The Effect of Target Purities on Grain Growth in Sputtered Copper Thin Films

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Grain growth rates in sputtered Cu thin films were found to be influenced by impurity levels of the sputtering targets. The Cu thin films with thickness of 100 nm or 1 \(\mu\)m were deposited on the rigid substrates by a sputter-deposition technique using the Cu target with purity of 99.99\% (4N) or 99.9999\% (6N), then subsequently annealed at room temperatures. The microstructures of the Cu films were analyzed by scanning-ion microscopy and the sheet resistivities was measured by a four-point probe method. Significant grain growth and reduction of the electrical resistivities was observed during room-temperature storage in these sputtered Cu films. For the Cu films with a thickness of 1 \(\mu\)m, the grain growth rates of the Cu films were not influenced by the impurity levels of the targets. However, for the films with a thickness of 100 nm, the rate of the grain growth in the 6N-Cu films was found to be slower than that in the 4N-Cu films. This was contradictory to the grain growth mechanism of bulk Cu. The grain growth rates of the Cu films at room temperature, which were strongly influenced by the existence of a small amount of impurities in the Cu films, were well explained by the difference of the strain relaxation mechanisms in the films.

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1. Introduction

Copper is attractive as an interconnect material for current Si ultra-large scale integrated (ULSI) devices with line width of less than 130 nm. Lower electrical resistivity and higher reliability are the advantages of using copper (compared to conventional Al-alloy) as the interconnect material. However, we are concerned about the use of Cu interconnects in sub-50 nm devices, because the resistivity of the Cu interconnects would increase rapidly by reducing the line width as predicted by theories.\(^1\)\(^-\)\(^3\) The reason for this increased resistivity was believed to be that the relatively long mean free path (\(\sim 39 \text{ nm}\)) of the conducting electrons in copper. Upon reducing the line width of the Cu interconnects down to less than 100 nm, the mean free path of the electrons in copper approaches the line width and the electrons are scattered by the surfaces, interfaces, and/or the grain boundaries, leading to a drastic resistivity increase. A device designer requires interconnect resistivity of less than 2.2 \(\mu\)Qcm to realize high-speed ULSI devices with 65-nm-wide interconnects.\(^4\) In order to realize nano-scale Si-devices, development of low-resistivity ultra-narrow copper interconnects is essential. Our recent experimental results suggest that the grain boundary scattering primarily increased the resistivity of the Cu thin films,\(^5\)\(^6\) indicating that large-grained films are essential for low-resistivity ultra-narrow copper interconnects. Therefore, understanding the grain-growth mechanisms in the Cu thin films is extremely important for reducing the electrical resistivity of the Cu interconnects.

After film deposition, the Cu films were annealed at elevated temperatures. Only a few grains grew locally at the expense of the smaller neighboring grains.\(^7\) This bimodal grain growth, which led to an inhomogeneous grain size distribution, was conventionally called “abnormal grain growth”.\(^7\) Many researchers observed the abnormal grain growth in the Cu thin films during annealing at elevated temperatures after film deposition.\(^8\)\(^-\)\(^10\) In the electroplated Cu films widely used in manufacturing Si-ULSI devices, this abnormal grain growth is observed even at room temperature storage.\(^11\)\(^-\)\(^18\) Cabral et al.\(^15\) and Ueno et al.\(^17\) observed simultaneously relaxation of stress (introduced in the electroplated Cu film) and grain growth during room-temperature storage. Harper et al.\(^16\) suggested that the stress change was caused by the volume change associated with the elimination of grain boundaries using a grain-growth model proposed by Chaudhari.\(^19\) Gross et al.\(^12\)\(^-\)\(^14\) and Brongersma et al.\(^18\) suggested that organic additives added to plating solutions which contained the Cu films during electrodeposition might enhance grain growth in electroplated Cu films at room-temperature storage.

We previously reported that room-temperature grain growth occurred in Cu films prepared by a sputtering technique. We concluded that the organic additives (needed for electroplating) were not the only primary factor causing Cu grain growth.\(^20\) Because the Cu films have intrinsic strain when deposited on the rigid substrates, the strain introduced in individual grains of the Cu film was concluded to be the primary factor to induce abnormal grain growth.\(^20\) Strain in the polycrystalline metal films is generally relaxed by several deformation (or strain relaxation) mechanisms, which are influenced by film microstructure and impurities in the films. Thus, if the strain is the primary factor that enhances grain growth at room temperature, the grain-growth rate in the sputtered Cu films would be affected by the purities in the Cu films and the grain-growth rates are different for the films sputter-deposited using Cu targets with different impurity levels.

The purposes of the present study are to study the effect of the impurities on the grain growth during room-temperature storage and to understand the abnormal grain-growth mechanism in the sputter-deposited Cu thin films. We deposited Cu films with thicknesses of 100 nm and 1 \(\mu\)m on the rigid substrate by the sputter-deposition technique using Cu targets with purity of 4N (99.99\%) and 6N (99.9999\%). The microstructures were analyzed by focused ion beam...
(FIB) spectroscopy and the electrical measurements were carried out by a four-point method. These studies provide a guideline for developing low-resistance Cu films with large grain size.

2. Experimental Procedures

(100)-oriented Si wafers, which were coated with 60 nm-thick Si$_3$N$_4$ layers by chemical-vapor deposition, were used as the substrates. The substrates with the Si/Si$_3$N$_4$ structure were ultrasonically cleaned with acetone and isopropyl alcohol (IPA) for 3 min/each and dried with N$_2$ gas. Next the substrates were mounted on the sample holder attached in the load-lock chamber of a direct current magnetron-sputtering system. After the load-lock chamber was evacuated, the substrates were transferred in the deposition chamber with the base pressure of about $1 \times 10^{-6}$ Pa. The Cu films with thickness of 100 nm or 1 μm were deposited by sputtering onto the Si/Si$_3$N$_4$ substrates which were cooled by water during the depositions. The working pressure during the deposition was kept to be about $5 \times 10^{-1}$ Pa. The purity of the Cu target used in the experiment was 4N (99.99%) or 6N (99.9999%). Table 1 gives the impurity concentrations detected in the Cu targets and sputter-deposited films. The major impurities in the 4N and 6N-targets are Ag and S. Note that the impurity levels between the targets and films are similar.

The samples were annealed isothermally at room temperature in air and/or annealed at 623 K in a 5% H$_2$/N$_2$ mixed-gas ambient. Microstructural analysis of the Cu films was carried out by a scanning-ion microscope (SIM) in the focused ion-beam (FIB) system. The electrical resistance in the Cu film was measured by a four-point probe method.

3. Experimental Results

3.1 Cu films with thickness of 100 nm

Figures 1(a)–(c) show the plan-view SIM images of the 100 nm-thick 4N-Cu film deposited on the Si/Si$_3$N$_4$ substrate after storage at room temperature for 3, 7, and 308 h, respectively. The as-deposited Cu films are found to have mixed large and fine grains as shown in Fig. 1(a). The majority of the grains are extremely small (< 20 nm), which is about one-fifth of the film thickness. Large grains with sizes in the range of 100 nm to 1 μm are observed locally. As the storage time increased, the large grains grew at the expense of the small grains and the fraction of the fine-grained area decreased as seen in Figs. 1(a)–(c). The large grains continued to grow, while the surrounding small grains were stable. These bi-modal grain growth rates result in an inhomogeneous grain size distribution along a direction parallel to the film surface.

Figures 2(a)–(c) are the plan-view SIM images of the 100 nm-thick 6N-Cu films deposited on the Si/Si$_3$N$_4$ substrates annealed at room temperature for (a) 3 h, (b) 7 h, and (c) 308 h.

| Table 1 Impurity concentrations detected in Cu targets and sputter-deposited films. |
|-----------------|-----------------|-----------------|-----------------|
| Element        | (4N-Cu target) | (4N-Cu film)    | (6N-Cu target) | (6N-Cu film)    |
| Ag             | 8.0            | 10              | 0.07           | 0.08            |
| S              | 5.4            | 3               | 0.1            | 0.05            |
| P              | <1.0           | 0.2             | <0.001         | <0.001          |
| Si             | <1.0           | 0.05            | 0.04           | 0.04            |
| Fe             | 1.8            | 2               | 0.07           | 0.4             |
| O              | 1.1            | —               | 0.6            | —               |

Fig. 1 Plan-views of SIM images of 100 nm-thick 4N-Cu films deposited on the Si/Si$_3$N$_4$ substrates annealed at room temperature for (a) 3 h, (b) 7 h, and (c) 308 h.
4N-Cu film. Even after storing for 324 h, small grains are observed locally.

Figure 3 shows changes of the electrical resistivities (\(\rho\)) during room temperature storage of the 4N-Cu and 6N-Cu films with thicknesses of 100 nm. The resistivity of the as-deposited 4N-Cu film is 3.35 \(\mu\Omega\)-cm. At the initial stages of the storage, the resistivity drastically decreases. After 100 h, the rate of the decrease becomes extremely slow; the \(\rho\) values decrease over a period of 300 h to reach a value of about 2.55 \(\mu\Omega\)-cm in 4N-Cu film. The \(\rho\) value of the as-deposited 6N-Cu film is 3.75 \(\mu\Omega\)-cm and the rate of the resistivity decrease in the 6N-Cu film is smaller than the 4N-Cu film. The \(\rho\) value of the 6N-Cu film after storage for 300 h is 2.75 \(\mu\Omega\)-cm. Considering the results shown in Figs. 1 and 2, the reduction of the \(\rho\) values could be explained by the reduction of the grain-boundary density in the films due to grain growth, as observed previously. Thus, the grain growth rate of the 6N-Cu film is smaller than that of the 4N-Cu film.

3.2 Cu films with thickness of 1 \(\mu\)m

Figures 4(a)–(c) and Figs. 5(a)–(c) are the plan-view SIM images of the 1 \(\mu\)m-thick Cu films sputter deposited using Cu targets with purity of 4N and 6N, respectively. Although the grain growth rates of the 1 \(\mu\)m-thick 4N-Cu film and the 1 \(\mu\)m-thick 6N-Cu film are almost identical, the rate of 1 \(\mu\)m-thick 4N-Cu film is slower than that of the 100 nm-thick 4N-Cu film (Fig. 1). The effect of the film thickness on the grain growth in the Cu films sputter deposited on the rigid substrates was studied previously with the FIB system. The large strain close to the substrate was found to enhance the growth of the grains located at the bottom of the film. When the film thickness was large, the strain close to the top film surface was almost relaxed. Therefore, as the film thickness increased, the grain growth rate close to the top surface became slow. After annealing at room temperature, the 1 \(\mu\)m-thick 4N and 6N Cu films were observed to have the same grain sizes as shown in Figs. 3(c) and 4(c), respectively, although the 100 nm-thick films had different sizes (Figs. 1(c) and 2(c)).

Figure 6 shows changes of the electrical resistivities (\(\rho\)) of the 1 \(\mu\)m-thick 4N-Cu and 6N-Cu films during room-temperature storage. The resistivity of the 4N-Cu film is higher than that of the 6N-Cu film. Considering the microstructures (grain size or grain boundary density) shown in Figs. 4 and 5, the high \(\rho\) values of the 4N-Cu films could be explained by large the electron scattering of impurities rather than difference in the microstructures. Therefore, primary factors of the
electron scattering of the 100 nm- and 1 μm-thick Cu films would be the grain boundaries and impurities, respectively. This is a reason why the 4N- and 6N-Cu films showed different resistivity changes during room temperature storage as shown in Figs. 3 and 6.

4. Discussion

Before we discuss the effect of the target impurities on the Cu grain growth, we will explain the driving force for grain growth in sputter-deposited Cu films.

4.1 Driving force for grain growth in Cu films

From the present SIM observations, the as-deposited Cu films were found to have very fine grains (<20 nm). Such a fine-grained structure is thermodynamically unstable because the film has a high density of grain boundaries with large boundary energy. This high grain boundary energy provides a macroscopic driving force \( P \) for grain growth, which is given by \( P = 3\gamma/d \) where \( d \) is the grain size and \( \gamma \) is the grain boundary energy per unit area.\(^{22}\) For a grain with \( d = 10 \) nm and \( \gamma = 0.6 \) J/m\(^2\) [Ref. 22], one obtains \( P = 1.8 \times 10^{18} \) J/m\(^3\). If sufficient thermal energy is given to the film to migrate...
the grain boundaries, grain growth is thus facilitated reducing this large grain boundary energy. We reported previously that significant grain growth was observed during room-temperature storage in sputtered Cu films deposited on the rigid substrates, but no grain growth was observed during room-temperature storage in the free-standing Cu films.

Previous experimental results suggest that the grain growth in the Cu films could not occur at room temperature unless additional energetic assistance was given to the films. Intrinsic strains, which were introduced into the films from the substrates, were found to provide the energetic assistance for grain growth in Cu films bonded to the rigid substrates.

4.2 Effect of impurities on grain growth in Cu films

The effect of impurities on room-temperature grain growth in the Cu films is discussed by correlating the grain growth and the strain-relaxation mechanisms in the films. As mentioned above, the grain growth in the Cu films could not occur at room temperature unless additional energetic assistance by strain was given to the film and strain energy in the Cu film provided a macroscopic driving force for the grain growth. However, if the strain exceeds the elastic limit of the film, plastic deformation will occur to relax the strain in the film. The strain in the film can be relaxed by several deformation (or strain relaxation) mechanisms which may operate simultaneously.

To discuss the strain relaxation in Cu films, deformation mechanism maps which was developed by Ashby were constructed. Four possible strain-relaxation mechanisms were taken into account for the calculations: dislocation glide, dislocation climb, Harper-Dorn creep, and diffusional creep. To calculate the relaxation rates of these mechanisms in Cu thin films, the equation used for bulk Cu must be modified for the thin film case. A deformation mechanism map calculated for a 3 μm-thick Cu film with average grain size of 3 μm and a 10 nm-thick Cu film with average grain size of 10 nm is shown in Figs. 7(a) and (b), respectively, where tensile stress ($\sigma$) is normalized by shear modulus ($\mu$) of copper. Contours of the constant strain-relaxation rates are shown by fine lines. These maps clearly indicate that the grain-boundary diffusional creep is dominant at the room-temperature region, especially in films with small thickness and small grain size. Note that strain relaxation by surface diffusion is not considered in these maps. However, the influence of the surface diffusion will become larger in films with small thickness.

In the case of thin films, part of the strain will be relaxed mainly by the diffusional creep at the grain boundaries or the film surfaces. The effective driving force for grain growth is the residual strain energy. If the total strain in films is relaxed by plastic deformation mechanisms, the effective driving force (driving energy) for the grain growth will decrease. This implies that the grain growth rate becomes small in the film, which can relax the strain easily by using plastic-deformation mechanisms.

Generally, it is believed that impurities segregate at the grain boundaries or the triple point of grain boundaries to suppress grain boundary migration and that grain growth rates in the films with low impurity are much faster than in films with poor purity. The impurities in the films also have the effect on the diffusion rates at the grain boundaries or the film surfaces. In the case of high-purity 6N-Cu films, if strain in the films can be relaxed by the interfacial diffusional creep mechanism, the effective driving force for grain growth will be smaller than that of low-purity 4N-Cu films. As the film
thickness increases, the strain close to the film surface becomes smaller, and the influence of the grain boundaries and the surfaces will become weaker. Therefore, the influence of the impurities for the grain growth rates was not strong in thick Cu films.

5. Conclusion

The present results indicate that the amounts of the intrinsic strain introduced from the substrate and the strain-relaxation mechanisms were the key factors for controlling grain growth in the Cu films. When the intrinsic strain was relaxed by the grain boundary diffusional creep mechanism, a small amount of impurities in the films influenced the strain-relaxation rates. Therefore, grain growth rates at low temperatures were found to be affected by the amounts of impurities which segregated at the grain boundaries in the Cu films. These results suggest that the impurities in the Cu films and the film thickness were found to control the driving energy for the grain growth and that to prepare giant-grained Cu films, a method should be developed to suppress the intrinsic strain relaxation caused by plastic deformation.

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