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Orientation-controlled phase transformation of Bi_2O_3 during oxidation of electrodeposited Bi film

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Abstract

High-temperature fluorite structure Bi_2O_3 is a well-known solid electrolyte owing to its high oxygen ion conductivity. In this study, Bi_2O_3 thin film was prepared by the oxidation process of the electrodeposited metallic Bi film. The crystal structures of the oxidized Bi films varied with the applied voltages during the electroplating process. Pure α-Bi_2O_3 was obtained when the oxidation was conducted for the metallic Bi film electrodeposited at -0.1 V. Only β-Bi_2O_3 was observed as a -0.5 V electrodeposited Bi film was oxidized. The crystal structure of Bi_2O_3 obtained by oxidation of metallic Bi film may dominantly be affected by the orientation of as-electrodeposited Bi film. Such kind of process is favorable to the preparation of functional ceramic with specific crystal structure.

Keywords: B. Crystal growth; C. X-ray diffraction; D. Crystal structure

1. Introduction

Bi_2O_3 is recognized as the best oxygen ionic conductor. Its high conductivity is highly dependent on its crystal structure and the concentration of oxygen vacancies. Many studies investigated the phase transformation of the Bi_2O_3 [1–4]. δ-Bi_2O_3, which is only stable at high temperature (723–823 °C), exhibits defective fluorite structure with the concentration of oxygen vacancies as high as 25 mol%. At temperatures lower than 723 °C, monoclinic α-Bi_2O_3 was obtained. In addition, β- and γ-phases were also examined at low temperature (about 350 °C) while cooling from a high-temperature with a rapid cooling

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rate. Except for the heat treatment conditions, some other parameters may also be changed to control the growth behaviors of the material. For example, the single crystalline δ-Bi_2O_3 film could be obtained by electrodeposition on a Au single crystal [5]. The single crystalline sapphire is usually used as the substrate for the preparation of the metal oxide single crystal in the deposition process because the lattice constants of sapphire is very close to that of substrates. In some previous studies, the effect of the metal surface characteristics on the growth behaviors of the oxide was pointed out [6]. It was suggested that the surface oxygen atoms would take part in the formation of oxide; the mass transport of oxygen and metal ions would limit the growth of oxide layer. For this reason, an appropriate orientation of the substrate can guide the growth of the material with a specific orientation. In this study, the Bi_2O_3 thin film with the specific preferred orientation was prepared by oxidation of electrodeposited Bi film. The underlying mechanisms of the oxide growth behaviors are also discussed through the structural relationship between Bi and Bi_2O_3.

2. Experimental procedure

A Pt thin film (20 nm thick) was deposited by e-beam evaporation on the n-type Si as the working electrode, and a Pt sheet was used as the counter electrode. The reference electrode was silver/silver

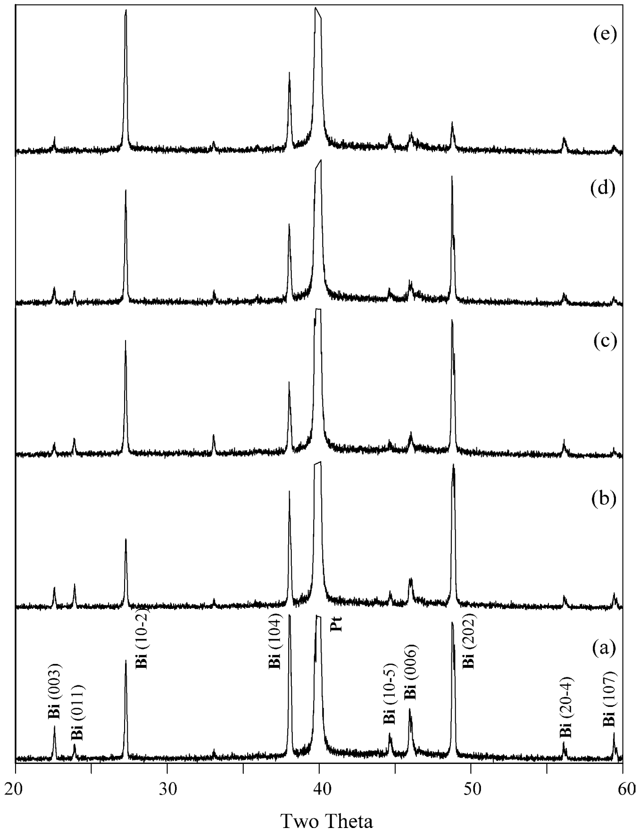

Fig. 1. XRD traces of electroplated Bi thin films at: (a) −0.1 V, (b) −0.2 V, (c) −0.3 V, (d) −0.4 V and (e) −0.5 V.

chloride. The electrodeposition was conducted in a conventional three-electrode cell (potentiostat/galvanostat meter, EG&G 263A). The electrolyte solution was composed of 48.57 g $Bi(NO_3)_3 \cdot 5H_2O$, 700 ml ethylene glycol and 300 ml distilled water. To ensure electrodeposition process more stable, the solution was stirred for 1 day to dismiss the additional bubbles produced during the mixing of the electrolyte. The electrochemical process was applied at voltages ranging from −0.1 to −0.5 V for 30 min to prepare metallic Bi thin film. To obtain bismuth oxide, the electroplated Bi thin films were heat-treated at 350 °C for 12 h in air. In addition, the heating rate was controlled at l °C/min to minimize the thermal stress of the material during the oxidation process. In order to examine structure variation and oxidation reaction of the electroplated metallic Bi obtained at various applied voltages, the crystal structures of the samples were analyzed using Regaku Multi Flex X-Ray system. The Cu Kα radiation was used and the scanning rate was set at 2 °C/min at a 2θ range between 20 and 60°. The lattice parameters were refined using the least-square method. The microstructure of the samples was examined using SEM.

3. Results and discussion

3.1. Prefer orientation of metallic Bi thin film

Fig. 1 showed the XRD traces of electroplated Bi thin films obtained at applied voltages ranging from −0.1 to −0.5 V. All the patterns reveal pure metallic Bi with rhombohedral structure. The reflection of Pt was also found at 39.8°. The intensities of certain reflections of the metallic Bi, such as $(1\,0\,\bar{2})$, (1 0 4) and (2 0 2) varied with the applied voltages. It is well-known that the electroplating process was significantly affected by the applied voltage because the nucleation and growth rate as well as the size of the critical

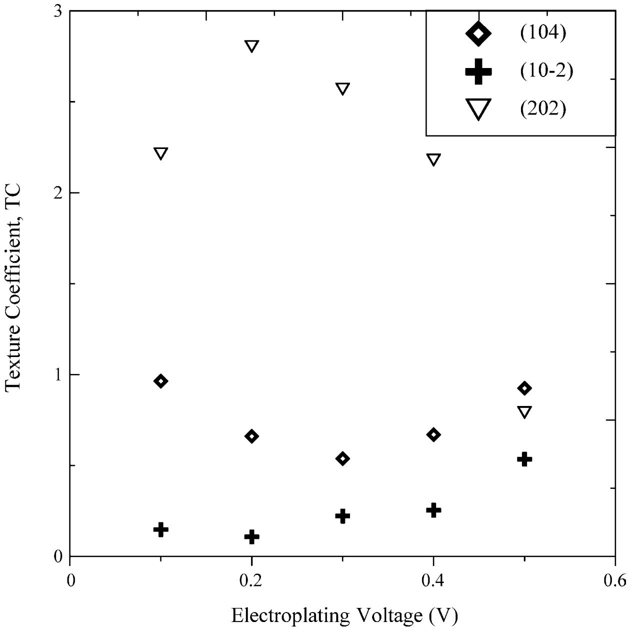

Fig. 2. Texture coefficients of $(1\,0\,\bar{2})$, (1 0 4) and (2 0 2) planes of electroplated Bi thin films at −0.1 V to −0.5 V.

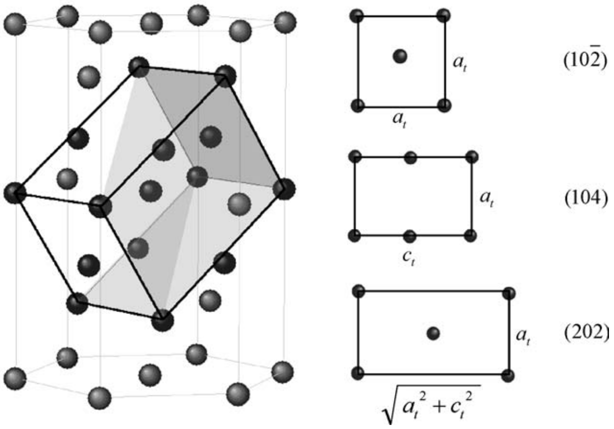

Fig. 3. Crystal structure of rhombohedral Bi and the atomic configurations of (1 0 $\bar{2}$), (1 0 4) and (2 0 2) planes.

nucleus are varied with the over-potential [7,8]. As shown in Fig. 1, the intensity of (1 0 $\bar{2}$) increased but (1 0 4) and (2 0 2) decreased as the applied voltages became more negative. For a polycrystalline film, the relatively higher intensity indicated the specific planes are well-aligned structure.

According to Harris method, texture coefficient values (TC) of (1 0 $\bar{2}$), (1 0 4) and (2 0 2) planes were estimated and drawn versus the applied voltages as shown in Fig. 2. The (2 0 2) and (1 0 4) planes are of the higher TC values than (1 0 $\bar{2}$) at −0.1 to −0.5 V. As we knew, the prefer orientation during deposition process is mainly determined by the surface energy. Consequently, the growth orientation of the thin film is based on the reducing of surface and strain energies, which are mainly determined by the atomic configuration of the specific plane. Rhombohedral Bi can be drawn in a hexagonal symmetry with the lattice parameters $a_h = b_h = 0.455$ nm and $c_h = 1.186$ nm, as shown in Fig. 3 [9]. Take other symmetry into consideration, rhombohedral Bi can be also regarded as a pseudo-tetragonal lattice with the parameter $a_t = 0.455$ nm, $b_t = 0.474$ nm, $c_t = 0.657$ nm, $\alpha_t = 93.37^\circ$, $\beta_t = 90.03^\circ$ and $\gamma_t = 90^\circ$, as shown in Fig. 3. Based on the atomic density, (1 0 $\bar{2}$) $(2/a_t^2)$ is more compact than (1 0 4) $(2/a_t \times c_t)$ and (2 0 2) $(2/a_t \times \sqrt{b_t^2 + c_t^2})$. Hence, (1 0 $\bar{2}$) is of a higher surface energy than (1 0 4) and (2 0 2) owing to the more broken bonds. As shown in Fig. 2, $\mathrm{TC}_{(2\ 0\ 2)}$ increases at −0.1 to −0.2 V but decreases at −0.2 to −0.5 V. In addition, $\mathrm{TC}_{(1\ 0\ 4)}$ decreases at −0.1 to −0.3 V but increases at −0.3 to −0.5 V. It implied that the prefer orientations of (2 0 2) and (1 0 4) are controlled by the adjustment of the surface and the intrinsic stress. However, the growth of (1 0 $\bar{2}$) plane is mainly affected by the over-potential owing to its relative higher surface energy. Hence, the $\mathrm{TC}_{(1\,0\,\bar{2})}$ increases with the increasing applied voltages meaning that the growth of (1 0 $\bar{2}$) plane requires relative higher driving force.

3.2. Microstructure of Bi thin film

Fig. 4 shows the morphologies of metallic Bi film obtained at different applied voltages. Most of the films are composed of isolated grains. The average grain size increases as the applied voltage became more negative. At −0.5 V, the metallic Bi film became more continuous than those obtained at −0.1 to −0.4 V. During the electrodeposition, the final average grain size usually determined by the growth competition between large and small grains. The results in Fig. 4 indicate that the growth of the most

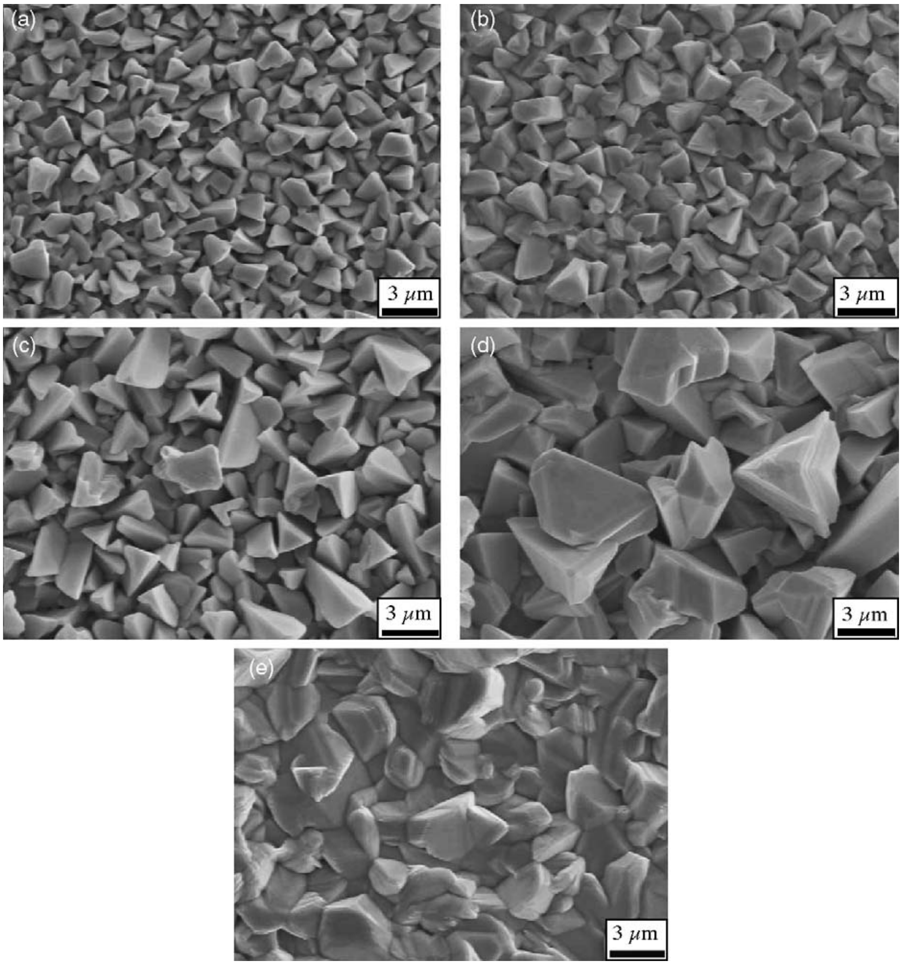

Fig. 4. SEM micrographs of electroplated Bi thin films at: (a) −0.1 V, (b) −0.2 V, (c) −0.3 V, (d) −0.4 V and (e) −0.5 V.

small grains are retarded by the neighboring large grains under a large over-potential, leading to the larger average grain size.

3.3. Oxidation of Bi thin film

Fig. 5(a–c) show the morphologies of oxidized Bi film electrodeposited at a low over-potential (−0.1 to −0.3), the average grain size are larger and many parts of the oxidized film became more continuous (compared with the results in Fig. 4(a–c)). Because the heat treatment temperature is higher the melting point of metallic Bi (271.3 °C), the results in Fig. 5(a–c) implies that grain growth occurs during the heat treatment. Similar growth behaviors should occur during oxidation of metallic Bi film electrodeposited at a higher over-potential (−0.4 to −0.5). Nevertheless, the average grain size shown in Fig. 5(d and e) seem to be smaller than those shown in Fig. 4(d and e). Though the heating rate is controlled at 1 °C/min to minimize the thermal stress of the material during the oxidation process, some additional stresses will

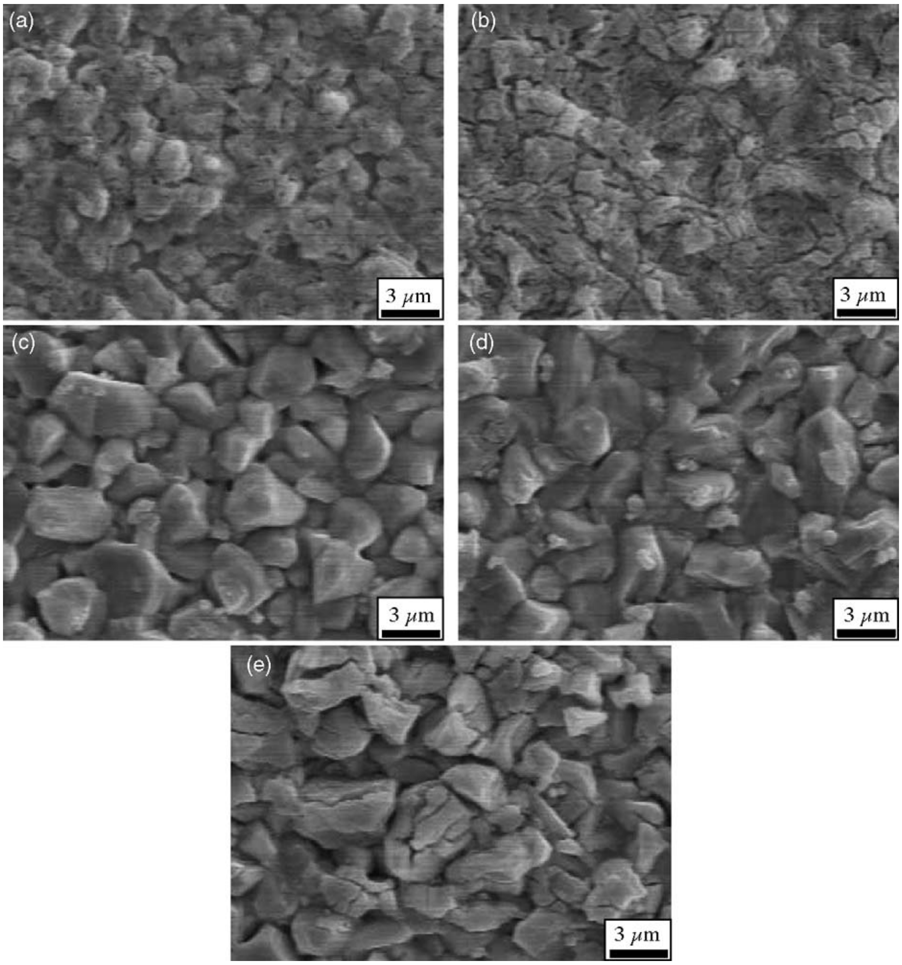

Fig. 5. SEM micrographs of oxidized Bi thin films electroplated at: (a) −0.1 V, (b) −0.2 V, (c) −0.3 V, (d) −0.4 V and (e) −0.5 V.

still be induced because of the volume expansion when metallic Bi transform to Bi_2O_3. Besides, the intrinsic stresses within the metallic Bi film electrodeposited at a more negative voltage should be higher as a result of the higher growth rate of the deposit under a larger over-potential. These stresses will be released by the formation of cracks along the grain boundary or passing through the grain, leading to the smaller grain size shown in Fig. 5(d and e).

Fig. 6 shows the XRD traces of oxidized Bi films electrodeposited at applied voltages. Pure α-Bi_2O_3 was obtained when the oxidation was conducted for the metallic Bi film electrodeposited at −0.1 V, as shown in Fig. 6(a). The α-Bi_2O_3 was of a monoclinic structure and a thermal equilibrium phase from room temperature to 723 °C. When the −0.2 to −0.4 V electrodeposited Bi film was oxidized, the oxide was composed of α-Bi_2O_3 and β-Bi_2O_3, as shown in Fig. 6(b–d). Only β-Bi_2O_3 was observed as a −0.5 V electrodeposited Bi film was oxidized as shown in Fig. 6(e). In the previous literatures, β-Bi_2O_3 of tetragonal structure was generally prepared by rapid cooling after heat treatment [4,10,11]. In the present study, pure β-Bi_2O_3 could easily be produced just by the oxidation of metallic Bi film electrodeposited at

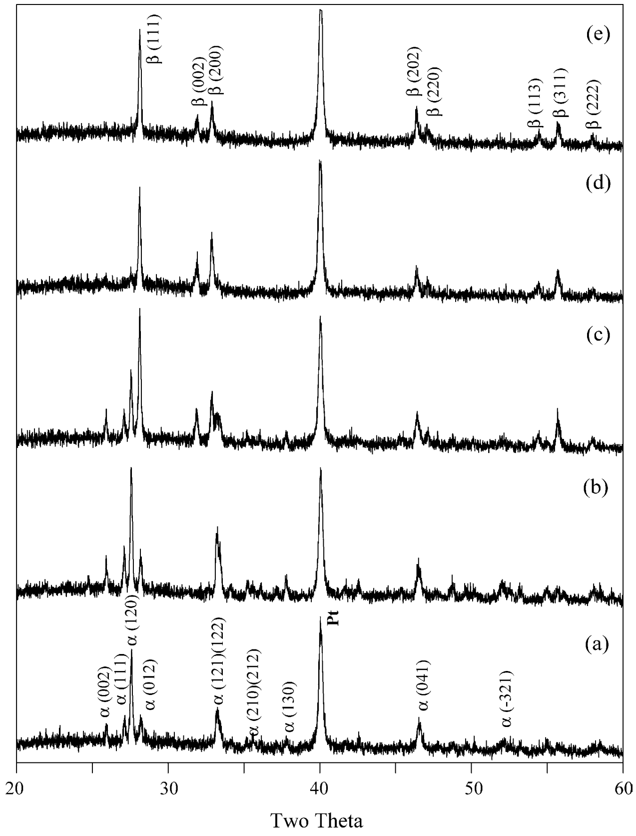

Fig. 6. XRD traces of oxidized Bi thin films electroplated at: (a) −0.1 V, (b) −0.2 V, (c) −0.3 V, (d) −0.4 V and (e) −0.5 V.

a more negative voltage. According to those described in Fig. 1, the results in Fig. 6 also imply that the (2 0 2) preferred orientation of metallic Bi is favorable to the formation of α-Bi_2O_3 while (1 0 $\bar{2}$) preferred orientation of metallic Bi is favorable to the formation of β-Bi_2O_3.

3.4. The formation of *β*-Bi_2O_3

According to the results as mentioned above, an attractive phenomenon should be emphasized here. Even though the heat treatment condition was fixed, the phase ratio of oxidized film still varied when the oxidation was conducted for the metallic Bi film electrodeposited at different voltages. Consequently, the crystal structure of Bi_2O_3 obtained by oxidation of metallic Bi film may dominantly be affected by the orientation of as-electrodeposited Bi film. In order to investigate the structural relationship between the as-electroplated Bi and the as-produced bismuth oxide during oxidation reaction, a schematic diagram was drawn in Fig. 7. The Bi atoms are not in a close-packed arrangement in rhombohedral symmetry and some free space is available. Since Bi_2O_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 prefer oriented planes. In Fig. 6, the β-Bi_2O_3 formed obviously from the oxidation of Bi film with (1 0 $\bar{2}$) prefer orientation. On the other hand, α-Bi_2O_3 was obtained when Bi film

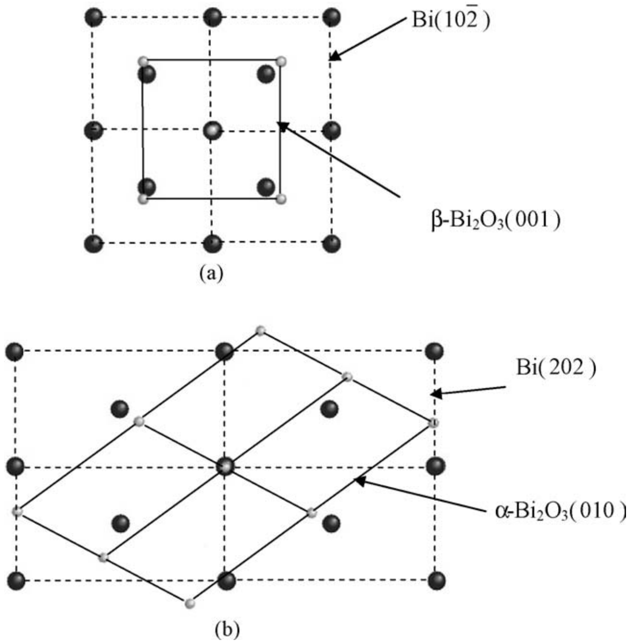

Fig. 7. Schematic diagrams of coherent relationship between (a) Bi(1 0 $\bar{2}$)/β-Bi_2O_3(0 0 1) and (b)Bi(2 0 2)/α-Bi_2O_3(0 1 0).

was preferably oriented along (2 0 2) plane. These result indicated that the Bi atoms along (1 0 $\bar{2}$) is closely matched with Bi ions on the plane of (0 0 1) in β-Bi_2O_3 as shown in Fig. 7(a). Also, the Bi atoms along (2 0 2) plane is consist with Bi ions on the plane of (0 1 0) in α-Bi_2O_3 as shown in Fig. 7(b). The crystal structure of the Bi_2O_3 is determined by the oxidation reaction without greater deformation on the Bi/Bi_2O_3 interface. Consequently, the prefer orientations of the specific atomic planes cause the formation of favored oxide during oxidation process.

4. Conclusions

In this study, the Bi_2O_3 thin film with the specific crystal structure was prepared by oxidation of electrodeposited Bi film. During the preparation of metallic Bi film, the preferred orientation of Bi film varied from (2 0 2) to (1 0 $\bar{2}$) as the applied voltage became more negative. After oxidation, the phase ratio is different even though the heat treatment condition was fixed. Only β-Bi_2O_3 was obtained on the metallic Bi film with (1 0 $\bar{2}$) preferred orientation, while only α-Bi_2O_3 was obtained on the metallic Bi film with (2 0 2) preferred orientation. Therefore, during the oxidation, the crystal structure of the Bi_2O_3 can be controlled by the orientation of the metallic Bi film.

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