HABIT MODIFICATION CAUSED BY 2-ThIOURACIL DURING THE ELECTRO-DEPOSITION OF COPPER ON COPPER (100) FACE

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The mode of action of addition agents in modifying the habit of electrodeposits at the molecular level has been reported. Usually the addition agents are found to increase the cathodic overpotential during the deposition process. In the present report, the effect of 2-thiouracil during the electrodeposition of copper from acid sulphate bath on copper (100) single crystal plane, with respect to both surface topography and electrokinetic parameters has been studied. The notable feature is that this compound causes a reduction in overpotential and brings beneficial changes in the brightness of the deposit.

The copper single crystal was machined and polished in 1:1 aqueous orthophosphoric acid bath at a constant cell potential of 1.2 V. The electrolytic bath whose purity was controlled had the composition 0.25 M CuSO₄ · 5H₂O, 0.1 M H₂SO₄ and the required concentration of 2-thiouracil. The deposition was carried out at 2, 5, 10 and 15 mA cm⁻² to a thickness of 3.6 μ at 25 ± 1°C. The overpotential during the deposition process was recorded using an Elico digital pH meter with reference to a freshly prepared copper electrode. The surface appearance after the deposition was examined using a phase contrast microscope at a magnification of 625 x.

In the case of pure solution at low current densities (2 and 5 mA cm⁻²) a layer type of growth was obtained as noticed by earlier workers. It was observed that the distance between steps in the layer type of deposit decreased, as the concentration of 2-thiouracil was increased from 10⁻⁶ to 10⁻⁷ mol l⁻¹. When the concentration of 2-thiouracil was 10⁻⁷ mol l⁻¹, the layer type of deposit was completely transformed into ridge type of deposit. The ridges were perpendicular to the layers. At a concentration of 10⁻⁶ mol l⁻¹, very narrow ridge growth was observed. When the concentration of 2-thiouracil was increased to 10⁻⁵ mol l⁻¹, the deposit became polycrystalline. Further addition of 2-thiouracil made the surface dirty grey and non-uniform.

At higher current densities (10 and 15 mA cm⁻²), in case of pure solution, the deposit consisted of pyramids in the background of layers (Fig. 1). At a concentration of 10⁻⁶ mol l⁻¹ of 2-thiouracil, the number of pyramids slightly decreased and layers were observed. When the concentration was increased to 10⁻⁵ mol l⁻¹, truncated pyramids and layers were observed. At a concentration of 10⁻⁴ mol l⁻¹, the pyramidal growths completely disappeared and the distance between the layers became very small. When the concentration of 2-thiouracil was increased to 10⁻³ mol l⁻¹, only ridge growth was noticed. At 10⁻³ mol l⁻¹, the ridges were still narrow (Fig. 2) and at a concentration of 10⁻² mol l⁻¹, a uniform bright deposit was observed. Further increase in concentration to 10⁻¹ mol l⁻¹, resulted in a polycrystalline deposit (Fig. 3). If the concentration of 2-thiouracil in the bath was further increased, the deposit became dull grey and non-uniform.

Fig. 1. Pyramids in the background of layers when copper is deposited on copper (100) face from pure solution at 10 mA cm⁻² (magnification 625 x).

Fig. 2. Narrow ridges when copper is deposited on copper (100) face from acid sulphate bath containing 10⁻⁴ mol l⁻¹ of 2-thiouracil at 10 mA cm⁻² (magnification 625 x).
The overpotential value during the deposition in presence of 2-thiouracil was always less than that of the pure solution at the corresponding current density studied. The Tafel relationship holds good at low and moderate concentrations of 2-thiouracil, but at very high concentrations it was not valid. The calculated value of Tafel slope at various concentrations of 2-thiouracil studied was 120 ± 5 mV agreeing with the value determined in the case of pure solution by Bockris et al. A decrease in the value of exchange current density was noticed in the presence of 2-thiouracil.

The above results indicate the remarkable effect of 2-thiouracil on the habit modification of copper electrodeposited. At low concentrations of 2-thiouracil in the bath, the transport mechanism may be due to the formation of 1:1 complex, which may get discharged at a faster rate, compared to the discharge of copper ions in pure solution, resulting in a decrease in overpotential. At higher concentrations, copper mercaptide may be formed as revealed by the disappearance of the absorption peak, characteristic of S-H group in the I.R. spectra of the compound obtained with copper sulphate solution and 2-thiouracil. The copper mercaptide may get adsorbed on the active sites and may hinder growth leading to shortered layers and finally ridges. Finally the copper mercaptide obstructs the incorporation of copper adions and leads to random nucleation resulting in a polycrystalline deposit.

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A CONVENIENT SYNTHESIS OF MELITERNATIN

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Methylation of 3,6,7,3',4'-pentahydroxy-5-methoxyflavone(I) obtained by the selective methylation of chelated 5-hydroxyl of 3,5,6,7,3',4'-hexahydroxyflavone(I), followed by the methylation of the resulting 3-hydroxy-5-methoxy-6,7,3',4'-dimethylenedioxyflavone (III) gave 3,5-dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV) identical with an authentic sample of meliternatin.

This paper reports an unambiguous and a convenient synthesis of meliternatin isolated from *Melicope tenuata* and thus provides further confirmation of constitution assigned to this compound and its demethylation product which were considered as 3,5-dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV) and 3-hydroxy-5-methoxy-6,7,3',4'-dimethylenedioxyflavone(V) identical with a sample of meliternatin. The earlier synthesis of this flavone(IV) reported by Fukui et al. was cumbersome and also involved large number of steps with poor yield. The present synthesis consists of two parts: The first part involved the preparation of 3,6,7,3',4'-pentahydroxy-5-methoxyflavone(II) by the selective methylation of the chelated hydroxyl in quercetagetin(I). As such the hexahydroxyflavone(I) could have been directly methylated to 3,5-dihydroxy-6,7,3',4'-dimethylenedioxyflavone(VI) which then on methylation should give 3,5-dimethoxy-6,7,3',4'-dimethylenedioxyflavone(IV). However, during such a methylation, the formation of the isomeric 3,7-dihydroxy-5,6,3',4'-dimethylenedioxyflavone(VII) along with the required flavone(VI) could not be ignored. In order to rule out the possibility of the formation of VII, it was considered necessary to protect this C₅-hydroxyl in I by alkylation before methylation.