Effect of Cl^- Ions on the Crystallization Process in Acid Copper Sulfate Baths

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The effect of Cl^- ions on the epitaxial growth of copper from acid sulfate baths was examined by measuring the changes in orientation indexes of various crystal facets of copper deposits and also analyzing the cross sections of the deposits. For the deposits from the bath in the presence of 1.0 mM Cl^- , well-defined epitaxial growth was maintained in the thick deposits, and it was explained by considering the suppression of nucleation in the copper deposition reaction.

1 Introduction

The exchange current density and surface diffusion of ad-atoms seem to be important factors in the nucleation and growth mode of depositing metals¹⁾. The larger the exchange current density and surface diffusion rate, the smaller the nucleation density on the metal surface. In the previous paper²⁾, Cl^- has been found to increase the exchange current densities of charge transfer reactions and to accelerate the copper deposition and dissolution reactions in an acid copper sulfate bath. It is interesting to know the effect of Cl^- ions on the crystallization of copper from an acid sulfate bath as a function of exchange current density. In this paper, the effect of Cl^- ions on the epitaxial growth of copper from acid sulfate baths was examined by measuring the changes in orientation indexes of various crystal facets of copper deposits and also by analyzing the cross sections of the deposits.

2 Experimental

The copper (40 μm) was deposited on the rotating disc electrode with a demountable disc (2.27 cm^2) made of rolled copper sheet. The rolled copper disc, which had either (110) or (100) preferred orientation, was electropolished in 50% phosphoric acid and washed with re-distilled water before use. The copper deposits obtained were examined by an X-ray diffraction method using $\text{Cu-K}\alpha$ radiation (20 kV, 10 mA),

and the cross sections of the deposits were examined by a scanning electron microscope. The solution tested in the present study was composed of 0.2 M $\text{CuSO}_4 + 0.5 \text{ M } \text{H}_2\text{SO}_4$, unless otherwise noted. The other experimental conditions were the same as described elsewhere²⁾. The orientation indexes of (111), (100), (110) and (113) facets as a measure of the preferred orientation of the deposits were determined from the X-ray diffraction intensities by the Wilson's method³⁾.

The orientation index was obtained in the following manner; The intensity I (scale reading) for the particular diffraction line in the X-ray diffraction profiles is divided by the sum of the intensities for all the lines corresponding to the main crystal facets to give an intensity fraction IF, e.g.,

$$\text{IF}_{111} = \frac{I_{111}}{I_{111} + I_{200} + I_{220} + I_{311}}$$

Other IF fractions can also be calculated from the intensities referred to the standard copper (ASTM card). They were $\text{IFR}_{111} = 0.532$, $\text{IFR}_{200} = 0.245$, $\text{IFR}_{220} = 0.106$ and $\text{IFR}_{311} = 0.090$. The IF term for the particular diffraction line of the deposit divided by the IFR term gives the orientation index as;

$$\text{Orientation index}_{111} = \frac{\text{IF}_{111}}{\text{IFR}_{111}}$$

If the deposits were entirely random in orientation, the orientation index for each plane would be 1.0.

3 Results and Discussion

Figure 1 shows the effect of current density on the orientation indexes of various crystal facets of the copper deposits obtained from the

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Fig. 1 Effect of current density and chloride ions on the orientation indexes of various Cu crystal facets of the copper deposits (40 μm)

Substrate copper has (110) preferred orientation

acid sulfate baths in the presence (1.0 mM) or absence of Cl^- ions. The substrate copper has (110) preferred orientation and orientation index of (110) is about 5. For the deposits with no chloride, (110) orientation index increased and gave a maximum value in the region of low current density, and then decreased gradually with increased current density, while orientation indexes of (111), (100) and (113) facets have minimum values in the low current density region. The (110) preferred orientation of substrate disappeared in the high current density region.

On the other hand, for the copper deposits obtained with 1.0 mM Cl^- concentration, the preferred orientation of (110) was pronounced over the wide current density region. The orientation indexes of (111), (113) and (100) facets were found to be extremely small compared with that of (110) facets.

The copper deposits formed on the copper substrate with (100) preferred orientation are shown in Fig. 2. For the copper deposits

Fig. 2 Effect of current density and chloride ions on the orientation indexes of various Cu crystal facets of the copper deposits (40 μm)

Substrate copper has (100) preferred orientation

obtained from the pure CuSO_4 bath, (100) preferred orientation seemed to diminish gradually with an increase of current density. On the other hand, with an addition of 1.0 mM Cl^- , the orientation index of (100) facet was maintained at high values over the wide region of polarization current. Under these conditions, the orientation index of (110) increased slowly and those of the other facets remained to be low values.

For the copper deposits formed in the different concentration baths such as 0.2 M CuSO_4 + 2.0 M H_2SO_4 , 0.5 M CuSO_4 + 1.0 M H_2SO_4 , and 1.0 M CuSO_4 + 0.5 M H_2SO_4 , the same results were obtained.

It is well known that the activation overpotentials as well as crystallization overpotentials of copper deposition on different crystal planes are in the order⁴⁻⁶⁾

$$\eta(110) < \eta(100) < \eta(111)$$

Further, the overpotential on the crystal plane (311) would be larger than that on (110), because the (110) crystal plane has more active sites than the (311) plane. If copper were electrodeposited on a polycrystalline copper plate without any nucleation reaction, the orientation

index of (110) would increase because of the difference in the growth rates of the various crystal facets, as the deposit becomes thicker. Thus, the increase of (110) orientation indexes for the copper deposits in Fig. 1 is explicable by considering the suppression of nucleation in the copper deposition reaction. The maintenance of high values in the orientation indexes of (100) observed for the deposits with an addition of 1.0 mM Cl^- in Fig. 2 is also explained in the same way.

Fig. 3 shows the cross sections of the copper deposits formed on the (100) plane at a current density of 75 mA cm^{-2} . The pictures, A and B correspond to the deposits obtained from the

Fig. 3 SEM micrographs of the cross sections of copper deposits

(A) no chloride ions and (B) 1.0 mM Cl^-
Deposition parameters: 75 mA cm^{-2} current density, 600 rpm rotation speed of disc electrode, 30°C , $0.2 \text{ M CuSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$

bath with or without Cl^- , respectively. It is difficult to distinguish the grain size of the deposits from each other in the deposits. The epitaxy in the deposit, however, can be clearly seen in the etched patterns. For the copper deposits obtained from a pure sulfate bath, the epitaxial growth disappeared in the early stage of the deposition. While, for the copper deposits obtained from the same bath in the presence of 1.0 mM Cl^- , well-defined epitaxial growth was maintained in the thick deposits.

4 Conclusion

For the copper deposits from the acid copper sulfate bath in the presence of Cl^- ions, well-defined epitaxial growth was maintained in the thick deposits, and it was explained by considering the suppression of nucleation in the copper deposition reaction.

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電気化学工業と電力貯蔵方式・調査報告書

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☆本報告書は、エネルギー問題の重要性に鑑み、電気化学工業において多面的に省資源・省エネルギー対応を図ると共に、電気事業にとっても極めて有効な方策の一つとして共通な課題である電力貯蔵方式について行った調査報告書です。

☆内 容 ○電気事業の現状 ○電気化学工業の現状 ○二次電池による電力貯蔵 ○電力貯蔵用新型常温電池 ○燃料電池による発電 ○水電解-燃料電池の組合せによる電力貯蔵 ○総括

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