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Synthesis and properties of multiferroic $0.7BiFeO_3-0.3BaTiO_3$ thin films by Mn doping

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Abstract

Multiferroic $BiFeO_3-BaTiO_3$ thin films that simultaneously exhibit ferroelectricity and ferromagnetism at room temperature were prepared by chemical solution deposition. Perovskite single-phase $0.7BiFeO_3-0.3BaTiO_3$ thin films were successfully fabricated in the temperature range 600–700 °C on $Pt/TiO_x/SiO_2/Si$ substrates. As the crystallization temperature was increased, grain growth proceeded, resulting in higher crystallinity at 700 °C. Although the $0.7BiFeO_3-0.3BaTiO_3$ thin films exhibited poor polarization (P)−electric field (E) hysteresis loops owing to their low insulating resistance. The leakage current at high applied fields was effectively reduced by Mn doping at the Fe site of the $0.7BiFeO_3-0.3BaTiO_3$ thin films, leading to improved ferroelectric properties. The 5 mol% Mn-doped $0.7BiFeO_3-0.3BaTiO_3$ thin films simultaneously exhibited ferroelectric polarization and ferromagnetic magnetization hysteresis loops at room temperature.

Keywords: A. Sol-gel processes; C. Ferroelectric properties; C. Magnetic properties; D. Perovskites

1. Introduction

Recently, multiferroic $BiFeO_3$ thin films that simultaneously exhibit ferroelectricity and ferromagnetism have received much attention as promising materials for the development of new types of electronic devices [1]. However, the synthesis of pure $BiFeO_3$ without impurity phases is usually difficult owing to the low structural stability of perovskite $BiFeO_3$. In the case of $BiFeO_3$ thin films, the crystallization of the $BiFeO_3$ phase on a substrate often results in the formation of a bismuth-deficient second phase such as $Bi_2Fe_4O_9$, which degrades the surface microstructure, leading to poor electrical properties [2]. Moreover, it is difficult to evaluate the ferroelectric properties of $BiFeO_3$ at ambient temperature owing to low insulating resistance. In addition, $BiFeO_3$ is known to exhibit very weak ferromagnetism with relatively low magnetization [3]. Therefore, modification of its magnetic properties is also an important objective.

The design of $BiFeO_3-ABO_3$ solid solution systems is an effective means of improving the structural stability and several properties of $BiFeO_3$ films. Among several ABO_3 compounds, $BaTiO_3$ is a practical counterpart because it is a stable ferroelectric perovskite oxide. Thus, a solid solution of $BiFeO_3$ and $BaTiO_3$ is expected to achieve the desired structural stabilization and electrical and magnetic properties. Furthermore, doping $BiFeO_3$ thin films with functional elements (e.g., Mn) to improve their electrical and magnetic properties has been intensively studied [4,5]. However, the multiferroic properties of $BiFeO_3-BaTiO_3$ (BF–BT) thin films reported in the previous studies were not sufficient [6].

In this study, the fabrication of room temperature multiferroic BF–BT thin films on Si-based substrates has been performed by chemical solution deposition. Previous studies have reported that perovskite BF–BT maintains a rhombohedrally distorted crystal lattice when the content of $BaTiO_3$ is less than 33 mol% [7]. Therefore, the $0.7BiFeO_3-0.3BaTiO_3$ composition was selected to stabilize the perovskite structure and multiferroic properties caused by the associated crystal lattice distortion. The effect of Mn

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doping on several properties of the BF–BT thin films was also investigated.

2. Experimental procedure

$Bi(O^tC_5H_{11})_3$, $Fe(OC_2H_5)_3$, $Ba(OC_2H_5)_2$, $Ti(O^iC_3H_7)_4$, and $Mn(O^iC_3H_7)_2$ [Kojundo Chemical] were selected as starting materials for preparing precursor solutions. The required amounts of starting metal alkoxides corresponding to the $0.7Bi(Fe_{1-x}Mn_x)O_3-0.3BaTiO_3$ (Mn100x% BF–30BT) composition with 3 mol% excess Bi were dissolved in dehydrated 2-methoxyethanol. Thereafter, the mixed solution was heated at 90 °C for 18 h, yielding a 0.2 M precursor solution. The entire procedure was conducted under a dry N_2 atmosphere.

BF–BT thin films were fabricated by spin coating the Mn100x%BF–30BT precursor solution on $Pt/TiO_x/SiO_2/Si$ substrates. The resulting precursor films were dried at 150 °C for 5 min and calcined at 400 °C for 1 h (heating rate: 5 °C/min) under an oxygen flow. After five drying and calcining cycles, the films were crystallized at 600–700 °C for 30 min under an oxygen flow using rapid thermal annealing (180 °C/min). The coating and calcining cycles were repeated 10 times (including two heat treatments for crystallization), resulting in a film thickness of approximately 500 nm.

The crystallographic phases of the crystallized BF–BT thin films were identified by X-ray diffraction (XRD; Rigaku RAD RC) analysis using Cu Kα radiation with a monochromator. The surface morphology of the crystallized thin films was observed by atomic force microscopy (AFM; SII NanoTechnology, SPI3800N). Pt top electrodes of diameter 0.2 mm were deposited by DC sputtering onto the surface of the films followed by annealing at 400 °C for 1 h. The ferroelectric properties of the resulting thin films were measured 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 (Keithley 6517A). The magnetization behavior of Mn100x%BF–30BT thin film samples was evaluated using a superconducting quantum interference device (Quantum Design, Type-5).

3. Results and discussion

Fig. 1 shows the XRD profiles of Mn0%BF–30BT thin films fabricated on $Pt/TiO_x/SiO_2/Si$ substrates after heat treatment at 600–700 °C. All thin films crystallized in the perovskite BF–BT single phase with a random orientation. Crystallization in the perovskite single phase is caused by the stabilization of the perovskite phase by the formation of a solid solution with $BaTiO_3$. The reported formation of the $Bi_2Fe_4O_9$ phase in $BiFeO_3$ films is attributed to the low structural stability of perovskite $BiFeO_3$ and the volatility of Bi ions at high temperatures (>600 °C) [2]. The temperature range of crystallization in perovskite single-phase BF–BT is enlarged by the formation of a solid solution with $BaTiO_3$. In addition, the full width at half maximum of each diffraction line decreased with increasing crystallization temperature.

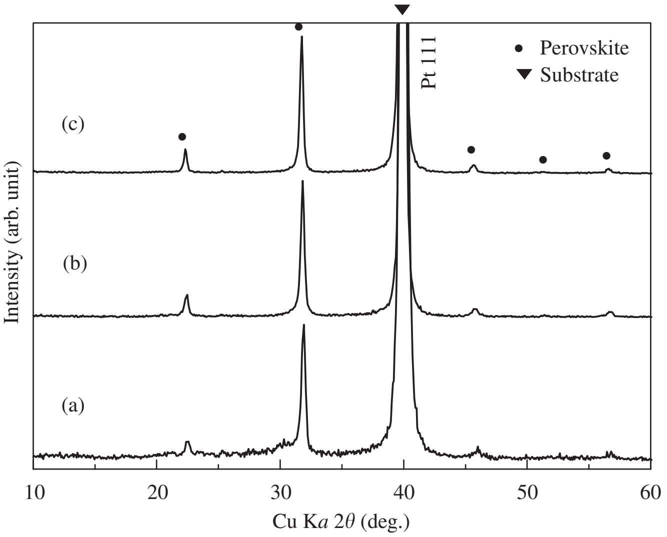

Fig. 1. XRD profiles of Mn0%BF–30BT thin films crystallized at (a) 600 °C, (b) 650 °C and (c) 700 °C.

Fig. 2 shows the AFM images of the Mn0%BF–30BT thin films prepared at 600–700 °C. All films had homogeneous surface morphologies. This may be ascribed to the suppression of the formation of a second phase such as $Bi_2Fe_4O_9$. Grain growth was enhanced and the grain size of the films increased from 30–60 nm (600 °C) to 80–160 nm (700 °C). The root mean square (RMS) roughness values of the Mn0%BF–30BT thin films ranged from 1.6 to 5.4 nm.

Perovskite $0.7BiFeO_3-0.3BaTiO_3$ thin films with a homogeneous microstructure were obtained by annealing at 700 °C. Thereafter, *P–E* hysteresis measurements were performed for the Mn0%BF–30BT thin films. Although the Mn0%BF–30BT films exhibited a ferroelectric hysteresis loop, a saturated *P–E* loop could not be obtained because a sufficiently high electric field could not be applied at room temperature. The Mn0%BF–30BT thin films exhibited relatively poor electrical resistivity. Therefore, to improve their insulating properties, Mn-modified BF–BT thin films were examined in this study. Improvement in the electrical properties of perovskite $BiFeO_3-PbTiO_3$ (BF–PT) films, especially insulating resistance, as a result of Mn doping has been reported by the authors [8]. In addition, Mn doping of the BF–BT thin films had no influence on the crystallization in perovskite BF–BT. Fig. 3 shows the leakage current density of the Mn0%BF–30BT, Mn3%BF–30BT and Mn5%BF–30BT thin films as a function of electric field. Curves of leakage current density as a function of the applied electric field curves for the thin films with and without Mn doping clearly exhibited different behavior. The leakage current density of the Mn0%BF–30BT films exhibited an abrupt increase with an applied field of approximately 30 kV/cm, whereas, in

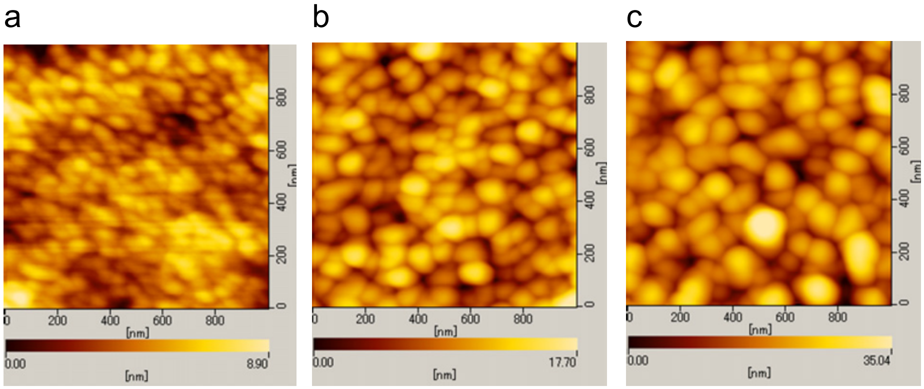

Fig. 2. AFM images of Mn0%BF–30BT thin films crystallized at (a) 600 °C, (b) 650 °C and (c) 700 °C.

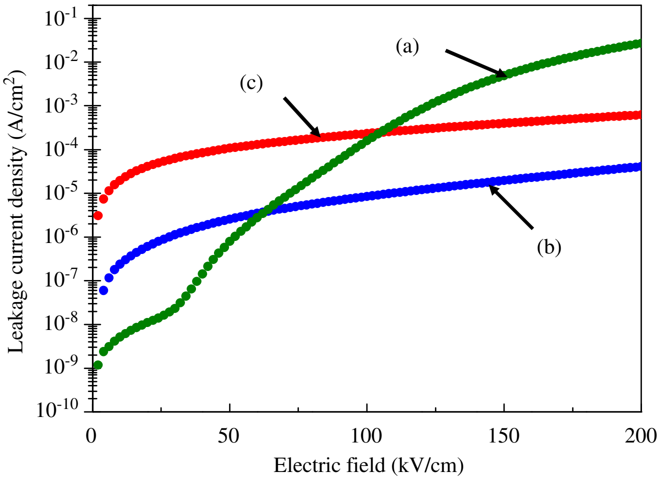

Fig. 3. Leakage current properties of (a) Mn0%BF–30BT, (b) Mn3%BF–30BT and (c) Mn5%BF–30BT thin films crystallized at 700 °C (measured at room temp.).

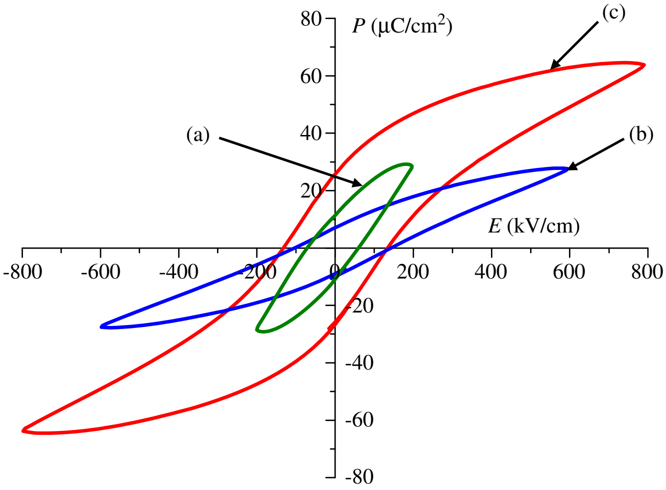

Fig. 4. Ferroelectric properties of (a) Mn0%BF–30BT, (b) Mn3%BF–30BT and (c) Mn5%BF–30BT thin films crystallized at 700 °C (measured at room temp.).

the low electric field region, BF–30BT0%Mn thin films exhibited a lower current density compared with the Mn3%BF–30BT and Mn5%BF–30BT thin films. Mn doping of the BF–BT films clearly decreased the leakage current at high applied fields, as shown in Fig. 3. The result represented by Fig. 3 is consistent with that reported for $BiFeO_3$ and Mn-doped $BiFeO_3$ thin films [4].

Fig. 4 shows the *P*–*E* hysteresis loops of the Mn0%BF–30BT, Mn3%BF–30BT and Mn5%BF–30BT thin films measured at room temperature. Among them, the Mn5% BF–30BT thin film exhibited a well-shaped hysteresis loop with a minor leakage component. This suggests that 5 mol% Mn doping of the $0.7BiFeO_3-0.3BaTiO_3$ thin films is an appropriate level for improving polarization properties. The Mn5%BF–30BT thin film exhibited a remanent polarization of 27 μC/cm². This value is larger than that of 0.67BF–0.33BT ceramics containing 0.1 wt% MnO_2 [9]. Similarly to the case of previously reported Mn-doped $BiFeO_3-Bi_{0.5}Na_{0.5}TiO_3$ (BF–BNT) thin films [10], Mn as a dopant might play an important role as an acceptor for trapping free carriers in the BF–BT thin films. However, Mn substitutes at the Fe^{3+} site as Mn^{2+}, which is accompanied by the formation of an oxygen vacancy. This might have a negative influence on the films under an increasing concentration of the Mn dopant. Thus, the optimum Mn and $BaTiO_3$ concentrations should be determined in future work. Furthermore, additional control of film orientation in the direction of polarization is essential for greater ferroelectric polarization.

The magnetic properties of the perovskite Mn-doped BF–30BT films were also evaluated. Fig. 5 shows the magnetization (*M*)–magnetic field (*H*) hysteresis loops of the Mn0%BF–30BT and Mn5%BF–30BT thin films. This measurement was performed at 300 K. The data is corrected for diamagnetic contributions from the substrate and sample holder. These films exhibited typical ferromagnetic characteristics. Such features can be explained by the typical *M*–*H* hysteresis loops of weak ferromagnetism (Fig. 5) showing magnetization at an applied field of 30 kOe and remanent magnetization and coercive field of 10 emu/cm³;

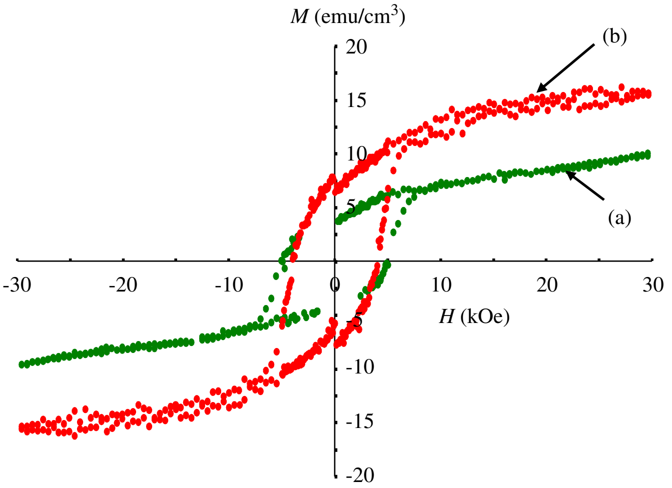

Fig. 5. Magnetic properties of (a) Mn0%BF–30BT and (b) Mn5%BF–30BT thin films crystallized at 700 °C (measured at 300 K).

3.8 emu/cm^3, 5.0 kOe and 16 emu/cm^3; 7.5 emu/cm^3, 4.0 kOe for Mn0%BF–30BT and Mn5%BF–30BT, respectively. The Mn5%BF–30BT thin film is considered to be multiferroic at room temperature on the basis of the results shown in Fig. 4. A $BiFeO_3$ single crystal was reported to exhibit a near-linear *M–H* relationship [3]. The typical polycrystalline $BiFeO_3$ samples also showed small magnetization and *M–H* hysteresis loops without spontaneous magnetization [11]. These results clearly suggest that the BF–BT films prepared in this study can be directed into a ferromagnetic state that exhibits remanent magnetization, unlike that previously reported for $BiFeO_3$. Similar magnetic behavior, including the presence of ferromagnetism, was observed in a previous study of magnetization in BF–PT thin films [12]. Kumar et al. reported on $(1-x)BiFeO_3-xBaTiO_3$ ceramics with ferromagnetic *M–H* hysteresis loops [13]. Although the XRD data indicates that the films in this study are pseudo cubic perovskite, their weak ferromagnetism depends on the structural distortion that occurred in BF–BT. On the other hand, the statistical distribution of the Fe^{3+} and Ti^{4+} ions at the octahedral sites also affects the magnetization and ferromagnetism of the films. It is equally possible that both crystal structure and Fe^{3+} ion distribution play an important role in the onset of ferromagnetism (*M–H* characteristics) in the current Mn0%BF–30BT and Mn5%BF–30BT thin films. Furthermore, Mn0%BF–30BT thin films exhibited smaller magnetization at 30 kOe. As reported in Takahashi et al. [5], the enhanced magnetization of the Mn5%BF–30BT thin films is considered to be caused by a magnetic structural change from spiral to collinear G-type antiferromagnetic ordering of $BiFeO_3$ caused by Mn doping. In addition, with respect to coercive force and magnetization values, there is a difference between the films with and without Mn doping. This is mainly caused by the defect structure of the films, especially the valence state of the Mn and Fe ions, and the amount of oxygen vacancies in these films. The grain size of the films is also an important factor because the grain boundary region of magnetic ceramics often affects the magnetization behavior and coercive force. The reason for these differences is not clear and is under investigation.

4. Conclusions

Room temperature multiferroic BF–BT thin films were successfully synthesized by chemical solution deposition. Following the formation of a solid solution with $BaTiO_3$, the BF–BT films directly crystallized in the perovskite single phase over a wide temperature range, leading to the formation of a homogeneous surface microstructure with higher crystallinity. Although the electrical resistivity of the Mn0%BF–30BT thin films was not sufficiently high, the leakage current density was effectively reduced at high applied fields by Mn doping. In particular, the Mn5%BF–30BT thin films simultaneously exhibited improved ferroelectric properties and typical ferromagnetic *M–H* hysteresis loops at ambient temperatures. Thus, Mn was found to be an effective functional element for improving electrical properties and enhancing the magnetization of the multiferroic BF–BT thin films.

Acknowledgments

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