Invited Paper

AMORPHOUS METALLIC ALLOYS: A NEW ADVANCE IN THIN-FILM DIFFUSION BARRIERS FOR COPPER METALLIZATION

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1. INTRODUCTION

Copper, which has a lower electrical resistivity and a higher resistance to electromigration than aluminum, is currently being evaluated for ULSI applications as a replacement for aluminum. Drawbacks to the use of copper include its strong tendency to oxidation, a high mobility in metals and semiconductors, and a high reactivity with silicon at temperatures as low as 200°C.

To overcome these problems, very effective diffusion barriers need to be developed. These barriers should have a low diffusivity for copper, a high thermal stability, and should lack a driving force for chemical reactions with Cu, silicon or silicides. Unlike aluminum, copper does not form stable intermetallic compounds with the transition metals of the V and Cr groups, and the mutual solid solubilities of these metals with Cu are low, so that these metals would seem to be a logical choice for barrier applications. It has long been known, however, that these arguments are misleading[1]. Previous studies have indeed shown Cu diffuses through grain boundaries and defects in a tantalum layer and into silicon at a relatively low temperature (450°C) causing a failure of devices[2,3].

The effectiveness of non-reactive and insoluble tantalum barriers can be improved by adding impurities like oxygen or nitrogen to stuff grain boundaries of the material in order to suppress fast grain boundary diffusion[4]. It is difficult, however to reproducibly improve the effectiveness of barriers by adjusting the level of impurities. Since amorphous alloys lack grain boundaries that can act as fast diffusion paths, they should offer an improved alternative for effective barriers [5-7]. In this paper we report on the properties and diffusion barrier performance of amorphous tantalum and tungsten silicides and tantalum-silicon-nitrogen ternary alloys [3,8] for Cu metallizations.

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2. PROPERTIES OF AMORPHOUS METALLIC THIN-FILM BARRIERS

Tantalum and tungsten silicides are deposited by rf sputtering of Ta_5Si_3 and W_5Si_3 targets in an argon plasma. The as-deposited film are amorphous, as indicated by both x-ray and electron diffraction. The atomic composition of the as-deposited tantalum silicide films is $Ta_{74}Si_{26}$. The concentration of oxygen and argon impurities as measured by 2 MeV ^4He backscattering spectrometry are approximately 3 and 2 at.%, respectively. The resistivity at room temperature of the 100 nm thick $Ta_{74}Si_{26}$ film deposited on oxidized silicon is about 230 µΩcm. The crystallization temperature of the $Ta_{74}Si_{26}$ films on oxidized silicon is about 900°C. The crystallization products consist mainly of Ta_2Si with some addition of metastable $Ta_{4.5}Si$[9]. The atomic composition of the as-deposited tungsten silicide film is $W_{80}Si_{20}$. This film contains about 2 at.% oxygen and 2 at.% argon. Its room temperature resistivity is about 200 µΩcm. The film crystallizes after annealing at 700°C for 1 hr.

The $Ta_{36}Si_{14}N_{50}$ films are deposited by rf reactive sputtering of the Ta_5Si_3 target in Ar/N_2 gas mixture [8]. The film contains about 3 at.% of argon and below 3 at.% oxygen. The resistivity of the $Ta_{36}Si_{14}N_{50}$ film is about 625 µΩcm. The as-deposited film on sapphire substrate is x-ray and TEM-amorphous and crystallizes at very high temperature, e.g., 1100°C. The crystallization product is a mixture of hexagonal Ta_2N, tetragonal Ta_5Si_3 and hexagonal Ta_3 $(Ta_{0.28} Si_{0.72})$[3].

3. THERMODYNAMICS

To predict the thermal stability of amorphous silicides with copper, we have calculated ternary M-Si-Cu phase diagram at 25°C and 700°C for both Ta and W. Details of the calculations are described in references 10 and 11. In those calculations only elemental and binary phases are considered due to the lack of data on possible ternary compounds. In addition, the phases are assumed to have zero homogeneity range and no solid solubility. Metastable silicides were not taken into account.

Figure 1 shows the calculated Ta-Si-Cu and W-Si-Cu ternary phase diagrams for 700°C. In the W-Si-Cu system, tie lines exist between Cu and all silicides. In the Ta-Si-Cu systems, tie lines exist between copper and all silicides except the Si-richest compound $TaSi_2$. Alternative possible tie lines which can be obtained by minimal adjustments in the thermodynamic data are given by dotted lines.

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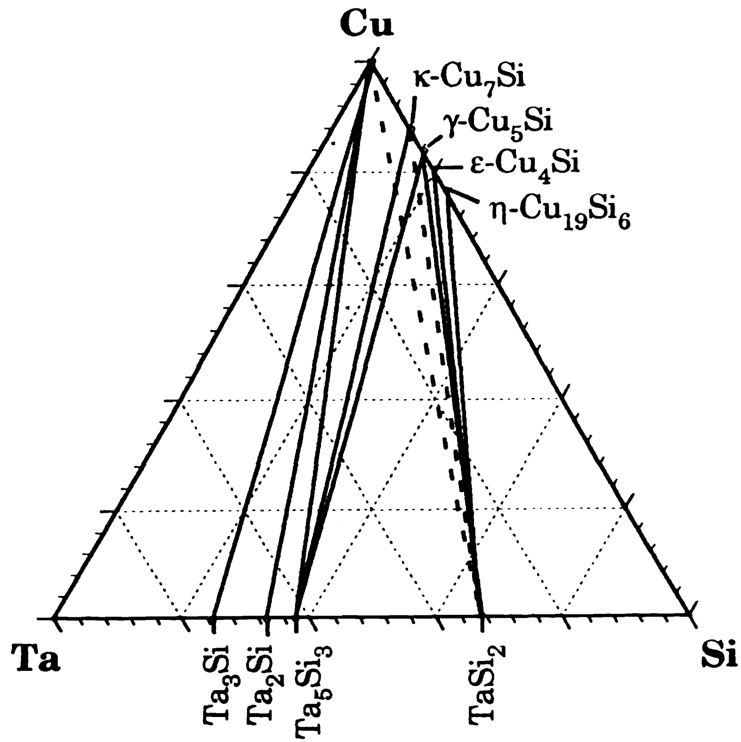

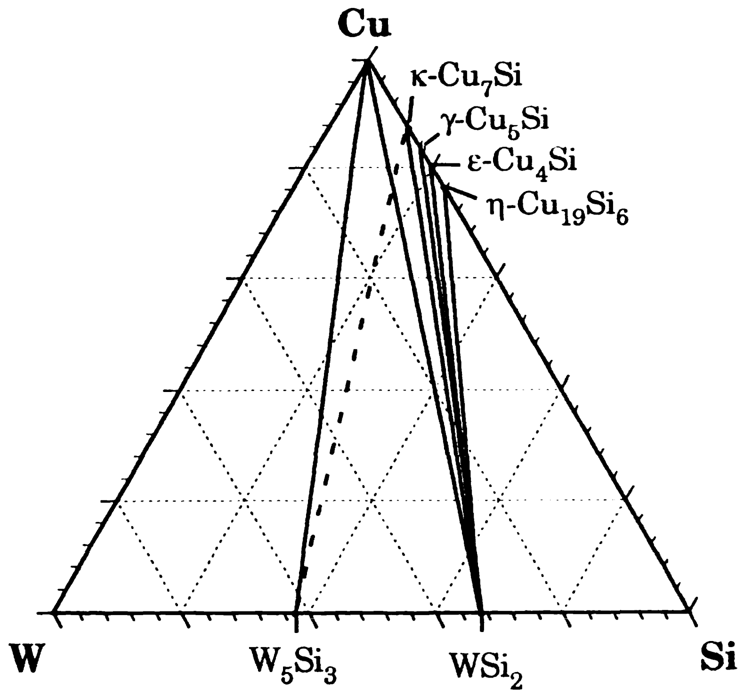

Fig. 1. Calculated Ta-Si-Cu and W-Si-Cu ternary phase diagrams for 700°C. Dashed lines denote alternate sets of thre possible lines.

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These diagrams reveal what kind of silicides should be chosen for Cu diffusion barriers in order to obtain a stable system. Specifically, according to the thermodynamics, tantalum and tungsten silicide diffusion barriers with at least 62.5% atomic metal contact should be used to prevent reaction with copper. An additional benefit of choosing metal-rich silicides lies in the fact that they tend to have higher crystallization temperature than their silicon-rich analogues[11].

4. DIFFUSION BARRIERS

Amorphous, metal-rich tantalum silicide possesses all three requirements needed for good diffusion barrier for copper. It is amorphous, so diffusivity for Cu should be low; it's crystallization temperature is high enough for most barrier applications (~900°C), and it is thermodynamically stable with Cu.

Figure 2 shows the I(V) characteristics of a shallow n^+p junction with the contact configuration Si substrate/$Ta_{74}Si_{26}$(100 nm)/Cu(500nm) as a function of temperature for 30 min vacuum annealing. The reverse leakage current of the diodes remains almost unchanged after annealing at 600°C. Diodes are shorted after annealing at 650°C. Backscattering spectra of the same metallization deposited on plain silicon confirm that the barrier fails structurally at 650°C but is maintained at 600°C and below.

The 650°C failure temperature is unexpectedly low since the amorphous $Ta_{74}Si_{26}$ alloy crystallizes at 900°C. To elucidate the reason, $Ta_{74}Si_{26}$ films with a Cu overlayer were deposited on oxidized silicon substrates and heated for 1 hr up to 1000°C. Figure 3 graphically summarizes the x-ray diffraction data after heat treatment for various thicknesses of the copper overlayer. It is clear from the graph that even a thin Cu overlayer lowers the crystallization temperature from about 900°C to 700°C. No copper silicides were observed in any samples investigated, which agrees with the predicted stability of Cu with tantalum-rich tantalum silicides. The likely scenario is that Cu promotes the crystallization of $Ta_{74}Si_{26}$ and that the barrier failure is connected with the (partial) crystallization of the barrier and the occurrence of rapid diffusion of copper into silicon via grain boundaries.

Similar results hold for tungsten silicide. The crystallization temperature of a plain $W_{80}Si_{20}$ film for 1 hr vacuum annealing is about 700°C. If a Cu overlayer induces premature crystallization in this system also, a reduced failure temperature of the amorphous $W_{80}Si_{20}$ barrier with a Cu overlayer is

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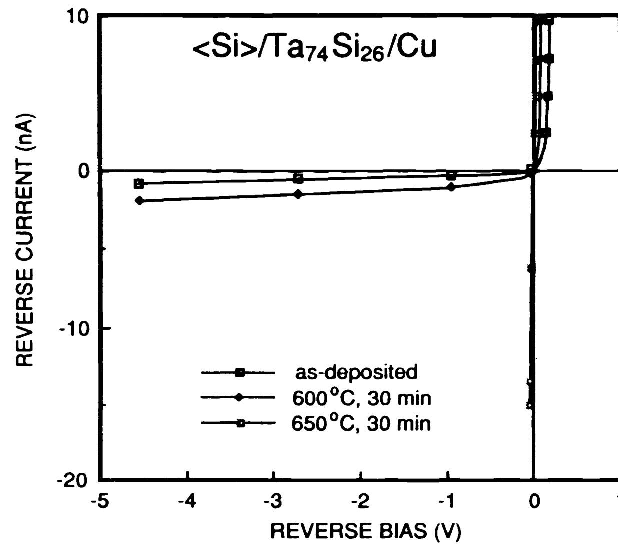

Fig. 2. The I-V characteristics of a shallow n^+p junction with a contact structure <Si>$Ta_{74}Si_{26}$(100nm)/Cu(500nm) as a function of temperature for 30 min vacuum annealing. The contact area is about 230 x 230 μm^2.

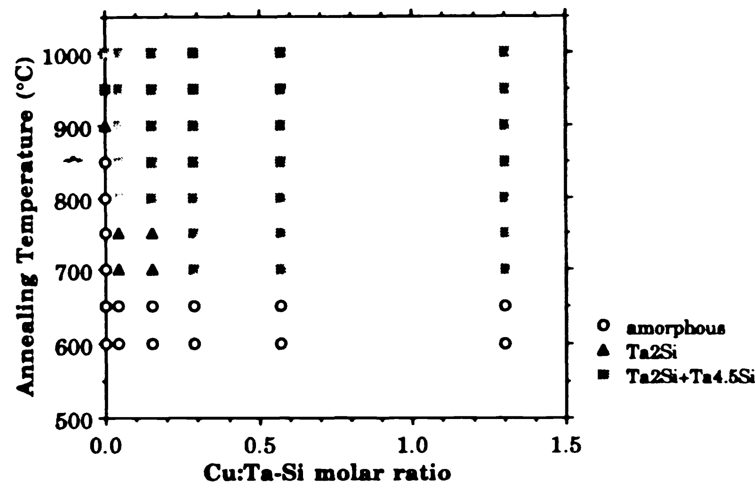

Fig. 3. Graphical summary of the compounds detected by x-ray diffraction after annealing a $Ta_{74}Si_{26}$ /Cu bilayer in vacuum for 1 hr with various copper overlayer thicknesses. At temperatures greatrer than 850°C, some copper was lost through evaporation.

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expected. Indeed, electrical measurements reveal that the Si/$W_{80}Si_{20}$(100 nm)/Cu(500) metallization fails already after 30 min annealing at 550°C in vacuum[12].

The high crystallization temperature of $Ta_{36}Si_{14}N_{50}$ alloy films (1000°C) suggests a potentially very high effectiveness of these films as diffusion barriers for Cu. However, the accelerated crystallization observed for the $Ta_{74}Si_{26}$ and $W_{80}Si_{20}$ in contact with copper also takes place for $Ta_{36}Si_{14}N_{50}$ in the <Si>/ $Ta_{36}Si_{14}N_{50}$/Cu metallization. As shown previously by TEM [3] the crystallization starts at the $Ta_{36}Si_{14}N_{50}$/Cu interface at 900°C and progresses in a laterally uniform way throughout the film. Once fully crystallized, the copper rapidly diffuses into silicon substrate and causes a failure of the devices. It should therefore be possible to further increase the time to failure or the failure temperature of the metallization by increasing the thickness of the barrier. Figure 4 shows the I(V) characteristics of the shallow junction with a contact of the structure <Si>/ $Ta_{36}Si_{14}N_{50}$(170)/Cu(500). The metallization is stable after annealing at 900°C for 30 min in vacuum. With the same metallization that is only 120 nm thick, a <Si>/ $Ta_{36}Si_{14}N_{50}$ barrier yields shallow junctions with a 8-fold increased leakage current after a similar heat treatment.

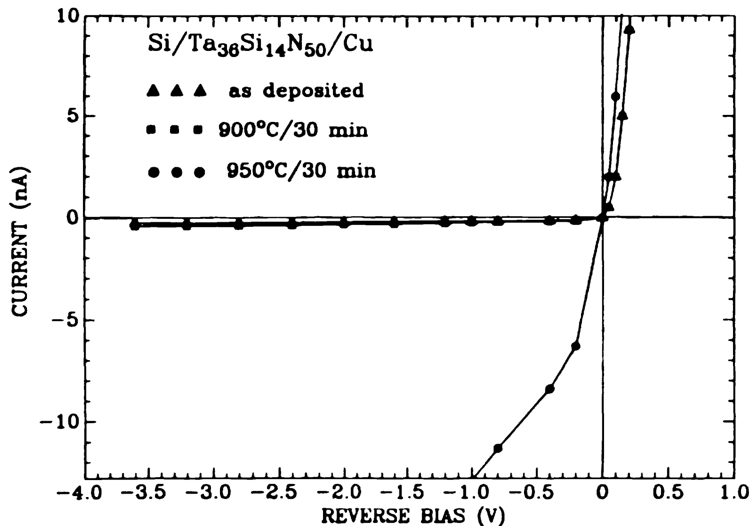

Fig. 4. The I-V characteristic of a shallow n^+p junction with a contact structure <Si>/$Ta_{36}Si_{14}N_{50}$(170 nm)/Cu(500 nm) as a function of temperature for 30 min vacuum annealing. The contact area is about 230 x 230 μm^2.

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In practical application, a contacting layer should be added to the metallization. Since $TiSi_2$ is used in industry, we tested the stability of a <Si>$TiSi_2$(30nm)/ $Ta_{36}Si_{14}N_{50}$(80 nm)/Cu(500 nm) metallization deposited on the same shallow junction diodes. The reverse current does not change after annealing at 900°C for 30 min, and increases about six fold after annealing at 950°C[13]. The same metallization, but without diffusion barrier, fails at 300°C.

5. CONCLUSIONS

Thin films of amorphous metallic alloys can be highly effective diffusion barriers between copper and silicon. However, in order to take advantage of their lack of fast diffusion paths, these barriers must have high crystallization temperatures and be thermodynamically stable with copper.

6. ACKNOWLEDGEMENTS

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