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THE EFFECT OF DITHIOTHREITOL ON THE GROWTH HABIT OF COPPER ELECTRODEPOSITS ON COPPER (111) PLANE

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AN investigation of the anisotropy with respect to morphology and electrode kinetics of copper electrodeposit on the (111) plane of copper deposited from highly purified solution of acidified copper sulphate containing very small concentrations of dithiothreitol (DTE) was made for the first time. Pyramids observed on (111) plane of copper when deposited changed to layers, ridges and polycrystalline type of growth as the concentration of DTE was increased.

Studies of a number of organic sulphur compounds as addition agents in copper plating have been reported in literature¹. However the role of individual groups in the performance of an addition agent has been only meagerly studied. Such studies of addition agents are important in understanding the basic growth mechanism on a molecular level in plating baths.

Recently it was reported that the brightening effect of mercaptoethanol was due to the presence of -SH group in the molecule². In order to study the group effect systematically, investigation with DTE was undertaken since it contains two -SH groups

$$\begin{array}{cccc} \text{CH}_2 & -\text{CH} & -\text{CH} & -\text{CH}_2 \\ | & | & | & | \\ \text{SH} & \text{OH} & \text{OH} & \text{SH} \end{array}$$

In the present work the effect of dithiothreitol on the growth habit modification of copper electrodeposited on (111) plane of a copper single crystal from an acid copper sulphate bath was studied. The (111) face of the copper cathode was mechanically polished on an emery paper finishing with 4/0 and then electropolished in 1:1 H₃PO₄. The depositions were carried out at

2.5, 7.5, 10 and 12.5 mA/cm² to a thickness of 3.6 μ on the plane from a (0.25 M CuSO₄ + 0.1 M H₂SO₄) bath with a known amount of freshly prepared DTE. The overpotentials (η) were measured with respect to a freshly prepared copper electrode acting as a reference electrode. The deposit was examined under a metallographic microscope. The other experimental details have been described earlier⁴.

In pure solution at 2 mA/cm², characteristic triangular pyramids and at 5, 7.5, 10 and 12.5 mA/cm² hexagonal block type of growth were observed as noticed by earlier workers^{5,6} (figure 1). The triangular type of growth transformed into small layers in the presence of 10⁻¹⁶ M/l of DTE and the layers changed to ridges at 5 × 10⁻¹⁶ M/l of DTE, (figure 2). When the concentration of DTE was increased to 10⁻¹⁵ M/l, the deposit became polycrystalline in nature (figure 3). At higher current densities 5, 7.5, 10 and 12.5 mA/cm² the hexagonal block type of structure observed in pure solution changed to circular layers, dragged pyramids and then to polycrystalline deposit with increasing concentration of DTE in the bath. However the critical concentration of DTE for the above transitions depended upon the current density of deposition. Interestingly the presence of DTE in the electrolyte reduced the overpotential value at all current densities. The η - log i relationship was linear in pure solution with a slope of 120 ± 10 mv. In solutions with DTE η - log i relation was linear up to 10⁻¹⁵ M/l of DTE, but deviated at concentrations > 10⁻¹⁵ M/l. The presence of DTE in the electrolytic bath may stimulate the electro-chemical-discharge reaction through a complex formation due to the oxidation of dithiothreitol

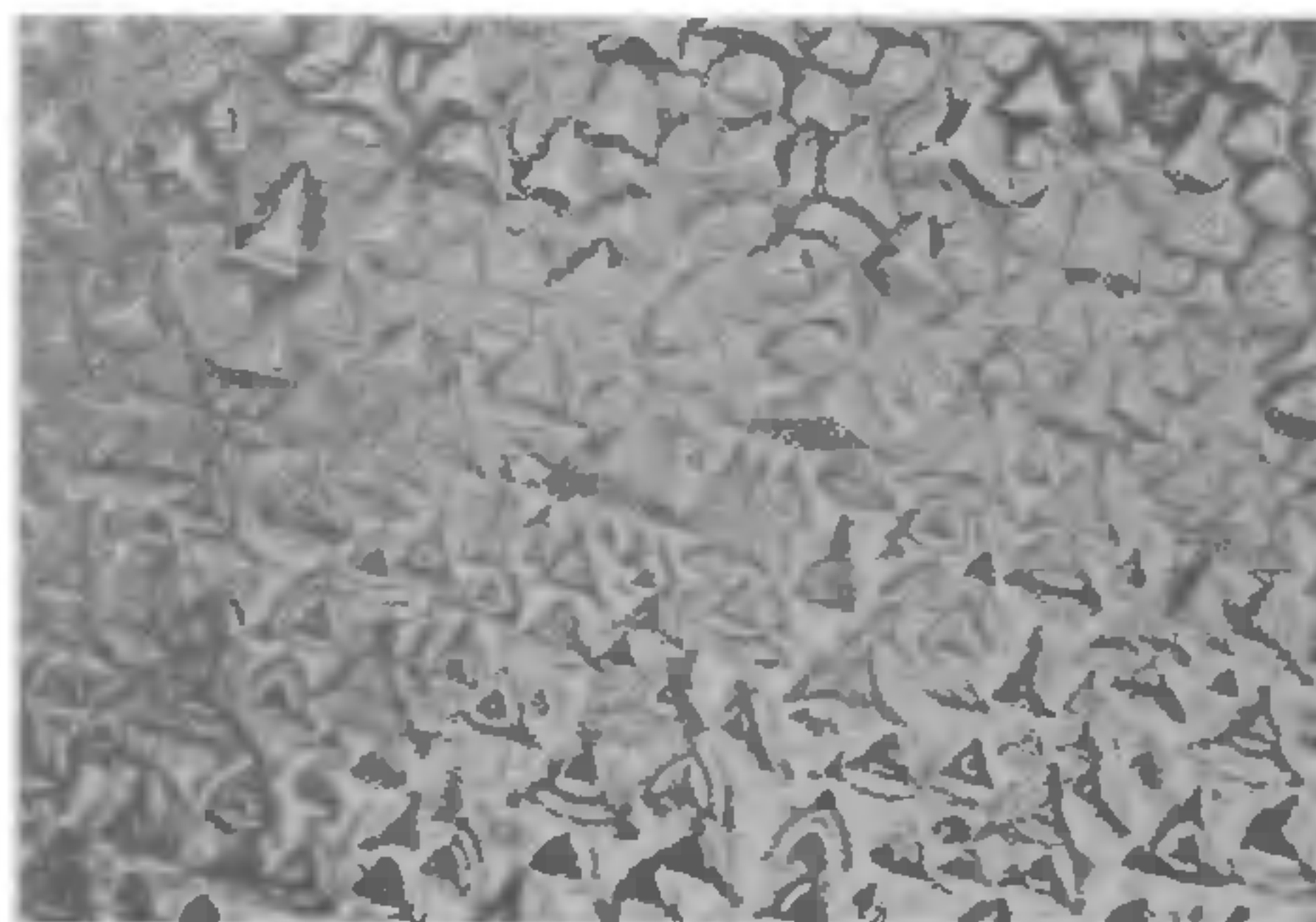


Figure 1. Triangular pyramids of copper deposited on copper (111) plane from pure copper sulphate bath at 2 mA/cm², × 625.



Figure 2. Ridge type of growth aligned in [110] direction when copper is deposited from acid copper sulphate bath in presence 5×10^{-16} m/l of DTE at 2 mA/cm, $\times 625$.



Figure 3. Polycrystalline type of deposit on copper (111) face from acid copper sulphate bath at 2 mA/cm² in presence of 10^{-15} m/l of DTE at 2 mA/cm, $\times 625$.

leading to a decrease in the overpotential values and accelerating the rate of transport of copper ions across the interface region resulting in changes in the morphology. The fact that the effect is apparent at a concentration as low as 10^{-16} M/l could be due to the presence of two -SH groups in the same compound. Such a low threshold concentration of an addition agent has not been reported earlier. The mechanism of habit modification due to DTE is under detailed investigation.

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LATE-PLEISTOCENE BEACH ROCK FROM URAN, MAHARASHTRA, INDIA.

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BEACH rock, popularly known as 'karal' in Konkan, is a common type of sedimentary formation in the littoral zone of the Konkan coast. Although, a good number of C-14 dates of beach rocks are available, the noteworthy beach rock formation from Uran has not been dated so far. Other beach rocks from Konkan have given a general age of Mid to Late Holocene epoch¹.

The beach rock found in the littoral zone, to the west of Uran ($18^{\circ}52'30''N$ & $72^{\circ}54'56''E$) is shelly-pebbly in nature and is well consolidated. Distinct laminations with alternate bands of fine and coarse material are seen in the exposed sections.

A representative lithosection (figure 1) exhibits about 1.8 to 2 m of exposed beach rock at the base, extending upwards through parts of dune (0.9 to 1.5 m), capped by red sandy soil. The reddish sandy soil perhaps implies pedogenesis after the formation of the beach rock. The soil-forming process must have caused the gradual elimination of $CaCO_3$ through time. Subsequently, the lamination and the shells disappeared. The red colour of the top layer indicates that the sands are old or at least that the sediments have been subjected to relative intense weathering for a