Nano Growth Mechanism of Electrolytic Copper Foils

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Introduction

Electrolytic copper foils have extensively been used in subtractive process of PCB. The surface roughness control is an important factor not only for adhesion but also for fine etching.

Crystal growth of electrolytic copper foils with macro steps lateral growth will be discussed in details with typical additives of geratin and Cl⁻. A systematic interpretation of nano crystal growth of electrolytic copper is given.

Experimental procedure

A (100) single crystal copper and titanium foil have been used as substrates. Electrolytic bath consists of 270g/L of CuSO₄ and 100g/L of H₂SO₄. 10ppm of geratin and 60ppm of Cl⁻ have been added as additives. The electrolytic copper have been observed by FESEM(Field Emission Scanning Electron Microscopy) and X-ray diffraction.

Results

(1) Fig.1 shows the FESEM micrograph of electrolytic copper deposited on the (100) single crystal substrate. The (100) planes grow parallel to the (100) single crystal substrate. The electrolytic copper grows with lateral growth of macro steps on the (100)(See white arrow in Fig.1).

(2) Fig.2(a) and (b) shows the electrolytic copper on titanium foils with geratin and Cl⁻ as additives, respectively. The electrolytic copper with geratin as additive have triangular pyramid in crystal shape(Fig2(a)). This crystal has (111) orientation from X-ray diffraction. The white arrow in Fig.2(a) shows the macro step growth along the (100).

The electrolytic copper with Cl⁻ as additive have triangular columnar in crystal shape(Fig.2(b)). One of the rectangle plane of this triangular columnar shape is parallel to the substrate. This has (110) orientation and the rectangular plane is (110). Again the macro step grow along the (100) and this is marked with white arrow in Fig2(b). The macro steps grow laterally along (100) both with geratin and CI⁻ additives.

(3) Fig.3 shows the cross sections of electrolytic coppers both with geratin and Cl⁻. The cross section with geratin consists of fine granular crystals. That with CI⁻ consists of columnar crystals.

The electrolytic copper with geratin have (111) orientation and the macro step growth direction is slant to the substrate(Fig.2(a)). This slant growth direction forms the granular crystals in cross section. The electrolytic copper with CI⁻ have (110) orientation and the macro step growth direction is perpendicular to the substrate(Fig.2(b)). This growth direction forms the columnar crystals in cross section.

(4) The growth direction of the electrolytic copper with geratin is slant to the substrate. Smoother surface roughness of this electrolytic copper forms with this growth direction. With CI⁻, the growth direction is perpendicular to the substrate and the electrolytic copper has rougher surface.

![Fig.1 FESEM micrograph of electrolytic copper on the (100) single crystal and growth mechanism.](image)

![Fig.2 FESEM micrograph of electrolytic copper on the titanium substrate and growth mechanism. a) with geratin additive, b) with Cl⁻ additive.](image)

![Fig.3 FESEM micrograph of cross section of electrolytic copper on the titanium substrate. a) with geratin additive, b) with Cl⁻ additive.](image)