Electrodeposition of copper on copper in the presence of dithiothreitol

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Studies of the –SH group effect present in dithiothreitol (DTE) with respect to morphology and electrode kinetics of copper electrodeposits on the (1 1 1) plane of a copper single crystal and polycrystalline copper from highly purified solutions of acidified copper sulphate were made. At 2.0 and 5.0 mA cm^{-2} there was a truncation of pyramids to layers and ridges and then to polycrystalline growth with an increase in the concentration of DTE in the bath. At higher current densities the change was from pyramids to thin hexagonal blocks, dragged pyramids and then to polycrystalline growth. Interestingly, the above morphological changes repeated at two different concentrations of DTE corresponding to two –SH groups present in the molecule. Levelling of the grains was observed at all current densities studied on a polycrystalline substrate. The electrode kinetic parameters have been correlated with the morphological changes and transport mechanisms have been proposed for different concentrations of the additive.

1. Introduction

It is seen from the literature that studies of the effect of additives with respect to the number of polarizable groups and aromatic rings present in the molecule are very few [1–3]. A detailed knowledge of individual group effect on reaction pathway, reaction products, complexation, and adsorption of organic compounds in the metal deposition porcess would help in selecting a suitable additive to obtain an electrodeposit with the desired properties. Furthermore, such studies would also aid in the understanding of the basic growth mechanism at a molecular level occurring in plating baths. With this in view a study with dithiothreitol (DTE) was undertaken. This compound was chosen because it contains two –SH groups and in previously reported work no additive containing two or more –SH groups had been studied. The effect of very small concentrations of DTE on the morphology and electro-kinetic parameters of copper electrodeposits at the (1 1 1) plane of a copper single crystal and on polycrystalline copper obtained from highly purified solutions was investigated. The observed morphological changes are correlated to kinetic parameters and a transport mechanism is proposed.

2. Experimental procedure

The cathodes used were polycrystalline copper and the (1 1 1) plane of a copper single crystal (supplied by Monocrystal Company). Prior to electrodeposition, the cathodes were electro-polished in a phosphoric acid bath [4]. The electrolytic bath (0.25M CuSO$_4$–0.1M H$_2$SO$_4$) was prepared and pure dithiothreitol (Bio-Rad) was added in various concentrations. The deposition of copper at a given current density was carried out to a thickness corresponding to 10 C cm^{-2} (3.6 μm). The overpotential was measured with reference to a freshly prepared copper electrode. The surface of the copper electrodeposits was examined under a metallurgical microscope at a magnification of 625× and photomicrographs were obtained. Details of the experimental procedure have been described elsewhere [5].

At a selected concentration of the addition agent, the bath solution was evaporated in a water bath (80°C) and the solid obtained was examined

by the IR method. The X-ray powder diffraction
pattern of the copper deposits was taken using a
Phillips X-ray generator. Standard procedures
were followed.

In the present study copper depositions on
polycrystalline and single crystal (1 1 1) surfaces
were studied in the current density range 2.0–10.0
mA cm^{-2}. The concentration of the additive was
changed from 10^{-18}–10^{-3} mol dm^{-3}. At 10^{-3} mol
dm^{-3} of DTE, a precipitate appeared in the
solution.

3. Results

3.1. *Morphology*

*3.1.1. Deposition on polycrystalline copper
cathode.* A characteristic type of deposit was
observed when the electrodeposition of copper
was carried out from a bath containing no
additives at all current densities (Fig. 1). Big grains
were observed at 2.0, 5.0 and 7.5 mA cm^{-2} and
small grains at 10.0 and 12.5 mA cm^{-2}. The grain
size decreased and the density of grains per unit
area increased with an increase in current density.
In the presence of 10^{-18}–10^{-17} mol dm^{-3} of DTE
in the bath, there was no significant change in the
morphology of the deposit. At a concentration
of 10^{-16} mol dm^{-3} of DTE and at 2.0 and
5.0 mA cm^{-2} levelling of grains started and the
effect continued up to the concentration of 10^{-14}
mol dm^{-3}. On increasing the concentration from
10^{-13} mol dm^{-3} to 10^{-9} mol dm^{-3} of DTE the
deposit became polycrystalline in nature. When
the concentration of DTE was further increased
to 10^{-8} mol dm^{-3} levelling of grains occurred and
the deposit consisted of fine grains (Fig. 2). If the
concentration of DTE is 10^{-5} mol dm^{-3} the
substrate surface becomes corroded. A similar
growth habit modification occurred at 7.5, 10.0
and 12.5 mA cm^{-2} with a gradual increase in the
concentration of DTE.

*3.1.2. Deposition on the copper single crystal
(1 1 1) face.* The variation in the growth habit of
the copper deposit as a function of current density
at the representative concentration and the
addition agent is shown in Table 1.

3.1.2.1. 2.0 mA cm^{-2}. The deposit obtained
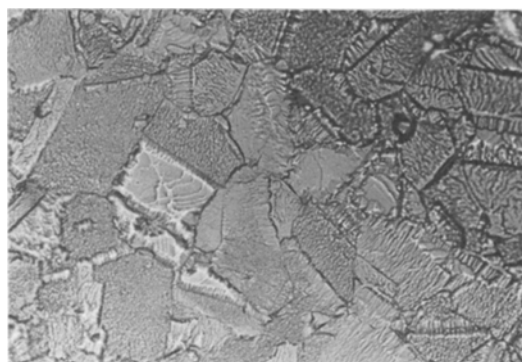from pure acid copper sulphate solution at

Fig. 1. A polycrystalline deposit on polycrystalline copper
from a pure acidic copper sulphate bath at 5.0 mA cm^{-2}
(×625).

2.0 mA cm^{-2} consisted of a triangular pyramidal
growth (Fig. 3). The presence of 10^{-18}–10^{-17} mol
dm^{-3} of DTE in solution caused little change in
the growth habit. At a concentration of 10^{-16} mol
dm^{-3}, the pyramidal type of growth changed
completely to ridge growth (Fig. 4). This type of
growth habit continued up to a concentration of
10^{-10} mol dm^{-3} and changed over to polycrystal-
line growth at 10^{-9} mol dm^{-3} of DTE. At 10^{-8} mol
dm^{-3} of DTE the ridge type of growth reappeared
and continued up to a concentration of 10^{-5} mol
dm^{-3} and became polycrystalline at a concen-
tration of 10^{-4} mol dm^{-3} of DTE in the bath.

3.1.2.2. 5.0 mA cm^{-2}. The growth habit of the
deposit obtained at 5.0 mA cm^{-2} was very similar
to that observed at 2.0 mA cm^{-2} except that the
density of pyramids per unit area was greater.
At 10^{-16} mol dm^{-3} of DTE in the electrolyte
dragged pyramids were observed (Fig. 5). The

Fig. 2. Levelling of grains when copper was deposited on
polycrystalline copper from sulphate bath containing
10^{-8} mol dm^{-3} of DTE at 7.5 mA cm^{-2} (×625).

Table 1. Type of deposits obtained at various current densities in the presence of DTE on the (1 1 1) plane of copper single crystal

Current density (mA cm^{-2})	Concentration of DTE (mol dm^{-3})	Type of deposit
2.0	pure solution	triangular pyramids
	10^{-16}	ridge growth
	10^{-10}	polycrystalline
	10^{-8}	ridge growth
	10^{-4}	polycrystalline
5.0	pure solution	triangular pyramids
	10^{-16}	dragged pyramids
	10^{-11}	polycrystalline
	10^{-8}	partial truncation
	10^{-4}	polycrystalline
7.5	pure solution	triangular and hexagonal pyramids
	10^{-16}	partial truncation
	10^{-10}	polycrystalline
	10^{-8}	partial truncation
	10^{-4}	polycrystalline
10.0	pure solution	hexagonal pyramids
	10^{-16}	partial truncation
	10^{-10}	polycrystalline
	10^{-8}	partial truncation
	10^{-4}	polycrystalline

dragging of pyramids increased with an increase in the concentration of DTE up to 10^{-13} mol dm^{-3}. The deposit became polycrystalline at 10^{-11} mol dm^{-3} of DTE in the bath. When the concentration of DTE was further increased to 10^{-8} mol dm^{-3} pyramidal growth with truncations reappeared and at 10^{-6} mol dm^{-3} the deposit was again poly-crystalline in nature.
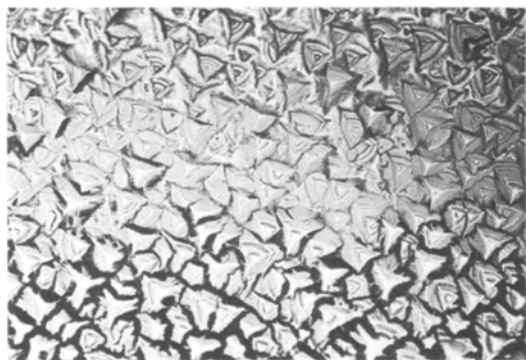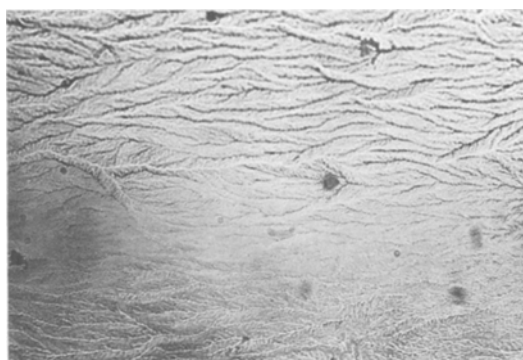
3.1.2.3. *7.5 and 10.0 mA cm^{-2}.* Truncated

Fig. 4. Ridge growth of copper deposited on copper (1 1 1) from acidic copper sulphate bath containing 10^{-16} mol dm^{-3} of DTE at 2.0 mA cm^{-2} ($\times$625).

hexagonal pyramids with occasional triangular pyramids were observed when copper was deposited from pure solution at these current densities (Fig. 6). In a bath containing 10^{-17} mol dm^{-3} of DTE, partial truncation of pyramids commenced which increased with an increase in concentration of DTE up to 10^{-13} mol dm^{-3} (Fig. 7). The deposit at 10^{-12} mol dm^{-3} of DTE became polycrystalline. Truncated pyramidal growth re-occurred at 10^{-10} mol dm^{-3} and finally the deposit changed to polycrystalline at 10^{-5} mol dm^{-3} of DTE (Fig. 8).

3.2. *Overpotential (η)*

The overpotential decreased with time and attained a constant value at all current densities studied. The Tafel plots of the pure solution and solutions containing 10^{-16} and 10^{-8} mol dm^{-3} of DTE are shown in Fig. 9. At high concentrations

Fig. 3. Pyramidal growth of copper deposited on Cu (1 1 1) from pure acidic copper sulphate bath at 2.0 mA cm^{-2} ($\times$625).
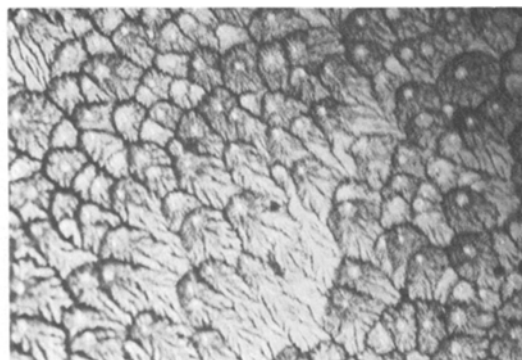

Fig. 5. Drag pyramids when copper is deposited on copper (1 1 1) from an acidic copper sulphate bath containing 10^{-16} mol dm^{-3} of DTE at 5.0 mA cm^{-2} ($\times$625).
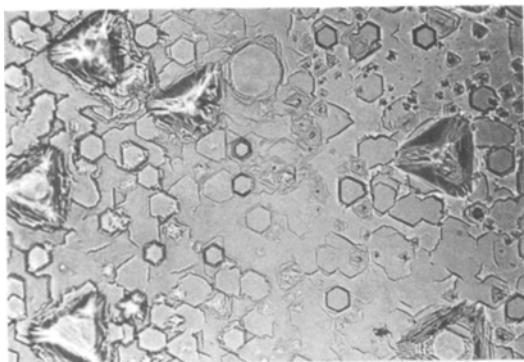
Fig. 6. Truncated hexagonal pyramids when copper is deposited on Cu (1 1 1) from an acidic copper sulphate bath at 10.0 mA cm^{-2} (×625).

Fig. 8. Polycrystalline copper deposit on Cu (1 1 1) from acidic copper sulphate bath containing 10^{-5} mol dm^{-3} of DTE at 10.0 mA cm^{-2} (×625).

of DTE deviations from the Tafel relationship were evident. Two minima in the overpotential values were apparent at all current densities. The critical concentration at which the minima occurred shifted to a lower value with an increase in current density and furthermore the over-potential value at the critical concentration was always less than that in the pure solution.

4. Discussion

DTE was effective at the low concentration of 10^{-16} mol dm^{-3} in bringing about growth habit modification of the copper deposit. Such a low threshold concentration for an additive has not been observed before. This could be due to the presence of two –SH groups in the same molecule. Plots of overpotential vs concentration of DTE in the bath (not shown) suggested the occurrence of two minima at all current densities studied as
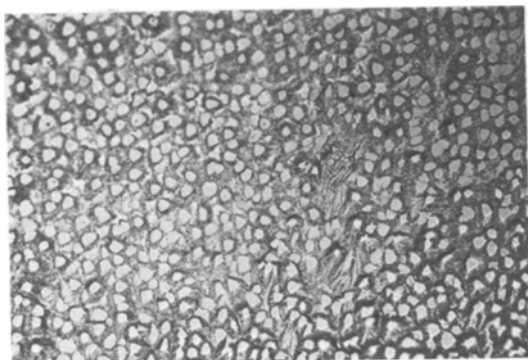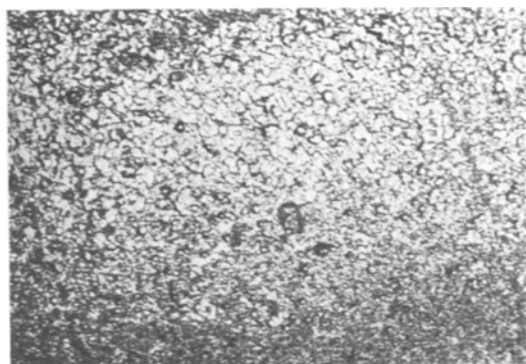
opposed to one minimum observed by previous workers, working with other sulphur-containing additives such as mercaptoethanol containing only one –SH group [3]. Furthermore, the behaviour of DTE was unique in that the observed morpho-logical changes on single crystal copper repeated at two different concentrations of the additive (Table 1).

Several mechanisms have been proposed by previous workers to explain the varying actions of addition agents during the electrodeposition process. Of these the surface adsorption theory and the complex ion theory, both proposed by Fischer [6] seem to be most pertinent. The observed $2RT/F$ values (120 ± 10 mV) for the Tafel slopes in pure solutions on the Cu (1 1 1) plane and on a polycrystalline surface is in accordance with the values observed by Conway and Bockris [7].
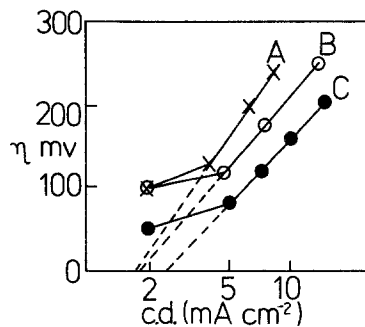

Fig. 9. Overpotential (η)–current density (c.d.) plot (Tafel relationship) for electrodeposition of copper on copper (1 1 1) plane from a pure solution and in the presence of DTE. (A) 10^{-8} mol dm^{-3} DTE, $b = 71$ mV; $i_0 = 1.5$ mA cm^{-2}; (B) 10^{-16} mol dm^{-3} DTE, $b = 70$ mV; $i_0 = 1.9$ mA cm^{-2}; (C) pure solution, $b = 120$ mV; $i_0 = 2.5$ mA cm^{-2}.

Fig. 7. Partial truncation of pyramids on Cu (1 1 1) from acidic copper sulphate bath containing 10^{-13} mol dm^{-3} at 10.0 mA cm^{-2} (×625).

The Tafel slope in the presence of low concentrations of DTE (10^{-18}–10^{-17} mol dm^{-3}) was found to be 120 ± 10 mV (the same as in pure solutions) indicating that there was no more change in the reaction path; i.e. the first electron transfer step is the rate determining step. At critical concentrations of DTE, however, the overpotential value during deposition was less than that in the pure solution suggesting that the presence of DTE in the bath stimulated the discharge process. The Tafel slope at the critical concentration of DTE increased to 10^{-8} mol dm^{-3} single electron transfer across the metal–solution interface. This could be due to the formation of a complex ion between the copper (II) ions and the ligand as given below.

$$Cu^{2+} + [HS-CH_2CHOH.CHOH.CH_2SH] \rightarrow$$

$$[Cu-S-CH_2.CHOH.CHOH-CH_2SH]^+ + H^+$$
$$\parallel$$
$$[Cu(DTE)]^+$$
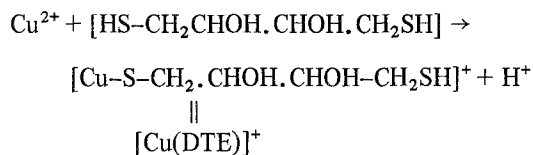
This complex may degrade to give Cu$^+$ ions, thereby facilitating the metal ion transfer and resulting in a decrease in the overpotential. Alternatively, the copper (I) ions could also be produced by the chemical reduction of copper (II) ions with DTE. Reduction of copper (II) ions using thiols containing the –SH group has been reported [8].

It is also possible that at the critical concentration corresponding to the second minimum, the copper ions instead of forming a [Cu(DTE)]$^+$ ion could form a neutral mercaptide, Cu(S.CH$_2$. CHOH)$_2$, which by physical adsorption on the cathode surface results in the observed lowering of the overpotential.

The formation of the mercaptide involving both –SH groups of the DTE molecule is supported by IR data. For example, the solid obtained after the evaporation of the bath containing 10^{-8} mol dm^{-3} of DTE showed no –SH absorption bands in the IR spectrum. The influence of the concentration of DTE on the growth habit of the deposit is shown in Table 1. Similar growth habit modifications are observed at two different concentrations of DTE. These correspond to the minima observed in the η–concentration plots.

The first transition in growth modification could be due to the [Cu(DTE)]$^+$ ion which may be adsorbed on the active sites of the Cu (1 1 1) plane and also on the apices of pyramids, causing truncation of pyramids and promoting horizontal growths as the steps cannot generate from the apices of the pyramids. This would give rise to small layer growths with the gradual disappearance of pyramids resulting in macrosteps and layers aligned along the (1 1 2) direction [9]. As the concentration of DTE increased to 10^{-8} mol dm^{-3} the growth of macrosteps would be hindered and copper anions may now diffuse along the (1 1 0) direction giving rise to ridge growth [10] (Fig. 10). At this concentration the degree of complexation may be large favouring a polycrystalline growth.

At still higher concentrations (10^{-4} mol dm^{-3} of DTE) the copper deposits contained inclusions, most probably formed by the reaction of copper (II) ions with DTE and precipitated on the active sites of the cathode favouring random nucleation and giving rough, nonuniform deposits.

5. Conclusions

Dithiothreitol in copper sulphate solutions strongly affects the growth habit and electro-kinetic parameters of copper deposition. As an addition agent DTE is unique in two ways

i. its threshold concentration is extremely low (10^{-16} mol dm^{-3}) and

ii. the structural changes in the deposit repeated themselves at two different concentrations of the additive

The presence of DTE in the bath appeared to stimulate the discharge process which at critical concentration seemed to involve a single electron transfer across the metal–solution interface.

Acknowledgements

References

[1] S. C. Barnes, *J. Electrochem. Soc.* **111** (1964) 296.
[2] D. R. Turner and G. R. Johnson, *ibid.* **109** (1962) 798.
[3] R. Lekshmana Sarma and S. Nageswar, *Surf. Technol.* **12** (1981) 377.
[4] P. Jacquet, *C. R. Acad. Sci.* **201** (1935) 1473.
[5] S. Nageswar and T. H. V. Setty, Proceedings of the Indian Academy of Science A, **LXXXI** (1968) 178.
[6] H. Fischer, *Z. Electrochem.* **54** (1950) 459.
[7] B. E. Conway and J. O'M. Bockris, *Electrochim. Acta* **3** (1961) 79.
[8] Saul Patai, 'The Chemistry of the Thiol Group, Part I', John Wiley & Sons, New York (1974) p. 274.
[9] A. Damjanovic, T. H. V. Setty and J. O'M. Brockris, *J. Electrochem. Soc.* **113** (1966) 429.
[10] R. Piontelli, G. Poli and G. Serravalle, 'Transaction of the Symposium on Electrode Processes', (edited by E. Yeager) John Wiley & Sons Inc., New York (1961) p. 67.