Effect of Si addition on the precipitation of Al_2Cu-phase in Al-Cu-Si thin films

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The effects of Si addition and of deposition temperature on the precipitation processes of Al_2Cu (θ) and Si particles in Al-Cu-Si alloy films were studied with *in-situ* hot stage transmission electron microscopy (TEM). Deposition of an Al-1.5Cu-1.5Si (wt%) film at 305°C, in the three-phase, Al(α)-Al_2Cu-Si region resulted in formation of fine, uniformly distributed spherical θ-phase particles due to the coprecipitation of the θ and Si phase particles during deposition. For deposition in the two-phase, Al(α)-Si region (435°C), fine θ-phase particles precipitated during wafer cooldown, while coarse Si nodules formed at the sublayer interface during deposition. *In-situ* heat treatment of the film revealed that excess Si existed in a supersaturated Al matrix. Si addition decreased film susceptibility to corrosion induced by the θ-phase precipitates, since extensive Cu segregation can be reduced by coprecipitation at 305°C and the Al matrix supersaturated with Si reduced galvanic action with respect to the θ-phase precipitate. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Aluminum interconnection lines 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]. In the binary Al-Cu alloy, we previously reported that the film deposited at 325°C, in the two-phase, Al(α)-Al_2Cu region, has large, irregular θ precipitates (~1.0 μm in length), whereas the film deposited at 465°C, in the single-phase Al(α) region, has fine, plate-like θ precipitates at the grain boundaries (GBs) [8]. 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. However, research on these subjects has never been reported in the literature.

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. The films were evaluated using *in-situ* heat treatments in transmission electron microscopy (TEM). Microstructure and corrosion properties are also correlated.

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 μm 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°C or 435°C. The films were deposited to a thickness of 0.75 μm for 40 sec at a deposition rate of ~1.1 μm/min. The wafers were not biased during deposition. From the Al-Cu-Si phase diagram [9], it can be seen that 305°C was in the three-phase, Al(α)-Al_2Cu-Si region and 435°C 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. Plan-view samples were prepared from around 500 μm thick wafers. An ultrasonic disc cutter was used to cut 3 mm diameter discs from the wafers. The discs were successively

ground, dimpled and polished from the Si side only. A final low angle ion milling was performed in a single sided specimen holder at 4 keV and 0.5 mA with a beam angle less than 8°. Specimens for the cross-section TEM studies were prepared in the usual fashion: sectioning, gluing, dimpling, and ion milling at 15° beam angle in a liquid-nitrogen cooling stage using a Gatan 600 Duomill. To produce a thin sample with uniform thickness, a final low angle ion milling was performed in a single sided specimen holder at 4 keV and 0.5 mA with a beam angle less than 6°. These samples were analyzed with a JEOL JEM 2000FX at 200 keV. Cu and Si distributions through the film thickness were analyzed by Auger electron spectroscopy (AES).

To study the precipitation processes of the θ and Si phase particles during subsequent thermal processes, the plan-view TEM specimens of the as-deposited films underwent *in-situ* heat treatments in a Philips 400 T TEM at 120 keV equipped with a heating stage. Heating temperatures were chosen from the ternary Al-Cu-Si phase diagram [9] to study growth of the θ and Si phase precipitates (380°C, Al(α)-Al_2Cu-Si region) and dissolution (450°C, Al(α)-Si region) and reprecipitation processes of θ-phase particles. The annealing cycle steps were: (1) heat to 380°C and hold for five min; (2) heat to 450°C and hold for five min; and (3) cool to 25°C. Photographs were taken upon completion of each heat treatment step.

3. Results

A plan-view TEM micrograph of the Al-1.5Cu-1.5Si film deposited at 305°C 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°C, 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

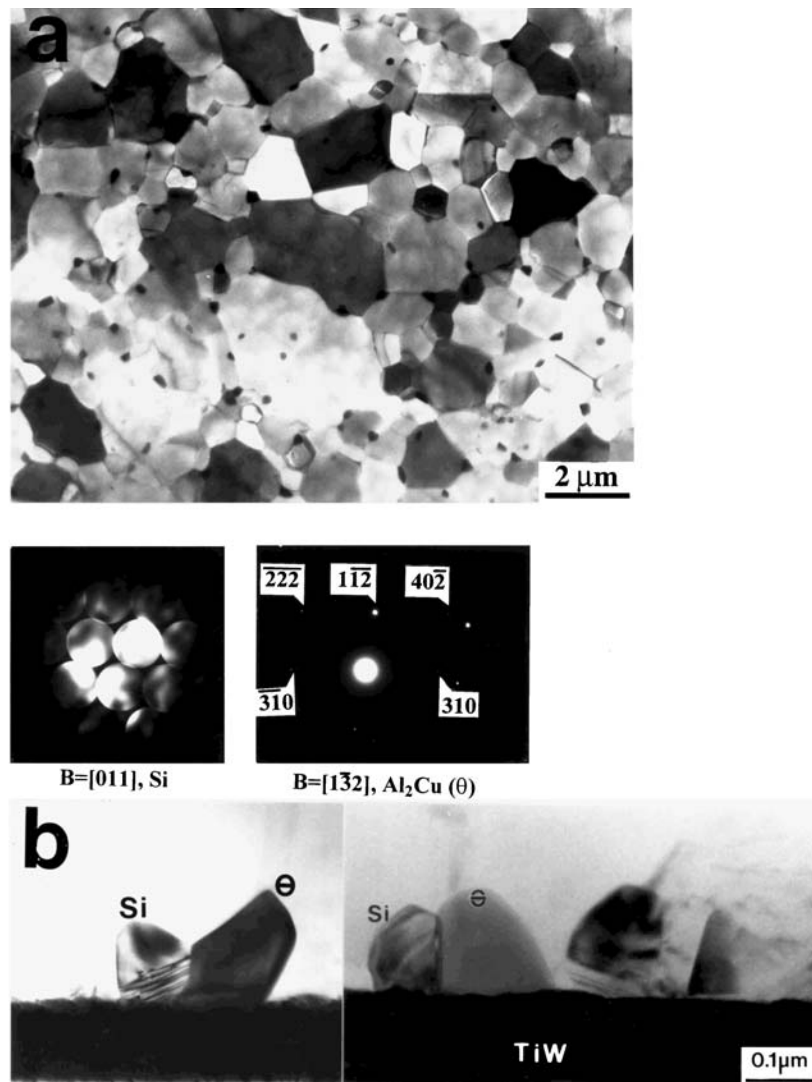

Figure 1 Microstructure of Al-1.5Cu-1.5Si film deposited at 305°C. (a) Plan-view TEM micrograph showing uniform distribution of the spherical Al_2Cu (θ) and Si phase precipitates throughout the film. (b) Cross-section TEM micrographs showing coprecipitation of the θ and Si phase particles at the sublayer interface. The zone axis of Al_2Cu diffraction patterns is slightly tilted from the exact [1, −3, 2] direction. The intensities of [−4, 0, 2], [2, 2, 2] spots are not strong enough to be seen in the picture and the indexing is not given to these spots.

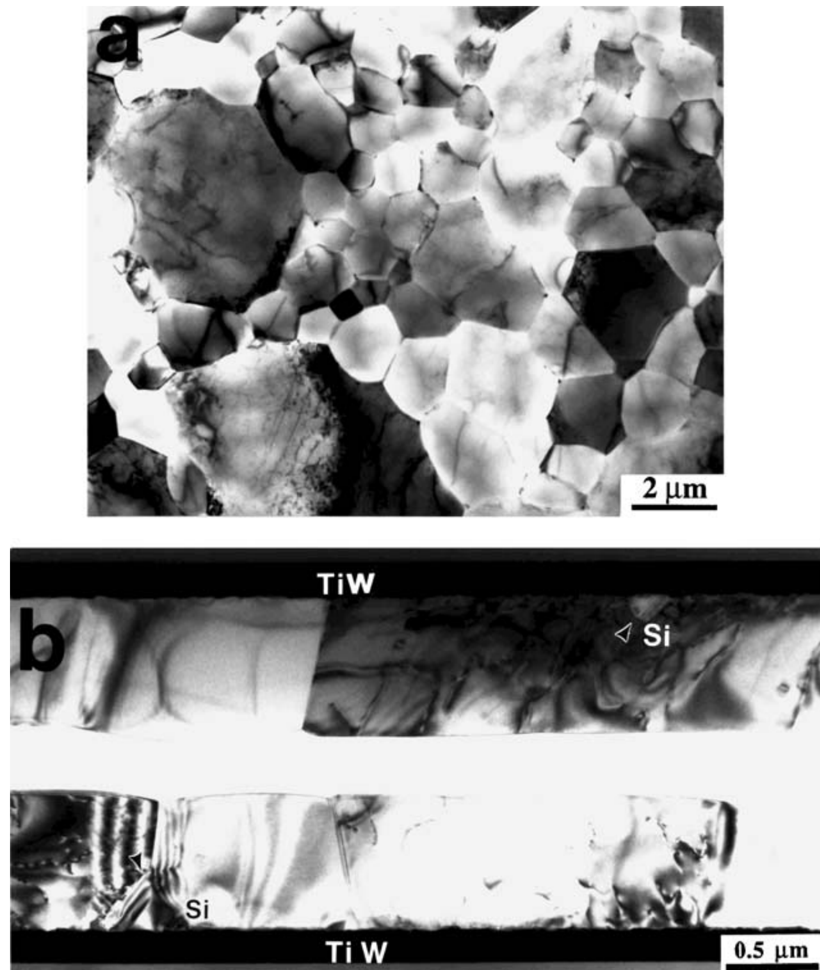

Figure 2 Microstructure of Al-1.5Cu-1.5Si film deposited at 435°C. (a) Plan-view TEM micrograph showing fine Al_2Cu (θ) phase precipitates at the grain boundaries (GBs) and triple points (TPs). (b) Cross-section TEM micrograph showing coarse Si precipitates at the sublayer interface.

in Fig. 1b. The Cu and Si distributions in the film determined by AES show a strong pileup of Cu and Si near the Ti-W sublayer interface for deposition at 305°C (Fig. 3a).

Fig. 2a shows a plan-view micrograph of the Al-1.5Cu-1.5Si film deposited at 435°C. 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 Cu and Si distributions determined by AES show that Cu is uniformly distributed through the thickness of the Al-1.5Cu-1.5Si film deposited at 435°C, but the Si distribution showed that it still remains piled-up at the Ti-W sublayer interface (Fig. 3b).

The as-deposited Al-1.5Cu-1.5Si film at 435°C underwent *in-situ* heat-treatments in the TEM. 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°C 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°C, the θ-phase precipitates rapidly dissolved into the Al matrix, while the Si precipitates continued to grow during holding at 450°C for five minutes (Fig. 4c). Upon cooldown, the θ-phase

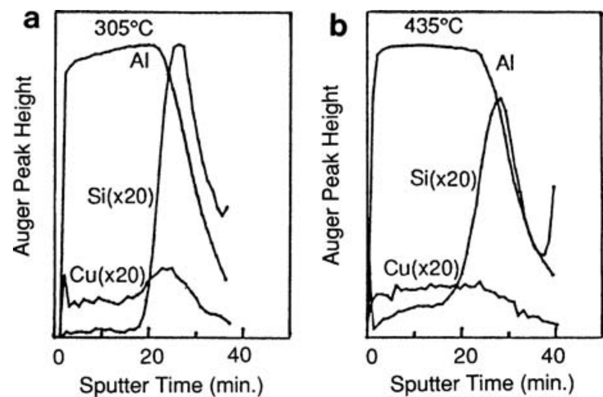

Figure 3 Depth distribution of Cu and Si in Al-1.5Cu-1.5Si film on a Ti-W sublayer, as determined by Auger electron spectroscopy. (a) 305°C deposition in the three-phase, Al(α)-Al_2Cu-Si region. (b) 435°C deposition in the two-phase, Al(α)-Si region.

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

The effect of Si addition and of the deposition temperature on the precipitate formation in Al-1.5Cu-1.5Si

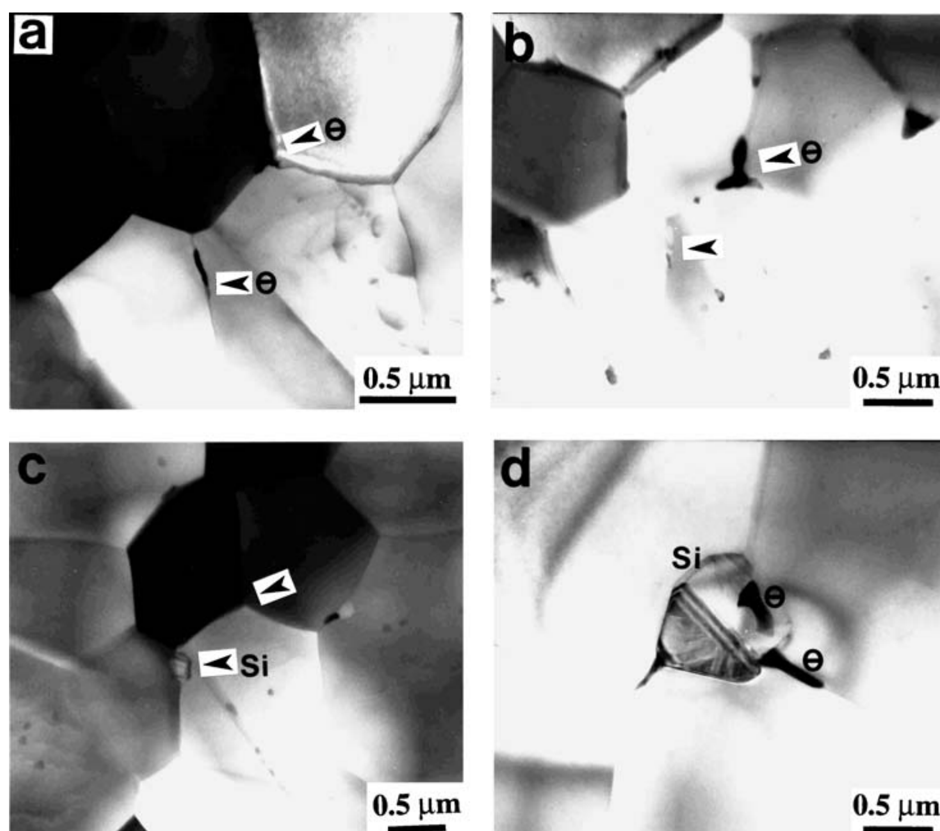

Figure 4 *In-situ* heat treatment of the Al-1.5Cu-1.5Si film deposited at 435°C for the following conditions; (a) 25°C, (b) 380°C and hold for 1 min, (c) 450°C and hold for 5 min, (d) 25°C. Coarsening, dissolution and reprecipitation processes of θ-phase particles are shown at the GBs. Precipitation of the Si particles is also shown at the GBs, twin boundaries, and within grains.

films can be understood by referring to the Al-Cu-Si phase diagram [9]. As can be seen from the phase diagram, Si added into an Al-Cu alloy does not form any interaction compounds with either Al or Cu. In addition, the Cu solid solubility does not change much with Si additions, as can be seen by comparing the Al-Cu phase diagram [10] with the Al-Cu-Si phase diagram [9]. The solid solubility of Si in Al is only ~0.1 wt% at 305°C and is only slightly higher than 0.4 wt% at 435°C. Thus, the addition of 1.5 wt% Si in Al results in formation of second phase Si during film deposition at either 305 or 435°C.

The Al-1.5Cu-1.5Si film is in the three-phase, Al(α)-Al_2Cu-Si region during deposition at 305°C. Excess Si can segregate and precipitate as elemental Si particles. The θ precipitates can also nucleate and grow during the film deposition. A pile-up of Cu and Si at the Ti-W sublayer interface is mainly due to the formation of interfacial θ and Si precipitates during deposition at 305°C (Fig. 3a). The Si addition resulted in a fine, uniform distribution of spherical θ precipitates in the Al-1.5Cu-1.5Si film deposited at 305°C. This is in direct contrast to the formation of coarse θ precipitates with an irregular shape, as we previously observed in an Al-1.5 Cu film deposited at 325°C [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 can result in a finer distribution of small θ precipitates. The interface between the θ and Si precipitates can also provide high diffusive path for the particle growth.

The Al-1.5Cu-1.5Si film was in the two-phase, Al(α)-Si region at the 435°C 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). The Si distribution indicated that it piled up at the Ti-W interface due to the formation of interfacial Si precipitates (Fig. 3b). However, the Cu profile is uniform throughout the film thickness for the deposition at 435°C. A similar trend was reported previously for the Al-1.5Cu film deposited at 465°C [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°C 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°C, 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

TABLE I Electrode potentials of aluminum solid solutions [11]. As measured against calomel electrode at 25°C

Al	−0.85 V
Al-1%Si	−0.81 V
Al-2%Cu	−0.75 V
Al_2Cu (θ)	−0.73 V
Al-4%Cu	−0.69 V

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°C (Fig. 4). Supersaturated Si segregated out as elemental Si nodules during heating at 380°C (Fig. 4b). The Si precipitates continued to grow during further heating at 450°C (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°C. As previously reported [8], the growth of the coarse θ-phase precipitate in Al-1.5Cu film during deposition in two-phase Al(α)-Al_2Cu region (325°C) 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°C 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 I shows standard electropotentials of Al metals and alloys in a solution of chloride ions with a calomel reference [11]. 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 I. *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°C) [9] 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 an Al-1.5Cu film resulted in a fine distribution of small θ-phase precipitates at a 305°C deposition temperature (three-phase, Al-Al_2Cu-Si region). This was due to the coprecipitation of θ and Si phase particles at the Ti-W sublayer interface. In the Al-1.5Cu-1.5Si film deposited at 435°C (two-phase, Al-Si region), the coarse, interfacial Si precipitates were observed at the sublayer interface along with fine θ-phase precipitates at the GBs. However, *in-situ* heating and cooling experiments of the film revealed that excess Si existed in a supersaturated Al matrix. Thus, 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°C and the matrix of Al-Si solid solution is less anodic than Cu-depleted Al matrix with respect to the θ-phase precipitate.

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