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MOCVD growth of epitaxial pyrochlore $Bi_2Ti_2O_7$ thin film

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Abstract

Growth of $Bi_2Ti_2O_7$ films on the substrates having cubic-structure was investigated by metal organic chemical vapor deposition (MOCVD). (1 0 0), (1 1 0) and (1 1 1)$SrTiO_3$ single crystals, (1 1 1)-oriented Pt- and $SrRuO_3$-coated (1 1 1)$SrTiO_3$ were used as substrates together with (1 1 1)Pt/TiO_2/SiO_2/Si. Peaks originated to $Bi_2Ti_2O_7$ phase were not detected on (1 0 0), (1 1 0) and (1 1 1)$SrTiO_3$ substrates. On the other hand, (1 1 1)-oriented $Bi_2Ti_2O_7$ phase was ascertained to be prepared on (1 1 1)Pt//(1 1 1)$SrTiO_3$ and (1 1 1)Pt/TiO_2/SiO_2/Si substrates in spite of the almost the same lattice parameters of $SrRuO_3$ and $SrTiO_3$ with Pt. From the pole figure measurement, $Bi_2Ti_2O_7$ films prepared on the (1 1 1)Pt//(1 1 1)$SrTiO_3$ substrates were ascertained epitaxial grown, (1 1 1)$Bi_2Ti_2O_7$//(1 1 1)Pt//(1 1 1)$SrTiO_3$, while that on the (1 1 1)Pt/TiO_2/SiO_2/Si were (1 1 1)-one-axis-oriented $Bi_2Ti_2O_7$ with in-plain random. The easy growth of (1 1 1)-oriented $Bi_2Ti_2O_7$ film on (1 1 1)Pt layer can be explain by the existence of the sub-unit in (1 1 1)Pt plane consist of three Pt atoms.

Keywords: Films; Capacitors

1. Introduction

Pyrochlore oxides ($A_2B_2O_7$) are known to have wide variety of composition together with wide variety of superior characteristics including superconductivity and high dielectric constant at high frequency.[1–3] Especially, some kind of materials having pyrochlore structure, such as $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$, has been widely investigated for high frequency capacitor.[4] Film form of these materials is suitable for increasing capacitance, so that the thin film researches become important of this materials. However, the epitaxial grown film has been hardly reported in spite of the fact the superior property is expected compared with the polycrystalline film. Therefore, the establishment of the growth method of epitaxial pyrochlore film is important for the improvement of the film property. Epitaxial film research is also important to understand the fundamental property of these materials due to the lack of the single crystal data. Taking account of the fact that the basic unit cell size of oxide pyrochlore is almost the same,[5] the suitable substrates for the epitaxial growth are expected to be common for many pyrochlore oxide films, just in case of perovskite oxide films.

Conductive underlying layers or substrates are essential for the electrical properties measurement of pyrochlore films. In addition, based on the fact that the pyrochlore film is oxide and expected to need high deposition temperature, the following are the candidates:

Type 1. Rutile type conductive oxides, such as IrO_2 and RuO_2.
Type 2. Perovskite type conductive oxides, such as $SrRuO_3$ and $La_{0.5}Sr_{0.5}CoO_3$.
Type 3. Precious metal, such as Pt.

We already reported the epitaxial growth condition of pyrochlore films on the substrates having rutile structure (Type 1) by metal organic chemical vapor depositions (MOCVD) [6]. In the present study, we investigated the epitaxial growth of $Bi_2Ti_2O_7$ films on other two types of substrates having cubic symmetry, Type 2 and Type 3. We selected Pt and $SrRuO_3$ in Type 1 and Type 2, respectively. These are known to be epitaxially grown on wide variety of substrates, such as Si, GaAs and so on.[7–9] This suggests the possibility of epitaxial growth of pyrochlore film on wide variety of substrates.

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2. Experimental

$Bi_2Ti_2O_7$ films were prepared at 600 °C by MOCVD. $Bi(CH_3)_3$[TRI Chemical], $Ti(O{\cdot}i\text{-}C_3H_7)_4$ and O_2 were used as source materials. The composition of the film was adjusted by controlling the input gas ratio of $Bi(CH_3)_3$ to $Ti(O{\cdot}iC_3H_7)_4$. (1 0 0), (1 1 0) and (1 1 1)$SrTiO_3$ single crystals were used as substrates to check the appropriate orientation in Type 2 substrates because it has a perovskite structure as same as $SrRuO_3$. Moreover, (1 1 1)-oriented epitaxial Pt and $SrRuO_3$ layers grown on (1 1 1)$SrTiO_3$ single crystals, (1 1 1)Pt//(1 1 1)$SrTiO_3$ and $(1\,1\,1)_c$$SrRuO_3$//(1 1 1)$SrTiO_3$, were also used as substrates, which were, respectively, grown at 550 °C and 750 °C by sputtering method and MOCVD, respectively. (1 1 1)Pt/TiO_2/SiO_2/Si having one-axis orientated Pt top layer was also used as a reference.

The constituent phase and the orientation of the films were measured by X-ray diffraction (XRD) θ–2θ scan and pole figure plots. Film thickness was observed by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows 2θ–θ XRD patterns of the Bi–Ti–O films prepared on (1 0 0), (1 1 0) and (1 1 1)$SrTiO_3$ substrates. These films thickness were ascertained to be 100 nm by the SEM observation for all films. However peaks originated to $Bi_2Ti_2O_7$ was hardly observed on XRD patterns except the weak unknown peaks for the films on (1 0 0) and (1 1 0) substrates as shown in Fig. 1(a) and (b), respectively. On the other hand, the peaks originated from the films were hardly detected for the film on (1 1 1)$SrTiO_3$ substrate as shown in Fig. 1(c). In addition, any obvious spots were not observed for all films by the pole figure measurement fixed at 2θ angle corresponding to $Bi_2Ti_2O_7$ *4 4 4*. These show that the crystalline pyrochlore phase was hardly observed not only to the substrate surface normal direction but also to other ones. These suggest that the films shown in Fig. 1 are hardly crystallized.

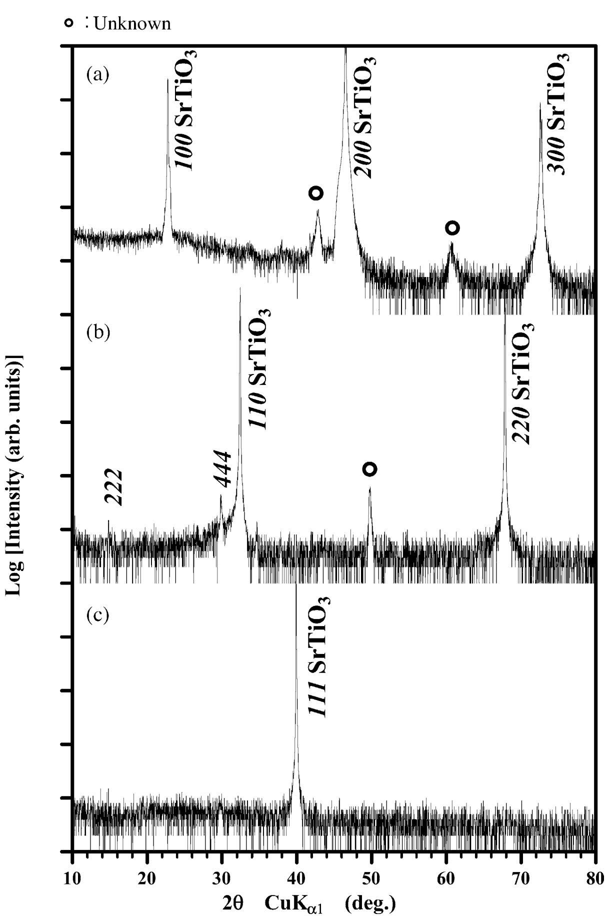

Fig. 1. 2θ–θ XRD patterns of the Bi–Ti–O film prepared on (a) (1 0 0), (b) (1 1 0) and (c) (1 1 1)$SrTiO_3$ substrates.

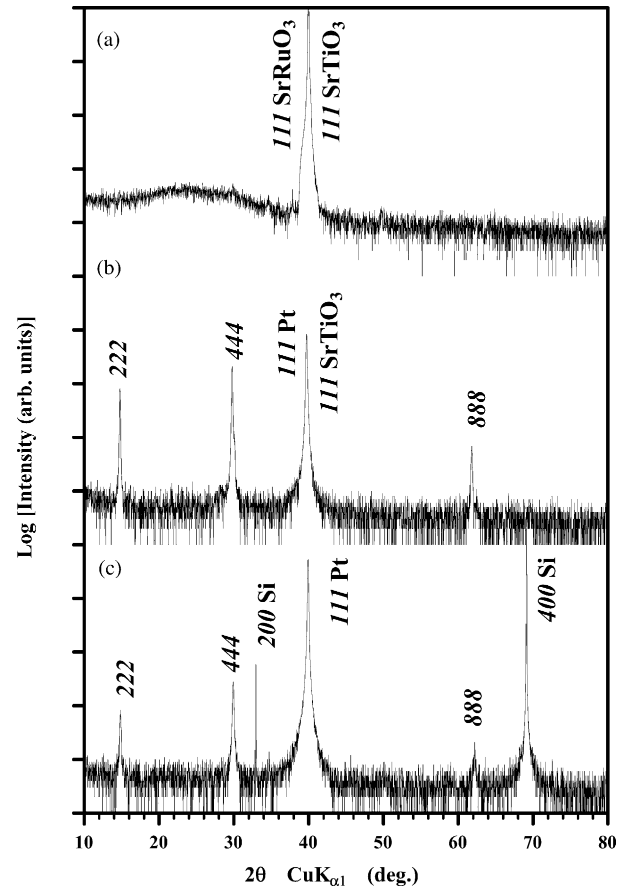

Fig. 2. 2θ–θ XRD patterns of the films deposited on (a) $(1\,1\,1)_c$$SrRuO_3$//(1 1 1)$SrTiO_3$, (b) (1 1 1)Pt//(1 1 1)$SrTiO_3$ and (c) (1 1 1)Pt/TiO_2/SiO_2/Si substrates.

Highly crystalline (1 1 1)-oriented $Bi_2Ti_2O_7$ phase was frequently reported on (1 1 1)Pt-covered (1 0 0)Si substrate.[10] Therefore, Bi–Ti–O films were tried to be deposited on (1 1 1)Pt-coated substrates, (1 1 1)Pt//(1 1 1)$SrTiO_3$ and (1 1 1)Pt/TiO_2/SiO_2/Si for the next step. $(1\,1\,1)_c$$SrRuO_3$//(1 1 1) $SrTiO_3$ was also used because the lattice parameter of $SrRuO_3$ was almost the same with Pt. Fig. 2 shows 2θ–θ XRD patterns of the films deposited on $(1\,1\,1)_c$$SrRuO_3$//(1 1 1)$SrTiO_3$, (1 1 1)Pt//(1 1 1)$SrTiO_3$ and (1 1 1)Pt/TiO_2/SiO_2/Si substrates. As shown in Fig. 2(a), peaks originated to $Bi_2Ti_2O_7$ were not detected on (1 1 1)$SrRuO_3$//(1 1 1)$SrTiO_3$ substrates as the same on (1 1 1)$SrTiO_3$ substrate. On the other hand, (1 1 1)-