In-plane dielectric properties of epitaxial $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.35\text{PbTiO}_3$ thin films in a very wide frequency range

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The in-plane dielectric properties of epitaxial $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.35\text{PbTiO}_3$ thin films deposited on MgO by pulsed-laser ablation were determined over a wide frequency range and compared with single crystals and ceramics. Depressed values of the dielectric constant, induced diffused phase transition, dielectric relaxation, and nonlinear behaviors were observed in the films. The overall dielectric behaviors of the films were found to be a mixture of that of relaxor ferroelectrics and normal ferroelectrics. The correlation of the microstructural features (mechanical clamping, small grain size, and epitaxial nature) and the dielectric behaviors was discussed.

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Lead magnesium niobate ($\text{Pb}[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3$, abbreviated as PMN) has been extensively studied since it was first synthesized in the late 1950s. Outstanding properties, such as high dielectric constant and very large piezoelectric coefficient, have been discovered in PMN-based ceramics and single crystals, making these materials very useful for electronic components, such as multilayer capacitors, actuator, and sensors, etc. To pursue the mechanism for the unique dielectric and piezoelectric behaviors of this compositionally and microstructurally complicated and diversified material family is rather challenging; and this may be an important reason for the materials being so attractive to materialists and physicists. The research effort for decades has led to the establishment of various models to interpret the origin of the special properties in PMN-based ceramics and single crystals. In the last few years, there has also been an increasing interest in the development of PMN-based thin films for microelectromechanical systems and electro-optical (EO) devices. Comparatively, the structure-property relationship in thin films is more complicated than that in bulk materials due to interface effect and size effect. So far, however, the investigation on the dielectric properties of PMN-PbTiO$_3$(PT) films in literature is rather limited.

In this letter, the in-plane dielectric properties of PMN-PT thin films were investigated. The nominal composition of the films was 0.65 PMN–0.35 PT, a composition near the morphotropic phase boundary (MPB), where the giant piezoelectric effect and large EO effect are observed. The dielectric characterization was conducted along an in-plane direction rather than along a regular out-of-plane direction not only because the in-plane dielectric behaviors had seldom been studied, but also because the actual devices may work under in-plane electrical fields.

The thin films were deposited by pulsed-laser deposition using a krypton fluoride (KrF) excimer laser (Lambda Physik COMPex 205) with a wavelength of 248 nm. Important processing parameters for the deposition were as follows: (a) Background vacuum $=10^{-7}$ Torr; (2) target: 0.65 PMN–0.35 PT ceramics; (3) atmosphere and pressure during deposition: high-purity O$_2$, 200 mTorr; (4) substrate (MgO) temperature $=660^\circ$C; and (5) laser beam energy density $=2\ J/cm^2$, repetition rate $=6\ Hz$. After deposition, the film was annealed in the chamber at $660^\circ$C for 10 min and then cooled down in O$_2$. The thickness of the film was 400 nm.

X-ray diffraction was performed on a Bruker AXS D8 Discover X-ray Diffractometer. The $\theta$–$2\theta$ scan of the sample revealed that PMN-PT has a pure perovskite phase. The off-axis $\phi$ scan of the (101) reflection of the PMN-PT film revealed that the film grew with a “cube-on-cube” epitaxy on the (001) MgO substrate. The lattice parameters of the films were determined. The films were found to have a tetragonal structure. The out-of-plane lattice parameter of the film was found to be 0.4029 nm, slightly smaller than the $c$-axis length of bulk 0.65PMN–0.35PT single crystal (0.4044 nm). On the contrary, the in-plane lattice parameter of the film was 0.4015 nm, slightly larger than the $a$-axis length of bulk 0.65PMN–0.35PT (0.4 nm). This lattice deformation in our PMN-PT film is believed to be a result of the lattice mismatch between PMN-PT and the substrate MgO (cubic symmetry, lattice parameter $=0.4190$ nm, larger than the lattice constant of PMN-PT). The result also implies that PMN-PT is stressed in tension in the film-substrate interface and in compression in the out-of-plane direction. The in-plane strain calculated from the measured lattice parameter is $-0.38\%$, an order of magnitude less than the lattice misfit ($\sim4.8\%$), which is consistent with observations in similar systems. The morphology of the films (not shown) was observed under atomic force microscope (AFM). The average grain size was found to be about 40 nm in diameter.

The in-plane dielectric properties of PMN-PT films were determined by using coplanar interdigital electrodes (IDE). The top electrodes were prepared by the deposition of an 80-nm-thick Au layer on the film surface followed by patterning using standard photolithography and wet chemical etching techniques. The electrode finger width was 10 $\mu$m.
and the finger gap was 5 μm. In order to avoid the possible influence of dielectric anisotropy of PMN-PT on the measurement results,20 the IDE fingers on all samples were kept to be parallel to the in-plane [010] direction of MgO substrate. Three commercial instruments—Agilent impedance analyzer 4194A, Hewlett Packard impedance analyzer 4291B, and Agilent network analyzer 8720ES—were employed in the dielectric measurements so that the tests could cover a wide frequency from 100 Hz to 10 GHz. The capacitance from the calculation of the capacitance of the sample to obtain the dielectric constant of the material was conducted by using a program that we developed based on Gevorgian’s model,21,22 which has established the relationship between the capacitance and the electrode sizes and the material properties. The dielectric constant (ε) versus temperature (T) dependence of PMN-PT films was determined at three frequencies: 1 kHz, 100 kHz, and 1 MHz. The maximum dielectric constant (ε_m) at these three frequencies was found to be 2720, 2480, and 2380, respectively. In the measurement frequency range, ε_m all occurred at about 158 °C, with a broadened peak around this temperature (T_m). A typical ε−T curve (measured at 1 MHz) is shown in Fig. 1. As for comparison, our experimental results on the films together with the literature data23 of PMN-PT single crystal and ceramics near the MPB are listed in Table I. As shown in this table, a significant depression in the ε value is observed in the films. The room temperature ε of the film is about 20% of the ε value of the single crystals and the ceramics. The peak value ε_m of the film remains only about 4% of ε_m of the single crystal or 7% of ε_m of the ceramics.

While T_m for the three forms of PMN-PT are almost the same, there are noticeable differences in the shape of peaks. 0.65PMN−0.35PT single crystal behaves like a normal ferroelectric and exhibits a sharp ε−T peak.18 The ε−T peak of ceramics is less sharp.17 For our PMN-PT films, the peak is quite broad. In the literature,24,25 the ε−T relationship of PMN-based materials was often empirically fitted into the following equation: 1/ε−1/ε_m=(T−T_m)/C, where r and C are constants. The constant r is roughly a measure of the “normality” of ferroelectricity, with values ranging from 1 (normal ferroelectric) to 2 (“relaxor”). Our regression using literature data17,18 has revealed that r (0.65PMN-0.35PT single crystal)≈1 and r (ceramic) ≈1.4; both values are reasonable and understandable. For our sample, we have found r (film)≈2. The (1/ε−1/ε_m) vs (T−T_m)^2 data points of our thin films could be well fitted to a straight line, as shown in the inset of Fig. 1. This result implies that the typical relaxor characteristics of diffused phase transition (DFT) are induced in these compositionally “normal” ferroelectric films. However, they are not absolute relaxor ferroelectrics since T_m does not change with the frequency of the measurement.

The room-temperature ε−f relationship of PMN-PT films is shown in Fig. 2. The dielectric constant decreases as the frequency increase, followed by a dramatic drop starting at about 300 MHz. When f < 300 MHz, ε is found to keep a linear relationship with ln f: ε(f)=ε(∞)+A ln f=1315−23.75 ln f, a behavior which is likely related to the reversible domain-wall motion.26 When f > 300 MHz, the films exhibit a Debye relaxation: ε(f)=ε(∞)+[ε(0)−ε(∞)]/[1+(2πfτ_0)^2]=96.5+782.5/[1+(2π×9×10^11×f)^2]. The value of the relaxation time obtained from the regression, τ_0, is quite reasonable in physics. The Debye-like relaxation in the low-gigahertz frequency region in our PMN-PT film is a result of ion vibration (phonon) that is probably the ferroelectric soft-mode movement in the material.27

When domain-wall motion exists in the system, a hysteresis effect should be expected. We did observe such an
effect as a strong dependence of \( \varepsilon \) on the dc bias over a frequency range from 100 Hz to 50 MHz in our films. As shown in Fig. 3, the film exhibits a butterfly-shaped \( \varepsilon - E \) and \( \tan \delta - E \) dependence (\( E \) is defined as the ratio of dc bias over finger gap). The electric field of the occurrence of \( \varepsilon \) (maximum), \( E_m \), which actually corresponds to the coercive field (\( E_c \)), was found to be about 14.1 kV/cm at this frequency. In the frequency range of observation, \( E_c \) was found to be almost independent on \( f \). The maximum dielectric tunability \( \Delta \varepsilon / \varepsilon = (\varepsilon_{\text{max}} - \varepsilon_{\text{min}}) / \varepsilon_{\text{max}} \) is found to be 49\% at 1 MHz. In the whole measurement range, the value of the tunability varies within 45\%--55\%, showing a noticeable trend of decrease with the increase of frequency.

The experimental results shown above indicate that the PMN-PT films did not behave either as a typical relaxor ferroelectric or a typical “normal” ferroelectric. Instead, the in-plane dielectric properties are much like a mixture of the two. The mechanism is not yet clear. Nevertheless, the following three microstructural features should be very important factors to consider: (1) The lattices are epitaxially aligned in three directions; (2) the grain size is about 40 nm in diameter, only about 100 times larger than a lattice cell; and (3) the film is mechanically clamped on the substrate. Because of the aligned nature of the lattice, the film did not exhibit strong frequency dispersion; and its coercive field is almost frequency independent. The clamping effect and the small grain sizes (thus, the films have a larger amount of the low-\( \varepsilon \) grain boundaries than single crystals and ceramics) are responsible for the depression of the \( \varepsilon \) value. The grain size may have a certain distribution, leading to a diffused phase transition. More theoretical work is still undertaken.

In summary, the in-plane dielectric properties of epitaxial 0.65PMN–0.35PT thin films grown on MgO have been determined over a wide frequency range. The films exhibit a depressed value of \( \varepsilon \) and an induced diffused phase transition. At room temperature, a dielectric relaxation with frequency and a strong dielectric nonlinearity against dc bias were observed. The overall dielectric behaviors of the films were neither a typical relaxor ferroelectric nor a normal ferroelectric.

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\[ \text{TABLE I. Comparison of the dielectric properties of 0.65PMN-0.35PT thin films with single crystals and ceramics.} \]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Single crystal along 001-direction (Ref. 18)</th>
<th>Ceramics (Ref. 17)</th>
<th>Films in-plane along 010-direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon ) (at room temperature)</td>
<td>5000 (1 KHz)</td>
<td>5230 (1 KHz)</td>
<td>1160 (1 KHz)</td>
</tr>
<tr>
<td>( \varepsilon_m )</td>
<td>65,000 (1 KHz)</td>
<td>1030 (100 KHz)</td>
<td>980 (1 MHz)</td>
</tr>
<tr>
<td>( T_m )</td>
<td>( \sim 160^\circ \text{C} )</td>
<td>( \sim 160^\circ \text{C} )</td>
<td>( \sim 158^\circ \text{C} )</td>
</tr>
<tr>
<td>Peak shape at MPB</td>
<td>Sharp</td>
<td>Less sharp</td>
<td>Board</td>
</tr>
</tbody>
</table>

23Due to the strong anisotropy of PMN-PT, a fairer comparison can be made between the permittivity along the [010] direction of the film and the same direction of the single crystal. Technically this is difficult due to (1) the lack of single-crystal data and (2) the difference between the electric-field distribution along an in-plane direction in a thin film and that in a bulk single crystal.