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Bi Concentration Dependence of Structural, Ferroelectric and Magnetic Properties of $BiFeO_3$ Films

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ABSTRACT

Bi-rich $BiFeO_3$ films were fabricated by chemical solution deposition followed by a post-deposition annealing at 823 K in air. Not only the polycrystalline $BiFeO_3$ phase but also the bismuth oxide phases were formed at high excess Bi contents. This suggested that the Bi atoms were not significantly evaporated. The remanent polarization decreased as the excess Bi contents increased at 90 K, though the remanent polarization of 33 $\mu C/cm^2$ was still obtained at the excess Bi contents of 30 at.%. The magnetization monotonically decreased as the excess Bi content increased. It could be considered that the optimal Bi content is the stoichiometric value of $BiFeO_3$ in the preparing way of the CSD followed by the annealing at 823 K.

Keywords: $BiFeO_3$ film; Bi; remanent polarization; magnetic property

INTRODUCTION

Multiferroic $BiFeO_3$ films have been attracted much interest as one of the candidates for a future multi-valued memory material because the $BiFeO_3$ films that have coupled ferroelectric and magnetic order parameters leading to a magneto-electric (ME) effect. Therefore, recently many study concerning to the $BiFeO_3$ films has been reported [1–5]. However, the physical parameters such as the remanent polarization and the saturation magnetization are different in each report. In these reports [2–4], the Bi rich target and the precursor solution have been used for pulse laser deposition (PLD) and chemical solution

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deposition (CSD) methods as the starting materials because of the low melting temperature of Bi element ($T_m = 547$K). However, the optimal content of Bi for the ferroelectric and the magnetic properties are not discussed in detail. As well known, in PZT films of the typical ferroelectric material's case, ferroelectric properties is affected by a lead content [6]. In the present study, we investigate the Bi content dependence of the ferroelectric and the magnetic properties of the $BiFeO_3$ films prepared by the CSD method.

EXPERIMENTAL PROCEDURE

The Bi_xFeO_3 ($1 \leq x \leq 1.3$) films were fabricated by CSD method using the precursor solution with Bi:Fe ratios from 1.0:1.0 to 1.3:1.0 were prepared. These precursor solutions were spin-coated onto the Pt(150nm)/Ti(5nm)/SiO_2/Si(001) substrates. The coated substrates were dried at 423 K for 1 min and calcined at 623 K for 5 min in air. These processes were repeated 5 times. The annealing was carried out at 823 K for 10 min in air. In order to make a capacitor structure, top Pt electrodes were deposited by electron beam evaporation. The top Pt electrode size was 100 μm in diameter. The crystal structure was determined by an x-ray diffraction (XRD: $2\theta/\theta$, Cu-$K\alpha$; PANalytical X'Pert MRD). The surface morphology of the films was observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM; JEOL JSM-6380). The composition of the specimen was analyzed by an x-ray spectroscopy (EDS) attached to SEM. The ferroelectric hysteresis loops were performed by making use of a ferroelectric tester (TOYO Corporation FCE-1A type) with a single triangular pulse of 100 kHz at room temperature and 2 kHz at 90 K (aixACCT TF-2000). Leakage current density was measured at room temperature using a pA meter (HP 4140B). A driving voltage was applied to the bottom electrodes. The magnetic properties were measured by a vibrating sample magnetometer (VSM: Tamagawa Corporation) at room temperature. The magnetic field was applied parallel to film surface.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the Bi_xFeO_3 ($1 \leq x \leq 1.3$) films after annealing at 823K for 10 min in air. Below the excess Bi content of 15 at.%, many diffraction peaks due to the $BiFeO_3$ phase were observed, which indicating that the $BiFeO_3$ films have a polycrystalline structure with random orientation and the influence of the strong 111-texture of the bottom Pt electrode layer on the $BiFeO_3$ orientation was not observed. By contrast, not only the $BiFeO_3$ diffraction peaks but also the secondary phases of β-Bi_2O_3 and Bi_2O_4 were formed above the excess Bi contents of 20 at.%.

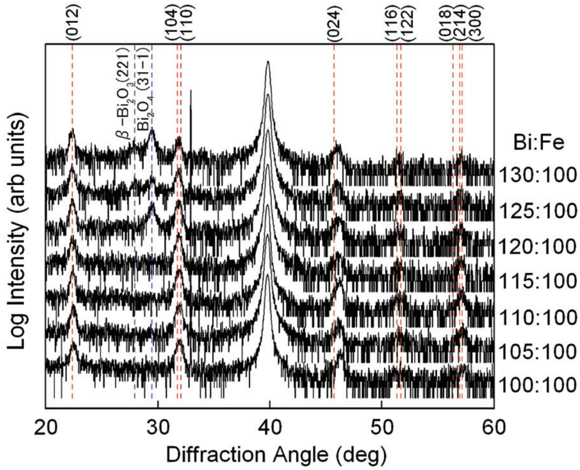

Figure 1. XRD patterns for the various excess Bi Composition.

Figure 2 show the AFM images of the $BiFeO_3$ films with various excess Bi contents. Below the excess Bi content of 15 at.%, a few micron size of the grains were formed and the size of the grains were increased at the excess Bi

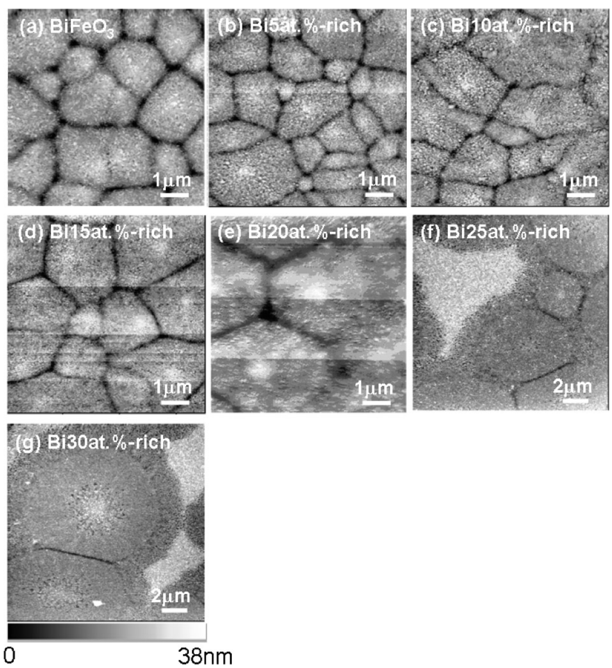

Figure 2. AFM image for various excess Bi Composition.

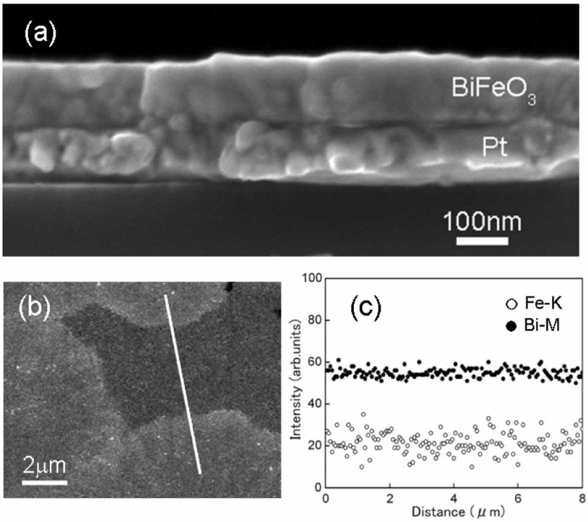

Figure 3. Cross-sectional SEM image (a); plan view of SEM image (b) and the profile of the composition of the composition fo the surface (c) for the film specimen with the excess Bi composition of 30 at.%.

content of 20 at.%. Then, the lotus sheets of around 20 μm in diameter appeared at the excess Bi contents above 25 at.% [Fig. 2(f), 2(g)]. According to the line profile crossed the lotus sheet for the 30%-Bi-rich specimen; it revealed that the lotus sheets had concaved structure. In order to understand the formation of the lotus sheets, we measured the line profile of the composition crossing the lotus sheet and observed the cross sectional SEM image.

Figure 3(a) shows the cross sectional SEM image of the specimen with the excess Bi contents of 30 at.%. In the cross sectional SEM image, difference of the contrast could not be observed around the interface of the lotus sheet. The SEM image on the surface, the contrast related to the lotus sheets were observed as shown in Fig. 3(b). We analyzed the composition of the surface of the film crossing the lotus sheet. The result is shown in Fig 3(c). The composition ratio of Bi and Fe was almost constant in each position, indicating that the concaved structure of the lotus sheet was not attributed by the inhomogeneously-distributed composition. Now, the reason of the formation of the lotus sheet on the surface at the high excess Bi composition is unclear.

Figure 4(a), 4(b) and 4(c) show the ferroelectric hysteresis loops at room temperature for the specimen with the various Bi contents. In order to reduce the influence of the leakage current component on ferroelectric hysteresis shape at room temperature, the ferroelectric hysteresis loops were measured using the high frequency system of 100 kHz (TOYO Corporation FCE-1A). When comparing with the ferroelectric hysteresis loops using the low frequency system,

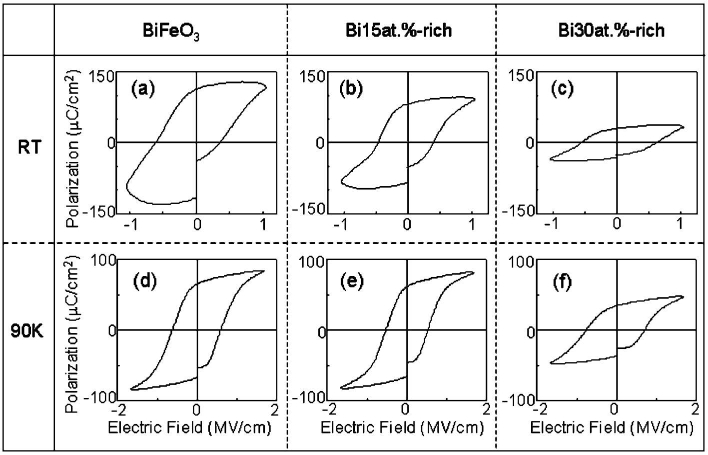

Figure 4. Bi Compostion dependence of ferroelectric hystersis loops at room temperature (a) and at 90 K (b).

the high frequency of 100 kHz system is successful to reduce the influence of the leakage current component, though the $P - E$ hysteresis loop of the $BiFeO_3$ film shown in Fig. 4(a) seems to be still expanded due to the leakage current component. The $BiFeO_3$ film with the excess Bi contents of the 15 at.% showed the relatively constricted shape of the ferroelectric hysteresis loop was observed implying that the leakage current density was changed by the excess Bi contents. The remanent polarization and the electric coercive field are summarized in Fig. 5(a). The electric coercive field of the $BiFeO_3$ film might be decreased at the excess Bi contents of around 10 at.%.

The other way to reduce the leakage current components and measuring the accurate ferroelectric hysteresis loops is decreasing the measuring temperature. Figure 4(d), 4(e) and 4(f) show the ferroelectric hysteresis loops measured at 90 K for the various excess Bi contents. Each ferroelectric hysteresis loop was measured at applied the electric field of 1.7 MV/cm. The ferroelectric hysteresis loops with high squareness were obtained in each excess Bi composition due to the suppression of the leakage current. The remanent polarization and the electric coercive field measured at 90 K are summarized in Fig. 5(b). The remanent polarization at 90 K of the non excess Bi specimen film was 66 $\mu C/cm^2$ at the electric field of 1.7 MV/cm. The remanent polarization of the $BiFeO_3$ film decreased as the excess Bi composition increased, though the remanent polarization around 33 $\mu C/cm^2$ was still retained at the 30%-Bi-rich specimen, in which the secondary bismuth oxide phases in the film coexisted. The electric coercive field of the $BiFeO_3$ film decreased at the excess Bi contents of around 10 at.%. These results suggest that Bi elements hardly lose from

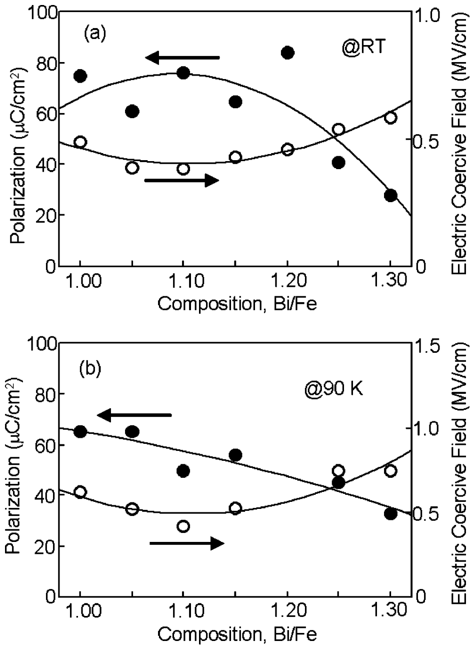

Figure 5. Bi composition dependence of the ramanent polarizatkion and electirc coercive field measured at room temperature (a) and at 90 K (b).

the film body during the heat treatment of 823 K and excess Bi never improved the crystallinity in the $BiFeO_3$ system.

Figure 6 shows the magnetic hysteresis loops of the Bi_xFeO_3 ($1 \leq x \leq 1.3$) films measured at room temperature. Each of the magnetic hysteresis loops showed the typical weak ferromagnetism. The spontaneous magnetization as well as the magnetic coercivity did not appeared at room temperature. Figure 7 shows the excess Bi composition dependence of the magnetization at 14 kOe estimated from the $M - H$ curves. The magnetization at 14 kOe linearly

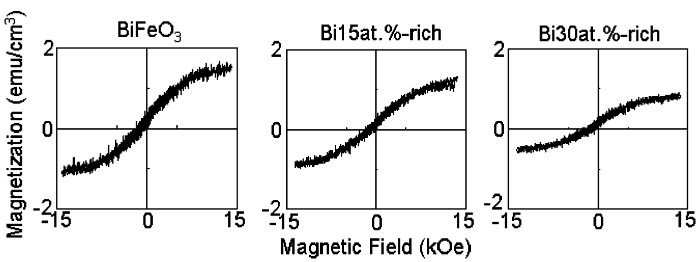

Figure 6. $M - H$ curves for the various Bi compositions.

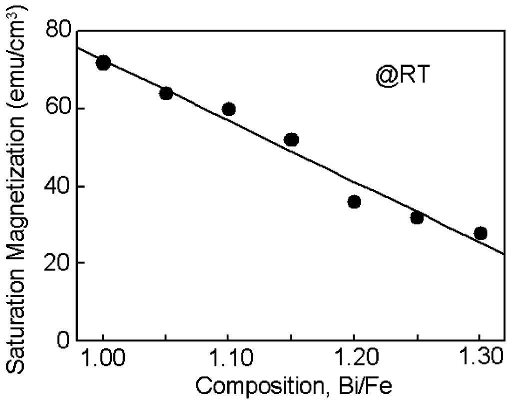

Figure 7. Bi composition dependence of the magnetization at 14 KOe measured at room temperature.

decreased as the excess Bi content increased. Although non-magnetic material of the Bi oxide phase was not formed at the excess Bi contents below 20 at.%, the saturation magnetization was started to decrease at the excess Bi content of 5 at.%. Therefore, it could be considered that the nonmagnetic Bi cluster and/or Bi oxide nanoparticles, which could not be possible to detect by the conventional x-ray diffraction measurement, was formed even at low excess Bi contents. These results revealed that the excess Bi did not significantly evaporated at the annealing condition of 823 K for 10 min. In this study, it could be concluded that optimal Bi contents of $BiFeO_3$ film is the nominal stoichiometric composition of $BiFeO_3$ when using the CSD method with the post deposition annealing at 823 K in air.

CONCLUSIONS

Bi-rich $BiFeO_3$ specimens have been fabricated by CSD method on Pt(150nm)/Ti(5nm)/SiO_2/Si(100) substrates followed by the post-deposition annealing at 823 K for 10 min. The XRD measurements revealed that the secondary phases of β-Bi_2O_3 and Bi_2O_4 were formed above the excess Bi contents of 20 at.%. The microstructure study using AFM and SEM indicated that the lotus sheet with concavity structure appeared on the surface of the film at the excess Bi contents above 25 at.%,. Although the effect of the leakage current on the ferroelectric hysteresis loops are reduced by using the high frequency system of 100 kHz, all of the ferroelectric hysteresis loops looks like still including the leakage current components at room temperature. By contrast, the leakage current component was strongly suppressed by decreasing the measuring temperature to 90 K. The remanent polarization decreased as the excess Bi content increased at 90 K, though the 33 $\mu C/cm^2$ of the remanent polarization was still observed at the excess Bi content of 30 at.%, in which the secondary phases of bismuth oxide coexisted. The magnetic measurement indicated that the nonmagnetic Bi cluster and/or Bi oxide nanoparticles, which were not be possible to detect by the conventional x-ray diffraction measurement, were formed even in the specimens with the small amount of the excess Bi. From these results, it suggested that the excess Bi did not significantly evaporate at the annealing process of 823K for 10 min in air. Thus, it could be concluded that optimal Bi content of $BiFeO_3$ film is the nominal stoichiometric composition of $BiFeO_3$. No need to add the excess Bi in the CSD process for the large remanent polarization.

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