there is a rule: they form at a temperature which is about one-third to one-half that of the lowest melting point in the binary phase diagram[77]. This rule resembles the rule which defines the temperature below which grain boundary diffusion dominates (Section 3). The two rules obviously have a common source.

(iii) How rapidly do compounds form? There are several answers.

(a) Square root of time growth ($\propto t^{1/2}$) is typical of a growth process which is limited by atomic transport across the newly formed compound layer. The dimetal silicides of nickel, palladium, platinum and cobalt, the monosilicides of nickel, platinum and cobalt, the germanides Pd_2Ge and PdGe and a number of metal compounds such as $TiAl_3$, VAl_3, Ag_2Al and CrPt all grow by this law.

(b) Linear growth with time ($\propto t$) is typical of a growth process which is limited by an interfacial reaction. The disilicides of vanadium, tungsten,

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*For the purpose of this discussion, metals with some limited solid solubility are considered as cases intermediate between these two.

chromium and molybdenum have been reported by some to grow in this way, but conflicting results have been obtained.

(c) The reaction rates are all thermally activated. Activation energies vary substantially but in an orderly way.

It is worth reflecting on point (b). The reproducibility of the results becomes doubtful when we are dealing with the early transition metals (titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten). These metals are among the most reactive ones. There is a strong possibility that traces of oxygen or nitrogen in the film deposition system or in the annealing ovens find their way into the films and affect the results. That oxygen does indeed affect the growth kinetics of reactive films has been observed and substantiated for VSi_2[78] and $Ti_xW_{1-x}Si_2$[34]. Wagner *et al.*[79] have investigated the reaction of vanadium films deposited and annealed under ultra-clean conditions. They found non-linear growth rates for VSi_2 which are higher than those reported earlier and appear to have a different activation energy. Furthermore, they observed that the reaction can be induced at temperatures as low as 440 °C. Vanadium films which are not prepared and annealed in ultrahigh vacuum will react much more slowly at these temperatures. That vanadium reacts at such low temperatures is consistent with the observation that the reaction rates are thermally activated. Such processes have no low temperature threshold. Impurities (such as hydrogen, oxygen, nitrogen, water vapor and CO_2) may well be the cause of the sluggishness of thin film reactions below the Tammann temperature. While the kinetics seem to be sensitive to impurities, the compound formed in the reaction is usually not affected.

Another factor which certainly influences thin film reactions is stress. The formation of the new compound is accompanied by volumetric changes. The resulting compound may have mechanical and thermal parameters which differ from those of either of the films. It is known, for example, that in the thermal oxidation of silver exposed to an oxidizing atmosphere the application of stress affects the oxidation rate. Such effects are to be expected in solid thin film reactions as well.

More is known about the structural aspects of solid film reactions. In general terms, reactions tend to have structural memory. A good example is provided by the behavior of a nickel film on a silicon substrate[80]. If this substrate is a polycrystalline or amorphous film of silicon, or a silicon single crystal of ⟨100⟩ orientation, the growth rate is about four times faster than on a ⟨111⟩ single-crystal substrate. The growth is always proportional to the square root of the time. This means that the transport-limited reaction varies with the conditions existing outside the layer. This surprising result is explained by structural differences in the nickel silicide. On a ⟨111⟩ substrate the average grain size of the compound is about twice as large as in the other cases[80]. Baglin *et al.*[81] describe another example where an increase in the grain size of one of the films (silver) leads to a decrease in the rate of growth of the compound (Ag_2Al). A different case is provided by the reaction of palladium films with silicon. The rate of growth of the Pd_2Si layer is the same on ⟨100⟩-, ⟨110⟩- and ⟨111⟩-oriented single-crystal wafers or on evaporated (amorphous) silicon films[82]; yet the structure of the resulting Pd_2Si film depends on the substrate. On ⟨111⟩-oriented single-crystal wafers the Pd_2Si is nearly epitaxial, but it is much less so in the other cases[83]. When two appropriately chosen metal films are deposited epitaxially onto each other, the compound obtained after reaction has a nearly single-crystalline structure, *e.g.* PtCr formed from platinum and chromium[84].

In summary, there are general trends, rules and patterns in solid film reactions. The details are complex, however. Our understanding of the subject is mainly phenomenological and fragmentary.

Most of the practical metallization schemes contain compound-forming thin film couples. (In the IBM SLT system shown in Fig. 12 the Al/Cr couple forms compounds.) The present understanding of reactions between thin solid metal films is not yet sufficient to establish logical schemes of selection and prediction. It was even less satisfactory years ago when metallization systems had to be developed to satisfy the needs of the industry. It is clear that under such conditions failures were inevitable, but there were also successes. These were studied and out of the studies a barrier concept evolved which seemed at first to side-step the issue, because the barriers were obviously not stable. In fact, it was easy to see that they would fail. Herein lay their usefulness.

DuMond and Youtz made their experiment a success by reformulating the problem. Restating the problem of the diffusion barrier similarly transforms compound formation by thin film couples into a successful basis for diffusion barriers.

6.2. *Compound-forming barriers* (*sacrificial barriers*)

To understand the concept of this type of barrier, we must first recognize that no barrier can fulfil its function forever. When two materials A and B are separated by X because A and B would intermix if X were removed, the barrier X only retards the point in time when A and B will eventually intermix. This ultimate state of equilibrium is not eliminated by X, it is only made less accessible. Once this fact is recognized, the real question becomes how long a barrier will serve its purpose. In all the cases discussed so far, the intention was that the presence of the material X would move the point of mixing far into an unspecified future (tens of years? hundreds of years?). In the case of the sacrificial barrier, the length of its useful life becomes predictable. To an extent, such a state of affairs is satisfying: the point of possible failure is foreseeable.

Figure 14 illustrates the concept of the sacrificial barrier. The metal X can react with both A and B. The thin film reactions with both A and B must be laterally uniform and must be fully characterized: the compounds formed, the rates of reactions and the activation energies must all be known. It then becomes straightforward to predict after how long at any given temperature the barrier X will be fully consumed. The behavior of the system beyond this point cannot be predicted from the simple assumptions made so far, but the conservative estimate is that the metallization system will fail catastrophically. For any prescribed time–temperature cycle, it is possible to determine the minimum amount of material required for X to prevent its total consumption. As long as this does not occur, a separation of A and B is, in fact, accomplished.

A successful application of this concept is demonstrated in Fig. 15[85]. When an aluminum layer is deposited on a film of polycrystalline silicon the resulting bilayer is inherently unstable. Even at 150 °C aluminum permeates the polysilicon and

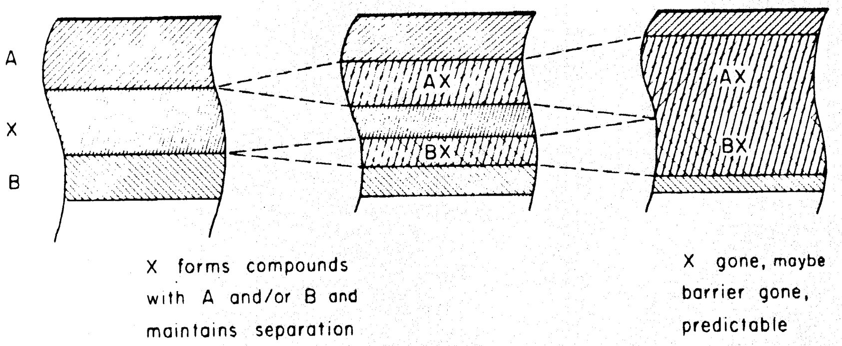

Fig. 14. If the reactions of the barrier layer X with A and B are each fully characterized and laterally uniform, the point at which the layer X has been fully consumed is predictable. As long as this point is not reached, a separation of A and B is in fact accomplished. For any prescribed time–temperature cycle there is a minimum thickness of X which will assure separation and this amount can be predicted.

modifies its doping. Aluminum and silicon do not form a compound and their eutectic temperature is relatively low (577 °C), so that grain boundary effects are expected to set in at about 100–200 °C. At higher annealing temperatures the thin film couple becomes structurally unstable (Fig. 15, top). This phenomenon is important because many MOSFETs are constructed in this way. The interpenetration of aluminum and silicon can be prevented by interposing a layer of titanium. At 450 °C titanium reacts negligibly with silicon but it forms $TiAl_3$ with aluminum. As long as some unreacted titanium remains, the contact retains its structural integrity (Fig. 15, center). If all the titanium is consumed, structural reordering reappears (Fig. 15, bottom). The rate at which the thickness Δx of the compound $TiAl_3$ increases with time t is known quantitatively ($\Delta x = (Dt)^{1/2}$, where $D = 1.5 \times 10^{15} \exp(-1.8\ \text{eV}/kT)\ \text{Å}^2\ \text{s}^{-1}$). For instance, at 450 °C a layer of 1250 Å of titanium is consumed in 1 h of annealing. To survive this test, a thicker titanium layer would be required. The same barrier effect would also be accomplished with vanadium[85]. Since aluminum reacts roughly 20 times slower with vanadium than with titanium, the same protective action is offered with 210 Å of vanadium.

Bower describes another application of the Ti–Al reaction in a sacrificial barrier[86]. There, the direct contact between an aluminum film and the bare silicon in a window of the field oxide is prevented by interposing a titanium layer. To our knowledge, this was the first description of the concept of the sacrificial barrier.

In the two previous examples, the barrier layer reacts with only one of the two adjacent metals. Olowolafe *et al.*[87] have recently described a sacrificial barrier application where the barrier metal (chromium) reacts on both sides, one being a palladium layer and the other an aluminum film.

The advantage of the sacrificial barrier is its adaptability. Many binary metal combinations form compounds, so that the choice of materials is wide and can take into consideration other constraints which are important for the proper functioning of the barrier. However, there is always a need to ascertain that the compounds formed in the reaction are compatible with those constraints. In the case of an electrical contact, for instance, it is imperative that the compounds be good conductors, but thermal and mechanical properties and corrosion resistance are other factors to consider. We have also assumed throughout that in the layer X itself the diffusion of A and B is slow enough to be negligible compared with the growth of the compound layers. All reacting materials may not fulfil this condition.

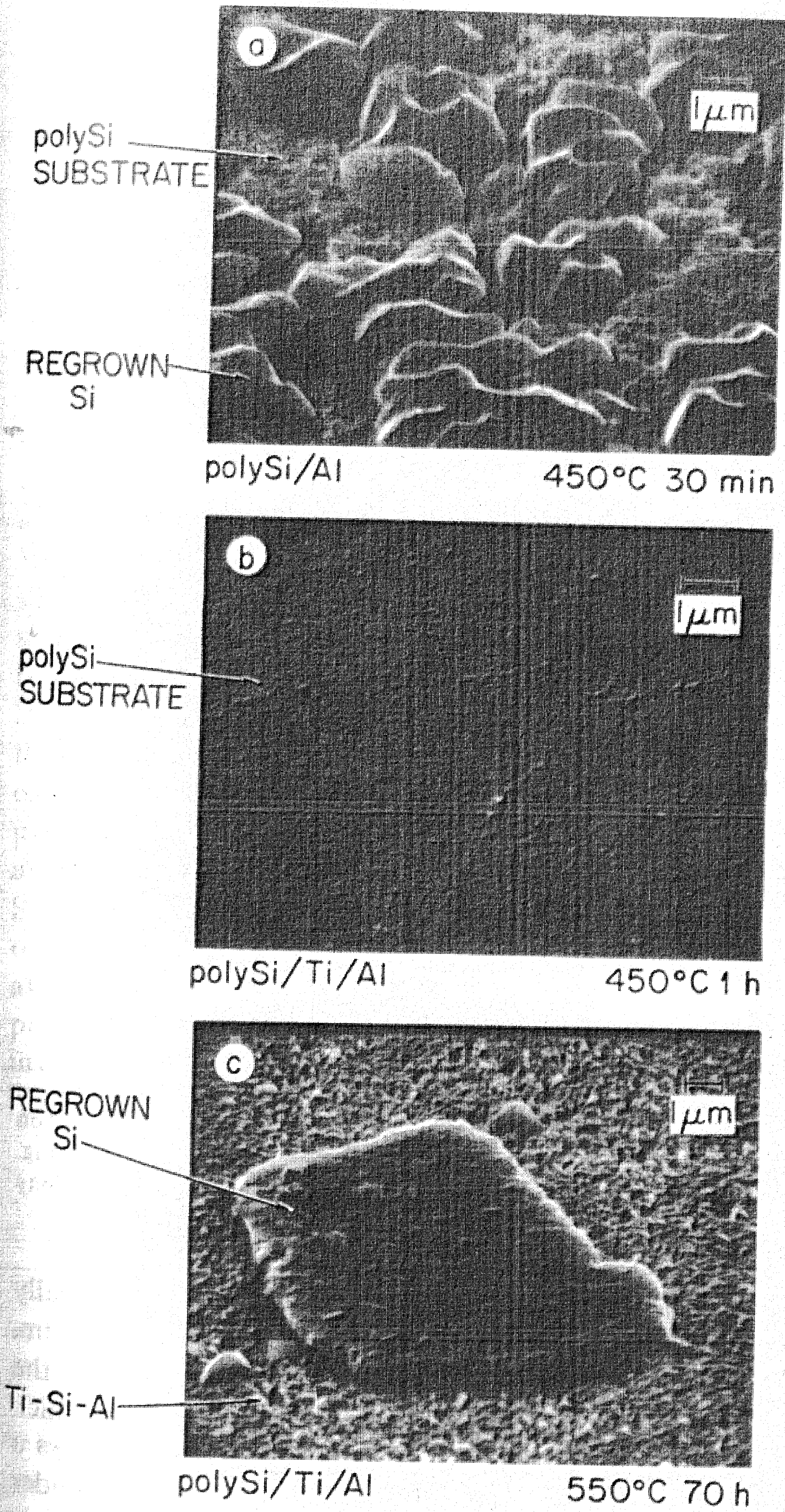

Fig. 15. When a polycrystalline silicon film is covered by an aluminum film the fine-grained polycrystalline silicon forms larger crystallites in the aluminum film upon annealing at 450 °C for 30 min. (a) The surface morphology of the silicon after the aluminum has been chemically etched away. A layer of vanadium interposed between the polysilicon and the aluminum film acts as a sacrificial barrier (which reacts only with the aluminum film) and suppresses the intermixing of silicon and aluminum. (b) The surface morphology of the polysilicon after annealing at 450 °C for 1 h and removing both the aluminum and the titanium layer chemically. (c) If the vanadium layer is fully consumed, the barrier action breaks down; this figure was obtained by the same procedure as (b) (from ref. 85).

7. EFFECT OF IMPURITIES

The effect of impurities on diffusion barriers is a subject of major significance. The subject is treated last because it is understood least. Evidence is mounting which suggests that some barriers actually work by virtue of the impurities they contain.

7.1. *Stuffed barriers*

Some immiscible layers do not act as barriers because of the rapid diffusion along grain boundaries and other structural defects (see Section 4). An obvious stratagem is to try to plug the easy paths with appropriate atoms or molecules ("stuffing" the barrier, see Fig. 16). There is evidence indicating that this can indeed occur. The interpretation of these observations in terms of atomistic mechanisms is largely conjectural, but the resulting effects are striking.

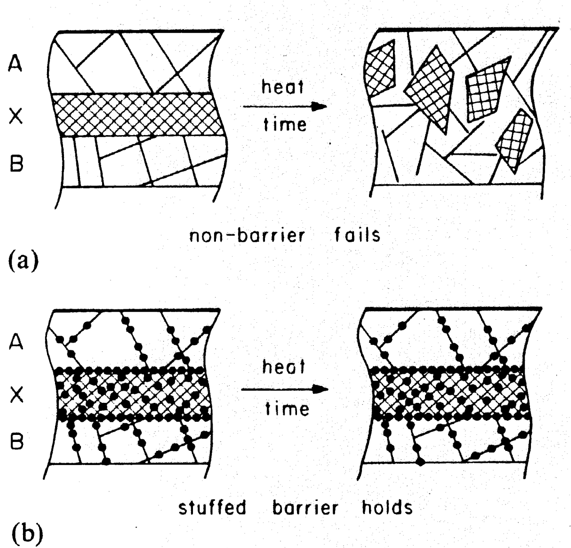

Fig. 16. (a) A non-barrier X of a metal which has no mutual solid solubility with the metals A and B on either side fails because of the extended structural defects which act as fast diffusion paths (see also Fig. 2). (b) When these paths are plugged by suitable impurities, the stuffed barrier can successfully withstand the heat treatment.

In Section 4.1 it is stated that molybdenum and gold, which are mutually insoluble, nevertheless intermix because of structural defects in the film. Molybdenum cannot therefore prevent the diffusion of gold across it, but the Ti/Mo/Au triple layer constitutes a widely applied metallization scheme which seems to work well. On closer scrutiny it appears, however, that oxygen plays a major role in this system[16]. When titanium and molybdenum are deposited under good high vacuum conditions, the two metals readily intermix by grain boundary diffusion. When gold is added on top of the molybdenum film, we find that gold and titanium readily combine at 600 °C across the virtually unperturbed molybdenum layer. However, if the titanium is exposed to oxygen before the molybdenum layer is deposited, intermixing between titanium and molybdenum is not observed. The implication is that the Ti/Mo/Au barrier system may owe its blocking capacity to the presence of oxygen. How interpenetration across the molybdenum layer is stopped is unclear, but it is certain that with pure layers of titanium and molybdenum the barrier will not work. Realizing this problem, Nowicki and Wang[88] have deposited the molybdenum film by reactive r.f. sputtering and controlled incorporation of nitrogen. The barrier properties are thereby significantly improved. Reactive r.f. sputtering is clearly one possible method of stuffing a barrier. In the present case, nitrogen may possibly be incorporated in such large amounts as to form an MoN compound. It has been shown by Nowicki *et al.*[89] that nearly stoichiometric Mo_2N can form during sputtering in residual pressures of 10^{-5} Torr. Shoji had suggested this earlier[90]. The distinction between a stuffed barrier and a compound barrier is not a sharp one.

A well-documented case is that of a platinum film on a silicon single-crystal substrate[91]. During annealing at 600 °C in an inert atmosphere such as nitrogen, the whole platinum film is transformed into PtSi (Fig. 17(a)). In an oxygen atmosphere the reaction comes to a halt about 500 Å below the surface (Fig. 17(b)). What happens is that oxygen permeates the platinum layer and reacts with the silicon. A uniform layer of SiO_2, possibly containing PtSi as well, is formed and stops the reaction. It can easily be shown that this layer does not result from a reduction of PtSi after all the platinum has reacted to form PtSi: the fully reacted layer only develops a surface oxide when exposed to oxygen (Fig. 17(a)). The very thin platinum layer which remains as the reaction in oxygen approaches completion evidently becomes permeable to oxygen, so much so that it actually promotes the formation of SiO_2 until all diffusion paths for platinum and silicon are blocked by SiO_2 in the interface. This effect is most important in practice. The SiO_2 layer protects the PtSi below from attack by chemical etchants, and this is one of the desirable properties which has led to the widespread application of PtSi as a primary contacting material. A better understanding of the process could be profitable in pointing out ways by which the same desirable effect could be induced in other metal silicides.

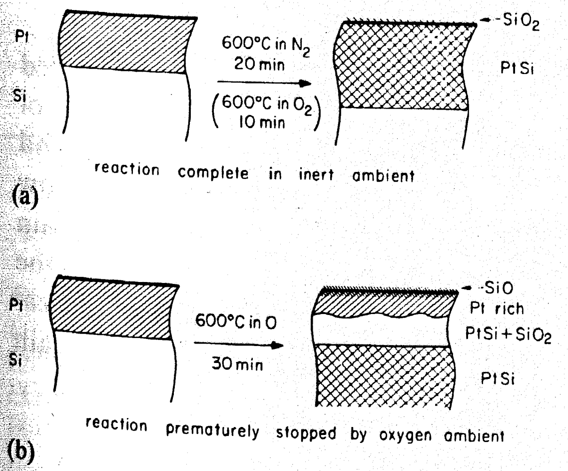

Fig. 17. (a) A film of platinum on a silicon substrate reacts completely to form PtSi upon heat treatment at 600 °C for 20 min in an inert atmosphere. (b) In an oxidizing atmosphere the reaction stops about 500 Å short of completion because an SiO_2 layer develops. The unreacted platinum does not form by reduction of completely reacted PtSi in a second annealing step at 600 °C for 10 min in O_2, *i.e.* permeation of the platinum by oxygen is responsible for the premature termination of the reaction in (b).

Stuffed barriers may be present more often than is recognized. For instance, it has been observed that in a Ti/Rh/Au trilayer gold diffuses into the rhodium and reaches concentrations of 3–4 at.% even at room temperature[20]. Gold and rhodium are immiscible in the solid phase, so the result is as expected. When the layer sequence is Ti/Au/Rh, however, and rhodium is the exposed surface, no room temperature diffusion of gold into the rhodium film is observed. Such an effect could be due to the permeation of rhodium by undetected contaminants. A similar observation relates to Ti/Pd thin film couples in which palladium is at the surface[92]. When annealed at 390 °C in vacuum for 2 h, the layers form a compound (probably $TiPd_3$). The same annealing treatment in air produces very little change, save for the appearance of oxygen close to the Ti–Pd interface. Oxygen apparently permeates the palladium film and blocks further diffusion. Rhodium and palladium are neighboring elements in the periodic table and palladium is well known for its permeability to hydrogen.

Very recently, Revitz and Totta[93] have described a technique for producing Ta/Au/Ta trilayers which implements the idea of a stuffed barrier explicitly. The trilayer is used as a metallization on silicon chips. The deposition of the bottom layer of tantalum is interrupted after half the film has been laid down and the film is exposed to air at 150 °C to form a very thin oxide layer. This treatment suppresses all risk of an Au–Si eutectic formation across the tantalum layer during subsequent annealing at places where the trilayer is in direct contact with silicon. In this example, the bottom tantalum layer is purposely contaminated to achieve the desired barrier effect between gold and silicon. The contact resistance of the trilayer is not perceptibly altered by the oxidation.

In the related situation of tungsten films on bare silicon, Chang and Quintana[94] found a uniform layer of tungsten silicide after annealing the sample, as expected for a silicide-forming metal. However, a thin layer of native oxide on the silicon is enough to change the reaction to a grain-boundary-dominated, rapid and laterally non-uniform permeation of the tungsten film by silicon. The interface oxide decreases the rate of silicide formation but not the out-diffusion of silicon along grain boundaries.

Electromigration is one of the effects related to the concept of the stuffed barrier. This effect also depends on grain boundary diffusion. Small additions of copper to aluminum or of tantalum to gold reduce electromigration damage and lengthen barrier lifetimes. The improvement is due to the fact that at low temperatures tantalum, for example, segregates very strongly at the grain boundaries of the gold[95]. We suspect that, by related effects and causes, the characteristics of stuffed barriers could be altered by the application of an electrical current, or that electrical currents could induce the preferential population of grain boundaries and stuff a barrier. These ideas seem worth pursuing.

7.2. *Concluding comments*

It was stated in connection with the structural defects of a thin film that the procedures applied in the fabrication process can be a critical factor in the success or failure of a barrier. That comment applies equally to impurities which may be incorporated into a film during its deposition or subsequent processing. There is a significant practical consequence which follows from this observation. Imagine that a titanium layer is deposited in a sputtering system whose vacuum is not particularly good. Imagine further that the next metallization step is the deposition of a film of platinum or gold. It could be that the result is an acceptable metallization system, because the residual nitrogen or oxygen provides the reactive ambient necessary to create a titanium nitride or oxynitride layer between the two metallization steps. Improving the cleanliness of the titanium deposition would then reduce the effectiveness of the barrier[96]. The practical message is that processes used in the construction of a successful barrier should not be modified before the mechanism of operation of that barrier is clearly established and before it can be decided whether the proposed change will assist or hinder the process.

ACKNOWLEDGMENTS

I am indebted to R. S. Nowicki for assistance in the preparation of this paper. W. N. Cheung (Caltech) assembled the material reported in Fig. 10. Dr. D. Gupta (IBM) and Dr. A. K. Sinha (Bell Laboratories) offered criticism, and J. W. Mayer gave encouragement. Tables I–III owe their existence to J. N. Zemel's gentle prodding. The work was supported financially by the Office of Naval Research (L. R. Cooper).

This help and support are thankfully acknowledged.

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