Sono-electroplating of Bismuth Film From Bi(III)-EDTA Bath

A. Chiba† and T. Kojima
Department of Materials Chemistry, Yokohama National University 79-5, Tokiwadai, Hodogaya-Ku, Yokohama 240-8501, Japan

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BiOCH₃COO and EDTA-4Na were dissolved in 2 mol/dm³ CH₃COOH-2 mol/dm³ CH₃COONa buffer solution, and was adjusted to pH 4.1 by adding 2 mol/dm³ CH₃COOH or 2 mol/dm³ CH₃COONa. 100 cm³ of this electrolyte was used. Electroplated film was obtained in the range of 10-100 mA/cm². Sono-electroplating was carried out smoothly, because the mass transfer accelerated with ultrasonic agitation and Bi ion was supplied to electrode surface. The mass transfer and crystallization processes were most affected with micro-jet and shock wave pressure. Best conditions of sono-electroplating were 0.10 mol/dm³ BiY³⁺, pH 4.0-5.5, 298 K and 10 mA/cm². Exchange current density and reaction rate constant in the sonication increased compared with that in the stationary state. As for this, an electron reaction became fast by the micro-jet or a shock wave pressure. The plated film was smoothness and denseness in sonication compared with that in stationary state. It was concluded that main factor that the surface became smooth was shock wave pressure.

Keywords: Electrochemical method; Bi; Metallic film; Surface morphology; Sonication

I. INTRODUCTION

Bi is a scarce metal with an abundance in earth about the same as Ag, and a semi metallic element with unusual electronic properties due to its highly anisotropic fermi surface, low carrier concentrations, and small carrier effective masses. Bi has specific electrical, physical and chemical properties. Coatings of Bi may be particularly useful because of physical and chemical properties. Thin films had shown large magneto resistance [1–3], thermoelectric efficiency [4] and interesting quantum effects [5]. Bi is also used in electrochromic devices [6, 7] and for magneto resistance [1–3], thermoelectric efficiency [4] and interesting quantum effects [5]. Bi has specific electrical, physical and chemical properties. Coatings of Bi may be particularly useful because of physical and chemical properties. Thin films had shown large magneto resistance [1–3], thermoelectric efficiency [4] and interesting quantum effects [5]. Bi is also used in electrochromic devices [6, 7] and for magneto resistance [1–3], thermoelectric efficiency [4] and interesting quantum effects [5].

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II. EXPERIMENTAL

The substrate was Cu sheet (99.9% and 0.3 mm thick) with an active area of 1 cm × 1 cm. The counter electrode was Pt plate with an active area of 2.5 cm × 4 cm, and placed 3 cm from the working electrode. The Cu substrate was polished with No. 2000 emery paper and immersed in 6 mol/dm³ HNO₃ solution for several seconds, then rinsed with distilled water and air-dried before the experiments. BiOCH₃COO and EDTA-4Na were dissolved in 2 mol/dm³ CH₃COOH - 2 mol/dm³ CH₃COONa buffer solution, and was adjusted to pH 4.1 by adding of 2 mol/dm³ CH₃COOH or 2 mol/dm³ CH₃COONa. 100 cm³ of the electrolyte was used. The cell, 6 cm in diameter and 7 cm in height, was placed in an ultrasonic tank. The electrolyte maintained at 298 k. The sonication was stable in solution because the stability constant was 26.5.

III. RESULTS AND DISCUSSION

The main reaction of Bi(III) and EDTA ion in pH 4.1 solution was Eq. (1). Bi(III)-EDTA complex (BiY³⁺) was stable in solution because the stability constant was 26.5. The solubility limit of BiY³⁺ was 0.15 mol/dm³ in buffer solution (pH 4.1).

\[ \text{Bi}^{3+} + \text{H}_2\text{Y}^{2-} \rightarrow \text{BiY}^+ + 2\text{H}^+ \]  (1)

A. Cathodic polarization curve

Figure 1 shows the cathodic polarization curves. Polarization in the sonication state was reduced comparing with the stationary state because sonication was strongly
agitation. The limiting current density was about 55 mA/cm² in the sonication state, and about 15 mA/cm² in the stationary state. It was concluded that thickness of diffusion layer was thin with sonication. Table I shows the electrochemical parameters. The exchange current density, $i_0$, was larger with sonication comparing with that without sonication. It was concluded that thickness of electric double layer reduced with shockwave pressure and micro-jet in cavitation effects. Transfer coefficient, $\alpha$, reduced. These results may be related to increasing of agitation.

### B. Current density

Figure 2 shows the effects of current density and bath temperature on the current efficiency with sonication. Current efficiency was about 98% at 10 mA/cm² and 298 K, and below 25 mA/cm² at 313 and 333 K, and decreased with increasing of current density over 25 mA/cm² at all temperatures. Dendrite was deposited over 50 mA/cm² at 298 and 313 K, and over 75 mA/cm² at 333 K. Figure 3 shows the effect of pH on the current efficiency. The current efficiency was about 85-100% at 10 mA/cm² in the range of pH 4.0-5.5. The current efficiency was about 80% at 30 mA/cm² and about 60% at 50 mA/cm² in pH 4.1. The current efficiency decreased with increasing of pH over pH 4.5. Plated film was dendrite over pH 5.0 at 30 and 50 mA/cm². Figure 4 shows the effect of BiY⁻ concentration on the current efficiency. The current efficiency was about 45% in 0.01 mol/dm³, and increased with increasing of concentration, and was about 90% in range of 0.05-0.10 mol/dm³ at 10 mA/cm². The current efficiency was about 20% in 0.01 mol/dm³, and increased slowly with increasing of concentration and was about 55% in 0.10 mol/dm³ at 50 mA/cm².

### C. Texture coefficient

Figure 5 shows the effect of current density on the texture coefficient of electrodeposited film with sonication. The texture coefficient of (014) plane decreased and that of (102) plane increased with increasing of current density. The texture coefficient of (110) plane increased at 100mA/cm². The texture coefficients of other planes were almost constant. Figure 6 shows the effect of pH on the texture coefficient of electroplated film with sonication.
FIG. 4: Effect of BiY- concentration on the current efficiency with sonication.

Each planes with the exception of (014) and (102) plan were almost constants. The texture coefficient was not affected with pH.

D. Surface morphology

Figure 7 shows the surface morphology of plated film after electrolysis of 10 mA/cm². Surface was smoothness and denseness in the sonication state comparing with that in the stationary state. Grain size was about 46.8 nm in the stationary state and 35.9 nm in the sonication state with X-ray analysis. It was concluded that particles were destroyed because the particle and particle had collision with the micro-jet and shock wave pressure on the terrace of surface.

E. Growth process of plated film

Figure 8 shows the growth process of plated film. Surface was smoothness and denseness with increasing of charge because particle crushed down with the shockwave pressure. For one example, the contact theory of elastic body was examined. The diameter of contact circle (a) indicated Eq. (2) when solid (radius: r) press to flat plate with pressure W:

\[ a^3 = \frac{3}{4} W r \left( \frac{1 - \sigma_1^2}{E_1} + \frac{1 - \sigma_2^2}{E_2} \right), \]  

where, \( E_1 \) and \( E_2 \) are Young's modules, \( \sigma_1 \) and \( \sigma_2 \) are Poisson's ratio of ball and plate. When Bi particle assumed globosity of 20 nm dia. and Bi film was flat plate.

Figure 9 shows the effect of pressure on the contact area. The particle shaved destruction or a part off with the shock wave pressure, and the size decreased. Thereafter, the particle moved to kink of surface by the micro-jet. The particles could be plug up in more small clearance.
[BiY\textsuperscript{−}]: 0.1 mol/dm\textsuperscript{3}, Current density: 50 mA/cm\textsuperscript{2}, pH: 4.1, Temperature: 298 K, Sonication: 28 kHz

FIG. 8: Growth process of deposited film with sonication.

FIG. 9: Area of an osculating circle when Bi particle pressed by some pressures and model of film growth.

IV. CONCLUSION

1. Best conditions of sono-electroplating was 0.10 mol/dm\textsuperscript{3} BiY\textsuperscript{−}, pH 4.0-5.5, 298 K and 10 mA/cm\textsuperscript{2}.

2. Polarization was smaller and limiting current density increased about 3.7 times compared with that in stationary state. The mass transfer and crystallization processes were most affected as diffusion layer was reduced with micro-jet and shock wave pressure with cavitation.

3. The texture coefficient of (014) plane decreased, and that of (110) and (022) planes increased with increasing of current density.

4. Grain size was reduced from 46.8 nm in the stationary state to 35.9 nm in the sonication state. The surface was smoothness and denseness in the sonication state. It was concluded that main cause that a surface was smoothness by the shock wave pressure.

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