FABRICATION OF Bi$_2$O$_3$ THIN FILM BY THERMAL-ENHANCED ELECTROPLATING

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ABSTRACT

High-temperature fluorite structure Bi$_2$O$_3$ is a well-known solid electrolyte due to its high oxygen ion conductivity. The stabilization of cubic Bi$_2$O$_3$ may be enhanced by adding rare earth oxide. It was thought that phase transformation was caused by the presence of oxygen vacancies. In this study, Bi$_2$O$_3$ thin film was prepared by oxidation on the electroplated Bi. The effect of applied voltage on crystallization of metallic Bi thin film was investigated. The oxidation reaction of Bi with various crystalline orientations is discussed. Two preferred orientations, (102) and (202), appeared in XRD. After oxidation, β-Bi$_2$O$_3$ and α-Bi$_2$O$_3$ appeared due to the specific atomic configurations of (102) and (202). The microstructure observed by SEM showed microcracks due to lattice expansion from phase transformation. The volume changes from rhombohedral Bi to β-Bi$_2$O$_3$ and α-Bi$_2$O$_3$ were estimated to be 16.73% and 19.14%.

INTRODUCTION

Bi$_2$O$_3$ is recognized as the best oxygen ionic conductor. Its high conductivity depends greatly on its crystal structure and concentration of oxygen vacancies. δ-Bi$_2$O$_3$ exhibits defective fluorite structure. The concentration of oxygen vacancies in δ-Bi$_2$O$_3$ is as high as 25 mol% (1-4). Unfortunately, this structure is only stable at high temperatures (723°~823°C). At temperatures lower than 723°C, monoclinic α-Bi$_2$O$_3$ was obtained. In addition, β- and γ-phases were also examined at low temperature (about 350°C) while cooling rapidly from high temperature. Many studies have investigated the phase transformation of Bi$_2$O$_3$ (5-8). Under controlled conditions, functional ceramic would also be obtained by oxidation of metal. In some studies of metal oxidation, the effect of the metal surface on the structure of the growing oxide was examined. It was also suggested that surface oxygen atoms take part in the formation of oxide and the mass transport of oxygen and metal ions limits the growth of oxide layer. In this work, a specific preferred orientation on Bi thin film is regarded as the reaction surface to discuss the effect of the oxidation reaction on the phase transformation of Bi$_2$O$_3$.

EXPERIMENTAL PROCEDURE

Electroplating of Metallic Bi Thin Film

A deposited Pt layer served as the working electrode in a conventional three-electrode cell for electrodeposition using a potentiostat/galvanostat meter (EG&G 263A). Pt plate was used as the counter electrode. The electrolyte solution was composed of 48.57 g Bi(NO$_3$)$_3$·5H$_2$O, 700 mL ethylene glycol and 300 mL distilled water. To ensure a stable
electrodeposition process, the solution was stirred for one day to dismiss excess bubbles. The electrochemical method was applied at voltages ranging from -0.1 to -0.5 V versus the Ag/AgCl reference electrode for 30 minutes to fabricate metallic Bi thin film.

**Oxidation at High Temperature**

To obtain bismuth oxide, the electroplated Bi thin films were heat-treated at 350°C for 12 hr in air. In addition, the heating rate was controlled at 1°/min to minimize the thermal stress of the material during the oxidation process.

**Material Characterization**

To examine structural variations and oxidation reactions of the electroplated metallic Bi obtained at various applied voltages, crystal structures of the samples were analyzed using Regaku Multi Flex X-ray system. The CuKα radiation was used, and the scanning rate was set at 2°min⁻¹ at a 2θ range between 20° to 80°. The lattice parameters were refined using the least-squares method. The microstructure of the samples was examined using SEM.

**RESULTS AND DISCUSSION**

**Effect of Applied Voltage on Crystal Structure of Electroplated Bi Thin Film**

Figure 1 shows the XRD traces of electroplated Bi thin films obtained at applied voltages
ranging from -0.1 to -0.3 V. All the patterns reveal pure metallic Bi with rhombohedral structure. In addition, the reflections of Pt and silicon double diffraction were also found at 39.8° and 33.1°. The intensities of certain reflections varied with the applied voltages. Since the growth behavior of metal during electroplating process is significantly affected by the rate of nucleation and growth rate, the growth behavior of the thin film would be affected by the applied driving forces. As seen in Figure 1, the intensity of (102) increased with increasing applied voltages but (202) decreased. For a polycrystalline film, the relative higher intensity indicated that the specific planes are well-aligned structure. During the electroplating process, the deposition of species would be controlled by nucleation or growth. In addition, the nucleation was also affected by the surface configuration. A surface with relaxed configuration had greater surface energy and is favored for nucleation. Because the atomic configuration of (102) is more compact than that of (202), it is thought to be a favored plane for growth at higher applied voltages. However, (202) would be a favored plane for nucleation at lower applied voltages.

**Effect of Crystal Structure on Phase Transformation During Oxidation Process**

As seen in Figure 2, both α- and β-Bi$_2$O$_3$ were obtained after oxidation of metallic Bi thin film. After oxidation, the oxide formed from sample electroplated at -0.1 V, revealed pure α-Bi$_2$O$_3$ as shown in Figure 2(a). α-Bi$_2$O$_3$ was of monoclinic structure and a thermal equilibrium phase from room temperature to 723°C. As the applied voltage increased to -0.5 V, the grown oxide was of more β-Bi$_2$O$_3$, Figure 2(e). β-Bi$_2$O$_3$ was of tetragonal structure and obtained only with a rapid cooling rate from a high temperature. However, the crystal structure of Bi$_2$O$_3$ after heat-treatment from electroplated Bi was mainly affected by the orientation of Bi film.

To investigate the structural relationship between the as-electroplated Bi and the as-produced bismuth oxide during an oxidation reaction, a schematic diagram was drawn (Figure 3). The Bi atoms are not in a close-packed arrangement in rhombohedral symmetry; some free space is available. Because Bi$_2$O$_3$ is an oxygen ionic conductor,
oxygen ions would diffuse through the oxide layer easily. Hence, the structure of bismuth oxide formed may be affected by the arrangement of Bi atoms in the preferred oriented planes. In Figure 3, the β-Bi₂O₃ formed from the oxidation of Bi film with (102) preferred orientation. On the other hand, α-Bi₂O₃ was obtained when Bi film was preferably oriented along the (202) plane. These results indicate that the Bi atoms along (102) are closely matched with Bi ions on the plane of (100) in β-Bi₂O₃. Also, the Bi atoms along the (202) plane are consistent with Bi ions on the plane of (100) in α-Bi₂O₃.

**Microstructure Observation**

Figure 4 shows the top view of micrographs of the metallic Bi thin film prepared at -0.3 V

**Figure 4.** Micrographs of top view on metallic Bi thin film prepared at -0.3 V, (a) before and (b) after oxidation.
before and after oxidation. Some cracks caused by the volume change during the oxidation reaction were observed on the surface. According to the theoretical density of metallic Bi, α-Bi₂O₃ and β-Bi₂O₃, the ratio of volume change would be estimated:

\[
\text{volume change} = \frac{m \times \frac{M_{\text{BiO}_3}}{d_{\text{BiO}_3}}}{m \times \frac{M_{\text{Bi}}}{d_{\text{Bi}}}}
\]

M and d represent molecular (atomic) weight and theoretical density, respectively. The volume changes from Bi to α-Bi₂O₃ and β-Bi₂O₃ were 16.73% and 19.14%. Hence, the lattice expansion due to the insertion of oxygen would cause the micro crack in the Bi₂O₃ thin film.

CONCLUSIONS

The following conclusions may be drawn based on the results of this work:

- Metallic Bi thin film revealed crystalline orientations of (102) and (202) planes varied with the applied voltage in the electroplating process.
- As the oxidation reaction was carried out on Bi thin film, the one with (102) preferred orientation formed β-Bi₂O₃. On the other hand, the Bi film with (202) preferred orientation formed α-Bi₂O₃.
- The favored reaction plane would produce specific crystal structure of Bi₂O₃. (102) and (202) preferred specimens formed β-Bi₂O₃ and α-Bi₂O₃ respectively.
- The lattice expansion during phase transformation from rhombohedral Bi to β-Bi₂O₃ and α-Bi₂O₃ taken place owing to the significant volume change 16.73% and 19.14%.

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