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Bi electrodeposition under magnetic field

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Abstract

Bi was galvanostatically electrodeposited in a hydrochloric acid solution in the presence and absence of a 0.5 T field. The effects of magnetohydrodynamics (MHD) convection were focused on the concentration overpotential as well as the current efficiency. The morphological and microstructural variation of electrodeposited Bi thin film was also investigated. Dendritic growth enhanced at higher current density was considerably suppressed by superimposition of a 0.5 T field, while the effect on the crystal microstructure was not confirmed.

Keywords: Bi; Electrodeposition; Magnetic field; Ionic mass transfer; Current efficiency

1. Introduction

The introduction of magnetic field into the electrochemical processing may open the large potential applications. Enhanced mass transfer [1,2], better electrodeposit quality [3–5] and control of corrosion [6,7] are just some of effects. In addition, the magnetic field may offer a powerful scientific tool in the research field on electrochemical reaction kinetics [8].

A number of studies have been reported on metal electrodeposition in a magnetic field [3–5,9–19]. They focused on the morphology [3,4,16] and crystal microstructure of electrodeposited thin film [9–15], and kinetics [19], for example.

Devos et al. studied the preferred orientation of electrodeposited Ni thin film [12]. They concluded that magnetohydrodynamics (MHD) convection influenced the concentration of competitive adsorption of various species (e.g. hydrogen adatom), which determined the texture axis of electrodeposited Ni. Kyoto university team engaged in the pole figure measurement to find out the biaxial texture evolution of electrodeposited Ni and Fe thin films in a magnetic field parallel to the substrate [14,15]. They deduced that the texture evolution of electrodeposited metal was determined by the direction of MHD convection.

The characteristic morphological variation of electrodeposited metal was often observed in a magnetic field. The macroscopic dendrite shape of metals like Cu, Zn, Co, and Fe was significantly influenced by a magnetic field at the higher current density [3,4,17,18]. Under the mass transfer-limited condition, MHD convection must reduce the contribution of concentration overpotential to the morphological variations. Fe dendrites electrodeposited in a magnetic field sometimes show the extraordinary macroscopic shape variation [17]. When the thin film was electrodeposited, not only the size but also the shape of crystallite was modified by the superimposition of a magnetic field, for example, Fe [15,16] and ZnO [20]. Although the stirring effect of MHD convection was surely confirmed in the many studies, the interest is still remained on the macroscopic shape evolution.

We have examined the morphological and microstructual variations of electrodeposited Cu and Ag films by discussing the important contribution of concentration overpotential measured with the interferometry technique [21,22]. It is an interesting subject in the field of shape evolution to investigate systematically the characteristic morphological variations induced by the complicated interaction between electric and magnetic fields near the cathode surface.

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This paper deals with Bi electrodeposition in the presence and absence of a magnetic field. Bi is a semimetal and has the most diamagnetic property among all elements. The unique electronic properties like enormous magnetoresistance (MR) effects in thin films [23] and nanowire arrays [24,25] have been demonstrated. Bi is the most promising candidate to examine the evidence of magnetic field effect on diamagnetism during electrodeposition as contrasted with the ferromagnetic elements, Fe, Co, and Ni. The present work focuses on the magnetic field effects on the electrochemical processing of Bi thin film.

2. Experimental

The composition of electrolyte was adjusted to 0.32 M $BiCl_3$–4.9 M HCl. Au sheet (1 cm × 1 cm) with a thickness of 100 μm was used as the cathode. A conventional three-electrode cell was employed with a Ag/AgCl, KCl sat. (E = +0.20 V versus SHE) reference electrode through using a Luggin capillary. The electrolytic cell is schematically illustrated in Fig. 1. The working electrode was installed vertically and fixed to the inner wall of 3 cm long duct type of cell as well as a Bi counter electrode. They were faced to each other with 1 cm distance at the center of duct cell [26]. Electrodeposition was carried out galvanostatically in the range of 1.0–150 mA cm^{-2}. The anode stripping method measured current efficiency. The magnetic field of 0.5 T was applied to the electrolysis with a permanent magnet of Nd–Fe–B alloy. All experiments were performed at room temperature. Electrodeposited Bi thin film was rinsed carefully by ethanol and dried out. The crystal microstructure of electrodeposited Bi thin film was determined by X-ray diffraction using Co Kα radiation (λ = 1.78897 nm).

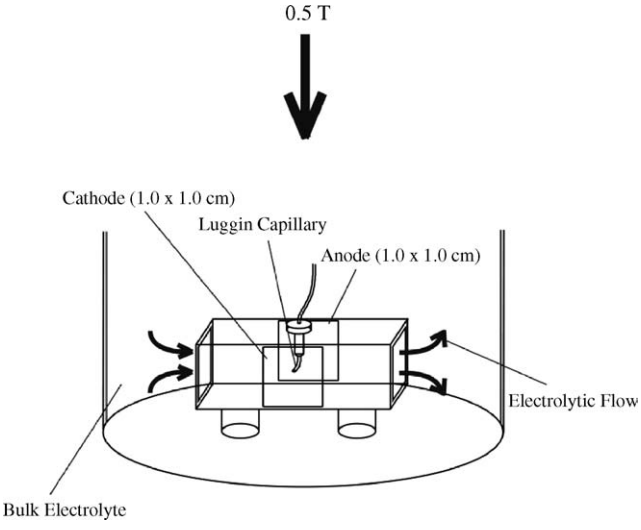

Fig. 1. Schematic illustration of the duct type of electrolytic cell. (A 0.5 T field was applied perpendicularly).

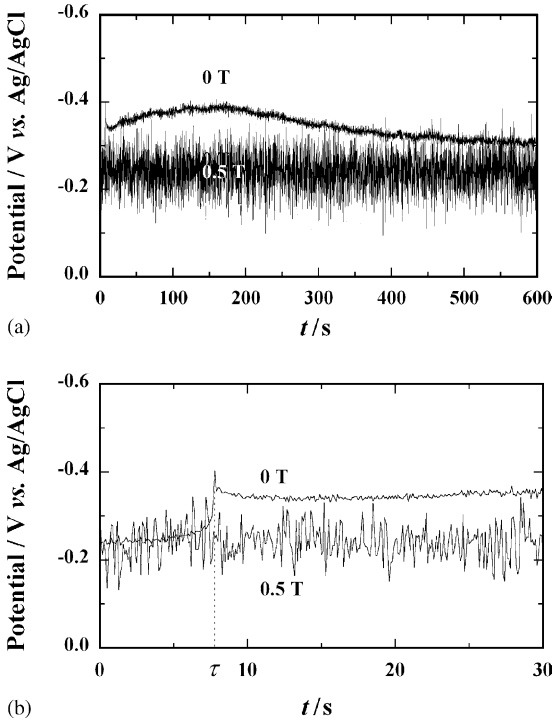

Fig. 2. Transient variation of electrode potential during Bi electrodeposition at 75 mA cm^{-2} in the presence and absence of a 0.5 T field. (a) Transient variation over 600 s and (b) over initial 30 s.

3. Results and discussion

Transient variation of electrode potential during Bi electrodeposition at 75 mA cm^{-2} is shown in Fig. 2. When the electrolysis started without magnetic field, the electrode potential suddenly jumped up by 0.1 V from E = −0.3 V around several seconds after starting the electrolysis as clearly demonstrated in Fig. 2(b). This duration period, τ (s), was significantly influenced by the applied current density. The potential then started gradually shifting to more negative direction to attain −0.4 V around t = 150 s (see Fig. 2(a)). Maintaining a constant potential of −0.4 V over 100 s, it was gradually recovered to −0.3 V at t = 600 s.

The superimposition of magnetic field, on the other hand, introduced a remarkable fluctuation of potential. It varied between −0.2 and −0.3 V with a frequency of 3 Hz. It was difficult to reduce such a significant fluctuation even if lead wires were completely sealed with Al foil. Kim and Fahidy found the current oscillation phenomenon during the magnetoelectrolysis [27]. They investigated the effect of the migration on it when Cu^{2+} was electrodeposited in $CuSO_4$–H_2SO_4 solution. The smaller ratio of the supporting electrolyte to the metallic ion tended to induce the oscillation. The current oscillation was observed at the ratio <40. In the present work, the electrode potential oscillation are noticed in the galvanostatic condition when [HCl]/[Bi^{3+}] is 15. Another possibility is described in Appendix A, although this value is within their criterion.