

SHORT COMMUNICATION

Role of 2-thiouracil as addition agent during the electrodeposition of copper on the copper (III) plane

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1. Introduction

Many addition agents have been proposed for the electrodeposition of copper in order to produce desired effects in the nature of the deposit. A few investigators [1–4] have carried out studies on the electrodeposition of copper on copper single-crystal substrates with the object of obtaining information on the mechanism of the action of these addition agents. Identification of the chemical species formed during the deposition also throws light on the role of the addition agent during the deposition process. In the present work the effect of controlled amounts of 2-thiouracil on the surface topography during the electrodeposition of copper on the copper (III) plane from an acid sulphate bath has been investigated. The overpotentials during the deposition process were measured in all the cases and the calculated electrode kinetic parameters were correlated with the morphological changes. The role of 2-thiouracil as an addition agent has been explained from the observed results.

2. Experimental procedure

The electrolytic bath consisted of a highly purified [5] solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.25 M) and H_2SO_4 (0.1 M) to which a fresh aqueous solution of 2-thiouracil (Sigma) of known concentration was added. The orientation of the copper single-crystal (III) plane was confirmed by X-ray diffraction. An atomically smooth surface was obtained by electropolishing with orthophosphoric acid for about 30 min at a constant cell potential of 1.2 V [6]. The electrodeposition was carried out on the (III) face at 2, 5, 10 and 15 mA cm^{-2} to a thickness corres-

ponding to 10 C cm^{-2} . A fresh crystal was used for each distinct concentration at every current density. The cathodic overpotential during the deposition process was noted with reference to a freshly prepared copper electrode at various time intervals of deposition using a vacuum tube voltmeter (Philips G.M. 90) with an accuracy of $\pm 5 \text{ mV}$. The use of a Luggin capillary in the deposition cell minimized any ohmic overpotential contribution. A correction for the concentration polarization was incorporated by taking the difference in the values of the overpotential with and without stirring. The morphology of the dried surface was examined under a phase contrast microscope at a magnification of $\times 625$ and photomicrographs were taken (reproduced here at $\times 600$). Each experiment was repeated to ensure reproducibility in the surface morphological features and overpotential values.

3. Results**3.1. Surface morphology**

The surface morphology of the deposit noticed during deposition from pure solution and in the presence of different concentrations of the addition agent at various current densities is given in Table 1 and Figs 1–6.

3.2. Overpotentials

In the absence of 2-thiouracil in the bath at all the current densities studied, the overpotential decreased with time up to a deposit thickness equivalent to 2 C cm^{-2} and then remained constant. When 2-thiouracil was present in the bath, the value of the overpotential was less

Table 1. Variation in surface morphology of deposit with differing current density and addition agent concentration

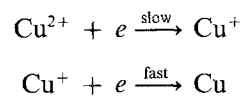
Current density (mA cm ⁻²)	Additive concentration (M)							
	0	10 ⁻¹⁰	10 ⁻⁹	10 ⁻⁸	10 ⁻⁷	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴
2	Triangular pyramids, layer base with macro-steps	Truncated pyramids and layers	Small truncated pyramids with more layers (Fig. 1)	Layers (Fig. 2)	Layers (smaller distance in between)	Narrow ridges	Polycrystals	
5	Triangular pyramids with macro-steps	Truncated pyramids	Truncated pyramids with layers	Layers	Layers	Ridges	Polycrystals	
10	Truncated hexagonal pyramids and occasional triangular pyramids	Hexagonal blocks (Fig. 3)	Truncated triangular pyramids	Steps (Fig. 4)	Layers	Ridges (Fig. 5)	Polycrystals (Fig. 6)	
15	Hexagonal blocks and occasional triangular pyramids with macro-steps	Fewer hexagonal blocks	Triangular pyramids	Steps	Layers	Ridges	Polycrystals	

than that of the pure solution at the corresponding current density. At low concentrations of 2-thiouracil the overpotential decreased with time and then reached a steady value as in the case of the pure solution. During the formation of layers, however, the overpotential increased with time and then remained constant. When ridge growth was observed there was no appreciable change in the value of the overpotential with time. The overpotential–log i relation was valid at low and moderate concentrations of 2-thiouracil (up to 10⁻⁵ M) and in all cases the

value of the Tafel slope was almost the same. (Fig. 7).

4. Discussion

Conway and Bockris have shown [7] that, in the case of copper deposition, the discharge mechanism is



with the first charge transfer as the rate control-

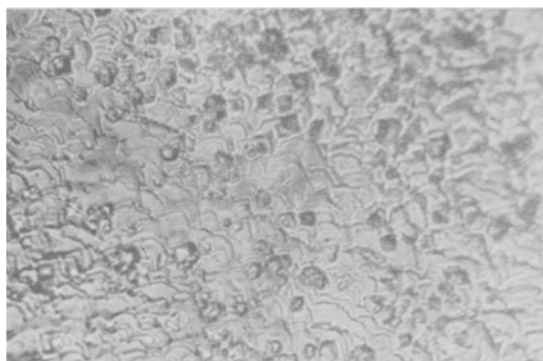


Fig. 1. Small truncated pyramids with more layers on the copper (III) plane from the acid sulphate bath with 10⁻⁸ M 2-thiouracil at 2 mA cm⁻². × 600.

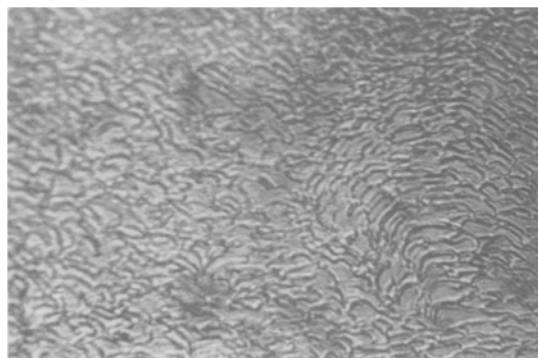


Fig. 2. Layers on the copper (III) plane from the acid sulphate bath with 10⁻⁷ M 2-thiouracil at 2 mA cm⁻². × 600.

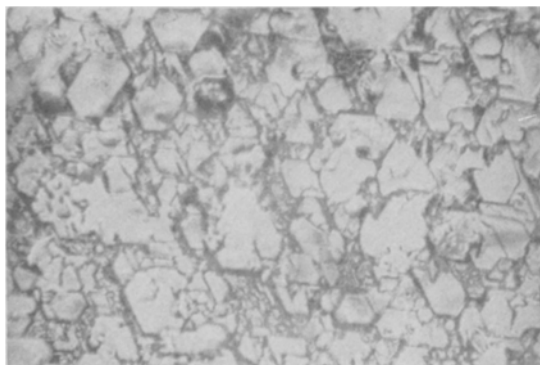


Fig. 3. Hexagonal blocks on the copper (III) plane from the acid sulphate bath with 10^{-9} M 2-thiouracil at 10 mA cm^{-2} . $\times 600$.



Fig. 5. Ridge type of growth on the copper (III) plane from the acid sulphate bath with 10^{-3} M 2-thiouracil at 10 mA cm^{-2} . $\times 600$.

ling step. The value of the Tafel slope obtained from the experimental results in the case of deposition from pure solution was found to be $120 \pm 10 \text{ mV}$ [8]. It is seen that the value of the Tafel slope in the presence of 2-thiouracil at the various concentrations studied is the same as that for pure solution. This shows that the electrochemical mechanism is not altered by adding 2-thiouracil to the bath, i.e. the first charge transfer is the rate determining step.

It is quite possible that 2-thiouracil increases the concentration of Cu^+ at the metal-solution interface, thereby favouring the discharge of the ions at a faster rate which results in a decrease in the value of the overpotential. At low concentration of 2-thiouracil due to the adsorption of the addition agent on the apexes of the pyramids, truncation starts because new steps cannot

spread from the apex and the truncated pyramids gradually turn into blocks. As the steps are more and more blocked by the adsorbed molecules, they move at a slower rate. On top of the first layer another step travels and catches up with the preceding one, favouring a bunching mechanism [9]. This leads to the formation of layers. At higher concentration, copper 2-thiouracil complex may be formed through nitrogen atoms and the thiocarbonyl sulphur atom [10]. The complex formed will be absorbed on the edges of the growing layer; the distance between successive layers decreases and ridges are formed. Finally the copper 2-thiouracil complex may codeposit on the active sites. Now the deposition takes place randomly with increase in the value of the overpotential and the resulting morphology is polycrystalline.

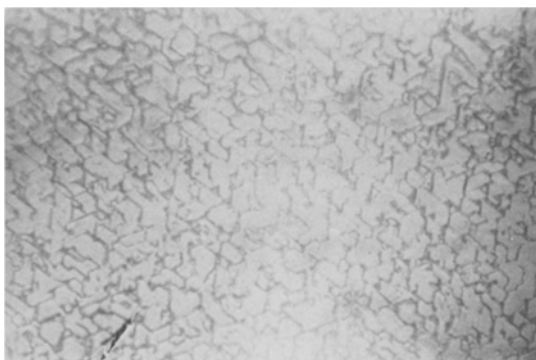


Fig. 4. Steps on the copper (III) plane from the acid sulphate bath with 10^{-7} M 2-thiouracil at 10 mA cm^{-2} . $\times 600$.



Fig. 6. Polycrystalline deposit on the copper (III) plane from the acid sulphate bath with 10^{-4} M 2-thiouracil at 10 mA cm^{-2} . $\times 600$.

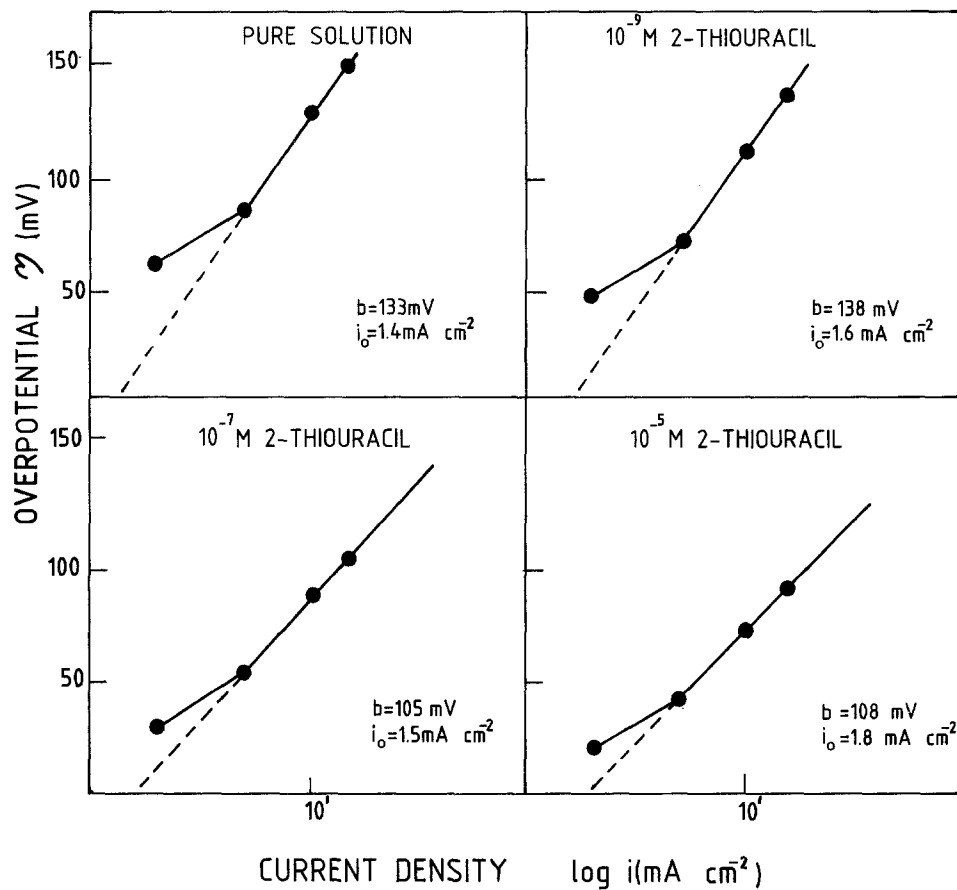


Fig. 7. Tafel relation for the deposition of copper on the copper (III) plane in the presence of 2-thiouracil.

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