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Citation	MATERIALS TRANSACTIONS (2010), 51(9): 1627-1632
Issue Date	2010
URL	http://hdl.handle.net/2433/148429
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Type	Journal Article
Textversion	publisher

Kyoto University

Materials Transactions, Vol. 51, No. 9 (2010) pp. 1627 to 1632
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Resistivity Reduction and Adhesion Increase Induced by Surface and Interface Segregation of Ti Atoms in Cu(Ti) Alloy Films on Glass Substrates

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Low-resistivity and excellent-adhesion Cu(Ti) alloy films were prepared on glass substrates. Cu(0.3∼4 at%Ti) alloy films were deposited on the substrates, and subsequently annealed in vacuum at 400°C for 3 h. Resistivity of the annealed Cu(Ti) alloy films was significantly reduced to about 2.8 μΩcm. Tensile strength of the Cu(Ti)/glass interface increased to about 60 MPa after annealing. The low resistivity and excellent adhesion resulted from Ti segregation at the film surface and the Cu(Ti)/glass interface. The segregated Ti atoms reacted with atmospheric oxygen at the surface and with oxygen in glass and/or from atmosphere at the interface, and formed a TiO_2 layer at the surface and a TiO_2 layer with a small amount of Ti_2O_3 and TiO at the interface. The layers were non-crystalline. Columnar grains in the alloy films were seen to enhance Ti segregation and subsequent Cu grain growth. The Cu grain growth also contributed to low resistivity of Cu(Ti) alloy films.
[doi:10.2320/matertrans.MAW201033]

(Received April 23, 2010; Accepted May 26, 2010; Published July 7, 2010)

Keywords: *copper titanium alloy film, titanium segregation, resistivity, adhesion, glass substrate*

1. Introduction

Developing better gate and interconnect materials to replace Mo(W) and Al(Nd)[1,2] alloys has been a critical issue as the size and resolution of thin film transistor liquid crystal displays (TFT-LCDs) increase.[3] Copper is an attractive candidate for the gate and interconnect materials in TFT-LCDs, because of its low resistivity and good electromigration resistance (high resistance to hillock formation). Copper has been evaluated for use in TFT-LCDs gate electrodes,[4,5] and the Cu-based TFT production process includes formation of a Cu/Mo bilayer gate electrode using wet etching of a sputter-deposited Cu/Mo bilayer. The process addressed Cu-related issues such as wet-etching difficulties and poor adhesion to dielectrics. Extensive efforts have been made to improve these Cu-related issues, for example, developing processes for production of Cu/M bilayers such as Cu/Co,[6] Cu/Mo,[7] Cu/Ti,[8] and Cu alloys such as Cu(Cr)[9] and Cu(In).[10,11] We similarly investigated the Cu alloying effect of a Cu(Ti) alloy film on Cu-related issues such as high resistivity due to impurity scattering, poor adhesion to glass, and poor oxidation resistance.

Low-resistivity Cu(Ti) interconnects were successfully prepared on dielectric/Si substrates for ultra-large scale integrated (ULSI) devices.[12–15] Copper interconnects have been used extensively in ULSI devices to reduce large resistance-capacitance delay and to improve poor device reliability. The large resistance increase is believed to be caused by small-grained Cu interconnects (numbers of grain boundaries) and large volume fraction of barrier layers in Cu interconnects.[16] One of the techniques to prepare thin barrier layers in Cu(Ti)[12–15] or Cu(Mn)[17,18] alloy films involves annealing at elevated temperatures. Supersaturated Cu(Ti) alloy films deposited on dielectric layers such as SiO_2, SiN, SiCO, SiCN, and SiOCH with low dielectric constants (low-k) were annealed at elevated temperatures, and thin Ti-rich layers were formed at the film surface and interface between the film and all the dielectric layers.[13,14] The Ti-rich barrier layers formed at the interface were found to consist of polycrystalline TiN for the annealed Cu(Ti)/SiN samples,[13] and amorphous Ti oxides with small amount of polycrystalline TiSi or TiC for other samples, indicating reaction of the Ti atoms with dielectrics. The primary factor to control composition of the Ti-rich barrier layers was concluded to be the C concentration in the dielectric layers.[12,14]

In this study, we have applied the technique of the thin Ti-based self-formed barrier formation using a Cu(Ti) alloy to seed the Cu metallization on glass substrates, and evaluated the performance. Adhesion of the Cu(Ti) layer to the glass was evaluated by stud pull tests. The microstructures of the annealed Cu(Ti)/glass samples were analyzed by Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) and correlated with the electrical properties of the Cu(Ti) films.

2. Experimental Procedure

Cu(Ti) alloy films were deposited on glass substrates (Corning, Inc., Eagle2000) by a radio frequency magnetron sputtering technique. Prior to film deposition, dust on the substrate surface was blown off using nitrogen gas. The base pressure prior to deposition was approximately 1×10^{-6} Pa, and the sputtering power and working pressure were kept at 300 W and about 1 Pa, respectively. The substrate holder was placed 100 mm above the target. To prepare the Cu(Ti) films,

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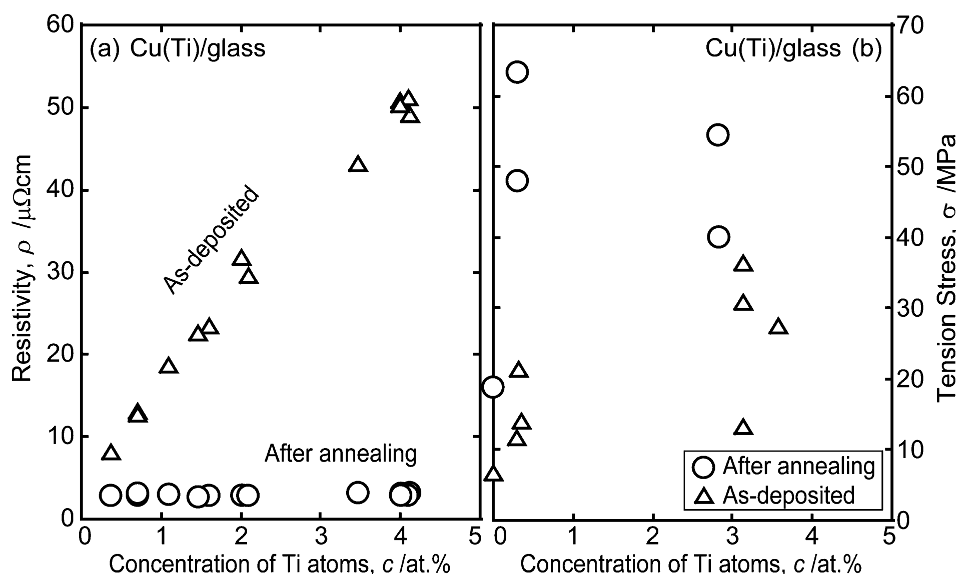

Fig. 1 (a) Resistivity of as-deposited and annealed Cu(Ti) alloy films deposited on glass substrates as a function of an initial concentration of Ti atoms. (b) Their tensile stresses in stud pull tests. The annealed samples were annealed at 400°C for 3 h (a) in vacuum and (b) in UHV.

small rectangular Ti plates were mounted on a Cu target. The purities of the Cu target and the Ti plates were 99.99% and 99.9%, respectively. Ti concentration in the as-deposited Cu(Ti) alloy films was in the range of 0.3∼4 at%. The film thicknesses were measured using TEM and RBS: the typical thickness of the Cu(Ti) alloy films was controlled to approximately 300∼400 nm. The samples were annealed in vacuum ($\sim 10^{-1}$ Pa) isothermally at 400°C for 3 h. The electrical resistivity in the Cu(Ti) films was measured by a four-point probe method. The adhesion of the Cu(Ti) layer to the glass was evaluated by stud pull tests using Shimadzu EZ Graph. Stud bars with an area of approximately 5 mmϕ were glued onto the films. Through annealing in vacuum at 400°C, oxide layers formed at the film surface, and the surface oxide layer was the weakest in the annealed samples. Before evaluating the adhesion of the Cu(Ti) layer to the glass, as-deposited samples produced only for the stud pull tests were annealed in an ultra-high vacuum (UHV) of $\sim 10^{-8}$ Pa to prevent formation of Ti oxide layers at the surface. The Ti segregation to the surface and interface was investigated by RBS. For the RBS measurements, $^4He^{2+}$ ion beams with energy of 2 MeV were impinged perpendicularly onto the film surfaces. The alloy film microstructures and crystalline phase were analyzed by XRD and TEM. To identify non-crystalline phases in the surface and interface layers, XPS measurements and Ar etching were simultaneously carried out. To alleviate difficulties in the measurement of the very thin interface layers, Ti concentration in the as-deposited Cu(Ti) alloy film was increased to 4 at%. The typical thickness of the alloy films was controlled to approximately 50 nm.

3. Results and Discussion

3.1 Resistivity and adhesion of Cu(Ti) alloy films on glass substrates

Cu(Ti) films prepared on glass substrates were a supersaturated alloy, as copper has a low solubility of about 0.3 at%Ti.[19] Resistivity of the as-deposited Cu(Ti) alloy films increased linearly with increasing initial Ti concentration (Fig. 1(a)). After annealing in vacuum at 400°C for 3 h, resistivity of the Cu(Ti) alloy films was significantly reduced to about 2.8 μΩcm, regardless of the initial Ti concentration of the Cu(Ti) alloy films (Fig. 1(a)). The as-deposited pure-Cu film showed weak adhesion with tensile stress less than 10 MPa, and the tensile stress of as-deposited Cu(Ti) alloy films increased with increasing Ti concentration (Fig. 1(b)). Adhesion of pure-Cu and Cu(Ti) films on glass substrates increased after annealing (Fig. 1(b)). The tensile stresses of the annealed pure-Cu/glass and Cu(Ti)/glass samples increased to about 20 and 60 MPa, respectively. The adhesion of the annealed Cu(Ti)/glass samples did not obviously vary with the initial Ti concentration of the Cu(Ti) alloy films. This suggests that an interface layer had formed between the Cu(Ti) layer and the glass surface through annealing, and that the interfaces of the layer strengthened the Cu(Ti)/glass interface. Thickness of the interface layer may not vary with the initial Ti concentration of the alloy film, or may not influence the adhesion. In this investigation, low-resistivity and excellent-adhesion Cu(Ti) alloy films could be formed on glass substrates, suggesting that those properties could potentially be applicable to TFT-LCDs.

3.2 Mechanism characterization of low resistivity and excellent adhesion for the annealed Cu(Ti) alloy films on glass substrates

Figure 2(a) shows RBS profiles of Cu(3.5 at%Ti)/glass samples before and after annealing in vacuum at 400°C for 3 h, together with that of Cu(4 at%Ti)/SiO_2 samples after annealing. Small peaks around channel 550 and large peaks around channel 700 were observed in the RBS profiles of the Cu(Ti)/glass and Cu(Ti)/SiO_2 samples after annealing, although there were no peaks in the RBS profile of the as-deposited Cu(Ti)/glass sample. The peak around channel 550

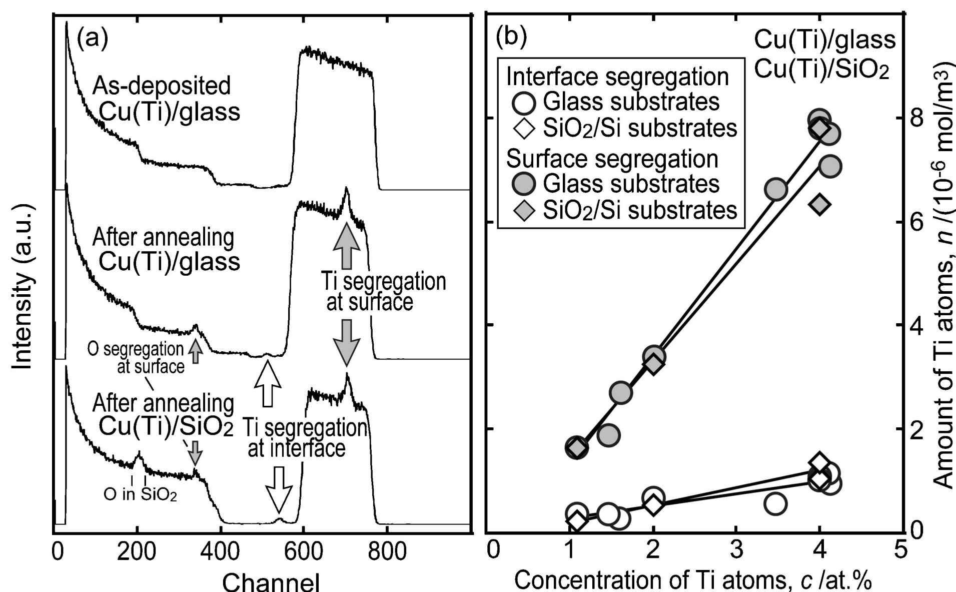

Fig. 2 (a) RBS profiles of Cu(3.5 at%Ti)/glass samples as-deposited and after annealing in vacuum at 400°C for 3 h, together with that of a Cu(4 at%Ti)/SiO_2 sample after annealing in Ar at 400°C for 3 h. (b) Molar amounts of Ti atoms segregated at the surface and interface of the annealed Cu(3.5 at%Ti)/glass and Cu(4 at%Ti)/SiO_2 samples. The molar amounts of Ti atoms were estimated from the Ti peaks at the surface and interface in the RBS profiles.

indicates Ti segregation at the interface, and that at 700 indicates Ti segregation at the surface in the annealed samples. Small peaks around channel 350 were observed in the RBS profiles of the Cu(Ti)/glass and Cu(Ti)/SiO_2 samples after annealing, indicating O segregation at the film surface. This suggests that Ti and oxygen atoms segregated at the film surface formed Ti oxides. The O segregation at the interface can occur similarly to the Ti segregation at the interface; however, the intensity of Ti peaks around channel 550 was significantly lower than that around channel 700, and similarly, the O peaks at the interface were too small to observe definitively in the RBS profiles. Based on the Ti peaks around channels 550 and 700 in the RBS profiles, amounts of Ti atoms segregated at the surface and interface in the Cu(Ti)/glass and Cu(Ti)/SiO_2 samples after annealing were estimated, and the results are shown as a function of the initial Ti concentration in Fig. 2(b) (Details of determination of the molar amount of Ti atoms based on the Ti peaks in the RBS profiles are not shown: see Ref. 14)). The molar amounts of Ti atoms segregated at both the surface and interface increased linearly with increasing initial Ti concentration. Thus, the excess Ti atoms exceeding Ti solubility in copper were removed from the supersaturated alloy films to the surface and interface, resulting in low resistivity in the Cu(Ti) alloy films. The molar amount of Ti atoms segregated at the surface was about eight times higher than that segregated at the interface in the Cu(Ti)/glass samples after annealing. This feature of Ti segregation at both the surface and interface was similar to that in the Cu(Ti)/SiO_2 samples after annealing.

To identify the Ti-based layers formed at the surface and interface of the Cu(Ti)/glass samples after annealing, XRD measurements were performed. Portions of typical XRD profiles of Cu(3.1 at%Ti)/glass samples before and after annealing are shown in Fig. 3(a). The $\{111\}_{Cu}$ peak was the only peak observed, and its peak intensity increased after annealing (Related $\{222\}_{Cu}$ peak was observed in higher-angle portions of the XRD profiles, not shown). This trend of the XRD profiles was observed in all Cu(Ti)/glass samples before and after annealing. Intensity of the $\{111\}_{Cu}$ peak in Cu(Ti)/glass samples before and after annealing increased with increasing initial Ti concentration (Fig. 3(b)). The increase in number of {111}-oriented Cu grains may be explained by the fact that the surface energy of $\{111\}_{Cu}$ decreases with increasing Ti concentration in Cu(Ti) alloy films.

Although formation of surface and interface layers in the Cu(Ti)/glass samples after annealing could not be identified by XRD measurements, cross-sectional TEM images confirmed that an approximately 50 nm-thick surface layer and an approximately 10 nm-thick interface layer were formed in the annealed samples (Fig. 4(a)). It is suggested that formation of a thin interface layer such as this could enhance the adhesion of the Cu(Ti) layer to the glass, while formation of the surface layer could prevent oxidation of the Cu(Ti) alloy films. A selected-area-diffraction (SAD) image obtained from the interface is shown in Fig. 4(b), surrounded by a broken circle. A few diffraction spots were seen in the upper part, and a halo pattern was observed in the center part. The diffraction spots must come from a crystalline Cu grain, and the halo pattern from the amorphous glass substrate. Similarly, no diffraction spots except those from Cu grains were observed in SAD images obtained around the thicker surface layers (not shown), indicating that the surface layer formed in the Cu(Ti)/glass samples after annealing is not a crystalline phase. Similarly, the interface layer cannot be a crystalline phase, although its volume fraction was obviously too small to identify.

To identify non-crystalline phases in the Cu(Ti)/glass samples after annealing, XPS measurements and Ar etching

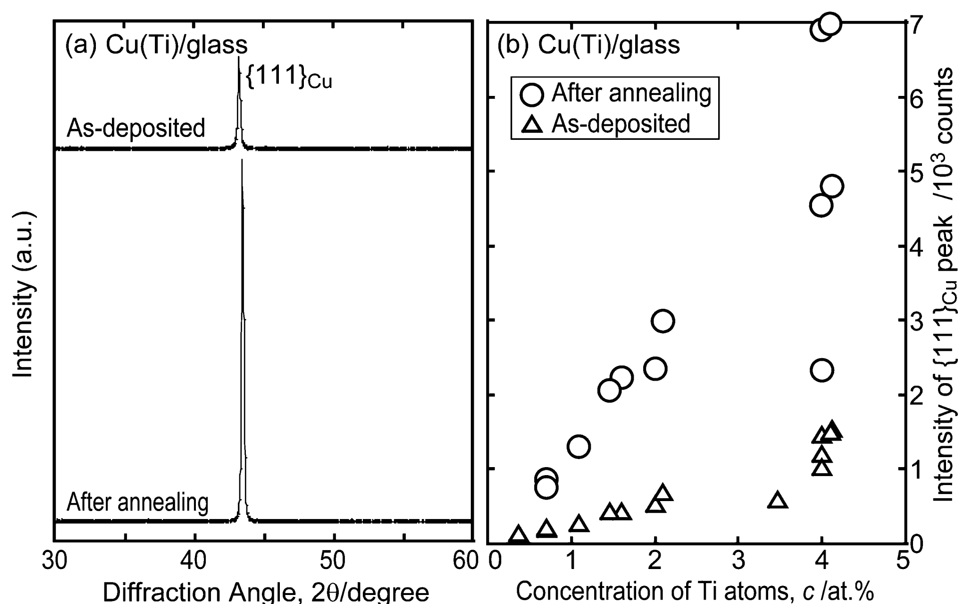

Fig. 3 (a) XRD profiles of as-deposited and annealed Cu(3.1 at%Ti) alloy films deposited on glass substrates. The annealed samples were annealed in vacuum at 400°C for 3 h. (b) Intensity of $\{111\}_{Cu}$ peaks in the XRD profiles of Cu(Ti) alloy films as a function of Ti concentration.

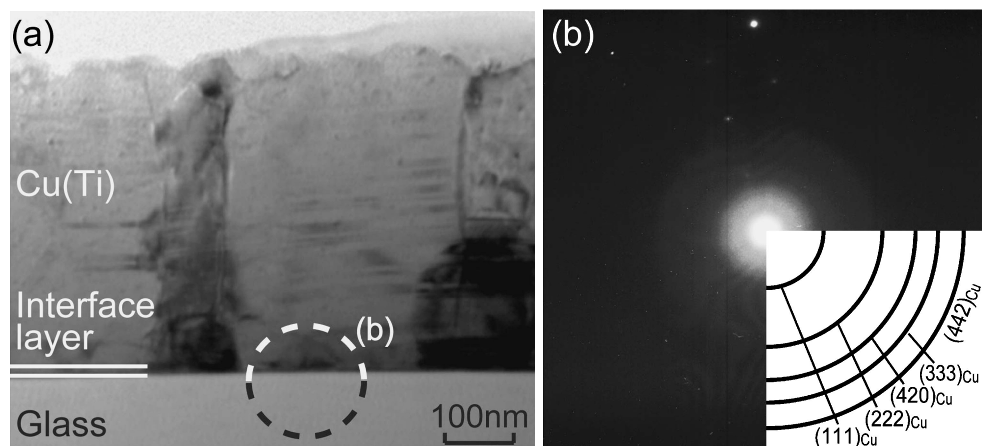

Fig. 4 (a) A cross-sectional TEM image for a Cu(4 at%Ti)/glass sample after annealing in vacuum at 400°C for 3 h. (b) a SAD image obtained in a broken circle in (a).

were simultaneously carried out. Figure 5(a) shows XPS depth profiles of the Cu(4 at%Ti)/glass sample after annealing in vacuum at 400°C for 3 h. The Ti and oxygen concentration peaks were observed at early etching time (indicating their surface segregation), but Cu and Si concentration were low enough to confirm that Cu and Si atoms did not exist at the film surface. This is in good agreement with the Ti and oxygen segregation at the film surface observed in the RBS profiles (Fig. 2(a)). Although the depth resolution of element identification in the present depth profiles was not good, the Ti and Si concentration in the Cu(Ti) alloy film was determined to be low. The O and Si concentration in the range of etching time between 110000 s and 210000 s can be explained by contribution of the glass substrate. A small Ti concentration peak was observed in the range of etching time between 220000 s and 250000 s (Fig. 5(b)), suggesting Ti segregation at the Cu(Ti)/glass interface. To characterize the Ti segregation at the surface and interface of the Cu(Ti)/glass samples after annealing, a portion (around the Ti 2p) of an XPS profile obtained near the surface is shown in Fig. 5(c), and near the interface in Fig. 5(d). Two obvious peaks were observed in both portions of the XPS profile, and the binding energies of both peaks indicate formation of TiO_2 phase. There are three candidates of Ti oxides, namely TiO, Ti_2O_3, and TiO_2, each with different binding energies. The refinement plots consisted of three components and a background plot placed upon the observed data (Figs. 5(c) and 5(d)). The TiO_2 layer was indicated as the only phase formed at the surface, while the Cu(Ti)/glass interface layer consisted of about 80 at% TiO_2, 10 at% Ti_2O_3, and 10 at% TiO. The layers were non-crystalline. This suggests that the segregated Ti atoms reacted with atmospheric oxygen at the surface and with oxygen in glass and/or from atmosphere at the interface, and oxygen concentration at the interface is suggested to be less than that at the surface.

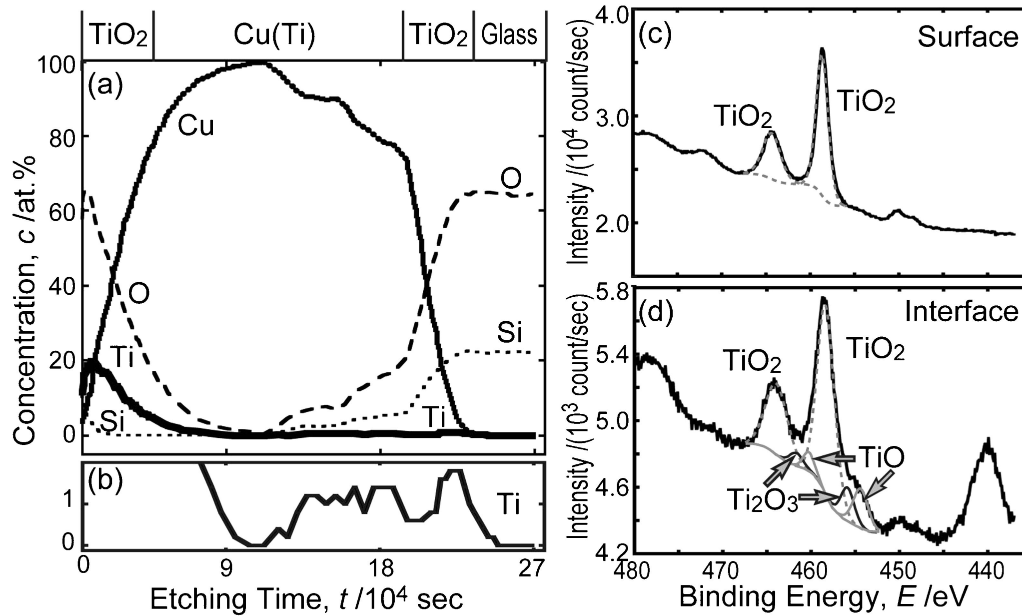

Fig. 5 (a) XPS depth profiles of the Cu(4 at%Ti)/glass sample after annealing in vacuum at 400°C for 3 h, and (b) an enlarged Ti profile. (c) and (d) Portions (around the Ti 2p) of the XPS profiles obtained near (c) a surface and (d) an interface of the same sample as (a) with refinement plots placed upon the observed data. The refinement plots consisted of three components of TiO_2, Ti_2O_3, and TiO.

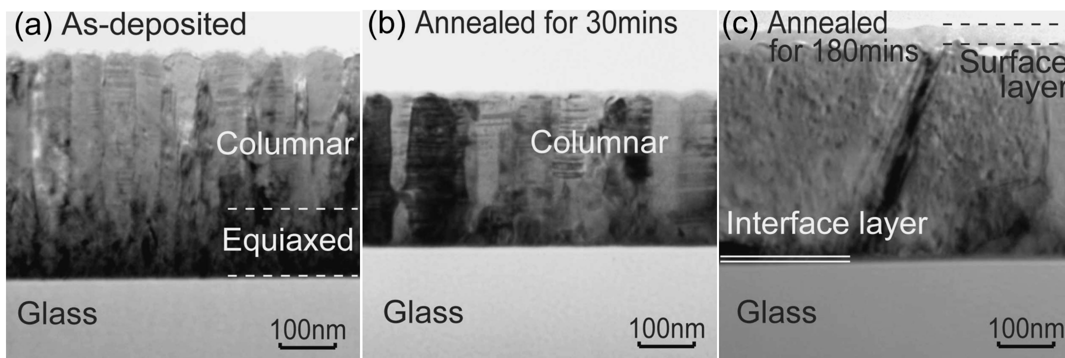

Fig. 6 Cross-sectional TEM images for Cu(4 at%Ti)/glass samples (a) as-deposited, (b) after annealing in vacuum at 400°C for 30 min, and (c) after annealing in vacuum at 400°C for 3 h.

3.3 Microstructure-related Ti segregation and grain growth

Ease of Ti diffusion into the surface and interface of the Cu(Ti) alloy films after annealing is essential for the observed low resistivity and excellent adhesion. In fact, a few of the Cu(Ti)/glass samples after annealing did not show such low resistivity as around 2.8 μΩcm, but instead showed higher resistivity of about 5 μΩcm (not shown). In the high-resistivity samples, the Ti segregation at the interface was lower than that in the low-resistivity samples. The Ti diffusion into the surface and interface was controlled by microstructures of the as-deposited samples and changes they had undergone during annealing. Typical microstructures of the Cu(4 at%Ti)/glass samples as-deposited and annealed for 30 min and 180 min are shown in Fig. 6. A cross-sectional TEM image of the as-deposited sample shows columnar grains in more than half of the upper part of the film and equiaxed grains between the columnar grains and glass substrates (Fig. 6(a)). The smaller volume fraction of the equiaxed grains in the as-deposited samples tended to reach the lower resistivity. The equiaxed grains had disappeared after annealing for 30 min (Fig. 6(b)), and columnar grains grew from the interface to the surface. This indicates that the columnar grain boundaries are an express pathway for the Ti diffusion, while grain boundaries around the equiaxed grains formed many triple points, which acted as roadblocks preventing the Ti diffusion from moving directly to the interface. The excess Ti atoms were removed through the columnar grain boundaries to the surface and interface, resulting in large grain growth in the sample after annealing for 180 min, as shown in Fig. 6(c). In the high-resistivity samples, fine columnar grains remained even after annealing for 180 min (similar to Fig. 6(b)). Thus, the formation of a fully columnar structure at the beginning of annealing is suggested to be essential for the ease of the Ti segregation and subsequent large grain growth. The Ti atoms might be gradually pinned at the grain boundary due to oxygen penetration through the grain boundary during the anneal, in

which case the Ti contamination at the grain boundary would lead to prevention of further grain growth. The smaller volume fraction of eqiaxed grains in the as-deposited samples is also a key for the faster formation of the fully columnar structure and Ti segregation.

4. Conclusions

The self-formation technique of Ti-based diffusion barrier in fabrication of ULSI interconnects was applied to obtain low-resistivity and excellent-adhesion Cu films prepared on glass substrates. Cu(0.3∼4 at%Ti) alloy films were deposited on glass substrates (Corning, Inc., EAGLE2000), and were subsequently annealed in vacuum at 400°C for 3 h. Resistivity of the annealed Cu(Ti) alloy films were significantly reduced to about 2.8 μΩcm. Tensile strength of the interface between Cu(Ti) alloy films and glass substrates increased to about 60 MPa in stud pull tests after annealing. The low resistivity and excellent adhesion resulted from Ti segregation at the film surface and the Cu(Ti)/glass interface after annealing, as confirmed by RBS analyses. The Ti segregation reduced Ti concentration in the Cu(Ti) alloy films. The segregated Ti atoms formed Ti-based layers at the surface and interface of the annealed Cu(Ti)/glass samples, as observed in cross-sectional TEM images. Although portions of XRD profiles obtained in the annealed Cu(Ti)/glass samples show only the $\{111\}_{Cu}$ peak, portions (around the Ti 2p) of the XPS profiles obtained near the surface of the annealed samples indicate only TiO_2 formation, and portions near the interface indicate TiO_2 formation with small amounts of Ti_2O_3 and TiO. Thus, amorphous TiO_2 layers formed at both the surface and interface of the annealed samples, suggesting that the segregated Ti atoms reacted with atmospheric oxygen at the surface and with oxygen in glass and/or from atmosphere at the interface. The Ti segregation could be enhanced in the columnar grains passing through the alloy films, which was formed at the beginning of annealing. Such a microstructural change is believed to be essential for removing the excess Ti atoms in the alloy films and subsequent Cu grain growth. The Cu grain growth also contributed to low resistivity of Cu(Ti) alloy films.

Acknowledgements

This work was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (Kohama). The authors also would like to thank Y. Sonobayashi and Prof. H. Sugimura, Dept. of Materials Science and Engineering, Kyoto Univ., for the XPS measurements.

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