Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 26 (2006) 2155–2159

www.elsevier.com/locate/jeurceramsoc

MOCVD growth of epitaxial pyrochlore $Bi_2Ti_2O_7$ thin film

Muneyasu Suzuki [a], Takayuki Watanabe [a], Tadashi Takenaka [b], Hiroshi Funakubo [a,*]

[a] *Department of Innovative and Engineered Materials, Interdisciplinary Graduate School, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midoriku, Yokohama 226-8502, Japan*

[b] *Faculty of Science and Technology, Tokyo University of Science, Yamazaki 2641, Noda, Chiba-ken 278-8510, Japan*

Available online 10 March 2006

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.

* Corresponding author.
E-mail address: funakubo@iem.titech.ac.jp (H. Funakubo).

0955-2219/$ – see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2005.09.103

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.

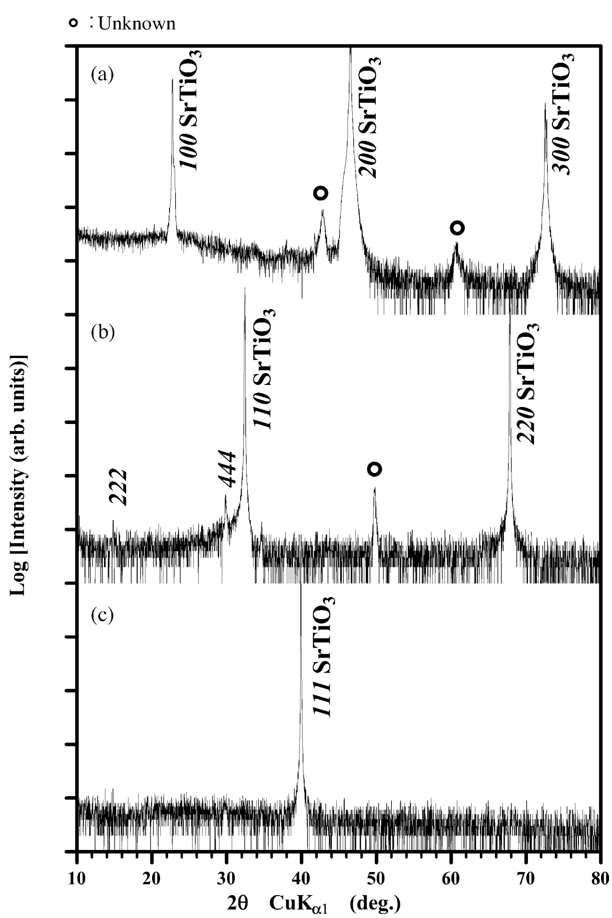

Fig. 1. 2θ–θ XRD patterns of the Bi–Ti–O film prepared on (a) (1 0 0), (b) (1 1 0) and (c) (1 1 1)$SrTiO_3$ substrates.

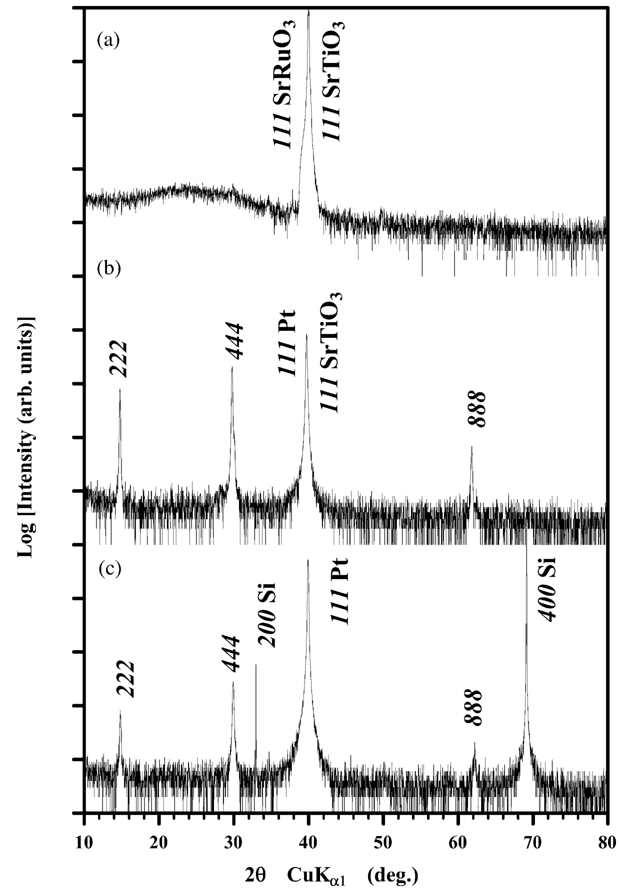

Fig. 2. 2θ–θ XRD patterns of the films deposited on (a) $(1\,1\,1)_c$$SrRuO_3$//(1 1 1)$SrTiO_3$, (b) (1 1 1)Pt//(1 1 1)$SrTiO_3$ and (c) (1 1 1)Pt/TiO_2/SiO_2/Si substrates.

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)-

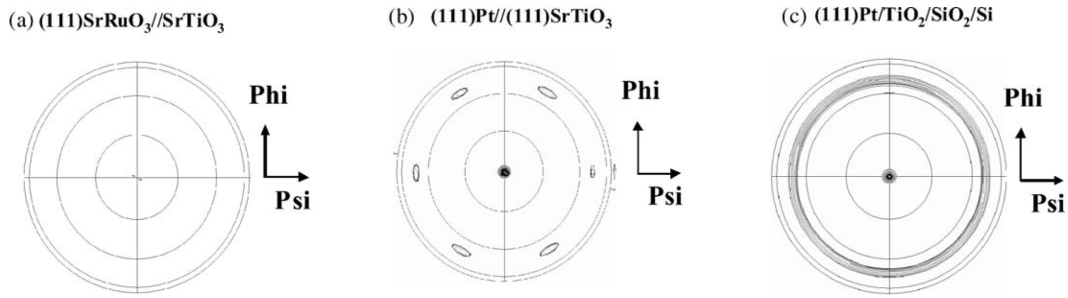

Fig. 3. Pole figure plots fixed at 2θ angle corresponding to *4 4 4* $Bi_2Ti_2O_7$ for the same films as shown in Fig. 2.

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. Rocking curve full width at half maximum (*FWHM*) of the $Bi_2Ti_2O_7$ *2 2 2* were 0.30° and 1.40° for the films prepared on (1 1 1)Pt//$SrTiO_3$ and (1 1 1)Pt/TiO_2/SiO_2/Si substrates, respectively. Fig. 3 shows pole figure plots fixed at 2θ angle corresponding to $Bi_2Ti_2O_7$ *4 4 4* for the same films shown in Fig. 2. No concentrated pole was confirmed for the films deposited on the (1 1 1)$SrRuO_3$//(1 1 1)$SrTiO_3$ substrate as shown in Fig. 2(a). However, concentrated spot at the center and the six holed ones at Psi = 70.5° at every 60° were observed on (1 1 1)Pt//(1 1 1)$SrTiO_3$ substrate as shown in Fig. 2(b), while one spot at the center and a ring pattern at Psi = 70.5° on (1 1 1)Pt/TiO_2/SiO_2/Si substrate were observed as shown in Fig. 2(c). This suggests that $Bi_2Ti_2O_7$ film prepared on the (1 1 1)Pt//(1 1 1)$SrTiO_3$ substrate was ascertained to be 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 substrate was (1 1 1)-one-axis-oriented $Bi_2Ti_2O_7$ film with in-plain random. These data clearly shows that (1 1 1)-oriented-$Bi_2Ti_2O_7$ films were easily deposited on the (1 1 1)Pt-coated layer. On the other hand, crystalline $Bi_2Ti_2O_7$ film was hardly observed on (1 1 1)$SrTiO_3$ and (1 1 1)$SrRuO_3$//(1 1 1)$SrTiO_3$ substrates in spite of the similar lattice parameter of $SrTiO_3$ and $SrRuO_3$ within Pt, 0.46%. This

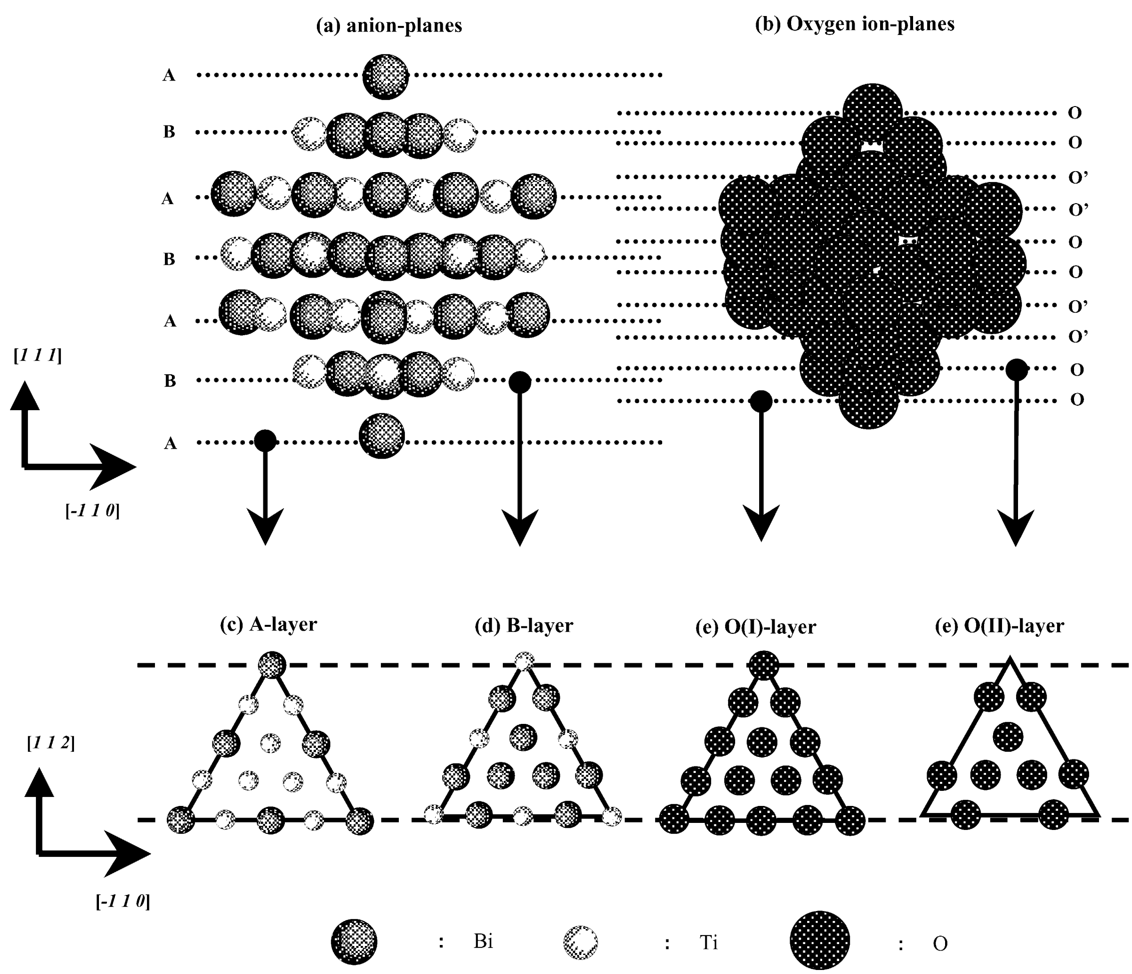

Fig. 4. The crystal structure of pyrochlore. Two kinds of anion layers and two kinds of cation layers are stacked along [1 1 1] direction without overlapping.

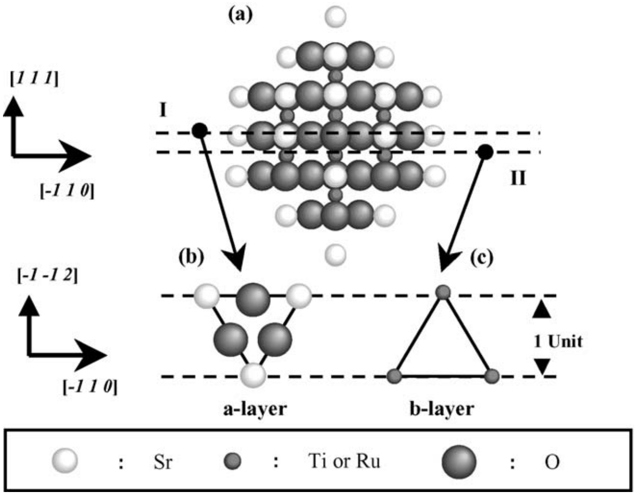

Fig. 5. The crystal structure of cubic perovskite structure.

suggests that atomic and ionic arrangements in the crystal structure play an important role, because Pt, $SrTiO_3$ and $SrRuO_3$ have simple face centered cubic (fcc) and perovskite structures, respectively.

Pyrochlore structure generally consists of the stacking of four kinds of ionic layers along [1 1 1] as shown in Fig. 4 (a) and (b) without overlapping each layer, two anion layers (A-layer (Fig. 4(c)) and B-layer (Fig. 4(d))) and two oxygen layers (O(I)-layer [Fig. 4(c)) and O(II)-layer (Fig. 4(f))). In more strict sense, $Bi_2Ti_2O_7$ took two times large lattice parameter of the general pyrochlore structure shown in Fig. 4. On the other hand, perovskite structure, such as $SrTiO_3$ and $SrRuO_3$, consists of two kinds of ionic layers along [1 1 1] as shown in Fig. 5. These layers are the negative charge layer consisting of O^{2+} and Sr^{2+} (a-plane), and the positive charge layers consisting of Ti^{4+} or Ru^{4+} (b-plane) as shown in Fig. 5(b) and (c), respectively.

In Pt case, Pt consists of the three types of the cubic closed packed layers with shifted by each other along [1 1 1] plane originated to the fcc structure. However, the atomic arrangement was basically the same as shown in Fig. 6(a), in which 3×3 unit cells are shown. By the comparison of the pole figure plot of $Bi_2Ti_2O_7$ *4 4 4* as shown in Fig. 3(b) with that of Pt *1 1 1*, the epitaxial relationship between $Bi_2Ti_2O_7$ and Pt is found to be shown in Fig. 6(a) and (b) in which 0.5×0.5 unit cells are shown in case of (1 1 1)$Bi_2Ti_2O_7$. Taking account of the face that (1 1 1)-oriented Pt films was epitaxially grown on (1 1 1)$SrTiO_3$, (1 1 1)Pt//(1 1 1)$SrTiO_3$ as shown in Fig. 2(b), the possible epitaxial relationship between (1 1 1)-oriented $Bi_2Ti_2O_7$ and (1 1 1)$SrTiO_3$ or (1 1 1)$SrTiO_3$ is considered to be almost the same orientation with Pt case as shown in Fig. 6(c). 3×3 unit cells were also shown in Fig. 6(c), for (1 1 1)$SrTiO_3$ and (1 1 1)$SrRuO_3$. In addition, based on the existence of the positive and the negative charge layers of $Bi_2Ti_2O_7$, the possible combinations between the film and the substrates are as follow:

(1) A-layer or B-layer of (1 1 1)$Bi_2Ti_2O_7$ match with b-layer of (1 1 1)$SrTiO_3$ or $SrRuO_3$ (upper series named Pattern-1 in Fig. 6).
(2) O(I)-layer and O(II)-layer of (1 1 1)$Bi_2Ti_2O_7$ match with a-layer of (1 1 1)$SrTiO_3$ or $SrRuO_3$ (bottom series named Pattern-2 in Fig. 6).

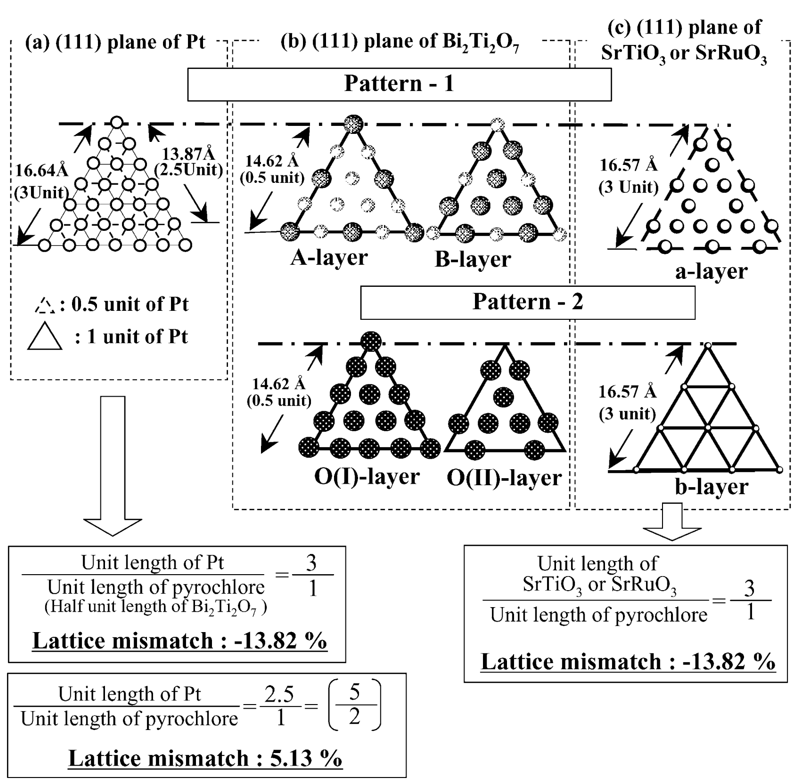

Fig. 6. Epitaxial growth consideration between pyrochlore and each substrate.

When 0.5 unit length of $Bi_2Ti_2O_7$ lattice match to 3 unit one of Pt and $SrTiO_3$ or $SrRuO_3$, as shown in Fig. 6(b) and (c), which correspond to the lattice match between 1 unit length of $Bi_2Ti_2O_7$ and 6 one of Pt, $SrTiO_3$ and $SrRuO_3$, the lattice mismatches were −13.82% and −13.35% along [−1 −1 2], respectively. These are too large for epitaxial growth in general sense. In addition, the small difference of these lattice mismatches between Pt, and $SrTiO_3$ or $SrRuO_3$ dose not explain the resultant growth difference on these substrates.

In case of Pt, sub-unit having half unit length consisting of three Pt atoms was observed as shown in dot line in Fig. 6(a), while one unit cell consist of nine atoms. Taking account of this sub lattice, 0.5 unit cell length of $Bi_2Ti_2O_7$ match with 5 half-unit-cell length of Pt with the lattice mismatch of 5.13%. The existence of this sub-unit cell in (1 1 1)Pt is considered to make easy grown of (1 1 1)-oriented epitaxial $Bi_2Ti_2O_7$ films on (1 1 1)Pt. On the other hand, the lack of these half unit cells of $SrTiO_3$ and $SrRuO_3$ is considered to make difficult the epitaxial growth of $Bi_2Ti_2O_7$ on these substrates. This corresponds to the 1 unit cell length of $Bi_2Ti_2O_7$ lattice matches with 5 one of Pt.

Formation of (1 1 1)-oriented pyrochlore phase was frequently reported in Pb-Zr-Ti-O system for the film prepared on (1 1 1)Pt-coated (1 1 1)Si substrate,[11] while pyrochlore phase was hardly reported in bulk ceramics. Frequency formation of (1 1 1)-oriented pyrochlore phase in films form is possible to be related to the (1 1 1)Pt top surface of the substrate. However, more detailed analysis of the interface between the film and substrate by TEM is essential together with the surface energy consideration.

4. Conclusions

Growth condition of $Bi_2Ti_2O_7$ films on various kinds of the substrates having cubic-structure was investigated. Epitaxial (1 1 1)-oriented $Bi_2Ti_2O_7$ films were confirmed to be deposited on (1 1 1)Pt//(1 1 1)$SrTiO_3$ substrates by XRD θ–2θ scans, but detectable $Bi_2Ti_2O_7$ peaks were not detected on (1 1 1)$SrTiO_3$ and (1 1 1)$SrRuO_3$//(1 1 1)$SrTiO_3$ substrates in spite of the almost same lattice parameters of these substrates. Top surface of Pt-layer makes easy growth of (1 1 1)-oriented $Bi_2Ti_2O_7$ phase. Face center cubic structure of Pt having subunit is considered to play an important role for the growth of epitaxial (1 1 1)-oriented $Bi_2Ti_2O_7$ film.

References

1. Shimakawa, Y., Kubo, Y., Hamada, N., Jorgensen, D. J., Hu, Z., Short, S. *et al.*, Crystal structure, magnetic and transport properties, and electronic band structure of $A_2Mn_2O_7$ pyrochlores (A = Y, In, Lu, and Tl). *Phys. Rev. B*, 1999, **59**, 1249–1254.
2. Takeda, T., Kanno, R., Yamamoto, Y., Takano, M., Izumi, F., Sleight, W. A. *et al.*, Structure-property relationships in pyrochlores: low-temperature structures of $Tl_2Ru_2O_{7-\delta}$ (δ = 0.00 and 0.05). *J. Mater. Chem.*, 1999, **9**, 215–221.
3. Khasanov, R., Eshchenko, G. D., Karpinski, J., Kazakov, M. S., Zhigadlo, D. N., Brütsch, R. *et al.*, Pressure effects on the transition temperature and the magnetic field penetration depth in the pyrochlore superconductor $RbOs_2O_6$. *Phys. Rev. Lett.*, 2004, **93**, 157004(1)–157004(4).
4. Lu, J., Stemmer, S. and Low-loss, Tunable bismuth zinc niobate films deposited by rf magnetron sputtering. *Appl. Phys. Lett.*, 2003, **83**, 2411–2413.
5. Subramanian, A. M., Aravamudan, G. and Subba Rao, V. G., Oxide pyrochlores—a review. *Prog. Solid State Chem.*, 1983, **15**, 55–143.
6. Suzuki, M., Watanabe, T., Takenaka, T. and Funakubo, H., Growth of pyrochlore $Bi_2Ti_2O_7$ epitaxial films and their electrical characterization. *Integr. Ferroelectr.*, 2004, **67**, 201–209.
7. Moon, K. B. and Ishiwara, H., Formation and electrical properties of heteroepitaxial $SrTiO_3/SrVO_{3-x}$/Si(1 0 0) structures. *Appl. Phys. Lett.*, 1995, **67**, 1996–1998.
8. Hou, Y. S., Kwo, J., Watts, K. R., Cheng, -Y. J. and Fork, K. D., Structure and properties of epitaxial $Ba_{0.5}Sr_{0.5}TiO_3/SrRuO_3/ZrO_2$ heterostructure on Si grown by off-axis sputtering. *Appl. Phys. Lett.*, 1995, **67**, 1387–1389.
9. Marvin, C. D., Ives, A. N. and Leung, S. M., In/Pt ohmic contacts to GaAs. *J. Appl. Phys.*, 1985, **58**, 2659–2661.
10. Watanabe, T. and Funakubo, H., Orientation control of metalorganic chemical vapor deposition-$Bi_4Ti_3O_{12}$ thin film by sequential source gas supply method. *Jpn. J. Appl. Phys.*, 2000, **39**, 5211–5216.
11. Brooks, G. K., Reaney, M. I., Klissurska, R., Huang, Y., Bursill, L. and Setter, N., Orientation of rapid thermally annealed lead zirconate titanate thin films on (1 1 1) Pt substrates. *J. Mater. Res.*, 1994, **9**, 2540–2553.