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An electroplating method for copper plane twin boundary manufacturing

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ABSTRACT

A twin boundary is a special kind of grain boundary that plays an important role in the deformation process of nanocrystalline metals, as it may affect the migration of atoms and electrons in polycrystalline solids, resulting in different electrical and mechanical properties. In this study, plane twin structures were introduced into an electroplated copper film by an electroplating method that inserts an interlayer film with a very small current density (<3 mA/cm^2). It was found that the small-current interlayer formed a demarcation line for copper grain growth, and enhanced the twin boundaries by self-annealing at room temperature. Based on this, a method was developed to manufacture multi-plane twin boundaries to improve electron migration. Transmission electron microscopy, focused ion beam analysis, and secondary ion mass spectrometry were employed to examine this interesting phenomenon.

1. Introduction

In sub-130 nm semiconductor device manufacturing, copper (Cu) is used as the interconnection metal as a replacement for aluminum, because it has higher conductivity and good reliability. Different from the metal-etching patternization that occurs in the aluminum (Al) metallization process, the Cu metal lines are produced by the damascene process, including the deposition of diffusion barriers and Cu metals, and the removal of overburden metals by chemical mechanical polishing. The electrochemical plating (ECP) method is widely used for the preparation of Cu metallization layers. In the field of Cu metallization reliability, electromigration (EM) due to the motion of atoms in an electrical field has been widely studied [1–5]. The effective diffusivity in Cu lines during EM mass flow is related to the microstructure and impurity content of the Cu metal, and is controlled by fast diffusion paths, such as interfaces and grain boundaries [5]. The activation energy for grain boundary transport is higher than that for surface transport [1]. For EM, the existence of narrow lines affects the atomic diffusion mechanism. For wide polycrystalline lines (>1 μm), the dominant diffusion mechanism is a mixture of grain boundary and surface diffusion, while for narrow ones (<1 μm) the dominant mechanism is surface transport.

In general, a tradeoff must be made between conductivity and mechanical strength. An electro-deposited Cu sample with a high density of nano-scale growth twins shows an ultrahigh tensile strength without affecting its electrical conductivity [6–11]. A twin boundary is a special kind of coherent boundary that may also be effective in blocking dislocation motions, similar to conventional grain boundaries that can be used to improve EM performance. However, twin boundaries are much more stable against migration than conventional grain boundaries, as their excess energy is one order of magnitude lower than that of grain boundaries. In addition, the strength of Cu increases with decreasing twin thickness [8]. Some studies carried out in situ ultrahigh-vacuum and high-resolution transmission electron microscopy, and observed EM induced atomic diffusion in the twin-modified grain boundaries. The triple point where a twin boundary meets a grain boundary has been shown to slow down grain-boundary and surface EM by one order of magnitude [9].

The quality of the electroplated Cu film depends on several factors, such as plating current density, Cu thickness, rotation speed and the chemistry of the plating solution [12–24]. Previous studies have shown that grains with a (111) crystallographic orientation have twin boundaries that form an angle of 60 °C, while (200) oriented grains have twin boundaries that intersect at an angle of 90 °C. A cross section of the Cu grain structure showed that the microstructure was comprised of large columnar grains that were generally of a height comparable to that of the film thickness, and the twins contained within such grains spanned the entire film thickness [21]. This earlier study pointed out that the formation of twin boundaries in nano-sized Cu grains is not controlled by grain size, but by grain growth. The twin boundaries could be annealing twins caused by irregularities in the stacking sequence during relatively fast grain growth [25].

2. Experimental procedure

In this study, a Cu electroplating bath including cupric sulfate of 0.25 mol/l, sulfuric acid of 1.8 mol/l and chloride ions of 50 ppm, was used as a standard solution. Organic additives, namely 10 ppm polyalkylene glycol (PAG) and 500 ppm bis-(3-sodiumsulfopropyl

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disulfide) (SPS) were added to this standard solution. The PAG is used as suppressors and SPS is used as accelerators. Before Cu electroplating, a 200-nm-thick oxide film was deposited on a bare silicon wafer, with a 200-nm-thick ionized-metal-plasma (IMP)-Cu film being used as a seed layer. The IMP deposition used inductively coupled Ar plasma to ionize sputtered atoms, which were highly directed by the potential difference between the plasma and substrate. The process pressure was controlled at 27 Pa. The gas purity was 99.9999%, and the gas flow was controlled within ±0.1 sccm by mass flow controllers, which guaranteed reproducible deposition conditions. After the deposition of the Cu seed layer, the wafer was electroplated under galvanostatic control at room temperature. After the Cu electroplating process, the samples were annealed at 200 °C for 90 s with 4% H_2/N_2 forming gas. The plating current and rotation speed are the major factors to affect the quality of Cu film during ECP process. Hence, the purpose of this study is to evaluate the effects of interlayers produced with various plating currents and rotation speeds on the formation of twin boundaries. The plating current is for 3 to 9 mA/cm^2 and rotation speed is 10 to 50 rpm. In addition, both single and multiple-layers were used to study the effects of film stacking. Transmission electron microscopy (TEM) experiments were performed in an FEI X-Twin Tecnai, operating at 200 kV and equipped with a Gatan heating holder. The heating and cooling rates used were 10 °C min^{-1}. High resolution TEM images were obtained in a JEM-2100F Electron Microscope to measure the structure of the twin boundary and a high-energy electron beam (~200 keV) interacts with an electron transparent (~100–150 nm thick) specimen to study the microstructure and composition. Focused-ion-beam (FIB) analysis was used for twin boundary detection and the operating voltage was on 30 kV. Secondary ion mass spectrometry (SIMS) of CAMECA IMS 7F was used to detect the interlayer impurity conditions for element analysis. The ion sources include O_2^+ (10 kV) and Cs surface ionization source (15 kV). The operating voltage was about 10–15 kV in the high vacuum system (1.33×10^{-7} Pa) and the samples were 1 cm × 1 cm.

3. Results and discussion

In this study, we found that twin boundaries were easily formed by control of the Cu electroplating process conditions. Fig. 1(a) shows the TEM image of the 2.4-μm-thick electroplated Cu film that was deposited at 35 mA/cm^2 and annealed at 200 °C for 90 s with 4% H_2/N_2 forming gas. In this case, no twin boundary appeared in the electroplated Cu film. On the other hand, Fig. 1(b) shows that there were clear twin grains with the width of 200 nm in the Cu film. In this case, an extra interlayer electroplated by a small current density of 3 mA/cm^2 was inserted in the Cu film. This small-current interlayer could block the grain growth of the electroplated Cu film, and thus enhance the formation of Cu twin boundaries.

In order to investigate the evolution of the twin boundary formation, the electroplated Cu films without post-annealing were examined by FIB. Fig. 2(a) to (f) shows the cross-section profiles of Cu films with different self-annealing times at room temperature. It can be seen that after 55-h of self-annealing, the grains of the electroplated Cu film grew and formed a twin boundary from the film surface toward the substrate, and stopped at the interlayer, as shown in Fig. 2(c). At the same time, the Cu grains under the interlayer did not grow, even after 64-h of self-annealing, as shown in Fig. 2(d). However, after 98 h and 145 h of self-annealing, as shown in Fig. 2(e) and (f), Cu twin boundaries were formed both below and above the interlayer. It can be seen in the images that, the twin boundaries were interrupted by the interlayer and formed independently.

In order to study the mechanism of the effects that the interlayer has on the formation of Cu twin boundaries, the interlayer was produced using different plating current densities and rotation speeds. In these cases, the annealing process was carried out after Cu electroplating. Fig. 3 shows the FIB cross-section images of the interlayers produced using different conditions. As the plating current density increased from 3 to 9 mA/cm^2, the Cu interlayer became weaker and disappeared at 9 mA/cm^2. When the plating current density was 9 mA/cm^2, less twin boundaries were formed. A lower plating current density produced a better interlayer for the twin boundary formation. On the other hand, when the rotation speed of Cu electroplating decreased from 50 to 10 rpm, the Cu interlayer became a little weaker. These results show that the plating current density was the major factor in enhancing the Cu interlayer and the formation of twin boundaries.

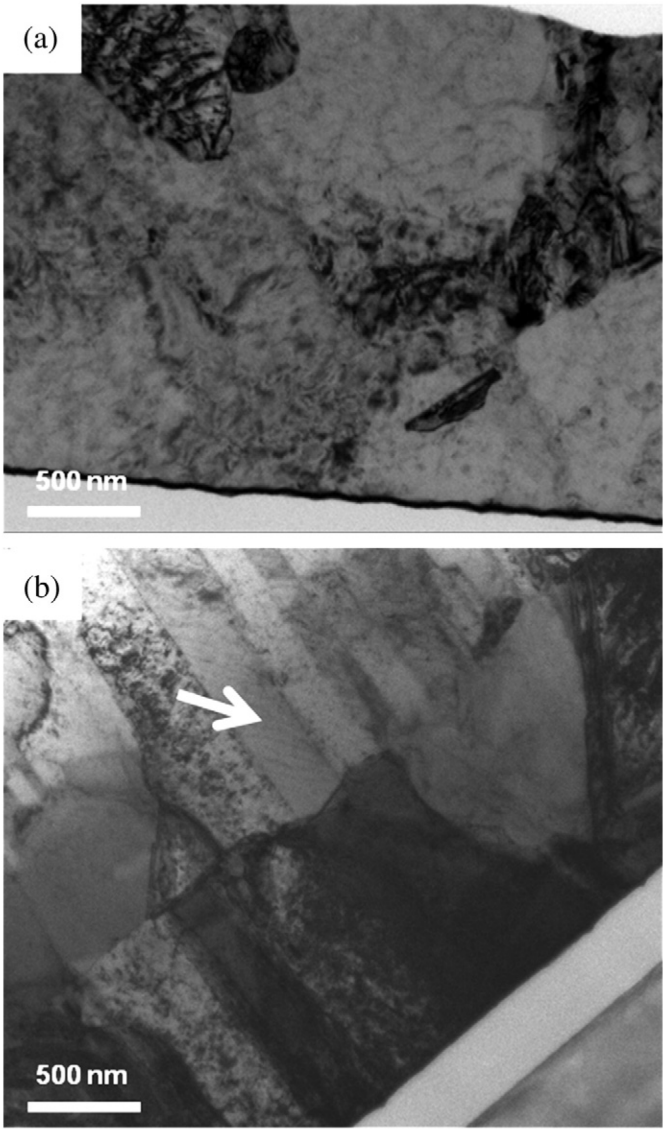

Fig. 1. TEM images of twin boundaries in 2.4-μm-thick electroplated Cu films produced at 35 mA/cm^2 (a) without an interlayer and (b) with an interlayer by plating current density of 3 mA/cm^2.

According to previous literature, certain amounts of impurities, like carbon, sulfur and chlorine will co-deposit into Cu film during the electroplating process. Stangl et al. pointed out that carbon has the ability to inhibit the grain growth of electroplated Cu film [20]. We prepared the samples with different electroplating current densities, and detected the impurities using SIMS, as shown in Fig. 4(a). The Cu film deposited at a lower electroplating current density contained more carbon. Fig. 4(b) shows that when a 3 mA/cm^2 interlayer was inserted in the electroplated Cu film, the carbon concentration of Cu increased from 9e20 to a peak value of 2.6e21 atom/cm^2. This is because the organic additives are hard to breakdown in lower current density

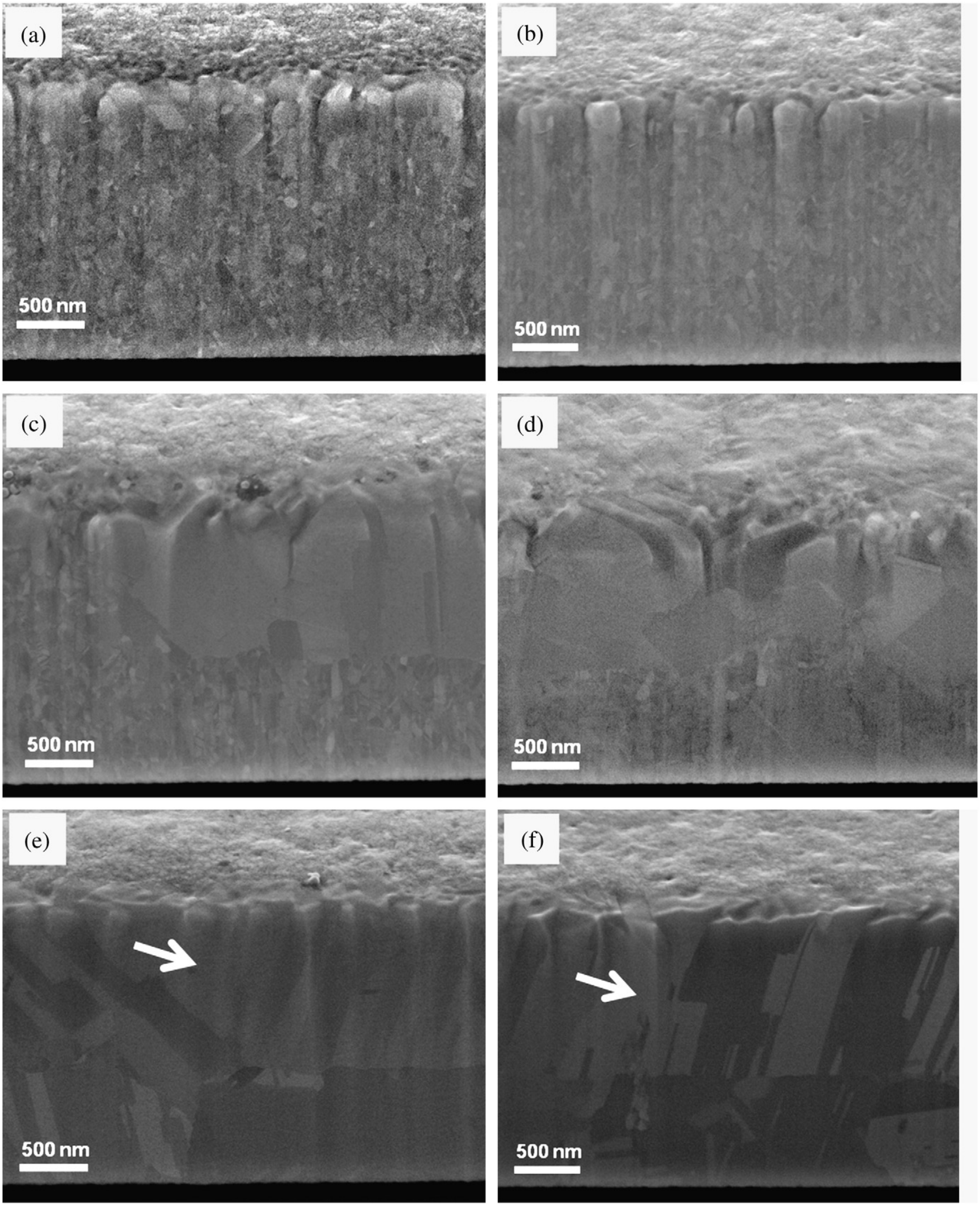

Fig. 2. FIB images of interlayer inserted electroplated Cu films with a self-annealing time of (a) 0 h, (b) 32 h, (c) 55 h, (d) 64 h, (e) 98 h and (f) 145 h.

during ECP process. At the same time, the higher rotation speed causes the organic additives easily diffusing to the Cu films. The data indicates that a lower plating current trapped more carbon in the Cu films, and then limited the Cu grain growth.

The sheet resistance also has different behavior with and without an interlayer, as shown in Fig. 5. The film deposited with an interlayer needed a longer time to reach stable sheet resistance, and had a higher sheet-resistance as compared with the film without an interlayer. This

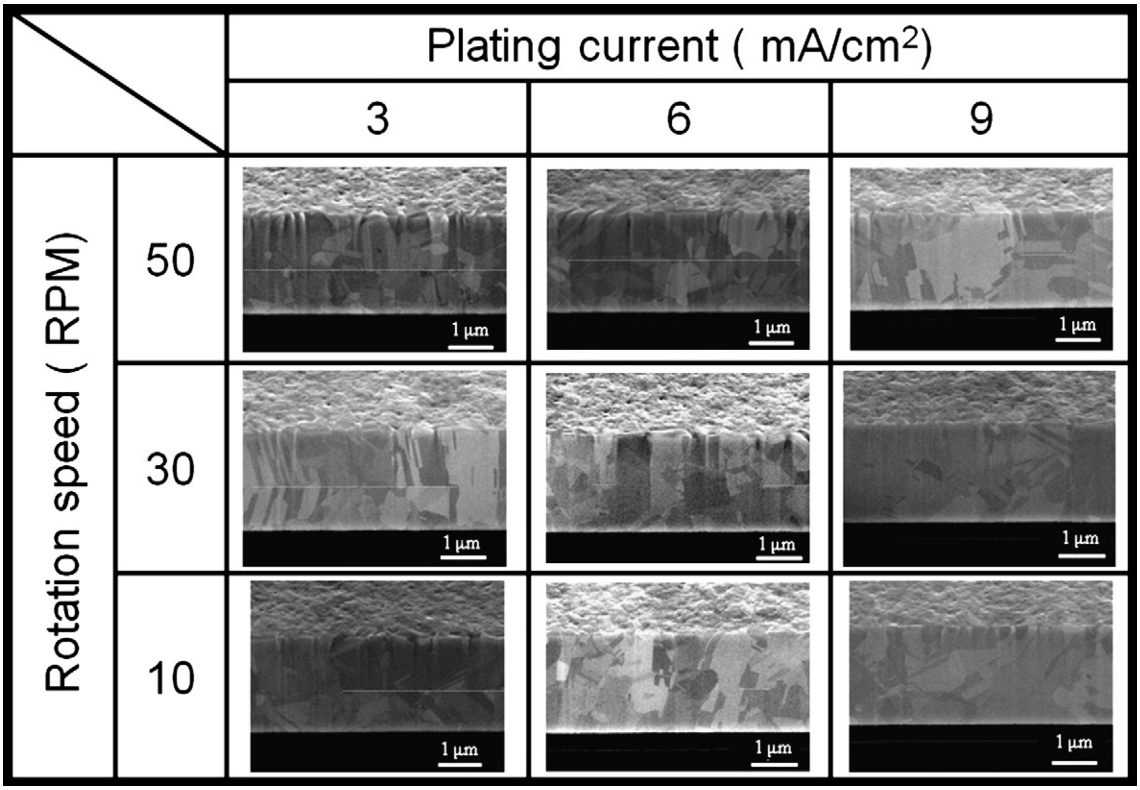

Fig. 3. Electroplated Cu film interlayers with different plating currents and rotation speeds. A lower plating current and higher rotation speed will lead to a better interface for twin boundary formation.

result indicates that the electroplated Cu film with an interlayer inhibited grain growth and induced more Cu twin boundary formation, causing an increase in sheet resistance.

Finally we demonstrated the formation of rich twin boundaries in the electroplated Cu film by inserting multiple interlayers, as shown in Fig. 6. This method could be applied in the semiconductor Cu electroplating process to improve interconnect reliability [9].

4. Conclusion

This study demonstrated a method to enhance the formation of twin boundaries in electroplated Cu films. The method is to insert a

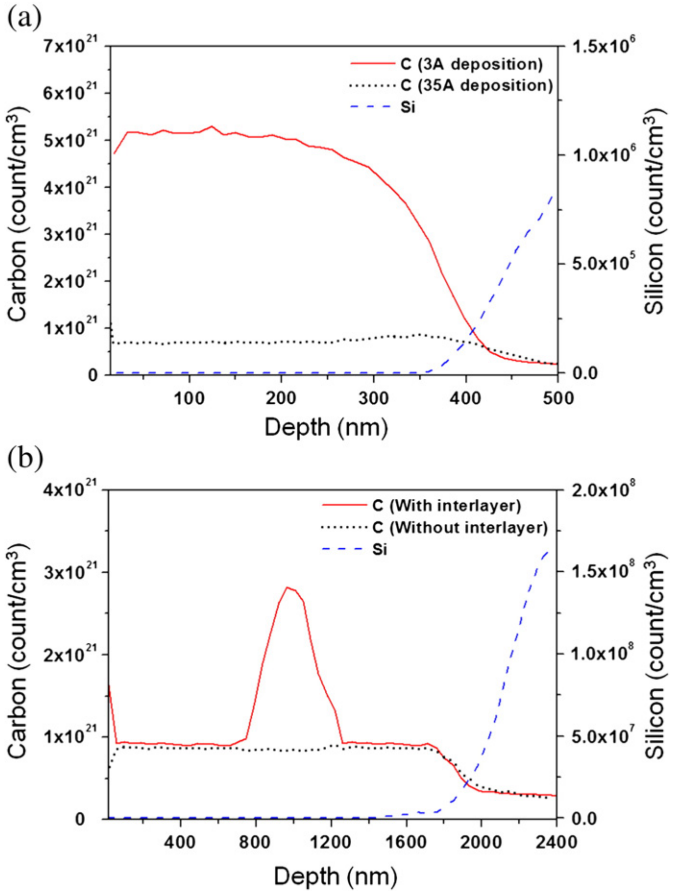

Fig. 4. Carbon SIMS impurity profile of the Cu films electroplated at (a) 3 and 35 mA/cm^2 and (b) with and without an interlayer.

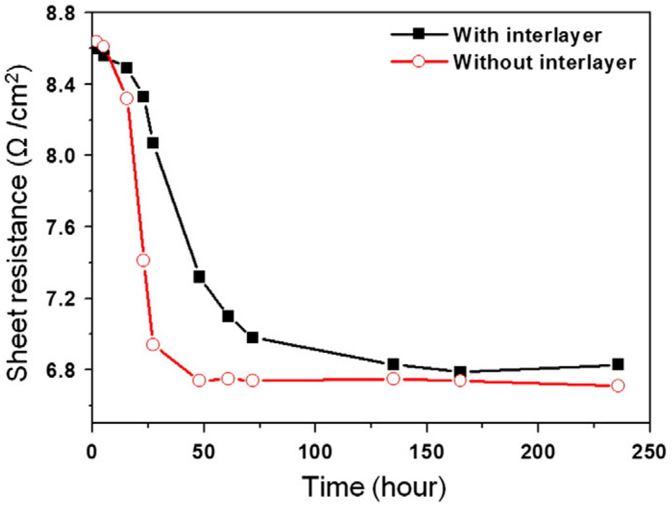

Fig. 5. Self-annealing effects on the resistance with and without an interlayer by sheet resistance measurement.

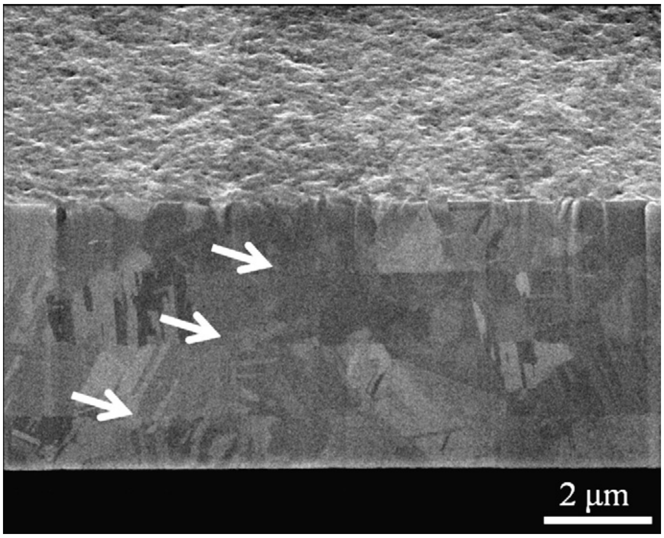

Fig. 6. FIB image of the electroplated Cu film with three inserted interlayers.

small-current interlayer in the Cu film. The low-current interlayer could trap higher-level carbon to limit Cu grain growth and enhance the formation of Cu twin boundaries. An electroplated Cu film with multi-interlayers was demonstrated in this study to produce rich twin boundaries.

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