

Ferroelectric polarization rotation in order-disorder-type

LiNbO₃ thin films

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Abstract

We observed ferroelectric polarization rotation in order-disorder-type LiNbO_3 (LNO) thin films. By introducing Li-vacancies via pulsed laser deposition, we fabricated LNO thin films with a freedom of ferroelectric polarization direction. The ferroelectric spontaneous polarization rotated from an out-of-plane to an in-plane direction with increasing Li vacancy concentration, within the hexagonal lattice framework. Partial inclusion of monoclinic phase was attributed for the inversion symmetry breaking along the in-plane direction.

INTRODUCTION

The ability to rotate spontaneous polarization in ferroelectrics provides a crucial insight in understanding and utilizing the piezoelectric and ferroelectric properties.

For example, at a morphotropic phase boundary (MPB), *i.e.*, a phase border between two phases with different polarization directions which shows an enhanced piezoelectric response, the ferroelectric polarization rotation should be necessarily accompanied [1-6]. Thus, the rotation of the ferroelectric polarization is closely coupled with the ferroelectric instability and piezoelectric elongation [5,6], which are imperative in improving the performances of ferroelectric sensors and energy harvesting devices.

More specifically, in ferroelectric oxide thin films, attractive ferroelectric phenomena have been observed as the polarization rotation is induced via elemental doping and/or epitaxial strain. An enhanced piezoelectricity was observed by doping Co in ferroelectric BiFeO₃ thin film, as the polarization direction rotated with the structural phase transition from a tetragonal to a monoclinic phase [7]. In PbTiO₃/CaTiO₃ superlattices, large dielectric constant was obtained at a specific tilt angle of the polarization direction, during the variation of the CaTiO₃ volume fraction [8]. In PbZr_{1-x}Ti_xO₃, epitaxial strain induced rotation of the electric dipole resulting in the structural twinning in the thin film [9,10]. More recently, a continuous rotation of the polarization was observed, realizing a polar vortex structure with converging dipoles in ferroelectric superlattices [11,12].

Up to now, such rotation of the polarization direction has only been demonstrated in displacive-type ferroelectrics. In a displacive-type ferroelectric, the lowest energy position can shift continuously, resulting in a systematic rotation of electric dipoles with structural modification. In an order-disorder-type ferroelectric, however, such rotation of microscopic electric dipoles is not expected. It is because the lowest energy position is more or less fixed, even above the ferroelectric transition temperatures. Therefore,

observation of the polarization rotation in an order-disorder-type ferroelectric would help expanding our knowledge on the ferroelectric oxides substantially.

LiNbO₃ (LNO) is a classic order-disorder-type ferroelectric material with its spontaneous polarization due to the displacement of Li and Nb ions along the *c*-axis direction of the hexagonal unit cell [13]. The structure belongs to *R3c* spacegroup at room temperature. It shows large remnant polarization of $\sim 70 \mu\text{C}/\text{cm}^2$, piezoelectric response of $\sim 6 \text{ pm}/\text{V}$ and attractive optical properties such as birefringence [13-18]. Photovoltaic effect related to the ferroelectricity has also been discussed in LNO, despite the wide band gap of $\sim 4 \text{ eV}$ [15]. The LNO lattice structure consists of Li-O trigon and Nb-O octahedron along the *c*-axis of the hexagonal unit cell. Li ions were found to play a dominant role in giving rise to the ferroelectric property according to a first-principles calculation [19]. The displacement of Li ions is either upward or downward relative to the triangular oxygen layer, resulting in the spontaneous polarization along the *c*-axis direction only. Nb atom also moves within the octahedral for additional contribution.

In order to examine the effect of the epitaxial strain and low dimension, and possible device applications, the growth of LNO thin film has been pursued using various substrates, including Si and Al₂O₃. Despite the large lattice mismatch (-7% , compressive), LNO thin films have been mostly grown on the sapphire substrates maintaining the same hexagonal structure [20-22]. In addition, LNO films have been grown on GaAs substrate or using buffer layers, such as ZnO and SiO₂, on Si substrates [23-25]. However, the thin films do not have ideal crystalline quality or show proper ferroelectricity expected from LNO bulk crystals. Hence, realization of the LNO thin films with good crystallinity would expand the possibilities for manipulating the ferroelectric properties and help us study the fundamental coupling between the charge dynamics and lattice structures.

In this paper, we present rotation of the spontaneous polarization direction in an order-disorder-type ferroelectric LNO thin film by introducing elemental vacancies.

The strong coupling between the chemical potential and the lattice structure induces rotation of the polarization within the LNO crystal. The unprecedented polarization rotation in an order-disorder-type ferroelectric could be understood in terms of inclusion of anti-site defects and local monoclinic LiNb_3O_8 structure which has off-centered ions along the in-plane direction. As a result, a LNO thin film with fully in-plane ferroelectric polarization could be obtained.

EXPERIMENTAL METHODS

Thin film growth

We fabricated (001) LNO thin films by pulsed laser deposition (PLD) under various $P(\text{O}_2)$ of 5-50 mTorr. The thin films were deposited on atomically flat (111) SrTiO_3 (STO) and Nb:0.5wt% doped (111) STO (Nb:STO) substrates at 600°C. Laser fluence of $\sim 1.5 \text{ J/cm}^2$ was used. The thickness of the thin films was about 75 nm confirmed from scanning transmission electron microscopy (STEM).

Structural characterization

X-ray diffraction (XRD) θ - 2θ and pole figure measurements were performed using high resolution XRD (Rigaku Smartlab). 2θ positions were aligned to the Bragg reflection conditions of SrTiO_3 (110) and monoclinic LiNb_3O_8 ($\bar{2}12$) at $2\theta = 32.3963^\circ$ and 32.2000° , respectively. Scanning transmission electron microscopy (STEM) was also performed on the two of our samples.

X-ray spectroscopy

Qualitative change in the stoichiometry was obtained by x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) at room temperature. XPS

was carried out with a monochromated Al- $K\alpha$ x-ray source ($h\nu = 1486.6$ eV) with the step size of 0.05 eV at a pass energy of 50.0 eV. The spot size was 400 μm . XAS, ...

Second harmonic generation

Second harmonic generation (SHG) at room temperature was performed in order to confirm the structural inversion symmetry breaking.

Piezoelectric force microscopy

Piezoelectric force microscopy (PFM) was conducted for the measurement of piezoelectric coefficient of the ferroelectric LNO thin films. Conducting Nb:STO substrates were used as the bottom electrode.

Electrical measurement

Electrical measurements were performed along the in-plane direction. Au electrodes were used with a distance of 75 μm . **IV measurements UV light with ~ 3.8 eV we measured in LNO thin films on STO substrate to minimize the leakage current, and used two Au electrode pad with a distance of $\sim 75\mu\text{m}$ along in-plane direction.**

RESULTS & DISCUSSIONS

We achieved systematic vacancy modulation in LiNbO_3 (LNO) thin films using pulsed laser deposition (PLD), while preserving the global hexagonal structural framework. Figure 1 shows the lattice and atomic structures of (001) LNO thin films grown on (111) STO (SrTiO_3) or Nb-doped STO substrates under different oxygen partial pressures ($P(\text{O}_2)$). Between $P(\text{O}_2)$ of 5 and 50 mTorr, phase pure LNO thin films have been deposited. All of the thin films were highly oriented along the LNO 00 l -direction, as evidenced from the x-ray diffraction (XRD) θ - 2θ scans (Fig. 1(a)). To the best of our knowledge, LNO thin film growth on STO (111) substrates has not been reported, partially due to the large lattice mismatch [26]. Ideally, STO (5.52 Å) substrate imposes

rather large tensile strain (+7%) with a larger in-plane lattice constant compared to that of bulk LNO (5.15 Å), which hampers the epitaxial growth. Nevertheless, a highly oriented crystal structure of the LNO thin film has been realized in this study, based on the same in-plane hexagonal symmetry and taking into account of chemical strain, which will be discussed later. While preserving the overall lattice framework, a variation in the $P(\text{O}_2)$ -induced systematic changes in the out-of-plane lattice constant, as shown in Fig. 1(b). In particular, the out-of-plane lattice constant of LNO thin film increased with increasing $P(\text{O}_2)$ from 5 to 30 mTorr, and then saturated. The large values of lattice constant compared to the bulk value (2.31 Å) might suggest off-stoichiometry in the thin films [27]. Specifically, Li vacancies have been widely discussed in LNO crystals due to the light-weight-nature of the element [28,29].

Upon performing scanning transmission electron microscopy (STEM), we could further confirm the microscopic atomic structure and strained nature of the LNO thin films. Figures 1(c)-1(f) show STEM images of the LNO thin films grown at 5 and 30 mTorr. The images are shown for the $(1\bar{1}0)$ cross-sectional plane of the STO substrates. From low resolution images (Figs. 1(c) and 1(d)), a coherently grown LNO thin films with hexagonal structure can be observed. In addition, the interface between the thin film and the substrate is not atomically sharp, and an intermixing layer with a thickness of ~1 nm could be observed. The intermixing layer might result from the large lattice mismatch as previously discussed. From the high resolution images (Figs. 1(e) and 1f), both the in-plane and out-of-plane lattice constants can be obtained. Surprisingly, the in-plane lattice constant of LNO thin films grown at 5 and 30 mTorr is the same (~5.23 Å), despite the existence of the amorphous-like intermixing layer. Since the out-of-plane lattice constant obtained from both XRD and STEM consistently shows ~1% of differences between the film grown at 5 and 30 mTorr, the identical in-plane lattice parameter suggests that the thin films are at least partially strained. Therefore, the thin intermixing layer, even though it might be amorphous, seems to transmit strain and facilitate the coherent growth of the LNO thin film. The lattice expansion due to the non-

stoichiometry, together with the existence of the intermixing layer, makes it difficult to apply the nominal lattice mismatch of 7% in our LNO thin films. The expanded lattice due to the chemical strain reduces the tensile strain from the substrate, again facilitating the coherent growth of the thin film. STEM images also clearly depict the displacement of Nb atoms along the out-of-plane direction, as expected from the normal polar crystal structure of bulk LNO, as schematically shown in Fig. 1(e). The displacement of Nb, together with the displacement of Li which was not observable for the current STEM measurements, should provide the microscopic origin of the ferroelectricity in LNO thin films.

As the stoichiometry determines the atomic and crystal structures, we measured x-ray photoemission spectroscopy (XPS) to obtain relative atomic concentrations. Figure 2 shows that **with the increase of $P(O_2)$, Li concentration decreased significantly, while Nb and O concentrations increased steadily within the LNO thin films.** As $P(O_2)$ increased from 5 to 50 mTorr, spectral weight of Li 1s decreased systemically as shown in Fig. 2(a). The low Li concentration suggests that the light-weight Li atoms scatter easily with ambient oxygen during the deposition at high $P(O_2)$. Nb and O concentrations have also been obtained (see Supplementary Fig. S1). The large modulation of Li concentration (from 19.8% to 11.2%) and the relatively large Nb concentration (from 26% to 30.1%), let us consider anti-site defects, *i.e.*, Nb ions replacing nominal Li ions in Li sites. Anti-site defect has been often considered in LNO crystals to describe the motion of ferroelectric domain walls [30,31]. Also, we could consider Li-deficient $LiNb_3O_8$ phase, which has also been reported for some PLD-grown thin films [32,33]. These considerations provide ways for understanding modulation of polar behavior in LNO thin films. Additionally, we could determine the oxygen concentration evidently increasing with the increase of $P(O_2)$ using XPS. Such systematic trend in stoichiometry of LNO thin film has also been confirmed using x-ray absorption spectroscopy (XAS). As shown in Supplementary Fig. S2, the valence state of Nb decreases from the nominal value of 5+, suggesting increase of Li and/or decrease of oxygen as $P(O_2)$ decreases.

The Li vacancies led to an unexpected, yet substantial rotation in the ferroelectric polarization direction in the LNO thin films. The rotation of the polarization direction was evidenced by measuring the structural symmetry breaking direction via second harmonic generation (SHG). SHG signal is emitted from dipoles induced by a polarized light applied on a crystal with broken inversion symmetry. We measured three different configurations of the SHG, i.e., $P_{in}P_{out}$, $S_{in}P_{out}$, and $S_{in}S_{out}$ (P - (S -) polarization is perpendicular (parallel) to the film surface). Among these, $P_{in}P_{out}$ and $S_{in}P_{out}$ configurations are relevant for understanding the polarization rotation and shown in the inset of Fig. 3(a). The experimental results from these two configurations can be fit using the relation,

$$I_{PP}(2\omega) = (a_1 + a_2[-3 \sin(\varphi) \cos^2(\varphi) + \sin^3(\varphi)])^2, \quad (1)$$

$$I_{SP}(2\omega) = (b_1 + b_2[-3 \sin(\varphi) \cos^2(\varphi) + \sin^3(\varphi)])^2, \quad (2)$$

based on the $3m$ symmetry of the LNO crystal, where $a_1 = \text{fn}(\chi_{zzz}, \chi_{zxx}, \chi_{xzx})$, $a_2 = \text{fn}(\chi_{yyy})$ and $b_1 = \text{fn}(\chi_{zxx})$, $b_2 = \text{fn}(\chi_{yyy})$ are the constants describing anisotropic symmetry breaking with the susceptibility tensors χ , and φ is the rotation angle [34]. The functions indicate that a_1 and b_1 (a_2 and b_2) are the constants for the symmetry breaking along the out-of-plane (in-plane) direction. The equations (1) and (2) further implies that when the crystal has predominantly out-of-plane symmetry breaking, a_1/a_2 and b_1/b_2 are larger than 1, and the SHG response shows typically 3-fold symmetry. On the other hand, when the crystal has in-plane symmetry breaking components, a_1/a_2 and b_1/b_2 are smaller than 1, and the SHG response shows 6-fold symmetry. The evident evolution of the SHG response from a 3-fold ($P(\text{O}_2) = 5$ mTorr) to a 6-fold ($P(\text{O}_2) = 50$ mTorr) symmetry, clearly suggests that the in-plane symmetry breaking components dominate the LNO thin film as more Li vacancies are induced. The anisotropic symmetry breaking constant obtained from the fitting of SHG signal is shown in Fig. 3(a). As expected, a_1 (a_2) decreases (increases) systematically, as $P(\text{O}_2)$ increases, indicating a rotation of polarization from an out-of-plane direction to an in-plane direction. We note that the a_1/a_2 value for the bulk LNO single crystal ($a_1/a_2 = \sim 2.5$) is considerably larger than that for

the LNO thin film grown at $P(\text{O}_2) = 5$ mTorr ($a_1/a_2 = \sim 0.7$) [34]. This suggests that even the thin film grown at the lowest possible $P(\text{O}_2)$ has considerable amount of in-plane symmetry breaking component, which is consistent with non-zero Li vacancies observed even in the film grown at $P(\text{O}_2) = 5$ mTorr, as shown in Fig. 2(b). The LNO thin film grown at $P(\text{O}_2) = 50$ mTorr shows the a_1/a_2 value of ~ 0.04 , indicating that the thin film has mostly in-plane symmetry breaking.

The rotation of the inversion symmetry breaking direction could further be confirmed using piezoelectric force microscopy (PFM) measured for both the out-of-plane and in-plane direction. The PFM result shows highly anisotropic distribution of the piezoelectric coefficients. The unpoled PFM images of the LNO thin film grown at $P(\text{O}_2) = 5$ mTorr in the upper insets of Fig. 3(b) indicate existence of both out-of-plane and in-plane polarization. On the other hand, the film grown at $P(\text{O}_2) = 30$ mTorr in the lower insets present polarization aligned predominantly along the in-plane direction. By counting the number of pixels on each PFM images, we came up with the histogram as shown in Fig. 3(b). For the LNO thin film grown at low $P(\text{O}_2)$, polarization direction can be considered as a mixture of both out-of-plane and in-plane direction. On the other hand, for the film grown at high $P(\text{O}_2)$, the polarization shows a strong peak along the in-plane direction only and is scattered along the out-of-plane direction. **The PFM result is remarkably consistent with the SHG signal, validating the substantial rotation of the ferroelectric polarization via control of Li-vacancies in the LNO thin films.**

By examining different crystal structures within the LNO polymorphs, we could obtain insight for the origin of the polarization rotation. In particular, the large amount of Li deficiency and relatively high Nb concentration in the LNO films grown at high $P(\text{O}_2)$ let us consider the Li-deficient LiNb_3O_8 phase with monoclinic structure. Indeed, XRD pole figure measurements show the evidence of the monoclinic phase within the LNO thin films, as shown in Fig. 4. When $2\theta = 32.3963^\circ$, the expected 6-fold symmetry of (104) LiNbO_3 diffraction peaks are shown along with the 3-fold (110) STO

substrate diffraction peaks, for the films grown at low $P(\text{O}_2)$ (Fig. 4(a)). On the other hand, when $2\theta = 32.2000^\circ$, a weak twin structure with a 2-fold symmetry could be observed, which is a reminiscent of the $(\bar{2}12)$ Bragg reflection of the monoclinic LiNb_3O_8 phase (Fig. 4(c)). For the LNO films grown at high $P(\text{O}_2)$, the peaks for the monoclinic phase grow in intensity (Fig. 4(d)), and are much broader in the sense that its trace could even be observed when $2\theta = 32.3963^\circ$ (Fig. 4(b)). Moreover, instead of the clear 6-fold symmetry diffraction peaks for the LiNbO_3 phase, a twinned 6-fold symmetry Bragg reflection peaks were obtained when $2\theta = 30.2000^\circ$. The twinning of the crystal might be associated with partially relaxed LNO with double domain [35]. This twinned 6-fold peaks are higher in intensity compared to the 2-fold peaks, indicating that the main structure of the LNO films grown at high $P(\text{O}_2)$ is still a hexagonal one, but with a slightly different structural parameters and twinning owing to the large difference in the Li and Nb concentrations and large in-plane ferroelectricity.

Unlike stoichiometric LiNbO_3 , the monoclinic LiNb_3O_8 can facilitate the in-plane polarization. In bulk, the monoclinic LiNb_3O_8 does not have any out-of-plane ionic displacement as observed for the hexagonal LiNbO_3 (See Supplementary Fig. S3). The absence of the out-of-plane ionic displacement can also be explained in terms of anti-site defect, which restores the inversion symmetry along the out-of-plane direction. Instead, an in-plane ionic displacement can be expected within the $P2_1/a$ structure. While the monoclinic LiNb_3O_8 structure belongs to a centrosymmetric point group, the symmetry breaking due to the off-centered ions along the in-plane direction could be expected with the application of epitaxial strain and elemental vacancies. In addition, the breaking of mirror symmetry can be anticipated, partially based on the observation of the twinned structure.

The in-plane symmetry breaking in LiNb_3O_8 phase would give rise to the in-plane ferroelectric polarization, consistent with our PFM and SHG results. Specifically, (i) the non-zero in-plane polarization for the thin films grown at low $P(\text{O}_2)$, (ii) the increase

of this in-plane polarization with increasing $P(\text{O}_2)$, and (iii) the decrease of the out-of-plane polarization with increasing $P(\text{O}_2)$ can be understood in terms of enlarged monoclinic phase within the LNO thin film due to absence of Li ions. This leads to the rotation of the direction of the spontaneous polarization in the order-disorder-type ferroelectric LNO.

The rotation of the spontaneous polarization direction can have wide implications in engineering various electronic applications, including the ferroelectric photovoltaic effect. In particular, an enhanced photoconduction with the hysteretic behavior was observed for the in-plane photoconductivity measurements of the LNO thin film grown at high $P(\text{O}_2)$. Figure 5 shows the $I(V)$ characteristics of the LNO thin films along the in-plane geometry. The inset in Fig. 5(a) presents the schematic sample geometry. The LNO thin film grown at low $P(\text{O}_2)$ exhibited a limited enhancement with the application of UV light, as shown in Fig. 5(a). The photoconductivity was highly suppressed with the small in-plane ferroelectric polarization present. The ratio between the light and dark current was less than two. On the other hand, for the film grown at high $P(\text{O}_2)$, an enhanced photoconductivity was observed with the ratio $I_{\text{light}}/I_{\text{dark}} = \sim 10$. In addition, a hysteretic $I(V)$ curve was obtained manifesting the effect of in-plane ferroelectric switching due to the polarization rotation. We further note that the overall low current level, which is advantageous for ferroelectric application, might be associated with low oxygen vacancy concentration for the film grown at high $P(\text{O}_2)$.

Summary

In summary, we could rotate the direction of the ferroelectric spontaneous polarization in the order-disorder-type LiNbO_3 thin films by varying the elemental concentrations. By increasing the oxygen partial pressure during the pulsed laser deposition, we could induce Li vacancies, which led to the partial formation of the LiNb_3O_8 phase. The ferroelectric polarization along the out-of-plane direction, expected for the hexagonal LiNbO_3 , tilted

systematically toward the in-plane direction with the introduction of the monoclinic LiNb_3O_8 phase in the thin films. Both second harmonic generation and piezoelectric force microscopy consistently supported the rotation of the spontaneous polarization direction based on the difference in the inversion symmetry breaking direction and anisotropic distribution of the piezoelectric coefficients, respectively. Our result can be beneficial in comprehending the ferroelectricity in the polymorphs of LiNbO_3 , especially for engineering large ferroelectric polarization via charge-lattice coupling in this classic ferroelectric material.

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Figure legends

Figure 1 | Lattice and atomic structures of LiNbO₃ thin films deposited under various oxygen partial pressures. (a) X-ray diffraction θ - 2θ scans for LiNbO₃ thin films grown on SrTiO₃ (111) substrate, without any impurity phases. (b) Change in the c -axis lattice constant as a function of oxygen partial pressure. Low resolution bright-field scanning transmission electron microscopy images for the LiNbO₃ thin film grown at (c) 5 and (d) 30 mTorr. Enlarged images for the films grown at (e) 5 and (f) 30 mTorr. The overall LiNbO₃ structure is preserved regardless of the different oxygen partial pressures used. The scale bars represent 1 nm.

Figure 2 | Relative atomic concentration of the elements in LiNbO₃ thin films. (a) X-ray photoelectron spectroscopy near the Li 1s state. With decreasing oxygen partial pressure during the growth, the reduction of binding energy is observed, indicating the introduction of Li vacancies. (b) Relative atomic concentration (%) as a function of oxygen partial pressure during the growth, revealing a systematic change in the stoichiometry.

Figure 3 | Polarization rotation. (a) Symmetry breaking factors (a_1 and a_2), calculated from fitting data which are classified as P_{in}P_{out} (black) and S_{in}P_{out} (red). a_1 and a_2 represent symmetry breaking along the out-of-plane and in-plane, respectively. The inset shows the experimental (symbols) and fit (lines) data of the second harmonic generation performed on LiNbO₃ thin films, indicating anisotropy in the structural symmetry breaking. (b) The distribution of the polarization phases are shown for the out-of-plane and in-plane piezo-force microscopy on LiNbO₃ thin films grown at 5 (upper panel) and 30 mTorr (lower panel), respectively. The insets show the anisotropic piezo-force microscopic images. The size of the images is $0.5 \times 0.5 \mu\text{m}^2$.

Figure 4 | XRD pole figure analysis. Pole figure measurements on the LNO samples grown at $P(\text{O}_2) =$ (a),(c) 5 and (b),(d) 30 mTorr. Two different 2θ configurations (a),(b)

32.3963° and (c),(d) 30.2000° are used. Hexagonal LiNbO₃ thin film phase with a 6-fold symmetry, monoclinic LiNb₃O₈ phase with a 2-fold symmetry, and cubic SrTiO₃ substrate phase with a 3-fold symmetry can be identified depending on the $P(O_2)$ and 2θ values.

Figure 5 | Anisotropic photoconductivity in the LiNbO₃ thin films. In-plane photoconductivity of the LiNbO₃ thin films grown at (a) 5 and (b) 50 mTorr, respectively. The large in-plane spontaneous polarization in LiNbO₃ thin film grown at high $P(O_2)$ results in hysteresis and enhanced photoconductivity.

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