



Microstructure and crystallographic characteristics of nanocrystalline copper prepared from acetate solutions by electrodeposition technique



R. SEAKR

Electroplating and Metal Finishing Technology Division,
Central Electrochemical Research Institute, Karaikudi-630 006, Tamil Nadu, India

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Abstract: Methane sulphonic acid is an alternative electrolyte for conventional sulphuric acid for copper deposition. The electrodeposition of copper from eco-friendly acetate-based electrolytes consisting of copper acetate, sodium acetate and methane sulphonic acid was dealt. Thamine hydrochloride (THC), saccharin and 4-amino-3-hydroxynaphthalene 1-sulphonic acid were used as additives in depositing electrolytes. The cathode current efficiency was calculated using the Faraday's law. Metal distribution ratio of the solutions was determined using Haring–Blum cell. These additives impact the surface morphology of deposited copper films by downgrading, the grain size was analyzed by scanning electron microscopy (SEM) and X-ray diffraction technique. XRD pattern acquired for electrodeposited copper film shows polycrystalline and face centered cubic structure (FCC). The crystal size of the copper film was calculated using the Debye–Scherrer's equation. The crystal size revealed that deposits produced from additive containing electrolytes exhibited the lowest grain size. Texture coefficient analysis studies revealed that all copper film deposits are polycrystalline and the crystals are preferentially oriented and parallel to the surface. A uniform and pin-hole free surface morphology and grain refining were brought about by the additives.

Key words: acetate; copper electrodeposition; additives

1 Introduction

Copper is one of the most significant non-ferrous materials, because it is widely used in electrical and electronic industries for production of tubes, wires, sheets and for making copper-based alloys. Although, copper deposits have an excellent conductivity because free and mobile electrons are more in copper lattice. Alkaline cyanide electrolytes are still used to electroplate copper and have various applications for the metal finishing industry [1]. In recent years a plenty of research has been realized and various alternatives have been proposed, such as chloride, amine-ammonia, sorbitol, fluoborate, pyrophosphate, EDTA, citrate, tatarate, ethylenediamine (EDA), triethanolamine (TEA) and glycine to replace the cyanide electrolytes for its environmental concerns, because of environmental, economic or some other limitations [2]. However, most of these proposals have not been taken to industrial level. QUINET et al [3] have studied the influence of saccharin and thiourea, on electrodeposition of copper from acid

sulphate solutions using various electrochemical methods. TOROK et al [4] have investigated the direct cathodic deposition of copper on steel wires from pyrophosphate solutions. Electroplating of copper from methane sulphonic acid electrolytes for interconnects in ultralarge scale (ULSI) and microelectrochemical systems (MEMS) applications [5]. CAO et al [6] have investigated the effect of chloride ion in the methanesulphonic acid electrolytes by using electron paramagnetic resonance (EPR) and various electrochemical techniques. Copper film is produced on AZ31 magnesium alloy by electrodeposition using copper hydroxide and citrate solution with the addition of sodium fluoride, SP, MZ and PEG [7]. Systematic studies on copper deposition on stainless steel from a sulphate electrolyte had been undertaken using square wave pulse current and direct current [8]. MANTRY et al [9] have studied the deposition potential of copper slag for different engineering and structural applications by plasma spray technique. The influences of gelatin on cuprous copper electrodeposition in ammonical alkaline solutions were investigated [10]. In electroplating bath

formulations, the presence of organic and inorganic compounds introduced in trace amounts, called additives, exerts significant effects on metal deposition. In fact, additives modify the crystal growth and improve the physical and mechanical properties of the electrodeposits. Some additives may inhibit or catalyze the electrodeposition process by forming complexes with metallic ions or increasing the polarization of metal electrodeposition due to their adsorption on active sites [11]. LOW and WALSH [12] have studied the normal and anomalous codeposition of copper–tin alloy from methanesulphonic acid solution in the presence of perfluorinated cationic surfactant. SEKAR et al [13] have investigated the results on copper depositing electrolytes characteristics such as electrolyte stability, galvanic displacement reaction of copper on mild steel, deposition current efficiency, metal distribution of the depositing electrolytes and deposit characteristics like adhesion, quality of the copper deposit, crystal size, orientation of the crystal and microstructure using scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). The effects of plating parameters such as characteristics of depositing solutions, quality of the deposits and throwing power of the depositing electrolytes were investigated [14]. IBRAHIM et al [15] have investigated the electrodeposition of copper from aqueous ammonia solutions onto steel substrates and its deposit characteristics were studied by various electrochemical techniques [15]. SIVASAKTHI et al [16] have investigated the detailed study of electrodeposition of copper from glycerol complex and the influence of additives in alkaline medium. Moreover, electrodepositions of copper from acetate-based electrolytes have not been studied in detail. Hence, the authors desired to investigate the detailed study of electrodeposition of copper from acetate electrolytes using methane sulphonic acid (MSA) complex bath. In this paper, results on cathode current efficiency (CCE), throwing power of the depositing electrolytes (TP) and deposit characteristics such as adhesion, crystal structure and surface morphology are reported.

2 Experimental

2.1 Electrodeposition of copper and cathode current efficiency measurements

The alpha brass metallic foil consists of 75% copper and 25% zinc, which was used for the present study. Surface preparation prior to electrodeposition is an essential process and can be achieved by standard mechanical and electrochemical methods [17,18]. The pretreated brass foils with dimensions of 7.5 cm × 2.5 cm × 0.1 cm (7.5 cm length, 2.5 cm width, and 0.1 cm thickness) were used as cathodes in an electroplating cell

consisting of two 99.99% pure copper as anodes on either side of the cathode. The depositing electrolyte consists of copper acetate ((CH₃COO)₂Cu·H₂O), methane sulphonic acid (CH₄O₃S), and sodium acetate (CH₃COONa) in the presence of various additives and the detailed electrolyte composition is given in Table 1. Doubly distilled water and analytical grade chemicals were used for the electrolyte preparation for the deposition of copper. The electrolyte was agitated mechanically throughout the experiment to progress the quality of the deposits. The plating bath was operated at room temperature and at different current densities. The cathodes were weighed before and after deposition; the deposition current efficiency and rate of deposition were calculated from the mass ratio of the copper deposits to the theoretically expected mass of copper deposits, which is based on the amount of current, according to the Faraday's laws of electrolysis.

$$m = \frac{QM}{nF} \quad (1)$$

where m is the mass of the deposits, Q is the electric charge passed, F is the Faraday constant (96485.3329 C/mol), M is the molar mass of the species and n is the electrical charge involved in the reaction.

Table 1 Formulation of various copper baths

Bath No.	Composition
A	100 g/L copper acetate, 90 ml/L methane sulphonic acid, 20 g/L sodium acetate
B	Electrolyte A + 0.25 g/L thiamine hydrochloride
C	Electrolyte A + 0.25 g/L saccharin
D	Electrolyte A + 0.2 g/L 4-Amino 3-hydroxy naphthale-sulphonic acid

2.2 Metal distribution of depositing solutions

The throwing power of the depositing electrolytes was determined using the Haring–Blum cell [19,20]. This is a rectangular cell consisting of two brass sheet cathodes with sizes of 5 cm × 5 cm × 0.1 cm filling the entire cross section at both ends of the cell walls, and one perforated copper anode of the same size. The latter was placed between the cathodes so that the distance from one of the cathode was one-fifth of its distance from the other. Values of throwing power (p) for different bath compositions were calculated using the Field's formula.

$$p = \frac{L - R}{L + R - 2} \times 100\% \quad (2)$$

where R is the metal distribution ratio of the near to far cathode and L is the ratio of the respective distances of the far to near cathodes from the anode.

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