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Multiferroic epitaxial Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ thin films: A relaxor ferroelectric/weak ferromagnet with a variable structure

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The authors report the structural, ferroelectric, and ferromagnetic properties of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ epitaxial thin layers grown on (001), (110), and (111) SrTiO$_3$ substrates by pulsed-laser deposition; films were of sufficient resistivity to enable high-field $P$-$E$ measurements. Findings are as follows: epitaxial strain results in (i) a dramatic increase in the spontaneous polarization $P_s$; (ii) a lattice structure that is dependent on substrate orientation; (iii) a slim-loop response and relaxor ferroelectric characteristics in the dielectric constant, both of which are nearly independent of crystallographic orientation; and (iv) a weak ferromagnetic moment, which is dependent on epitaxial mismatch. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357926]

Lead iron niobate, Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ (PFN), was discovered by Smolenskii et al. in the 1950s. It is a multiferroic transforming from a paraelectric (cubic) phase to a ferroelectric (rhombohedral) one at a Curie temperature of 385 K, concurrently from a paramagnetic state to antiferromagnetic (AFM) spin-order one at a Néel temperature of 143 K, and subsequently undergoing a secondary AFM—AFM transition at 19 K. The room temperature lattice structure of PFN single crystals is rhombohedral, with lattice parameters of $a_r=4.0123$ Å (or 4.058 Å) and $a_c=89.89^\circ$. It is a mixed B-site cation perovskite and accordingly could be anticipated to have relaxor ferroelectric characteristics similar to Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$, such as slim-loop polarization ($P$-$E$) characteristics and a polarization dynamics that scale to a Vogel-Fulcher or stretched exponential relations.

The dielectric, ferroelectric, and ferromagnetic properties of PFN bulk single crystals and ceramics have been reported. The maximum polarization is only $\sim 10$ $\mu$C/cm$^2$. The $P$-$E$ response is “nonsquare” yet hysteretic, the dielectric breakdown field is low, and the weak-field dielectric loss ($or$ $\tan \delta$) factors are quite high. These limited dielectric and ferroelectric properties of bulk crystals and ceramics are believed to reflect inferior dielectric insulation, presumptively attributed to conductive losses via valence band hopping due to Fe$^{3+} \rightarrow$ Fe$^{2+}$. In addition, the induced magnetization of PFN single crystals at 80 K has been reported to be $<100$ emu/cm$^3$ unders a magnetic field of $H=10^5$ Oe. Unlike a normal AFM, at lower fields of $H<2\times10^4$ Oe, the induced magnetization was not linear with applied $H$; rather, the $M$-$H$ response was slim loop with a saturation magnetization of $M_s=20$ emu/cm$^3$, indicative of a weak ferromagnetism with no remanence.

Nonepitaxial thin layers of PFN have been previously prepared by sol-gel and pulsed-laser deposition (PLD). Superior ferroelectric properties were reported in both cases, relative to bulk crystals and ceramics. Sedlar and Sayer found the maximum polarization to be $P_m=24$ $\mu$C/cm$^2$ for sol-gel films, and Gao et al. reported a value of $P_m=22$ $\mu$C/cm$^2$ for PLD films deposited on La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$. However, epitaxial PFN films have yet to be prepared and studied. The ferroelectric and ferromagnetic properties of epitaxial thin layers with large stictions have been shown to be significantly altered by epitaxial strain. An in-plane compressive stress can result in an increase of the out-of-plane remanent polarization; however, biaxial tension will result in decreased out-of-plane polarization. For example, the apparent value of $P_s$ was increased (by approximately ten times) to 60 $\mu$C/cm$^2$ for [001]-epitaxial BiFeO$_3$ (BFO) thin layers grown on SrRuO$_3$/SrTiO$_3$ (or SRO/STO) electrode/substrate, relative to [001]-oriented bulk crystals; also, for epitaxial BaTiO$_3$ thin layers, $P_s$ has been found to be increased to 80 $\mu$C/cm$^2$. Furthermore, epitaxial strain results in important structural and magnetic property changes, relative to those of corresponding bulk crystals. For example, (001), (101), and (111) epitaxial BFO thin layers are tetragonal $(T)$ monoclinic $A$ $(M_A)$, and $R$, respectively.

Here, we report the structural, ferroelectric, and ferromagnetic properties of epitaxial PFN thin layers grown on SrRuO$_3$/SrTiO$_3$ by PLD that were quite resistive. In order to ensure the stoichiometric ratio of different ions, we fabricated PFN targets using a single-step solid-state reaction method. First, powders of PbO, Fe$_2$O$_3$, and Nb$_2$O$_5$ of >99.9% purity were stoichiometrically mixed with a 5% excess of PbO and then milled, calcined at 850 °C for 3 h; remilled, powders sieved, targets pressed, and subsequently sintered at 920 °C for 3 h in a PbO-rich atmosphere. Epitaxial thin layers of PFN were then deposited on STO substrates with (and without) a SRO buffer (electrode) layer by PLD. The energy density of the KrF laser (Lambda 305i) was 1.2 J/cm$^2$, and the distance between target and substrate was 6 cm. A bottom SRO electrode was first deposited on the STO substrate at 650 °C at a growth rate 0.7 nm/min. Films of PFN were then deposited at 630 °C at a growth rate of 10 nm/min to an average layer thickness of $\sim 200$ nm. A top gold electrode was then deposited by sputtering. The crystal structure of the films was measured using a Philips X’pert system equipped with a two-bounce hybrid monochromator, an open three-circle Eulerian cradle, and a domed hot stage. Mesh and line scans were both obtained to confirm the epitaxial film’s orientation and phase purity. All measurements were referenced to the reciprocal lattice unit of $a^* = 2\pi/a = 1.635$ Å$^{-1}$. The following properties of the films were measured using the respective measurement systems: the polar-
had thicknesses of about 200 nm and resistivities of
investigation of polarization reversal. 
Such high layers. We achieved room temperature values on order of
vice 16, and 15 kV/mm, respectively. It is important to note that
respectively; correspondingly, the coercive fields were 16,
width half maximum mismatches as summarized in Table I: 
the epitaxial mismatch and the peak broadness are consistent with each other for the various ori-
ments, revealing that they are largest for the
broadness are consistent with each other for the various ori-
enplane parameters of the var-
next, the structure and surface morphology of the PFN thin films were measured by x-ray diffraction (XRD) and atomic force microscopy, respectively. XRD line scans of PFN thin layers grown on (001), (110), and (111) STO substrates buffered with a SRO thin layer are shown in Fig. 1(a). From this figure, we established that all of our thin layers were phase-pure perovskite and also epitaxial. Mesh scans (not shown) demonstrated good epitaxy on the substrate. The atomic force image shown in Fig. 1(b) reveals a surface roughness of ~10 nm and an average crystallite size of ~150 nm.

We summarize how the room temperature lattice structure of PFN films depends on orientation, as given in Table I. We found that (001) oriented films had a tetragonal (T) structure with lattice parameters of $a_{T}=4.010$ Å (in plane) and $c_{T}=4.071$ Å (out of plane); that (110) oriented films had an orthorhombic (O) structure with a doubled unit cell and lattice parameters of $a_{O}=5.696$ Å (in plane), $b_{O}=5.670$ Å (out of plane), and $c_{O}=4.025$ Å (in plane); and that (111) oriented films had a rhombohedral (R) structure with lattice parameters of $a_{R}=4.027$ Å (out of plane) and $\gamma=89.98^\circ$, which is similar to that previously reported for bulk PFN single crystals which is the R phase with $a_{R}=b_{R}=c_{R}$. The lattice mismatch ($\epsilon$) between substrate and film can be calculated as 
$\epsilon=[(a_{film}-a_{substrate})/a_{substrate}]\times100\%$. The lattice parameter of the STO substrate was $a_{substrate}=3.905$ Å. Using our respective values for the in-plane lattice parameter of the variously oriented films, we can estimate the epitaxial lattice mismatches as summarized in Table I: $\epsilon_{(001)}=4.26\%$, $\epsilon_{(110)}=3.20\%$, and $\epsilon_{(111)}=3.17\%$. In addition, the values of full width half maximum (FWHM) are also summarized in Table I. It can be seen that the FHWM was larger for the (001) films (0.16°) than for either the (110) or (111) films (0.05°–0.06°). The results for the epitaxial mismatch and the peak broadness are consistent with each other for the various orientations, revealing that they are largest for the (001) film and notably less for the (110) and (111) which are nearly equivalent to each other.

Figure 2(a) shows the $P-E$ response of PFN thin layers with out-of-plane orientations of (001), (110), and (111). The maximum polarization can be seen to achieve values approaching $70 \mu C/cm^2$ under electric fields of $E > 190$ kV/cm, which is much larger (nine times and three times) than that previously reported (bulk and thin layers, respectively). The remanent polarizations of the (001), (110), and (111) oriented thin layers were 18, 17, and 13 $\mu C/cm^2$, respectively; correspondingly, the coercive fields were 16, 16, and 15 kV/mm, respectively. It is important to note that the induced polarization under a constant field level was nearly equivalent for all three orientations. For example, consider $E=125$ kV/cm, the induced polarizations were 56, 54, and 47 $\mu C/cm^2$ for (001), (110), and (111) oriented films. These results clearly demonstrate that the polarization

![AFM image demonstrating the morphology of a typical PFN film.](image)

**FIG. 1.** (Color online) XRD and AFM results of PFN thin film. (a) Line scan over wide angles, demonstrating phase purity and good epitaxy; and (b) AFM image demonstrating the morphology of a typical PFN film.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\gamma$ (deg)</th>
<th>Structure</th>
<th>FWHM (deg)</th>
<th>$\epsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) STO</td>
<td>4.010</td>
<td>4.010</td>
<td>4.071</td>
<td>90</td>
<td>Tetragonal</td>
<td>0.16</td>
<td>4.26</td>
</tr>
<tr>
<td>(110) STO</td>
<td>5.696</td>
<td>5.670</td>
<td>4.025</td>
<td>90</td>
<td>Orthorhombic</td>
<td>0.06</td>
<td>3.20</td>
</tr>
<tr>
<td>(111) STO</td>
<td>4.027</td>
<td>4.027</td>
<td>4.027</td>
<td>89.98</td>
<td>Rhombohedral</td>
<td>0.05</td>
<td>3.17</td>
</tr>
</tbody>
</table>
of PFN epitaxial thin layers is nearly independent of orientation. It is not anisotropic, but rather nearly isotropic: in spite of the fact that the crystal structure and lattice parameters were different.

We then measured the temperature dependence of the dielectric constant for the various oriented films, as given in Fig. 2(b). The value of the dielectric constant ($\varepsilon \approx 1000$ at 300 K and $\varepsilon \approx 2000$ at 400 K) and its maximum ($T_C \approx 400$ K) can be seen to be nearly constant for the various orientations. This value of $T_C \approx 400$ K is consistent with prior investigations of bulk crystals/ceramics, although the value of $\varepsilon$ is notably smaller for the thin layers than reported for bulk PFN. In addition, the temperature dependence of $\varepsilon$ revealed a strongly diffuse or broadened phase transition for the slip-loop-like frequencies for a bulk PFN. In addition, the temperature dependence of $H$ on the higher the mismatch, the larger the magnetization.

This result confirms prior reports of high dielectric loss in the relaxor state is invariant to changes in apparent phase characteristics, with a Curie temperature of ~400 K; and a weak ferromagnetic moment, where the moment is seemingly dependent on epitaxial mismatch.

In summary, we have deposited epitaxial PFN thin layers on (001), (110), and (111) SRO/STO. Our results demonstrate a relaxor ferroelectric state, whose crystal lattice structure and lattice parameters are variable to epitaxial mismatch but whose polarization and dielectric constant are nearly independent. Specifically, we find that (i) the structure is dependent on the substrate orientation, (001), (110), and (111) films are $T$, $O$, and $R$, respectively; (ii) the value of $P_x = 70$ $\mu$C/cm$^2$ is notably larger than that of bulk crystals, nearly independent of film orientation and lattice structure, and possesses a weak ferromagnetic moment, where the moment is seemingly dependent on epitaxial mismatch.

This research work was supported by the Department of Energy and by Air Force Office of Scientific Research.

FIG. 2. (Color online) Polarization and weak-field dielectric constant of variously oriented PFN films. (a) Polarization as a function of $E$ at 300 K, where data for nonepitaxial films and bulk ceramics are illustrated by dashed line; (b) complex dielectric constant as a function of temperature taken at a measurement frequency of 1 kHz for variously oriented films, where the inset shows that of (110) films for various frequencies; and (c) magnetization as a function of $H$ at 5 K.