AMORPHOUS METALLIZATIONS FOR HIGH-TEMPERATURE SEMICONDUCTOR DEVICE APPLICATIONS

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Abstract – In this paper we present the initial results of work on a new class of semiconductor metallizations which appear to hold great promise as primary metallizations and diffusion barriers for high-temperature device applications. These metallizations consist of sputter-deposited films of high-T_g amorphous-metal alloys which (primarily because of the absence of grain boundaries) exhibit exceptionally good corrosion-resistance and low diffusion coefficients. Amorphous films of the alloys Ni-Nb, Ni-Mo, W-Si, and Mo-Si have been deposited on Si, GaAs, GaP, and various insulating substrates. The films adhere extremely well to the substrates and remain amorphous during thermal cycling to at least 500°C. Rutherford Backscattering (RBS) and Auger Electron Spectroscopy (AES) measurements indicate atomic diffussivities in the 10^{-19} cm^2/S range at 450°C.

INTRODUCTION

One of the most difficult problems associated with the design of semiconductor devices intended for high-temperature operation is that of finding a suitable metallization system for providing contacts to the semiconductor. Typical difficulties which limit the lifetime of semiconductor devices at high temperature include: (1) altered electrical behavior caused by inter-diffusion of metal and semiconductor; (2) dimensional changes or embrittlement caused by compound formation, or grain-growth; and (3) catastrophic metallization failure due to electromigration. These must be considered as *intrinsic* failure modes in the sense that, while they may vary in absolute and relative importance from one system to another, they must always be present to some extent. Furthermore, all of these failure modes involve diffusive transport within and/or among the metal and semiconductor layers, and increase roughly exponentially with increasing temperature. The design of high-temperature metallizations, therefore, necessarily involves a search for means to impede atomic diffusion within the metal-semiconductor system. The most common approach to the problem of limiting diffusion between dissimilar materials involves the use of intervening metallization layers which are intended to act as diffusion barriers. A well-known example is provided by the Ti-Pt-Au metallization which is used in the "Beam-Lead" technology [1,2]. This metallization (on Si) has survived brief stress-tests at over 400°C, but degrades rapidly at all temperatures above 350°C [2]. Similar results are obtained with many other diffusion barriers [3]. The reason for the failure of conventional passive diffusion barriers is simple, but has only recently become well-recognized: Diffusive transport in polycrystalline thin-films is dominated by diffusion along grain boundaries and dislocations at all realistic operating temperatures [4]. The barrier layer cannot be fully effective if it is, itself, a thin, polycrystalline film. Nicolet has recently given a comprehensive review of thin-film diffusion barriers [3], in which the importance of grain-boundary diffusion is highlighted. In addition to reviewing the shortcomings of traditional diffusion barriers, Nicolet discusses more sophisticated concepts including "stuffed barriers" (in which the grain boundary paths are blocked by suitable impurities) and "thermodynamically stable" barriers (which utilize stoichiometric compound barriers such as transition metal nitrides or borides). In the present paper, we present an alternative approach to the design of high-temperature metallizations. We propose the use of sputtered *amorphous* metal films, either as primary metallizations, or as thin diffusion-barrier layers between conventional polycrystalline films.

Amorphous metallizations are easily produced by sputtering from various transition-metal and transition-metal/metalloid alloys. As noted above, most of the inherent reliability problems of conventional metallizations are associated with polycrystallinity and atomic motion. In amorphous metals, there are no grain boundaries or dislocations, and diffusive transport is thus determined by bulk diffusion coefficients [5,6]. As a consequence, diffusive transport in amorphous metal films can be orders of magnitude slower than in polycrystalline films of comparable composition. It is primarily for this reason that we believe amorphous metal films constitute an interesting new class of materials for semiconductor metallization applications.

EXPERIMENTAL

Materials Selection

If amorphous films are to be useful in the proposed applications, it is necessary that they remain amorphous at the desired operating temperatures. Typically, the time constant for crystallization is of the order of ≤ 1 hour at the glass transition temperature, T_g, and extrapolates to several years at $T \leq 0.85\ T_g$ [5,6]. We have therefore focused on alloys having known or predicted T_g values of ≥ 500°C. Donald and Davies [7] have discussed various factors which promote glass-forming ability and high T_g values, and have published several useful tables of known glass-forming compositions. After consideration of the factors discussed by these authors, we selected the Ni-Nb, Ni-Mo, Mo-Si, and W-Si systems for investigation. A full discussion of our selection criteria has been given elsewhere [8].

The substrate requirements for successful vapor deposition of amorphous metals are easily satisfied by almost any crystalline or amorphous solid. The main requirement is that the substrate surface remain at a temperature well below T_g during deposition. This, in turn, requires that the substrate have a thermal conductivity adequate for rapid transfer of the heat-of-condensation to a heat sink. The fact that amorphous metals have been deposited successfully on such notably poor thermal conductors as pyrex ($\sigma \sim 0.01$ watts/cm°K) leaves little doubt that all common semiconductors ($\sigma \geq 0.1$ watts/cm°K) will provide adequate heat-sinking and be useable as substrates. Most of the work reported here was done using single-crystal Si substrates, although fully amorphous films have also been obtained on GaAs, GaP, Al$_2$O$_3$, glass, mica, Cu, and Al substrates.

Film Preparation

Amorphous metal films were deposited by RF sputtering using a Varian 980 diffusion-pumped sputtering system. This system uses a split circular cathode, 9" in diameter, with a 3 1/2" cathode-to-substrate spacing. In order to sputter alloys of uniform composition, 1/4" thick base cathodes of either Ni or Si were partially covered by 10 mil foil masks of Nb, Mo, or W, having uniform distributions of holes to expose an appropriate fraction of the base cathode. In initial work, the exposed areas of base-cathode and foil were approximately equal. For each of the four alloy-systems studied, the area ratios were subsequently ad-

justed to achieve the desired film composition using feedback from annealing studies and electron-beam microprobe measurements.

Sputtering was done using $\gtrsim 2 \times 10^{-4}$ Torr Ar pressure at a total RF power of $\leq 1kW$. Under these conditions the deposition rate was typically $\approx 300°A/min$. In order to provide a deposit which was sufficiently thick for X-Ray diffraction and electron microprobe measurements, a standard sputtering time of 30.0 min. was used. Thus, most of our films were approximately 1 µm thick. Compositional uniformity was found to be typically ±0.5 At% over a 1/4" × 3/4" sample area.

Routine Characterization

The as-deposited films were routinely characterized as to adhesion, film-thickness (stylus measurements), composition (electron beam microprobe measurements), structural order (X-Ray diffraction measurements)and electrical resistivity (4-point probe measurements). For semiconductor metallization applications, the adhesion and resistivity results are of particular interest: We find that the films adhere extremely well to the semiconductor substrates and are very resistant to scratching. No flaking or wrinkling was observed on any of these films in the as-deposited state, nor after thermal cycling between -200 and +500°C. SEM examination shows the surfaces to be smooth and featureless. Typical room-temperature resistivity values obtained for the as-deposited films are as follows:

Alloy	Composition	$\rho(\mu\Omega cm)$	$R_s (\Omega/\square)$
Ni-Nb	55-60 At%Ni	200-230	2.0-2.3
Ni-Mo	55 At% Ni	110-130	1.1-1.3
Mo-Si	60 At% Mo	160-200	1.6-2.0
W-Si	90 At% W	140-150	1.4-1.5

The sheet resistance values given in Col. 4 are scaled to a film thickness of 1µ. As expected, the resistivities of the amorphous films are somewhat higher than the resistivities of corresponding polycrystalline films (typically a factor of ~5 higher), but sheet resistances of the order of 1 $\Omega/\square$ are perfectly acceptable for many device applications. For those applications in which these resistivities are excessive, it may be possible to overcoat the amorphous metal with a layer of Au or Cu to provide a lower-resistance metallization.

Annealing and Crystallization

As the crystallization of amorphous metals is controlled by kinetic factors, any experimental value of the crystallization temperature. T_c, depends on the time-scale of the experiment. Fortunately, the characteristic time for crystallization is an extremely strong function of temperature, so that reasonable estimates of the maximum "operating temperatures" of amorphous metallizations can be obtained using relatively brief anneals. The results reported here were obtained by annealing the samples for one hour in evacuated quartz ampoules which also contained a small slug of Ti for gettering.

In order to determine the one-hour crystallization temperature of a given alloy composition, the following sequence was followed: The first anneal was performed at 400°C, after which the sample was removed from its ampoule for examination by X-Ray Diffraction (XRD). If there was evidence of crystallinity, the sputter-mask was altered to achieve a different alloy composition. (Crystallization temperatures below 400°C are of no interest at the present time). If there was no evidence of crystallization, the same sample was resealed in an ampoule and annealed at 500°C for 1 hour. This procedure was repeated at 100° increments until crystallization was detected. A new sample from the same batch

was then annealed at the penultimate temperature, measured for crystallinity, and reannealed at successively higher temperatures using 50°C increments. Finally, a third sample was used to find T_c to within 25°C.

Figure 1 shows a sequence of typical XRD scans for initially amorphous Ni-Mo films (~65% Ni). It is somewhat difficult to judge whether or not small features on the amorphous peak correspond to the early stages of crystallization. Massive crystallization, however, is unmistakably evidenced by the appearance of numerous sharp diffraction peaks. These comments are illustrated in Fig. 1 by the 600°C and 650°C traces: After annealing at 600°C, small bumps are seen at $2\theta = 39°$ and 45°. These features are reproducible, and apparently indicate a small volume-fraction of crystallites in an amorphous matrix. After the 650°C anneal, the 39° peak is quite strong, but the 45° peak is either missing or
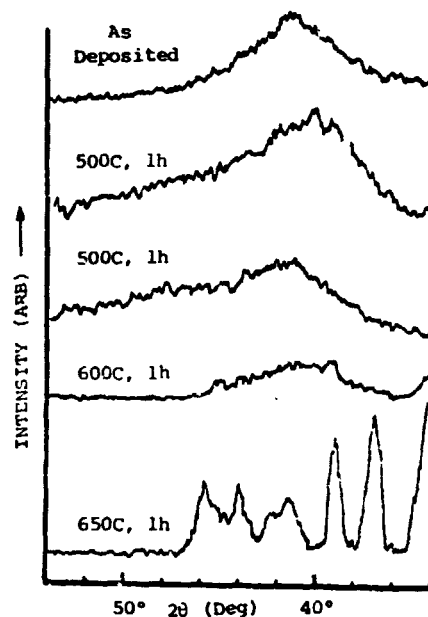

Figure 1. X-Ray Diffractometer scans of an initially amorphous film of Ni-Mo after 1h anneals at successively higher temperatures.

split into several peaks. It appears likely that the path of crystallization in the Ni-Mo system is complex, involving intermediate phases. Similar effects are seen in the other alloys as well. TEM investigations are planned for exploration of the crystallization mechanisms.

The results of the annealing studies to date are as follows:

Alloy	Composition	$T_0(°C)$	$T_1(°C)$
1) Ni-Nb	55 At% Ni	500	550
2) Ni-Nb	57 At% Ni	575	600
3) Ni-Mo	55 At% Ni	525	550
4) Ni-Mo	65 At% Ni	550	600
5) Mo-Si	60 At% Mo	550	600
6) W-Si	90 At% W	(Partially crystalline as deposited)	

The temperature T_0 is the highest 1-hour annealing temperature at which no evidence of crystallinity has been observed. T_1 is the lowest 1-hour annealing temperature at which some evidence of crystallinity has been observed. The W-Si alloys deposited to date have contained a small volume-fraction of microcrystalline phase in a predominantly amorphous matrix. Further re-

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finement of the composition is required. Nevertheless as will be shown in the next section, the largely amorphous W-Si films still function as effective diffusion barriers.

Diffusion

The diffusion of Au in amorphous metal films is of great practical interest because Au is widely used in multilayer metallizations and bonding wires for semiconductor devices. Au is also a prime candidate for use as an overlayer to reduce metallization resistances.

Au was ion-implanted into an amorphous Ni-Nb film which was subsequently annealed and measured by Rutherford Backscattering (RBS) to monitor any Au diffusion [9]. The amorphous film was deposited on a single-crystal Si substrate to a thickness of 1μ, and was composed of 56.5 At% Ni, 43.5 At% Nb. The implanted Au profile was Gaussian, with a peak concentration of 3.3 × 10^{20} cm^{-3} occurring ~400Å below the surface, and a "full width at half maximum" of 300Å. Since a Gaussian profile remains Gaussian during diffusion, it is straightforward to deduce diffusion coefficients from the half-widths of fitted Gaussian curves. Figure 2 shows a comparison of the Au profiles after 0.5 hours
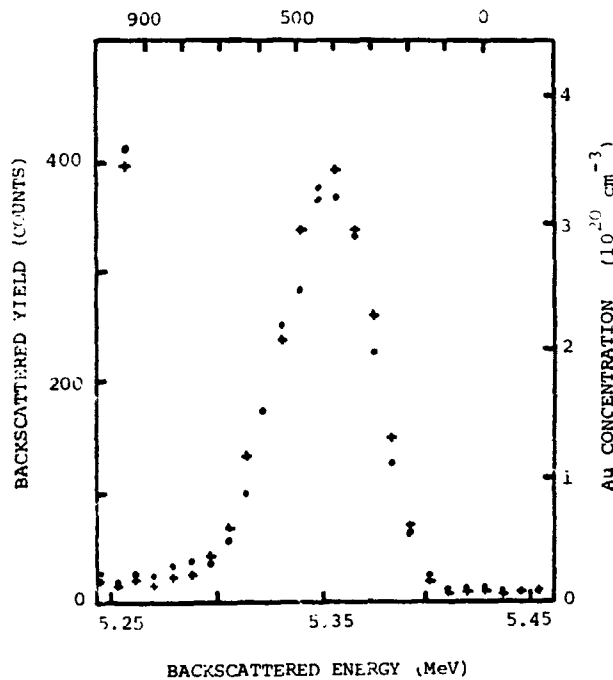
diffusion between amorphous metal films and overlayers of Cu or Au, and between amorphous metal films and semiconducting substrates are currently underway, and no quantitative results can be reported at this time.

In addition to the RBS measurements, we have used Auger Electron Spectroscopy (AES), together with Ar-ion sputtering to study interdiffusion. Figure 3 shows a series of AES profiles for an amorphous Ni-Nb film on which a ~750Å Cu layer was deposited. After 10 hours of annealing at 500°C, there was a slight broadening of the Cu/Ni-Nb interface, but no large-scale interdiffusion. After one hour at 600°C, however, the Cu,Ni, and Nb have thoroughly interdiffused, and the "interface" has moved very deeply (≳ 2000Å) into the Ni-Nb film. Other Ni-Nb films of the same composition were found to crystallize in one hour at 575°C. It is therefore clear that crystallization is responsible for the sudden, massive motion of Cu into the Ni-Nb (probably along grain boundaries). Similar results have been obtained with Au overlayers and with other amorphous alloys. It is interesting to note that we found essentially no interdiffusion between Au and amorphous W-Si despite the fact that the W-Si contained a detectable (but small) volume-fraction of microcrystalline phase. Thus, we believe that partially crystalline films can still function as effective diffusion barriers as long as the crystallites are well-separated by an amorphous matrix.

Figure 2. Comparison of the ion-implanted Au profiles after anneals of 30 minutes and 35 hours at 450°C, illustrating the extremely low rate of diffusion of Au in amorphous Ni-Nb at this temperature. The profile change can only be discerned by fitting Gaussian curves to the data.
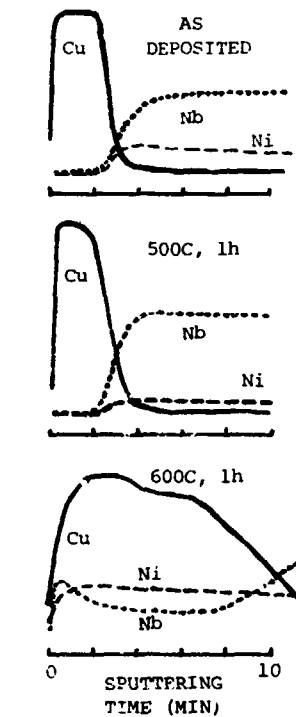

Figure 3. AES depth-profiles of Cu, Ni, and Nb. The top trace shows the as-deposited structure: A Cu layer on amorphous Ni-Nb. The middle trace shows that there was very little interdiffusion after 10 hours of annealing at 500°C. The bottom trace shows considerable interdiffusion after only 1 hour at 600°C. The rapid interdiffusion at 600°C is a consequence of crystallization.

and 35 hours of annealing at 450°C. Analysis of these and similar profiles obtained for longer annealing times gives a diffussivity of D ≈ 8 10^{-19}cm^2/sec for Au in this alloy at 450°C. Note that: (1) D ≤ 10^{-18} cm^2/s implies that an Au atom would require roughly 300 years to diffuse a distance of 1μ; and (2) the annealing temperature of 450°C is very near the estimated glass-transition temperature for this film: The one-hour crystallization temperature for films of this composition is in the neighborhood of T_c ≈ 550°C, and T_g must be ≲ T_c. Thus, our anneal temperature of 450°C is 2.88 T_g. Rutherford Backscattering studies of inter-

CONCLUSIONS

Amorphous metal films of appropriate compositions can be deposited on semiconducting and insulating substrates, and remain amorphous after one-hour anneals at temperatures in excess of 500°C. It is very important to note that the annealing temperatures used in this

study were specifically chosen to find the temperature ranges in which the alloys under investigation would crystallize on a time-scale of one hour $(T \geq 0.9T_g)$. At slightly lower temperatures, crystallization will not be observable on any reasonable laboratory time-scale. Our results also show that, as long as the films remain amorphous, they exhibit exceptionally low diffusivities. Indeed, the W-Si results show that films containing a small volume-fraction of microcrystallinity can still function as effective diffusion barriers. This observation is consistent with our basic working hypothesis that the advantages of amorphous metallizations stem from the absence of grain boundaries: As long as the volume-fraction of microcrystallinity is small, the crystallites will be separated by an amorphous matrix, preventing an interconnected network of grain boundaries. At some critical volume-fraction (which can be estimated from percolation-theory to be about 0.3 [10]), the crystallites will merge, and an essentially poly-crystalline film will result. Based on the work reported here, we conclude that films of high-T_g amorphous metal alloys are indeed viable candidates for use as high-temperature metallizations for semiconductor devices. We anticipate that this new class of semiconductor metallizations will find important applications as primary metallizations, interlayer diffusion barriers, and corrosion-resistant overlayers.

ACKNOWLEDGEMENTS

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