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Chemical Processing and Characterization of $Bi_4Ti_3O_{12}$-$BiFeO_3$ Thin Films

Yuko Komami, Tetsuo Shimura, Wataru Sakamoto and Toshinobu Yogo
EcoTopia Science Institute, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan,
Fax : 81-52-789-2133, E-mail : sakamoto@esi.nagoya-u.ac.jp

$Bi_4Ti_3O_{12}$-$BiFeO_3$-based compounds belong to the bismuth-layer-structured oxide family and are expected to show both ferroelectricity and weak ferromagnetism. In this study, $Bi_4Ti_3O_{12}$-$BiFeO_3$ thin films have been fabricated on $Pt/TiO_x/SiO_2/Si$ substrates by the chemical solution deposition. Homogeneous and stable $Bi_4Ti_3O_{12}$-$BiFeO_3$ precursor solutions were prepared by optimizing the starting metal alkoxide compounds and the processing conditions. $Bi_4Ti_3O_{12}$-$BiFeO_3$ (1:1) precursor films crystallized in the single phase of bismuth-layered $Bi_5Ti_3FeO_{15}$ structure with random orientation above 500℃. The crystallographic structure of $Bi_5Ti_3FeO_{15}$ thin film was confirmed by Raman spectroscopic analysis. The $Bi_5Ti_3FeO_{15}$ thin films exhibited typical ferroelectric P-E hysteresis loops.

Keywords : $Bi_4Ti_3O_{12}$-$BiFeO_3$, thin film, chemical solution deposition, ferroelectric properties

1. INTRODUCTION

Ferroelectricmagnetic materials are the special class of dielectric materials in which both ferroelectric and magnetic ordering exist simultaneously. Therefore, thin films of these materials offer a wide opportunity for potential applications in novel information storage memories, spintronic devices and new type of sensors.[1]

Bismuth-layer-structured oxide (BLSO) belongs to the family of Aurivillius-type structure, which is a regular intergrowth of $(A_{m-1}B_mO_{3m+1})^{2-}$ perovskite-like layers and $(Bi_2O_2)^{2+}$ slabs and m is the number of oxygen octahedra between bismuth oxide layers. These compounds have good structural stability, high Curie temperatures, and anisotropic characteristics.

Among several BLSO compounds, $Bi_4Ti_3O_{12}$(BiT) has a bismuth layered perovskite structure and is one of the most important lead-free materials which have excellent ferroelectric properties. In order to design a new material consisting of both ferroelectric and magnetic ordering, $BiFeO_3$ (BF) is combined with BiT to obtain $Bi_4Ti_3O_{12}$-$BiFeO_3$ (BiT-BF) compounds, because BF is reported to have both ferroelectric and antiferromagnetic natures.[2-4]

As a fabrication method of thin film, the chemical solution deposition (CSD) method using metal-organic compounds is known to be a useful thin film fabrication process to achieve the low-temperature fabrication and the precise control of chemical composition.[5,6]

Therefore, in this work, fabrication and characterization of BiT-BF (1:1) thin films on Si-based substrates have been carried out by the chemical solution deposition (CDS) method. The effects of several processing conditions on the surface morphology and the electrical properties of $Bi_5Ti_3FeO_{15}$ thin films were mainly investigated.

2. EXPERIMENTAL PROCEDURE

For preparing $Bi_4Ti_3O_{12}$-$BiFeO_3$ (1:1) precursor solutions, $Bi(O^tC_5H_{11})_3$, $Fe(OC_2H_5)_3$ and $Ti(O^iC_3H_7)_4$ were selected as starting materials. 2-methoxyethanol as a solvent was dried over molecular sieve and distilled prior to use. $Bi(O^iC_5H_{11})_3$, $Fe(OC_2H_5)_3$, and $Ti(O^iC_3H_7)_4$ corresponding to the $Bi_5Ti_3FeO_{15}$ composition were dissolved in absolute 2-methoxyethanol. 3mol% of excess Bi alkoxide was added to compensate for Bi loss during heating process. Acetylacetone was also added to the solution as a stabilizing agent. The mixed solution was heated at 100℃ to react the alkoxides. Then, this solution was concentrated to approximately 0.1M and used as a precursor solution. The procedure was conducted in a dry nitrogen atmosphere.

$Bi_5Ti_3FeO_{15}$ precursor films were prepared by spin-coating on $Pt/TiO_x/SiO_2/Si$ substrates using the $Bi_5Ti_3FeO_{15}$ precursor solutions. As-deposited $Bi_5Ti_3FeO_{15}$ precursor films were dried at 150°C for 5 min and calcined at various temperatures for 1 h at a rate of 10°C/min in an O_2 flow. And then, the calcined films were crystallized at 600-750°C for 1 h by rapid thermal annealing (RTA) at a rate of 180°C/min in an O_2 flow. Film thickness was adjusted to 250 nm by repeating coating/calcining process.

The crystallographic phases of prepared $Bi_5Ti_3FeO_{15}$ thin films were identified by X-ray diffraction (XRD) analysis using CuKα radiation with a monochromator and Raman microprobe spectroscopy. The surface morphology of thin films was observed using an atomic force microscope (AFM). Pt top electrodes were deposited onto the surface of the films by DC sputtering, followed by annealing at 400℃ for 30 min. The Pt layer of the $Pt/TiO_x/SiO_2/Si$ substrate was used as a bottom electrode. The electrical properties of the films were evaluated using a ferroelectric test system [FCE-1, Toyo Corp.] at room temperature.

3. RESULTS AND DISCUSSION

3.1 Effect of calcination temperature on surface morphology of BiT-BF thin films

In the CSD process, the elimination process of organic spiecies from precursor film is very important to obtain crystalline thin films with high quality. Figure 1 shows AFM images of $Bi_5Ti_3FeO_{15}$ thin films crystallized at 700℃ after calcined at various temperatures. Higher calcination temperature is effective to obtain thin films with smooth surface morphology. The main reason is considered that organic components of precursor film are completely eliminated through the higher temperature calcination. The removal of organic species is completed around 500℃ from the differencial thermal analysis (DTA) and thermogravimetry (TG) curves of BiT-BF precursor powder. For the fabrication of $Bi_5Ti_3FeO_{15}$ thin films, calcination temperature is determined to set at 500℃.

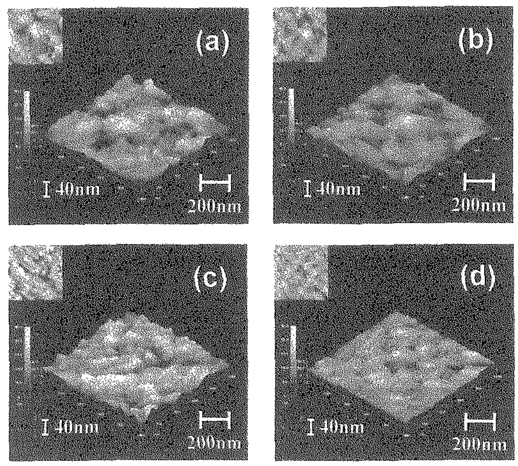

Fig.1 AFM images of $Bi_5Ti_3FeO_{15}$ thin films on $Pt/TiO_x/SiO_2/Si$ substrate crystallized at 700℃ after calcined at (a) 350℃, (b) 400℃, (c) 450℃ and (d) 500℃

3.2 Crystallization of BiT-BF thin films on substrates

Figure 2 illustrates XRD profiles of $Bi_5Ti_3FeO_{15}$ thin films fabricated on $Pt/TiO_X/SiO_2/Si$ substrates at various temperatures. These films crystallized into the Bi-layered perovskite single-phase above 500℃ and exhibited random orientation with an enhanced 119 reflection. As crystallization tempareture increased, crystallinity of thin films gradually increased. However, XRD patterns were not appropriate to judge whether $Bi_5Ti_3FeO_{15}$ crystallized to the desired m=4 structure or not. Because the XRD profiles of $Bi_4Ti_3O_{12}$ and $Bi_5Ti_3FeO_{15}$ are almost the same due to the presence of similar short-range crystal structures. Therefore, further investigation for the $Bi_5Ti_3FeO_{15}$ thin films is required.

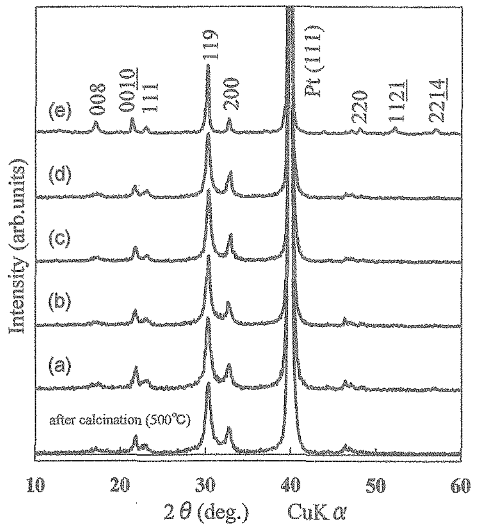

Fig.2 XRD patterns of $Bi_5Ti_3FeO_{15}$ thin films on $Pt/TiO_x/SiO_2/Si$ substrates crystallized at (a) 600℃, (b) 650℃, (c) 700℃, (d) 750℃ and (e) 800℃ [Calcination : 500℃]

3.3 Raman spectroscopic analysis of BiT-BF thin films

To understand the details of crystal structure of $Bi_5Ti_3FeO_{15}$ thin films, Raman microprobe spectroscopic measurements were performed. Figure 3 illustrates Raman spectra of $Bi_4Ti_3O_{12}$ (BiT) and $Bi_5Ti_3FeO_{15}$ thin films. Mode A and E indicate vibration of Bi (A site)-O bonds. Mode B and D are TiO_6 streching and vibration modes. Mode C corresponds vibration in pseudo-perovskite layer. In the case of $Bi_5Ti_3FeO_{15}$, the peak of mode B was shifted to lower wavenumber side. This comes from the substitution of iron for titanium site. This suggested that Fe obviously existed in the perovskite block. On the other hand, mode D was observed in $Bi_5Ti_3FeO_{15}$ and not in BiT. This mode results from the layered structure with m=4.[7] These results suggest that the $Bi_5Ti_3FeO_{15}$ thin films crystallized to the layered perovskite structure with m=4.

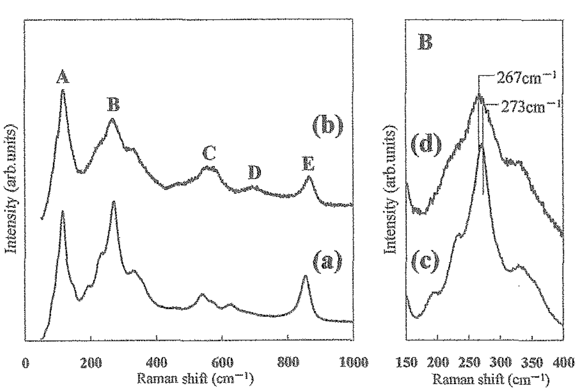

Fig.3 Raman spectra of (a), (c) $Bi_4Ti_3O_{12}$ and (b), (d) $Bi_5Ti_3FeO_{15}$ thin films

3.4 Surface morphology of $Bi_5Ti_3FeO_{15}$ thin films

Figure 4 shows AFM images of $Bi_5Ti_3FeO_{15}$ thin films crystallized at various temperatures after calcination at 500℃. RMS (root mean square) roughness values of the $Bi_5Ti_3FeO_{15}$ thin films crystallized at 600℃, 650℃, 700℃ and 750℃ were 1.9 nm, 3.2 nm, 3.8 nm and 4.0 nm, respectively. As the crystallization temperature increased, grain size of thin films gradually increased from about 50 nm to 100 nm. However, the surface morphology was degraded with increasing crystallization temperature.

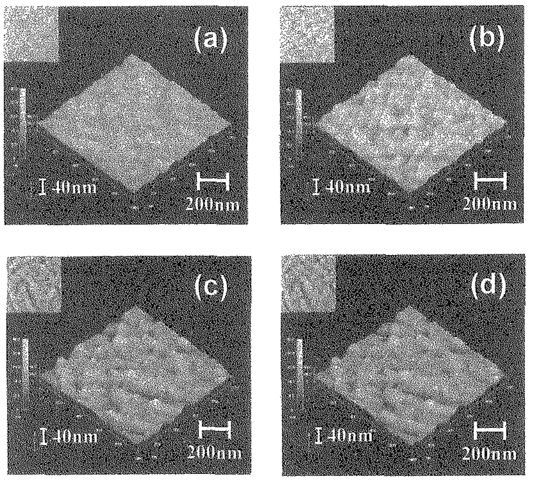

Fig.4 AFM images of $Bi_5Ti_3FeO_{15}$ thin films on $Pt/TiO_x/SiO_2/Si$ substrate calcined at 500℃ and crystallized at (a) 600℃, (b) 650℃, (c) 700℃ and (d) 750℃

3.5 Ferroelectric properties of synthesized films

P-E hysteresis measurement was performed to characterize the ferroelectric properties of the synthesized $Bi_5Ti_3FeO_{15}$ thin films. The measurement was done at an applied voltage of 10V and a frequency of 100Hz, and at room temperature. Figure 5 shows P-E hysteresis loops of the $Bi_5Ti_3FeO_{15}$ thin films crystallized at 600℃, 650℃ and 700℃ on $Pt/TiO_x/SiO_2/Si$ substrates. These films are approximately 250 nm in thickness. The $Bi_5Ti_3FeO_{15}$ thin films exhibited the typical ferroelectric P-E hysteresis loops as shown in Fig.5. The P_r values of the $Bi_5Ti_3FeO_{15}$ thin films increase with raising the crystallization temperature up to 700℃. However, the decrease of Pr value was observed for the $Bi_5Ti_3FeO_{15}$ thin film prepared at 750℃ (about 6 μ C/cm^2).

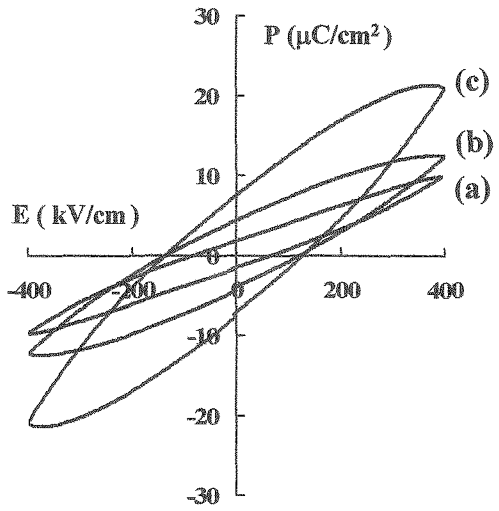

Fig.5 P-E hysteresis loops of $Bi_5Ti_3FeO_{15}$ thin films on $Pt/TiO_x/SiO_2/Si$ substrates crystallized at (a) 600°C, (b) 650°C and (c) 700°C

From the results described in the previous section, calcination at higher temperature enables to achieve smoother surface morphology because organic components of precursor film are completely eliminated through the appropriate temperature calcination process. On the other hand, with increasing crystallization temperature, the P_r values showed a peak at a fabrication temperature of 700℃. This can be explained by the grain size (crystallinity) and surface morphology of the crystallized films. Although the crystallization at higher temperature promotes the grain growth accompanied with the improvement of crystallinity of resultant thin films, the surface morphology is degraded as shown in Fig.4. Moreover, the P_r values of current $Bi_5Ti_3FeO_{15}$ thin films were less than 10 μ C/cm^2. Further improvement of ferroelectric properties and evaluation of magnetic properties of the $Bi_5Ti_3FeO_{15}$ thin films were required. Therefore, the doping of various ions to the $Bi_5Ti_3FeO_{15}$ thin films and the characterization of magnetization behavior are now in progress.

4. CONCLUSIONS

Ferroelectric $Bi_5Ti_3FeO_{15}$ thin films were successfully synthesized by the chemical solution deposition process. Homogeneous and stable $Bi_5Ti_3FeO_{15}$ precursor solutions were prepared by the selection of appropriate starting materials and a solvent. $Bi_5Ti_3FeO_{15}$ precursor thin films were found to crystallize in the desired Bi-layered structure (m=4) as single phases on $Pt/TiO_x/SiO_2/Si$ substrates above 500 ℃. $Bi_5Ti_3FeO_{15}$ thin films prepared by the optimized heating condition were found to exhibit the smooth surface morphology. The $Bi_5Ti_3FeO_{15}$ thin films exhibited ferroelectric P-E hysteresis loops. Ferroelectric properties of BiT-BF thin films were greatly influenced by the crystallinity and surface morphology of resultant thin films.

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