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<td>Li, Jiefang; Wang, Junling; Wuttig, M.; Ramesh, R.; Wang, Naigang; Ruette, B.; Pyatakov, A. P.; Zvezdin, A. K.; Viehland, D.</td>
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Dramatically enhanced polarization in (001), (101), and (111) BiFeO₃ thin films due to epitaxial-induced transitions

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Dramatically enhanced polarization has been found for (001), (101), and (111) films, relative to that of BiFeO₃ crystals. The easy axis of spontaneous polarization lies close to (111), for the various oriented films. BiFeO₃ films grown on (111) have a rhombohedral structure, identical to that of single crystals; whereas films grown on (101) or (001) are monoclinically distorted from the rhombohedral structure, due to the epitaxial constraint.

Ferromagnetoelastic materials have two order parameters. These are a spontaneous polarization \( P_s \) and a spontaneous magnetization \( M_s \). Of particular interest is BiFeO₃ (BF), which exhibits the coexistence of ferroelectric and antiferromagnetic (G-type) order up to quite high temperatures. In bulk single crystals, BiFeO₃ has a ferroelectric Curie temperature \( T_C \) of 850°C, and an antiferromagnet Néel temperature \( T_N \) of 310°C. The lattice structure of BiFeO₃ crystals is a rhombohedrally distorted perovskite, which belongs to the space group \( R3\text{c} \) (or \( C\text{6v} \)). The rhombohedral unit cell parameters are \( a_r = 3.96 \text{ Å} \) and \( \alpha_r = 60.6° \).

In this structure, the hexagonal (001) oriented films. BiFeO₃ has antiferromagnetic order. Microscopically, the antiferromagnetic spin order is not homogeneous. An incommensurate spin cycloid with a long wavelength \( \lambda \approx 600 \text{ Å} \) is present, which is oriented along \((111)_{\text{H}}\). The 3 m magnetic point group allows for a linear magnetoelectric effect \( \alpha_e \), but for BiFeO₃ the antiferromagnetic vector and linear magnetoelectric effect are both averaged to zero over \( \lambda \).

Recently, dramatically increased \( P_s \) and \( \alpha_e \) have been reported in epitaxial thin films of BiFeO₃ grown on (001). SrTiO₃. For example, the \( P_s \) of (001) BiFeO₃ thin films is \( \approx 0.6 \text{ C/m}^2 \)—which is \( \approx 20 \times \) larger than that of a bulk crystal. Clearly, heteroepitaxy induces significant and important structural changes. The lattice parameters, \( (c,a) = (4.005,3.935) \text{ Å} \), of thin films are not the rhombohedral ones of bulk single crystals and ceramics, \( (a_r = 3.96) \text{ Å} \).

FIG. 1. Reciprocal space scans for BiFeO₃ single crystals taken about various zones about (001). (a) \((H0L)\) zone; (b) \((HHL)\) zone; and (c) \((HHH)\) zone. The intensity is given on a log scale.
TABLE I. Summary of interplanar spacing and lateral correlation lengths oriented from small area reciprocal lattice scans for the variously oriented BiFeO$_3$ films and crystal. Peak splitting was observed along the (101) and (111), the relative intensities are designated by $I$, and the weaker peak is designated by brackets.

<table>
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<tr>
<th>Lattice spacing</th>
<th>Crystal</th>
<th>(111) film</th>
<th>(101) film</th>
<th>(001) film</th>
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<tr>
<td>$d_{(001)}$</td>
<td>3.958 Å</td>
<td>3.959 Å</td>
<td>3.984 Å</td>
<td>4.001 Å</td>
</tr>
<tr>
<td>$d_{(101)}$</td>
<td>2.783 Å ($I$=0.62)</td>
<td>2.810 Å</td>
<td>2.828 Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[2.809 Å ($I$=0.38)]</td>
<td></td>
<td>[2.816 Å ($I$=0.28)]</td>
<td></td>
</tr>
<tr>
<td>$d_{(111)}$</td>
<td>2.277 Å ($I$=0.87)</td>
<td>2.306 Å ($I$=1.00)</td>
<td>[2.278 Å ($I$=0.02)]</td>
<td>2.278 Å ($I$=0.90)</td>
</tr>
<tr>
<td></td>
<td>[2.306 Å ($I$=0.13)]</td>
<td></td>
<td>[2.307 Å ($I$=0.98)]</td>
<td>[2.304 Å ($I$=0.10)]</td>
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was chosen as the bottom electrode due to the closest lattice mismatch with the BFO structure. Films of SRO of 500 Å were deposited at 600°C in an oxygen ambient of 100 mTorr; and followed by the BFO film, deposited at 670°C in an oxygen ambient of 200 mTorr at the growth rate of 0.7 Å/s. The BiFeO$_3$ film thicknesses were all close to 2000 Å, which is necessary to reduce the influence of film thickness.$^{16}$ if the out-of-plane lattice parameters are to be compared. Chemical analysis was carried out by SEM x-ray microanalysis, indicating a cation stoichiometry in the BFO films of ∼1:1. Reciprocal lattice mapping was performed using a Phillips MPD system. Ferroelectric measurements were performed using a RT 6000 test system (Radiant Technologies).

Mesh scans that were taken about (001), (101), and (111) for a BiFeO$_3$ bulk single crystal are shown in Figs. 2(a)–2(c), respectively. A single peak was found along the (001), with $d_{(001)}$=3.958 Å. This is in agreement with previous reports of rhombohedral phase.$^{5,7,11}$ Peak splitting was found along the (101) with $d_{(101)}$=2.783 and 2.809 Å, and along the (111) with $d_{(111)}$=2.277 and 2.306 Å. The values of the interplanar spacings are summarized in Table I. These results evidence a polydomain rhombohedral state.

Mesh scan taken along (001), (101), and (111) are shown in Figs. 2(a)–2(c) for a (111) oriented BiFeO$_3$ thin film. Both a sharp peak from the SrTiO$_3$ substrate (illustrated by arrows) and a broad peak from the film (grey lines to guide eyes) can be seen in each figure. The values of $(HKL)$ were determined by referencing to the interplanar spacings of the bulk single crystal ($d_{(001)}$=3.958 Å, $d_{(101)}$=2.809 Å, and $d_{(111)}$=2.306 Å). The (111) oriented BiFeO$_3$ films were found to grow epitaxially on (111) SrTiO$_3$ substrates with values of the interplanar spacing of $d_{(001)}$=3.959 Å, $d_{(101)}$=2.810 Å, and $d_{(111)}$=2.306 Å. These interplanar spacings are equal to those of the bulk single crystal, as can be seen by comparisons in Table I. Apparently, the (111) BiFeO$_3$ films are in a single domain state with a rhombohedral structure.

The lattice structure of the (101) and (001) oriented BiFeO$_3$ thin films was found to be monoclinically distorted from the rhombohedral one. Mesh scans taken about (001), (101), and (111) are shown in Figs. 2(d)–2(f) for (101) films, and Figs. 2(g)–2(i) for (001) films, respectively. The values of the interplanar spacings are summarized in Table I. For both the (101) and (001) films, the values of $d_{(111)}$ were equal to those of the rhombohedral phase, whereas $d_{(101)}$ and $d_{(001)}$ were split. The (101) film is nearly single domain with $d_{(111)}$=2.307 Å (relative intensity, $RI$=0.98) and $d_{(101)}$=2.828 Å ($RI$=0.02), whereas the (001) film had a peak splitting about (111) and (101), with the dominant variant having values of $d_{(111)}$=2.277($RI$=0.9) Å and $d_{(101)}$=2.792 Å ($RI$=0.72). The value of $d_{(111)}$ is equal to that of one of the domain variants of the rhombohedral structure of the bulk crystal; whereas $d_{(110)}$ was notably different than that for the bulk single crystal. This splitting indicates domain formation, with two variants populated. For both (101) and (001) oriented films, pronounced deviations in the value of $d_{(001)}$ were found from that of the bulk rhombohedral lattice. The value of $d_{(001)}$ increased from 3.959 Å for the (111)
film, to 3.984 Å for the (101) film, to 4.001 Å for the (001) film.

A mesh scan about the $HLH$ zone around (001) is shown in Fig. 3 for the (001) oriented BiFeO$_3$ thin layer. This contour scan was taken only along the film peaks, avoiding those of the substrate. The contour lines in Fig. 3 are given in a logarithmic scale. Three peaks can be seen consisting of (i) a splitting of $a$ domains along ($H00$); and (ii) a splitting between $a$ and $c$ domains ($HOL$). These data give evidence that the stable phase of (001) oriented BiFeO$_3$ epitaxial thin layers is monoclinic. The monoclinic lattice parameters are $(a_m=b_m=c_m; \beta=90^{\circ})=(4.001 \, \text{Å}, 3.935 \, \text{Å}; 0.6^{\circ})$. This is the monoclinic $M_2$ structure. It should be noted that the monoclinic angle $\beta$ of the thin layer is nearly equal to that of the rhombohedral angle $\alpha$ of the bulk crystal. These results are preliminary to a further study of this film by synchrotron x-ray,19 which is now being carried out.

On (111), BiFeO$_3$ films grow in an unconstrained single domain condition. The crystal structure is rhombohedral and identical to that of bulk crystals. Films grown on either (101) or (001) are under significant epitaxial constraint. The crystal structure is monoclinically distorted from the rhombohedral structure. It should be noted that the monoclinic angle $\beta$ of the thin layer is nearly equal to that of the rhombohedral angle $\alpha$ of the bulk crystal. These results are preliminary to a further study of this film by synchrotron x-ray,19 which is now being carried out.

We also investigated the effect of orientation of this constrained crystallographic film state on the physical properties of BiFeO$_3$. The ferroelectric properties were characterized by a polarization hysteresis method. For each orientation, we observed hysteresis loops typical of a ferroelectric. We found a remanent polarization $P_r$ of $\sim 55 \mu$C/cm$^2$ for (001) films, $\sim 80 \mu$C/cm$^2$ for (101) films, and $\sim 100 \mu$C/cm$^2$ for (111) films. Figure 4 shows $3P_r(001)$, $2P_r(101)$, and $P_r(111)$ as a function of $E$ for the variously oriented films. In this figure, the values of the projected polarizations can be seen to be nearly equivalent. This confirms that the direction of spontaneous polarization lies close to (111), and that the values measured along (101) and (001) are simply projections onto these orientations. Clearly, similar to bulk crystals and ceramics, the spontaneous polarization is oriented close to (111). However $P_s$ is dramatically increased!

In summary, BiFeO$_3$ films grown on (111) have a rhombohedral structure, identical to that of single crystals, whereas films grown on (101) or (001) are monoclinically distorted from the rhombohedral by epitaxial constraint. The easy axis of spontaneous polarization lies close to (111) for the variously oriented films.

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19. G. Xu and G. Shirane (private communication).