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STABILITY OF AMORPHOUS Ir–Ta DIFFUSION BARRIERS BETWEEN Cu AND Si

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Thin-film amorphous Ir–Ta (a-IrTa) has been tested as a diffusion barrier between (100) Si and Cu. Sandwich structures of (100) Si/a-IrTa/Cu/a-IrTa were found to be stable during annealing in vacuum up to 700°C. At 750°C interdiffusion of Cu and Si took place as observed by Rutherford backscattering spectrometry. Using free-standing a-IrTa/Cu/a-IrTa samples for transmission electron microscopy, it was determined that the crystallization temperature of thin-film a-$Ir_{45}Ta_{55}$ is reduced from 900 to 750°C in the presence of Cu.

Although Al is the most widely used interconnect material in very large scale integrated (VLSI) circuit fabrication, its future potential is limited. As device dimensions become much smaller than 1 μm the *RC* time delay of the Al wiring will dominate the total chip delay. Copper is an obvious choice to replace Al for long and narrow interconnection since the lower resistivity (1.7 μΩ cm compared to 2.1 μΩ cm for Al) results in reduced signal delay times and higher operating frequencies compared to Al [1]. However, Cu is notorious for its contamination into Si devices, since it is not only a fast diffuser [2] but a deep level trap as well [3]. The necessity of diffusion barriers to prevent Cu penetration of devices and to control Cu corrosion has been recognized by several authors [1,4–6]. For instance, a Cu–10 at.% Ti alloy on top of $Si/SiO_2/W/TiN$ sample structures was nitrided at 800°C to form TiN-encapsulated Cu interconnects [6]. Also, SiON and SiN have been found to prevent Cu diffusion into Si substrates during annealing at 300°C in air [1]. Polycrystalline Ta was used as a conducting diffusion barrier by Hu et al. [4] and Cu/polyimide structures were found to be mechanically and electrically stable against 12 thermal cycles from room temperature to 400°C for 30 min. It is expected, however, that this barrier will fail at higher temperatures either by grain-boundary diffusion of Cu through the Ta or by $TaSi_2$ formation around 600–650°C [7].

In this paper we report on metallic amorphous Ir–Ta (a-IrTa) diffusion barriers between (100) Si substrates and Cu. A high failure temperature for (100) Si/a-IrTa/Cu structures is expected for several reasons. First, the absence of grain boundaries and extended defects in the amorphous alloy eliminates fast diffusion paths. Second, thin-film a-$Ir_{45}Ta_{55}$ exhibits crystallization temperatures as high as 900°C [8] and does not react with (100) Si substrates up to temperatures of 875°C [9] (see also p. 47 in ref. [10]). Furthermore, the a-IrTa/Cu system is expected to be chemically stable since no intermetallic compounds are known in either the Ir–Cu or the Ta–Cu system [11] and the heats of compound formation (at equiatomic composition) are positive and estimated by the macroscopic atom approach [12] to be +0 and +3 kJ/mol, respectively. On the other hand, the Ir–Ta system exhibits four intermetallic compounds [11] with heats of formation around −70 kJ/mol (and −50 for a-$Ir_{45}Ta_{55}$) [13] (see also p. 33 in ref. [10]). Therefore, a-IrTa barriers between Cu and (100) Si should be exceedingly stable.

Amorphous $Ir_{45}Ta_{55}$ alloys 300 Å thick were deposited in a dual electron gun evaporator with a base pressure less than 1×10^{-6} Pa. The composition of the alloys was monitored during deposition using a quadrupole mass spectrometer. The thickness of the deposited films was measured in situ using a quartz crystal monitor. The substrates ((100) Si and NaCl) were kept at liquid-nitrogen temperature during de-

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position. On top of these samples 500 Å of Cu was deposited. An additional 300 Å a-$Ir_{45}Ta_{55}$ capping layer was deposited. Compositional depth profiles were measured with 2 MeV He^+ Rutherford backscattering spectrometry (RBS). Transmission electron microscopy (TEM) analysis was done on the Ir–Ta/Cu (300/500 Å) and Ir–Ta/Cu/Ir–Ta (300/500/300 Å) samples evaporated onto the NaCl substrates. Before annealing the NaCl substrates were dissolved in de-ionized water and the films were mounted on molybdenum TEM grids. Anneals were carried out in a vacuum furnace (base pressure less than 1×10^{-5} Pa) for 30 min, up to 600°C uncapped, above 600°C samples were capped to prevent Cu evaporation.

No reaction was seen in RBS for anneals up to 600°C of the uncapped samples. TEM showed some Cu grain growth and the formation of a few pinholes in the Cu film. RBS spectra for higher-temperature anneals of capped films are shown in fig. 1. The surface peak positions of the elements are indicated by arrows. The Ir and Ta signals appear at the surface peak position in the spectrum of the as-deposited sample (solid line). Although the separate Ir and Ta peaks cannot be resolved in RBS because the masses of Ir and Ta are very close, the second (buried) Ir–Ta peak is separated from the first peak by the Cu layer. The Cu signal is below the Cu surface-peak position, as expected, as is the Si peak. The steep edges (of all peaks and the Si signal) indicate that the interfaces in the (100) Si/Ir–Ta/Cu/Ir–Ta samples are sharp. The spectrum of the sample annealed at 700°C for 30 min (dashed line) is almost identical to the spectrum of the as-deposited sample, indicating that no interdiffusion occurred. Dramatic changes are observed, however, after annealing at 750°C (dotted line). Copper disappears from the near-surface region and the two Ir–Ta peaks merge together. In addition Si is observed up to the surface. Whereas the sample surface after annealing at 700°C remained smooth, optical microscopy showed that after annealing at 750°C rectangular pits, measuring approximately 3×3 μm^2, were formed. Samples annealed at higher temperatures feature a larger density of these pits with sizes increasing up to 6×6 μm^2. This explains why Si is detected at the surface.

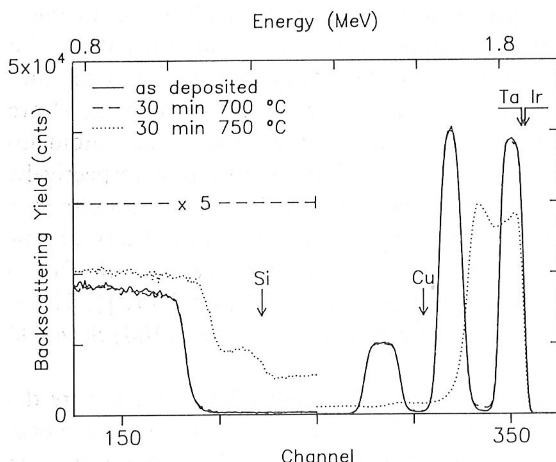

Fig. 1. 2 MeV $^4He^+$ RBS spectra of the (100) Si/a-$Ir_{45}Ta_{55}$/Cu/a-$Ir_{45}Ta_{55}$ samples. Scattering angle 135°, sample tilt 7°. Surface peak positions for Si, Cu, Ta, and Ir are indicated by arrows. After annealing at 700°C for 30 min in vacuum the sample structure appears stable. At 750°C Cu diffuses into the Si substrate.

TEM results for the free-standing a-$Ir_{45}Ta_{55}$/Cu/a-$Ir_{45}Ta_{55}$ films are presented in fig. 2. The pictures of fig. 2a were obtained after annealing at 650°C. These pictures are representative for all samples as deposited and annealed at temperatures up to 650°C. The bright-field image shows the Cu grains from the middle layer. The bright spots are small pinholes in the Cu layer, which are also observed in as-deposited samples. Growth of Cu grains or pinhole formation is not observed due to the suppression of Cu surface mobility by the Ir–Ta capping layer. The selected-area diffraction pattern shows broad halos, from the amorphous $Ir_{45}Ta_{55}$ alloy and diffraction lines from the polycrystalline Cu. After annealing at 700°C some β-Ta and fcc Ir crystals start to form, as seen in the bright-field image of fig. 2b. No changes could be observed in the diffraction pattern. After annealing at 750°C (fig. 2c), the temperature at which the reaction occurred in the (100) Si/a-$Ir_{45}Ta_{55}$/Cu/a-$Ir_{45}Ta_{55}$ samples, the bright-field image of fig. 2c shows an increasing number of newly formed crystals, and also additional spots due to β-Ta and fcc Ir are observed in the diffraction pattern. The reaction proceeds to completion at 850°C (fig. 2d). Cu is still present in the sample, but the amorphous Ir–Ta phase disappeared completely. The reaction products are identified as β-Ta and fcc Ir which are the same phases observed after crystallization of a-$Ir_{45}Ta_{55}$ at 900°C [8–10].

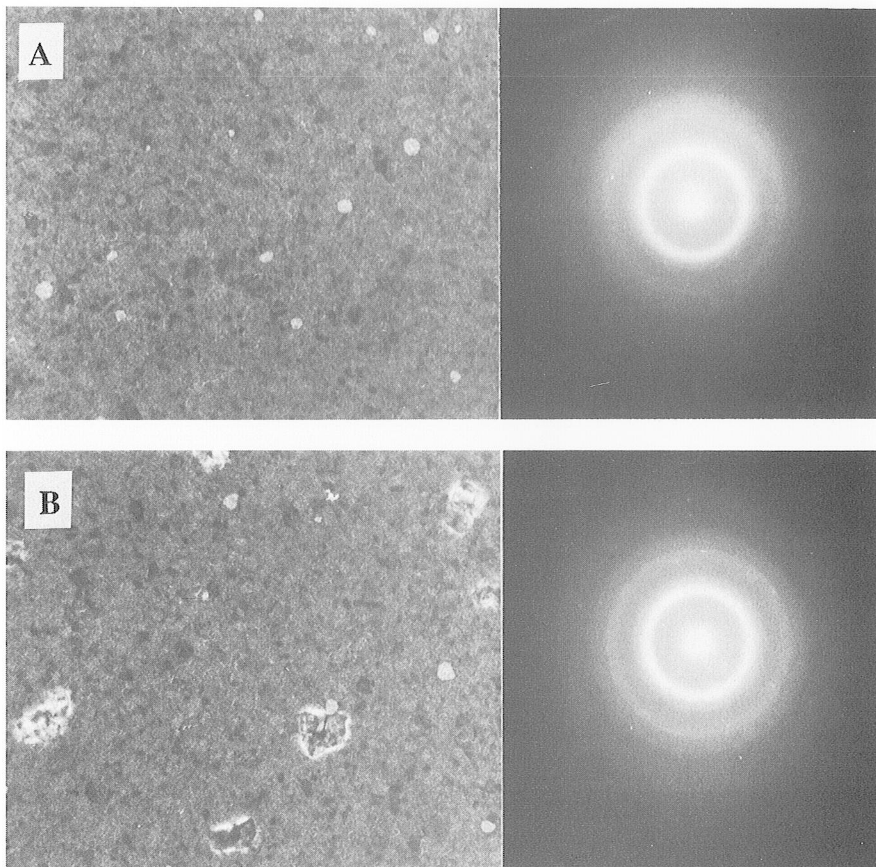

Fig. 2. TEM results obtained after isochronal annealing for 30 min of the free-standing a-$Ir_{45}Ta_{55}$/Cu/a-$Ir_{45}Ta_{55}$ sandwich structures. The bright-field images show an area of 1.1×0.9 μm^2. Also shown are the corresponding selected-area diffraction patterns. (a) After annealing at 650°C, only a-$Ir_{45}Ta_{55}$ and Cu are observed. The bright spots in the bright-field image are due to pinholes in the intermediate Cu layer. This sample is representative for all samples as deposited and annealed at temperatures up to 650°C. (b) After annealing at 700°C, some crystals of another phase are observed identified as β-Ta+fcc Ir. (c) After annealing at 750°C, the reaction proceeds. (d) After annealing at 850°C, the reaction is completed.

The crystallization temperature of a-$Ir_{45}Ta_{55}$ is reduced from 900 to approximately 750°C when in contact with a Cu film. If Cu diffuses into the a-$Ir_{45}Ta_{55}$ the mobility of Ir and Ta atoms may be enhanced which assists crystallization. Indeed, the heat of hole formation for Ta holes in IrTa is equal to 223 kJ/mol and in CuTa it is 210 kJ/mol, hence the crystallization temperature is expected to be reduced in copper-rich areas and at the a-IrTa/Cu interface. Once the a-IrTa crystallizes, Cu may diffuse along the grain boundaries and into the Si.

In conclusion, 300 Å thick a-$Ir_{45}Ta_{55}$ diffusion barriers in (100) Si/Cu contacts are stable against annealing at 700°C for at least 30 min in vacuum. At 750°C, a-$Ir_{45}Ta_{55}$ in contact with Cu crystallizes, and Cu can diffuse rapidly into the Si substrate. The high stability of the metallic a-IrTa buffer layer makes it a good candidate for application in future miniaturization of VLSI electronics.

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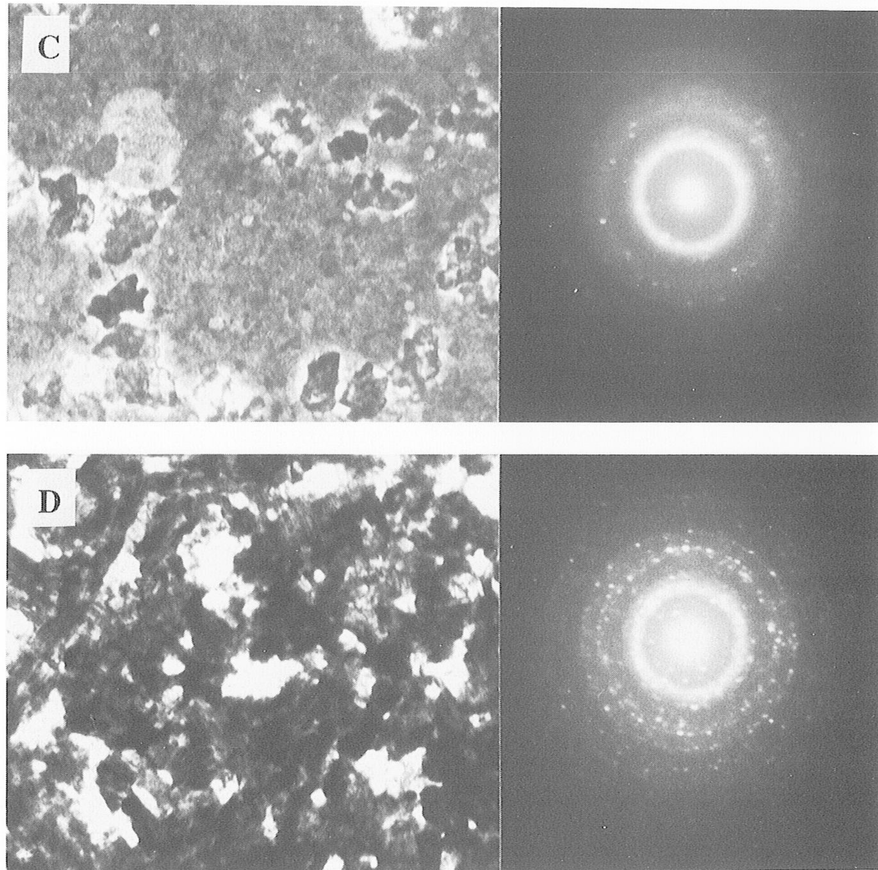

Fig. 2. continued

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