Controllable defect driven symmetry change and domain structure evolution in BiFeO$_3$ with enhanced tetragonality

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Defect engineering has been a powerful tool to enable the creation of exotic phases and the discovery of intriguing phenomena in ferroelectric oxides. However, the accurate control of the concentration of defects remains a big challenge. In this work, ion implantation, which can provide controllable point defects, allows us to produce a controlled defect driven true super-tetragonal (T) phase with a single-domain-state in ferroelectric BiFeO$_3$ thin films. This point-defect engineering is found to drive the phase transition from the as-grown mixed rhombohedral-like (R) and tetragonal-like (M$_C$) phase to true tetragonal (T) symmetry and induce the stripe multi-nanodomains to a single domain state. By further increasing the injected dose of the He ion, we demonstrate an enhanced tetragonality super-tetragonal (super-T) phase with the largest c/a ratio of $\sim$1.3 that has ever been experimentally achieved in BiFeO$_3$. A combination of the morphology change and domain evolution further confirms that the mixed R/M$_C$ phase structure transforms to the single-domain-state true tetragonal phase. Moreover, the re-emergence of the R phase and in-plane nano-scale multi-domains after heat treatment reveal the memory effect and reversible phase transition and domain evolution. Our findings demonstrate the reversible control of R-Mc-T-super T symmetry changes (leading to the creation of true T phase BiFeO$_3$ with enhanced tetragonality) and multidomain-single domain structure evolution through controllable defect engineering. This work also provides a pathway to generate large tetragonality (or c/a ratio) that could be extended to other ferroelectric material systems (such as PbTiO$_3$, BaTiO$_3$ and HfO$_2$) which might lead to strong polarization enhancement.

As a consequence of strong couplings and complex interplay between defects and the lattice, spin, charge and orbital degrees of freedom in complex oxides, defect engineering provides a plethora of splendid possibilities for creating a wealth of exotic phases and emergent physical phenomena.$^{1–12}$ In ferroelectric oxides, defect engineering is emerging as a powerful pathway to tailor structural transformation and manipulate material properties,$^{8–12}$ e.g., defect induced super-tetragonal PbTiO$_3$ and tetragonal-like BiFeO$_3$ thin films with giant tetragonality and enhanced polarization by the introduction of PbO$_{13}$ and Bi$_2$O$_3$ impurities,$^{14–16}$ respectively. The creation of novel domain states, the control of domain structure evolution, domain wall conduction and polarization switching as well as the enhancement of ferroelectric Curie temperature have also been realized through defect engineering.$^{17–22}$ However, these defects, introduced by changing growth conditions, cannot be precisely controlled. In recent years, the atomic-scale layer-by-layer growth techniques of oxide heterostructures have enabled the controllable introduction of planar defects—interfaces, leading to new modalities arising in superlattices, such as our recent discovery of polar vortices in PbTiO$_3$/SrTiO$_3$ superlattices$^8$ and domain configuration design in BiFeO$_3$/La-BiFeO$_3$ superlattices.$^{23}$ However, the post growth control of these planar defects is not allowed as they are...
imported during the growth process. Therefore, ion implantation, the standard technique to introduce accurately controlled defects post growth in semiconductor devices for the adjustment of electronic properties,24–26 is used in this work to study the controllable defect engineering of structure transformations and domain evolution in ferroelectric BiFeO3 thin films.

As one of the very few known room temperature multiferroic (ferroelectric and antiferromagnetic) materials,27,28 BiFeO3 exhibits rich phase diagrams which include bulk rhombohedral, rhombohedral-like, tetragonal-like and orthorhombic phases that have been theoretically predicted by density functional calculations and phase field simulations,29–31 and experimentally achieved through strain engineering (e.g., epitaxial strain and hydrostatic pressure)39–39 and defect engineering (such as substitutional defects and impurity defects),14,15,40–42 leading to a large number of intriguing properties.29,43–51 Among these, tetragonal-like BiFeO3 driven by epitaxial strain with a large c/a ratio (−1.23) is of great interest due to its giant spontaneous polarization up to 150 μC cm−2.42 Indeed, both theoretical calculations52–56 and experimental studies5,1,14,42,57–59 have demonstrated that ferroelectric oxides with giant tetragonality (or c/a ratio) possess a large polarization as a consequence of their large dipolar moment. However, despite considerable effort and dramatic progress in the research of tetragonal-like (Mc) BiFeO3, broad questions remain: (i) is it possible to stabilize tetragonal-like phase BiFeO3 in thick films while rhombohedral-like (R) phase BiFeO3 generally emerges due to strain relaxation in the films thicker than ~30 nm,29 (ii) is there a pathway to achieve the theoretically predicted true tetragonal (T) phase with a single domain state in the as-grown sample and (iii) could the c/a ratio (tetragonality) be further enhanced to obtain real super-tetragonal (super T) phase BiFeO3 that would lead to a larger spontaneous polarization? These challenges to be addressed are the main focus of this study.

Ion implantation, as a controllable defect engineering route, has enabled the ability to continuously tailor the structure phase transition, electric transport, magnetic properties, and the band gap in epitaxial oxide thin films by driving the out-of-plane lattice expansion while leaving the in-plane lattice epitaxially locked to the substrate.60–64 Very recently, it has also been demonstrated that He ion implantation can be used to control ferroelectric switching behaviors and enhance electrical resistivity in ferroelectric thin films (such as PbTiO3, PbZr0.52Ti0.48O3 and BiFeO3).65–67 However, the use of He implantation to simultaneously control the phase transition and domain structure evolution in BiFeO3 thin films remains elusive.

In this work, we start from BiFeO3 films with a mixed rhombohedral-like (R) and tetragonal-like (Mc) phase. We have discovered that controlled point defects, introduced by He ion implantation, can be used to drive the R-Mc-T-super T phase transition, enabling the formation of a true super-tetragonal phase in 70 nm-thick BiFeO3 films with enhanced tetragonality (c/a ratio ~ 1.3). Implanted He ions in the films enable not only the absence of the R phase but the transformation from the Mc structure to theoretically predicted true T symmetry.52,53 Further increasing the dosages can continuously enhance the c-axis lattice parameter from 4.65 Å to 4.93 Å and the c/a ratio from 1.22 to 1.3 (the largest tetragonality has ever been experimentally obtained in BiFeO3). It is also found that the in-plane nanoscale stripe domains (multi-domains) in the as-grown sample evolve to a single domain state after He implantation, which further confirms the Mc to true T phase transition. Moreover, the annealing process has enabled the re-emergence of the R phase and in-plane stripe nanodomains, demonstrating the reversible control of phase transition via He implantation.

We grew a series of epitaxial 70 nm-thick BiFeO3 films on LaAlO3 (001) substrates by pulsed laser deposition (PLD) at 680 °C under an O2 pressure of 100 mTorr and cooled under 1 atm oxygen atmosphere. After deposition, He ion implantation was carried out at 8 keV with a fluence from 5 × 1014 to 5 × 1015 ions per cm2. A combination of X-ray diffraction (XRD), reciprocal space mapping (RSM) and transmission electron microscopy (TEM) was used for the structural characterization. Morphology changes and ferroelectric domain structures were determined using atomic force microscopy (AFM) and piezoresponse force microscopy (PFM).

The topography of the as-grown sample, as shown in Fig. 1a, was imaged by using the AFM measurement, revealing the coexistence of the striped dark contrast R phase and bright contrast Mc phase matrix in the 70 nm-thick BiFeO3 film, which is consistent with previous work.29 The atomically flat terraces, one unit cell in height, confirm the high quality growth of the film, with a root mean square (RMS) roughness only of 0.2 nm. Interestingly, the striped R phase is greatly reduced after He implantation with the dose of 5 × 1014 ions per cm2, and it completely disappears with the implanted dose up to 5 × 1015 ions per cm2, as presented in Fig. 1b and c, respectively. We infer that there is an R-Mc phase transition induced via He implantation. To verify this hypothesis, X-ray reciprocal space mappings (RSMs) are carried out. RSM (002) reflections in Fig. 1d show the coexistence of R and T-like phases. The three-fold and two-fold splits along (103) and (113) RSMs (Fig. 1g and h) further confirm that the tetragonal-like structure is Mc phase in the as-grown sample, in agreement with previous work.31,35,39 Surprisingly, the mixed R and Mc phases evolve to a true tetragonal structure with an enhanced c/a ratio after He implantation (Fig. 1e, i and j). Although the nearly tetragonal phase was obtained by biaxial strain,58,69 this is the first report to achieve a true T phase in high quality pure BiFeO3 at room temperature, which has only been realized at high temperature or in chemical doping BiFeO3.31,70,71 Moreover, further enhancement of tetragonality (c/a ratio ~1.29) is obtained as the implanted He dose increases to 5 × 1015 ions per cm². Here we refer this tetragonal phase with an ultra-large c/a ratio to a true super-tetragonal (super-T) phase, which is different from the previously...
reported super-tetragonal like phase that is the Mc phase in fact.\textsuperscript{29,33,35,39,72,73} Typical X-ray $\theta - 2\theta$ scans show an obvious peak shift with the increasing implanted dosages, as shown in Fig. 1k, further confirming the Mc-T-super T symmetry changes driven by this controlled defect engineering route. Based on these XRD data (Fig. 1d–k), the dependence of the c/a ratio and c-axis with various He dosages is plotted in Fig. 1l. It shows the continuous enhancement of the c-axis

Fig. 1 (a–c) Morphology evolution in mixed phase BiFeO$_3$ (BFO) with the increase of implanted He dosages. (d–f) RSM (002) reflections corresponding to (a–c) samples reveal the He implantation (defect engineering) induced phase transitions and elongated out-of-plane (c-axis). (g–h) Three-fold and two-fold splits along (103) and (113) RSMs confirm the tetragonal-like Mc phase in the as-grown samples. (i–j) Single peak feature of (103) and (113) RSMs in the He implanted sample indicates the creation of the true tetragonal phase. (k) Typical X-ray $\theta - 2\theta$ scans of the as-grown and He implanted BiFeO$_3$ thin films on LaAlO$_3$ (LAO) substrates. (l) Dependence of the c/a ratio and c-axis lattice parameter with various He dosages.
lattice parameter from 4.65 Å to 4.93 Å and the c/a ratio from 1.22 to 1.29. These are the largest values of the c-axis and c/a ratio which have ever been experimentally achieved in BiFeO₃.

To understand the fine structure of these implanted films, atomic resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) studies were carried out. Fig. 2a shows a dark field cross-sectional STEM image of the implanted film with $2.5 \times 10^{15}$ He per cm², not only confirming the thickness (∼70 nm) of BiFeO₃ and the existence of a single phase (no contrast differences as prior work²⁹,⁷¹), but also revealing the maintenance of high-quality epitaxy with sharp interfaces after He implantation. A high-resolution Z-contrast image of the BiFeO₃/LaAlO₃ interface is shown in the bottom-right insets of Fig. 1a, illustrating the atomic-scale epitaxy between the BiFeO₃ and LaAlO₃ layers. This type of image is sensitive to variations in the atomic number and the intensity corresponds to the increasing Z number. Thus, the elements in decreasing order of brightness are Bi (83) and Fe (26), while O (8) is too light to be visible, which is confirmed in Fig. 1b using an ADF-STEM image and the corresponding EDS mappings. The selected area electron diffraction (SAED) patterns of implanted BiFeO₃ with He doses of $2.5 \times 10^{15}$ and $5 \times 10^{15}$ ions per cm² in Fig. 2c and d reveal the existence of a single T phase (i.e., absence of the R phase) and the enhancement of c/a ratios to 1.27 and 1.30, respectively. Further atomic structure of these implanted films is shown in Fig. 2e and f, presenting the strongly elongated out-of-plane lattice parameter driven by He implantation with almost no changes of the in-plane lattice parameter constrained by the substrate. Specifically, the c-axis changes from 4.65 Å to 4.93 Å and the c/a ratio is enhanced from 1.22 to 1.30, in contrast to the as-grown sample.

After successfully realizing the defect induced true super-tetragonal phase with giant tetragonality (c/a ∼ 1.30) in BiFeO₃ films, we next turn to study the domain structure evolution driven by this defect engineering effect. AFM images shown in Fig. 3 again confirm the morphology evolution with the increase of He doses. In the meantime, we probe the corresponding domain structures using piezoresponse force microscopy (PFM). The uniform out-of-plane (OOP) PFM contrast and the in-plane (IP) nanodomains shown in Fig. 3a indicate the Mc structure with a multi-domain state in the as-grown film, in accordance with previous work.³⁹,⁷⁴–⁷⁶ Both the implanted samples show the uniform OOP and IP contrasts (Fig. 3b and c), indicating the formation of a true T phase with a single domain state in agreement with our XRD and RSM
data. Therefore, the multi-domain to single domain structure evolution further verifies the Mc-T phase transition (this observation is distinct from the discovery of a multi- to a single-domain state change in (Ba,Ca)(Zr,Ti)O3 under an electric field which shows the ferroelectric rotation process without any structural change77). It is worth noting that although temperature-driven true T phase BiFeO3 has been reported,70,71 the domain structure has not been captured, inhibited by the unstable PFM scans at high temperature. Here we first time obtain the PFM images that reveal the single domain state in true T phase BiFeO3.

To explore the reversibility of phase transition and domain evolution induced by He implantation, high temperature annealing of the 5 × 10^{14} He per cm² dosed BiFeO₃ film was carried out at 550 °C under 1 atm oxygen atmosphere for 1 hour. A combination of the re-emergence of the dark-contrast R phase (Fig. 4a) and nanoscale stripe domains (Fig. 4c) indicates the reproduction of mixed R and Mc phases due to the release of He, which is confirmed with the (002), (103) and (113) RSMs shown in Fig. 4d, e and f, respectively. Schematics shown in Fig. 4g summarize the reversible control of the R-Mc-T-super T phase transition in BiFeO₃ via He ion implantation and high temperature annealing.

In summary, we have demonstrated the ability to control the defect-driven R-Mc-T-super T phase transition and multi-single domain evolution in BiFeO₃ thin films, enabling the cre-
ation of the single-domain-state, true super-tetragonal phase with enhanced tetragonality \((c/a \sim 1.30)\). The reversible phase transition and domain evolution have been revealed by high temperature annealing to release the implanted point defects. Our findings open a door to achieve giant tetragonality (or \(c/a\) ratio) in ferroelectric thin films which could be extended to other ferroelectric material systems (such as \(\text{PbTiO}_3\), \(\text{BaTiO}_3\) and \(\text{HfO}_2\)) which might lead to strong polarization enhancement. Moreover, the discovery of controlled defect engineered domain evolution in this work provides a future direction to create and manipulate exotic domain states (e.g., vortices and skyrmions) in ferroelectric and magnetic materials \textit{via} this approach.

Fig. 4  (a) Topography, (b) OOP PFM and (c) IP PFM images after annealing the implanted \(\text{BiFeO}_3\) at 550 °C under 1 atm oxygen atmosphere for 1 hour. (d) (002), (e) (103) and (f) (113) RSM reflections of the annealing sample shown in (a–c). (g) Schematics of the reversible control of the R-Mc-T-super T phase transition in \(\text{BiFeO}_3\) via He ion implantation and annealing which have been demonstrated in this work.
Author contributions

D.C. conceived and designed the project. S.Z. proposed the ion implantation/irradiation approach. C.C and C.L. fabricated and characterized the thin films. C.W. and U.K. conducted the He implantation experiments. X.C., C.X., N.W. and Y.Z. carried out the STEM measurements. J.Z., Z.L. and P.Y. contributed to the XRD and RSM data interpretation. Z.F., M.Q., M.Z., X.L. and G.Z. analyzed the PFM data. X.G. and J.-M.L. discussed the TEM and AFM data. D.C. and C.C. wrote the paper with contributions and feedback from all authors. All authors discussed the results and commented on the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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