TECHNICAL REPORT

EFFECT OF CYANIDE AND THIOCYANATE IONS ON THE RATE OF LAYER GROWTH FORMATION ON A COPPER (100) FACE

S. Nageswar

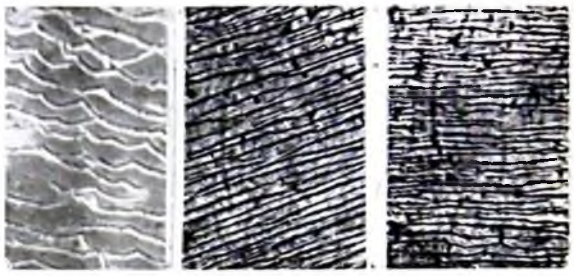
Dept. of Chemistry, Central College, Bangalore–560001

(Received in revised form Feb. 1978; accepted March 1978)

The layer type of structure is a common type of growth observed in electrodeposition process.[1,2] The layers may have regular shape with straight edges (steps) parallel to a certain crystallographic direction in the substrate, usually the one with low indices, but they may have irregular shape. Layer growth starts developing at an early stage of the deposition [3] and at an average thickness of the deposit of less than 1000° A, they become visible. The layers themselves may contain numerous microsteps [4,5,6]. The appearance of the layer growth depends on the orientation of the substrate. In the present work the rate of propagation of the layer growth on the (100) face of copper in pure solution of acid copper sulphate and in the presence of cyanide and thiocyanate ions are studied.

The experimental set up used in the present investigation was similar to that used in the earlier work [7]. The (100) plane of copper was mechanically polished on a emergy paper 4/0 and then electropolished in 1:1 orthophosphoric acid [8]. The deposition was carried out at various current densities on the (100) plane from 0.25M copper sulphate, and 0.1M sulphuric acid bath with a known amount of cyanide or thiocyanate ions. The surface appearance of the deposit was examined under a metallurgical microscope at a magnification of 625X. A series of photographs were taken and the average distance between the successive layers were measured.

It was noticed that the rate of propagation of layers was constant and was of the order of 3.079×10^{-5} cm/sec at 2mA/cm² (Fig.1). When the concentration of cyanide ions was 1×10^{-10} mol/l the rate of propagation of layers decreased to 1.234×10^{-5} cm/sec. With the increase of the cyanide ion concentration at 10^{-9} M/l in the bath, the layer type of growth changed completely to ridge growth. At a concentration of 10^{-8} M/l of cyanide ions layers reappeared and the rate of propagation was 1.468×10^{-5} cm/sec (Fig.2).



1 2 3

Fig. 1. Layer type of growth of copper deposited on a copper (100) face from acid copper sulphate bath at 2 mA/cm² (625×). Rate of propagation 3.079×10^{-5} cm/sec.

Fig. 2. Layer growth of copper deposited on a copper (100) face at 2 mA/cm² in presence of 10^{-8} m/l of CN^- (625×). Rate of propagation 1.468×10^{-5} cm/sec.

Fig. 3. Close layers when copper is deposited on a copper (100) face at 2 mA/cm² in presence of 10^{-6} m/l of CN^- (625×). Rate of propagation 1.234×10^{-5} cm/sec.

The rate remained constant up to 10^{-7} M/l of cyanide ions and further decreased to 1.234×10^{-5} cm/sec at a concentration of 10^{-6} M/l of cyanide ions in the bath (Fig.3). At concentration of 10^{-5} M/l the layers change over to ridge growth.

The growth rate of layers at 5mA/cm² was of the order of 4.311×10^{-5} cm/sec. When 1×10^{-10} M/l KCN was added to the bath the rate of growth of layers decreased to 1.468×10^{-5} cm/sec. With further increase in the concentration to 10^{-9} M/l, rate changed to 3.703×10^{-5} cm/sec. The rate remained almost constant upto a concentration of 10^{-7} M/l of cyanide ions in the bath and the layers change over to ridges at a concentration at 10^{-5} M/l of cyanide ions.

At the concentration of 1×10^{-10} M/l of thiocyanate ions, there was no significant change in the growth rate of layers. When the concentration was increased to 10^{-9} M/l of thiocyanate ions the rate of propagation of layers was 2.462×10^{-5} and 3.703×10^{-5} cm/sec at 2mA/cm² and 5 mA/cm² respectively.

These results indicate an interesting effect of cyanide and thiocyanate ions on the rate of layer growth formation on a copper (100) face. These results may be attributed to the adsorption of cyanide and thiocyanate ions.

The author is thankful to Dr. G.K.N. Reddy for his kind encouragement.

REFERENCES

1. Seiter, Fischer and Albert, Electrochem, Acta (1960) 2, 97.
2. Pick, Nature, 176 (1955) 693.
3. Vaughan and Pick, Electrochem, Acta (1960), 2, 130.
4. Pick, Storey and Vaughan, Electrochem, Acta (1960) 2, 167.
5. Howes, Proc. Phys. Soc. (1959), 74, 616.
6. A. Damjanovic, Paunovic and J'OM Bockris, J. Electroanal. Chem. 9 (1965), 93.
7. S. Nageswar and T.H.V. Setty, Proc. Ind. Acad. Sci. LXVIII (4) (1968) 178.
8. Jacquet, C R. Acad. Sci. Paris, 242 (1938).
9. S. Nageswar and T.H.V. Setty, Trans. SAEST. 7 (Jul) 1972.

