**Structural and Electrical Properties of Polycrystalline Bi(Fe_{0.6}Mn_{0.4})O_3 Thin Films**

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A 40% Mn-substituted BiFeO_3 (BFMO) thin film was deposited on a Pt(111)/Ti/SiO_2/Si(100) substrate by using a pulsed laser deposition method. The coexistence of rhombohedral and orthorhombic structures in the BFMO thin film was confirmed by using X-ray diffraction and Raman spectra investigation. The leakage current density of the BFMO thin film was larger than that of a pure polycrystalline BiFeO_3 (BFO) thin film. In order to understand the leakage current behaviors, the leakage current mechanisms were investigated. The leakage current mechanism of the BFO thin film was found to be space-charge-limited conduction (SCLC), followed by trap-filled conduction caused by the increasing electric field strength. On the other hand, trap-filled conduction was not observed in the BFMO thin film. A leaky ferroelectric hysteresis loop was observed in the BFMO thin film, but not in the BFO thin film.

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I. INTRODUCTION

Multiferroic BiFeO_3 (BFO) has a rhombohedral structure with R3c space group at room temperature and has a high Curie temperature ($T_c$) of $\sim$1130 K and a high Néel temperature ($T_N$) of $\sim$ 643 K [1, 2]. BFO has a G-type antiferromagnetism with a spatially-modulated spin structure [3]. In addition, BFO exhibits good ferroelectricity. For example, an epitaxial BFO thin film with a (111)-orientation exhibits a remnant polarization ($2P_r$) of $\sim$196.9 $\mu$C/cm$^2$ [4]. However, poor ferroelectric properties have often been observed in BFO thin films and are mostly related with high leakage currents caused by a charge transition from Fe$^{3+}$ to Fe$^{2+}$ and by the existence of Bi and oxygen vacancies [5, 6]. These poor ferroelectric properties of BFO thin films have been improved by impurity doping to compensate for the charge imbalance. As an example of this, improved ferroelectric property and leakage current were reported for a 3% Mn-doped BFO thin film [7].

Recently, BFO and BiMnO_3 (BMO) have been reported to be able to form a solid solution over the entire compositional range. The crystal structures of the solid solution were reported to be rhombohedral for BFO-rich, orthorhombic for an intermediate, and monoclinic for a BMO-rich solution. Azuma et al. reported that a Bi(Fe$_{1-x}$Mn$_x$)O$_3$ solid-solution ceramic has a phase transition between the rhombohedral and the orthorhombic structures at 20% Mn [8]. On the other hand, Ianculescu et al. reported that rhombohedral structure was retained up to Mn 40% [9].

Due to the controversial reports regarding the crystal structure of the BFO and BMO solid solution, we investigated the structure and the electrical properties of a 40% Mn-substituted BFO thin film that was grown on a Pt(111)/Ti/SiO_2/Si(100) substrate. The X-ray diffraction and the Raman spectrum of Bi(Fe$_{0.6}$Mn$_{0.4}$)O$_3$ (BFMO) thin film showed a crystal structure different from that of the BFO thin film.
II. EXPERIMENTAL

The BFO and the BFMO targets were fabricated by using a solid-state reaction with raw powders of Bi$_2$O$_3$ (99.999%), Fe$_2$O$_3$ (99.999%), and Mn$_2$O$_3$ (99.999%). Five mol% of Bi was added to the targets because of Bi volatility during high-temperature sintering. The BFO and the BFMO thin films were grown on Pt(111)/Ti/SiO$_2$/Si(100) substrates by using a pulsed laser deposition method with a KrF excimer laser at a laser repetition rate of 5 Hz. During the deposition, the substrate temperature was kept at 540 °C. Oxygen pressures of 30 mTorr and 10 mTorr were used for the growths of the BFO and the BFMO film, respectively. The thin films were characterized structurally by using an X-ray diffractometer (RIGAKU, Miniflex II) with Cu K radiation and a micro Raman spectrophotometer (JPR, NRS-3300). The Fe ion oxidation state was investigated by using X-ray photoelectron spectroscopy (XPS, VG Scientifics, ESCALAB 250). Leakage current densities were measured by using a semiconductor parameter analyzer (HP4145B), and the ferroelectric properties were measured by using a Sawyer-Tower circuit.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of the polycrystalline BFO and BFMO thin films. The BFO thin film was indexed as a pseudo-cubic structure because of incomplete (220) peak separation. The XRD pattern of the BFMO thin film was different from that of the pure BFO thin film. A slight shoulder on the right side of the (200) peak was observed in BFMO, which may suggest that BFMO is not a single phase. Due to the ambiguity of the XRD peaks, deciding the structures of the two thin films was difficult.

The Raman spectra of the BFO and the BFMO thin films measured at 150 K are shown in Figs. 2(a) and 2(b), respectively. The BFO thin film exhibited Raman active modes corresponding to a typical rhombohedral structure. For BFO with R3c space group, thirteen Raman active modes (4A$_1$+9E) have been reported [10]. The four peaks at 140 (A$_1$-1), 172 (A$_1$-2), 217 (A$_1$-3), and 429 (A$_1$-4) cm$^{-1}$, respectively, can be assigned to A$_1$-symmetry longitudinal-optical phonons. The peaks located at 76 (E-1), 262 (E-2), 275 (E-3), 307 (E-4), 345 (E-5), 369 (E-6), 470 (E-7), 521 (E-8), and 613 (E-9) cm$^{-1}$ are associated with E-symmetry transverse-optical phonons. On the other hand, orthorhombic structure has twenty-four Raman active modes (7A$_g$ + 7B$_{g1}$ + 5B$_{g2}$ + 5B$_{g3}$) [11]. Twelve Raman active modes, 143, 172, 221, 260, 289, 349, 369, 436, 474, 518, 614, and 649 cm$^{-1}$, were observed in the BFO thin film at 150 K. A$_1$ Raman active modes of rhombohedral structure were 143, 172, 221, and 436 cm$^{-1}$, and the E Raman active modes were 260, 349, 369, 474, 518, and 613 cm$^{-1}$. However, two observed Raman active modes at 289 and 649 cm$^{-1}$ were not matched with those of rhombohedral structure. The Raman active modes at 289 and 649 cm$^{-1}$ originated from the monoclinic structure, and have been reported in monoclinic BiMnO$_3$ [12]. This suggests the existence...