



Synergistic effects of gelatin and convection on copper foil electrodeposition



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ABSTRACT

Copper foil electrodeposition has been explored using a pure titanium rotating disk electrode (RDE) in acidic electrolytes containing gelatin and/or chloride ions under different convection conditions. In the plating bath without gelatin, the results indicate that stronger convection promotes hydrogen evolution, which reduces the current efficiency during copper plating. Gelatin restrains the growth of copper grains in the lateral direction parallel to the surface. This results in grain refinement on the shiny side, an increase in local grain misorientation and in internal stresses on both the shiny and the matte side, and a reduction in their internal stress difference. At strong convection conditions and with gelatin present, copper deposits as strip-like grains along the centrifugal direction of the cross section, and finally forms a spiral-shaped pattern on the matte side. The causes of these features are discussed in detail. The combined influences of hydrogen and gelatin adsorption are further elaborated in a model for a copper deposition. The current investigation suggests that a moderate convection (somewhat lower than 1000 rpm) and a concentration of 2 ppm gelatin in the plating bath are sufficient for copper foil fabrication in the presence of chloride ions (20 ppm).

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1. Introduction

Production of copper foils via electrodeposition is a key technique in the electronic industry [1] for printed circuit manufacture and circuit interconnections due to the low cost, high deposition rate and low toxicity [2] and [3]. All commercial electrodeposition baths contain additives to control the efficiency of copper foil production (e.g., to optimize the mass transport of reactants/products [4–6], or to change the surface reaction route [7,8]). Previous investigations have evaluated the effect of various organic additives such as thiorea [9,10], PEG (Polyethylene glycol)-chloride [11,12], SPS (bis (3-sulfopropyl) disulfide) [13,14], gelatin [15–17] and mixtures of different additives [18,19] on the copper deposition. Among them, gelatin is one of the safest additives in copper foil fabrication to meet the health considerations of toxic compounds used in industry [20]. Recently, gelatin was also used

as one of the additives in the electrodeposition of Sn–Cu alloys [16,21] and Sn–Bi alloys [22].

Gelatin, a grain refiner and hardener, is an additive that modifies electrochemical reactions and crystal growth of copper electrodeposits by preferential adsorption on surface protrusions [7,23]. Chlorides usually play a supporting role in the presence of gelatin [24]. Most research addressing the effect of gelatin on the copper electrodeposition process has been conducted at weak convection (or even static conditions), relatively low temperatures (20–40 °C) and low current densities (<100 mA cm⁻²). Koura et al. [25,26] proposed, via electrochemical impedance analyses, a two-step copper deposition reaction where the reduction of cupric ions (Cu²⁺ → Cu⁺ → Cu) proceeds with a hydrogen evolution reaction at a current density of 30 mA cm⁻² at 45 °C. Kondo et al. [27] demonstrated the formation of triangular pyramidal crystals and triangular columnar crystals, and proposed a crystal growth model for copper foils formed in unstirred electrolytes containing gelatin, chlorides and their combinations at a current density of 100 mA cm⁻² at room temperature.

It is noteworthy that industrial copper foil electroplating is quite different from damascene plating [7], electrorefining [28],

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Table 1
Base solution compositions.

Electrolytes	Composition	Electrolytes	Composition
A	1.3 M CuSO ₄ ·5H ₂ O, 1.4 M H ₂ SO ₄ + 20 ppm chloride ions (as HCl)	A'	1.4 M H ₂ SO ₄ + 20 ppm chloride ions (as HCl)
B	A+ 1 ppm gelatin	B'	A' + 1 ppm gelatin
C	A+ 2 ppm gelatin	C'	A' + 2 ppm gelatin
D	A+ 3 ppm gelatin	D'	A' + 3 ppm gelatin

and general copper coating electrodeposition [29,30] due to its higher cupric ion concentration (1.07–1.34 M Cu²⁺), higher current density (300–1200 mA cm⁻²) and higher plating temperature (57–60 °C). The behavior of additives at these conditions is assumed to be quite different compared with laboratory findings due to large differences in deposition conditions. However, only limited studies have investigated the effect of gelatin at conditions of high current density and strong convection. Osaka et al. [31,32] utilized a pint-sized apparatus to observe copper deposition with a columnar microstructure in the <110> direction in the presence of chloride and gelatin at 60 °C, a current density of 1.0 A cm⁻², and a flow rate of 2 m s⁻¹. Kondo [24] emphasized the significance of high current density with a high stirring rate through comparing the morphology and microstructure in these conditions with those at lower current density and unstirred condition. Hence, considering its profound industrial importance, fundamental studies on gelatin additive action on copper foil deposition are surprisingly few. In addition, the impact of convection on the gelatin effect is not fully understood. The combined effect of gelatin and chlorides on the nucleation and growth also needs to be clarified by means of more straightforward investigations.

Hydrogen evolution and the hydrogen gas release process in the cell design is one of the most critical items in copper foil fabrication. It causes serious troubles such as low current efficiency and may result in coarse foils containing voids. Angus [33] suggested that hydrogen bubbles evolving under the gelatin film result in current efficiencies significantly less than 100%. In addition, systematic investigations of copper electrodeposition have been initiated by Nikolic [34–36] on morphologies under conditions of hydrogen co-deposition (e.g., at various overpotentials and sulfate solutions of various H₂SO₄ concentrations). Although hydrogen evolution has been identified during copper electrodeposition [16,25], the impact of gelatin on this by-reaction during copper foil fabrication is still unknown.

Considering the important gaps of knowledge mentioned above, the main aim of this work was to perform a systematic investigation on the synergistic effects of gelatin and convection on copper foil deposition and its by-reaction (hydrogen evolution). This has been accomplished via an in-depth study of the electrochemical behavior, current efficiency, microstructure, local

misorientation and internal stress of copper deposits utilizing different electrochemical techniques (rotating disk electrode, chronoamperometry, cathodic polarization), mass measurements (microbalance), field emission scanning electron microscopy (FESEM), electron back-scattered diffraction (EBSD) and X-ray diffraction (XRD), respectively.

2. Experimental

Different solutions were studied, with detailed information in Table 1. Gelatin (analysis grade, granular, molecular weight of 10⁴–10⁵ Da) was purchased from Acros Organics, Belgium, and all other reagents (reagent grade) from Sinopharm Chemical Reagent Co. Ltd, China. Fresh solutions were prepared before each experiment to avoid their deterioration with time. All solutions were prepared using deionized water.

A rotating disk electrode (RDE) test system for electrochemical tests from PINE (AFMSRCE #2669), was employed using a Gamry Reference 600 potentiostat, a ϕ 5 mm titanium RDE working electrode, a 3 × 3 cm² platinum plate as counter electrode and a double-pipe saturated calomel electrode (SCE) reference electrode. Pure titanium was provided by MAGNETO special anodes Co. Ltd., Suzhou, China. The titanium disk was polished before each test with synthetic leather to ensure reproducible surface conditions. The distance between the counter and the working electrode was set to 20 mm.

In order to mimic industrial conditions during copper foil production, the jacketed beaker was connected to a circulating water bath to stabilize the temperature at 60 ± 1 °C during all electrochemical experiments. Three different convection conditions (100, 1000 and 1600 rpm) were investigated. Chronoamperometry (CA) at –300 mV (vs. SCE) and cathodic polarization with a scan rate of 5 mV s⁻¹ were performed from the open circuit potential (OCP) to –0.8 V (vs. SCE). All electrode potentials reported in this paper are referred to the SCE.

Copper foils were electrodeposited by performing CA as described above. The copper foils were withdrawn from the plating bath immediately after deposition, rinsed with deionized water, dried using a cool air breeze and stripped from the cathode substrate before weighing and characterization. The copper foil

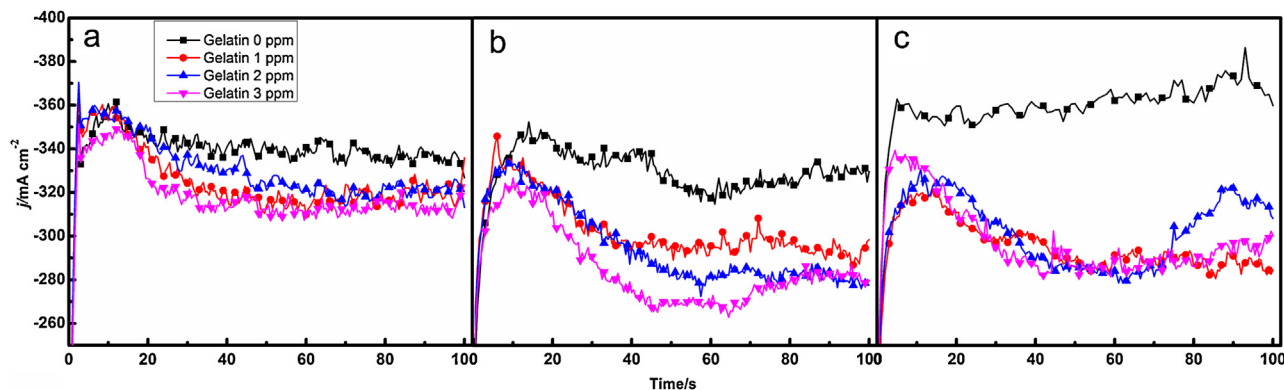


Fig. 1. Chronoamperometric curves (deposition potential: –300 mV) vs. time at different rotating speeds: (a) 100 rpm; (b) 1000 rpm; (c) 1600 rpm in base solutions A–D (containing 0, 1, 2 and 3 ppm gelatin, respectively).

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