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Strain dependent microstructural modifications of BiCrO₃ epitaxial thin films

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Abstract

Strain-dependent microstructural modifications were observed in epitaxial BiCrO₃ (BCO) thin films fabricated on single crystalline substrates, utilizing pulsed laser deposition. The following conditions were employed to modify the epitaxial-strain: (i) in-plane tensile strain, BCO_{STO} [BCO grown on buffered SrTiO₃ (001)] and in-plane compressive strain, BCO_{NGO} [BCO grown on buffered NdGaO₃ (110)] and (ii) varying BCO film thickness. A combination of techniques like X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (TEM) were used to analyse the epitaxial growth quality and the microstructure of BCO. Our studies revealed that in case of BCO_{STO}, a coherent interface with homogeneous orthorhombic phase is obtained only for BCO film with thicknesses, $d < 50$ nm. All the BCO_{STO} films with $d \geq 50$ nm were found to be strain-relaxed with an orthorhombic phase showing $\frac{1}{2}$ $\langle 100 \rangle$ and $\frac{1}{4}$ $\langle 101 \rangle$ satellite reflections, the latter oriented at 45° from orthorhombic diffraction spots. High angle annular dark field scanning TEM of these films strongly suggested that the satellite reflections, $\frac{1}{2}$ $\langle 100 \rangle$ and $\frac{1}{4}$ $\langle 101 \rangle$, originate from the atomic stacking sequence changes (or “modulated structure”) as reported for polytypes, without altering the chemical composition. The unaltered stoichiometry was confirmed by estimating both valency of Bi and Cr cations by surface and in-depth XPS analysis as well as the stoichiometric ratio (1 Bi: 1Cr) using scanning TEM - energy dispersive X-ray analysis. In contrast, compressively strained BCO_{NGO} films exhibited monoclinic symmetry without any structural modulations or interfacial defects, up to $d \sim 200$ nm. Our results indicate that both the substrate-induced in-plane epitaxial strain and the BCO film thickness are the crucial parameters to stabilize a homogeneous BCO phase in an epitaxially grown film.

1. Introduction

Multiferroic oxides possessing more than one ferroic order parameter have promising properties, both for fundamental and technological aspects [1]. These materials may be applied in integrated microelectronic devices, spintronic based magnetic field sensors, piezoelectric transducers, etc [2,3]. Among the known multiferroic materials, Bi-based perovskite oxides, such as BiMeO_3 (Me = Fe, Cr, Mn, etc), have been extensively studied due to their high magnetic and ferroelectric (FE) ordering temperatures [4,5]. One of the above mentioned materials that possesses intrinsic multiferroic properties is BiCrO_3 (BCO) [6,7,8]. BCO has not been explored much yet, unlike BiFeO_3 (BFO), which is quite appealing due to its large FE polarisation at room temperature (RT) [9,10,11,12]. In contrast to BFO, the existing literature on the synthesis and FE studies of BCO is very limited. Reports on the presence or absence of FE ordering in BCO at RT have led to controversial and ambiguous results [13,14]. Furthermore, enhanced FE and magnetic moments for the theoretically predicted B-site ordered double perovskite, $\text{Bi}_2(\text{FeCr})\text{O}_6$ [15] have led to a great deal of experimental efforts to synthesize bulk and thin films of these compounds. In general, the synthesis of B-site ordered perovskites has been tackled by fabricating artificial superlattices or heterostructures, consisting of BFO and BCO thin films [16]. This has proven challenging, both in bulk and thin film form, mainly due to the difficulty in stabilising a phase pure BCO without predominating growth defects and coexistence of different crystallographic structures as reported in the literature. Phase pure BCO ceramics can be synthesized only by using high-pressure techniques, requiring about 6 GPa [6]. Some of the few reports on BCO are summarized here: (i) Belik *et al.* [17] have reported that bulk BCO ceramics exhibit a monoclinic (C2/c) crystal symmetry at RT, which transforms into an orthorhombic symmetry (Pnma) at

around 420 K . However, later, the same authors [18] noted that the monoclinic BCO phase retains about 10 to 15 volume percentage of an orthorhombic phase, suggesting multiple phase coexistence in BCO, (ii) Goujon *et. al.* [19] have pointed out the presence of ~10 nm sized twinned domains within the monoclinic BCO phase, indicating its defective growth behaviour, (iii) Niitaka *et. al.* [20], in contrast, have suggested a distorted non-centrosymmetric crystal structure with C2 symmetry for BCO that could plausibly induce a FE structural distortion and (iv) David *et al.* [21] have recently shown that in case of BCO epitaxial thin films, an inhomogeneous strain distribution and oxygen-related defects within the BCO film can stabilize the coexistence of several distinct phases such as: monoclinic (C2/c) and orthorhombic (Pbnm), similar to the crystal structures already reported for bulk BCO, and an “unknown” third phase giving rise to superlattice diffraction spots and whose crystal structure has not been identified so far. However, the nature and the origin of such multiple structural coexistences in BCO remain ambiguous.

Therefore, detailed knowledge in the crystal structure of BCO is fundamental to understand its FE properties [13,14], as well as studying B-site ordered multiferroic heterostructures based on BCO and BFO [15]. The present work focuses on the fabrication and microstructural analysis of BCO epitaxial thin films fabricated under different in-plane strain conditions, i.e., tensile and compressive strain. All the fabricated BCO films were investigated using a variety of techniques: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM) and high resolution transmission electron microscope (HRTEM). Our results show that the BCO films grown under an in-plane tensile and compressive strained conditions exhibit different crystallographic structures at RT. In addition, we found that in-plane tensile

strained BCO thin films exhibit local structural modulations, directly correlated to the BCO layer thickness.

2. Experimental details

Epitaxial BCO thin films were fabricated by pulsed laser deposition (PLD) with a KrF excimer laser ($\lambda \sim 248$ nm) using a laser fluence of ≈ 2 J/cm². The BCO films were grown under an optimised conditions as follows: (i) substrate temperature (T_s) $\sim 650^\circ\text{C}$ to 700°C , (ii) oxygen partial pressure (p_{O_2}) ~ 1.3 to 2.6 Pa and (iii) laser frequency of 3 to 5 Hz. Metallic SRO bottom electrodes (15 - 25 nm thick) were first deposited onto the substrates as a buffer layer, so that the BCO films could be subjected to electrical measurements in the future. Two different single crystalline and oriented substrates were used, to impose the following in-plane strain conditions, (i) tensile strain: BCO grown on SrRuO₃ (SRO) buffered SrTiO₃ (001) (STO) [BCO_{STO}] and (ii) compressive strain: BCO grown on SRO-buffered NdGaO₃ (110) (NGO) [BCO_{NGO}]. The number line in Fig. 1(a) shows the pseudocubic in-plane lattice constants, a_{pc} (in Å) for BCO, SRO, NGO (110) and STO (001) substrates [2,22]. The orthorhombic NGO (110) substrate (pseudo-cubic with $a_{\text{pc}} \sim 3.867$ Å) imposes an in-plane compressive strain of approx. -1.08% , whereas STO (001) ($a_{\text{cubic}} \sim 3.905$ Å) imposes an in-plane tensile strain ($+0.64\%$) on BCO. To achieve atomically flat terraces having a single unit cell step height, both types of substrates were pre-treated: NGO (110) was thermally annealed at 1000°C for 2h, whereas STO (001) was chemically etched using a NH₄F-buffered HF solution followed by thermal annealing (950°C to 1000°C for 2h). Both BCO_{STO} and BCO_{NGO} films were fabricated under similar growth conditions (with various thickness of BCO film, d ranging from 10 to 200 nm). Some of the BCO_{STO} films ($d > 50$ nm) were subjected to post deposition annealing at higher oxygen partial

pressures. Surface morphology of the fabricated films was investigated using an AFM (DI 5000, Veeco) operated in the tapping mode. The surface topography of the pre-treated STO (001) is displayed in Fig. 1(b). The surface morphology of the SRO-bottom electrode fabricated onto STO (001), followed the step and terrace-like substrate morphology, indicating that step-flow growth took place [Fig. 1(c)]. The crystallinity and epitaxial nature of all the BCO films were analysed by high resolution XRD studies (Philips X' Pert MRD, Cu K_{α} radiation). A VG Scientific 220 i-XL ESCALAB spectrometer was used for surface and in-depth XPS analysis with a monochromatized Al K_{α} source ($h\nu=1486.6$ eV) at 70 W. The spot size was about 180 μm in diameter and a pressure of 10^{-7} Pa was maintained in the chamber during analysis. The full spectra (0-1350 eV) were obtained with constant pass energy of 150 eV and high resolution spectra with constant pass energy of 40 eV. High resolution XPS spectra were fitted and quantified using the AVANTAGE software provided by ThermoFisher Scientific. Microstructural data were investigated using TEM (JEOL 4010 at 400 kV) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging was acquired on a C_s -corrected FEI-TITAN 80-300 microscope at 300 kV. Both cross-sectional and plan-view TEM samples were prepared by standard mechanical and ion beam polishing procedures [23]. The stoichiometric ratios of cations (1Bi:1Cr) were confirmed for both BCO_{STO} and BCO_{NGO} films, by STEM - energy dispersive X-ray (EDX) line scans; excluding the possibilities of Bi volatility under the present growth conditions (not shown here).

3. Results and discussion

The representative XRD data for the BCO_{STO} ($d \sim 85$ nm) and BCO_{NGO} ($d \sim 160$ nm) samples is displayed in Figs. 2(a) and 2(b), respectively. Phase pure and highly oriented epitaxial growth could be envisaged for both the films, without any minor

secondary phases of Bi_2O_3 or Cr_2O_3 , etc. The reflections around $\text{STO}(003)$ and $\text{NGO}(330)$ are enlarged as inset in Figs. 2(a) and 2(b), respectively, to clearly reveal the presence of close peak splitting corresponding to the BCO and SRO phases, which indicates an oriented growth with their c-axis normal to STO. In addition, the BCO_{NGO} XRD exhibit a minor peak (*), possibly arising due to the misaligned grains of the perovskite structure with different orientation during strain relaxation [Fig. 2(b)]. The out-of-plane lattice constant for both BCO_{STO} and BCO_{NGO} from the $\theta/2\theta$ XRD scan is $\sim 3.88 \text{ \AA}$ and 3.9 \AA respectively, in agreement with the reported values of BCO epilayers [18]. The rocking curve analysis performed along the (004) reflection (not shown here) displayed a full width at half maximum of approx. 0.2° , indicating a textured-type growth nature for all BCO films fabricated onto the STO and NGO substrates. The epitaxial growth of BCO films was further confirmed using the conventional Φ -scan analysis that clearly indicated a cube-on-cube growth of BCO and the SRO buffer layer onto both types of substrates.

Reciprocal space mapping (RSM) analysis was performed to reveal the nature of lattice misfit strain and to estimate the in- and out-of-plane lattice constants. Figures 3(a) - 3(d) depict the RSM images recorded along the asymmetric (203) reflection for both BCO_{STO} and BCO_{NGO} films, respectively. The RSM plot for BCO_{STO} does not exhibit a distinct, separate (203) peak for BCO [Fig. 3(a)]. Instead, the BCO (203) reflection is shown as a broad peak that is closely located around the STO (203) peak, thus revealing a good lattice constant matching with STO. The intensity and broadness of the BCO (203) reflection decreased with the thickness of the BCO layer [Figs. 3(a) - 3(c)]. A coherent and strained growth of BCO could be envisaged only for the layer thicknesses below 50 nm, as depicted in Fig. 3(c). The nearly circular peak above the STO reflection in Figs. 3 (a) – 3 (c) corresponds to SRO (203), which indicates a

strained and coherent growth of the SRO buffer layer of less than 25 nm thickness. Figure 3(d) depicts the RSM analysis of a BCO_{NGO} film. The RSM image clearly revealed a partial strain relaxation for the studied BCO_{NGO} film with thickness, $d \sim 160$ nm and also revealed the splitting of the BCO (203) peak corresponding to the monoclinic-type distortion. This type of monoclinic splitting is very similar to that reported for compressively strained BiFeO₃ epitaxial thin films [24]. The RSM analysis revealed that the out-of-plane and in-plane lattice constants for the BCO_{NGO} film adopt pseudocubic values of approx. 3.9 Å and 3.87 Å, respectively, in correlation with the $\theta/2\theta$ XRD scan.

Figure 4(a) is the AFM topography image for BCO_{STO}, ($d \sim 85$ nm) which shows smooth and dense morphological features without any pore or crack formation at the surface; the RMS roughness value is 0.7 nm. In addition, this AFM image reveals an interesting surface structure with micron-sized rectangular blocks having two different azimuthal orientations perpendicular to each other. Inside these rectangular blocks, stripe-like features are clearly observed that could possibly be due to the texture-like epitaxial growth. In fact, the size of these rectangular blocks decreased with decreasing film thickness for BCO_{STO}. Figure 4(b) depicts the AFM image for a BCO_{NGO} film ($d \sim 160$ nm), whose surface morphological features differed much from that of BCO_{STO} films, since it revealed a dense and grainy characteristics. This is probably due to the morphology of the bottom electrode (SRO), which did not grow in step-flow regime on NGO substrates. The RMS roughness for the BCO_{NGO} film was found to be below 0.8 nm.

An XPS analysis was carried out for one of the BCO_{STO} ($d \sim 100$ nm thick) films, to analyse the cationic valency and the oxygen homogeneity both from the BCO

film's surface to the depth across the BCO/SRO and SRO/STO interfaces. The in-depth XPS profiling was performed by combining a sequence of Ar⁺ ion etching followed by the XPS data acquisition from the etched surface. Figure 5(a) – 5(c) depicts the high resolution XPS spectra of Bi *4f*, Cr *2p* and O *1s* core levels respectively. The Bi *4f* photoemission spectra exhibited two peaks at the binding energy (B.E) of 159.1 eV and 164.4 eV corresponding to *4f*_{7/2} to *4f*_{5/2} transition of Bi³⁺ [25]. However, additional shoulder peaks (marked by arrows) associated with the major Bi *4f* peaks at the lower B.E values of 157.3 and 162.5 eV, emerge due to the partial Bi reduction via breakage of Bi-O bonds and oxygen dissociation during the Ar⁺ sputtering that leads to the metallic Bi bonding [Fig. 5(a) inset]. The Cr *2p* core level spectra displayed two peaks at B.E ~ 576.7 eV and 586.6 eV, which are attributed to the *2p*_{3/2} and *2p*_{1/2} excitation levels, respectively [Fig. 5(b)]. The estimated B.E peak positions for both Bi *4f* and Cr *2p* levels are in correlation with the reported values for Bi³⁺ and Cr³⁺ ions in several perovskites like BiFeO₃, Bi₄Ti₃O₁₂, LaCrO₃, (La_{1-x}Sr_x)CrO₃ or (Pr_{1-x}Ca_x)CrO₃, etc. [26, 27,28], thus suggesting a +3 oxidation states for all the Bi and Cr ions in the BCO film. Similarly, Fig. 5(c) depicts the in-depth O *1s* core level spectra which exhibit the B.E peak at ~ 530.3 eV. The peak positions and asymmetries of various core level spectra were analyzed after the Gaussian fittings as shown in Fig. 5(d)-5(f) [for sputter depth of 22 nm from BCO surface]. The analysis of the peak intensity and positions for all the fitted Bi *4f*, Cr *2p* and O *1s* core level spectra at different BCO film depths suggested homogeneous oxygen distribution excluding the possibilities of multiple oxidation states for Cr or Bi ions as well as the secondary phase segregation. Further, the in-depth XPS analysis for this BCO_{STO} sample showed a nearly constant ratio of Bi, Cr and oxygen contents (atomic %) throughout the 100 nm depth of the heterostructure, beyond which the XPS signals of Sr *3d* and Ru *3d* core level signals corresponding to

the SRO buffer layer dominated [Fig. 6]. In-depth XPS data was performed until the STO substrate surface was reached, wherein, high Sr and Ti core level signals were obtained.

Figure 7(a) is a bright field (BF) TEM image displaying an overview for a $d \sim 130$ nm thick BCO_{STO} cross-section sample. The inset in Fig. 7(a) corresponds to the selected area electron diffraction (SAED) pattern acquired for the whole BCO_{STO} heterostructure along the [001]_{STO} zone axis. Analysis of the main SAED pattern revealed that the BCO_{STO} film exhibit an orthorhombic crystal structure and its estimated pseudo-cubic lattice constants revealed that the BCO_{STO} film experiences an in-plane lattice tensile strain. Further, the epitaxial relationship is $(100)_{\text{STO}} \parallel (100)_{\text{SRO}} \parallel (101)_{\text{BCO}_{\text{ortho}}}$ and $[001]_{\text{STO}} \parallel [001]_{\text{SRO}} \parallel [010]_{\text{BCO}_{\text{ortho}}}$, indicating a coherent “cube on cube” growth of the pseudocubically considered BCO layer on SRO-buffered STO. The BF image showed significant changes in contrast within the BCO film, which suggests a strained or defective growth of the BCO phase (see area marked by the white box). To analyse these regions, HRTEM images were acquired from areas such as the one highlighted by the white box in Fig. 7(a) and shown in Fig. 7(b). Several Fast Fourier transforms (FFT) were calculated from within the HRTEM image. Figures 7(c) and 7(d) display the FFTs calculated from those areas highlighted as 1 and 2, respectively in Fig. 7(b). Figure 7(c) shows the main BCO orthorhombic [010] unit mesh with $\frac{1}{2}$ satellite reflections (indicated by arrows) along $\langle 100 \rangle$. The presence of such satellite reflections indicates a possible cell doubling with a supercell parameter of 7.8 Å. Figure 7(d) indicates the [010] main orthorhombic unit mesh, similar to that of Fig. 7(c), but with $\frac{1}{4}$ satellite reflections appearing at a diagonal (45°) with respect to the orthorhombic diffraction spots along $\langle 101 \rangle$ (as marked by arrows). The FFT patterns possessing satellite reflections strongly indicated the

possibility of structural modulations within the main orthorhombic phase for the 130 nm thick BCO_{STO} film.

A plan-view TEM analysis was carried out for this BCO_{STO} ($d \sim 130$ nm) film. An overview BF image of BCO_{STO} as displayed in Fig. 8(a) clearly showed 90° oriented texture-like growth features whose averaged size is in correlation with the rectangular blocks observed in the corresponding AFM image. The SAED pattern in Fig. 8(b) exhibits a square perovskite structure which is associated with presence of extra satellite reflections (similar to those shown in Fig. 7) along two perpendicular crystallographic directions, wherein, the later originate due to the presence of twinned lattice planes. Further, the HAADF-STEM was used to characterise the apparently defective regions as observed by cross-sectional TEM and the BCO/SRO interface. From the overview of the BCO_{STO} film [Fig. 9(a)] the contrast variations, previously seen in Fig. 7, were not present and, more importantly, it should be noted that no change in the crystal structure of BCO was evident from our high-resolution HAADF imaging. The latter gives an indication that the defective areas observed in cross-sectional TEM (Fig. 7) originate from the modulated lattice structure. Further, the BCO layer of this sample exhibits defect lines perpendicular to the BCO/SRO interface, as marked by the white boxes in Fig. 9(a). Figure 9(b) is a zoomed-in image of the area marked as “1” in Fig. 9(a) to demonstrate that the defective line is formed by four edge-type dislocations originating from the BCO/SRO interface. Figure 9(c) is a high-resolution HAADF image of the top dislocation in Fig. 9(b), that shows its Burgers circuit with a vector of $b = a[101]$. The edge-type dislocation displayed in Fig. 9(c) is representative for all dislocations observed in different areas of the BCO_{STO} film.

To investigate the possibility of structural modulation within the orthorhombic BCO phase, a detailed analysis using HAADF-STEM imaging was performed on the cross-sectional and planar view samples (not shown) for $d \sim 130$ nm thick BCO_{STO} film. Figure 10(a) depicts a high-resolution HAADF image extracted from the top of the BCO_{STO} layer, wherein no apparent structural differences could be observed. We point out that although the HAADF parameters were set to reach Z-contrast, contributions from the B-site (Cr) ions were not evident, possibly due to the large difference in atomic numbers of Cr and Bi and also the large thickness of the BCO_{STO} film. However, its corresponding FFT pattern (inset) revealed 45° oriented satellite reflections, similar to those observed from the SAED patterns of the cross-sectional TEM. Furthermore, the HAADF image was processed using Digital Micrograph software to filter and create two lattice images by selecting (i) the main reflections (as marked by the red circle in the inset) and (ii) 45° oriented satellite reflections (as marked by the blue circles). The resulting lattice images are displayed in Figs. 10(b) and 10(c), respectively, both with their corresponding zoomed-in views as an inset. In Fig. 10(b), a cubic lattice pattern is observed, similar to the original HAADF image which is expected to arise from the A site cation (Bi). However, Fig. 10(c) revealed a hexagonal-like pattern for all its structure. Next, in Fig. 10(d), these two lattice images are combined to obtain a false colored image, wherein, the red color is assigned to the main diffraction spots and blue for satellite reflections. It is evident that the two lattice images corresponding to the main orthorhombic lattice and the extra diffraction spots do not superimpose, but rather occupy different lattice positions, suggesting no crystal structural changes. From this analysis, we conclude that within the orthorhombic BCO_{STO} phase, there exists a modulated hexagonal-like lattice pattern that possibly arises from the Cr-O sublattice. Further, such a lattice structural modulation gives rise to the 45° oriented $\frac{1}{2}$ and $\frac{1}{4}$ extra

superlattice reflections. The latter can be attributed to an “intergrowth” or “modulated structure”, i.e. stacking sequence variations similar to those seen in polytypes. Polytype structures are considered to arise from different stacking of atomic layers within the same crystal structure and with no change in overall chemical composition [24]. Formations of such polytypes have been reported in several alkaline-earth perovskites like BaCrO_3 [29], BaRuO_3 , etc. [30,31], but, so far, no such report exists in case of the Bi-based perovskite oxides. Further, there have been ample evidences from the earlier studies [28-30] that the polytypes are revealed by extra satellite reflections and/or streak formations in the SAED pattern [32]. Moreover, this will explain why no structural changes are observed in our HAADF images.

Changes in microstructure with respect to the layer thickness were observed for BCO_{STO} film thicknesses varying from 10 to 130 nm (Fig. 11). Here we show the TEM data only for the 85 and 25 nm thick BCO_{STO} films [Figs. 11(a) and 11(c)]. The BF image of the 85 nm thick BCO_{STO} film exhibited in the vicinity of the top surface several areas with dark contrast, probably strained regions (marked by a circle) in addition to the presence of edge-type dislocations that originate at the BCO/SRO interface, similar to those of Fig. 9(a). All the BCO_{STO} films grown with thickness below $d \approx 50$ nm do not exhibit any evidences of edge-type dislocations. As displayed in Fig. 11(c), a coherent growth and sharp BCO/SRO interface without any contrast variation were observed for all these films. The analysis of the SAED patterns acquired from the whole sample in the case of the thicker BCO_{STO} [Fig. 11(b)] strongly suggested that the strained dark contrast regions were responsible for the satellite diffraction spots (marked by arrows), indicating a structural modulation. This was seen only for BCO_{STO} films of thicknesses $d \gtrsim 50$ nm that are strain relaxed. For BCO_{STO} samples with BCO

layers below 50 nm thickness, the strained dark contrast regions disappeared and the edge-type dislocation density considerably decreased. They exhibited a homogeneous orthorhombic crystal structure, observed in its SAED [Fig. 11(d)]. A similar TEM analysis was carried out for BCO_{STO} films that were subjected to post deposition annealing treatments at higher oxygen partial pressures. We observed no significant modification in the microstructure due to post deposition oxygen annealing (not shown here).

To unravel the role of epitaxial strain on the structural modulation, BCO films were grown on an orthorhombic NdGaO₃ (110) [NGO] substrate with and without the SRO buffer layer. A large thickness (d up to 200 nm) of BCO_{NGO} thin films was particularly chosen to verify whether the compressive epitaxial strain relaxation stabilises a homogeneous BCO phase without any structural modulation. Figure 12 displays the TEM data set for a 160 nm thick BCO film fabricated onto 15 nm thick SRO buffered NGO (110) substrate. The high-resolution HAADF image [Fig. 12(a & 12b)] shows an overview of the sample, wherein both the BCO/SRO and SRO/STO interfaces appear smooth. Thus, our TEM studies suggest that the thick and strain-relaxed BCO_{NGO} film does not exhibit any extended defects such as dislocations or twinning or the spacing between the dislocations must be quite large. Figure 12(c) is the SAED pattern for the BCO_{NGO} sample, which indicates the epitaxial growth and more importantly no extra superlattice diffraction spots (“structural modulation”) could be observed. Indexing of the SAED pattern showed that the compressively strained BCO_{NGO} films exhibit a monoclinic crystal structure with an epitaxial relationship: $(110)\text{NGO} \parallel (100)\text{SRO/BCO}$ and $[011]\text{NGO} \parallel [001]\text{SRO/BCO}$. The monoclinic BCO_{NGO} films, fabricated up to $d \sim 200$ nm, exhibited no structural modulations, in

contrast to the BCO_{STO} ($d > 50$ nm) films. In addition, the presence of the SRO buffer layer up to thickness ≤ 25 nm, seems to play an insignificant role in altering the epitaxial strain on the BCO films, in case of both STO and NGO substrates.

In summary, at the macroscale, our structural and chemical analysis of both BCO_{STO} and BCO_{NGO} films, using the high resolution $\theta/2\theta$ XRD, RSM (203) scan, XPS and STEM-EDX analysis, respectively, revealed a highly oriented epitaxial growth with a stoichiometric cationic ratio (1 Bi : 1 Cr) and no oxygen inhomogeneity both at the film's surface as well as at the cross-sectional regions of the BCO heterostructure. In contrast, our TEM studies showed some interesting results. The crystallographic phase content of the tensile strained BCO_{STO} films was found to be an orthorhombic structure, whereas the BCO_{NGO} films exhibit a monoclinic symmetry. Thus, in contrast to the previous reports on multiple phase coexistence within the BCO bulk [17-20] or thin films [21], the present work suggests a variation in crystal structure, depending on whether the BCO films experienced tensile (BCO_{STO}) or compressive (BCO_{NGO}) in-plane strain. The tensile-strained orthorhombic BCO_{STO} films of thicknesses, $d \gtrsim 50$ nm exhibit a high density of edge-type dislocations originating near the BCO/SRO interface, which could be attributed to the semicoherent growth and an epitaxial strain relaxation. The HAADF-STEM analysis of those strain relaxed BCO_{STO} ($d \gtrsim 50$ nm) films with $\frac{1}{2} \langle 100 \rangle$ and $\frac{1}{4} \langle 101 \rangle$ extra satellite reflections suggested changes in the atomic lattice sequences or modulation similar to polytypes [24]. We point out that only those strain relaxed BCO_{STO} films exhibit extra satellite diffraction spots or structural modulation within the main orthorhombic phase. Further, the epitaxial strain modification via the layer thickness suggested that the presence of structural modulation critically depends on the BCO film thickness and it is thus inevitable to

limit its thickness, d below 50 nm, in order to stabilise a homogeneous orthorhombic phase. Such films would grow coherently with least interfacial defects.

The in-plane epitaxial strain was further altered by fabricating compressively strained BCO films on NGO (110) substrate with or without SRO buffer layer. Our TEM studies showed that BCO_{NGO} films with d up to 200 nm grown under an in-plane compressive strain have a monoclinic crystal structure. Although, the RSM analysis of BCO_{NGO} with larger layer thicknesses ($d \sim 160$ nm) showed the strain relaxed monoclinic (203) peak splitting [Fig. 3(d)], we do not observe any defective BCO/SRO interfaces in HRTEM. For BCO_{NGO} films, the interfacial regions analysed using STEM-HAADF also showed a coherent interface without any structural defects as well as misfit or edge-type dislocations. More importantly, compressively strained BCO_{NGO} films exhibit no superstructure diffraction spots in SAED patterns unlike the tensile strained BCO_{STO} films. All these results suggest that in case of compressive strain induced by NGO (110) substrate, the strain relaxation of BCO does not induce any structural modulation. We note in this context that, as suggested by David et al. [21] the inhomogeneous strain distribution or relaxation would lead to the prevalence of structural modulations in case of the tensile strained BCO_{STO} films.

4. Conclusions

Growing non-defective and relatively thick BCO epitaxial films that possess homogeneous crystal structure is a prerequisite to study their electrical properties, eliminating the large contributions from leakage current. The present study showed that it is possible to stabilise an epitaxial BiCrO₃, one of the metastable phases of Bi-based multiferroic oxides by PLD utilizing the substrate induced strain. Furthermore, an

appropriate choice of the substrate to fabricate an in-plane strained epitaxial BCO film as well as its thickness (in case of BCO_{STO}) are crucial parameters to obtain either an orthorhombic or monoclinic phase, and also may give insight into the fabrication of B-site ordered BCO superlattices or heterostructures with other isostructural compounds like BiFeO₃, BiMnO₃ etc.

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FIGURE CAPTIONS

Fig. 1. (a) Line graph showing the pseudocubic a-axis lattice constants (in Å) for BCO and SRO (above the number line) and NGO and STO substrate (below the number line).^[2,22] (b) AFM topography image of a chemically etched and annealed SrTiO₃ (001) substrate with the corresponding line scan as inset. (c) AFM surface morphology of a 20 nm thick SrRuO₃ film grown on STO (001).

Fig. 2. XRD scans for (a) BCO_{STO} and (b) BCO_{NGO} films; the (003) reflection is enlarged and shown as an inset.

Fig. 3. (a) - (c) RSM analysis along (203) for BCO_{STO} films with thickness 130 nm, 85 nm and 25 nm, respectively, and (d) RSM for 160 nm thick BCO_{NGO} film.

Fig. 4. AFM morphology of epitaxial BiCrO₃ films grown on SrRuO₃ buffered (a) SrTiO₃ (001) [BCO_{STO}] (RMS roughness: 0.7 nm) and (b) NdGaO₃ (110) [BCO_{NGO}] (RMS roughness: 0.8 nm). All the images are 4 x 4 μm². The height scale for both the images is 10 nm.

Fig. 5. XPS data for (a) Bi 4*f*, (b) Cr 2*p* and (c) O 1*s* core level spectra for a 100 nm thick BCO_{STO} film. Inset in (a) denotes the enlarged portion of one of the Bi-metallic shoulder peaks due to Ar⁺ sputtering (indicated by arrows). Their corresponding Gaussian-Lorentzian fittings (red solid lines) of core level XPS spectra recorded at the BCO film's depth of 22 nm are depicted in (d), (e) and (f) respectively.

Fig. 6: In-depth XPS analysis that shows the atomic % with respect to depth of the BCO(100nm)/SRO/STO heterostructure.

Fig. 7. (a) BF image of a 130 nm thick BCO_{STO} and its corresponding SAED pattern (inset), (b) HRTEM image from the area enclosed by the white box in (a), (c) and (d) FFT patterns from areas marked as 1 and 2 respectively, in (b). The satellite reflections are marked by arrows.

Fig. 8. Plan-view TEM micrograph for the 130 nm thick BCO_{STO} film. (a) BF image and (b) SAED pattern.

Fig. 9. (a) Overview HAADF-STEM image indicating two dislocation lines enclosed in the white boxes, (b) zoomed-in HAADF-STEM image taken from the dislocation line marked as 1 in (a), and (c) HAADF-STEM image from the top

dislocation enclosed in the box in (b), showing an edge-type dislocation and its Burgers circuit.

Fig. 10. (a) HAADF-STEM image of BCO_{STO} film with its corresponding FFT pattern as an inset, indicating the main reflections within the red circle and the extra reflections within three blue circles. b) Filtered image created using the main reflections. c) Filtered image created using the extra reflections. d) False color image combining (b) and (c), with red and blue, respectively.

Fig. 11. Cross section BF TEM images for two BCO_{STO} films with different thicknesses: (a) 85 nm and (c) 25 nm. The respective SAED patterns for (b) 85 nm and (d) 25 nm.

Fig. 12. BCO_{NGO} film (S)TEM data: (a) sample overview, (b) high-resolution and (c) SAED pattern.
