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Oxidation Resistive Cu Films by Room Temperature Surface Passivation with Thin Ag Layer

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A displacement-deposited Ag layer was investigated as an oxidation barrier in damascene Cu structure for high performance interconnection. A 40 nm thick bright and continuous Ag film was formed at the surface of electrodeposited Cu by immersing the copper film into the silver displacement solution. The Ag film at Cu surface significantly blocked oxygen diffusion into the Cu film and retarded oxidation. More importantly, an elevated barrier performance for oxygen diffusion through elimination and stuffing of grain boundaries of Cu was observed upon annealing in a 400°C N_2 atmosphere. Outward Cu diffusion through Ag layer controlled Cu oxidation when the surface was passivated with Ag layer.
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Copper's low resistivity and good electromigration property make it an ideal substitute for a conventional aluminum alloy as an interconnection material.[1,2] However, copper film cannot form a self-passivation layer under oxidizing conditions. Likewise, it is readily oxidized to cuprous or cupric oxide once exposed to air. Copper oxide is a semiconducting material with higher resistivity than pure copper. Thus, passivation of exposed copper film surface under oxidizing conditions is an important issue in the copper metallization processes.

Various attempts have been made to solve this problem, including ion implantation,[3-5] formation of surface silicides,[6] bilayer annealing,[7] and alloying the copper with Al or Mg.[8-10] Doping with Al or Mg is considered as the best method. This method includes the codeposition of Cu with Al or Mg. It can be performed easily using the physical vapor deposition (PVD) process. However, it is difficult to alloy copper with Al or Mg using other deposition methods such as chemical vapor deposition (CVD) or electrodeposition, whereby copper metallization in damascene structure is implemented due to its own superfilling capability. In particular, codeposition of Cu with Al or Mg during aqueous acidic Cu electrodeposition is essentially forbidden since Al and Mg cannot be deposited from aqueous solution.[11] Accordingly, it is necessary to develop a new passivation method that is compatible with the present damascene process.

In this study, a thin Ag film was deposited onto exposed Cu surface using the galvanic displacement deposition method. During galvanic displacement deposition, electrons are supplied through the dissolution of substrate Cu metal to convert the Ag^+ in the aqueous solution into Ag. Therefore, after chemical mechanical planarization (CMP) in the damascene process, this galvanic displacement deposition method can be used for Cu surface-selective passivation method. Figure 1 presents a schematic illustration of this process. This study examined the effect of Ag galvanic displacement deposition and annealing on the resistance to oxidation of electrodeposited Cu film.

Experimental

The study used Cu (seed, 70 nm)/TiN, 10 nm/Ti, 15 nm/Si as substrate structure. Cu and TiN was deposited through hollow cathode magnetron (HCM) PVD and metallorganic chemical vapor deposition (MOCVD), respectively. Four different kinds of samples were prepared from this substrate to test oxidation resistance: (a) electrodeposited copper, (b) annealed electrodeposited copper, (c) silver-passivated electrodeposited copper, and (d) annealed silver-passivated electrodeposited copper (Table I). Prior to electrodeposition onto the Cu seed layer, the substrate was pretreated with a 1:200 NH_4OH solution for 30 s to remove the native copper oxide.[12] Each wafer was then rinsed with deionized (DI) water and dried in an N_2 stream. The electrolyte for copper deposition was composed of 0.2 mol/L $CuSO_4$ and 1.0 mol/L H_2SO_4. Cu bar and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. Copper was deposited at a constant -0.2 V, which is optimized to the electrolyte, using a PAR 263 potentiostat (EG&G Princeton Applied Research Corporation). The Cu film electrodeposited for 400 s was about 1000 nm thick.

The solution for Ag galvanic displacement deposition was composed of 0.059 mol/L $AgNO_3$, 0.58 mol/L $(NH_4)_2SO_4$, and 523 mL/L NH_4OH, that were used to supply Ag ions, adjust pH, and dissolve the Cu film, respectively. A thin Ag layer was deposited on an electrodeposited copper layer by dipping the sample into the Ag solution for 20 s. Annealing was done at 400°C for 30 min in an N_2 stream.[13] The oxidation of four different kinds of samples was induced at 300°C for 4, 9, and 25 min. The oxidation resistance of each sample was then compared according to oxide thickness and change in sheet resistance. Oxide thickness and change in sheet resistance were measured using field emission scanning electron microscopy (FESEM) and four-point probe, respectively. On the other hand, X-ray diffraction (XRD) and Auger electron spectroscopy (AES) were used to analyze the crystallinity and oxygen contents of the samples.

Results and Discussion

Displacement of Cu with Ag occurred spontaneously upon immersion of Cu film into the displacement solution. The following reaction results in the formation of uniform and shiny Ag layer coating on Cu film

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2 + 2Ag(s) \qquad [1]$$

Figure 2 shows the AES depth profile and XRD spectra of a displacement-deposited Ag layer on Cu film. Displacement for 20 s produced a 40 nm Ag layer deposition. Both the Cu and Ag are face centered cubic (fcc) structures with similar lattice parameters of 361.49 and 408.53 pm, respectively. The reaction stoichiometry and lattice parameters indicate that the 40 nm Ag layer was deposited at the expense of about 18 nm Cu layer from the surface. Figure 2a clearly shows that the deposited Ag layer is very thin and surface-restricted. The texture of the deposited Ag layer showed a very strong (111) peak (Fig. 2b), which indicates a strong texture inheritance from the underlying Cu layer. Since these two metals are highly conductive and the major conductor is the underlying thicker Cu film, the sheet resistance after the displacement reaction was reduced by around 2%.

To investigate the oxidation resistance of Cu films, four samples assigned as a to d in the experimental section were used. Oxidation was performed at 300°C atmospheric condition for 4, 9, and 25 min.

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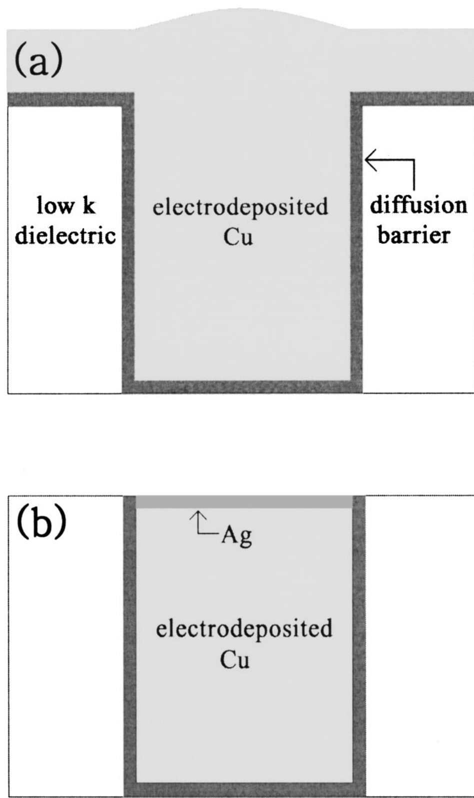

Figure 1. Schematic illustrations of (a) as-deposited damascene Cu structure and (b) surface passivated Cu after CMP and Ag displacement deposition.

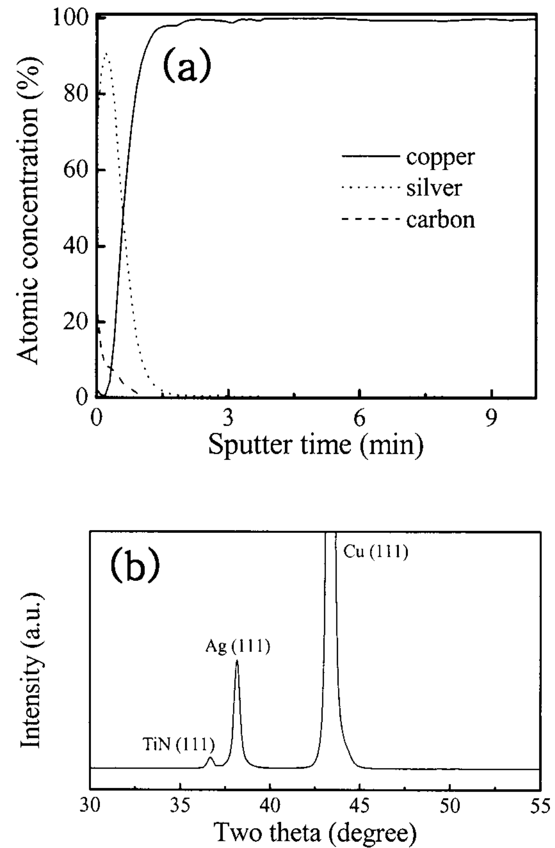

Figure 2. (a) AES depth profile of Ag displacement-deposited Cu film and (b) its XRD spectra.

Figure 3 presents the changes in sheet resistance according to oxidation time. R_o and R_s are sheet resistances of as-prepared and after oxidation, respectively. Sample a with Cu/TiN/Ti/Si structure and without annealing showed a drastic increase in sheet resistance. Though the copper oxide is a semiconducting material it has a much higher resistivity than pure Cu, which is the reason for increase in sheet resistance after oxidation. A slight improvement in oxidation resistance was observed when the sample Cu/TiN/Ti/Si was annealed prior to oxidation (Fig. 3b). Regardless of annealing, oxidation of the Cu layer was significantly inhibited by the capping of Cu surface with 40 nm thick Ag layer (Fig. 3c and d). In the case of the annealed Ag/Cu/TiN/Ti/Si structure d, resistance to oxidation was higher compared to the case without annealing (Fig. 3c). This implies that heat-induced changes in microstructure contributed to oxidation resistance.

Figure 4 shows the cross-sectional FESEM images of the four types of samples and corresponding AES depth profiles after oxidation for 9 min. Since the thermal expansion coefficient of pure copper was about two to eight times higher than that of copper oxide and silicon (0.23, 0.03, 0.12/0.07/0.07, and 0.03×10^{-4}/K for Cu, Cu_2O, CuO (monoclinic, a/b/c), and Si, respectively), the thermal oxidation and cooling process resulted in cracks between each layer. Thus, the FESEM images define the boundaries between pure copper and oxidized copper. Similar phenomena regarding cracks between copper and its oxide was reported in another study.[14] Almost all Cu in sample a was oxidized after 9 min thermal oxidation resulting in a very thin Cu film just above the TiN barrier layer. For the annealed sample b, the oxidation of copper was retarded com-

Table I. Four different kinds of samples.

Sample	Structure	Processes
a	Cu/TiN/Ti/Si	Cu electrodeposition
b	Annealed Cu/TiN/Ti/Si	Cu electrodeposition → anneal
c	Ag/Cu/TiN/Ti/Si	Cu electrodeposition →Ag displacement deposition
d	Annealed Ag/Cu/TiN/Ti/Si	Cu electrodeposition →Ag displacement deposition→anneal

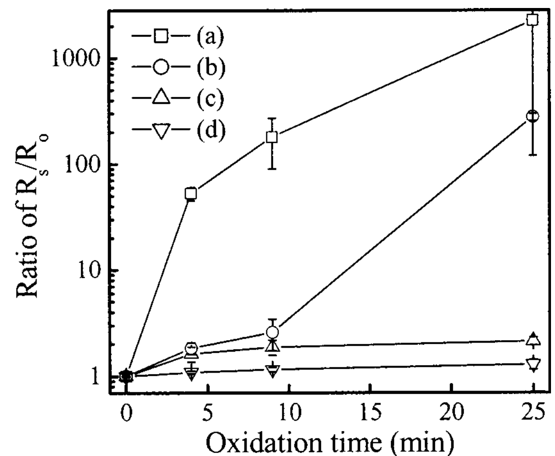

Figure 3. Sheet resistance changes of four types of samples according to the oxidation time; (a) Cu/TiN/Ti/Si, (b) annealed Cu/TiN/Ti/Si, (c) Ag/Cu/TiN/Ti/Si, and (d) annealed Ag/Cu/TiN/Ti/Si. (R_s: sheet resistance after oxidation, R_o: sheet resistance of as-prepared.)

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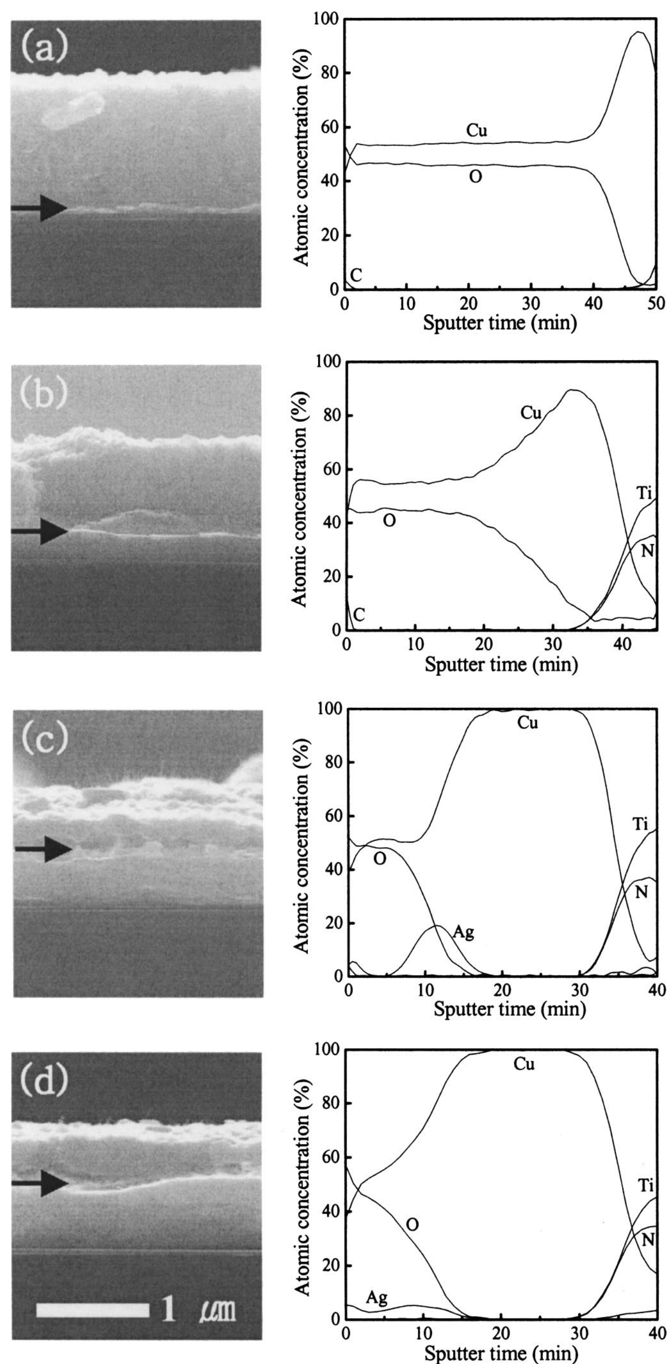

Figure 4. Cross-sectional FESEM images and corresponding AES depth profiles of four types of samples after 9 min oxidation at 300°C atmospheric conditions; (a) Cu/TiN/Ti/Si, (b) annealed Cu/TiN/Ti/Si, (c) Ag/Cu/TiN/Ti/Si, and (d) annealed Ag/Cu/TiN/Ti/Si.

pared to sample a. Nonoxidized Cu layers of samples c and d were much thicker than those without Ag passivation layer after thermal oxidation. The AES depth profiles of samples c and d show that the Ag profile was somewhat different from that of the as-plated Ag presented in Fig. 2a. In sample c, the Ag layer after thermal oxidation was positioned at an interface between pure copper and copper oxide. This implies that the Ag passivation layer served as a diffusion barrier of oxygen and copper to prevent interaction between them and that the outward diffusion of Cu through the Ag layer is preferred to that of the atmospheric oxygen to within the film. In sample d, a slight increase in pure Cu thickness was observed. Ag distribution within the film was also very broad compared to the narrow profile in c. This indicates that heat-induced (annealing) changes in film structure improved the function of Ag layer as a diffusion barrier.

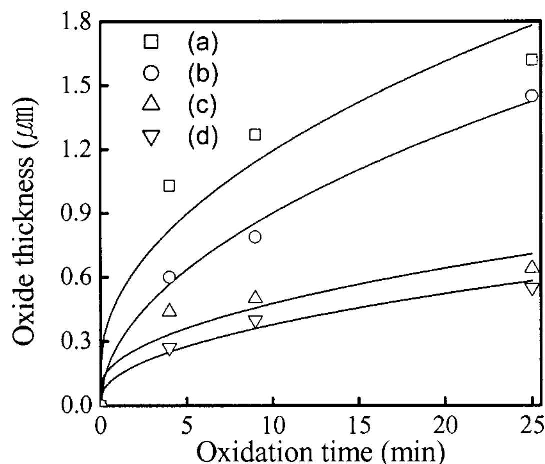

Figure 5. Oxide thickness of four types of samples according to oxidation time; (a) Cu/TiN/Ti/Si, (b) annealed Cu/TiN/Ti/Si, (c) Ag/Cu/TiN/Ti/Si, and (d) annealed Ag/Cu/TiN/Ti/Si.

Oxidation of pure copper and its progress are determined through oxygen diffusion within the copper film. In particular, one of the most important diffusion paths is grain boundary. Heat-induced grain growth decreases the number density of grain boundaries. Similarly, the improvement in oxidation resistance of sample b was attributed to the elimination of paths for oxygen diffusion. Upon passivation of the Cu surface with Ag layer, it served as a simple but effective barrier for oxygen diffusion as shown in Fig. 4c. In this case, Cu oxidation was more affected by the diffusion of Cu to the surface through the Ag layer. In the case of sample d, cumulative effects from the elimination of grain boundary through grain growth and the stuffing of grain boundary with covering Ag to close up the diffusion path are expected. Previous studies have already reported the stuffing of grain boundary with foreign metal, particularly for TiN with Al.[15] Stuffing and grain growth cut off oxygen diffusion more effectively than that in sample c, though copper diffusion through the Ag layer determined the whole oxidation process after covering the surface with Ag layer.

Measurement of oxide thickness from FESEM images according to oxidation time validated these results about the different aspects of each sample (Fig. 5). The fitting lines in Fig. 5 implied that the oxide thickness of all samples was proportional to the square root of oxidation time. This indicates that the diffusion of reactants was the determining step for all oxidation reaction. Ag-free samples a and b underwent fast oxidation controlled by oxygen diffusion. On the other hand, Ag-covered samples c and d passed through a very slow oxidation that is controlled by copper diffusion through the Ag layer. The improvement of barrier property to oxygen diffusion through grain boundary stuffing and grain growth was attributed to the thinner oxide thickness of d compared to c.

Conclusions

The AES and XRD analyses revealed that surface-restricted, high quality thin Ag layer could be obtained from the displacement reaction between electroplated Cu film and Ag ions. The study investigated the characteristics of displacement-deposited Ag layer as an oxidation barrier of Cu. Oxidation of Cu in Ag/Cu/TiN/Ti/Si structure was efficiently blocked compared to Cu/TiN/Ti/Si, since the Ag passivation layer served as an oxygen diffusion barrier. Grain growth of Cu film induced through 400°C thermal annealing also contributed to block oxygen diffusion. Annealed Ag/Cu/TiN/Ti/Si

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structure showed the best performance, with the combined effects of grain growth and Ag stuffing of the grain boundaries of Cu film.

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