

Preparation and Properties of Ferroelectric $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ Thin Films by Chemical Solution Deposition

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Ferroelectric $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ and $0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\text{-}0.3\text{BaTiO}_3$ thin films have been prepared by the chemical solution deposition. Perovskite single-phase thin films with homogeneous surface morphology were successfully fabricated at 700°C on $\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$ substrates. Although typical polarization (P)-electric field (E) hysteresis loops were observed for $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ thin films, their insulation resistance was relatively low at room temperature. Mn doping for Fe site of the $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ was very effective in improving the leakage current property at high applied fields and the surface morphology of the resultant thin films. 5 mol% Mn-doped films exhibited larger ferroelectricity at room temperature. Furthermore, at a low temperature of -190°C , the remanent polarization (P_r) of the 700°C -prepared $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ and $0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\text{-}0.3\text{BaTiO}_3$ thin films were approximately 30 and $46 \mu\text{C}/\text{cm}^2$, respectively.

Key Words: $\text{BiFeO}_3\text{-BaTiO}_3$, chemical solution deposition, thin film, ferroelectric properties

1. INTRODUCTION

Recently, ferroelectric BiFeO_3 -based thin films have been receiving much attention, because large remanent polarizations more than $50 \mu\text{C}/\text{cm}^2$ were reported for BiFeO_3 thin films fabricated by pulsed laser deposition [1-3]. However, the synthesis of pure BiFeO_3 without impurity phases is usually difficult due to the low structural stability of perovskite BiFeO_3 with a relatively low tolerance factor. In the case of BiFeO_3 thin films, the crystallization of the BiFeO_3 phase on substrates often results in the formation of a bismuth-deficient second phase such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ which degrades the surface morphology owing to exaggerated grain growth, leading to poor electrical properties [4]. Therefore, the fabrication of the perovskite BiFeO_3 single phase thin films is important for achieving the desired large ferroelectricity. Moreover, the low electrical resistivity of BiFeO_3 makes the observation of the ferroelectric polarization (P)-electric field (E) hysteresis loop very difficult.

Therefore, $\text{BiFeO}_3\text{-ABO}_3$ solid solution systems have

attracted great attention as a means to improve the structural stability. Among perovskite ABO_3 compounds, BaTiO_3 is one of the stable ferroelectric perovskite oxides. A solid solution of BiFeO_3 and BaTiO_3 is expected to achieve the desired structural stabilization and excellent electrical properties. Furthermore, recently, Mn-doped BiFeO_3 thin films were studied for the improvement of their ferroelectric properties [5].

In this work, the fabrication and characterization of $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ thin films on Si-based substrates have been carried out by chemical solution deposition. Rhombohedrally distorted perovskite structure of $\text{BiFeO}_3\text{-BaTiO}_3$ is reported to maintain by the BaTiO_3 composition less than 33 mol% [6]. Therefore, $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ composition was selected from the view point of stability of perovskite structure with crystal distortion to achieve the desired ferroelectricity. We investigated the crystallization, surface morphology and ferroelectric properties of chemically derived $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ thin films on $\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$

substrates. Effect of Mn doping to the Fe site of $\text{BiFeO}_3\text{-BaTiO}_3$ thin film were also examined.

2. EXPERIMENTAL PROCEDURE

$\text{Bi}(\text{O}^i\text{C}_5\text{H}_{11})_3$, $\text{Fe}(\text{OC}_2\text{H}_5)_3$, $\text{Ba}(\text{OC}_2\text{H}_5)_2$, $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$ and $\text{Mn}(\text{O}^i\text{C}_3\text{H}_7)_2$ were selected as starting materials for the preparation of precursor solutions. The appropriate amounts of $\text{Bi}(\text{O}^i\text{C}_5\text{H}_{11})_3$, $\text{Fe}(\text{OC}_2\text{H}_5)_3$, $\text{Ba}(\text{OC}_2\text{H}_5)_2$, $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$ and $\text{Mn}(\text{O}^i\text{C}_3\text{H}_7)_2$ corresponding to the $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ and $0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\text{-}0.3\text{BaTiO}_3$ compositions with 3 mol% of excess Bi were dissolved in absolute 2-methoxyethanol. Then, the mixed solution was refluxed for 18 h yielding a 0.2 M brown colored precursor solution. The entire procedure was conducted in a dry N_2 atmosphere.

Thin films were fabricated using the precursor solution by spin coating on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates. As-deposited precursor films were dried at 150°C for 5 min and calcined at 400°C at a rate of $5^\circ\text{C}/\text{min}$ for 1 h in an oxygen flow. The calcined films were then crystallized at 700°C for 30 min in an oxygen flow using rapid thermal annealing. The thickness of the BF-BT films was adjusted to be approximately 500 nm by repeating the coating / calcining cycle.

The crystallographic phases of prepared BF-BT thin films were identified by X-ray diffraction (XRD) analysis using $\text{Cu K}\alpha$ radiation with a monochromator. The surface morphology of the crystallized thin films was observed by atomic force microscopy (AFM). The Pt top electrodes with a diameter of 0.2 mm were deposited by DC sputtering onto the surface of the BF-PT films followed by annealing at 400°C for 1 h. The measurement of the ferroelectric properties of the thin films at various temperatures was conducted in a wafer cryostat (Sanwa, WM-363-1) under vacuum (1.0 Pa) using a ferroelectric test system (FCE-1, Toyo Corp.). The current density-electric field characteristics of the films were also evaluated using an electrometer / high-resistance meter.

3. RESULTS AND DISCUSSION

3.1 Crystallization of $\text{BiFeO}_3\text{-BaTiO}_3$ (BF-BT) thin films on substrates

Figure 1 illustrates XRD patterns of $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ (BF-30BT) and $0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\text{-}0.3\text{BaTiO}_3$

(BFM-30BT) thin films fabricated on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates after heat treatment at 700°C . Both of the thin films crystallized in the perovskite $\text{BiFeO}_3\text{-BaTiO}_3$ (BF-BT) single phase with random orientations. The crystallization in perovskite BF-BT is due to the stabilization of the perovskite phase by the formation of a solid solution with BaTiO_3 . The reported formation of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase in BiFeO_3 films is attributed to the low structural stability of perovskite BiFeO_3 and the volatility of Bi ion at high temperatures. In addition, 5 mol% Mn doping to the BF-BT solid solution system is found to have no affect to the crystallization in perovskite BF-BT.

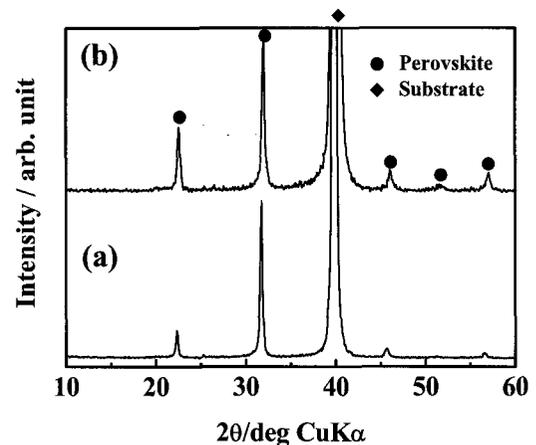


Fig. 1 XRD patterns of $0.7\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3\text{-}0.3\text{BaTiO}_3$ thin films on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates after heat treatment at 700°C (a) $x=0$, (b) $x=0.05$

3.2 Surface morphology of BF-BT thin films

Figure 2 shows AFM images of BF-30BT and BFM-30BT thin films prepared at 700°C on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates. Both films had homogeneous surface morphologies. This may be ascribed from suppressing the formation of second phase such as $\text{Bi}_2\text{Fe}_4\text{O}_9$. The root-mean-square (RMS) roughness values of the BF-30BT and BFM-30BT thin films were found to be 6.3 and 3.8 nm, respectively. It turned out from Fig. 2 that Mn-doped thin film had larger grain size and smaller surface roughness, which indicates Mn enhanced the grain growth and improved the surface morphology.

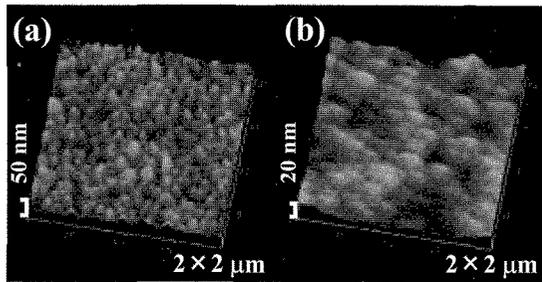


Fig. 2 AFM images of $0.7\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3-0.3\text{BaTiO}_3$ thin films on Pt/TiO_x/SiO₂/Si substrates after heat treatment at 700°C (a) $x=0$, (b) $x=0.05$

3.3 Leakage current properties of BF-BT thin films

In the case of BiFeO₃-based thin films, it is significant to investigate the leakage current property including the effect of Mn doping, because the difficulties in ferroelectric measurements due to the low resistivity of the films mainly originated from their leakage current. Figure 3 shows the leakage current properties of $0.7\text{BiFeO}_3-0.3\text{BaTiO}_3$ (BF-30BT) and $0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3-0.3\text{BaTiO}_3$ (BFM-30BT) thin films. Leakage current density-applied electric field curves of the samples with and without Mn doping showed clearly different behavior. Although, in low electric field region, BF-30BT thin films had lower current density than that of BFM-30BT thin films, Mn doped films had better insulating properties in high applied field area. The decrease of conductive species such as Fe²⁺ ion in BF-BT is considered to be the main origin of the hopping

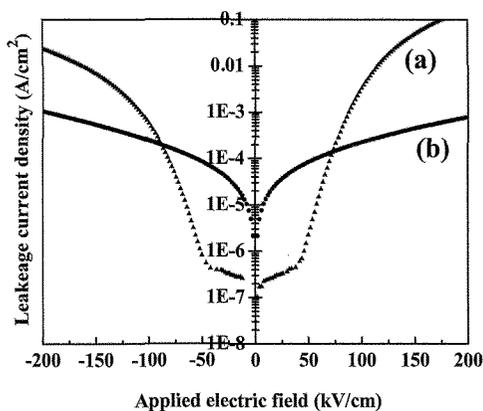


Fig. 3 Leakage current properties of $0.7\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3-0.3\text{BaTiO}_3$ thin films on Pt/TiO_x/SiO₂/Si substrates (a) $x=0$, (b) $x=0.05$

between Fe²⁺ and Fe³⁺. In this case, doped Mn effectively depressed the hopping conduction as an acceptor. The result in Fig. 3 is consistent with that reported for BiFeO₃ and Mn-doped BiFeO₃ thin films by Singh et al. [5]. Although the elucidation of the dominant mechanism of the leakage current is difficult as mentioned by Pabst et al. [7], the Mn doping effect should be clarified. Therefore, the valence state of Mn-doped BiFeO₃-BaTiO₃ is now under investigation by soft-X-ray absorption spectroscopy [8].

3.4 Ferroelectric properties of BF-BT thin films

P-E hysteresis measurements were also performed to characterize the ferroelectricity for BF-30BT and BFM-30BT thin films crystallized at 700°C. Figure 4 shows the *P-E* hysteresis loops of BF-30BT and BFM-30BT thin films measured at room temperature. Although BF-30BT thin films showed typical ferroelectric hysteresis loops, high electric fields cannot be applied because of its low insulating resistance. This is related with the result of leakage current shown in Fig. 3(a). On the other hand, BFM-30BT thin films showed larger ferroelectricity. As mentioned in the previous section, one of the major problems of BiFeO₃-based thin films is their low electrical resistivity, which affects the measurement of ferroelectric properties at room temperature. This is derived mainly from the valence fluctuation of Fe³⁺ to Fe²⁺ generating oxygen vacancies for charge compensation. The hopping electrons between Fe³⁺ and Fe²⁺ in BF-BT degrade the insulation resistance of

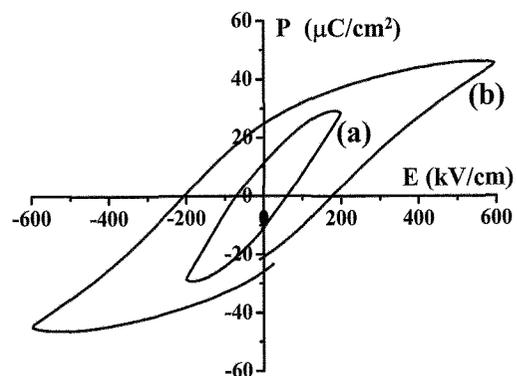


Fig. 4 *P-E* hysteresis loops of 500 nm-thick $0.7\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3-0.3\text{BaTiO}_3$ thin films on Pt/TiO_x/SiO₂/Si substrates measured at room temperature and 1 kHz (a) $x=0$, (b) $x=0.05$

resultant thin films.

Since the electrical resistivity was supposed to be high enough to characterize net ferroelectricity of the synthesized thin films, ferroelectric measurement at low temperature was then performed. Figure 5 shows the P - E hysteresis loops of BF-30BT and BFM-30BT thin films measured at -190°C . These thin films exhibited relatively saturated ferroelectric hysteresis loops compared with those at room temperature shown in Fig. 4. The remnant polarization (P_r) and coercive field (E_c) of the 700°C -prepared BF-30BT thin film were approximately $30\ \mu\text{C}/\text{cm}^2$ and $170\ \text{kV}/\text{cm}^2$, respectively. On the other hand, the BFM-30BT thin film prepared at 700°C exhibited larger P_r values around $45\ \mu\text{C}/\text{cm}^2$. To realize a practical application of the BF-BT thin films, the improvement of ferroelectric properties at ambient temperature is strongly required. Effect of BaTiO_3 concentration in BF-BT and the optimization of Mn doping amount are currently in progress.

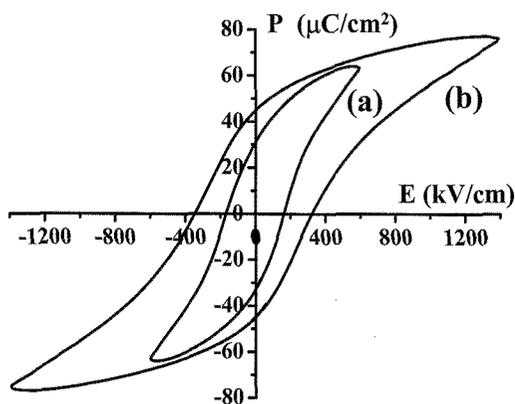


Fig. 5 P - E hysteresis loops of 500 nm-thick $0.7\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3\text{-}0.3\text{BaTiO}_3$ thin films on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates measured at -190°C and 1 kHz (a) $x=0$, (b) $x=0.05$

4. CONCLUSIONS

Ferroelectric $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ thin films were successfully synthesized by the chemical solution deposition. Perovskite $\text{BiFeO}_3\text{-BaTiO}_3$ single-phase thin films with homogeneous surface morphology could be fabricated by optimizing the several processing conditions. Electrical resistivity of the $0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$ thin films was not sufficiently high around room temperature.

By Mn doping, the leakage current behavior was changed and the leakage current density decreased, particularly at high applied fields. Mn doping to the Fe site of $\text{BiFeO}_3\text{-BaTiO}_3$ thin films were effective to improve the ferroelectric properties and the surface morphology of the resultant thin films.

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