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本研究課題による研究成果は学術誌 Applied Physics Letters に投稿済みですが、現在査読中です。以下の、投稿しました原稿をもって研究報告書に変えさせていただきます。

X-ray diffraction study of polycrystalline $BiFeO_3$ thin film under electric field

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Abstract

Diffraction measurements using 12.4 keV X-ray of synchrotron radiation have been performed in $(001)_{pc}$- and $(110)_{pc}$-oriented polycrystalline 350-nm-thick $BiFeO_3$ thin film on Pt /TiO_2 /SiO_2 /Si substrate under electric field in air at RT. Unipolar rectangular pulse voltage having 150 nsec width and 804.09 nsec period have been applied to $BiFeO_3$ with Pt top electrode. Diffraction peak of $(001)_{pc}$ [$(110)_{pc}$] plane shifts from 14.602^o [20.520^o] to 14.588 [20.505^o] due to piezoelectric response when 12 V [11 V] pulse is applied. Piezoelectric constants (d_{33}) of $(001)_{pc}$-oriented and $(110)_{pc}$-oriented domain estimated from these peak shifts are 27.8 pm/V and 26.4 pm/V, respectively.

Recently, multiferroic materials have been much attracted considerable interest because of simultaneous coexistence of (anti)ferroelectricity, (anti)ferromagnetism and ferroelasticity for device applications such as nonvolatile memory, actuators and infrared sensor. These properties are due to their strong coupling between electric polarization and elastic strain.[1-3] To improve these properties and explore new materials, their transient phenomena including domain wall motion have been well investigated.[4] Among many multiferroic materials, $BiFeO_3$ (BFO) with ABO_3 type perovskie structure shows good ferroelectric properties. In BFO, the $6s^2$ lone pair of Bi^{3+} has strong covalent characteristics of Bi – O bond for stabilizing noncentrosymmetric-distorted structure which takes an important role for ferroelectricity. Single crystal BFO has rhombohedrally distorted perovskite structure belonging to space group of *R3c* with lattice parameter of a = 0.562 nm and α = 59.35°.[5] It shows spontaneous polarization (P_s) of only 3.5 μC/cm^2 and 6.1 μC/cm^2 along [001] and [111] direction at 77K, [6] respectively, because ferroelectric hysteresis measurement in bulk BFO is difficult due to its high coercive field and high leakage current. However, we have reported polycrystalline BFO thin film on $Pt/TiO_2/SiO_2/Si$ substrate deposited by pulsed laser deposition (PLD) shows giant remanent polarization (P_r ~ 152 μC/cm^2) at 90 K.[7] This P_r value is extremely large compared to P_r of epitaxial BFO thin films and predicted by the first-principles calculation.[8, 9] Therefore, electric-field-induced phase transition is expected in polycrystalline BFO thin film, and investigations of structural properties of polycrystalline BFO thin films under electric field are required.

Recently, time-resolved synchrotron X-ray scattering studies of the dynamics in ferroelectrics have been carried out by many workers. Especially, nonlinear piezoelectric effect in high electric field region, domain wall motion and fatigue process in epitaxial $Pb(Zr,Ti)O_3$ thin films have been investigated using time-resolved synchrotron X-ray diffraction measurements under electric field.[10-12] However, there is no report of the time-resolved X-ray measurements in polycrystalline thin films. In this letter, we have reported electric-field-induced strain of polycrystalline $BiFeO_3$ (BFO) thin film using time-resolved synchrotron X-ay diffraction under electric field.

350-nm-thick BFO thin film has been prepared on Pt (200 nm)/TiO_2 (50 nm)/SiO_2 (600 nm)/Si (625 μm) substrate by PLD with ArF excimer laser (λ =193 nm). Substrate temperature and O_2 pressure were fixed at 500°C and 0.12 Torr during BFO deposition, respectively. 200-nm-thick Pt electrodes (ϕ 185 μm) have been prepared by RF magnetron sputtering at RT through a shadow mask. Two-dimensional XRD (2D-XRD) pattern of the BFO thin film measured by Bruker D8 Discover with GADDS (General Area Detector Diffraction Solution) indicates that the obtained BFO thin film was $(001)_{pc}$- and $(110)_{pc}$-oriented polycrystalline thin film (Fig.

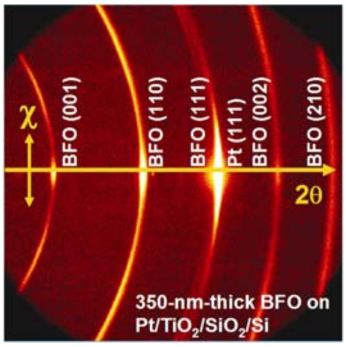

FIG.1 2D-XRD patterns of polycrystalline BFO thin film using CuKα radiation.

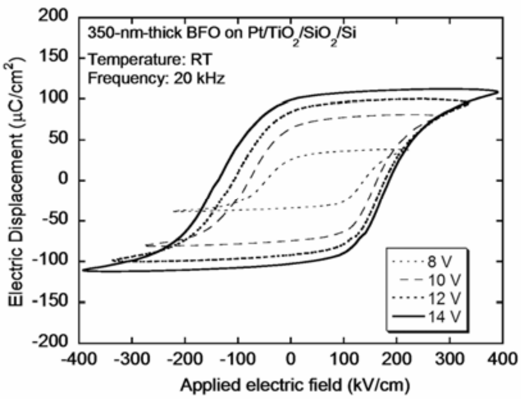

FIG. 2. *D-E* hysteresis loops of polycrystalline BFO thin film at room temperature

1). Before Time-resolved X-ray diffraction measurements, conventional *D*-*E* hysteresis characteristics at RT using bipolar 20 kHz triangular voltage measured by ferroelectric test system (Toyoechnica FCE-1) were shown in Fig. 2. Ferroelectric hysteresis loops were obtained over 8 V maximum applied voltages. And the remanent polarization (P_r) was 103 μC/cm^2 with a maximum applied voltage of 14 V. This ferroelectric property at RT shows good agreement with previous report.[7] Time-resolved X-ray diffraction measurements in air at RT were performed using a six-axis diffractometer and avalanche photodetector for high speed detection at beamline BL13XU for surface and interface structures, in synchrotron radiation facility SPring-8.[13] To obtain enough diffracted X-ray intensity, measurement time used was 50 sec at every 2θ points. Therefore, for preventing from time dependent dielectric breakdown and heating damage to sample capacitor, unipolar rectangular shape pulse voltage with 150 nsec width was repeatedly applied with a period of 804.09 nsec. The pulses were synchronized with synchrotron radiation source, and applied to top Pt electrode by high speed ferroelectric test system (Toyotechnica FCE-HS3) and tungsten needle probe. An X-ray of 12.4 keV was selected with a Si (111) double-crystal monochromater, and in addition, the beam was focused on Pt top electrode. Diffracted X-ray intensity profiles as a function of time at BFO $(001)_{pc}$ peak (2θ: 14.500^o) with applying 12 V pulse and at BFO $(110)_{pc}$ peak (2θ: 20.440^o) with applying 11 V pulse were shown in Figs. 3(a) and 3(b), respectively (where pc subscript denotes pseudocubic indices). The intensity was clearly changed with applying voltage, and the rise time of the intensity was about 50 nsec in both of intensities at 14.500^o and at 20.440^o. Such a long response time is constrained by *RC* time constant of the sample capacitor and measurement system. These results indicate that time-resolved X-ray diffraction measurements under electric field were performed in polycrystalline thin film. Figures 4(a) and 4(b) show voltage dependence of θ-2θ scan around BFO $(001)_{pc}$ and BFO $(110)_{pc}$ diffraction peaks during voltage application. These peaks were shifted to lower angle as increasing applied voltage. When 12 V and 11 V pulse voltage were applied, BFO $(001)_{pc}$ and BFO $(110)_{pc}$ diffraction peaks were slightly shifted from 14.602^o to 14.588^o and from 20.520^o to 20.505^o, respectively, These results indicated that both of $(001)_{pc}$- and $(110)_{pc}$-oriented domains in BFO thin films are expanded in perpendicular to the film plane because of electric-field-induced strains. Figures 5 shows electric-field-induced strain of BFO $(001)_{pc}$- and BFO $(110)_{pc}$-oriented domains estimated from peak shifts. The strain in both of $(001)_{pc}$- and $(110)_{pc}$-oriented domains increased linearly. Therefore, these electric-field-induced strains are due to piezoelectric responses, in addition, there is no electric field induced phase transitions in these applied voltage regions at RT. The d_{33} component of piezoelectric tensor is described

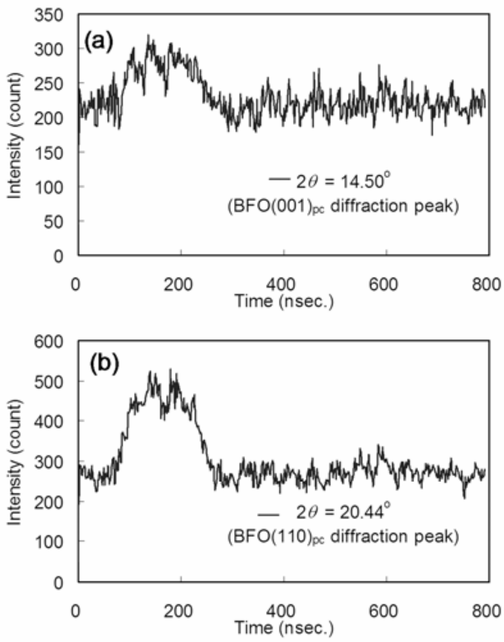

FIG. 3 Diffracted X-ray intensity profiles as a function of time (a) at BFO $(001)_{pc}$ diffraction peak (2θ: 14.500^o) under 12 V, 150 nsec width and 804.09 nsec period pulse application and (b) at BFO $(110)_{pc}$ diffraction peak (2θ: 20.440^o) under 11 V, 150 nsec width and 804.09 nsec period pulse application

by coupling of piezoelectric strain ε_3 and applied electric field E_3 along the direction of measured strain ε_3 as $\varepsilon_3 = d_{33} E_3$. The d_{33} components of $(001)_{pc}$- and $(110)_{pc}$-oriented domains estimated from Fig. 5 were 27.8 pm/V and 26.4 pm/V, respectively. These values were smaller value compared to the value measured by scanning probe microscope in previous report.[8] Moreover, in these voltage regions, *D-E* hysteresis loop does not fully saturate as shown in Fig. 2. Thus, piezoelectric responses with minor hysteresis loop were obtained in these results. However, time-resolved X-ray diffraction measurement under electric field was done in polycrystalline BFO thin film.

In summary, X-ray diffraction under electric field using 12.4 keV synchrotron radiation have been measured in $(001)_{pc}$- and $(110)_{pc}$-oriented polycrystalline 350-nm-thick $BiFeO_3$ thin film on Pt (200 nm)/TiO_2 (50 nm)/SiO_2 (600 nm)/Si (625 μm) substrate. When 12 V [11 V] pulse voltage have been applied, diffraction peak of $(001)_{pc}$ [$(110)_{pc}$] plane shifts from 14.602° [20.520°] to 14.588 [20.505°] due to piezoelectric response. The piezoelectric constants (d_{33}) of $(001)_{pc}$-oriented and $(110)_{pc}$-oriented domain estimated from these peak shifts were 27.8 pm/V and 26.4 pm/V, respectively. However, *D-E* hysteresis loop did not fully saturated in these voltage regions.

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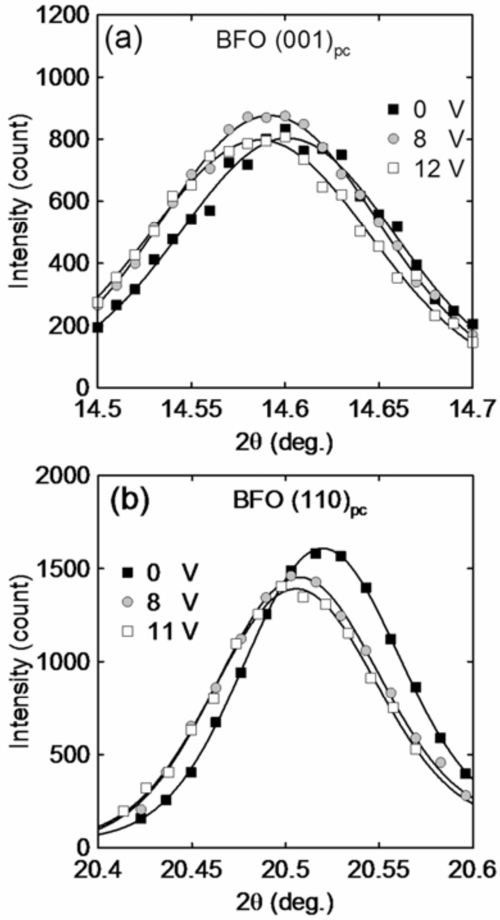

FIG. 4. Voltage dependence of θ-2θ XRD patterns around (a) BFO $(001)_{pc}$ diffraction peak and (b) BFO $(110)_{pc}$ diffraction peak under 150 nsec width and 804.09 nsec period pulse application

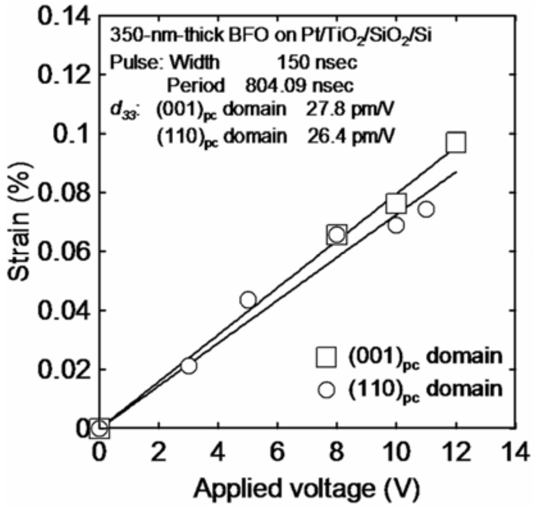

FIG. 5. Voltage dependence of electric-field-induced strain of (a) $(001)_{pc}$- and (b) $(110)_{pc}$-oriented domains

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