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> Phys. Rev. Materials **3**, 094410 — Published 23 September 2019 DOI: 10.1103/PhysRevMaterials.3.094410

Optical response of BiFeO₃ films subjected to uniaxial strain

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The impact of single axis lattice expansion on the optical response of BiFeO₃ films is examined. Low-energy He implantation is used to tailor morphotropic phases of BiFeO₃ films and study changes in their optical spectra with continuously increasing lattice expansion. He ion implantation of epitaxial rhombohedral (R) - and tetragonal (T) - like BiFeO₃ films induces uniaxial out-of-plane strain that, on R-like films, eventually leads to a complete R-T phase transition. This approach allows us to provide new insights into the optical response of BiFeO₃ films. Strain doping of Tlike films leads to a significant redshift of the optical absorption spectra that is theoretically explained by a lowering of Fe 3d t_{2g} states. R-like films, on the other hand, show a less pronounced sensitivity to uniaxial strain and a blueshift of about 250 meV at the strain-induced R-T transition. The results demonstrate that straindoping allows a deeper examination of the optical properties of epitaxial phases that are otherwise impossible to access by standard epitaxy.

The stabilization of various polymorphs with vastly different properties has spurred immense research interest in BiFeO₃ (BFO) over the last decade. In classical morphotropic piezoelectric materials, rhombohedral and tetragonal phase variants can energetically compete to form a mixed phase regime with improved functional properties.^{1–3} A similar strain-driven morphotropic phase boundary was found in epitaxial BFO films on substrates imposing moderate to large compressive in-plane strain⁴. Films under compressive strain less than ~4% typically grow in a quasi-rhombohedral BFO polymorph (R). This bulk R-like phase has been studied in detail for its room temperature

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multiferroic properties, including a large ferroelectric polarization^{5,6}, antiferromagnetism or cycloidal spin structure with a high Nèel temperature^{7,8}, and complex magnetoelectric coupling^{9,10}. The discovery of the quasi-tetragonal polymorph (T) in films grown under compressive strain >4% spurred renewed interest in BFO; because this T phase is structurally characterized by an extraordinarily high c/a ratio that does not exist in bulk¹¹. The enormous tetragonality implies that the T polymorph should possess vastly different physical properties than its R counterpart. While improved functionality, such as greatly increased ferroelectric polarization^{12,13} has been observed, experimental difficulties in placing the lattice into specific symmetries while collecting magnetic or electronic structure have limited direct observation of supertetragonal behaviors.^{14–16}

Previous work demonstrated that low energy He ion implantation can be used to introduce uniaxial strain in epitaxial oxide thin films.^{17,18} Strain doping of BFO films recently showed it is possible to exert continuous control of morphotropic phase composition, i.e. the direct transformation of R- to T-films post-synthesis.¹⁹ Uniaxial out-of-plane lattice expansion induced by strain doping thereby offers an excellent opportunity to generate a full array of strain states that are otherwise impossible to achieve by biaxial in-plane strain via standard epitaxy. This can then be used to provide deeper access to the electronic structure of BFO under symmetry manipulation.

Optical spectroscopy is a simple yet efficient approach to get access to details on the electronic band structure of thin films. In this work, strain doping is used to understand how the optical response of R- and T-BFO polymorphs evolve under the influence of uniaxial strain. A substantial change in the optical absorption with a significant reduction of the optical band gap of about 60 meV / % lattice expansion is observed in T-BFO. Uniaxial expansion of R-BFO generates a blueshift of the optical band gap of about 250 meV which can be attributed to a large electronic reconstruction through the strain-induced R-T transition.

Experimental Details

To stabilize the R and T phases of BFO, 20nm thick epitaxial films are deposited on (001) oriented $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) and LaAlO₃ (LAO) substrates, respectively. X-ray diffraction (XRD) confirms that all films are grown coherently with

their substrates, with a compressive in-plane strain of -2.5% for LSAT, and -4.6% for LAO. The film structures are in perfect agreement with previous reports on epitaxial BFO films—with the film on LSAT growing in an R-like state^{20,21} and the film on LAO growing in a T-like state.²² Uniaxial out-of-plane lattice expansion is then iteratively applied to the films using low energy He ion irradiation.^{17,18,23} Figure 1a shows θ -2 θ XRD scans around the pseudocubic (pc) 001 reflections of the films on LAO and LSAT with varying doping levels. The T-BFO peak of films on LAO shifts continuously towards lower diffraction angles, which means that the out-of-plane lattice parameter gradually increases with increasing He doping. This behavior is expected for a uniaxial lattice expansion along the c direction. A small broadening of the film peaks is observed. This broadening is caused by a slightly inhomogeneous strain profile which is likely related to a non-linear ion implantation profile. Simulations of the data indicate that the total variation of the out-of-plane strain across the film thickness is only about 30 per cent. On LSAT, the XRD scans show a shift of R-BFO lattice reflections for low He doses, followed by the emergence of a second diffraction peak at intermediate doses that grows in intensity at the expense of the R-BFO peak. This indicates an R-T phase transformation under strain doping that leads to a full conversion into T-BFO at higher doping levels. This can also be seen in **Figure 1b** where the *c* parameter determined from the positions of the film peaks is plotted versus the dosage applied to the BFO film. While the lattice parameter of the BFO/LAO film is already large in the as-grown strain state and increasing moderately with He doping, the lattice of the BFO/LSAT film shows an extraordinary expansion due to the phase transition towards the highly tetragonal Tlike BFO polymorph. This response is in perfect agreement with previous work which demonstrated tailoring of morphotropic BFO phases with strain doping.¹⁹



Figure 1. Structural characterization of BFO thin films upon He ion irradiation. (a) θ - 2θ scans around the 002_{pc} peaks of BFO thin films on LAO and LSAT substrates under different helium dosage. (b) The out-of-plane lattice constant *c* as a function of helium dose. A large nonlinear lattice expansion due to the R-T crystal phase transition is clearly visible on LSAT at intermediate doses.

This large area of previously inaccessible structural phase space covering phase and symmetry from rhombohedral to tetragonal enables a continuously variable pallet from which to measure. Spectroscopic ellipsometry is used to determine the optical constants in an energy range 1.2 - 5 eV across this structure regime to give new insights into the optical behavior of BFO. Since interface roughnesses are small relative to film thickness, it is possible to determine the optical constants of the films by fitting the response data to a simple two-layer model consisting of the substrate and film. The impact of straggle doping into the substrates was also found to be unimportant by intentionally implanting He into bare LAO and LSAT substrates and determining their optical properties - no significant change was found after implantation.²⁴ Thus, in the model system, the optical properties of the substrates (LAO and LSAT) are fixed to the parametric data determined independently from ellipsometry measurements and fitted to the BFO layers by Kramers-Kronig consistent B-splines with 16 data points over the full energy range.

Results and Discussion

Energy-dependent ellipsometric angles Ψ and Δ were recorded across the full range of structure space described above. Figure 2a shows examples of as-grown and heavily

expanded films. Significant differences between the films are clearly visible, in particular in the intermediate 2 - 3.5 eV energy range. This range is within the visible/near visible spectrum of light and is what makes ferrites, in particular BFO, interesting for photovoltaic and photocatalytic applications. Tuning optical responses by He implantation may thus enhance functionalities.



Figure 2. Ellipsometric spectroscopy data for films on LAO and LSAT. (a) Ellipsometric parameters Ψ and Δ for as-grown films (solid lines) and films dosed with $9x10^{15}$ He/cm² (open symbols). (b) Real and imaginary part of the dielectric function determined by fits to the ellipsometry data as described in the text.

Figure 2b shows the real (ε_1) and imaginary (ε_2) part of the dielectric function determined from the fits to the ellipsometry data for the undosed and heavily dosed BFO films on LAO and LSAT. The results on the undosed films are in perfect agreement with previous experimental work.^{25,26} The characteristic peak of the dielectric constant near 3 eV is related to the excitation of electrons above the band gap. The broad dielectric loss spectrum indicates the presence of several absorption bands that have been ascribed to charge excitations mainly from O 2p to Fe 3d states.^{26,27} For films on LAO and LSAT, strain doping leads to an overall reduction of the dielectric constant and dielectric loss.²⁸ This reduction is not supported by theoretical predictions based on pure strain effects but can simply be explained with a decreased polarizability caused by the random introduction of noble He ions at interstitial sites of the perovskite lattice. Similar observations have been made in studies on other dielectric film materials.²⁹



Figure 3. Tauc-plots of the absorption coefficient versus the photon energy for BFO/LAO and BFO/LSAT. The optical band gaps of the undosed (solid) and dosed films (dotted lines) are determined by extrapolating the linear range of the data to zero.

In general, despite their greatly different lattice structure, as-grown R and T films show surprisingly similar absorption spectra that are offset from each other by ~300 meV. Theoretical methods have failed to reproduce this blueshift and actually predict a reduction of the bandgap.^{12,30} Recent work suggests that the enhancement of the optical bandgap in T-BFO could be associated with an increase of the electronic band gap.^{26,27} In **Figure 3** the absorption coefficient of the BFO films is depicted in a Tauc-plot. Extrapolating a linear line to zero allows for the determination of the optical band gap, E_g , as shown in the figure. The spectra of R- and T-BFO are best described by direct bandgaps, with values of about 2.75 eV and 3.05 eV, respectively.^{25,31} In this work, the bandgaps of as-grown R- and T-BFO film are 2.72 eV and 2.99 eV, respectively, and are thus in good agreement with previous studies. Since the blueshift of the highly tetragonal T phase with respect to the bulk-like R phase is mainly attributed to strain effects, the optical response of BFO polymorphs to strain has been investigated in more detail by growing epitaxial films on various substrates. However, these previous works reveal no clear dependence.³² A major drawback of heteroepitaxy is that it only allows discrete strain states given by available substrates and does not permit the strain tunability needed to continuously track changes of optical properties due to strain. Furthermore, standard epitaxy is always bound to a three-dimensional elastic reaction of the material, meaning that imposing compressive inplane strain will come along with an out-of-plane lattice expansion due to Poisson's effect. Uniaxial strain via he implantation works around these experimental challenges. As uniaxial strain is applied, the peak of the dielectric constant as well as the onset of the absorption band shifts to a slightly lower photon energy for the BFO film on LAO, i.e. the optical band gap of T-BFO films is effectively lowered. The bandgap is reduced by ~170 meV as the film is fully expanded. On the other hand, the band gap of the R film increases by ~120 meV as the BFO film is fully expanded.



Figure 4. Response of optical band gaps to He ion implantation. Open triangles and squares show the experimentally determined band gaps of the films on LSAT and LAO, respectively, as a

function of the He dosage. The blue and red bands are guide to the eyes to illustrate the different response between the polymorphs of BFO.

To understand this disparate strain response between R- and T-BFO, it is instructive to compare the optical band gap as it evolves under uniaxial lattice expansion for each starting phase (**Figure 4**). The band gap of T-BFO continuously decreases under strain doping. The decrease amounts to a reduction of about 60 meV / % lattice expansion. The R-film on LSAT has a lower virgin band gap value than the as-grown T-film. As the film expands, it initially shows a reduction in bandgap; however, as uniaxial strain increases and the R phase transitions to mixed and R and T phases the bandgap begins to increase. Under the highest expansion the film is fully transitioned to pure T-BFO and again reacts to increased lattice expansion with a decrease in optical band gap. The red-blue-red shift that occurs with increasing uniaxial expansion in the film grown on LSAT can then be understood to be a direct consequence of the change to the symmetry of the crystalline phase.

To better understand how uniaxial strain-induced phase transition impacts electronic states, the evolution of the bandgap should be considered. The structural transition between R- and T-BFO induces a blueshift of 250 meV, which is in very good agreement with experimental studies on biaxially strained thin films.^{25,27,31,32} The fact that uniaxial and biaxial strain effects have a similar impact indicates that the blueshift is primarily caused by symmetry breaking of the FeO₆ octahedron rather than changes of the unit cell dimensions alone. Density functional calculations have been able to reproduce the optical properties of biaxially strained thin films quite accurately 26,27 and revealed that in both, T-and R-BFO, the valence band maximum (VBM) is mainly composed of O 2p states but is relatively unaffected by epitaxial strain or structural changes between BFO polymorphs. The conduction band minimum (CBM), however, is a hybridization of unoccupied Fe 3d and O 2p states and is thus particularly sensitive to Fe-O distance changes. In R-BFO, all three anti-bonding Fe 3d t_{2g} states are nearly degenerate and contribute equally to the CBM, while in highly tetragonal BFO the 3d t_{2g} split due to the FeO₅ like coordination, with the d_{xz} and d_{yz} states moving up in energy. These states hybridize with the O 2p states and are the most optically active, thus leading to an increase of the optical band gap during the R-T transition.

While the blue shift observed across the R- to T-transition induced in BFO/LSAT films can be very well understood in terms of global band structure changes, the reduction of the optical band gap for R- and T-BFO with increasing He dose is an open question. Experimental and theoretical studies on uniaxial strain are sparse and most work has focused on the effect of biaxial epitaxial strain. Naively, one would expect a uniaxial out-of-plane lattice expansion to induce similar effects as biaxial compressive stress as they both increases the tetragonality (c/a) of the perovskite unit cell. Theoretically, biaxial compressive strain has been suggested to cause a slight increase of the electronic band gap in R-BFO.²⁷ This is also supported by the general trend in ferroelectric perovskites where a polarization rotation from in-plane to out-of-plane generally increases the band gap.³³ Experimentally, however, compressive strain in epitaxial R-BFO films has been shown to have little to no effect on the optical band gap.^{32,34} Still, the reduction in band gap observed in uniaxial lattice expansion experiments is not in agreement with effects caused by biaxial strain. This shows that uniaxial strain may act in a fundamentally different way. While the dominating roles of structural transition and phase type are clearly observed in this work, it is important to consider how secondary structural effects induced by the He ion implantation process might impact bandgap. As an example, He ion implantation can modify oxygen octahedral rotations in perovskites,¹⁸ which can change orbital overlaps and consequently reduce electronic band gaps.^{35,36} Similarly, strain doping has been shown to cause a series of structural phase transition in T-BFO that can be linked to a rotation of the polarization vector towards out-of-plane.¹⁹ Most polar perovskites possess lower electronic band gaps in their tetragonal phase than in their rhombohedral phase. This is in line with the decrease of the optical band gap found for the implanted films on LAO. Apart from complex lattice distortions to the perovskite structure, He implantation typically leads to the creation of lattice defects. Defects such as oxygen vacancies, interstitials or site reversals^{37,38} could produce defect states below the CBM and increase optical absorption within the ideal band gap of BFO.

This work explores the optical response of BiFeO₃ in a previously inaccessible structure phase space between the rhombohedral to tetragonal regimes. Strain doping via He implantation leads to uniaxial lattice expansion of T-BFO films grown on LAO,

whereas films grown on LSAT substrates undergo a R to T transformation on top of the regular lattice expansion. Neither continuously controllable uniaxial lattice expansion nor continuous variation across the morphotropic phase transition, are features that can be studied independently by heteroepitaxy. Uniaxial strain lowers the optical band gap of T-BFO by as much as 60 meV / % lattice expansion. On the other hand, the R-T phase transition induces a blue shift of approximately 250 meV, a value that indicates large electronic changes associated with the structural modifications during the phase transition. These results provide new insights into the role of the morphotropic phase composition in dictating optical and electronic properties in BFO, while demonstrating a clear path toward designing application-specific optical responses.

Methods Summary

The 20 nm thick BFO films are grown by pulsed laser deposition from a $Bi_{1,1}FeO_3$ target on commercial LAO, LSAT substrates at a deposition temperature of 700°C. Au films of 20 nm thickness are deposited on top of the BFO thin films to serve as a buffer and neutralization layer for helium ion implantation. Helium is implanted using a *SPECS IQE 11/35* ion source at an energy of 4 keV. After implantation, the Au layers are mechanically removed and the films are characterized by X-ray diffraction mappings using a *Panalytical X'Pert* thin film diffractometer with Cu K α radiation. The spectroscopic ellipsometry measurements where conducted with a *M-2000 J.A. Woollam* ellipsometer.

Acknowledgements

Experiment design, sample synthesis, strain modification and structural characterization were supported by the US Department of Energy (DOE), Office of Basic Energy Sciences (BES), Materials Sciences and Engineering Division and the Quantum Condensed Matter Division. Ellipsometry completed by SFR was financially supported by ANCS within PN 16 14 03 02 contract and mobility grants of the Romanian Ministery of Research and Innovation, CNCS – UEFISCD MC-2018-0561 and MC-2017-0791. AH was supported by the Deutsche Forschungsgemeinschaft (DFG), SFB 762, Functional

Oxide Interfaces.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

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