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Visualization of dielectric constant-electric field-temperature phase maps for imprinted relaxor ferroelectric thin films

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The dielectric phase transition behavior of imprinted lead magnesium niobate–lead titanate relaxor ferroelectric thin films was mapped as a function of temperature and dc bias. To compensate for the presence of internal fields, an external electric bias was applied while measuring dielectric responses. The constructed three-dimensional dielectric maps provide insight into the dielectric behaviors of relaxor ferroelectric films as well as the temperature stability of the imprint. The transition temperature and diffuseness of the dielectric response correlate with crystallographic disorder resulting from strain and defects in the films grown on strontium titanate and silicon substrates; the latter was shown to induce a greater degree of disorder in the film as well as a dielectric response lower in magnitude and more diffuse in nature over the same temperature region. Strong and stable imprint was exhibited in both films and can be utilized to enhance the operational stability of piezoelectric devices through domain self-poling. © 2016 AIP Publishing LLC.

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Understanding the dielectric behaviors in relaxor ferroelectrics (FEs) is of great importance not only for studying thermally induced phase transitions, but also for high performance electromechanical actuators and sensors. Relaxor FEs, in contrast to conventional FEs, are characterized by suppression of long-range ordering of the spontaneous polarization and derive their dielectric behaviors from localized polar nano-regions. The polar nano-regions persist above a temperature $T_{\text{max}}$, at which the relative dielectric constant ($\varepsilon_r$) is maximum, whereas they become frozen into a disordered glassy state at temperatures below $T_{\text{max}}$. Especially, in the vicinity of the morphotropic phase boundary, where relaxor-based FEs undergo a structural transition induced by changes in chemical composition, large dielectric responses and exceptional electromechanical properties have been observed. For solid-solutions of the prototypical relaxor FE Pb(Mg1/3Nb2/3)O3 with the normal FE PbTiO3 (PMN-PT), ultrahigh piezoelectric coefficient of 2000–3000 pC/N is reported. Recently, high-performance piezoelectric MEMS (micro-electromechanical systems) devices have been demonstrated by exploiting PMN-PT thin films on SrTiO3 (STO)-buffered Si substrates, exhibiting strong piezoelectricity and a good figure of merit ($\varepsilon_r^2 / \varepsilon_f \varepsilon_0$) for energy harvesting applications. In particular, the enhanced figure of merit was aided by a large imprint of $\sim$40 kV/cm, which suppressed $\varepsilon_r$ at the zero-field condition; tuning the system to exhibit stronger imprint may further suppress $\varepsilon_r$, in turn augmenting the energy harvesting performance of such films operating in the $e_{31}$ mode.

Imprint strongly affects the dielectric behaviors of relaxor-based FE thin films. Imprint, which manifests as a lateral shift in polarization ($P$)-electric field ($E$) hysteresis loops, originates from the presence of internal electric fields. Given that the relative dielectric permittivity, $\varepsilon_r$, is proportional to $dP/dE$, the dielectric behaviors in imprinted relaxor FE thin films are also shifted along the $E$-axis in accordance with the magnitude and direction of the internal electric fields. In order to understand the dielectric behaviors in specimens with imprinted hysteresis, an external $E$ bias with the same magnitude and the opposite direction should be applied to compensate internal fields while measuring the $T$-dependence of the dielectric responses. Because this is rarely done, the influence of the imprint on the dielectric properties and its temperature-dependent stability is not well studied.

In this work, three-dimensional (3D) dielectric maps were visualized in order to investigate the imprint effect on the dielectric response of relaxor FE PMN-PT thin films. This was accomplished by repeatedly measuring $\varepsilon_r$-$E$ loops with increasing $T$ and then constructing 3D $\varepsilon_r$-$E$-$T$ phase maps by integrating the measured dielectric hysteresis loops with respect to $T$. Based on the constructed dielectric maps, the relationship between structural and dielectric properties in the PMN-PT thin films is discussed in conjunction with disorder inside the films.

For this aim, two epitaxial 0.70PMN-0.30PT thin films with different strain states were prepared using rf magnetron sputtering. Through a comparison with bulk PMN-PT, it was...
found that a Pt (40 nm)/PMN-PT (500 nm)/SrRuO₃ (100 nm) film on a STO (001) substrate is under in-plane compressive strain [Fig. 1(a)], whereas another Pt (40 nm)/PMN-PT (500 nm)/SrRuO₃ (100 nm) film on a STO-buffered Si substrate is under in-plane tensile strain [Fig. 1(b)]. Detailed information on the in-plane and out-of-plane lattice constants is given in supplementary Table S1. The in-plane and out-of-plane strain (Fig. 1(a)) indicates high crystalline quality. The in-plane epitaxy was confirmed via rocking curves [supplementary Figs. S1(a) and S1(b)], and along with the out-of-plane rocking curves [supplementary Figs. S1(c) and S1(d)] indicating high crystalline quality. Electrical measurements were performed in Pt/PMN-PT/SrRuO₃ capacitors 100 µm in diameter. P–E hysteresis loops were collected by applying triangular pulse fields with the amplitude of 240 kV/cm at a frequency of 1 kHz using a Precision Multiferroic tester (Radiant Technologies, Inc.). Dielectric constant and loss data were recorded under ac fields with the amplitude of 50 mV and the frequency of 100 kHz using a precision LCR meter (Hewlett Packard 4284A).

FIG. 1. Structural characterization of 500-nm-thick epitaxial 0.7PMN-0.3PT films. Reciprocal space maps show the in-plane strain states of 0.7PMN-0.3PT films on (a) STO and (b) STO-buffered Si (001) substrates. Both films exhibit phase purity and in-plane epitaxy as indicated by X-ray diffraction. 20-θ scans, as shown for the film on (c) STO and (d) STO-buffered Si (001) substrates, respectively.

Figures 2(a) and 2(b) show P–E and \( \varepsilon_r–E \) hysteresis loops of PMN-PT thin films on STO and STO-buffered Si (001) substrates at room temperature, respectively. A larger remanent polarization (\( P_r \)) of \( \sim 27.3 \mu C/cm^2 \) was observed in the PMN-PT films on STO (001) substrates than that of \( \sim 9.7 \mu C/cm^2 \) in PMN-PT films on STO-buffered Si (001) substrates. Considering that the films on STO and STO-buffered Si substrates are under in-plane compressive and tensile strain with respect to bulk PMN-PT (\( P_{r,bulk} \sim 30 \mu C/cm^2 \)) (not shown here), respectively, the difference in \( P_r \) between the PMN-PT films is attributed to a strain effect. In contrast, in dielectric hysteresis loops, the maximum dielectric constant (\( \varepsilon_r,max \sim 1380 \)) in the PMN-PT films on STO (001) substrates is smaller than that (\( \sim 1750 \)) in the films on STO-buffered Si (001) substrates, although the effective tunability, \( (\varepsilon_r,max/\varepsilon_r,min) \), is comparable between the two films. Interestingly, for the PMN-PT films on STO-buffered Si (001) substrates, a strong imprint of \( \sim –65 kV/cm \) is observed in both P–E and \( \varepsilon_r–E \) hysteresis loops. Note that imprint in the PMN-PT films on STO (001) substrates is \( \sim –15 kV/cm \). Furthermore, the \( T \) dependence of the imprint is quite different for the PMN-PT films on STO and STO-buffered Si (001) substrates [Figs. 2(c) and 2(d)]. For the PMN-PT films on STO substrates, the absolute value of the imprint decreases with increasing \( T \), whereas it is almost constant in the films on STO-buffered Si substrates. This \( T \) dependence of the imprint emphasizes the necessity of \( E \) sweep in \( T \)-dependent dielectric response measurements in relaxor FE thin films.

3D maps of \( \varepsilon_r, E \), and \( T \) in PMN-PT thin films are shown in Fig. 3. To achieve this, \( \varepsilon_r–T \) loops were obtained by sweeping electric fields from negative to positive bias in a stepwise manner at room temperature as shown Fig. 2(b);
this procedure was repeated at discrete $T$ intervals of 10°C to yield comprehensive 3D dielectric maps. For more details of this measurement technique, see supplementary Fig. S2.16. It was found that the true maximum values ($\varepsilon_{\text{r,max}}$, $E_{\text{max}}$, and $T_{\text{max}}$) in $\varepsilon_{\text{r}}$–$E$–$T$ phase maps deviated from those at zero-field due to imprint. For the PMN-PT films on STO and STO-buffered Si substrates, $\varepsilon_{\text{r,max}}$ are 5150 and 1810, $E_{\text{max}}$ are $-15$ and $-60$ kV/cm, and $T_{\text{max}}$ are 185 and 110°C, respectively.

Figs. 4(a) and 4(b) show that the dielectric behaviors in the PMN-PT films on STO-buffered Si substrates are more diffuse in both $E$- and $T$-axes than those on STO substrates. Figures 4(c) and 4(d) represent cross-sectional $T$-dependent dielectric responses on the planes of $E = E_{\text{max}}$ and $E = 0$. For both PMN-PT samples, it is clearly shown that dielectric responses at the electrically loaded condition are much larger than those at the zero-field condition in a wide range of $T$.

To examine the strain effect on dielectric phase transition in PMN-PT thin films, the dielectric behaviors of thin film samples were compared with that of bulk PMN-PT. This was done for the conditions where the internal fields in the thin films are compensated to facilitate comparison to the zero field data for bulk PMN-PT. As shown in Fig. 5(a), the dielectric permittivity in PMN-PT thin films is one order of magnitude smaller than the bulk value, consistent with a substrate clamping effect. A shift in $T_{\text{max}}$ is also observed in the two PMN-PT film samples; the PMN-PT films on STO-buffered Si substrates exhibit a maximum in $\varepsilon_{\text{r}}$ at a slightly lower $T$ ($\Delta T_{\text{max}} \sim -20$°C), whereas the shift is towards higher $T$ for the films on STO substrates ($\Delta T_{\text{max}} \sim 55$°C). Such changes in $T_{\text{max}}$ by substrate-induced strain are consistent with previous reports for epitaxial PMN-based films. The $T$-dependent dielectric loss [Fig. 5(b)] also had a shifted $T_{\text{max}}$, almost identical to that in $T$-dependent dielectric permittivity data.
Dielectric peak broadening, indicative of a “smearing” out of the dielectric phase transition, was observed in both PMN-PT thin films, though it is more pronounced in the films on STO-buffered Si substrates. While the presence of an effective “dead” layer at the surface of a dielectric film has been demonstrated to suppress and broaden the dielectric response near \( T_C \), these results may also be a consequence, at least in part, of the epitaxial quality of the PMN-PT thin films. Note that incorporation of defects during growth can result in inhomogeneous strain fields within the film, broadening the phase transition. Structural data (full-width half-maximum (FWHM) in rocking curve measurements and unit cell volume in the supplementary Table S1) demonstrate that the film quality is inferior to that of the PMN-PT films on STO substrates, probably due to the existence of oxygen vacancy defects. The formation energy of oxygen vacancies in complex oxide films is reduced by tensile strain, supporting this conclusion.

It is important to consider the origin of the internal fields in PMN-PT thin films. In normal and relaxor FEs, various mechanisms for the internal field development have been proposed, including the existence of charged defects (trapped charges, defect dipole complexes), film/electrode interface effects (charge injection, the formation of passive or “dead” layers), the generation of built-in potential owing to asymmetric top and bottom electrodes, composition gradients, and flexoelectric fields induced by strain gradients. Note that both PMN-PT thin films in this work have the same Pt top and SrRuO\(_3\) bottom electrodes, suggesting that this alone cannot explain the large discrepancy in the magnitude of the imprint exhibited between the films on STO and STO-buffered Si substrates. Furthermore, the flexoelectric coefficient of PMN-PT would be insufficiently large to produce internal fields of the magnitude observed. Considering that the strain states in two PMN-PT samples are relaxed throughout the film thickness, any flexoelectric field would...
be negligible. Thus, considering that the PMN-PT thin films on STO-buffered Si substrates incorporate a number of vacancy defects, the internal fields may be attributed to composition gradients, charge trapping, or defect dipoles.

In summary, 3D $e_r$–$E$–$T$ phase maps of relaxor FE films with internal field bias were constructed. It was revealed that the shape and position of a $e_r$ peak in dielectric behaviors of PMN-PT thin films are quite different from the bulk properties depending on the strain state. Consequently, the construction of such 3D dielectric phase maps is crucial to visualizing the dielectric responses, as they can be strongly modified by internal fields. Furthermore, the internal bias field developed in the relaxor FE films is comparatively stable as a function of $T$. For applications to piezoelectric thin-film devices, the robust internal fields are of practical interest, leading to enhanced domain stability over a wide $T$ range.\[31\]

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16See supplementary material at http://dx.doi.org/10.1063/1.4944774 for X-ray diffraction data and visual explanation of permittivity measurements.