ELECTRODEPOSITION OF COPPER ON COPPER SINGLE CRYSTAL (100), (110) AND (111) PLANES IN PRESENCE OF THIOSEMICARBAZIDE

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ABSTRACT

Thiosemicarbazide (TSC), present in small quantities in acid copper sulphate bath, modifies the growth habits of copper on copper single crystal planes and reduces cathodic polarization. On (100) plane a transition from layer type of growth to ridge type and from ridges to pyramidal type and finally to polycrystalline type was noticed. On (110) plane ridges change to platelet type then finally to polycrystalline type. On (111) plane at low current densities triangular pyramids formed in pure solution transforms to hexagonal pyramids and to polycrystalline type. At high current densities hexagonal pyramids change to layer type, which transforms to nonsymmetrical pyramids and polycrystalline deposit at critical concentration of the addition agent. The transitions noticed depend on the concentrations of TSC and current density. These changes in morphology are attributed to the adsorption of TSC on the substrate.

It is known^{1, 2} that the epitaxial growth of copper depends largely on the orientation of the substrate and on the bath conditions. It is further shown³⁻⁵ that in purified solutions characteristic growth occurs when copper is deposited on oriented copper surfaces. It is noticed³⁻⁷ also that habit modification takes place when deposition conditions are altered.

Addition agents used in plating baths to increase brightness, smoothness, etc., usually increase the cathodic polarization.⁸ There are, however, certain compounds which reduce the cathodic polarization.⁹ Thiosemicarbazide not only modifies the growth habits of copper on copper single crystal planes but also reduces the cathodic polarization when it is present in small quantities in acidified copper sulphate bath.

EXPERIMENTAL

Preparation of highly purified solutions, electrolytic cell and general procedure are as in the earlier work.¹⁰ Known amount of TSC is added to highly purified 0.25 M $\text{CuSO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ and used.

RESULTS

Deposition on a (100) Face

At 2, 5 and 10 mA/cm²—Layer type of deposit was obtained (Fig. 1) when copper was deposited on a (100) face of copper single crystal from highly purified acid copper sulphate bath at 2, 5 and 10 mA/cm², however the distance between the layers is large at 2 and 5 mA/cm² but small at 10 mA/cm². Layers with decreased distance between them were noticed when TSC was present in the bath in small quantities. When TSC content was increased edge striations in these layers were noticed (Fig. 2). As the concentration of TSC was further increased more and more edge striations took place and a transition from layer to ridge type was noticed (Fig. 3). The layers completely broke up at striated points and gave ridge type of deposit (Fig. 4) when TSC was further increased. These ridges were aligned along [110] direction. Further increase in TSC content produced pyramidal type of growth (Fig. 5). Twinning of these pyramids (Fig. 6) and polycrystalline type of deposit (Fig. 7) resulted at higher concentration of TSC in the bath at all current densities.

Thus it was observed that a transition takes place from layer type of deposit to ridge type of deposit, from ridge type of deposit to pyramidal type of deposit, from pyramidal type to polycrystalline type of deposit in presence of TSC at three current densities mentioned above.

At 2 mA/cm², a transition from layers to ridges was observed at 4×10^{-8} M TSC, which then transformed to pyramids at 5×10^{-8} M. Finally, polycrystalline deposit was noticed at 1.5×10^{-6} M TSC.

In presence of 2.5×10^{-7} M TSC layers transformed to ridges when copper was deposited at 5 mA/cm². These ridges change to pyramidal type at 7.5×10^{-7} M in turn which transforms completely to polycrystalline type at 4×10^{-6} M TSC.

A transition at 10 mA/cm² from layers to ridges was noticed at 6.5×10^{-7} M TSC. Ridges change to pyramidal type at 8×10^{-7} M TSC and polycrystalline type was obtained at 5×10^{-6} M.

At 15 and 20 mA/cm².—Layers, truncated pyramids (Fig. 8) were observed when copper was deposited from highly purified acid copper sulphate bath at 15 mA/cm². When the TSC content in the bath was increased from 10⁻⁸ M to 10⁻⁶ M the number of truncated pyramids decreased and blocks were observed. At 10⁻⁶ M the number of truncated pyramids decreased and more of blocks were observed. Layers in the background gradually changed to ridge type of deposit (Fig. 9). At 1.5×10^{-6} M only ridge type of deposit was noticed (*cf.* Fig. 4). Further increase in TSC content to 2.5×10^{-6} M pyramids with steps on their sides with ridge background appeared. At 5×10^{-6} M the surface was completely covered with stepped pyramids. Twinning of these pyramids took place when TSC content in the bath was increased to 7.5×10^{-6} M. Small flat and twinned pyramids completely covered the surface at 10⁻⁵ M. At 1.5×10^{-5} M, polycrystalline type of deposit resulted.

At 20 mA/cm² no regular transitions were observed when TSC was present in the bath, however there was gradual increase of block type of deposit. Twinned block type of deposit with occasional truncated pyramids were observed at 10⁻⁵ M of TSC. At 2.5×10^{-5} M polycrystalline type of deposit resulted.

Deposition on a (110) Face

At 5 mA/cm².—Ridge type of deposit (*cf.* Fig. 4) was observed when copper was deposited on a copper single crystal (110) face from highly purified acid copper sulphate bath as noticed earlier. They were aligned along [100] direction. When TSC content in the bath was varied from 10⁻⁸ M to 10⁻⁷ M these ridges become shorter. Further increase of TSC to 5×10^{-7} M there was a transition from ridges to platelets. At 10⁻⁶ M concentration of TSC complete platelet type of deposit (Fig. 10) was observed. These platelets broke up with further increase of TSC and resulted in a polycrystalline type of deposit at 2.5×10^{-6} M. It is shown¹⁰ that the type of growth did not change at different densities when copper was deposited on copper (110) from acid copper sulphate bath containing TSC except that the direction of ridges changes from [100] direction to [110] at 10 and 15 mA/cm². Hence further work was not carried out.

Deposition on a (111) Face

At 5 mA/cm².—Triangular pyramids with steps on their sides appeared (Fig. 11) when copper was deposited from highly purified acid copper sulphate bath on a copper single crystal (111) face. When TSC in the bath was

increased from 10^{-10} M to 10^{-9} M, the number of pyramids per unit area increased otherwise there was not much change in the deposit morphology. At 10^{-8} M a tendency for twinning of these pyramids was observed but at 10^{-7} M more of twinning of these pyramids was observed as seen in Fig. 12. At 10^{-6} M of TSC there were occasional truncated triangular pyramids. On further increase in TSC content more of truncation of these twinned triangular pyramids was observed. At 10^{-5} M and above these triangular pyramids gradually transformed to hexagonal type of pyramids. At 7.5×10^{-5} M hexagonal pyramids with polycrystalline background appeared. The deposit consisted of more polycrystalline deposit with some truncated hexagonal pyramids when TSC was increased further. At 3×10^{-4} M the deposit was polycrystalline type.

At 10 and 15 mA/cm².—When deposited from highly purified acid copper sulphate bath truncated hexagonal pyramids with occasional triangular pyramids were observed at these current densities (Fig. 13). As the concentration of TSC in the bath increased the triangular pyramids got twinned and the number of hexagonal pyramids decreased. The triangular pyramids got truncated and truncated hexagonal pyramids grew side ways and produced macrosteps (Fig. 14) when the concentration of TSC was further increased. When the content of TSC was increased distorted pyramids appeared and these were twinned (Fig. 15). Finally polycrystalline type of deposit was observed at critical concentration of TSC.

At 10 mA/cm² truncated hexagonal and triangular pyramids transformed to macrosteps at 10^{-5} M TSC, which then changed to distorted pyramidal type at 4×10^{-5} M and finally to polycrystalline deposit at 4×10^{-4} M.

Truncated hexagonal and triangular pyramids obtained in pure solution changed to macrosteps at 2.5×10^{-5} M TSC at 15 mA/cm². These macrosteps changed to distorted pyramidal type at 5×10^{-5} M TSC. Finally only polycrystalline deposit resulted at 5×10^{-4} M TSC.

At 20 mA/cm².—Both truncated hexagonal and occasional triangular pyramids (*cf.* Fig. 13) were observed when deposited from pure solution. There was no change in the type of deposit when TSC was present in the bath upto a concentration of 10^{-5} M, however, there was increase of number of triangular pyramids. Large number of triangular pyramids with occasional truncated hexagonal pyramids (Fig. 16) were observed as the concentration of TSC was further increased. Some of the triangular pyramids were truncated. Twinning of these triangular pyramids resulted in polycrystalline type of deposit at critical concentration of TSC (7.5×10^{-4} M).

More of TSC is needed to bring about the transformation on (111) face compared to those on (100) and (110) face.

OVERPOTENTIALS

On a (100) face.—When copper was deposited on a (100) face of copper single crystal, from highly purified solutions the overpotential increased with time and attained a steady value at all current densities investigated as observed by earlier workers.^{4,10,11} The steady value of overpotential was attained more or less at the same thickness of the deposit ($2C/cm^2$) at all current densities. When TSC was present in the bath same trend of increasing and attaining a steady state was observed. However overpotential was always lower at corresponding current densities in presence of TSC compared to pure solution. When ridge type of deposit grows the overpotential was practically constant from the beginning. The same trend was observed even when pyramids and polycrystalline type of deposits developed. However there was not much change in the values of overpotential during deposition from pure solution and in presence of TSC during deposition at 20 mA/cm^2 .

The Tafel slope was found to be $125 \pm 5\text{ mv}$ when deposited from highly purified solutions. There was no significant change in the values of Tafel slope and exchange current density when TSC is present in solution. The values of Tafel slopes and exchange current densities are shown in Table I.

On a (110) face.—The overpotential slightly increased and reached steady state value quickly during deposition on (110) face when deposited from pure solution.⁴ There was no change in the trend of variation of overpotential with time when TSC was present in the bath. The value of overpotential also did not change.

On a (111) face.—The overpotential values at all current densities on a (111) face decreases and attains a constant value after some time when deposited from highly purified solution.^{4,10} When morphology of the deposit was affected by the presence of TSC the overpotential value was always lower compared to pure solution. However the same trend in change of overpotential with time was observed in presence of TSC. The steady state was attained more or less at the same thickness of the deposit.

The values of Tafel slope was found to be $130 \pm 5\text{ mv}$ when deposited from highly purified solution for both initial and final values of overpoten-

tial.^{4, 10} The value of tafel slope and exchange current density (i_0) did not change much in presence of TSC. The values of Tafel slopes and exchange current densities are given in Table I.

TABLE I

Tafel slopes (b) and exchange current density (i_0) in presence of TSC

Plane	Concentration of TSC	Tafel slope (b) (mv)		Exchange current density (i_0) mA/cm ²	
		Initial	Steady	Initial	Steady
(100)	Pure solution	125.3	120.0	3.0	1.8
	10 ⁻⁸ M	136.5	140.0	2.4	2.0
	10 ⁻⁷ M	144.0	140.0	3.0	2.3
	10 ⁻⁶ M	141.0	141.7	2.7	2.3
(111)	Pure Solution	132.5	130.5	1.3	1.5
	10 ⁻⁶ M	145.0	144.0	2.0	1.3
	10 ⁻⁵ M	146.0	142.0	2.0	1.5
	10 ⁻⁴ M	144.0	144.9	2.8	1.8

DISCUSSION

It is known¹² that the morphology of electrodeposits may change because of the change of electrochemical parameters such as Tafel slope, exchange current density, etc., or due to adsorption of the addition agent on the surface of the substrate or both.

The above results indicate that there is no significant change in the Tafel slopes and exchange current densities in presence of TSC on all the three planes. Hence the mechanism of charge transfer has not changed in presence of TSC, *i.e.*, the first electron transfer is the rate determining step even in presence of TSC. Therefore the above changes in the growth habits of copper electrodeposits may be due to only adsorption of TSC or the products produced during electrolysis.

Llopis¹³ have shown by radio tracer method the presence of sulphur in copper deposits when deposited from acidified copper sulphate containing thiourea. Hence it can be assumed that TSC molecule, which is nothing

FIGS. 1-8

FIGS. 9-16

but amino-thiourea, may hydrolyse to give urea and hydrogen sulphide, or may be reduced at the cathode forming NH_4CN and hydrogen sulphide. Cu^{++} ions may react with hydrogen sulphide forming CuS . Since solubility product of CuS is very low (8.5×10^{-45} M) the CuS will precipitate out on the cathode surface, relatively at low sulphide ion concentration. This precipitated CuS may get adsorbed at active sites on the cathode surface, and block the diffusion of adions or reduce the velocity of the movement of steps. Either way it interferes with normal crystal growth and thus bring about change in the deposit morphology.

The layers observed in pure acidified copper sulphate solution will transform to ridge type because of the hindrance of step movement on the surface by adsorbed film of CuS . The adions under this condition could only move along $[110]$ direction on (100) face and crystallize at growth sites resulting in the ridge type of deposit. Here it is noticed that the cathodic polarization both on (100) face and (110) face are same during ridge type of growth and this supports the above observed fact. When TSC content in the bath is increased to a critical value, the CuS film may completely cover the active sites on the surface. Then the copper adions may nucleate on adsorbed film and growth of non-symmetrical pyramids on (100) face and platelet type of deposit on (110) face may form while the substrate still influences the growth. The frequency of nucleation may increase with the increase of TSC content and this will result in twinning of pyramids. More and more twinning takes place with the increase of TSC content. At a critical concentration, the twinned growth gives rise to polycrystalline type of deposit, as concluded by Setty and Wilman¹⁴ for silver deposits.

On (111) plane at low current densities, regular triangular pyramids form. When TSC is present in the bath the number of such pyramids increased for the given area because of an adsorbed film of CuS on the surface which increases the growth nuclei. As the concentration of TSC is increased in the bath CuS may get adsorbed on the apex of these pyramids also. This prevents the vertical growth and the pyramids truncate. The truncated pyramids may now grow side ways. Further increase prevents this growth and there would be more nucleation producing blocks or nonsymmetrical pyramids which may get twinned. This twinned type may give rise to polycrystalline type of deposit.

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EXPLANATION OF PLATES IX AND X

PLATE IX

- FIG. 1. Copper deposited from acid copper sulphate bath on a (100) face at 2 mA/cm² 625 ×.
- FIG. 2. Copper deposited from acid copper sulphate bath + 10⁻⁹ M TSC on a (100) face at 2 mA/cm² 625 ×.
- FIG. 3. Copper deposited from acid copper sulphate bath + 2 × 10⁻⁸ M TSC on a (100) face at 2 mA/cm² 625 ×.
- FIG. 4. Copper deposited from acid copper sulphate bath + 2.5 × 10⁻⁸ M TSC on a (100) face at 2 mA/cm² 625 ×.

- FIG. 5. Copper deposited from acid copper sulphate bath + 6×10^{-8} M TSC on a (100) face at 2 mA/cm², 625 $\times$.
- FIG. 6. Copper deposited from acid copper sulphate bath + 2.5×10^{-7} M TSC on a (100) face at 2 mA/cm², 625 $\times$.
- FIG. 7. Copper deposited from acid copper sulphate bath + 1.5×10^{-6} M TSC on a (100) face at 2 mA/cm², 625 $\times$.
- FIG. 8. Copper deposited from acid copper sulphate bath on a (100) face at 15 mA/cm², 625 $\times$.

PLATE X

- FIG. 9. Copper deposited from acid copper sulphate bath + 10^{-8} M TSC on a (100) face at 15 mA/cm², 625 $\times$.
- FIG. 10. Copper deposited from acid copper sulphate bath + 10^{-6} M TSC on a (110) face at 5 mA/cm², 625 $\times$.
- FIG. 11. Copper deposited from acid copper sulphate bath on a (111) face at 5 mA/cm², 625 $\times$.
- FIG. 12. Copper deposited from acid copper sulphate bath + 10^{-7} M TSC on a (111) face at 5 mA/cm², 625 $\times$.
- FIG. 13. Copper deposited from acid copper sulphate bath on a (111) face at 10 mA/cm², 625 $\times$.
- FIG. 14. Copper deposited from acid copper sulphate bath + 10^{-5} M TSC on a (111) face at 10 mA/cm², 625 $\times$.
- FIG. 15. Copper deposited from acid copper sulphate bath + 5×10^{-5} M TSC on a (111) face at 10 mA/cm², 625 $\times$.
- FIG. 16. Copper deposited from acid copper sulphate bath + 5×10^{-5} M TSC on a (111) face at 20 mA/cm², 625 $\times$.