Evaluation of the Crystallinity of Grain Boundaries of Electronic Copper Thin Films for Highly Reliable Interconnections

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Abstract
The change of the crystallinity of grain boundaries of the electroplated copper thin films used for the various interconnections in electronic products was evaluated quantitatively by applying an electron back-scattering diffraction analysis. It was found that the crystallinity of the electroplated films varied drastically depending on the electroplating conditions such as the composition of solute, temperature of the plating, the current density during electroplating, the surface material on the substrate, and so on. The change of the crystallinity of the films caused the drastic variation of both the electrical and mechanical reliability of the films.

Introduction
Electronic products such as mobile phones and PCs have been miniaturized continuously and their functions have been improved drastically. [1] Electroplated copper thin films have started to be applied to not only interconnections in printed wiring boards, but also thin film interconnections and TSV (Through Silicon Via) in semiconductor devices because of its low electric resistivity and high thermal conductivity.

However, both electrical and mechanical properties of the electroplated copper thin films, such as resistivity, Young’s modulus and the tensile strength, were found to vary drastically comparing with those of the conventional bulk copper. [2]–[5] The reason for the variation of these physical properties was that the electroplated copper thin films mainly consisted of fine columnar grains with porous grain boundaries which were easily etched off by ion beams. Such microcolumnar structure with porous grain boundaries changes both their electrical and mechanical properties significantly from those of bulk material based on the high resistance and low strength caused by porous grain boundaries. In addition, cooperative grain boundary sliding phenomenon causes super plasticity of thin films. [6] These variation and fluctuation of the mechanical and electrical properties of the electroplated copper thin films should degrade the reliability of electronic devices seriously.

From this point of view, it is necessary to clarify the effect of their micro-texture on their mechanical and electrical properties and to establish a method for controlling their mechanical and electrical properties in order to assure the reliability of electronic products. In this study, both the electrical and mechanical properties of the electroplated copper films were investigated experimentally considering the change of their micro texture. The change of the crystallinity of the polycrystalline copper thin-film interconnections was observed by using an EBSD (Electron Back-Scattering Diffraction) method. In particular, it was found that the quality of grain boundaries in the interconnections changed drastically during their manufacturing process depending on the electroplating conditions and thermal history after the electroplating. In addition, the crystallographic quality of the interconnections was found to be degraded seriously by the stress-induced migration of the component elements.

Sample Preparation
The dependence of the electrical reliability of the electroplated copper thin film interconnections on thermal history was then investigated. The thin film interconnections were made by damascene process for electromigration (EM) test as shown in Fig. 1. First, 1.5-μm thick SiO2 layer was deposited on a Si wafer by Plasma-CVD. Next, the SiO2 layer was locally etched off to make thin trenches whose depth was 1.0 μm. Thin Ta and Copper layers were deposited by sputtering. The trench was filled by electroplated copper film. Electroplated copper thin films used in this study were prepared as follows. The composition of a plating bath used for electroplating was controlled by diluting CuO powder of 80 g, the H2SO4 of 186 g with purified water of 1000 ml. The test films were electroplated on stainless steel under the constant current density from 10 mA/cm2 to 100 mA/cm2 at 30°C. Finally, the excess copper layer was mechanically-polished to make isolated interconnections. In addition, some films were annealed after the electroplating in pure Ar gas at 200°C and 400°C for 30 minutes.

The as-electroplated films mainly consisted of fine grains as shown in Fig. 2(a). On the other hand, the average grain size of the films annealed at 200°C increased drastically as shown in Fig. 2(b). Therefore, the recrystallization of the films started to occur at temperatures lower than 200°C. The average grain size increased further after the annealing at 400°C.
400°C (Fig. 2(c)). Thus, recrystallization of the electroplated copper thin films started to occur at temperatures higher than 200°C.

The change of the quality of the annealed films was evaluated by X-ray diffraction and EBSD analysis. The measured results are summarized in Table 1. Since the FWHM (Full width at half maximum) was decreased by about 20%, the quality of the annealed films improved clearly. However, the characteristic of grain boundaries of the film annealed at 200°C was almost the same as that of the films annealed at 400°C as shown in Table 1, even though the average grain size of the annealed films increased with the increase of the annealing temperature. In addition, the ratio between high angle (random) grain boundaries and \( \Sigma 3 \) CSL (Coincidence Site Lattice) grain boundaries was almost the same between the films annealed at 200°C and 400°C. Thus, the crystallinity of the annealed films was almost constant when the annealing temperature was higher than 200°C.

**Mechanical Properties of Electroplated Copper Films**

A simple uni-axial tensile test was performed using EZ Gragh (made by Shimazu Corporation). The films were attached on a jig. The width of each specimen was 2.5 mm and its length was 5.0 mm, respectively. A tensile test was performed at room temperature under a constant strain rate of \( 10^{-4} \text{s}^{-1} \).

Figure 3 shows the typical stress-strain curves obtained by the tensile test. An as-electroplated film fractured without clear plastic deformation and thus, it was rather brittle. The stress-strain curve of the annealed films changed drastically comparing with that before annealing. The yield stress of the annealed films decreased drastically from about 270 MPa (before annealing), to about 140 MPa (after annealing at 200°C), and to about 80 MPa (after annealing at 400°C), respectively. The main reason for this change can be attributed to recrystallization of the annealed film, i.e. grain coarsening and the improvement of the grain boundary integrity as shown in Fig. 2.

The fatigue test was performed by using Magnetic Micro Testing system MMT-101NV10 (made by Shimazu Corp.). The fatigue test condition was as follows. The cyclic uni-axial tensile load was applied to the film using a sine wave and the stress ratio was fixed at 0.1. The frequency of the fatigue test was fixed at 1.5 Hz.

Figure 4 summarizes the change of the fatigue strength of the electroplated copper thin films. In the low cycle region between about \( 10^2 \) cycles and \( 10^5 \) cycles, the fatigue strength of the annealed films decreased drastically. The fatigue strength of the film annealed at 200°C was similar to that of the film annealed at 400°C in the low cycle region. In high cycle region, however, the fatigue strength of the films annealed at 200°C was almost same as that of the as-electroplated films. On the other hand, the fatigue strength of the films annealed at 400°C improved clearly in high cycle region. Thus, the fatigue strength of the films also varied drastically due to the thermal history after the electroplating.

Figure 5 shows typical examples of the fatigue fracture surfaces of each film. Neither striation pattern (slip line) nor dimple was observed in the fracture surface of the as-electroplated films as shown in Fig. 5 (a). This result indicates that fatigue cracks seemed to propagate along grain boundaries and the fatigue fracture mode of the as-electroplated film was brittle intergranular fracture. But both clear striation patterns (slip lines) and dimples were observed in the fracture surface of the films annealed at 400°C as shown in Fig. 5 (d). This surface clearly indicates that plastic deformation occurred and fatigue cracks propagated in grains. Therefore, this fracture mode was a typical ductile transgranular fracture mode. On the other hand, two kinds of the fracture surface were observed in the films annealed at...
Fig. 5. Cross-sectional SEM photographs of the fracture surface of the electroplated copper thin films after their fatigue test: (a) As-electroplated, (b) Annealed at 200°C and fractured in low cycle region, (c) Annealed at 200°C and fractured in high cycle region, (d) Annealed at 400°C

200°C. Some striation patterns (slip lines) and dimples were observed on the fracture surface obtained in low cycle region as shown in Fig. 5(b). This fracture surface was similar to that of the film annealed at 400°C. This result indicates that this fatigue fracture mode was a typical ductile transgranular fracture mode. However, a brittle fracture surface was observed in high cycle region as shown in Fig. 5(c). This fracture surface was similar to that observed in the as-electroplated films. This brittle fracture mode was caused by the porous grain boundaries in the electroplated films. Even though grain coarsening occurred by annealing at 200°C, the porous and brittle grain boundaries still remained in the films, probably around the fine grains. These results indicate that the crack propagation path during the fatigue fracture was determined by the crystallinity of grain boundaries. The film annealed at 200°C consisted of the porous and brittle grain boundary and coarsened grains. As a result, there were two kinds of the fatigue fracture mode.

Electrical Properties of Electroplated Copper Films

The electrical resistance of the interconnection was found to vary depending on the current density during electroplating. The resistivity of the electroplated copper thin films was higher than that of bulk copper and it increased monotonically with increase of the current density. It was about twice when the current density was 10 mA/cm². The electromigration test was applied to the interconnections. The current density applied to the interconnection during the test was varied from 1 MA/cm² to 10 MA/cm².

Abrupt electrical open failure caused by local fusion was often observed in the as-electroplated films within a few hours as shown in Figs. 6 and 7(a). Since there were a lot of porous grain boundaries in the as-electroplated film, the local high Joule heating should have caused the fusion at one of the porous grain boundaries. Actually, it was confirmed that the open failure rate increased linearly with the square of the amplitude of the applied current density as shown in Fig. 8.

On the other hand, the lifetime of the annealed interconnections became longer than that of the interconnection without annealing because the diffusion of copper atoms was enhanced significantly after the annealing of change of the fracture mode clearly indicates the improvement of the crystallographic quality of grain boundaries in the annealed interconnections.

However, the stress-induced migration occurred in the annealed interconnections as shown in Fig. 9. Hillocks appeared without current loading on the surface of the annealed interconnections 72 hours later at even room temperature after the annealing as shown in Fig. 9(b). The number of hillocks had increased continuously for about 6 months as shown in Fig. 9(d). This stress-induced migration was caused by high tensile residual stress which occurred in the film during cooling process after the annealing due to the constraint of the shrinkage of the films by rigid oxide around them. These results clearly indicated that the control of both the micro-texture and residual stress is indispensable for improving the reliability of the electroplated copper thin film interconnections.

Thus, the residual stress of each film was measured after electroplating and annealing. The residual stress in thin films was determined based on the elastic deformation of a substrate after deposition and annealing of the thin films without patterning. Assuming that the residual stress in the...
Fig. 9 Change of the surface morphology of the annealed electroplated copper thin film interconnection caused by stress-induced migration

Fig. 10 Change of the electrical resistivity of the interconnection due to stress-induced migration

 deposited or annealed film was uniform, the residual stress in the film was calculated by the measured change of the radius of the substrate. The residual stress of the as-electroplated films changed drastically depending on the current density during electroplating. The residual stress of the film electroplated at current density of 50 mA/cm² was much higher than that at current density of 10 mA/cm² and it was about 90 MPa. On the other hand, the residual stress in each film increased significantly after the annealing at 400°C, and it reached almost the same value of about 250 MPa. Since this value was much higher than the yield stress of the films annealed at 400°C as shown in Fig. 3, this residual stress was high enough to cause stress-induced migration in the films. The residual stress in the annealed films after 6 months was found to decrease to the stress lower than the yield stress of about 90 MPa, and no further growth of hillocks was observed. This result clearly indicates that the formation of hillocks was dominated by the high tensile stress caused by the annealing.

In addition, the stress-induced migration caused the increase of the electrical resistivity of the interconnections as shown in Fig. 10. The resistivity increased continuously during 6 months, and it reached almost twice of the initial value when the interconnection was electroplated at 50 mA/cm². It was also found that the abrupt fracture of the interconnection due to the local fusion appeared again during the EM test after the hillock formation. This result clearly indicates that not only hillocks but also voids segregated in the interconnection during the stress-induced migration of copper atoms, and thus, caused the abrupt failure.

Fig. 11 Change of distribution of IQ value depending on the current density during electroplating

Observation of the Change of the Crystallinity of the Electroplated Copper Thin Films

A novel evaluation method of the crystallinity of grain boundaries was proposed by analyzing the quality of Kikuchi lines obtained from the conventional EBSD analysis. [7] This method can evaluate the porous and brittle grain boundaries by IQ (Image Quality) and CI (Confidence Index). Both IQ and CI values are the parameters which are calculated from the observed result of the Kikuchi pattern obtained from the area where electron beams penetrate during EBSD analysis. The space resolution of the EBSD analysis determines the spatial resolution of the IQ and CI values. The IQ value indicates the crystallinity of the measured area. It is average intensity of Kikuchi lines obtained from the measured area during EBSD analysis. The CI value indicates the position of a grain boundary in the measured area. The CI value varies from 0 to 1. When the crystallinity of the two grains are close, this CI value becomes almost 0. On the other hand, the CI value is 1, when the measured area consists of one grain. Thus, the position of the grain boundaries is determined by this CI value, and the crystallinity of the film around the grain boundaries is evaluated by the IQ value quantitatively. In this study, the diameter of an electron beam was fixed at 50 nm, and it was scanned two-dimensionally on each interconnection.

Figure 11 shows the change of the distribution of the IQ values as a function of the current density during electroplating. It is clear that the crystallinity of the electroplated copper thin film was improved by decreasing the current density. The average grain size of the film electroplated at 10 mA/cm² was much larger than that at 50 mA/cm². In addition, the IQ value of the film electroplated at 10 mA/cm² was much higher than that at 50 mA/cm². Thus, it was confirmed that the current density during electroplating is one of the dominant factors that determine the crystallinity of the electroplated films.

Figure 12 shows the change of the crystallinity of the electroplated copper thin film interconnections due to the annealing. In this figure, dark blue area corresponds to the area with low IQ value and low CI value, and thus porous grain. Dark blue area corresponds to the area with low IQ value and low CI value, and thus porous grain boundary. It is clearly seen that the most areas of the as-electroplated
Fig. 12 Change of the crystallinity of the electroplated copper thin film interconnections evaluated by the combination of the IQ and CI values

(a) As-electroplated                   (b) Annealed at 400°C

Fig. 13 Change of the crystallinity of the electroplated copper thin films evaluated by the combination of the IQ and CI values (Red areas indicate the grain boundaries with low crystallinity.)

interconnection consisted of the dark blue area as shown in Fig. 12(a). This result indicates that the crystallinity of this interconnection was quite low. There were a lot of fine grains and grain boundaries with low crystallinity. On the other hand, the color of the most area of the interconnection annealed at 400°C turned from dark blue to red as shown in Fig. 12(b). This result indicates that the crystallinity of the most coarsened grains was improved.

Figure 13 shows the change of the color map in the typical measured area of the films as a function of annealing temperature. The area painted by red indicates the area with low CI value and low IQ value and this area consists of the grain boundaries with low crystallinity. There are a lot of red areas in grains and along grain boundaries in the as-electroplated film (Fig.13 (a)). This result indicates that the film consisted of the low crystallinity of both grain and grain boundaries. When the film was annealed at 200°C, the number of the grain boundaries colored by red decreased drastically as shown in Fig.13 (b). However, there still remained the continuous poor grain boundary network in this film. This result clearly indicates that the porous, in other words, brittle grain boundaries could not be eliminated completely by the annealing at 200°C. It was confirmed by EBSD analysis that the most porous grain boundaries remained at high angle (random) grain boundaries. The color of grain boundaries at Σ3 CSL grain boundaries was found to change from red to black. The most red areas disappeared after the annealing at 400°C as shown in Fig. 13(c). Black marked areas, in other words, high quality grain boundaries existed along both high angle grain boundaries and CSL Σ3 grain boundaries. Therefore, it can be concluded that the crystallinity of grain boundaries was improved significantly by annealing at 400°C.

However, the crystallinity of the film was degraded again due to the stress-induced migration as shown in Fig. 14. The formation of many hillocks on the surface of the film indicates that a lot of vacancies remained in the film. Since the local fusion occurred in this degraded film as shown in Fig. 13, the vacancies should have segregated around grain boundaries where the diffusion of copper atoms was accelerated by the stress-induced migration. Therefore, it was concluded that the crystallinity of the grain boundaries of the electroplated copper thin films varies the reliability of the film. It is very important, therefore, to improve the quality of their crystallinity in order to assure the reliability of products.

Improve the Crystallinity of the Electroplated Copper Thin Films

The reason for the low crystallinity of the electroplated copper thin-film interconnections was attributed to the low quality of the base copper film deposited on the tantalum layer which was used for the diffusion barrier of copper into silicon dioxide and silicon. The low crystallinity was considered to be caused by large mismatch in the lattice constant between copper and tantalum. The mismatch was about 18%. Thus, a new material, ruthenium, was introduced between the tantalum layer and the electroplated copper layer. The mismatch between tantalum and ruthenium was about
8%, and that between copper and ruthenium was about 6%. This low mismatch among the three-stacked layers should improve the quality of atomic configuration in each layer.

Figure 15 summarizes the change of the crystallinity of the electroplated copper interconnections as functions of base material and current density during electroplating. It was found that the average IQ value of the films grown on the ruthenium layer was about 30% higher than that on the copper layer regardless of the current density during electroplating. This result clearly indicates that the crystallographic quality of the base material for electroplating dominates the crystallinity of the electroplated copper thin films. In addition, the improvement of the crystallinity decreased the electrical resistivity of the electroplated films as shown in Fig. 16. Thus, the crystallinity of the electroplated copper films directly influences the resistivity of the films. This improvement of the crystallinity also improved the lifetime of the interconnection during the electromigration test. No abrupt failures were observed in the as-electroplated copper interconnections grown on the ruthenium layer regardless of the current density during electroplating. Beside, no open failures occurred for 10 hours even under the current density at 10 MA/cm². In addition, no open failures due to stress-induced migration were observed for 6 months after the annealing at 400°C. This was because that the residual stress in the annealed film was less than the yield stress of the annealed film. It was confirmed that the crystallinity of the electroplated films changed drastically, and ruthenium is one of the effective material for improving the crystallinity of the films.

Conclusions

Both the electrical and mechanical properties of the electroplated copper thin film interconnections varied drastically depending on not only the electroplating condition, but also the thermal history after the electroplating. This was due to the change of the crystallinity of the electroplated copper thin films. It is, therefore, very important to control the micro texture and the crystallinity of the electroplated copper thin film interconnections to assure the reliability of electronic products. A novel method for evaluating the local change of the crystallinity of the annealed films in nano-scale was proposed by using the combination of the IQ and CI values obtained from the EBSD analysis, which can evaluate the crystallinity of a grain and a grain boundary quantitatively. The change of these values corresponded to the changes of mechanical and electrical properties of the electroplated copper thin films due to annealing after electroplating. Therefore, the quality of grain boundaries can be evaluated by using the proposed combination of the IQ and CI values clearly, and thus, this method is effective for evaluating the crystallinity of grain boundaries of the film and thus, the change of mechanical and electrical properties of the electroplated copper thin films. The introduction of a ruthenium layer as the base material for the electroplating is one of the effective methods for improving the crystallinity of electroplated copper thin films and thus, the reliability of electronic products.

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References