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Effect of Lattice Misfit Strain on Crystal System and Ferroelectric Property of BiFeO$_3$ Epitaxial Thin Films

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Abstract. The effects of the lattice misfit strain on the crystal system and the ferroelectric properties of BiFeO$_3$ epitaxial thin films were investigated. The misfit strain was controlled by the introduction of a buffer layer. When the film thickness of BiFeO$_3$ is 130 nm, the lattice parameter of the film was controlled by the lattice misfit. Furthermore, when the thickness is 900 nm, it was found that the crystal system of the film with misfit of -1.3 % was monoclinic, and that with a misfit of 0.5 % was rhombohedral. From the evaluation of the ferroelectric properties, it was found that the coercive electric field of the films with a misfit of 0.5 % was smaller than that with misfit of -1.3 %. Moreover, the polarization switching behavior and the leakage current at the microscopic region of the films were investigated using scanning probe microscopy. The results suggest that the lattice misfit causes the generation of defects in the grain and affects the polarization switching behavior.

1. Introduction

Lead-free ferroelectric BiFeO$_3$ is one of the promising materials for memory and piezoelectric devices because BiFeO$_3$ has a huge spontaneous polarization as large as $\sim$100 $\mu$C/cm$^2$ and high Curie temperature ($T_C$$\sim$850 °C) [1-4]. There are various attempts to engineer the properties of BiFeO$_3$. Especially, there are lots of reports about engineering the crystal structure and ferroelectric properties of BiFeO$_3$ thin films by substitution [5-8]. For example, substitution and solid solution of materials with tetragonal structure are conducted to explore the Morphotolopic phase boundary (MPB) composition [7]. On the other hand, it is also reported that while crystal system of BiFeO$_3$ is rhombohedral in bulk structure, there are some cases that it becomes tetragonal or monoclinic in film form due to substrate clamping effect [9-11]. Therefore, it is important to reveal the effect of substrate clamping on the crystal system and ferroelectric properties of the films. The influence of lattice strain from substrate on lattice parameter, crystal system, and ferroelectric properties of BiFeO$_3$ thin films has also been reported. In the reports, the lattice strain of BiFeO$_3$ film is controlled by substrates with various lattice parameter and orientation, film thickness, and fabrication of membrane structure [12-15]. However, there are few reports about the structural and ferroelectric properties of BiFeO$_3$ with small lattice misfit. In this paper, the lattice misfit is controlled by the introduction of a buffer layer The effects of lattice misfit strain on the crystal system and the ferroelectric property of the films were investigated. In particular, domain switching behavior and microscopic conduction were studied.

2. Experimental Procedure

Bottom electrode, buffer layer and BiFO$_3$ were deposited by pulsed laser deposition (PLD). The
stoichiometric targets were ablated by using an ArF excimer laser (Lambda Physik COMPex102) with a wavelength of 193 nm. BaTiO₃ epitaxial films were deposited on (001) SrTiO₃ substrates as the buffer layer. The buffer layer was annealed after the deposition so as to be released from substrate clamping [16]. Epitaxially grown SrRuO₃ bottom electrode with 5-nm-thick was deposited on the buffer layer so that its lattice constant becomes identical to that of the buffer layer by epitaxial restriction. Finally, BiFeO₃ epitaxial films were deposited at a growth temperature of 500 °C and an oxygen pressure of 1 mTorr. 130- and 900-nm-thick films with and without the buffer layer were fabricated. The crystal system of the films was investigated by reciprocal space mapping (RSM) of a x-ray diffraction (XRD; Panalytical X-pert Pro). The piezoelectric response and domain switching behavior of the films were investigated using piezoelectric force microscopy (PFM).

3. Results and Discussion

Results of XRD 2θ-ω scan of the 130-nm-thick BiFeO₃ thin films without and with buffer layer are shown in Figs. 1(a) and 1(b), respectively. (001)BiFeO₃ films were obtained on the both samples. The c lattice constant of BiFeO₃ decreases by introduction of the buffer layer. It is suggested that the decrease of c lattice constant is caused by in-plane tensile strain from the bottom layer. The in-plane lattice parameter of the films was also investigated using RSM of XRD (not shown here). From the result, the a lattice constant of the BaTiO₃ buffer layer is determined as 3.98 Å. Therefore, the lattice misfits of a BiFeO₃ single crystal on SrRuO₃/SrTiO₃ and SrRuO₃/BaTiO₃/SrTiO₃ are -1.3 % and 0.5 %, respectively. Moreover, the a and c lattice parameters of the BiFeO₃ films with a misfit of -1.3 % are 3.91 Å and 4.05 Å, which indicates that the film is tetragonal. On the other hand, the a and c lattice parameters of the BiFeO₃ films with the misfit of 0.5 % are 3.96 Å and 3.95 Å, which indicates that the film is pseudo-cubic. In the same way, results of XRD 2θ-ω scan of the 900-nm-thick BiFeO₃ thin films with misfits of -1.3 % and 0.5 % are shown in Figs. 1(c) and 1(d), respectively. Fig. 1(c) indicates that the BiFeO₃ film with a misfit of -1.3 % consists of two kinds of phases with different lattice parameter. The result of RSM indicates that the two phases are tetragonal lattice clamped by the substrate (bottom electrode) and relaxed lattice. The relaxed lattice has an angular distortion and the c lattice parameter is larger than the a lattice parameter. Therefore, it is suggested that the relaxed lattice is monoclinic. On the other hand, one diffraction peak is observed in the 2θ-ω scan of the film with the buffer layer. For detail analysis, the diffraction intensity of BiFeO₃ 004 in RSM was projected along ω and the

![Figure 1](image1.png)  
Figure 1. XRD patterns of (a) 130-nm-thick BiFeO₃ thin film without buffer layer, (b) with buffer layer, (c) 900-nm-thick films without buffer layer, and (d) with buffer layer, respectively.

![Figure 2](image2.png)  
Figure 2. Integrated profiles obtained from reciprocal space mapping of 900 nm-thick-film with misfit of 0.5 % in 004 diffraction at (a) Φ=0° and (b) 45° (dotted) and pattern fitting using Pseudo Voigt function (solid line), respectively.
integrated intensity is resolved by fitting using Pseudo Voigt function at Φ=0° and 45° as shown in Figs. 2(a) and 2(b). From the fitting results, it was found that the integrated profiles at Φ=0° and 45° have two and three diffraction peaks, respectively, indicating that the existence of two sets of c-plane with different tilt angle of 0.59° and 0.90° at Φ=0° and 45°, respectively. As reported in Ref. 17, the tilt indicates the four distortion directions along 111 of the rhombohedral phase suggesting that lattice parameter and crystal system can be controlled by lattice misfit and film thickness.

The ferroelectric properties of the films were evaluated. Pt top electrodes with a diameter of 100 μm were deposited on the BiFeO₃ thin films through a metal mask by RF magnetron sputtering. The electrical measurements were conducted using the Sawyer–Tower circuit and LCR meter. However, it was difficult to evaluate the dielectric property of the films due to the large leakage current. In particular, the leakage current of the 130-nm-thick films is larger than that of the 900-nm-thick films. Therefore, the relationship between the microscopic structure and the leakage current of the 130-nm-thick films was investigated by current mapping using atomic force microscopy (AFM) with Pt/Cr-coated probe. AFM images of the 130-nm-thick BiFeO₃ thin films with misfits of -1.3% and 0.5% are shown in Figs. 3(a) and 3(b), and the results of the leakage current mapping measured simultaneously at an applied bias electric field of 150 kV/cm are shown in Figs. 3(c) and 3(d). The electrical measurement using SPM was performed in the region without top electrodes. The results indicate that the both films show large leakage current in particular grains. No obvious relationship between the surface morphology and the leakage current is observed. However, in the case of the film with a misfit of 0.5%, the amount of the grains with large leakage current is smaller than that of the film with a misfit of -1.3%. There are many reports about the morphology and domain structure of BiFeO₃ films and the influence of the structure on the electric properties [18, 19]. In particular, it was reported that the domain walls were much more conductive than inside of the domains [20]. To discuss the relationship between the domain structure and local conductivity, the domain structure was observed using PFM. The measurement was conducted at various dc electric field and ac oscillations with a frequency of 4 kHz. Figs. 4(a)-4(d) show the domain mapping images of the films under dc electric field from 0 to 230 kV/cm. In these figures, upward and downward domains are displayed as black and white, respectively. These results indicate that the grain consists of single domain for all films. Therefore, the domain wall exists at the grain boundary in these
films, and the origin of leakage current is different from specific conductivity of the domain wall of BiFeO$_3$. Moreover, there are some domains which do not switch even at 230 and 110 kV/cm in the 130- and 900-nm-thick films with a misfit of -1.3 %, respectively. As shown in Fig. 3, the films with a misfit of -1.3% have grains with large leakage current at the interface between bottom electrodes and the films. It appears that the leaky grains generated by the dislocation, which is introduced by misfit strain, affect the domain switching behavior.

4. Conclusions

The structural and ferroelectric properties of BiFeO$_3$ epitaxial thin films with various film thickness and lattice misfit were investigated to reveal the influence of the lattice misfit on the properties. The misfit is changed by introduction of a BaTiO$_3$ buffer layer. It was found that the crystal system can be controlled from monoclinic to rhombohedral by the misfit. The decrease of density of the grain with large leakage current and the coercive electric field was observed in the films with lower misfit. The results suggest that the lattice misfit cause the generation of defects in the grains and it affects the polarization switching behavior.

References