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Direct piezoelectric properties of BiFeO₃ epitaxial films grown by combinatorial sputtering

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Abstract. We have proposed that BiFeO₃ films are suitable for piezoelectric vibration energy harvesting applications, because of the low dielectric permittivity and excellent ferroelectricity. In this paper, the improvement of the piezoelectric properties of the domain-engineered BiFeO₃ films was discussed. The (100) epitaxial films were prepared at growth temperatures between 500 and 650°C on Nb-doped (100) SrRuO₃ single crystals. The combinatorial sputtering method was employed in order to prevent Bi defects during high-temperature deposition. The domain structure and ε₃₁,⊥ piezoelectric coefficients of the films were characterized by a piezoelectric force microscopy and direct piezoelectric response, respectively. The highest ε₃₁,⊥ coefficient of -4.3 C/m² and figures of merit of 14 GPa were obtained in the film deposited at 600°C, which has the highest domain wall density. This suggests that the introduction of the domain walls is effective to enhance the piezoelectric properties of BiFeO₃ films.

1. Introduction

Recently, vibration energy harvesters (VEHs) are receiving a considerable amount of interest [1, 2]. While the various transduction mechanisms for VEHs exists such as electromagnetic and electrostatic, the piezoelectric effect has the feature of the direct conversion of the applied strain energy into a useful electric energy [2]. The typical structure of the piezoelectric VEHs is a cantilever with a mass at the free end. The electromechanical coupling factor of the piezoelectric films in this structure is given by

\[ k^2 = \frac{(1 - \nu)^2 \varepsilon^{\perp}_{31,f}}{Y \varepsilon_0 \varepsilon_r}, \]  

where ε₃₁,⊥ is the transverse effective piezoelectric coefficient, ε₀ is the permittivity of vacuum, εᵣ is the relative permittivity, Y is Young’s modulus, and ν is the passion ratio [3]. We have proposed that BiFeO₃ films are suitable for piezoelectric VEH (pVEH) applications, [4, 5] because it has a high spontaneous polarization (~100 µC/cm²) and a low dielectric permittivity (~100) [6, 7]. Piezoelectric MEMS VEH using sol-gel derived BiFeO₃ films showed a maximum output power of 10 µW/mm²/G² [3, 8]. This result is comparable to those of the best-performing VEHs using other piezoelectric films [9, 10].

While it is indicated that BiFeO₃ films are promising for pVEH applications, the further improvement of the piezoelectric properties of BiFeO₃ films needs to facilitate device design. The general approach to enhance the piezoelectric properties is the exploration of the morphotropic phase boundary (MPB). For example, on the (100) epitaxial films of the solid solution system of BiFeO₃, BaTiO₃, and SrTiO₃
reported $d_{33(AFM)}$ coefficient of 83 pm/V was reported [11]. The effect of rare-earth substitution for BiFeO$_3$ epitaxial films was also investigated, and $d_{33(AFM)}$ coefficient of 110 pm/V was reported on Sm$^{3+}$ substituted films [12]. Our approach is the engineering of the domain configuration. In ferroelectric single crystals, the excellent piezoelectric properties are obtained in a direction not parallel to the spontaneous polarization [13]. It was indicated that this mechanism is effective for piezoelectric films also [14]. We have reported that the $e_{31,f}$ coefficient of (100) BiFeO$_3$ epitaxial film (-3.5 C/m$^2$) is 2.7 times higher than that of the (111) film (-1.3 C/m$^2$), which indicates that the engineered-domain configuration is effective for BiFeO$_3$ films [4].

For the further improvement of piezoelectric properties, we employed a combinatorial sputtering method [15] to obtain stoichiometric films regardless the growth conditions because it is known that Bi is easily volatile during the deposition. The relationship between the growth condition, crystal structure, domain structure and piezoelectric properties are discussed.

2. Experiment

The schematic illustration of the combinatorial sputtering method is shown in Fig. 1. To fabricate the films with a gradient of Bi/Fe ratio in-plane direction, Bi$_{1.1}$FeO$_3$ ceramic and pressed powder of Bi$_2$O$_3$ were used as the targets, which have a diameter of 2-inches. RF power of 30W and 5W was applied, respectively, at the same time. Nb-doped (100) SrTiO$_3$ single crystals were used as the substrates. The growth temperature was varied from 500 to 650 °C. The films with a thickness of about 300 nm were obtained for the deposition of 5h. The crystal structure of the films was investigated by x-ray diffraction (XRD) of 2-$\theta$ scan and reciprocal space mapping. The surface morphology and ferroelectric domain structure were observed by scanning probe microscopy (SPM). The effective transverse piezoelectric coefficient, $e_{31,f}$, was characterized by direct piezoelectric response based on substrate bending method [16].

3. Results and Discussion

XRD analysis indicated that the (100) BiFeO$_3$ epitaxial films with cube-on-cube relationship were obtained at the growth temperature from 500 to 650 °C. Significant change in the phase development...
against the composition was not observed. Figure 2 shows the surface morphology of these films. At the deposition temperature of 500 ºC, the smoothest surface is observed at the position (d). Above 600 ºC, the smoothest surface is observed at the position (e). These results can be explained by the change of the film composition because it is well known that for BiFeO₃ films the surface roughness drastically increases by the off-stoichiometry. Since the volatilization of Bi during the deposition increases with increasing the growth temperature, the position where the film has the stoichiometric composition shifts to the side of the Bi₂O₃ target.

The domain structure of the BiFeO₃ films was observed by piezoelectric force microscopy using SPM. The (100) BiFeO₃ films have a rhombohedral structure with a spontaneous polarization along the <111> direction. Since the conductive SPM probe was placed parallel to the <110> direction of BiFeO₃ in this measurement, the lateral piezoelectric response has four possible directions with respect to the in-plane direction. Figure 3(a) and 3(b) shows the mapping images of the vertical and lateral converse piezoelectric response of the BiFeO₃ films with the stoichiometric composition. At the deposition temperature of 500 ºC, the domain has a round shape with a size of around 100 nm, which is almost same as the grain size. This indicates that the grain growth is insufficient and the most of the domain walls exist at the grain boundary. At 550 and 600 ºC, the domain size observed by the vertical piezoelectric response increases to 100-500 nm and the domains have a polygon shape. The domain size observed by the lateral piezoelectric response is bit smaller than that observed by the vertical piezoelectric response. The (100) BiFeO₃ films with rhombohedral structure have the three types of domain walls as shown in figure 3(c). While 180° and 109° domain walls exist between the upward and downward domains, only 71° domain walls exist between the domains with the same vertical component. The domain observation for the films deposited at 550 and 600 ºC indicates that the part of the domain walls is 71° walls. At 650 ºC, the domain has an elongated shape with a width of 200-300 nm and a length of 500~1000 nm. The domain sizes observed by vertical and lateral piezoelectric response are almost same, which indicates that the domain walls consists of 180° and 109° domain walls.

**Figure 3.** Mapping images of (a) vertical and (b) lateral converse piezoelectric responses of the BiFeO₃ films and (c) types of the domain wall (DW).

**Figure 4.** Growth temperature dependence of e₃₁,f coefficient, dielectric constant and FOM of the BiFeO₃ films.
The $\varepsilon_{31,f}$ coefficient and dielectric constant of these films are shown in figure 4. The $\varepsilon_{31,f}$ coefficient increases with increasing the deposition temperature up to 600 °C, then decreases at 650 °C. The highest $\varepsilon_{31,f}$ coefficient at 600 °C is -4.3 C/m², which is comparable to the best result for BiFeO$_3$ films [6]. We have revealed that the intrinsic contribution in the $\varepsilon_{31,f}$ coefficient for the (100) BiFeO$_3$ films is about -2 C/m², and that the other component in the $\varepsilon_{31,f}$ coefficient is caused by 71° domain walls. The results presented in this paper are consistent with this. The dielectric constant of the films gradually increases from 100 to 200 with increasing the growth temperature. The figure of merit (FOM) for VEH application, which is given by $\varepsilon_{31,f}^2/\varepsilon_0\varepsilon_r$, is also shown in figure 4. As can be seen, the highest FOM of 14 GPa was obtained at the growth temperature of 600 °C, at which the highest $\varepsilon_{31,f}$ coefficient and domain wall density are obtained. Given the thickness of the BiFeO$_3$ films (~300 nm), these results are quite promising, because the obtained FOM (14GPa) is comparable to the typical PZT film with a thickness more than 1 µm. Thus, it can be concluded that the control of the domain structure is the key to obtain high $\varepsilon_{31,f}$ coefficient and FOM.

Conclusion
Direct piezoelectric properties of (100) BiFeO$_3$ epitaxial films grown by combinatorial sputtering was investigated. The films with smooth surface were obtained at the growth temperature from 500 to 650°C. It was found that the density of 71° domain walls increases between 550 and 600°C. The high $\varepsilon_{31,f}$ coefficient (-4.3 C/m²) and FOM (14 GPa) for VEH application are obtained in the films deposited at 600°C. The results obtained in this study suggests that increase of the density of 71° domain walls is effective to improve the piezoelectric properties of (100) BiFeO$_3$ epitaxial films.

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