Electrodeposition of Copper on Copper (111) Plane in Presence of 2-mercaptoethanol

R. LEKSHMANA SARMA AND S. NAGESWAR

Department of Chemistry, Central College, Bangalore University, Bangalore-560 001

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IT is known that the nature of the metal, the crystallographic orientation of the electrode surface and the both composition affect the nature of electrodeposits. In the study of electrode process on polycrystalline electrodes, the electrode behaviour is a kind of rough average of various crystal planes having different structure and electrochemical properties. Hence it is desirable to use a single crystal plane, of pure, metal whose working electrode surface prossesses a well defined crystal orientation.

The kinetics and growth habit of Copper deposits have been studied by Bockris and others[1-2]. Triangular pyramids and hexagonal blocks were observed on (111) face of Copper single crystal. Several addition agents[3-4] have been used to get the desired Physjcal Properties of deposits. However many of these addition agents increase the cathodic overpotential of the deposition process. Very few compounds have been reported, which decrease the cathodic overpotential. Turner and Jhonson[5] hove shown that the Presence of Sulphur compounds affects the nature of electrodeposits and the electrochemical Pa.ameters : The purpose of the present work is to study the effect of 2-mercaptoethanol at suitable concentrations on the (111) plane of copper on the growth habit modification and the kinetic parameters such as Tafel slope and exchange current density.

EXPERIMENTAL

The experimental procedure has been described in detail earlier[6]. An atomically smooth (111) face of copper (checked by X-ray diffraction) was prepared by electropolishing in a phosphoric acid bath[7]. An electrolytic bath of composition 0.25 M $CuSO_4$ and 0,1 M H_2SO_4 was used. Desired amount of 2-mercaptoethanol (Fluka, AG) was added whenever necessary. The deposition of copper at given current density was carried out to a thickness of 3.6μ and the overpotential was recoided using V.T.V.M. with reference to freshly prepared Copper electode with an accuracy of $\pm$5 mV. The surface appearance of the electrodeposit was examined under a metallurgical microscope at a magnification of 625X and photomicrographs were taken.

The solid obtained when 2-mercaptoethanol of higher concentration added to acid copper sulphate solution, was separated, purified and studied using IR spectra. (Carl Zeiss UR 10 infrared spectrophotometer).

RESULTS

Surface Morphology at 2 mA/cm² : A triangular pyramidal type of deposit with a layer base was observed when copper was deposited from pure solution (Fig. 1). Upto a concentration



FIG. 1 A triangular pyramidal type of deposit with a layer base when copper is depositkd on copper (III) plane from pure acid copper sulphate bath at 2 mA/cm² (Magnification 625 X)

of 10^{-10} mol/l., of 2-mercaptoethanol, there was no significant change in the type of growth. At this concentration the pyramids got slightly truncated. On increasing the concentration to 10^{-9} mol/l, twinned triangular pyramids were noticed (Fig. 2). When the concentration was changed to 10^{-8} mol/l, the pyramids changed to layers (Fig. 3). With further increase of concentration to 10^{-6} mol/l, triangular pyramids were observed in a background of polycrystalline deposit. At a concentration 10^{-5} mol/l, the deposit became polycrystalline (Fig. 4).

Surface Morphology at 5 mA/cm² : When copper was deposited at 5 mA/cm². from a pure solution, triangular pyramids were observed. The density of pyramids per unit area was greater than that obtained at 2 mA/cm². At a concentration of 10^{-10} mol/l, of 2-mercaptoethanol, the pyramids got twinned (of : Fig. 2). At a concetration



FIG. 2 Twinned triangular pyramids when copper is deposited on copper (III) plane from acid copper sulphate bath in presence of 10^{-9} mol/l, of 2-mercaptoethanol at 2 mA/cm² (Magnification 625 X)

of 10^{-9} mol/l, pyramids with layer base were observed. On further increase of concentration of 2 mercaptoethanol to 10^{-7} mol/l, a layer growth was observed (of : Fig. 3). When the concentration was changed to 10^{-6} mol/l, dark pyramids



FIG. 3 Layer type of deposit when copper is deposited on copper (III) plane from acid copper sulphate bath in presence of 10^{-8} mol/l, of 2-mercaptoethanol at 2mA/cm² (Magnification 625 X)

were observed in a background of polycrystalline deposit. At a concentration of 10^{-5} mol/l, the deposit observed was polycrystalline.



FIG. 4 A polycrystalline type of deposit when copper is deposited on copper (III) plane from acid copper sulphate bath in presecce of 10^{-5} mol/l, of 2-mercatoethnol at 2 mA/cm² (Magnification 625 X)

Surface Morphology at 10 mA/cm² : A large number of truncated hexagonal pyramids were deposited from a pure acid copper sulphate bath at a current density of 10 mA/cm² (Fig. 5). When



FIG. 5 Truncated hexagonal pyramids when copper is dnposited on copper (III) plane from pure acid copper sulphate bath at 10 mA/cm² (Magnification 625 X)

the concentration of 2-mercaptoethanol was 10^{-10} mol/l, the hexagonal pyramids lost their shape. At a concentration of 10^{-7} mol/l, triangular pyramids in the background of layers appeared. On increasing the concentration to 10^{-6} mol/l, ridge growth was observed (Fig. 6). On further increase in concentration to 10^{-5} mol/l, dark pyramids were observed in a background of polycrystalline deposit.

Surface Morphology at 15 mA/cm² : In pure solution at a current density of 15 mA/cm², hexagonal block with occasional triangular pyramids in a layer background were observed. When the



FIG. 6 Ridge type of deposit when the copper is deposited on copper (III) plane from acid copper sulphate bath in presence of 10^{-6} mpl/l. of 2-mercaptoethanol at 10 mA/cm^2 (Magnification 625 X)

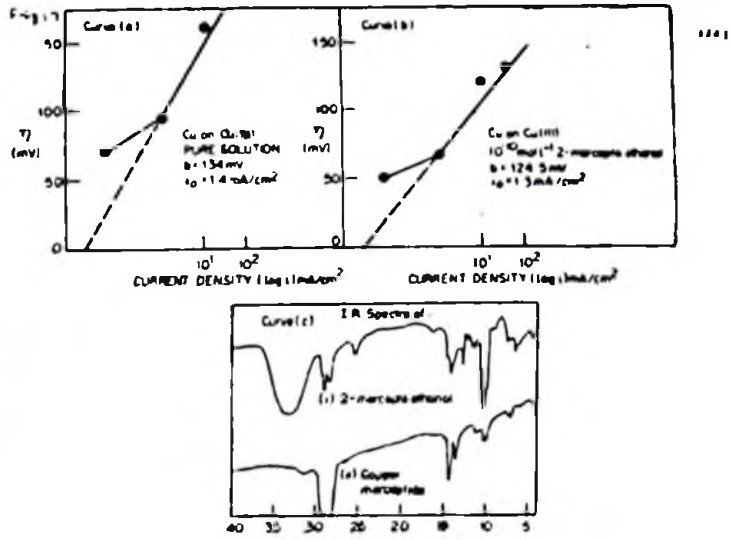


Fig. 7

concentration of 2-mercaptoethanol was 10^{-9} mol/l, twinned pyramids were observed. On increasing the concentration to 10^{-7} mol/l, triangular pyramids in a background of layers were noticed. On increasing the concentration to 10^{-6} mol/l, ridges were formed. On further increase of concentration to 10^{-5} mol/l, dark pyramids were observed in a background of polycrystalline deposit.

Overpotentials : The overpotential in pure solution decreases with time and attains a steady value at all current densities. In presence of low concentration of 2-mercaptoethanol, the overpotential is less than that of pure solution. The overpotential increases and then attains a steady value, during the transition from pyramidal to layer type of growth. The overpotential was almost steady during the formation or ridge type of growth. The Tafel relationship holds good only at low concentration of 2-mercaptoethanol, At higher concentration of 2-mercaptoethanol, the Tafel relation does not hold good.

I.R. Spectra : The spectrum of pure 2 mercaptoethanol shows the —SH stretching frequency at 2550 cm^{-1}. In the spectrum of the compound obtained with copper sulphate solution and 2-mercaptoethanol, there was disappearance of the absorption peak characteristic of —SH group (Fig. 7[c]).

DISCUSSION

Simultaneous participation of two electrons in the discharge of metalllic ions leads to high overpotential. If one electron takes part in the discharge act or if a process may break down number of successive one electron steps, the overpotential will be low[8]. The observed 2 RT/F values for the Tafel slope in pure solution on (111) plane of copper is in accordance with the following mechanism :

$$Cu^{2+} + e \xrightarrow{\text{Slow}} Cu^{+}$$

$$Cu^{+} + e \xrightarrow{\text{Fast}} Cu$$

as found by Bockris et al[9].

At low concentration of 2-mercaptoethanol, the value of the Tafel slope does not change from that of pure solution and there is decrease in overpotential value (Fig. 7[a] & [b]). The following transport mechanism may take place through a single electron transfer.

$$Cu^{++} + HS-CH_2-CH_2-OH \longrightarrow$$
$$\longrightarrow Cu^{+} - (S-CH_2-CH_2-OH) + H^{+}$$

The released chelating ligands sterically hinder deposition of neighbouring growth sites[10]. At low concentrations of 2-mercaptoethanol, there is likelihood of the formation of a 1 : 1 complex which may get absorbed on the substrate surface. This reveals that absorption is a pre-requisite for the transport mechanism[11].

At higher concentration, the transport mechanism may occur (as revealed by IR spectra) through the formation of copper mercaptide.

$$Cu^{++} + 2\,HS-CH_2-CH_2-CH \longrightarrow \begin{matrix} \diagup\, S-CH_2-CH_2-OH \\ Cu \\ \diagdown\, S-CH_2-CH_2-OH \end{matrix} + 2H^+$$

The copper mercaptide precipitates out at the interface region leading to an increase in overpotential. The copper mercaptide gets adsorbed [12-13] on the active sites of the Copper (111) face and also on the apexes of the pyramids. Thus the vertical growth of pyramids is hindered. leading to truncated pyramids. Further growth may occur sideways as the steps cannot generate from the apexes of the pyramids. This may give rise to layer type of growth. Further the copper mercaptide affects the growth of steps, preventing the layer growth and favouring the growth of adions in (110) direction leading to ridge growth.

At still higher concentration the transport mechanism may proceed with the precipitation of CuS.

$$2\,Cu^{++} + 2\,[HS-CH_2-CH_2-OH] \longrightarrow 2\,CuS + \begin{matrix} CH_2-CH_2-OH \\ | \\ CH_2-CH_2-OH \end{matrix} + 2\,H^+$$

CuS may precipitate in the form of triangular pyramids[14 15]. This obstructs the incorporation of copper adions and leads to random nucleation, resulting in a polycrystalline deposit.

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