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New non-cyanide acidic copper electroplating bath based on glutamate complexing agent

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ABSTRACT

Highly adherent and compact copper coatings on steel substrates were successfully produced by electrodeposition using noncyanide bath based on glutamate as a complexing agent. The investigation was conducted using potentiodynamic cathodic polarization, cyclic voltammetry, in situ-anodic linear stripping voltammetry and chronoamperometry techniques. The results from the potentiodynamic cathodic polarization show polarization characterized by the presence of a current plateau (limiting current, i_{lim}) in the potential range −0.65 to −0.83 V_{SCE}, as a result of the deposition limitation by the diffusion process. The present glutamate bath has a higher cathodic current efficiency than that of cyanide baths. The electrochemical kinetic data confirms that the Tafel slopes of the solution containing glutamate ions are higher (821.1–849.9 mV decade^{-1}) than that without MSG (738.5 mV decade^{-1}). The relative invariance of α_c, observed for increasing glutamate ion concentrations, suggests that the Cu electrodeposition pathway is not affected by the presence of glutamate. However, the rate of Cu^{2+} deposition on the steel surface from glutamate bath, is much higher than that on the glassy carbon surface. Copper coatings with very different morphologies can be obtained from the glutamate bath by simply manipulating the applied current density. X-ray diffraction analysis and SEM observations revealed that monosodium glutamate (MSG) does not vary the texture of the electrodeposited copper. However, it depends greatly on the deposition parameters such as the applied current density, pH and bath temperature. High hardness of copper deposits was obtained both at low concentration of MSG and at low current density. Baths contained glutamate ions exhibited a slight decrease in the throwing power.

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1. Introduction

Copper electrodeposition is widely used in industry for the fabrication of printed wiring boards, electronic devices, silicon chip interconnect material, on-chip metallization, plating on plastics and electroforming [1–3]. Moreover, steel wire can be coated with copper for a high electric conduction [1]. Recently, the electroplating of copper has gained a lot of attention as a replacement for aluminum in the electronic industry. Copper thin film coatings are also used in the manufacture of the hard disk read heads. The electrodeposition method has the advantages of being less expensive, highly productive and readily adoptable in comparison with other methods e.g. PVD, CVD and sputtering [1,4].

A simple sulfuric acid copper sulfate bath cannot be used for direct cathodic deposition of copper onto steels, as the adherence and structure of the first thin copper deposit will not be good enough to build up a thick, compact and sound copper surface layer afterwards [5]. This problem was avoided by using copper cyanide electroplating baths, which hinder the direct chemical reduction of copper by shifting the reduction potential to more negative values. However, cyanide solutions are not generally suitable for thick copper deposits. In addition, cyanide solutions have the disadvantage of being strong pollutants because of their toxicity and waste treatment problems [1]. For this reason, several attempts have been made to electrodeposit copper using various complexing agents, such as citrate, glycine, sorbitol, EDTA, ammonia, thiosulfate and tartrate [6–12]. In this work, monosodium glutamate (MSG) was used as a complexing agent in the electrodeposition of copper from an acid sulfate bath. It is an attractive compound due to its ability to form complexes with copper and give the solution buffering behavior. To the best of our knowledge this is the first trial of copper deposition from baths based on the presence of glutamate ions. The characterization of glutamate-based electrolytes in acid solution represents an interesting challenge because they offer alternatives to the toxic cyanide baths for copper or copper alloy plating.

2. Experimental

The copper electrodeposition was achieved galvanostatically at room temperature on a steel sheet cathode from a solution containing: 0.1 M $CuSO_4 \cdot 5H_2O$, 0.5 M Na_2SO_4, 0.1 M MSG, 15 g/L PEG, pH 2.0, t =

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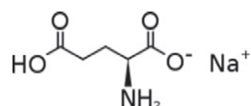
10 min, and at 20 °C. The steel used in this study is a carbon steel with a chemical composition (in wt.%) of 0.370% C, 0.210% Si, 0.660% Mn, 0.014% S, 0.076% Cr, 0.010% Ti, 0.057% Ni, 0.008% Co, 0.160% Cu, with the reminder iron (Fe).The anode was a platinum sheet which has the same dimension as that of the cathode (2.5 cm × 3.0 cm).The plating cell used was a rectangular Perspex trough (11 × 3 cm) with vertical grooves on each of the side walls to fix the electrodes. Monosodium glutamate (MSG) was added to the sulfate bath as a complexing agent. It is the sodium salt of glutamic acid [$HO_2CCH_2CH_2CH(NH_2)CO_2Na$]. MSG is a flavor enhancer commonly added to Chinese food, canned vegetables, soups and processed meats. It has the following chemical structure:



Monosodium glutamate (MSG)

The pH of the electrolytic solution was achieved to the desired value using 1:1 vol. H_2SO_4 (sp.gr. 1.84 g/cm^3). However, most of the experiments were carried out at pH 2.0. Sodium sulfate was added to the electroplating bath to enhance the conductivity. Polyethylene glycol, (PEG), (Merck, MW 10,000) was used as an additive at a concentration of 15 g/L. Polyethylene glycol is usually incorporated into industrial plating bath as an additive which suppresses copper deposition especially in the presence of chloride ions [13,14].The calculations of the cathodic current efficiency, F% of copper deposition was described in an earlier publication [15].The throwing power is a measure of an electroplating solution's ability to plate to a uniform thickness over an irregularly shaped cathode. The T.P. of the electrolytic solutions was calculated using a Haring–Blum rectangular cell (19.5 × 2.5 cm), with a 2.5 cm solution depth. One anode is fixed between two cathodes where the ratio of the near-to-far distance was 1:3. The T.P. % was calculated from the empirical formula [16]

$$\text{T.P.\%} = (\text{L}-\text{M}/\text{L}+\text{M}-2) \times 100. \quad (1)$$

where L is the current distribution ratio (3:1) and M is the metal distribution ratio (weight of the metal deposit on the near cathode divided by the weight of the metal deposit on the far cathode). The values of M were plotted versus L and the throwing index (T.I.) of each electrolytic solution was proposed to be the reciprocal of the slope of this plot. All experiments were carried out using unstirred solutions. All of the electrochemical experiments were carried out using a computer assisted potentiostat/galvanostat (SI 1287 Solartron). The potentials were measured versus a SCE. The potentiodynamic cathodic polarization curves were recorded by sweeping the potential in the negative potential direction with a scan rate of 10 mV s^{-1}. A classic three-electrode cell was used for the voltammetric experimental runs. The working electrode was a glassy carbon electrode (GCE) (area = 0.1963 cm^2) enclosed in a PVC cylinder. The counter-electrode was a platinum wire. In situ-anodic stripping voltammetry (ALSV), measurements were carried out as in the earlier publications [17,18].The chronoamperometry (current–time transients) measurement was carried out at different applied potentials and different MSG concentrations. The texture of the copper coatings was analyzed by a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA), Ni filter and CuKα radiation. The surface morphology of the copper deposits was examined with a Philip XL-40FEG field emission SEM. The Vickers micro-hardness of the copper deposit was determined by an indentation technique at 100 gf load with a diamond pyramid indenter technique using a TukonSerieS B200 microhardness tester. Adhesion characterization of the deposited copper film was carried out using Pull Off Adhesion Tester. The Positest Adhesion Tester (Model AT-M) is designed to measure the bond strength of applied coatings. The Positest Adhesion Tester can be used in accordance with the following National and International Standards ASTM D 4541, AS/NZS 1580.408.5, EN 13144, ISO 4624 supersedes EN 24624 & NF T30-062, ISO 16276-1, JIS K 5600-5-7 & NF T30-606.

3. Results and discussions

3.1. Cathodic current efficiency

The ratio of the weight of metal actually deposited to that, which would have resulted if all the current had been used for deposition, is called the cathode current efficiency (F). Visual observation of copper electrodeposited in the presence of glutamate showed an improvement in the appearance of copper deposits. The applied current density studied had the following range 0.3–1.3 mAcm^{-2}. The cathodic current efficiency was found to be close to 100%. However, it depends to somehow, on the plating parameters e.g., the applied current density, the pH and the bath temperature. For example, the F% was decreased from 100% at 0.3 mAcm^{-2} to 80% at 1.3 mAcm^{-2}. High H_2 evolution is observed at high current density, and a decrease in F% is expected. However, the deposit is dull and not well adhered to the steel substrates at current densities higher than 0.9 mAcm^{-2}.

On the other hand, increasing the pH value from pH 2.0 to pH 4.0 decreased greatly the F% from 96% to 68%. Increasing pH value, leads to an increase of H^+ dissociation from the glutamate molecule, consequently, the free Cu^{2+} ions decreases and the F% is expected to decrease. In contrast, it was found that raising the bath temperature from 20 °C to 60 °C increased slightly the F% from 96.4% to 100%.

It is well known that the acid copper sulfate, copper fluoborate and copper pyrophosphate baths have cathodic efficiency of 100%. On the other hand, cyanide-type copper plating baths having F ranging from 50 to 90% depends upon the bath composition [19]. Moreover, copper deposited from citrate baths having F > 96% [6]. However, the present glutamate bath has an acceptable and higher efficiency than that of cyanide bath.

3.2. Potentiodynamic cathodic polarization curves and Tafel lines

The polarization curves of copper deposition on to steel substrates from acidic bath in the absence and presence of MSG (0.0125–0.1 M) were measured and the results are given in Fig. 1. It is observed that the polarization curves are characterized by the presence of a current plateau (limiting current, i_{lim}) in the potential range from −0.65 to −0.83 V_{SCE}, as a result of the deposition limitation by the diffusion process. Behind the limiting current, a rapid increase of current is observed at high negative potentials due to the hydrogen evolution. From the inspection of the data, a marked shift in the polarization curves towards

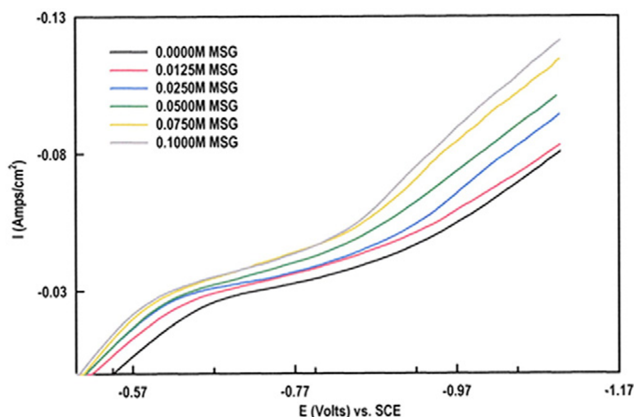


Fig. 1. Potentiodynamic cathodic polarization curves onto steel substrate during copper electrodeposition in the absence and presence of different concentrations of MSG.

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