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Micro-structure and ferroelectric properties of $BiFeO_3$ thin films formed on Pt-coated r-plane sapphire substrates

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Abstract Magnetoelectric $BiFeO_3$ (BFO) materials exhibit ferroelectric and ferromagnetic properties simultaneously, therefore they have a potential to be applied in magnetic as well as ferroelectric devices. BFO thin films were formed by depositing sol-gel solutions on Pt-coated r-plane sapphire dielectric substrates. We did not observe any secondary phase such as $Bi_2Fe_4O_9$ on the r-plane sapphire substrates, which is generally observed on Si substrates. We observed small ferroelectric grains of about 0.1 μm on Pt/sapphire structures. The leakage current density in BFO films was found to be decreased dramatically after optimizing process conditions of stoichiometric BFO chemical solution. The leakage current densities were in the range of 10^{-7} A/cm^2 at room temperature and 10^{-9} A/cm^2 at 80 K under 0.4 MV/cm applied electric field. The main reason for low leakage current is considered to be reduction of oxygen vacancies due to the presence of exclusive Fe^{3+} valance state in the films. An applied electric field higher than 0.5 MV/cm was required to pole the BFO films, which made it difficult to obtain the saturated polarization at room temperature. We could measure the saturated remanent polarization in the BFO films at 80 K and the obtained remanent polarization was 100 μC/cm^2.

Keywords Magnetoelectrics · $BiFeO_3$ thin films · Chemical solution deposition · Micro-structure · Ferroelectrics properties

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Introduction

Multiferroic $BiFeO_3$ (BFO) is reported to exhibit antiferromagnetic ordering with Neel temperature (T_N) of about 370°C and ferroelectric ordering with Curie temperature (T_C) of about 850°C [1]. The lattice structure of a BFO crystal is a rhombohedrally distorted perovskite, which belongs to the space group R3c with unit cell parameters $a_r = 5.364$ Å and $\alpha_r = 0.6°$ [2]. The crystallization temperature of BFO films is lower than 550°C and five-minute-annealing in a nitrogen atmosphere is sufficient to obtain crystalline BFO films, which is suitable for implementing BFO capacitors on CMOS logic circuits [3]. Spontaneous polarizations in a single crystal have been measured at 80 K to be 3.5 μC/cm^2 along a (100) direction and 6.1 μC/cm^2 along a (111) direction [4]. The enhanced polarization of about 100 μC/cm^2 was observed in the thin films fabricated by pulsed laser deposition [5, 6] as well as chemical solution deposition [3]. An enhanced polarization value is advantageous for the fabrication of high-density ferroelectric random access memory device.

BFO prepared from mixed oxide materials always contains impurity by-products. The phase diagram studies on the Bi_2O_3-Fe_2O_3 binary system show that BFO is an incongruent compound [7, 8]. The phase formation of BFO starts around 300°C and it mainly consists of three phases γ-Bi_2O_3, $BiFeO_3$ and $Bi_2Fe_4O_9$ [9]. Because it is difficult to form a pure BFO phase, one of the major problems of BFO thin films is low electrical resistivity and it affects the measurement of ferroelectric/ferromagnetic properties at room temperature (RT). The relatively high conductivity of BFO is attributed to valence fluctuation of Fe ions (Fe^{3+} to Fe^{2+}), creating oxygen vacancies for charge compensation [10]. Improved leakage current in BFO films has been achieved through optimizing process conditions of stoichiometric chemical solution [3].

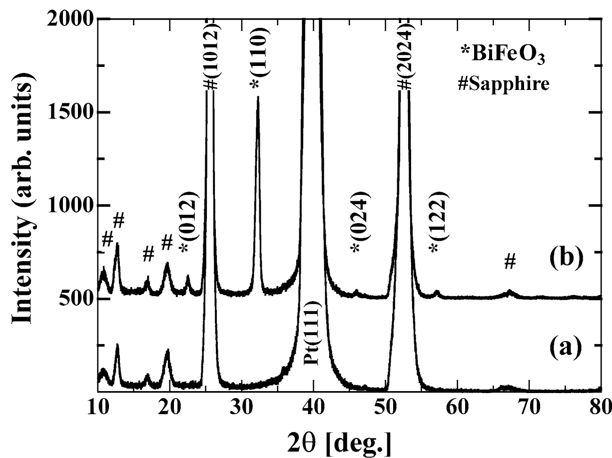


Fig. 1 X-ray diffraction patterns of (a) Pt/sapphire (b) $BiFeO_3$/Pt/ sapphire structures

In this paper, we will discuss the micro-structure and ferroelectrics properties of BFO thin films fabricated on Pt-coated (1012)-oriented r-plane sapphire substrates.

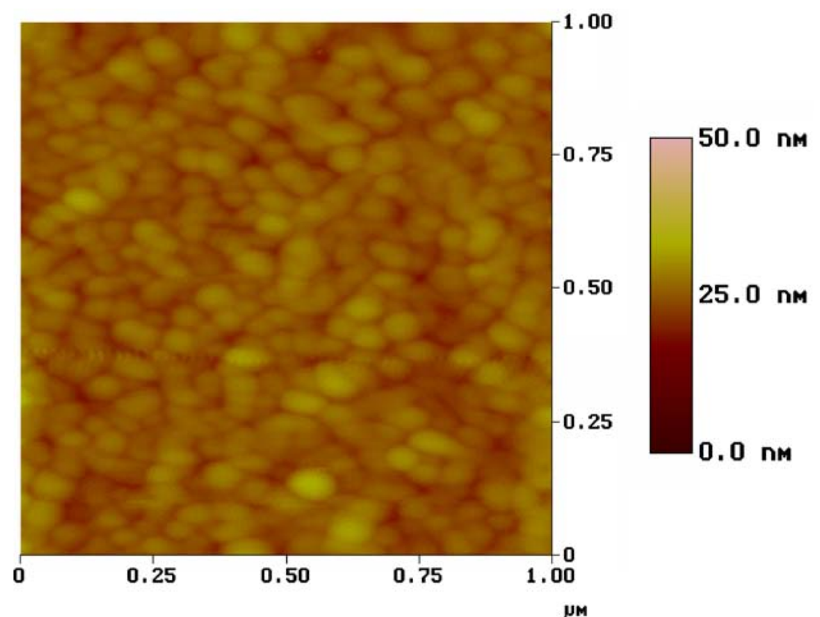
Experimental details

First, we deposited a 100-nm-thick Pt bottom electrode on sapphire substrate at 500°C using a sputtering system. BFO thin films were formed by depositing sol-gel chemical solution on the Pt/sapphire structures. The stoichiometric solution of $BiFeO_3$ (Toshima MFG Co. Ltd.) was spin-coated at 3000 rpm for 30 s, dried at 240°C for 3 min, and prefired at 350°C for 10 min in air. This process was repeated several times to obtain the films of desired thickness and then the films were annealed at 550°C for 5 min in a nitrogen atmosphere. The electron beam evaporation was used for depositing Pt top electrodes of 3.14×10^{-4} cm^2 and 0.785×10^{-4} cm^2 areas through a shadow mask. The crystalline structure of the films was investigated with a multipurpose X-ray diffractometer (X,Pert-Pro MPD, Philips). The electrical properties of the film capacitors were measured using a standardized ferroelectric test system (Radiant Technologies, RT66a) and an HP4156A precision semiconductor parameter analyzer (Hewlett-Packard). The surface morphologies of the films were determined using atomic force microscopy (AFM).

Result and discussions

Figure 1 shows X-ray diffraction (XRD) patterns of (a) Pt/sapphire and (b) $BiFeO_3$/Pt/sapphire structures. The XRD peaks of BFO thin films were indexing using a rhombohedral structure. X-ray diffraction patterns of the BFO film indicate mixed orientation with preferred orientations along (110) axes. We did not observe any secondary phase such as $Bi_2Fe_4O_9$ phase on sapphire substrate, which was generally observed on Si substrate [3]. Other peaks which appear in the patterns belong to the Pt/sapphire structure, as shown in the figure. It can also be seen that BFO films are well crystallized in 5-min-annealing at 550°C in a N_2 atmosphere and a single phase perovskite structure is obtained on sapphire substrate. The reduction of secondary phase on sapphire substrate may be due to smooth surface morphology of bottom Pt electrode. Although we observed highly (111)-oriented Pt thin films on the r-plane substrate with a nearly 4-folded symmetry, the Pt surface on the sapphire substrate was smoother than that on Si substrate. That is, the RMS (root-mean-square) values

Fig. 2 Surface morphology of a $BiFeO_3$ thin film on Pt/sapphire substrate annealed at 550°C for 5-min in a N_2 atmosphere



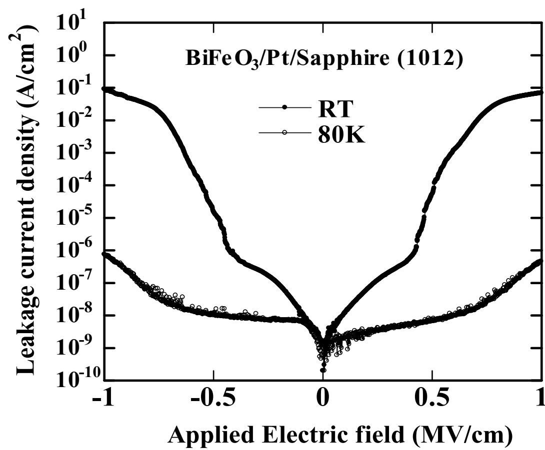


Fig. 3 Current-voltage (I - V) characteristics of Pt/$BiFeO_3$/Pt thin film capacitors on sapphire substrate at RT and 80 K

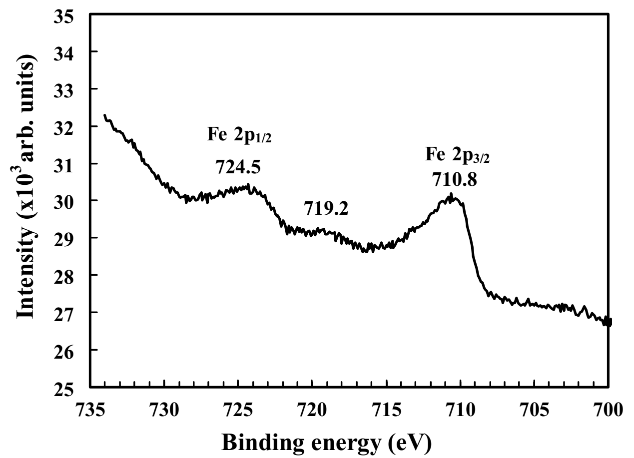


Fig. 4 XPS spectra of Fe 2p state in a $BiFeO_3$ film deposited on sapphire substrate

on sapphire and Si substrates were 0.35 nm and 0.7 nm respectively. It was also found that the small changes in the growth parameters were very sensitive to the orientation of the BFO films and these changes affected the insulating and ferroelectric properties significantly.

The surface morphology of the films was studied using AFM. Figure 2 shows the surface morphology of a BFO film on Pt/sapphire substrate annealed at 550°C for 5 min in a N_2 atmosphere. We could observe well distinguished ferroelectric grains of about 0.1 μm in the BFO film, which shows that the crystalline phase of BFO is obtained under such small thermal budget conditions as 550°C for 5 min in a N_2 atmosphere. The RMS value of the surface roughness (Rrms) was about 4 nm.

Figure 3 shows I–V characteristics of Pt/BFO/Pt/sapphire thin film capacitors measured at (a) RT and (b) 80 K. The leakage current densities in BFO films were greatly decreased under our growth conditions. In the lower electric field than 0.4 MV/cm, the current densities were on the order of 10^{-7} A/cm^2 at RT and lower than 1×10^{-8} A/cm^2 at 80 K. The obtained RT value was 4 orders-of-magnitude lower than typical reported values in pure BFO films [11, 12]. The leakage current density at RT increased rapidly as we applied electric field higher than 0.4 MV/cm. At 80 K, the leakage current density at 1 MV/cm is 7×10^{-7} A/cm^2 on sapphire substrate. The main reason for reduction of leakage current in our films may be the reduction of the oxygen vacancies.

The valance state of Fe ions was investigated using X-ray photoelectron spectroscopy (XPS). The XPS spectrum from 700 to 735 eV is shown in the Fig. 4. The 3/2 and 1/2 spin-orbit doublet components of the Fe 2p photoemission are located at 711 and 724.5 eV in Fig. 4, respectively, which are associated with Fe^{3+} valance state [13]. The positions of the Fe 2p line and satellite are 711, and 719 eV for Fe^{3+}

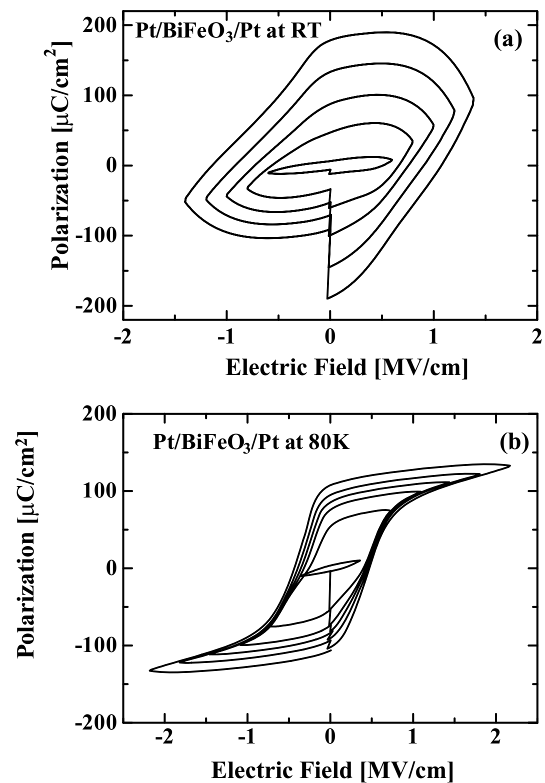


Fig. 5 Polarization-electric field (P-E) hysteresis loop of Pt/$BiFeO_3$/Pt thin film capacitors on sapphire substrate at (a) RT and (b) 80 K

and 709.5, and 716 eV for Fe^{2+} respectively [14]. This result shows that our BFO films have only Fe^{3+} valance state and it is identical with XPS spectra for BFO films grown by PLD [12, 14].

The polarization-electric field (P-E) hysteresis loops of BFO films were measured at room temperature as well as at 80 K. The BFO films show a coercive field around 0.5 MV/cm, which is much higher than that of typical ferroelectric materials. We are required to apply the electric field

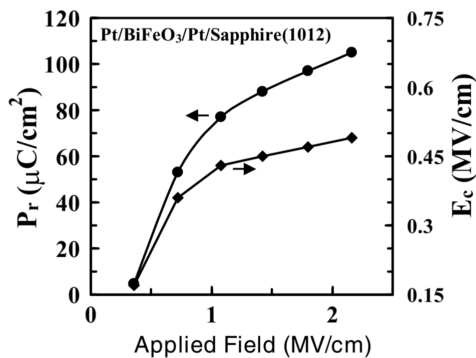


Fig. 6 Electric-field dependence of remanent polarization and coercive field in Pt/$BiFeO_3$/Pt thin film capacitors on sapphire substrate at 80 K

higher than 0.5 MV/cm to pole the BFO films. At RT it was difficult to determine the exact polarization value because of existence of the leakage current component, as shown in Fig. 5(a). At 80 K on the other hand, the leakage current of the range of 10^{-7} A/cm^2 was observed at an applied field of 1 MV/cm and because of the low leakage current, we could measure well saturated rectangular-shaped hysteresis loops, as shown in Fig. 5(b). Figure 6 shows the electric-field dependence of remanent polarization and coercive field for Pt/$BiFeO_3$/Pt/sapphire thin film capacitors at 80 K. The well saturated remanent polarization was obtained for electric fields higher than 0.5 MV/cm at 80 K. The saturated remanent polarization and coercive field at 2 MV/cm were about 100 μC/cm^2 and 0.5 MV/cm, respectivily.

Conclusions

BFO thin films were formed by depositing sol-gel solutions on r-plane (1012)-oriented sapphire substrates. We did not observe any secondary phase such as $Bi_2Fe_4O_9$ on r-plane sapphire substrate, which was generally observed on Si substrate. We observed small ferroelectric grains of about 0.1 μm on Pt/sapphire substrate. The leakage current density in BFO films was found to be decreased dramatically after optimizing process conditions of stoichemistric BFO chemical solution. The leakage current densities were in the range of 10^{-7} A/cm^2 at room temperature and 10^{-9} A/cm^2 at 80 K under 0.4 MV/cm applied electric field. The leakage current density at RT increased rapidly when the applied electric field was increased beyond 0.4 MV/cm, while the leakage current density at 80 K was 7×10^{-7} A/cm^2 at 1 MV/cm. The main reason for low leakage current is considered to be reduction of oxygen vacancies due to the presence of exclusive Fe^{3+} valance state in the films. The BFO films showed the coercive field around 0.5 MV/cm, which made it difficult to obtain the saturated polarization at room temperature. We could measure the saturated remanent polarization in the BFO films at 80 K and the obtained remanent polarization was as large as 100 μC/cm^2.

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