Effect of Annealing Atmosphere on Void Formation in Copper Interconnects

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1. Introduction

Recently, extensive efforts have been made to replace aluminum by copper for the interconnect materials of the Si-ULSI (Ultra-Large Scale Integrated) devices. Copper is attractive as the interconnect materials of the future Si-ULSI devices with linewidth of less than 0.10 μm. The advantage of Cu over conventional Al-alloy using as the interconnect materials is that copper has lower electrical resistivity and higher reliability. However, we have serious concern with reliability of the ultra-narrow Cu interconnects, because the reliability of interconnects is strongly influenced by the film microstructure. Especially, void formation in the Cu interconnects is a very important issue for reliability.

Electromigration (EM)1–4) and stressmigration (SM)5,6) which have been observed in Al-alloy interconnects were concluded that these EM and SM caused void formation (or growth). EM is a phenomenon which involves atomic fluxes induced by electric current in Al-alloy wires. Atomic diffusion induced by stress gradient in the interconnect materials introduced by thermal expansion mismatch between the interconnect metals and the passivation materials is defined as SM. Since the melting point (1083 °C) of Cu is higher than that (660 °C) of Al, it is considered that Cu has higher resistance for atomic diffusion by EM and SM. However, in the electroplated (EP) Cu films, which are widely used in the manufacturing Si-ULSI devices, large voids have been often observed after heat treatment.7) In addition, there are several reports that micro-voids existed even in the as-deposited EP-Cu films, leading to failure of the ultra-narrow Cu interconnects. Stress-induced voids were believed to enhance significantly the accumulation of EM damage.8) This implies that the micro-voids in Cu interconnects would also enhance EM failure. Therefore, in order to realize the highly reliable Cu interconnects, it is very important to prepare the void-free EP-Cu films by understanding of the origin of void formation or the growth behavior of voids in the Cu interconnects.

The void formation which was induced by the imperfect filling in vias or trenches during Cu deposition was well discussed. However, the micro-voids were frequently observed even in the blanket Cu films, implying that the micro-voids are not formed due to imperfect filling in vias or trenches during Cu deposition. Sekiguchi et al.9) and Alers et al.10) explained that the formation of the micro-void was caused by the stress induced in the Cu interconnects during heat treatments. Nawafune et al.10) reported that the organic additives such as polyethylene glycol (PEG), which were incorporated in the EP-Cu films, were the origin of the micro-voids. Although there were a few reports concerned with the micro-void formation in Cu films, key factors which induced the micro-void formation were not identified.

In bulk copper materials which contain a small amount of oxygen, cracks or pores are observed at grain boundaries after annealing in atmosphere containing hydrogen.11) This phenomenon, which is called “hydrogen embrittlement”, was explained that hydrogen diffused into copper and reacted with oxygen to form water vapor. In the case of the electroplated Cu interconnects, it was reported that the additive-derived impurities of C, N, O, S and Cl were incorporated in the films.12) These previous experimental results indicated that the microstructure of EP-Cu films is influenced by annealing atmosphere and that micro-voids are formed by the mechanism similar to that for the hydrogen embrittlement observed in bulk Cu materials.

The purpose of the present study is to search a primary factor which induces void formation in the Cu interconnects. We focused our research on the effect of the oxygen contained in the Cu films for void formation, so we prepared the samples of Cu/CuO/Cu layered structure by the sputter-deposition technique, and annealed in hydrogen atmosphere.13) The microstructures were observed by transmission electron microscopy (TEM) and scanning ion microscopy (SIM). We proposed a new model of void formation in the Cu interconnects based on the idea different from traditional models of such as EM or SM voiding.

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2. Experimental Procedures

(100)-oriented Si wafers, which were covered with chemical vapor deposited (CVD) Si$_3$N$_4$, were used as the substrates. Prior to sputter-deposition, the substrates with Si/Si$_3$N$_4$ structure were ultrasonically cleaned with acetone and IPA (isopropyl alcohol) for 3 min/each. After blowing with dry N$_2$ gas, the substrates were mounted on the sample holder and immediately loaded into the load-lock chamber of the radio-frequency (rf) magnetron sputtering system. After the load-lock chamber was evacuated, the substrates were transferred in the deposition chamber, where the base pressure was about $2.7 \times 10^{-6}$ Pa. The samples with Si/Si$_3$N$_4$/Cu/CuO/Cu layered structure were prepared by the sputter-deposition technique. The deposition conditions are summarized in Table 1. The CuO films with 100 nm thickness were deposited by reactive sputtering on the Cu films with 1500 nm thickness, and the Cu films with 500–1500 nm thickness were deposited on the CuO layers. These sandwich-structural samples were annealed isothermally at temperatures ranging from 300 to 400°C in 5% H$_2$/N$_2$ mixed gas atmosphere or in Ar gas atmosphere. Microstructural analyses of the samples before and after annealing were carried out by scanning ion microscopy (SIM) or transmission electron microscopy (TEM). Cross-sectional SIM and TEM observations were performed with the samples prepared by a focused ion beam (FIB).

3. Results and Discussion

3.1 Microstructural analysis of Cu/CuO/Cu films

In order to discuss the effects of annealing gas atmosphere on the growth of micro-voids in Cu films, the samples with PVD-Cu(1500 nm)/CuO(100 nm)/PVD-Cu(1500 nm) layered structure were investigated. Figure 1(a) shows a cross-sectional SIM image of the as-deposited Cu/CuO/Cu sample. The CuO layer is appeared as dark contrast in the center of the sample. Although the average grain size of the as-deposited PVD-Cu films was about 100 nm in diameter, the large grains (∼300 nm) were observed at the bottom of the lower Cu layer. It is considered that these grains grow during storage at room temperature induced by the stress introduced into the film from the substrate.\(^1\) When the sample is annealed at 400°C for 10 min in Ar atmosphere, the CuO layer is stable as shown in Fig. 1(b). However, when the sample is annealed at 400°C for 10 min in H$_2$/N$_2$ mixed gas atmosphere, the CuO layer disappears and large voids are formed at the region where the CuO layer was originally located as indicated by the arrows in Fig. 1(c). These experimental results clearly indicate that the voids are formed in the CuO layer when annealed in hydrogen atmosphere.

The rate of void formation depended on the thickness of the upper Cu layer. As shown in Fig. 2, the rate of void formation increases with decreasing thickness of the upper Cu layers. The present result suggests that hydrogen diffuse through the upper Cu films and react with the CuO layers to form water vapor, causing the void formation in the Cu films. Using the diffusion coefficient of oxygen in Cu reported by Wohlbier\(^15\) and that of hydrogen in Cu reported by Hukai,\(^16\) the diffusion distances of oxygen and hydrogen in Cu during annealing at 400°C for 30 min were estimated to be less than 1 nm and about 1 mm, respectively. Hydrogen diffusion through
The upper Cu films is fast enough to react with the CuO layers to form water vapor during the heat treatment. The equation for copper oxide reacting with hydrogen is given by,

\[ CuO + H_2 \rightarrow Cu + H_2O \]  

(1)

or

\[ Cu_2O + H_2 \rightarrow 2Cu + H_2O. \]  

(2)

Once H\(_2\)O is formed in the Cu film during annealing at high temperatures in hydrogen atmosphere as indicated in eq. (1) or eq. (2), it is difficult for H\(_2\)O molecules to diffuse in the Cu film even along the grain boundaries. Sawada et al.\(^{17}\) suggested that H\(_2\)O was formed in the copper oxide film deposited on silicon wafer after annealing in hydrogen atmosphere. For bulk copper materials, Koïwa et al. experimentally revealed the presence of water in hydrogen embrittled Cu wire using differential scanning calorimeter (DSC).\(^{11}\) These results support our present model.

The growth process of the voids during annealing at 360°C in H\(_2\)/N\(_2\) mixed gas atmosphere is shown in Fig. 3. After annealing for 10 min, small voids (∼50 nm) are formed in the CuO layer (Fig. 3(a)). By subsequent annealing for 20 min, the CuO layer disappears and large voids, which elongate along the direction parallel to the film surface, are formed at the region where the CuO layer was originally located (Fig. 3(b)). The shape of these voids become equiaxed after annealing for 40 min (Fig. 3(c)). The present observation suggests that the driving force for the void growth is reduction of total surface (or interface) free energy of the void. Since there is no mass transports between the bubbles by diffusion of H\(_2\)O molecules in the Cu film, it is considered that the void growth rate is controlled by transport of Cu atoms. Especially, interfacial diffusion of Cu around the bubbles controls the void growth when they are small.

Figure 4 shows cross-sectional and plan-view SIM images of the sample with a thin upper Cu layer after annealing at 400°C in H\(_2\)/N\(_2\) gas atmosphere. As shown in Fig. 4(a), “pores” are locally formed on the Cu film surface. The cross-sectional SIM image of Fig. 4(b) shows that the voids grow at the surface to form “pores”. With subsequent annealing, large voids were obseved on the surface of the upper Cu film. This large deformation of the film is due to high internal pressure accumulated in the bubbles. A high density of cracks along the grain boundaries were observed at the surface of the swellings as shown in Fig. 5. The formation of cracks along the grain boundaries is similar to that observed previously in hydrogen embrittled bulk Cu materials,\(^{11}\) suggesting that the annealing at high temperature in H\(_2\) atmosphere affected the mechanical properties of the Cu interconnects.

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Fig. 2 Cross-sectional SIM images of Si/Si\(_3\)N\(_4\) (100 nm)/PVD-Cu (1500 nm)/PVD-CuO (100 nm)/PVD-Cu(x nm) samples which were annealed at 360°C for 10 minutes in 5% H\(_2\)/N\(_2\) mixed gas atmosphere. The symbol (x) denotes the thicknesses of the upper PVD-Cu film, which were (a) 500 nm, (b) 1000 nm and (c) 1500 nm, respectively.

Fig. 3 Cross-sectional SIM images of Si/Si\(_3\)N\(_4\) (100 nm)/PVD-Cu (1500 nm)/PVD-CuO (100 nm)/PVD-Cu (500 nm) samples which were annealed at 300°C in 5% H\(_2\)/N\(_2\) mixed gas atmosphere for (a) 10 minutes, (b) 20 minutes and (c) 40 minutes, respectively.
3.2 Microstructural analysis of Cu/CuO (native oxide)/Cu films

In order to investigate the effect of hydrogen on the void formation in Cu films which contain a small amount of oxygen, the PVD-Cu/CuO (native oxide)/PVD-Cu samples were prepared. After the Cu film with 50 nm thickness was deposited by sputtering on the thin Si$_3$N$_4$ substrate (~60 nm), the sample was exposed in air for 10 hours to form a native oxide layer on the surface of the PVD-Cu film. Then a Cu film with 50 nm thickness was deposited on this sample and annealed at 400°C for 10 min. (This layered structure was prepared to simulate to the EP-Cu samples containing a native oxide layer at the seed-Cu/EP-Cu interfaces or organic additives incorporated in the EP-Cu films.) Figure 6 shows plan-view TEM images of the Cu/CuO (native oxide)/Cu sample after annealing in Ar atmosphere (Fig. 6(a)) or H$_2$/N$_2$ atmosphere (Fig. 6(b)). The micro-voids are clearly observed inside a large grain of Cu films after annealing in H$_2$/N$_2$ gas atmosphere. The average size of these voids is about 20 nm in diameter. However, no voids are observed in the sample annealed in Ar atmosphere. The present result suggests that if a small amount of oxygen is contained in Cu interconnect materials, annealing at elevated temperatures in hydrogen gas atmosphere forms voids which would influence the reliability of ultra-narrow Cu interconnects which were prepared by an electroplating method.

Since the CVD-Cu films were reported to contain large amounts of impurities such as oxygen or carbon compared with the electroplated Cu films, the void formation by a water bubbling mechanism is more serious for the CVD-Cu films. Sa-Kyun Rha et al. studied the microstructures of the CVD-Cu films which were annealed in Ar atmosphere or H$_2$/Ar atmosphere. A high density of micro-voids was formed in the CVD-Cu films after annealing in H$_2$/Ar atmosphere. Their results agree with our experimental results.

The detailed mechanism for the void growth, especially, how H$_2$O bubbles grow in the Cu films, is not fully understood at the moment. However, we believe that chemical reaction between impurities in the Cu films and hydrogen at high temperatures induces growth of micro-voids in the Cu thin film.
4. Conclusions

The effect of annealing atmosphere on the void formation in the Cu films were studied by analyzing the microstructure of the Cu films containing oxygen which were prepared by the sputtering technique. Existence of the copper oxides in the Cu films formed voids after annealing at elevated temperatures in hydrogen atmosphere, which was believed to be caused by formation of the H$_2$O bubbles in the Cu films. Even a small amount of oxygen such as the native oxide in the Cu film resulted in the formation of the micro-voids in the Cu films. The growth rate of the bubbles increased with increasing annealing temperature. The bubbles caused large deformation of the films due to high internal pressure in the bubbles. The present experiment suggested that existence of the impurities within the Cu films and annealing in hydrogen atmosphere are very unique combination to form micro-voids in the Cu interconnects.

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13) T. Ohnishi: unpublished work.