# Enhanced Piezoelectricity in Tetragonal $BiFe_xCo_{1-x}O_3$ Epitaxial Thin Films

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$BiFeO_3$ (BFO) has attracted much attention because of its room-temperature multiferroic properties with a ferroelectric Curie temperature ($T_C$) of ~830 ºC and an antiferromagnetic Néel temperature ($T_N$) of ~370 ºC. Concerning the electrical properties, although its spontaneous polarization is as large as ~100 μC/cm$^2$, its piezoelectric constant ($d_{33}$~60 pm/V) is far smaller than those of lead containing piezoceramics such as $Pb(Zr,Ti)O_3$ (PZT). An improved piezoelectric response is expected in the solid solution of rhombohedral BFO and tetragonal $BiCoO_3$, $BiFe_xCo_{1-x}O_3$ (BFCO), due to the presence of morphotropic phase boundary [1] similar to PZT. We have successfully prepared epitaxial BFCO thin films on $SrRuO_3$(SRO)/$SrTiO_3$(STO)(001) substrates by pulsed laser deposition (PLD) method, and demonstrated that the $d_{33}$ value of the BFCO thin film increases with increasing Co content $x$, reaching ~100 pm/V at $x$=0.10 [2]. However, it decreased to ~80 pm/V when $x$ was further increased to 0.15. It was suggested that BFCO phase with giant $c/a$ ratio found in the film degraded the piezoresponses. Therefore, in order to improve the piezoresponse further, it is crucial to obtain a giant-$c/a$-phase-free BFCO film with the largest Co contents. In this study, the crystal structure and electrical properties of epitaxial BFCO thin film with $x$=0.12 were investigated.

BFCO thin film with $x$=0.12 and a thickness of 200 nm was grown on the SRO/STO (001) substrate by focusing a KrF excimer laser pulse (λ=248 nm/5 Hz/1.5 Jcm$^{-2}$pulse$^{-1}$) onto a rotating target at substrate temperature of 700 °C under oxygen pressure of 15 Pa. Stoichiometric target at a cation ratio was used. The crystal structure of the BFCO film was studied by x-ray diffraction (XRD; Rigaku SmartLab). Local displacement versus electric-field ($d$–$E$) hysteresis loops were measured by detecting the vertical motion of an atomic-force-microscope (Agilent Tech. Agilent 5420) cantilever with a conducting tip connected to a ferroelectric test system (Toyo FCE).

θ/2θ x-ray diffraction (XRD) pattern of the BFCO thin film indicated a single-phase perovskite structure without any traces of the giant-$c/a$ phase. The out-of-plane lattice parameter was 4.015 Å, which is larger than its bulk values. This can be ascribed to the presence of in-plane compressive stress induced by the SRO/STO substrate. To study the detailed crystal structure, reciprocal space mapping (RSM) was measured around 003 and 113 STO, and the results are shown in Fig. 1. Only one reflection was detected from the BFCO film in both the 003 and 113 RSMs. Because the $q_z$ of both the reflections are the same, the crystal structure of the BFCO film is determined to be tetragonal. The out-of-plane lattice parameter $c$, in-plane lattice parameter $a$, and the distortion angle $\beta$ as determined from the RSM data are shown in

Fig. 2(a) together with those of BFCO films with x=0 to 0.15 as reported previously [2]. The lattice parameters of BFCO film with $x$=0.12 fall between those of BFCO films with x=0.10 and 0.15. Dependence of displacement on electric filed ($d$-E) was measured at room temperature with a scanning frequency of 1 kHz. The effective $d_{33}$ estimated from the slope of the $d$-E curve is shown in Fig. 2(b) together with those of BFCO films with $x$=0 to 0.15. It is demonstrated that the effective $d_{33}$ for the BFCO film with $x$=0.12 reached as high as about 130 pm/V.

References

[1] M. Azuma et al., Jpn. J. Appl. Phys., **47**, 7579 (2008).
[2] H. Hojo et al., submitted.

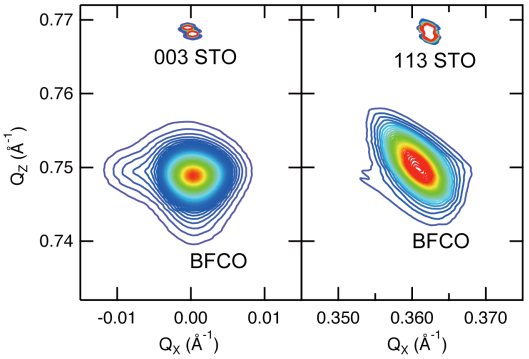


FIG.1 Reciprocal space mapping around 003 and 113 STO for BFCO thin films with $x$ = 0.12.

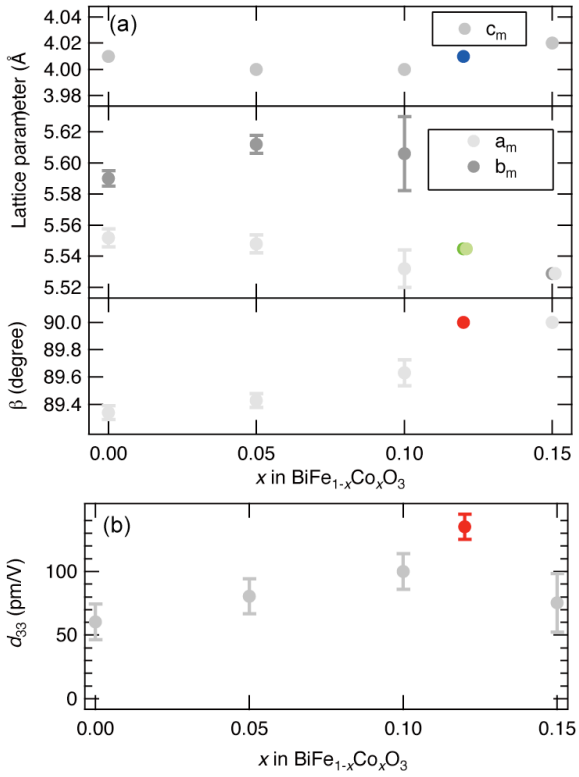


FIG.2 (a) Lattice parameters and axis angle and (b) effective piezoelectric constant $d_{33}$ as a function of the cobalt contents. Data for BFCO films with $x$=0, 0.05, 0.10 and 0.15 are from Ref. [2].