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GROWTH AND OXIDATION OF THIN FILM Al_2Cu

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ABSTRACT

Al_2Cu thin films (~382 nm) are fabricated by melting and resolidifying Al/Cu bilayers in the presence of a ~ 3 nm Al_2O_3 passivating layer. X-ray Photoelectron Spectroscopy (XPS) measures a 1.0 eV shift of the $\text{Cu}2p_{3/2}$ peak and a 1.6 eV shift of the valence band relative to metallic Cu upon Al_2Cu formation. Scanning Electron Microscopy (SEM) and Electron Back-Scattered Diffraction (EBSD) show that the Al_2Cu film is composed of 30-70 μm wide and 10-25 mm long cellular grains with (110) orientation. The atomic composition of the film as estimated by Energy Dispersive Spectroscopy (EDS) is $67\pm2\%$ Al and $33\pm2\%$ Cu. XPS scans of $\text{Al}_2\text{O}_3/\text{Al}_2\text{Cu}$ taken before and after air exposure indicate that the upper Al_2Cu layers undergo further oxidation to Al_2O_3 even in the presence of ~5 nm Al_2O_3 . The majority of Cu produced from oxidation is believed to migrate below the Al_2O_3 layers, based upon the lack of evidence for metallic Cu in the XPS scans. In contrast to Al/Cu passivated with Al_2O_3 , melting/resolidifying the Al/Cu bilayer without Al_2O_3 results in phase-segregated dendritic film growth.

INTRODUCTION

Al_2Cu is a common precipitate in Al rich Al/Cu systems and known to have strong effects on both the corrosion resistance of Al(Cu) alloys and the electromigration reliability of Al(Cu) interconnects.¹⁻⁴ The precise mechanisms for corrosion initiation at Al_2Cu precipitates in Al-Cu alloys are not well understood, but may depend upon the galvanic relationship to the matrix, the properties of the oxide at the surface and/or the changes they induce in the local solution chemistry. In order to enable studies of the properties of pure theta phase Al_2Cu and (it's) oxide, we have fabricated thin films by melting/re-solidifying Al/Cu bilayers. We find that the phase formation and morphology depend upon the type of oxide present at the Al surface before melting, and that the oxidation of Al_2Cu is considerably different from that of pure Al.

EXPERIMENTAL

Al/Cu bilayers were prepared by sequential Cu (100.0 nm) and Al (281.9 nm) deposition using electron-beam evaporation of 99.9999% pure Cu and Al, respectively, in

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a vacuum chamber; the background pressure of the system was $< 1 \times 10^{-8}$ Torr, and the pressure during film deposition was $\sim 1 \times 10^{-6}$ Torr. The films were grown on a thermally oxidized Si (100) substrate at ambient temperature, at a growth rate of ~ 0.1 nm/s. The bilayer was melted at 580 °C for 10 min in vacuum, followed by cooling for re-solidification at ~ 10 °C/s. X-ray Photoelectron Spectroscopy (XPS) was performed in situ using an Al K α source (300 W) and a VG100AX electron energy analyzer (20 eV pass energy); the resolution measured for the Au4f $_{7/2}$ peak was 1.3 eV. The binding energy scale was calibrated with metallic Au4f $_{7/2}$ (84.0 eV), Ag3d $_{5/2}$ (368.3 eV), and Cu2p $_{3/2}$ (932.6 eV) peaks. The morphology and composition were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) in a JEOL JSM-845A microscope with an Oxford Link Isis attachment. The grain orientation in the films was determined using Electron Back-Scattered Diffraction (EBSD) measured and indexed by an Oxford Opal system. The quantity of Al and Cu in the Al/Cu bilayers was determined with Rutherford Back-scattering Spectrometry (RBS).

RESULTS AND DISCUSSION

Melting and re-solidification of thin Al/Cu bilayers (Al:Cu $\sim$ 2:1) covered with native oxide, i.e. Al $_2$ O $_3$ /Al/Cu, results in continuous Al $_2$ Cu film formation as evidenced by XPS, EDS, and SEM. Figure 1 shows Cu2p XPS and valence band (VB) spectra of (a) a metallic Cu film and (b) the Al $_2$ O $_3$ /Al/Cu after melting and re-solidification. Metallic Cu shows a Cu2p $_{3/2}$ peak at 932.6 eV, a Cu2p $_{1/2}$ peak at 952.4 eV, and a VB peak at 2.7 eV. After melting/re-solidification, these peaks shift to higher binding energies; Cu2p $_{3/2}$ to 933.6 eV, Cu2p $_{1/2}$ to 953.5 eV, and VB to 4.3 eV, indicating Al $_2$ Cu formation.⁵ These chemical shifts are not caused by Cu oxidation or surface charging; Cu2p satellite peaks, characteristic of CuO, do not appear in this spectrum, and the Cu2p $_{3/2}$ binding energy (BE) would be 932.5 eV if Cu $_2$ O were formed.⁶ The Cu LMM AES peak of the heated sample appears at 918.4 eV (Figure 2b), compared to 918.6 eV for metallic Cu (Figure 2a), 918.1 eV for CuO, and 916.2 eV for Cu $_2$ O.⁶ The Al2p peak at 72.9 eV does not shift, as expected for Al $_2$ Cu formation;⁵ this also confirms there is no significant surface charging during the XPS scan for this sample.

We also observe an Al2p peak at 75.8 eV, corresponding to Al $_2$ O $_3$. The native oxide (Al $_2$ O $_3$) in the Al $_2$ O $_3$ /Al/Cu sample was formed from a 5 day air exposure, which results in a thickness of ~ 3 nm as estimated from the Al2p peak intensity. The relative intensity of this oxide peak is increased after the melting/resolidification, resulting in an estimated thickness of 5 nm.⁷ The thickening of Al $_2$ O $_3$ layer may be caused by continued Al oxidation due to the high reaction temperature and/or due to the presence of more conductive Cu. It may also be caused by oxidation of Al $_2$ Cu formed from the reaction; we have observed binding energies characteristic of Al $_2$ Cu at the Al/Cu interface of very thin Al/Cu bilayers and in Al codeposited with Cu at ~ 30 °C, indicating that Al $_2$ Cu formation starts far below the 580 °C annealing temperature. In fact, our in-situ TEM study shows a crystalline diffraction pattern consistent with Al $_2$ Cu at 370 °C.⁸

An SEM image of the annealed Al $_2$ O $_3$ /Al/Cu (Figure 3a) clearly shows a continuous Al $_2$ Cu film with cellular grain growth. We observed that the width of Al $_2$ Cu cellular grains

depends strongly on cooling rate; the grains shown in Fig. 3(a) are 30-70 μm wide and 10-25 μm long. EBSD patterns taken from several different areas of the film show that the cellular grains have preferred (110) orientation (Fig. 3(d)). In situ TEM studies of melting and re-solidification of $\text{Al}_2\text{O}_3/\text{Al}/\text{Cu}$ samples show that nanometer sized polycrystalline grains of Al_2Cu are formed below 200 $^\circ\text{C}$ and grow in size until melting.⁸ Crystalline (110) grains are formed upon cooling from the melt, where the grain size increases with cooling rate.⁸

Melting and re-solidification of thin Al/Cu bilayers ($\text{Al}:\text{Cu}\sim 2:1$) in situ, without exposure to air or oxygen, results in phase-segregated dendritic film growth. An SEM image of the Al/Cu sample heated in situ is shown in Figure 3(b). Three distinctive regions are observed: bright dendrites interspersed with dark dendrites, and a small fraction of segregated islands. EDS analysis indicates that the atomic composition of the bright dendrites is $62\pm 2\%$ Al, $38\pm 2\%$ Cu, which is close to the composition of Al_2Cu . The atomic composition for the dark dendrites is $93\pm 2\%$ Al, $7\pm 2\%$ Cu, and that for the bright islands is $33\pm 2\%$ Al, $67\pm 2\%$ Cu.

The influence of the type of surface oxide on the microstructure was further investigated by forming an oxide in the vacuum chamber prior to melting and re-solidification. An Al/Cu bilayer was exposed to an oxygen plasma generated by an electron cyclotron resonance (ECR) source for 10 min in situ. Compared to the air-formed aluminum oxide, the oxide grown with the oxygen plasma has a lower $\text{Al}2\text{p}$ binding energy as indicated by XPS; the $\text{Al}2\text{p}$ BE is 75.6 eV for the air-formed oxide (Figure 4a) and 74.7 eV for the plasma-formed oxide (Figure 4(b)). Thickness estimates based on XPS results⁷ indicate that the plasma-formed oxide is ~ 2 nm thicker than the air-formed oxide. However, once exposed to air, $\text{Al}-\text{O}$ bonding in the plasma-formed oxide becomes similar to that in the air-formed oxide, as indicated by the $\text{Al}2\text{p}$ BE shift to 75.8 eV (Figure 4c). No obvious change in either thickness or oxygen content upon air exposure was noted for the ECR formed oxide. In situ melting and re-solidifying the Al/Cu bilayer covered by a plasma-formed oxide does not result in a continuous Al_2Cu film. A phase-segregated film, composed of islands and bright dendrites dispersed with dark dendrites, is produced as shown in Figure 3(c). The portion of segregated islands is much higher in this film than in the film grown without oxide. The atomic composition, estimated by EDS, is $42\pm 2\%$ Al, $58\pm 2\%$ Cu for the bright islands, $76\pm 2\%$ Al, $24\pm 2\%$ Cu for the bright dendrites, and $94\pm 2\%$ Al, $6\pm 2\%$ Cu for the dark dendrites.

The fact that continuous, phase pure Al_2Cu is produced upon cooling from the melt only in the presence of an air-formed oxide (i.e. $\text{Al}_2\text{O}_3/\text{Al}/\text{Cu}$), suggests that native Al_2O_3 is structurally rigid and chemically stable at temperatures up to 580 $^\circ\text{C}$. By contrast, the ECR plasma-formed oxide is chemically and structurally less stable at these temperatures, and does not keep the Al/Cu films from phase-segregating after melting and re-solidification. These results suggest that the stability of the oxide rather than the thickness is the key factor in controlling the resulting morphology.

The oxide formed on Al_2Cu must support electron transfer during localized corrosion of Al at Al_2Cu precipitates in $\text{Al}(\text{Cu})$ alloys. A thorough understanding of this process requires knowledge of the structural and electrical properties of the oxide. Previous studies show conflicting results on Al_2Cu oxidation. Li et. al. claimed no oxidation of Al_2Cu , based on RBS and x-ray diffraction analyses of an $\text{Al}_2\text{Cu}/\text{Al}$ bilayer on an SiO_2 substrate.⁹

Scully et. al. suggested that Al_2Cu oxidation results in Cu dispersed in Al_2O_3 , based on their XPS and AES measurements on cast Al_2Cu .¹⁰ Chiu et. al. observed Al_2Cu oxidation to Al_2O_3 and Cu in an Al film containing Cu (1 weight %) and Si (0.5 weight %), where the Cu was located primarily at the $\text{Al}_2\text{O}_3/\text{Al}$ interface, as determined by cross sectional TEM, secondary ion mass spectroscopy (SIMS), and EDS.¹¹

A comparison of the XPS scans of $\text{Al}_2\text{O}_3/\text{Al}_2\text{Cu}$ taken before and after a 3 day air exposure is shown in Figure 5, where the $\text{Al}_2\text{O}_3/\text{Al}_2\text{Cu}$ samples were prepared by annealing $\text{Al}_2\text{O}_3(\text{native})/\text{Al}/\text{Cu}$, as mentioned above. Following air exposure, the $\text{Al}2\text{p}/\text{Cu}3\text{p}$ XPS shows increased $\text{Al}2\text{p}$ intensity for Al_2O_3 (75.6 eV BE) and decreased $\text{Al}2\text{p}$ intensity for Al_2Cu (72.8 eV BE), Figure 5 (a). The $\text{Cu}3\text{p}$ shoulder in Figure 5 (a) ($\text{Cu}3\text{p}_{3/2}$ at 75.9 eV BE and $\text{Cu}3\text{p}_{1/2}$ at 78.4 eV BE for Al_2Cu) shows a clear intensity decrease after oxidation in air. The 3 day air exposure results in an increase in oxide thickness from ~5 nm to ~8 nm, as estimated by XPS peak fitting.⁷ Figure 5 (b) shows a dramatic decrease in the $\text{Cu}2\text{p}$ intensity after air exposure. However, the $\text{Cu}2\text{p}$ peaks are not shifted, and no indication of CuO or Cu_2O formation is observed. These results suggest that Al_2Cu undergoes oxidation to form Al_2O_3 and Cu even under ~5 nm of Al_2O_3 , unlike the $\text{Al}_2\text{O}_3(\text{native})/\text{Al}$ system, which passivates at ~3 – 5 nm. Decreased intensities but no chemical shift for $\text{Cu}2\text{p}$ and Cu LMM peaks Figure 2(c) indicate that the majority of Cu produced from Al_2Cu oxidation either migrates below the photoelectron escape depth or is converted to Al_2Cu beneath the oxide layer. Note that the Al/Cu bilayer used in this study was Al rich by a few percent, which could provide a source of Al for the reaction with Cu. Recall, as mentioned above, that Cu and Al atoms can exhibit bonding characteristic of Al_2Cu when mixed at the nm scale even at a room temperature.

We have recently used x-ray reflectivity¹² and current-voltage measurements¹³ to characterize the electronic properties of the oxide on these $\text{Al}_2\text{O}_3/\text{Al}_2\text{Cu}$ thin films. The electron density and conductivity are both much higher than expected for pure Al_2O_3 , suggesting that a small amount of a conductive impurity, such as Cu, may reside in the oxide layer. This high conductivity may also explain the enhanced oxidation of Al_2Cu relative to pure Al, i.e. a thicker oxide can grow before passivation occurs. Angle-resolved XPS measurements, designed to increase our sensitivity to Cu species in the oxide layer, are currently underway in order to address this question.

CONCLUSIONS

In summary, large-grained, phase-pure, thin films of Al_2Cu have been fabricated by melting and re-solidifying Al/Cu bilayers capped with an air-formed Al_2O_3 layer. SEM and EBSD show that the Al_2Cu is composed of 30-70 μm x 10-25 mm sized, (110) oriented grains. Annealing the Al/Cu bilayers without an oxide layer or with an ECR plasma-formed oxide layer results in phase-segregated films. This suggests that capping the Al/Cu bilayer with a chemically and structurally stable Al_2O_3 layer prior to annealing is a key step to prevent film de-wetting. Al_2Cu was further oxidized in air to form Al_2O_3 even under an existing ~5 nm thick oxide layer, as determined by XPS. The majority of Cu produced upon Al_2Cu oxidation is believed to migrate below the photo-electron escape depth (~10 nm) or to form Al_2Cu beneath the Al_2O_3 layer. A residual amount of Cu may still reside in

the oxide layer, which could explain the high electrical conductivity observed and the formation of a thicker Al_2O_3 layer relative to the oxide formed on pure Al.

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Fig. 1. $\text{Cu}2p$ and Valance Band XPS of (a) a metallic Cu film and (b) an $\text{Al}_2\text{O}_3/\text{Al}/\text{Cu}$ bilayer taken after melting at 580°C for 10 min. then cooling to re-solidify. The 1.0 eV shift of $\text{Cu}2p$ peaks and VB peak shift to 4.3 eV indicate Al_2Cu formation.

Fig. 2. Cu LMM AES spectra of (a) a metallic Cu film, (b) melted/re-solidified $\text{Al}_2\text{O}_3/\text{Al}/\text{Cu}$ and (c) melted/re-solidified $\text{Al}_2\text{O}_3/\text{Al}/\text{Cu}$ after 3 day air exposure.

Fig. 3. SEM image of Al_2Cu formed from the Al/Cu bilayer in the presence of (a) air formed Al_2O_3 , (b) no oxide, and (c) ECR-formed oxide. Continuous Al_2Cu film formation occurs only in (a). (d) EBSD pattern of the Al_2Cu film shown in (a).

Fig. 4 Al₂p XPS of aluminum oxides formed (a) in air, (b) by exposure of Al to an ECR oxygen plasma and (c) after exposing the plasma-formed oxide to air for 18 hours. Note that the ECR plasma-formed oxide has an Al₂p peak at a 1.0 eV lower BE than the air-formed oxide.

Fig. 5 $\text{Al}2p$ and $\text{Cu} 2p$ XPS and VB of Al_2Cu taken (a) before and (b) after air exposure.