MICROSTRUCTURAL ANALYSIS OF COPPER THIN FILMS FOR CHARACTERIZATION OF STRESS-INDUCED VOIDING MECHANISMS

by

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Abstract

The amount of twin formation of electroplated and thermally treated copper thin films was evaluated by electron back-scattering diffraction (EBSD) analysis. The result establishes the importance of twin formation in the analysis of stress-induced voiding, and indicates that with the inclusion of a copper alloy co-element, twin formation was significantly reduced relative to pure-copper. Furthermore, the thermal stress hysteresis curve of the Cu-Sn(0.01wt%) thin film indicated a higher flow stress than that of pure-copper. These indications are consistent with the theory of suppressed grain deformation and reduced grain boundary elimination by particle pinning of grain boundaries during microstructure evolution of electroplated copper thin film. With the growth of the grains inhibited, both boundary filling and vacancy generation issues are suppressed, and the number of twin boundaries as void nucleation sites are reduced. Thus, the copper alloy film is believed to be more resistant to stress-induced voiding.

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CHAPTER I. INTRODUCTION

1.1 Overview

In the past five years, copper has replaced aluminum as the interconnect metal of choice in microchip fabrication.   The main advantage of copper is its low electrical resistivity and high resistance to electro-migration and stress-migration, (in comparison with aluminum.)   Lower resistance means that smaller and more tightly packed metal lines can carry the same amount of current. This leads to fewer levels of metal, faster speed, and lower production costs.

The chief drawback to copper is its high diffusivity. To prevent copper from diffusing into transistors, it must be encapsulated in a barrier film, usually a derivative of tantalum or titanium. In addition, to reduce the extra parasitic capacitance in denser circuits, dielectrics with lower dielectric constants must be used. The spin-on-coat process of low-k dielectric material requires furnace annealing to cure the film.

During this thermal processing, however, the copper is mechanically confined in the bulk layer by the barrier metal and in the vias/trenches by sidewalls. As the copper and dielectric materials are heated and cooled, their different thermal coefficients of expansion lead to a mismatch in the residual stress of the copper in the bulk layer and trenches. The mismatch leads to stress migration and eventually stress induced voiding (SIV) in the copper during chip operation. Voids increase the resistance and lead to chip failure. Obviously, this causes a severe problem in chip reliability.

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The current project investigates the stress characteristics of bulk copper films in an attempt to characterize the origins of stress voiding. This project also demonstrates that

SIV may be suppressed by replacing copper with a copper alloy. I investigated tin as a first likely candidate. The alloy reduces the overall change in grain size during thermal cycling, thereby suppressing the effects of mechanical confinement. My contribution to the project was to design the relevant experiments, perform the metrology, and interpret the results.

1.2 Background

1.2.1 Copper Plating

Electrochemical plating (ECP) is presently the most popular method used for Cu deposition in semiconductor fabrication processes. The electrodeposition of copper (or any other metal) is achieved by placing a piece of conducting material into a solution (electrolyte) containing copper ions. The conductor is placed in electrical contact with a power supply, and current passes through both the conductor and the solution. This induces a reaction between the copper ions and the conducting surface to form a metal on the surface of the conductor. In the present experiments, the conducting surface used is a silicon wafer containing a thin layer of copper deposited by sputtering. As copper is plated on the cathode (negative electrode), copper goes into the solution at the anode (positive electrode) as copper(II) ions, maintaining a constant concentration of copper(II) ions in the electrolytic solution. Figure 1 shows a diagram of a typical plating setup with the relevant chemical reactions shown next to the cathode and anode.

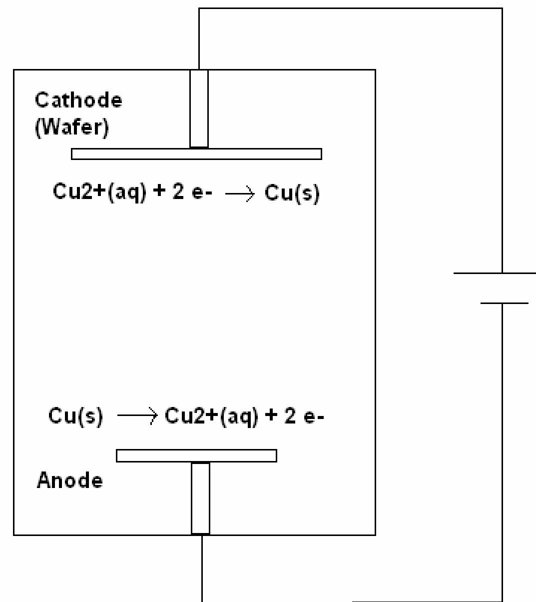

Figure 1. Schematic of copper electroplating chamber and process.

1.2.2 Damascene Process

Microchips fabricated using copper interconnects are made using the damascene process. In the damascene process, a dielectric layer is first deposited and then etched using photolithographic techniques. Etching the dielectric layer leaves a pattern of trenches into which copper is then deposited by plating. Electroplating, of course, deposits a copper film covering both etched and non-etched areas; so after plating, the whole surface must be polished down until the only copper remaining resides in the trenches. The resulting copper lines (in the trenches) form the circuit through which current will pass in a fully functioning microchip. These trenches are where the thermal

expansion and contraction of copper is most critical, due to the increased mechanical confinement.

Until copper replaced aluminum as an interconnect metal, aluminum was first deposited and then space was etched for the dielectric, the reverse of the damascene process. Even though the aluminum process in many respects is less technically challenging and certainly more thoroughly studied, it cannot be used for copper. This is because copper is not easily etched. Since the more difficult damascene process must be used for copper plating, the process must be much more carefully controlled in order to properly fill trenches and prevent excessive stress migration during annealing.

1.2.3 Stress Induced Voiding (SIV)

Stress migration failure was not originally expected for Cu, since it normally has lower diffusivity than aluminum. However, voiding in passivated (encapsulated) copper films was observed in the very first attempts to fabricate copper interconnect structures. [1] In films that are mechanically confined, as in the damascene process, thermomechanical stresses are induced during cooling after thermal annealing. After cooling, the film is in a state of hydrostatic tension. The resulting stress is the driving force behind both void nucleation and subsequent morphological evolution. [2]

The phenomenon of stress-induced voiding is generally understood as a result of stress mismatch in materials [3] and structures [4] in copper interconnects. Copper is mechanically confined in the trenches and via holes by sidewall barrier metal and encapsulation dielectric film. This results in stress mismatch after thermal cycling, which leads to stress-induced voiding during the subsequent process steps and chip operation.

Microstructural analysis of copper thin film is increasingly important for understanding stress-induced voiding kinetics. Microstructure dependence of stress-induced voiding in copper thin films mainly comes from its effects on vacancy diffusion and void nucleation [5-8]. The grain boundaries themselves are full of vacancies, and the free volume released by grain growth as the result of grain boundary elimination creates sizeable voids [5]. Also, the grain boundary is one of the fast diffusion paths in copper interconnect, and the diffusivities are influenced by the misorientation angle of grain boundaries [6, 7]. Moreover, twin boundaries have been found to be nucleation sites for stress-induced voiding due to thermal stress concentration at their interfaces [8]. So, copper films with larger grains (fewer grain boundaries) that also maintain strong crystallographic orientation and minimum twin formation are preferred for stress-induced voiding resistance in copper interconnects.

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Many methods have been suggested to suppress stress voiding in copper interconnects. Most of these involve either altering the geometry of the line/via structure, changing the dielectric materials to improve passivation, or optimizing the thermal cycling process in an attempt to make it more robust.[5] In addition, it has been theorized that the inclusion of a small amount of a second metal in copper thin films during electroplating and its subsequent segregation at grain boundaries by thermal treatment suppresses the copper grain boundary diffusivity. Also, in addition to possibly creating interstitial defects in the copper crystallite lattice, the alloyed co-element may fill the vacancies inherent at grain boundaries. The co-element thereby affects both the grain size distribution and thermal-mechanical properties (i.e. flow stress) of the copper thin films by particle pinning of grain boundaries. [9] In the present study, a Cu-Sn(0.01wt%) thin film was subjected to

grain size, grain orientation, and twin fraction analysis by electron backscattering diffraction (EBSD) [10] and compared to those of pure-copper thin films to evaluate the potential advantage for stress-induced voiding.

Chapter II. EXPERIMENTAL SETUP

2.1 Process Characteristics

800 nm copper thin films were deposited by electroplating over PVD copper seed (125 nm) with PVD Ta (25 nm)/Thermal-SiO_2 (500 nm) underlayers on Si-substrate using a process after that of Padhi *et al.* [11]. In the copper alloy experiment, tin-sulfate along with anti-oxidation stabilizer was dosed into the electroplating bath to incorporate tin into copper thin film while electroplating. The samples were annealed at various annealing conditions for 1min in a forming gas ambient immediately following the deposition. Forming gas is dilute H_2 in an inert gas. Tin incorporation in the copper thin film was confirmed by secondary ion mass spectroscopy (SIMS) analysis. Copper lattice spacing calculation, during in-plane strain analysis by x-ray diffraction (XRD), was also employed to complement the SIMS analysis result. EBSD was applied for grain size and grain orientation analysis, and twin fraction was also acquired from the EBSD grain-orientation images.

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2.2 Experimental Setup

2.2.1 300 mm Center to Edge Annealing Experiment

Three experiments were performed to characterize the possible causes of stress migration failure in copper interconnects. The first was an analysis of the differences in the center and edge of 300-mm copper-plated wafers. It had been previously observed that the highest rate of stress migration failure results from chips fabricated on the edge of 300-mm wafers, while chips fabricated in the center show a dramatic reduction in

failures due to stress induced voiding. Extensive microstructure analysis was therefore performed after the samples were annealed in various ways. Table 1 shows the matrix of annealing conditions used in this experiment. Note that the cool-down rate is changed by varying the distance between the wafer and the cooling plate, which is at a constant temperature.

	Low	***Mid***	***High***
Anneal Temp.	150 C	180 C	210 C
Anneal Time	30 sec.	60 sec.	90 sec.
Cooling Rate	3850 steps 30 sec	3800 steps 30 sec	3500 steps 60 sec

Table 1. Matrix of annealing conditions used in 300 mm center to edge experiment.

2.2.2 200 mm Cu and CuP Anode Experiment

In the second experiment, the microstructural properties of 200-mm wafers were analyzed with two different metal compositions used as anodes during plating. There are two anodes currently used in industry for plating 200-mm copper wafers. The first and most common is a high purity uniform copper wafer. The second, less commonly used anode is composed of copper doped with phosphorus. The phosphorus is included to prevent adverse competing reactions at the anode. Applied Materials uses pure copper anodes, but their chief competitor uses copper phosphorus and seems to have a greater resistance to stress migration.

2.2.3 200 mm CuSn experiment

The third experiment was similar to the anode experiment described in the previous section, except that a chemical difference is introduced in the electrolyte bath rather than changing the anode. I chose tin as the dopant in this experiment since I thought that it may be co-deposited with the copper and integrate into the microstructure of the plated copper film. (This turned out not to be the case because of a steep deposition potential curve due to underpotential effects. The tin was merely flowed in.) The microstructure of this film was then compared to the standard film.

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Chapter III. RESULTS

3.1 Experiment 1: Comparison of Center to Edge

Figure 2 shows that the wafer stress is not significantly different in the center than at the edge after plating and annealing. This suggests that local stress in the copper may not be the reason for stress migration failure. Typical tensile stress measurements for the ECP films at both center and edge of the wafer were between 85 and 90 GPa.

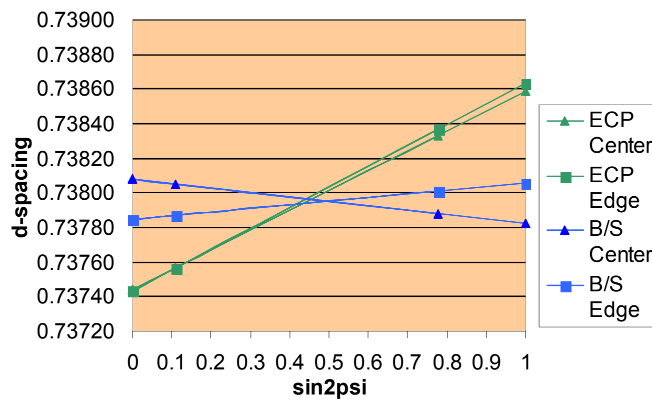

Figure 2. Stress difference between center of edge of 300 copper plated wafer and sputtered copper barrier/seed film.

Table 2 shows the measured crystallite size from XRD in the <111> orientation at both the center and edge of the wafer after annealing. While the barrier/copper seed layer shows uniform crystallite size, the plated copper shows a significant increase in crystallite size near the wafer center. Table 3 shows the strength of the <111> preferred orientation. While the crystallites at the edge with <111> orientation show stronger texture (i.e. narrower peaks) there are relatively much fewer of them. This is indicated by the high percentage of random and other orientations at the wafer edge.

Wafer	Location	FWHM	Corrected FWHM*	Crystallite Size (Å)
B/S	Center	0.221	0.092	473
	Edge	0.222	0.093	476
ECP	Center	0.172	0.043	942
	Edge	0.158	0.029	751

Table 2. Crystallite size of copper ECP film after annealing as measured by XRD.

Wafer	Location	10% (degrees)*	50% (degrees)*	63% (degrees)*	90% (degrees)*	% Random	Other Orientations
B/S	Center	0.46	2.6	3.4	6.6	<5%	None
	Edge	0.40	2.3	3.0	6.0	<5%	None
ECP	Center	0.71	3.6	4.8	8.8	37%	(511) and others
	Edge	0.42	2.4	3.2	6.0	60%	(511) and others

Table 3. Strength of <111> crystallite orientation at wafer center and wafer edge measured by XRD. The table indicates the angular spread in the measured diffraction peak containing 10, 50, 63, and 90 percent of the peak. The narrower the peak, the stronger the texture.

Figure 3 shows EBSD generated pole figures that indicate that the wafer center has much stronger <111> texture than the wafer edge after annealing, confirming the XRD analysis shown above.

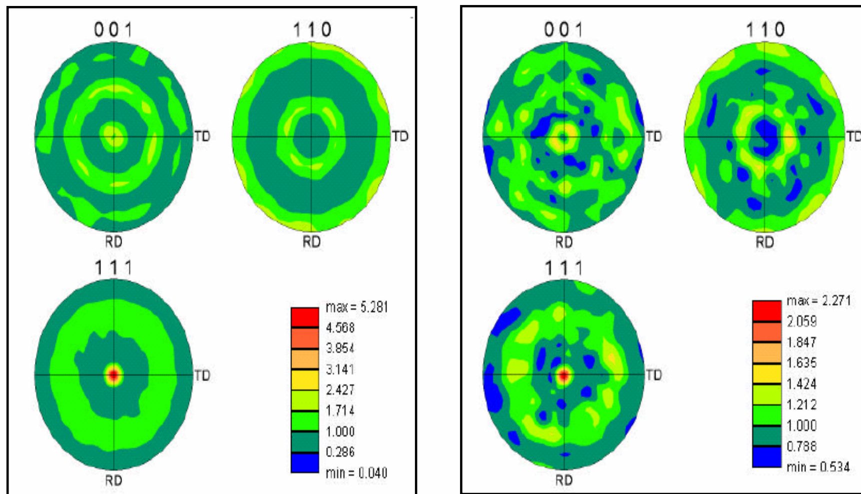

Figure 3. Representative EBSD pole figures of 300 mm wafers after annealing at wafer center (a) and edge (b).

The grain size distribution was also found to vary among different annealing conditions. Notably, when the same data are graphed excluding twin grain boundaries, the average grain size at the wafer edge is significantly higher than the average grain size at the center.

Figure 4 shows the resulting grain size distribution from the matrix of annealing conditions shown in table 1, as measured by EBSD.

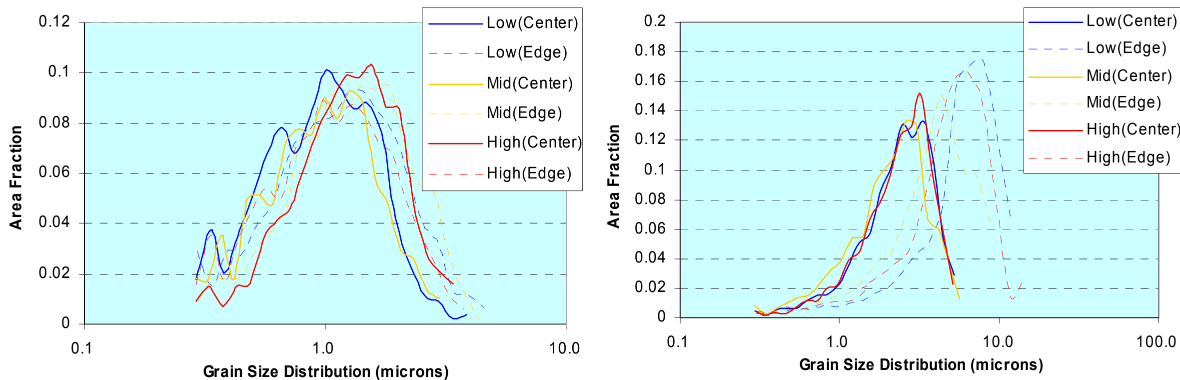

Figure 4. Grain size distribution different among different post ECP anneal conditions shown in table 1.

These data reveal that with the same thermal treatment, the lattice structure at the wafer edge is much more likely to deform to a more negative free energy, twin-boundary state. This suggests that the lattice was in a higher energy state upon deposition and required less energy input during thermal cycling to induce plastic deformations. As indicated by the grain texture measurements, this is probably due to weaker texture and hence lower binding energies. As more heat is applied, the observed disparity in twin formation from center to edge increases. Excessive grain growth and the corresponding weaker texture are likely the cause of stress migration failure at the wafer edge.

3.2 Experiment 2: Comparison of Copper anode with the Copper-Phosphorus Anode on Microstructure of Copper Films

Figure 5 shows lattice strain and spacing measurements for wafers plated using a copper anode system as opposed to a copper-phosphorus anode. Although the in-plane strain (slope) in on the same order of magnitude (about 100GPa), the copper on the wafers deposited using with the copper-phosphorus anode show different lattice spacing (intercept) at the wafer edge than those produced with the customary pure copper anode.

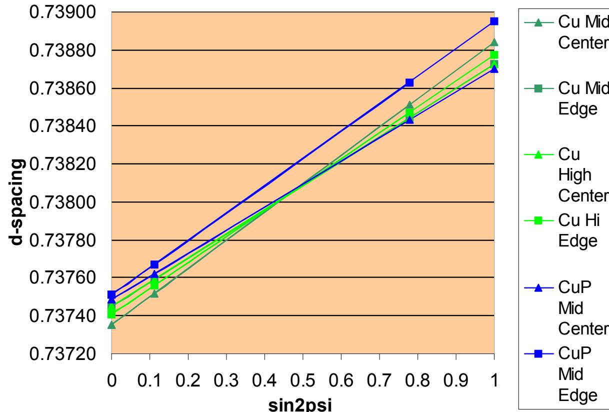

Figure 5. Lattice spacing of Cu and CuP as measured by XRD

Wafer	Location	Stress (Gpa)
CuP	Center	91.2
	Edge	108.1
Cu Mid	Center	111.47
	Edge	95.71
Cu High	Center	95.70
	Edge	102.46

Table 4. Local Stress of Cu and CuP ECP films

Secondary ion mass spectroscopy (Figure 6) revealed slightly higher amounts of phosphorus in the copper films plated with the copper-phosphorus anode, suggesting that the increased lattice parameter near the wafer edge shown in figure 5 may be due to increased amounts of phosphorus. Recall that the center vs. edge texture data from experiment 1 reveal weak texture at the wafer edge, implying excess volume due to grain boundary misalignment. This suggests that the phosphorus may be accumulating at the grain boundaries. X-ray diffraction further revealed the average crystallite size in the copper plated with a phosphorus anode to be roughly half as large as the crystallites

plated with the pure copper anode. (450 vs. 900 angstroms). This was also found to be consistent with surface roughness and hardness analysis, which showed that the phosphorus wafers had both harder and rougher surfaces. This suggests that the phosphorus precipitates to the grain boundaries to fill excess volume and raises the critical free energy necessary for both plastic and elastic deformation.

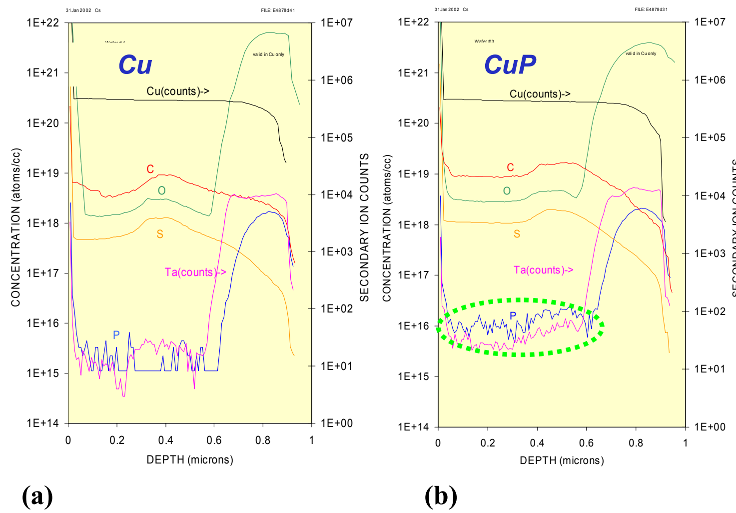

Figure 6. Depth profile of impurity concentrations in the electroplated copper thin films by SIMS analysis: (a) Cu and (b) CuP

X-ray diffraction texture analysis (Table 5) show that the pure copper wafers have strong <111> orientation, while the phosphorus doped wafers have only moderate <111> orientation. In addition, the pure copper wafers show significant <511> twinning, and additional "other" orientation. Hence, even though, the phosphorus doped films have weaker texture, they show much lower amounts of <511> twinning and random components, suggesting that the grain boundaries have been effectively pinned during thermal annealing. Electron backscattering pole figures (Figure 7) also reveal the strong <111> texture in both films.

Wafer	Location	10% (degrees)*	50% (degrees)*	63% (degrees)*	90% (degrees)*	% Random	Other Orientations
CuP	Center	0.16	0.94	1.3	3.3	13	(511) trace
	Edge	0.21	1.2	1.7	3.8	13	(511) trace
Cu	Center	0.11	0.75	1.1	2.4	20	(511) and others
	Edge	0.13	0.62	0.88	2.1	23	(511) and others

Table 5. Strength of Cu and CuP ECP films <111> crystallite orientation at wafer center and wafer edge measured by XRD.

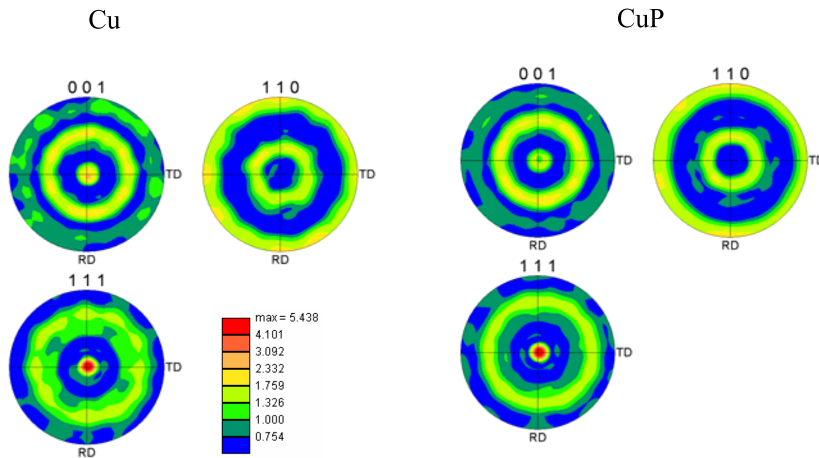

Figure 7. EBSD generated pole figures for Cu and CuP ECP films.

3.3 Experiment 3: CuSn Microsructure Analysis

3.3.1 Film Composition Analysis

SIMS analysis indicated uniform distribution of tin incorporated across the bulk of the electroplated copper thin film without significantly affecting the other impurity concentrations, i.e. oxygen and carbon, as shown in Figure 8.

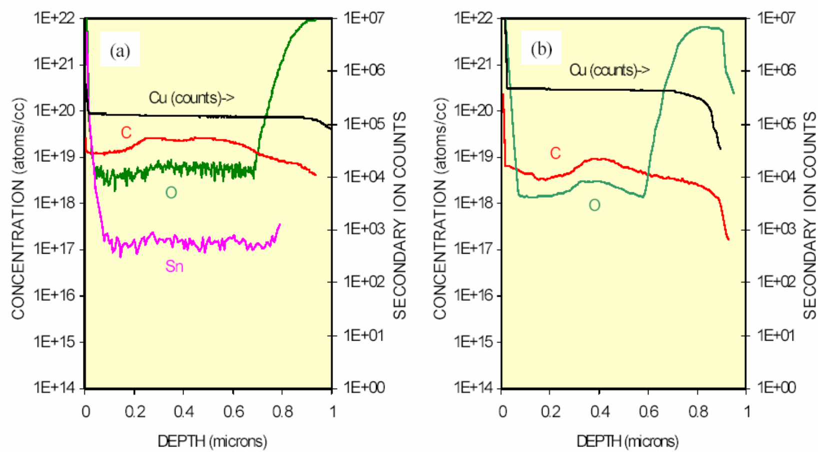

Figure 8. Depth profile of impurity concentrations in the electroplated copper thin film by SIMS analysis: (a) Cu-Sn and (b) pure-copper. Tin concentration is uniformly distributed across the bulk of the copper film, and the increase of oxygen (by tin oxidation in the plating bath) and carbon (by dosing tin anti-oxidation stabilizer) impurities is considered to be insignificant.

Based on the SIMS data, the weight percentage of tin in the copper thin film was calculated as shown in figure 9, which confirmed ~100ppm (by weight) of tin uniformly incorporated across the bulk of the copper film.

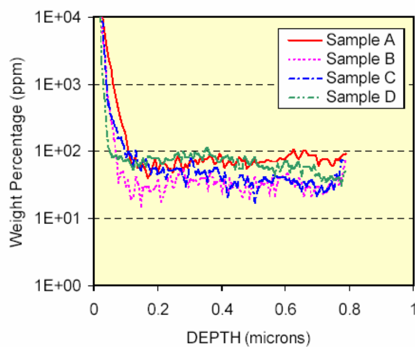

Figure 9. Depth profile of tin concentration, by weight percentage, in the electroplated copper thin film by SIMS analysis. Indicated ~100ppm of tin uniformly incorporated across the bulk of the copper film.

XRD in-plane strain analysis revealed decreased lattice spacing of the Cu-Sn thin film, as shown in figure 10, while obtaining the same magnitude of in-plane strain as the pure-copper thin film (see table I). This is possibly due to the interaction of the incorporated tin with the copper crystallite lattice structure, and thought to be consistent with the results of grain size analysis by EBSD, explained below, and film hardness observations, which showed that the Cu-Sn film has smaller grains and greater hardness in polishing process. This suggests that the tin possibly precipitates at copper grain boundaries filling excess volume and pinning the grain boundaries, which results in an increase of the critical energy necessary for grain growth, thereby affected the lattice spacing.

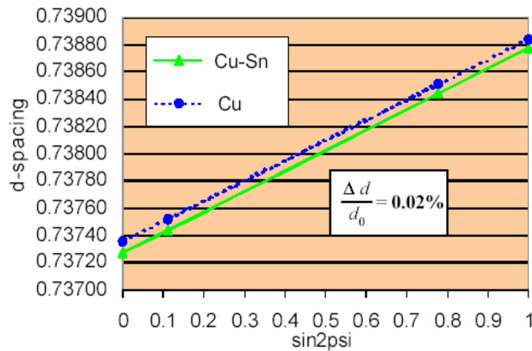

Table I. Cu-Sn vs. pure copper in-plan strain values obtained by XRD analysis

Sample	Strain (MPa)
Cu	111.47
Cu-Sn	112.60

Figure 10. XRD plot for in-plane strain analysis of the electroplated copper thin films. ~0.02% decrease in lattice spacing observed with the Cu-Sn thin film compared the pure-copper thin film.

3.3.2 Film Microstructural Analysis

EBSD pole figures indicate that the Cu-Sn thin film has a similarly strong (111) grain orientation as the pure-copper thin film, as shown in figure 11.

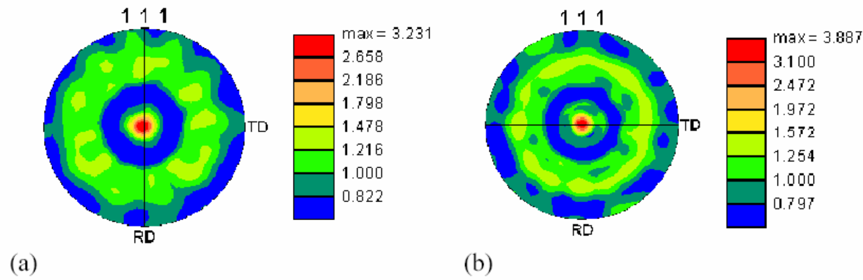

Figure 11. EBSD (111) pole figures of the electroplated copper thin films: (a) Cu-Sn and (b) pure-copper. Both the Cu-Sn and pure-copper thin films showed (111) preferred orientation, although both contain slight random components.

EBSD grain-orientation images of both the Cu-Sn and pure-copper thin films were analyzed to determine grain-size distribution. Comparing the two grain-size distributions shown in figure 5, it is apparent that the Cu-Sn thin film has smaller grains than the pure-copper thin film.

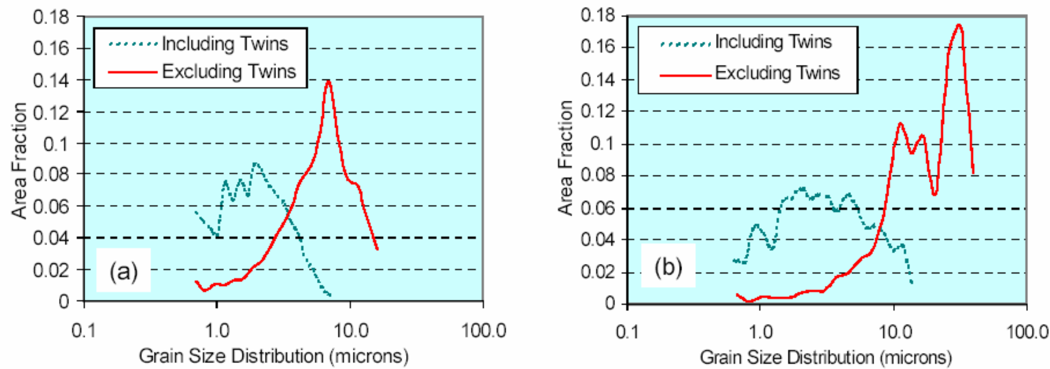

Figure 12. Grain size distribution plots from EBSD grain-orientation image analysis of the electroplated copper thin films: (a) Cu-Sn and (b) pure-copper. The Cu-Sn film showed significantly smaller grain size and lower twin fraction than the pure-copper film.

The EBSD analysis result of smaller grains with the Cu-Sn thin film after the same thermal annealing process, also suggests improved thermal-mechanical stability of the Cu-Sn thin film over the pure-copper thin film. A thermal stress hysteresis curve was obtained to determine the flow stress (the maximum stress at elastic-plastic flow transition) of the two films, and the result is shown in figure 6. The higher flow stress of the Cu-Sn thin film consisting of smaller grains was confirmed to be consistent with Hall-Petch model for grain size dependence of yield stress.

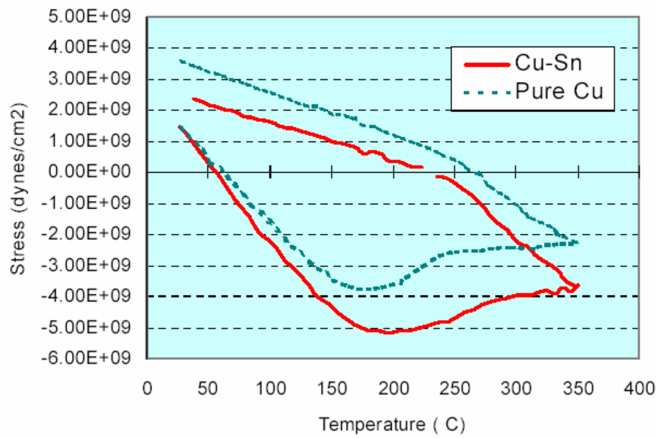

Figure 13. Thermal stress hysteresis curves of the electroplated thin films. A significant increase of flow stress is seen with the Cu-Sn film compared to the pure-copper film.

Finally, as seen in the grain size distribution difference between the two different grain boundary definitions (including vs. excluding twin boundaries as grain boundaries) in figure 5, the overall fraction of twinned grains is smaller with the Cu-Sn film compared to the pure-copper film. This suggests that the inclusion of tin increased the resistance of

the copper thin film to plastic deformation and hence twin formation. The twin fractions for the Cu-Sn and pure-copper thin films were calculated to be 0.67 and 0.72, respectively. The number fractions of ∑3 boundaries were 0.56 and 0.59 for the Cu-Sn and pure-copper thin films, respectively, while overall number fraction of CSL boundaries was 0.79 for both films. This result also indicates the advantage of Cu-Sn film over pure-copper film in suppressing the formation of ∑3 boundaries where the stress-induced voiding is believed to nucleate.

3.4 Conclusions

Microstructural analysis of electroplated copper thin films revealed that a copper-tin alloy has a potential advantage over pure-copper in the suppression of stress-induced voiding. The small amount of tin co-deposited from the copper electroplating bath apparently becomes segregated to the grain boundaries, where it fills vacancies and lowers the grain-boundary energy and diffusivity, effectively pinning the grain boundaries. This serves to suppress the grain growth, and the resulting small grain size raises the flow stress and improves the thermomechanical stability of the thin film. In addition, since grain-boundary twinning is caused by single-grain deformation during grain growth, the suppression of grain growth also results in less twin formation. Both of these effects, the improved thermal-mechanical stability and the decreased twin content, contribute to the suppression of stress-induced voiding in copper-tin alloy thin films.

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