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Effect of Si Addition on the Microstructure of Al-Cu-Si Alloy for Thin Film Metallization

반도체 metallization용 Al-Cu 합금의 미세구조 천이에 미치는 Si 첨가영향

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Abstract

The effects of Si addition on the precipitation processes of in Al-Cu-Si alloy films were studied by the transmission electron microscopy. Deposition of an Al-1.5Cu-1.5Si (wt. %) film at 305℃ resulted in formation of fine, uniformly distributed spherical θ-phase particles due to the precipitation of the θ and Si phase particles during deposition. For deposition at 435℃, fine θ-phase particles precipitated during wafer cooldown, while coarse Si nodules formed at the sublayer interface during deposition. The film susceptibility to corrosion is discussed in relation to the film microstructure and deposition temperature.

1. Introduction

Aluminum interconnects are commonly alloyed with Cu and Si to improve their properties for the multi-level metallization in integrated circuits. Cu addition enhances resistance to electromigration[1] and hillock growth[2]. However, excess Cu can result in the formation of Cu-rich Al_2Cu (θ) precipitates, which can increase corrosion susceptibility due to the galvanic action between the θ precipitate and adjacent Cu-depleted matrix during wet and dry processing.[3,4] Si was originally added to the Al film to retard diffusion of Si from the Si substrate into the interconnection layer.[5] But excess Si can result in formation of elemental Si particles in the Al lines, which degrades electromigration resistance[6], and causes high resistance points[7]. The use of diffusion barrier layers, such as Ti-W and TiN, significantly reduced the need for Si in Al, however Si is still commonly added to Al as well as Cu. An unanticipated beneficial side effect of Si additions to Al-Cu films is their improved resistance to corrosion induced by θ-phase particles during device processing, but the mechanism for this improvement is not clearly understood.[3] The addition of Si in Al-Cu alloy could alter the precipitation kinetics and microstructures significantly due to the changes in chemical energy for the formation of θ-phase precipitate.

In view of these considerations, careful examination of the film microstructure is required to understand the effect of Si addition on the various aspects of film properties. In this work, the effects of adding Si and deposition temperature on the formation of the θ and Si phase precipitates are reported in Al-Cu alloy interconnection lines.

2. Experimental

Films with a composition of Al-1.5Cu-1.5Si (wt%) were studied to examine precipitate formation during thermal processing. The substrates used were oxidized Si wafers coated with 0.15 mm Ti-W film. Al-alloy films were sputter deposited to a thickness of 0.75 μm on top of a Ti-W film in a single wafer deposition system. The wafers were heated during deposition at either 305℃ or 435℃. From the Al-Cu-Si phase diagram[8], it can be seen that 305℃ was in the three-phase, Al(α)-Al_2Cu-Si region and 435℃ was in the two-phase, Al(α)-Si region. The microstructures of films were characterized in both the as-deposited and annealed conditions by plan-view and cross-section TEM.

3. Results

A plan-view TEM micrograph of the Al-1.5Cu-1.5Si film deposited at 305℃ is shown in Fig. 1a. The film consisted of small spherical particles and equiaxed aluminum grains. The particles were either the θ-phase or elemental Si precipitates. The planar distribution of the fine θ precipitates were uniform throughout the film, compared to the Al-1.5%Cu film deposited at 305℃, which was previously reported by the author[8]. In a film cross-section view of Fig. 1b, it can be seen that the θ and Si particles coprecipitated during deposition at the Ti-W sublayer interface. The internal morphology of the Si precipitate was highly twinned, as shown in Fig. 1b.

Fig. 2a shows a plan-view micrograph of the Al-1.5Cu-1.5Si film deposited at 435℃. A fine, uniform distribution of the θ precipitates was observed only at the GBs and triple points (TPs). Coarse Si precipitates (0.2-0.4 μm in diameter) were also observed in the cross-section view of Fig. 2b.

The as-deposited Al-1.5Cu-1.5Si film at 435℃ underwent *in-situ* heat-treatments in the. Fig. 4a shows the as-deposited film microstructure in which the plate-like θ precipitates are located at the GBs and TPs. Upon heating to 380℃ and holding for five minutes, the θ precipitates grew, as shown in Fig. 4b. At the same time, Si precipitates started to nucleate and grow at the GBs, twin boundaries, and within the Al grains. Upon further heating to 450℃, the θ-phase precipitates rapidly dissolved into the Al matrix, while the Si precipitates continued to grow during holding at 450℃ for five minutes (Fig. 4c). Upon cooldown, the θ-phase particles reprecipitated at the interface between Si precipitates and GBs (Fig. 4d). The morphology of the Si precipitates was spherical and the internal structure was highly twinned, but the θ precipitates retained a plate-like morphology.

4. Discussion

For the Al-1.5Cu-1.5Si film, a pile-up of Cu and Si at the Ti-W sublayer interface is due to the formation of interfacial θ and Si precipitates during deposition at 305℃. The Si addition resulted in a fine, uniform distribution of spherical θ precipitates in the Al-1.5Cu-1.5Si film deposited at 305℃. This is in direct contrast to the formation of coarse θ precipitates with an irregular shape, as we previously observed in an Al-1.5Cu film deposited at 325℃.[8] These differences in microstructure and distribution are due to the coprecipitation of θ and elemental Si phase particles, as shown in a film cross-section view of Fig. 1b. We speculate that the coprecipitation of the θ and Si phase particles can significantly reduce the activation energy for the nucleation of both θ and Si precipitates if a significant reduction of the interfacial free energy is possible. This will increase the nucleation rate of both the θ and Si precipitates. Thus, an increasing nucleation rate with a constant growth rate, which is temperature dependent, can result in a much finer distribution of small θ precipitates.

The Al-1.5Cu-1.5Si film was in the two-phase, Al(α)-Si region at the 435℃ deposition temperature. The 1.5 wt. % Cu is totally soluble in Al solution but excess Si can segregate out and precipitate as Si nodules during deposition. Thus, the fine θ-phase particles can precipitate during wafer cooldown (Fig. 2a). However, the Cu profile is uniform throughout the film thickness for the deposition at 435℃. A similar trend was reported previously for the Al-1.5Cu film deposited at 465℃.[8] Thus, Si addition in the Al-1.5Cu-1.5Si film seemed to have little effect on the nucleation and growth of the θ-phase particles when it precipitated during wafer cooldown from the two phase region after 435℃ deposition.

The solid solubility of Si in Al at room temperature is less than 0.01 weight percent. Although coarse Si precipitates were observed at the sublayer interface in the Al-1.5Cu-1.5Si film deposited at 435℃, there was no evidence that all of the excess Si solute segregated out and precipitated into Si nodules. The excess Si solute may exist in a supersaturated condition in the Al matrix of the as-deposited film upon completion of the vapor phase sputter deposition at high rate (1.1 μm/min). This is supported by the nucleation and growth of Si precipitates during the *in-situ* heating and cooling experiments of the Al-1.5Cu-1.5Si film deposited at 435℃ (Fig. 4). Supersaturated Si segregated out as elemental Si nodules during heating at 380℃ (Fig. 4b). The Si precipitates continued to grow during further heating at 450℃ (Fig. 4c). Upon cooldown, the plate-like θ-phase particles reprecipitated at the interface between Si precipitates and GBs (Fig. 4d). This also suggests that the coprecipitation of θ and Si phase particles is energetically favored.

The effect of Si additions on the film corrosion susceptibility during device processing can also be considered. Weston et al.[3] found that the corrosion induced by the θ-phase precipitate can easily occur when an as-deposited film was rinsed in plain, deionized water after exposure to standard positive photoresist developers. They found that the presence of Si in the Al-Cu film significantly reduced corrosion susceptibility of the alloy films. First, the correlations between microstructure and susceptibility to corrosion are discussed for the Al-1.5Cu-1.5Si film deposited at 305℃. As previously reported[8], the growth of the coarse θ-phase precipitate in Al-1.5Cu film during deposition in two-phase Al(a)-Al_2Cu region (325℃) can result in an extended Cu-depleted region adjacent to the precipitate. However, the addition of 1.5 wt. % Si into the Al-1.5Cu film will significantly suppress the growth of θ-phase precipitates during deposition at 305℃ due to the coprecipitation of θ and Si phase particles (Fig. 1b). This can substantially reduce the galvanic action between the θ-phase precipitate and Al matrix, since the extent of the non-uniformity of the Cu distribution may be reduced by the coprecipitation process.

The correlation between Si additions and corrosion susceptibility of the film will now be discussed. Table 1 shows standard electropotentials of Al metals and alloys in a solution of chloride ions with a calomel reference.[10] It shows that a decreasing copper concentration in Al solid solution makes the alloy more anodic. However, Si solute added into an Al solid solution makes the alloy less anodic in comparison with a Cu-depleted Al matrix (with respect to the θ-phase precipitate), as shown in Table 1. *In-situ* heating and cooling experiments (Fig. 4) of the Al-1.5Cu-1.5Si film revealed that excess Si existed in the supersaturated Al matrix of the as-deposited film. Thus, an Al matrix supersaturated with Si is less anodic compared to the Cu-depleted Al matrix. This will reduce the galvanic action between the θ-phase precipitate and the Al matrix supersaturated with Si, resulting in a film with less corrosion susceptibility than the binary Al-Cu films. It was explained that Si additions to Al-Cu films are conducive to reducing film susceptibility to corrosion, but other detrimental effects on the film properties, such as electromigration and electrical resistivity should be considered. Considering these effects, the addition of excess Si beyond the solid solubility limit (e.g. ~0.5 wt. % at 450℃)[8] at the temperature of thermal processing would not be entirely positive, since the formation of Si precipitates and the resulting reduction in grain size can increase electromigration susceptibility and film resistivity. Quantitative information on such effects of Si will require further studies on correlations between film properties and microstructure.

5. Conclusions

Si additions into Al-Cu films can improve film resistance to corrosion because the extensive Cu segregation into coarse θ precipitates can be reduced for deposition at 305℃ and the matrix of Al-Si solid solution is less anodic than Cu-depleted Al matrix with respect to the θ -phase precipitate.

6. References

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Table 1. Electrode Potentials of Aluminum Solid Solutions.[10] As Measured Against Calomel Electrode at 25℃.

Al	-0.85 V
Al-1%Si	-0.81 V
Al-2%Cu	-0.71 V
Al_2Cu (θ)	-0.73 V
Al-4%Cu	-0.69 V

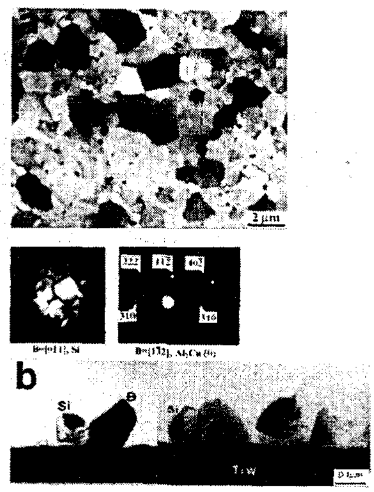

Fig 1. Microstructure of Al-1.5Cu-1.5Si film deposited at 305℃. (a) Plan-view TEM micrograph showing uniform distribution of the spherical Al_2Cu (θ) and Si phase precipitates throughout the film. (b) Cross-section TEM micrographs showing coprecipitation of the θ and Si phase particles at the sublayer interface.

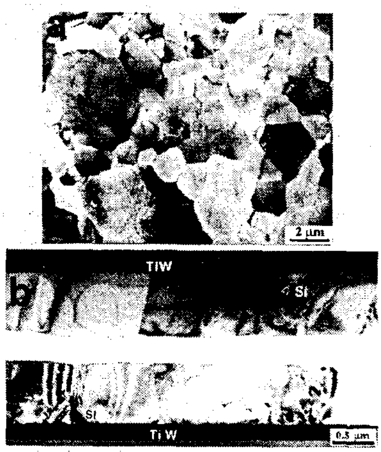

Fig 2. Microstructure of Al-1.5Cu-1.5Si film deposited at 435℃. (a) Plan-view TEM micrograph showing fine Al_2Cu (θ) phase precipitates at the grain boundaries (GBs) and triple points (TPs). (b) Cross-section TEM micrograph showing coarse Si precipitates at the sublayer interface.

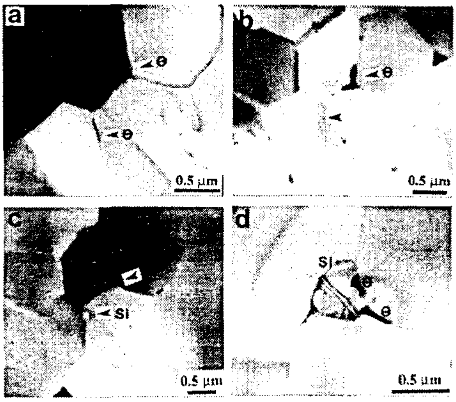

Fig 3. *In-situ* heat treatment of the Al-1.5Cu-1.5Si film deposited at 435℃ for the following conditions; (a) 25℃, (b) 380℃ and hold for 1 min, (c) 450℃ and hold for 5 min, (d) 25℃. Coarsening, dissolution and reprecipitation processes of θ-phase particles are shown at the GBs. Precipitation of the Si particles is also shown at the GBs, twin boundaries, and within grains.