The Effect of Copper Dissolution in Acidic Electrolyte on the Formation of Nanotwin in Pulse Electrodeposited Copper

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The effect of Cu dissolution during pulse electrodeposition process on the generation of high density nanoscale twin structure was investigated. During off-time, the density of nuclei was reduced by acidity of electrolytes. The reduction in the density of nuclei could suppress the formation of nanocrystalline structure, which is commonly observed at pulse electrodeposition, and the twin structure was generated to reduce the accumulated strain energy during on-time in grains. We confirmed the effect of the dissolution of Cu on the twin generation by measuring the mechanical strength and electrical resistivity of Cu deposits obtained at different pH, with which, the dissolution rate of Cu was controlled.

The dissolution rate of Cu during off-time was applied as 0.5 A/cm², therefore, the average current density of PC-ED was 23.8 mA/cm². The current density of DC-ED varied from 0.1 to 3.5 by adding sulfuric acid. The deposition bath was basically fixed as ~10 μm. However, the film thickness only for tensile test was ~120 μm, because of the load cell of tensile tester applied in this work. The capacity of the load cell is 1 ton which is not for thin films. The electrical resistivity would not strongly depend on the film thickness if the film thickness is over micrometer unit. The highly purified copper sheet (99.99%) was selected as a soluble anode for electrodeposition. The distance between cathode and anode was adjusted as 3.0 cm. The electrolyte was comprised of copper sulfate (1.0 M) without any other additives, and the pH was varied from 0.1 to 3.5 by adding sulfuric acid. The deposition bath was mechanically stirred with 200 rpm during pulse electrodeposition. The film thickness was measured by mechanical testing with quartz crystal microbalance (QCM, QCM200, Stanford Research Systems). The confirmation of the nanotwin structure was performed with transmission electron microscope (TEM, JEM-2100F, JEOL). The samples for TEM observation were prepared by jet-polishing and ion-milling method to minimize the potential damage to the microstructure during sample preparation. The position of TEM samples was well-controlled. The TEM images were observed at the middle depth (~5 μm) of 10 μm Cu films, and the depth position was confirmed by optical microscope observation. Mechanical strength and electrical resistivity could be the basic and essential property to indirectly identify the density of nanotwin Cu. Therefore ultimate tensile strength (UTS) of true stress was calculated from the engineering stress and cross-sectional area of the fractured samples. The engineering stress, film thickness, and film width were measured by tensile tester (RB-301 Unitech M., R&B Inc.), optical microscope (KH-7700, HIROX co., ltd.) and vernier calipers, respectively. Samples for tensile test were prepared in the shape of dog-bone, and the gauge length was 6.0 × 10⁻³ cm with the gauge length as 15 mm. Electrical resistivity was calculated from sheet resistance and film thickness.

Experimental

Nanotwin Cu films were deposited by PC-ED on Cu (200 nm) / Ti (50 nm) layers, which was prepared on glass substrates. The size of deposited Cu film was 2.5 cm × 1.0 cm, and the thickness was basically fixed as ~10 μm. However, the film thickness only for tensile test was ~120 μm, because of the load cell of tensile tester applied in this work. The capacity of the load cell is 1 ton which is not for thin films. The electrical resistivity would not strongly depend on the film thickness if the film thickness is over micrometer unit. The highly purified copper sheet (99.99%) was selected as a soluble anode for electrodeposition. The distance between cathode and anode was adjusted as 3.0 cm. The electrolyte was comprised of copper sulfate (1.0 M) without any other additives, and the pH was varied from 0.1 to 3.5 by adding sulfuric acid. The deposition bath was mechanically stirred with 200 rpm during pulse electrodeposition. The film thickness was measured by mechanical testing with quartz crystal microbalance (QCM, QCM200, Stanford Research Systems). The confirmation of the nanotwin structure was performed with transmission electron microscope (TEM, JEM-2100F, JEOL). The samples for TEM observation were prepared by jet-polishing and ion-milling method to minimize the potential damage to the microstructure during sample preparation. The position of TEM samples was well-controlled. The TEM images were observed at the middle depth (~5 μm) of 10 μm Cu films, and the depth position was confirmed by optical microscope observation. Mechanical strength and electrical resistivity could be the basic and essential property to indirectly identify the density of nanotwin Cu. Therefore ultimate tensile strength (UTS) of true stress was calculated from the engineering stress and cross-sectional area of the fractured samples. The engineering stress, film thickness, and film width were measured by tensile tester (RB-301 Unitech M., R&B Inc.), optical microscope (KH-7700, HIROX co., ltd.) and vernier calipers, respectively. Samples for tensile test were prepared in the shape of dog-bone, and the gauge length was 6.0 × 10⁻³ cm with the gauge length as 15 mm. Electrical resistivity was calculated from sheet resistance and film thickness.

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Almost ten years ago, the synthesis of Cu thin film having ultrahigh mechanical strength as well as low electrical resistivity was proposed by L. Lu et al. Such fascinating physical and electrical properties of Cu are mainly caused by the formation of high density twin structures with nanoscale, therefore this unique Cu has been called as nanotwin Cu. Nanotwin Cu has become a promising candidate for many applications in electronic industries such as advanced interconnect materials, electrodes of rechargeable batteries, core materials for flexible devices, and others.^{1,10} So far, many techniques have been established to prepare nanotwin Cu such as pulse current electrodeposition, magnetron sputtering, and multilayer deposition.^{9,20} Among them, the pulse current electrodeposition (PC-ED) is one of the effective techniques, because the nucleation density could be easily controlled, and the process is cost-effective due to no need for complicated and expensive equipment for high temperature and vacuum systems. After Dr. Lu et al. succeeded in synthesizing nanotwin Cu by PC-ED, and represented an outstanding mechanical and electrical properties compared to those of nanocrystalline and coarse-grained Cu in 2004,^{4} many studies proposed the formation mechanism of nanotwin structures. Dr. Tu’s group reported the formation of nanotwin Cu by relaxing the film stress during off-time in PC-ED. The formation mechanism of nanotwin structure based on the stress relaxation is not sufficient to explain the formation of large grain Cu with nanotwin instead of nanocrystalline Cu in high overpotential conditions. The relationship between the overpotential and the size of nucleation is given by the equation

\[ \eta = \frac{zE}{2s} \frac{1}{\rho s} \left( \frac{\alpha}{e} \right)^{\frac{1}{z}} \]  

where \( \eta \) is the overpotential, \( s \) is the critical radius of the surface nucleus, \( \rho \) is the number of electrons involved in the reaction, the charge of one electron (1.602 × 10⁻¹⁹ C) and the overpotential, respectively. According to the equation, the nucleation size is inversely proportional to the overpotential. The overpotential is also proportional to the current density depending on the Butler-Volmer equation. \(^{2,11,12}\) In case of PC-ED, the peak current density at off-time is very high as few hundreds mA/cm², which is normally much stronger than the current density applied in direct current electrodeposition (DC-ED). Due to significantly higher nucleation density caused by high overpotential, typically very fine grain structure, such as nanocrystalline, would be generated in PC-ED conditions. However, when nanotwin Cu structure is obtained by PC-ED, most of grains are substantially large, and hard to find nanocrystalline structures. The study about stress relaxation of electrodeposited Cu during off-time is not enough to explain why large grain Cu with nanotwin is formed instead of nanocrystalline structure at very strong peak current density in PC-ED. The nanocrystalline Cu might be recrystallized during the off-time (1.0). However, the phenomenon has been not experimentally proven clearly.

In this research, we investigated the effect of Cu dissolution during off-time in PC-ED on the formation of twin structure by observing physical and electrical properties of pulse-electrodeposited Cu obtained at different electrolyte pH.

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which were measured by four point probe (CMT-SR1000N, CHANG MIN co., ltd.) and surface profiler (P-1, TENCOR instruments), respectively. Scanning electron microscope (SEM, S-480, HITACHI) was employed to investigate the grain size of electrodeposited Cu films.

**Results and Discussion**

Stress relaxation during off-time is an important factor to form nanotwin in electrodeposited Cu.\(^8\)\(^,\)\(^12\) However, it is insufficient to explain why the formation of nanotwin structure is preferred, instead of the formation of nanocrystalline structure in PC-ED as described in the introduction part. Therefore, the effect of another factor which is the effect of dissolution in off-time period was investigated.

During Cu electrodeposition, the strain energy could be induced on grains, because of high film stress which was accumulated during the film growth. This strain energy might be released by the deformation of microstructures, such as twin formation or recrystallization.\(^12\) If PC-ED is applied, comparably high peak current density would be applied, which effectively increases the density of small nuclei as well as enhances the growth rate due to the high overpotential. It can, in turn, cause nanocrystalline structures producing large amounts of grain boundaries, without high density twin. This strongly implies that if the nucleation rate is too fast, only nanocrystalline would be formed, and it is difficult to obtain large grains with nanotwin structure. Therefore a certain factor to reduce the nucleation rate at high peak current density must exist to obtain nanotwin structure with comparably big grain size, which could be the dissolution during off-time.

Figure 1 illustrates the schematics about the development of nanotwin structure with pulse current. At the beginning, large numbers of nuclei and grains with various sizes generate on the surface during on-time (Figure 1A). The stress induced by applied high overpotential would be released by creating the nanoscale twin during off-time, however there could be comparably small grains or nuclei without having twin, because they could not have enough volume to generate the stress to form the twin structures. All of the grains would be affected by pH of electrolyte, particularly small grains and nuclei might be much more due to its large surface area per unit volume. In low pH condition, small grains and nuclei could be completely dissolved in electrolytes (This is only extreme assumption. They would not be completely dissolved in the experiments), which results in decreasing the number of small grains, and comparably large grains only could survive (Figure 1(B1)). As process A to B1 are repeated, large grain Cu with high density nanotwin would be obtained (Figure 1(C1)). The size of large nanotwin grains might be not changed even after aging owing to mesostability of nanotwin (Figure 1(D1)). However, in the case of high pH, the small grains and nuclei would not be dissolved during off-time (Figure 1(B2)). After repetition of process A to B2, big grains having nanotwin and grown middle size grains could be coexisted (Figure 1(C2)). The middle grains might be disappeared by coarsening or grown by recrystallization after aging due to high surface energy, possessing comparably small amount of annealing twin (Figure 1(D2)). S-C. Chang et al. observed the reduction in electrical resistivity of electrodeposited Cu film in additive-free conditions during aging time.\(^15\)

In order to confirm the dissolution of Cu in acidic electrolytes, in-situ mass change of electrodeposited Cu during PC-ED was investigated with QCM. Figure 2 represents the mass change during electrodeposition, and the decrease in mass during off-time periods was clearly confirmed as shown in the enlarged inset graph. The change of dissolution rate as a function of pH is shown in Figure 3. As expected, the dissolution rate decreased with increasing pH, and the significant dissolution was not found at pH 3.5. The current efficiency, which was calculated with Faraday equation, was approximately 22%. The rest of the charge seemed to be consumed to hydrogen evolution, which was caused by the high overpotential. However, no hydrogen embrittlement phenomenon was found, and it was confirmed that the mass reduction measured by QCM was only Cu dissolution. Therefore, the effect of hydrogen evolved by high overpotential on the Cu films

**Figure 1.** The schematics of the formation mechanism of nanotwin Cu.

**Figure 2.** Mass change of electrodeposited Cu during PC-ED in-situ measured by QCM.

**Figure 3.** Dissolution rates of deposited Cu as a function of pH.
would be minimal. According to these results, it was confirmed that the electrodeposited Cu was significantly dissolved in highly acidic electrolytes during off-time in PC-ED, and the dissolution rate was highly affected by electrolyte pH.

There was a precedent to analyze twin fraction by employing EBSD.\textsuperscript{11} However, EBSD is not appropriate for quantitatively analyzing twin fraction owing to the significant detection limit of resolution as the author also mentioned.\textsuperscript{11} Therefore, in order to (indirectly but reasonably) show the variation of nanotwin density of entire Cu films, we tried to use the combination of mechanical strength, electrical resistivity and TEM images.

Comparison of the mechanical strength and the electrical resistivity might be one of the effective parameters to confirm the generation of nanotwin structure in pulse current conditions. According to Hall-Petch relation, the mechanical strength is inversely proportional to the average grain size, because grain boundaries serve as sites to lock the movement of dislocations.\textsuperscript{16,17} Twin boundaries act as dislocation-locking sites even more effectively than grain boundaries,\textsuperscript{18–20} therefore the increase in strength of pure Cu might be the results of either nanotwin generation or nanocrystallization. However, the electrical resistivity only increases, when the density of incoherent boundaries, in other word, grain boundaries, increases owing to the electron scattering at the boundaries, and the scattering at the coherent boundary such as twin boundary is minimal. These facts imply that, if there are high density nanotwin without nanocrystallines, the mechanical strength would be enhanced without significant degradation of electrical resistivity.\textsuperscript{1}

Figure \textit{4} and \textit{5} represent the variation of mechanical strength (UTS) and electrical resistivity of Cu pulse-electrodeposited at different pH and off-time (inset). The properties were measured in as-deposited condition. As pH increased, the mechanical strength decreased, and the electrical resistivity slightly increased. It implies that when pH increased, the density of nanotwin decreased with increasing the grain boundary density, because of comparably low dissolution rate of Cu at higher pH. The twin boundary is a coherent boundary so that the influence of twin boundary on the electrical resistivity is minimal, therefore the increase in the electrical resistivity might be the contribution of nanocrystallines (small grains which was not dissolved during off-time).\textsuperscript{4} The variation of the mechanical and electrical properties indicates that the density of nanotwin has been decreased with enhancing pH. We also varied off-time at pH 1.0 which can control the amount of dissolution per cycle. As off-time gets longer which means an increase in the dissolution amount, UTS increased, and electrical resistivity slightly decreased. The mechanical and electrical properties of DC-ED samples were not significantly affected by pH variation. UTS and electrical resistivity of DC-ED samples in the range of pH 0.1\textasciitilde3.5 were 317.7\pm17.5 MPa and 1.87\pm0.03 \(\mu \Omega\cdot\text{cm}\), respectively. UTS of all PC-ED samples showed much higher than those of DC-ED, and the electrical resistivity showed a little bit higher. It seems to be the result from the existence of nanotwin structure. The variation of the mechanical and electrical properties indicates that the density of nanotwin has been decreased with decreasing dissolution rate.

The TEM images visually ensured the nanotwin density variation of Cu films electrodeposited by direct current, pulse-electrodeposited at low pH (0.1) (B) and high pH (3.5) (C) (Figure \textit{6}).
of DC-ED sample was very low in comparison with that of PC-ED samples. Nanotwin structure was observed much more at low pH sample than at high pH sample. However, there was not big difference of grain size between low and high pH samples on SEM images (Figure 7), and the average grain size of low and high pH samples were measured as 0.359 \( \mu m^2 \) and 0.340 \( \mu m^2 \), respectively. This might be attributed to the grain growth during the sample-preparation time for SEM or TEM observations, which was approximately for 12 hours. In order to confirm the assumption, the variation of electrical resistivity of the Cu films after 2 days from the deposition were investigated (Figure 8). The significant decrease in the electrical resistivity was found at high pH sample. This result means that a lot of small grains in high pH sample might be coarsened or recrystallized, which caused a decrease in the electrical resistivity. On the other hand, the electrical resistivity of low pH sample containing high density nanotwin slightly decreased after 2 days, because it already consisted of comparably big grains with nanotwin, which did not have enough driving force for coarsening or recrystallization. There was a negligible change in electrical resistivity after 2 days in DC-ED films.

**Conclusions**

We have investigated that the effect of Cu dissolution for achieving high density Cu nanotwin in pulse electrodeposition. During off-time, dissolution of Cu was obvious in highly acidic electrolytes, so that some of generated nuclei could be disappeared. If the same average current density was applied, much stronger stress could be applied during on-time in PC-ED than DC-ED, because of high peak current density, and the possibility of forming nanoscale twin structures would be significant. The effect of dissolution was verified by observing the variation of twin density, and measuring mechanical and electrical properties of Cu films. The density of nanotwin increased with increasing dissolution rate. As the dissolution rate increased, the mechanical strength increased, whereas electrical resistivity decreased, which also strongly implies that twin density increased. The decrease in electrical resistivity after 2 days was more significant in high pH sample than low pH sample, which means high pH sample has small grains which could be recrystallized to bigger grains without having nanotwin.

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