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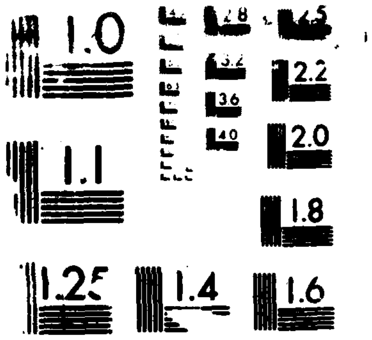

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THIN-FILM DIFFUSION BARRIERS
FOR
METAL-SEMICONDUCTOR CONTACTS

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ABSTRACT

The notion of a diffusion barrier is discussed as it applies to thin films, and to metal/semiconductor contacts in particular. The electrical requirements on the barrier material are easily met; those of the thermodynamic stability of the barrier and of the low atomic diffusivity in the barrier are not. The critical influence of the deposition process on the latter property is pointed out. Several different ways to solve the problem are discussed by examples.

INTRODUCTION

To impart stability to a metal-semiconductor contact by inserting a kinetic barrier in the form of a thin film is difficult, because the barrier layer has to be limited to a thickness of the order of 100 nm or less. The time required to penetrate through a given thickness by a diffusion process scales with the square of the thickness. A 1 mm thick diffusion barrier that will fail after 10 years does so already after 3 sec when reduced to 100 nm. Very low atomic diffusivities are thus essential for thin-film diffusion barriers. In addition, a thin-film diffusion barrier must also meet conditions that are imposed on its physical and chemical characteristics by virtue of its function in the contact and on a chip, as well as by practical requirements of manufacturing. Compromises are therefore unavoidable. To find acceptable ones requires an appreciation of the issues and trade-offs involved.

This paper considers briefly some of these questions. For comprehensive treatments and references, the reader is referred to recent reviews [1-3].

A diffusion barrier does not eliminate the thermodynamic instability of a metal-semiconductor combination. A diffusion barrier is a "kinetic barrier", that is, it retards the rate of progression of a degradation process and thereby provides stability which is necessarily only temporary. Whether a diffusion barrier should be included in the design of a device is an economic issue. This paper concerns itself only with the technical aspects of thin-film barriers.

CONCEPTS

An electrical contact to a semiconductor must fulfill two major conditions: (i) It must satisfy a prescribed electrical characteristic, and (ii) this characteristic must be stable in time. In the implementation of Fig. 1, both these conditions must be met by the same layer X. Although the scheme is simple, it is easier by far to find acceptable solutions to both requirements by solving each condition separately.

This engineering approach naturally leads to the generic contact scheme shown in Fig. 2. The contacting layer determines the electrical characteristics of the contact (ohmic or rectifying). The material of this layer is selected to realize a prescribed electrical interface with the semiconductor that satisfies the requirements imposed on the contact by device considerations. In addition, this contacting layer/semiconductor

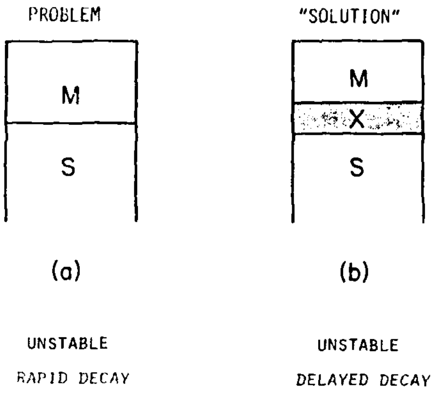

Fig.1 A thin-film diffusion barrier has a typical thickness of 100 nm or less. It does not remove an existing instability but only retards its rate of progression. When the layer X is in immediate contact with the semiconductor, X must satisfy electronic requirements at the barrier/semiconductor interface, as well as requirements imposed on its structure to fulfill its role as a diffusion barrier.

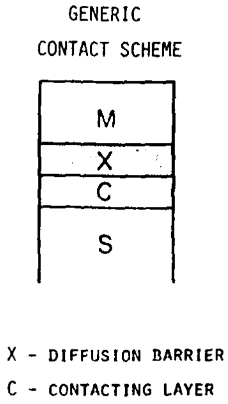

Fig.2 In this generic scheme of an electric contact, the diffusion barrier layer X serves to minimize the atomic interaction between the metal layer M above the barrier and the structure below it. The contacting layer C optimized the electrical characteristics of the contacting layer/semiconductor interface (ohmic or rectifying).

configuration has to be able also to sustain subsequent processing steps without significant degradation. In silicon VLSI circuits, this contacting layer is typically made of a transition metal silicide. For GaAs and other III-V compounds, satisfactory contacting layers are presently lacking; to find some is the subject of ongoing searches. The thin-film diffusion barrier minimizes the interaction between the metallic overlayer and the contact configuration below. Ideally, the diffusion barrier is electronically transparent and atomically opaque. Conceivably, a good thin-film diffusion barrier can serve well on devices involving different semiconductors and metal overlayers. Contacting layers, in contrast, are semiconductor-specific.

"Electrically transparent" means that the voltage drop across the barrier layer should be negligibly small. Assuming a current flow of 10E6 A/cm^2 perpendicularly to the plane of a 100 nm film, and an acceptable voltage drop of 25 mV (=kT/q), resistivities on the order of 1 mOhm-cm or less are sufficient to qualify a material electrically. This condition is met by many substances, and includes heavily doped semiconductors, amorphous metallic alloys, and conducting oxides. To meet the electrical requirement of a diffusion barrier is thus easy; even poor electrical conductors are admissible for this purpose.

To appreciate when and how atoms diffuse through solid films is essential to the design of effective thin-film diffusion barriers. There are many possible diffusion mechanisms in solids. Their relationship to atomic diffusion in thin films is depicted schematically in Fig. 3. At high temperatures, diffusion mechanisms through the bulk of the material dominate. At low temperatures, diffusion along extended defects of the material (such as grain boundaries or dislocations) is faster than through the bulk. The activation energy for these processes typically scales with the melting point of the element [4]. The temperature of transistion from bulk to defect mechanisms depends on the density of these extended defects, and lies typically near half the absolute melting point for polycrystalline materials. More important than the actual location of this transistion point is the recognition that if defects determine the diffusivity, the diffusivity becomes a function of the manner in which the film is deposited, because it is the deposition process that determines the defect structure of a film. In working with and discussing thin-film diffusion barriers, it is therefore essential to pay as much attention to the methods of film deposition as to the choice of the material.

IMPLEMENTATIONS

Stuffed Barrier

How important the deposition method is in determining the performance of a thin-film barrier was demonstrated by an experiment with a Ti-W film deposited between a Si substrate and a Au overlayer by rf sputtering with argon [5]. Two depositions were made in which all sample processing steps were identical, except for the reduced base pressure achieved in one case over the other by a longer pump-down period before back-filling with argon (see Fig.4). A subsequent thermal annealing of the two samples under an SEM microscope revealed that the barrier deposited with the lower base pressure (samples shown on the left side of the frames in Fig. 4) failed to prevent Au-Si intermixing at temperatures at which the other sample showed no signs of degradation. An AES analysis indicated that the good barrier contained about 5 at.% oxygen impurity and the poor one only 2 at.%. The better performance of the good barrier may thus have had its origin in the elevated content of oxygen (although other impurities - not monitored in the experiment - may have been at cause as well).

If one assumes that a polycrystalline material consists of cubic grains

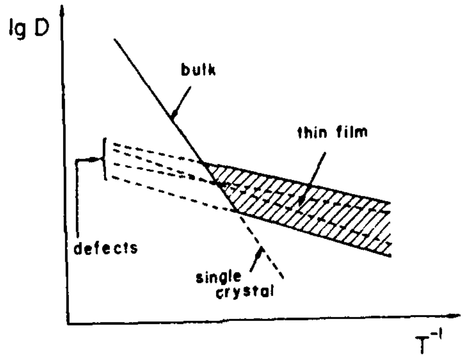

Fig.3 Typical dependence of atomic diffusivity in a solid as a function of reciprocal absolute temperature. At elevated temperatures, bulk processes dominate. At low temperatures, diffusion is primarily along extended defects. Their number and nature depend on the deposition process of the film. Diffusivity in thin films at low temperatures thus is a process-dependent quantity.

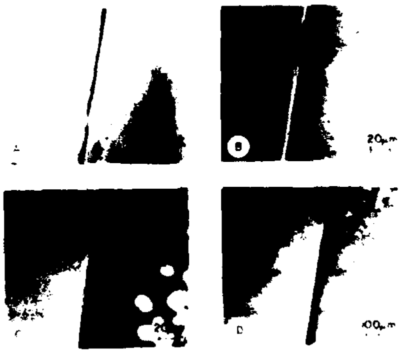

Fig.4 The notion of a stuffed diffusion barrier explains why seemingly small variations in a thin-film deposition process can lead to major differences in behavior (from [5]).

50 nm on edge, it takes only 1.6 at.% of impurity atoms to completely decorate all grain boundaries. A full decoration may not be necessary to impede the transport of atoms along fast diffusion paths, and there may not be as many extended defects to plug as this simple geometric model assumes. The main point of the argument is that a total of less than 1 at.% of impurities may have a big effect on the atomic diffusivities of thin films.

A number of experiments performed on films deposited in UHV systems with and without intentionally added impurities suggests that thin films of elemental metals are poor diffusion barriers when they are pure, because fast diffusion paths will promote rapid interdiffusion. With impurities, however, the same elemental film may serve well. Films whose good diffusion barrier performance depends on the presence of minor foreign constituents have been referred to as "stuffed barriers" to indicate that their effectiveness rests on impurities. Stuffed barriers are valid solutions to the thin-film diffusion barrier problem. The danger lies in not recognizing that a barrier is of this type.

Tungsten seems to be an exception to the rule that pure elemental thin films are poor diffusion barriers. How little impurity is needed to alter the diffusivities along fast diffusion paths is not normally known. Tungsten may be particularly sensitive in this respect. To clarify this issue, in general, requires careful experiments in UHV systems with ultra-pure metallic charges and an accurate tracing of impurities. Conclusive experimental evidence that a solute segregates along defects and alters diffusivities there has so far been obtained only in a few instances [4]. Until such experiments are carried out for W, the reason for its good diffusion barrier properties remains uncertain.

The notion of the stuffed barrier is a useful concept that explains experimental observations simply, but one should be aware that it has yet to be validated in most instances by direct experimental proofs relating cause and effect.

Refractory Compound Barriers

The only alternative to elemental films is that of compounds and alloys. These materials are usually polycrystalline as well, so that fast diffusion paths exist there also. What is new here is that compounds can have very high melting points. Since the activation energy for diffusion along extended defects tends to scale with the melting point, polycrystalline materials with a high melting point are advantageous for diffusion barrier applications.

Interstitial alloys form a group of refractory compounds that have shown much promise as thin-film diffusion barriers. They are binary alloys of the early transistion metals (Ti, V, and Cr goups) with the metalloids B, C, and P [6,7], they are metallic in character and have extremely elevated melting points. They must therefore be synthesized as part of the deposition process. Deposition by chemical vapors and reactive sputtering are the most common methods.

TiN has been studied most for thin-film diffusion barrier applications. Its commercial use in electrical contacts goes back to the beam-lead technology of the 60's, but interest in its systematic investigation and application is of recent date. Successful applications have been reported in III-V solid-state injection lasers, GaAs microwave devices, and Si-based semiconductor devices and VLSI circuits (see Fig. 5). TiN also forms upon thermal annealing of Ti films in a nitrogen ambiant if oxygen is absent. This fact is exploited in combination with rapid thermal annealing to simultaneously form a self-aligned $TiSi_2$ contacting layer to a shallow junction in a contact opening, and a TiN layer above it as a diffusion barrier [9]. Over the field oxide, a conducting layer (of a general composition Tin_xO_y) forms that is subsequently removed, or that can serve as

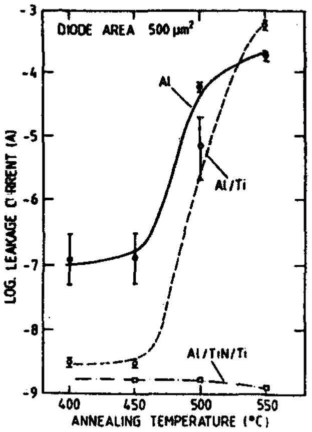

Fig.5 A successful application of the reactively sputtered refractory compound TiN as a thin-film diffusion barrier (from [8]). The figure shows the leakage current of a reverse biased Si n^+p junction with Al/Si, Al/Ti/Si and Al/TiN/Ti/Si contact systems as a function of the temperature of an annealing treatment in flowing argon for 15 min.

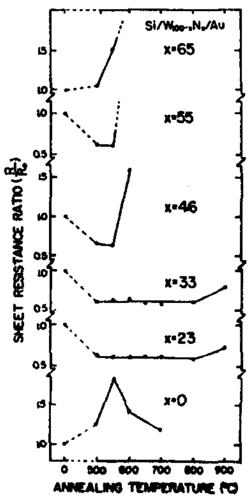

Fig.6 A successful application of the amorphous alloy $W_{100-x}N_x$ as a thin-film diffusion barrier between a Au overlayer and a Si substrate (from [11]).

a local interconnection. On Si with an Al overlayer, a TiN barrier of about 100 nm can prevent degradation upto about 500 °C for 30 min annealing.

The TiN/Al system is thermally unstable; the dominant failure mode is a locally triggered reaction. One difficulty of TiN films that are reactively sputtered in a argon/nitrogen gas mixture is the large compressive stress (on the order of GPa). Kanamori has recently reviewed the properties of TiN thin films for diffusion barrier applications [10]. Solute atoms and/or non-stoichiometric composition can of course lead to segregation along grain boundaries as well; the distinction between compound barriers and stuffed barriers may then be difficult to make.

Amorphous Alloy Barriers

Amorphous metallic alloys are attractive as diffusion barriers because they have no extended structural defects of the kind that produce fast diffusion paths in cyrstalline materials. (Recent research indicates, however, that not all amorphous materials have necessarily low atomic diffusivities.) Amorphous materials are also metastable. This is not a serious obstacle; some amorphous metallic alloys are known to crystallize above 600 to 800°C. One difficulty is that amourphous alloys tend to react, so that it is important to minimize their reactivity.

Pure metals are not amorphous at room temperature. Amorphous metallic alloys are therefore necessarily multi-elemental. One class of amorphous metallic alloys combines two transistion metals. Because near-noble transistion metals react readily at fairly low temperatures with Si, binary alloys that do not contain these metals are preferable for contacts to Si devices [11]. Another class of amorphous metallic binaries combines transistion metals with metalloids (B,C,P,Si). Current research suggests that some of these alloys have promising properties for diffusion barrier applications.

An example is N-W which, in its crystalline form, is an interstitial compound. In the composition range of 10 to 30 at.% N, reactive sputtering produces the amorphous phase [12]. Such a film, about 100 nm thick, has prevented metallurgical interactions between a Au overlayer and a Si substrate above 700 °C annealing for 30 min (see Fig.6). The Au-Si eutectic temperature is 360 °C. A highly pinhole-free film is required to endure this treatment.

CONCLUSION

As this sketchy review indicates, the subject of thin-film diffusion barriers for metal-semiconductor contacts combines structural, chemical and electronic aspects of materials. When the two basic requirements of a contact, meaning its electrical characteristics and its thermal stability are met by two distinct layers, as shown in Fig. 2, the constraints on the electrical resistivity of the diffusion barrier material are weak. This opens the way to many possible choices of materials, including doped semiconductors, metallic alloys, and conducting oxides in crystalline or amorphous forms. Only few have been investigated so far.

A thorough experimental investigation of any particular system is a demanding undertaking that normally has to include details of the film deposition process. These particularities of the subject make it likely that continued good progress can be expected from investigations of new materials and/or deposition techniques inspired by ideas and concepts outlined in this paper. The clear understanding of these concepts on a fundamental level will advance at a moderate pace only. Progress there requires carefully planned experiments, executed with the advanced tools of thin-film synthesis and analysis that modern materials research now has, and dedicated financial backing.

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