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Crystal Growth of Electrolytic Cu Foil

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Electrolytic copper deposited on $(100)_{Cu}$ single crystals forms pyramidal crystals that grow parallel to the substrate at low current density without stirring. With stirring and higher current density, slanting platelet crystals with $(111)_{Cu}$ orientation are formed. Chloride and gelatin are typical additives for electrolytic copper foils and the electrolytic copper foils are formed on a titanium substrate with a stirring rate and high current density. With gelatin, triangular pyramidal crystals form with $(111)_{Cu}$ orientation. The triangle-shaped side planes of the crystals are the $(100)_{Cu}$, and platelet crystals exist along the $(100)_{Cu}$. With chloride and gelatin, triangular columnar crystals with the $(110)_{Cu}$ orientation are formed. The triangle-shaped side planes of the crystals are the $(100)_{Cu}$ and the platelet crystals again exist along the $(100)_{Cu}$. These platelet crystals are bound by macrosteps, and they are the growth sites. The morphology of electrolytic copper foils on the titanium substrate does not change with higher current densities and stirring rates. It was also found that chloride changes deposit orientations in the concentration range of less than 10 ppm.

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Electrolytic copper foils have been widely used as the conductors for printed circuit boards (PCBs). About 90% of the copper foils have been produced by the electrolytic process because finer line etching is possible with thinner electrolytic copper foils. Additives play a major role in controlling the properties of electrolytic copper foils.

Carneval *et al.*[1] investigated the effect of morphology and orientation of electrolytic copper deposits by using different anions. Lamb *et al.*[2] investigated numerous electrolytic conditions and pointed out that additives have a critical influence on the cross-sectional microstructures. Barkley *et al.*[3] observed the electrolytic copper deposit morphology on copper single crystal by atomic force microscopy (AFM). It was shown that chloride (Cl^-) has an important role in the faceting electrolytic copper deposits and a monoatomic layer growth model was given.

Cl^- and gelatin are typical additives for electrolytic copper foils. Koura *et al.*[4,5] proposed pyramidal crystal growth with Cl^- and gelatin. Osaka *et al.*[6] also reported the role of Cl^- and gelatin for electrolytic copper foils. Kondo *et al.*[6] recently proposed the crystal growth model of electrolytic copper foil with Cl^- and gelatin. Unfortunately, our previous experiments were done with lower current densities and in an unstirred bath. However, electrolytic copper foils are produced in high current densities and with a high stirring rate in actual production. The electrolytic copper foil is initially deposited on the titanium substrate and then removed from the substrate. Mechanical adhesion between resin and electrolytic copper foil, and anisotropic etching are the critical properties for electrolytic copper foils. These properties are related to the morphology, microstructure, and crystal structure of the metal. Morphology, microstructure, and orientation are determined by the crystal growth mechanism.

Both $(100)_{Cu}$ single crystal and titanium were used as cathode substrates. The role of Cl^- and gelatin on the morphology, orientation, and crystal growth of electrolytic copper foils were investigated at high current densities and high electrolyte stirring rate. We propose a crystal growth model of electrolytic copper foils.

Experimental

Both the electrolytic copper deposits and electrolytic copper foils were deposited with constant current (Hokuto denko, HA-151). Anodes were made of copper plate and two kinds of cathodes were used; the titanium substrate and the $(100)_{Cu}$ single-copper crystal substrate. The baths consist of the basic bath of $CuSO_4 \cdot 5H_2O$ and H_2SO_4 and additives are gelatin and chloride (Cl^-) (Table I). The bath temperature was kept at 40°C. The current densities and stirring rates of the electrolyte were varied. The deposit thickness of electrolytic copper deposits on the $(100)_{Cu}$ single-copper crystal substrate was kept as 1 μm, and electrolytic copper foils on the titanium substrate was 30 μm.

The $(100)_{Cu}$ single-copper crystal (Goodfellow Co.) was used as one of the substrates. Surface treatment of the $(100)_{Cu}$ single-copper crystal is the critical factor for obtaining a good deposit. The surface treatment is done with three polishing steps as follows.[7] Mechanical polishing of the surface initially with emery paper and secondary polishing with diamond particles of 3 μm diam. Next, chemical mechanically polishing the surface with OP-S suspended solution, H_2O_2, and NH_3 on Straus MD-Chem cloth available from Struers Co. The surface was then rinsed in ethanol and deionized water.

The deposit morphologies were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4300). The crystal orientations of the deposits were analyzed by X-ray diffraction (XRD) (Rigaku-denki, RINT2000) and thin film XRD (Rigaku-denki, RINT2500). The relative XRD is defined as follows. *A* represents for area of the individual X-ray peak

$$\text{Relative X-ray intensity} = \frac{A_{\text{Individual peak area}}}{A_{\text{Largest peak area}}}$$

Results

Electrolytic copper deposits on the $(100)_{Cu}$ single crystal.—Figure 1a shows FESEM micrographs of deposits with 60 ppm Cl^- in addition to the basic bath. The deposits are formed at the lower current density of 10 mA/cm^2 and in an unstirred bath. Pyramidal crystals of several micrometers in diameter are formed. These pyramidal crystals consist of stacked square platelet crystals. The edges of the platelet crystals are macrosteps. The platelets grow parallel to the $(100)_{Cu}$ substrate, and the platelet size decreases with respectively higher stacking levels.

Figure 1b shows XRD patterns for the deposits. Since the $(200)_{Cu}$ diffraction produces the strongest intensity, the plane of the platelet crystals, which are parallel to the substrate, is the $(100)_{Cu}$.

Table I. Bath compositions.

Chemicals		Concentration
	Basic bath	
$CuSO_4 \cdot 5H_2O$		270 g/L
H_2SO_4		100 g/L
	Additives	
Gelatin		0, 10 ppm
Cl^-		0, 10 ppm

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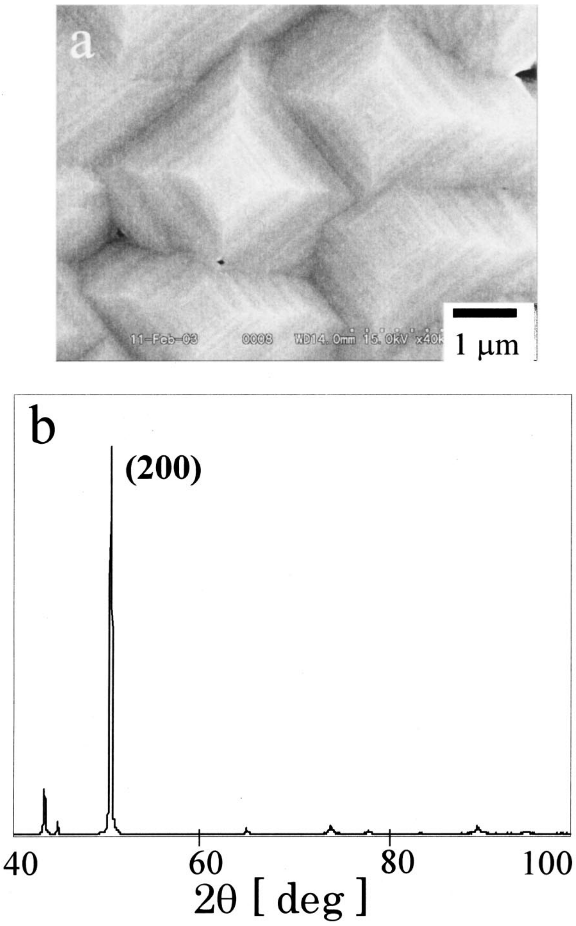

Figure 1. FESEM micrograph and X-ray of the electrolytic copper deposit on the $(100)_{Cu}$ single-crystal substrate.

Electrolytic copper deposits on the $(100)_{Cu}$ single crystal with stirring rate and higher current density.—Figure 2 shows FESEM micrographs of deposits formed at 10 mA/cm^2 with different stirring rates. Without stirring, pyramidal crystals are formed (Fig. 2a). The thin-film XRD pattern for the deposit is shown in Fig. 2c. The $(111)_{Cu}$, $(200)_{Cu}$, $(110)_{Cu}$, and $(311)_{Cu}$ diffractions exist in the thin-film XRD and intensity of the $(111)_{Cu}$ is almost the same as that of the $(200)_{Cu}$. At 500 rpm, however, slanting platelet crystals form at the side of the pyramidal crystals (arrow in Fig. 2b). Thin-film X-ray intensity of the $(111)_{Cu}$ is larger than the intensity at $(200)_{Cu}$.

Figure 3 shows FESEM micrographs of deposits formed at different current densities in an unstirred bath. At 10 mA/cm^2, pyramidal crystals of stacked platelet crystals form (Fig. 3a). The $(111)_{Cu}$, $(200)_{Cu}$, $(110)_{Cu}$, and $(311)_{Cu}$ diffractions exist and the intensity of the $(111)_{Cu}$ is almost same as the $(200)_{Cu}$. At 50 mA/cm^2, however, slanting platelet crystals form at the side of the pyramidal crystals (see Fig. 3b, arrow). Thin-film X-ray intensity of the $(111)_{Cu}$ again is larger than the $(200)_{Cu}$. Slanting platelet crystals have the $(111)_{Cu}$ orientation.

The $(100)_{Cu}$ orientated deposits, pyramidal crystals, are parallel to the $(100)_{Cu}$ single-crystal substrate and grow epitaxially to the $(100)_{Cu}$ single-crystal substrate. This epitaxial growth occurs at 0 rpm stirring rate and 10 mA/cm^2 lower current density. At a higher stirring rate of 500 rpm or higher current density of 50 mA/cm^2, however, the epitaxial growth breaks down and the $(111)_{Cu}$ oriented slanting platelet crystals start to form. These $(111)_{Cu}$ orientated crystals are caused by twin or misfit formation in the $(100)_{Cu}$ orientated crystals which originally grows epitaxially to the $(100)_{Cu}$ single-crystal substrate.

Electrolytic copper foils on the titanium substrate at higher current density and stirring rate.—Figure 4 shows FESEM micrographs of deposits formed with different current densities and different stirring rates. At 10 mA/cm^2 of current density and 0 rpm of stirring rate and with 200 mA/cm^2 and 800 rpm (Fig. 4a,b), the deposit morphologies are almost identical. On the titanium substrate, the deposit morphology should not change with higher current densities and stirring rate except the formation of dendrites.

Electrolytic copper foils orientation on titanium substrate with Cl^-.—Figure 5 shows the relation between Cl^- concentration in the bath and relative X-ray intensities of the electrolytic copper foils. The relative X-ray intensities change up to 10 ppm of Cl^- concentration. Without Cl^-, the $(111)_{Cu}$ has the strongest diffraction intensity, however, the intensities of $(111)_{Cu}$ and $(100)_{Cu}$ decrease as the Cl^- concentration increases of up to 10 ppm. On the other hand, the $(110)_{Cu}$ intensity increased drastically within the Cl^- concentration of 1 ppm. Electrolytic copper foil crystal orientation is very critical with Cl^-.

Electrolytic copper foils on titanium substrate with Cl^- and gelatin.—Figure 6 is a FESEM micrograph of electrolytic copper foils formed with Cl^- and gelatin on a titanium substrate at 200 mA/cm^2 current density and 800 rpm stirring rate. Triangular pyramidal crystals of 0.1 µm in crystal diameter form with gelatin (Fig. 6a). Triangular columnar crystals of 5 and 2 µm in crystal diameters form with Cl^-, and gelatin and Cl^- (Fig. 6b,c). The two triangle planes of these triangular columnar crystals are right-angle isosceles triangles. Furthermore, the plane of these triangular columnar crystals, which is parallel to the substrate, is one of three other rectangular planes (see the illustration of triangular columnar crystal in Fig. 6).

Figure 7 shows the result of thin film XRD of the electrolytic copper foils shown in Fig. 6a,b,c, respectively. With gelatin in Fig. 7a, the copper foil has a $(111)_{Cu}$ orientation, since the diffraction intensity of $(111)_{Cu}$ is stronger than other diffractions. With Cl^- and gelatin and Cl^- of Fig. 7b and c, the electrolytic copper foils have $(110)_{Cu}$ orientation, since the $(110)_{Cu}$ is stronger than other diffractions.

Crystal growth of electrolytic copper foils.—Now the growth models of the electrolytic copper foils with Cl^- and gelatin are discussed. Figure 8a is a schematic illustration of face-centered cubic (fcc) copper cubic crystal structure. The circles in Fig. 8a do not represent the copper atoms and the schematic illustration includes several million unit cells. Side planes of the cubic crystal are the $(100)_{Cu}$. Electrolytic copper deposits grow with macrosteps along $(100)_{Cu}$ on the $(100)_{Cu}$ single crystals (Fig. 1). This macrostep growth along the $(100)_{Cu}$ plane holds even on the $(100)_{Cu}$ of electrolytic copper foils on titanium substrates.

Figure 8b and c are the schematic illustration of copper crystals with Cl^- and gelatin. Triangular pyramidal crystals with gelatin (Fig. 6a) has the $(111)_{Cu}$ orientation (Fig. 7a). The $(111)_{Cu}$ is parallel to the substrate and $(100)_{Cu}$ are triangle-shaped side planes of triangular pyramidal crystals. Platelet crystals of several 10 nm in thickness exists on one of the $(100)_{Cu}$ (Fig. 6a) and these platelet crystals are the macrosteps along $(100)_{Cu}$ (Fig. 8b).

The triangular columnar crystals with Cl^-, and Cl^- and gelatin (Fig. 6b,c) have the $(110)_{Cu}$ orientations (Fig. 7b,c). Cl^- changes the electrolytic copper foil crystal orientation (Fig. 5). $(110)_{Cu}$ is parallel to the substrate, and $(100)_{Cu}$ are the triangle-shaped side planes of triangular columnar crystals. Again platelet crystals exists on one of the $(100)_{Cu}$ (Fig. 6b,c) and these platelet crystals are the macrosteps along $(100)_{Cu}$ (Fig. 8c).

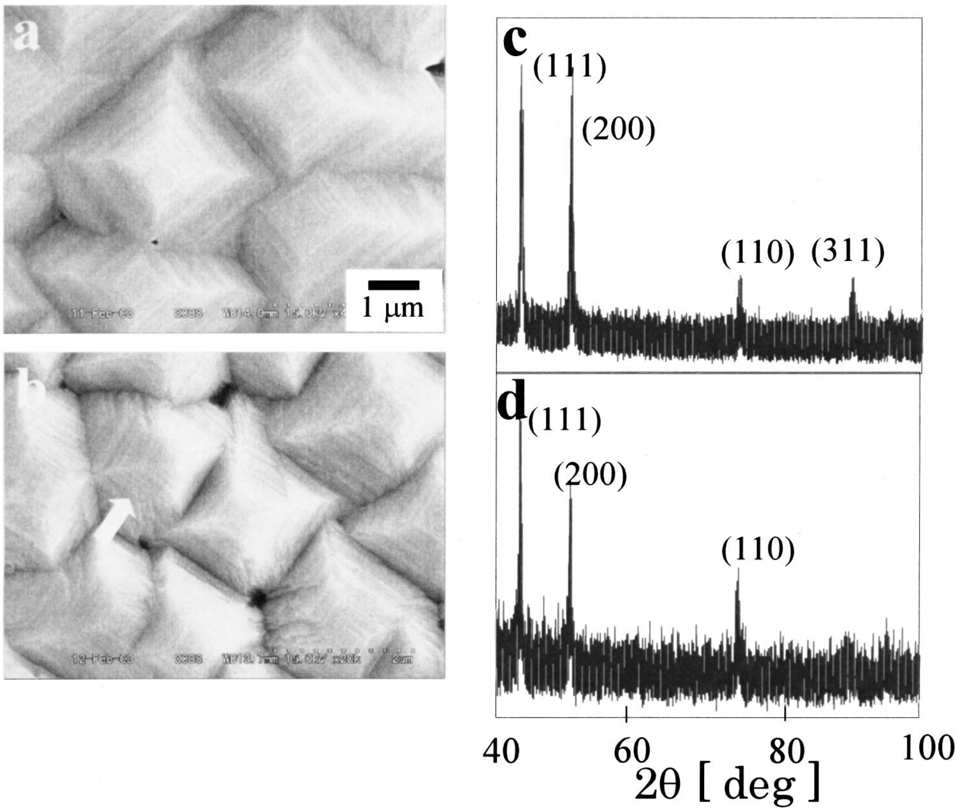

Figure 2. FESEM micrographs and thin-film XRD images of the electrolytic copper deposits on the $(100)_{Cu}$ single crystals at different stirring rates. (a,c) 0 and (b,d) 500 rpm.

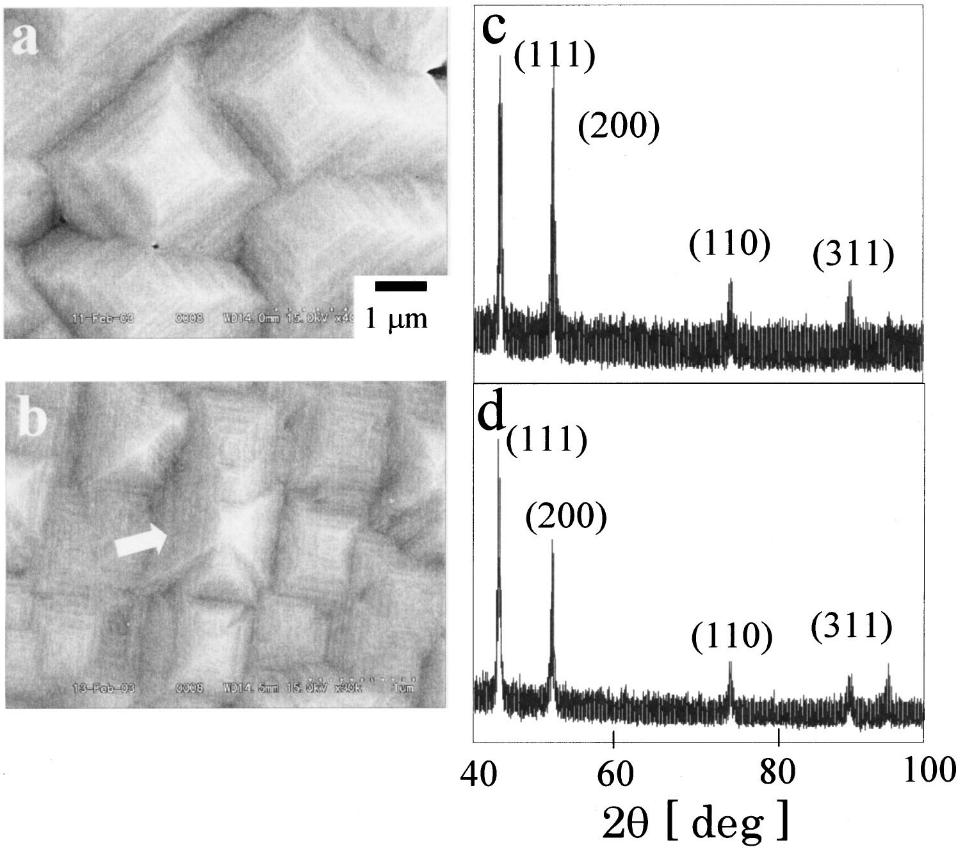

Figure 3. FESEM micrographs and thin film XRD images of the electrolytic copper deposit on the $(100)_{Cu}$ single crystals at different current densities. (a,c) 10 and (b,d) 50 mA/cm^2.

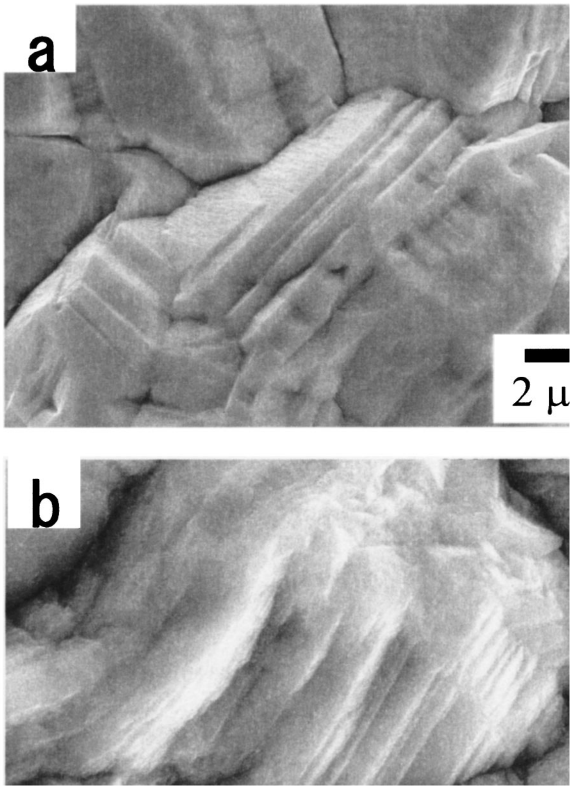

Figure 4. FESEM micrograph of the electrolytic copper foil on titanium substrate at different current densities and different flow rates. (a) 0 rpm, 10 mA/cm^2, (b) 800 rpm, 200 mA/cm^2.

Conclusions

The role of chloride and gelatin additives on the morphology, orientation, and growth of electrolytic copper foils are investigated at high current densities and high electrolyte stirring rates. A crystal growth model of electrolytic copper foils is proposed.

Electrolytic copper deposits on the $(100)_{Cu}$ single crystal is made up of pyramidal crystals, which consist of stacked platelet crystals. These crystal are formed at lower current density of 10 mA/cm^2 and in an unstirred bath. From X-ray diffraction, these pyramidal crystals grow parallel to the $(100)_{Cu}$ single-crystal substrate.

At a higher stirring rate of 500 rpm and a higher current density of 50 mA/cm^2, the slanting platelet crystals form at the side of these pyramidal crystals. From thin film XRD, these slanting platelet crystals have their orientation of $(111)_{Cu}$.

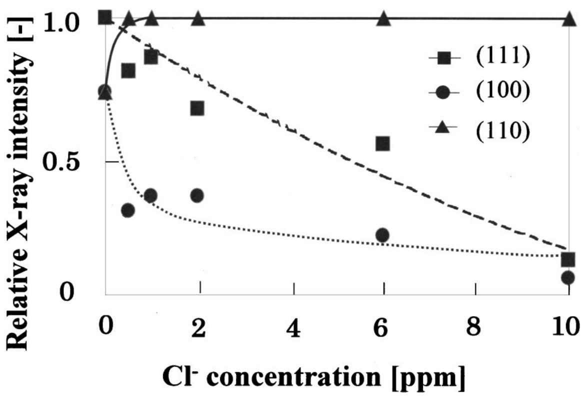

Figure 5. Effect of chloride concentration on the orientation of the electrolytic copper foil.

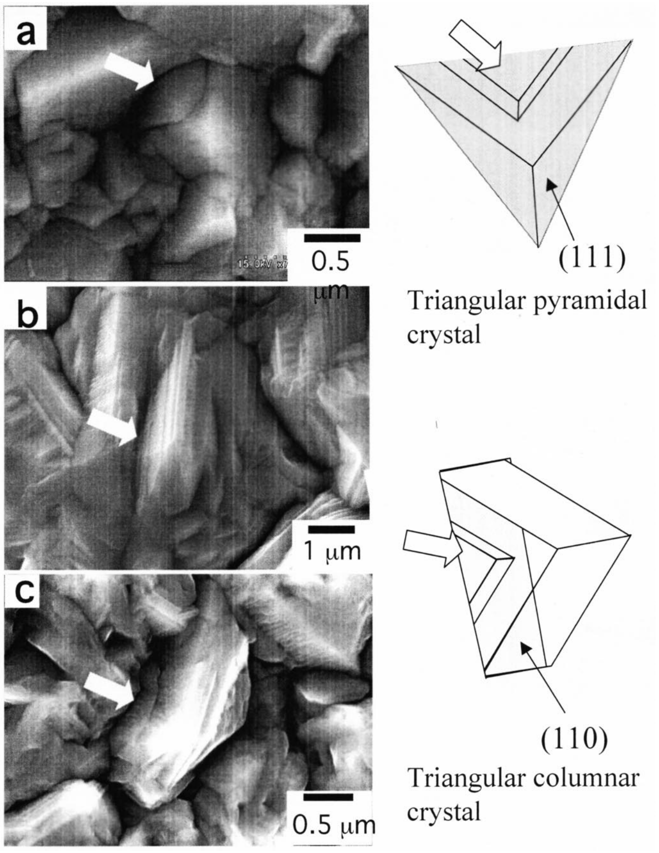

Figure 6. FESEM micrograph of electrolytic copper foil on titanium substrate. (a) Gelatin, (b) chloride, and (c) gelatin and chloride.

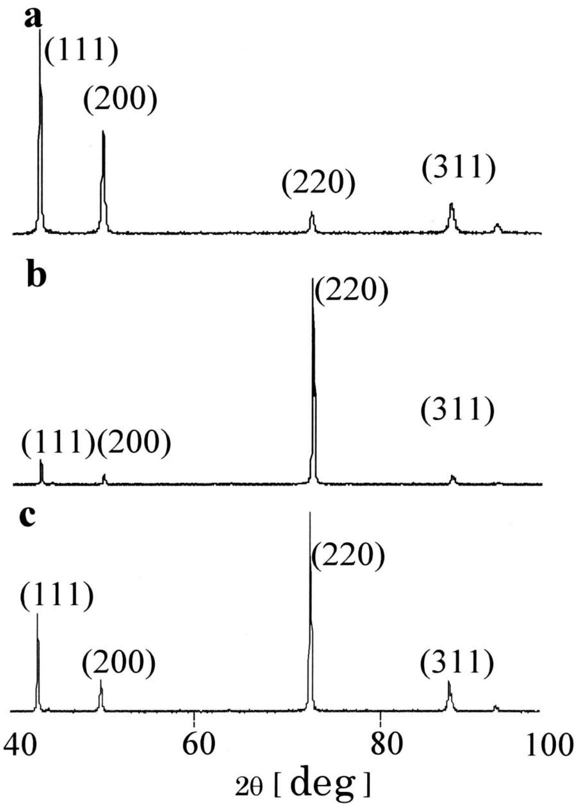

Figure 7. Thin-film XRD patterns of electrolytic copper foil. (a) Gelatin, (b) chloride, and (c) gelatin and chloride.

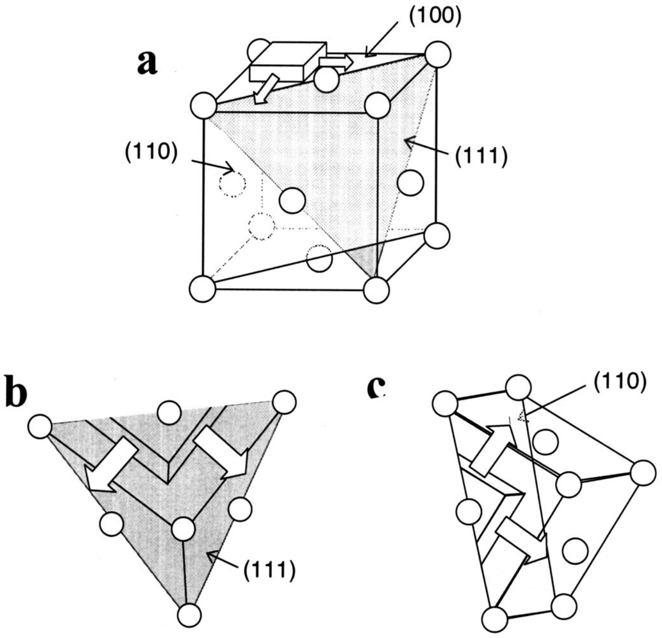

Figure 8. Electrolytic copper foil crystal growth mechanism of the $(100)_{Cu}$ macrostep. (a) $(100)_{Cu}$ lateral growth on the Cu(100) single crystal, (b) $(111)_{Cu}$ orientation on titanium substrate, and (c) $(110)_{Cu}$ orientation on titanium substrate.

The $(100)_{Cu}$ orientated deposits, pyramidal crystals, grow epitaxially to the $(100)_{Cu}$ single-crystal substrate. At higher stirring rates or higher current densities, however, epitaxial growth breaks down and the $(111)_{Cu}$ oriented slanting platelet crystals start to form.

The morphology of electrolytic copper foils on titanium substrate, does not change at higher current densities and stirring rate.

Chloride and gelatin are the typical additives for the electrolytic copper foils and electrolytic copper foils are formed on titanium substrate at higher stirring rates and current densities. With gelatin, the triangular pyramidal crystals form and the $(111)_{Cu}$ is parallel to the titanium substrate. Triangle-shaped side planes of the crystals are the $(100)_{Cu}$. A platelet crystal exists on one of these $(100)_{Cu}$. With chloride, gelatin, and chloride, the triangular columnar crystals form and the $(110)_{Cu}$ is parallel to the substrate. Triangle-shaped side planes of the crystals are the $(100)_{Cu}$. Platelet crystals, again, exist on these $(100)_{Cu}$.

Electrolytic copper deposits grow with the platelet crystals along $(100)_{Cu}$ on the $(100)_{Cu}$ single-crystal substrates. These platelet crystals exist on the $(100)_{Cu}$ of electrolytic copper foil deposits are the macrosteps, and they are the growth sites.

The chloride determines the crystal orientations of electrolytic copper foils and the orientation change is effective up to 10 ppm chloride concentration.

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