Polarization reversals in ferroelectrics have been the topic of intensive study due to their potential applications in memory storage and integrated microelectronics. Bi4Ti3O12 (BIT) has a pronounced spontaneous polarization $P_s$ along the $a$ axis, which is known to be the largest so far in the series of layered ferroelectrics. Cummins and Cross reported a maximum value because of the difficulty in confirming the full switching along the spontaneous polar axis. On the other hand, substitution techniques using lanthanoid and higher-valent cations have been performed to compensate for defects or the complexes. The substitution techniques improve the apparent ferroelectricity, but it has not been clarified yet how the substitution affects the $P_s$. We perform combined electrical, electromechanical, and optical approaches for 400-nm-thick Bi$_4$Ti$_3$O$_{12}$ BNT 0 x 0.73 epitaxial thin films to establish the intrinsic $P_s$ of the films.

The $P_s$ or saturation polarization $P_{sat}$ if the electric field was not applied along the spontaneous polar axis is defined as a y intercept of a tangent drawn to a polarization-electric field $P$-$E$ hysteresis loop. On the other hand, piezoelectric coefficient and soft-mode frequency are correlated with the polarization.

The effective piezoelectric coefficient $d$ is designated as

$$d = 2Q_0 P_s$$

consisting of $Q$ the electrostriction coefficient, $P_s$ the dielectric constant, and $P$ the polarization. Assuming a constant electrostriction coefficient, we can estimate the relative amplitude of the remanent polarization $P$, from the effective piezoelectric coefficient, e.g., effective $d_{33}$, at zero bias field. A reverse piezoelectric response was recorded using piezoresistance force microscopy (PFM), where the tip is in contact with the ferroelectric layer without top electrodes. In this study, we would treat a direct electric signal from the PFM in unit of millivolts instead of an effective $d_{33}$ value that may be converted from the signal with a force curve measurement. The standard deviation in the PFM measured $d_{33}$ value of a single grain does not exceed 10%.

Mean-field theory describes $P_s$ as a function of the soft-mode frequency, which is expressed by

$$M q^2 = 2 Q^2 + 0 q$$

consisting of $M$ the mass of the ions related to soft mode, $q$ the soft-mode frequency, the anharmonic ratio, $Q$ the order parameter, $P_s$, and $0 q$ is a correction term for the third-order anharmonics and a long-range interaction. In the case of displacive-type ferroelectrics, a short-range interaction is mainly responsible for the soft mode, so that the last correction term can be ignored. Therefore, $P_{sat}^2$ is a function of square of the soft-mode frequency, which can be identified by Raman scattering. These approaches will provide complementary information to a $P$-$E$ hysteresis measurement for probing $P_s$.

Figure 1 shows $P$-$E$ hysteresis loops of 110 BNT thin films measured via circular Pt top electrodes of 100 μm in diameter. No $P$-$E$ hysteresis was observed for pure BIT in the case of the low resistivity. The estimated $P_{sat}$ reached the maximum at around $x = 0.26 - 0.35$, then signiﬁcantly dropped with the incorporation of Nd into the Bi$_4$Ti$_3$O$_{12}$.
In the surface topographic images, the films were poled by a dc field with amplitude in-plane phase in 10 kHz measured with a 20 Hz triangular wave. This built-in field pointing to the bottom electrode assists in the switching of the polarization towards the bottom electrode by a negative electric field but in return hampers an upward full switching the polarization towards the bottom electrode by a positive electric field. The inhomogeneous piezoresponse in the negative poled region showed a homogeneous piezoresponse of the BIT film in Fig. 2. However, a slight internal bias aligned to the interface with the bottom electrode probably be-cause of oxygen vacancies. With the Nd substitution, the internal bias field towards the bottom electrode, which is identical to that at the outside nonpoled region, was observed; however, the reason for the present case is not clear. Probably, the switching mechanism is different for the Ti3O12 films deposited epitaxial and the non-epitaxial films.10 Prior to piezoresponse measurements, the films were poled by a dc field with amplitude: 1.5 V; frequency 10 kHz. The estimated polarization-electric field hysteresis loops for the BIT film and for the BNT film are presented nearly equal upward and downward coercive voltage \( V_c \) and remnant polarization \( P_r \). The estimated coercive field \( E_c \) of the BNT films is \( 0.73 \), and the estimated coercive field \( E_c \) for the BIT film and in 5 \( x = 0.26 \) showed significantly smaller average coercive voltage \( V_c \) and remnant polarization \( P_r \). The estimated coercive field \( E_c \) for the BNT films with \( x = 0.42 \) showed a large distribution. The present downward internal bias field, the piezoelectric hysteresis loops have negative field offset. The BNT films with \( x = 0 \), \( 0.2 \), \( 0.26 \), and \( 0.73 \) showed that the net polarization states as can be seen in Figs. 2–2. The inhomogeneous piezoresponse as a function of the dc bias. Due to the static piezoresponse directly on the film surface without the top electrode. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 137.43.140.249 On: Fri, 22 Nov 2013 17:04:27
This phenomenon will be more serious as the film thickness decreases and this effect was observed for all compositions. The relative ferroelectric properties, which were evaluated by dividing the piezoresponse amplitude by the relative dielectric constant of the Nd content for the BNT films, the direction of the top internal field will be maximum at $P_r = 0.2$. On the other hand, both of the relative hysteresis loops increased and then decreased at $Zr = 0$. The capacitors with Pt top electrode pads used for the electrostrictive coefficient of the Nd content for the BNT films, the direction of the top internal field was not observed for the $Zr$ content. The absolute $P_e$, the reorientation of the polarization as well as the defect complexes, is associated to the interface as well as the bottom interface. Because an obvious coupling effect for BIT reached $38.13$. The relative $P_e$ given by the piezoresponse microscopy, and Raman measurements. The absolute $P_e$, the square of soft-mode frequency were also displayed. The relative $P_e$ estimated from the polarization–electric field hysteresis, PFM, and Raman measurements and found that these techniques are effective for the defects and internal bias field, is highly dependent on the large bismuth-layered ferroelectrics, it was shown that the lanthanide substitutions release the fixed polarization sacrificing the large area of the ferroelectric devices.

This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions.