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# Thickness dependent microstructural modifications of BiCrO<sub>3</sub> epitaxial thin films

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Detailed thickness dependent microstructural investigations were carried out on the epitaxial BiCrO<sub>3</sub> (BCO) films grown under different substrate induced in-plane strain conditions, e.g., SrRuO<sub>3</sub> buffered SrTiO<sub>3</sub> (001) [BCO<sub>STO</sub>] & NdGaO<sub>3</sub> (110) [BCO<sub>NGO</sub>]. A combination of techniques such as the high resolution transmission electron microscopy (HRTEM), X-ray diffraction ( $\omega/2\theta$ ,  $\phi$ -scan) and reciprocal space mapping (RSM) were to characterise the structural and growth quality of BCO films.. The thickness dependent microstructural analysis showed that BCO films grown under in-plane tensile strained conditions [BCO<sub>STO</sub>], a homogeneous orthorhombic phase could be achieved only below critical thicknesses of 50 nm. Whereas, BCO<sub>STO</sub> films  $\geq$  50 nm were strain relaxed and revealed the presence of structural heterogeneity having orthorhombic symmetry along with the presence of (i)  $\frac{1}{2}$  superlattice extra reflections along  $\langle 100 \rangle$  having a supercell parameter of  $\sim 7.8$  Å and (ii)  $\frac{1}{4}$  satellite reflections appearing at  $45^\circ$  from the main diffraction spots, along  $\langle 101 \rangle$ . Using STEM-HAADF analysis we confirmed the superlattice modulation are due to stacking sequence changes as those seen in polytypes and they do not alter the oxygen homogeneity, chemical valence and stoichiometry of Bi and Cr ions (surface and in-depth XPS analysis). On utilizing the NGO substrates, we obtain in-plane compressively strained, BCO<sub>NGO</sub> films having monoclinic crystal symmetry without any misfit or edge-type defective regions and structural heterogeneities like polytypes which in turn, indicate the role of substrate in the local structural modifications.

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## I. INTRODUCTION

Multiferroic oxides that possess more than one ferroic order parameters have promising research interest both from fundamental and technological aspects<sup>[1]</sup>. These materials find potential application as integrated microelectronic devices, spintronic based magnetic field sensors and piezoelectric transducers, etc.<sup>[2,3]</sup> Among the known multiferroic materials, the Bi-based perovskite oxide such as BiMeO<sub>3</sub> (Me = Fe, Cr, Mn, etc), have been extensively studied due to its high magnetic and ferroelectric (FE) ordering temperatures.<sup>[4,5]</sup> One of the above mentioned materials that possess an intrinsic multiferroic property is bismuth chromite, BiCrO<sub>3</sub><sup>[6,7,8]</sup> (BCO). BCO has not been fully explored yet, unlike BiFeO<sub>3</sub> (BFO), which exhibit a room temperature (RT) multiferroic property with large FE polarisation<sup>[9,10,11,12]</sup>. In contrast, there exists a very limited literature on synthesis and FE studies of BCO. Reports on the presence or absence of the FE ordering in BCO at RT have led to controversial results.<sup>[13,14]</sup> Further, an enhanced FE and magnetic moments in the theoretically predicted 1:1 B-site ordered double perovskite, Bi<sub>2</sub>(FeCr)O<sub>6</sub><sup>[15]</sup> have led to enormous research interests in various other Bi-based multiferroic oxides. However, the successful fabrication and multiferroic studies of such an ordered double perovskite by way of fabricating artificial superlattice or heterostructures of single layers of BFO and BCO thin films<sup>[16]</sup> are difficult mainly due to the limited understanding on the crystal structure, growth and microstructural investigations of BCO thin films.

One of the main challenges about BCO has been its synthesis in the bulk and thin film form. Phase pure BCO ceramics could be synthesized only using a high-pressure techniques that requires 5 to 6 GPa.<sup>[6]</sup> Recently, Belik et. al.<sup>[17]</sup> have reported that the BCO ceramic exhibit a monoclinic, C2/c crystal symmetry at RT, which transform into an orthorhombic symmetry, Pnma at 420 K and that it exhibits a canted-type antiferromagnetic (AFM) ordering with a weak parasitic ferromagnetic moment below the critical temperature of 109

K. However, it was later noted by the same authors<sup>[18]</sup> that about 10 to 15 volume percentage of BCO can retain an orthorhombic phase within the monoclinic crystal structure which, in turn reveals the multiple phase coexistence in the bulk high pressure synthesised BCO ceramics. Further, Goujon *et. al.*<sup>[19]</sup> have reported that the monoclinic structure of BCO ceramics exhibit twinning with domain size of  $\sim 10$  nm, that indicates a defective growth nature of BCO phase. In contrast to the aforementioned reports, Niitaka *et. al.*<sup>[20]</sup> suggested that the BCO exhibit a distorted non-centrosymmetric crystal structure with C2 symmetry, that can plausibly induce a FE structural distortion. However, till date, there exists no consistent crystal structure information for BCO and furthermore, existence of FE distortion is very controversial and not completely understood.

Among the few existing studies on BCO epitaxial thin films, David *et al.*<sup>[21]</sup> have recently pointed out that inhomogeneous strain distributions and oxygen defects within the BCO film can stabilize the coexistence of several distinct phases such as: (i) monoclinic (C2/c) and (ii) orthorhombic (Pbnm), similar to the crystal structures already reported for bulk BCO, and (iii) an “unknown” third phase having super structural extra diffraction spots and whose crystal structure could not be identified so far. However, the nature and the origin of such structural coexistence remain ambiguous till date. Hence detailed microstructural analysis of BCO phase is inevitable to explore its ferroelectric properties<sup>[13,14]</sup> or to study B-site ordered heterostructures<sup>[15]</sup>. The present work focuses on fabrication, microstructural analysis of BCO epitaxial thin films fabricated under different in-plane strained conditions. i.e., tensile (BCO grown on SrRuO<sub>3</sub> (SRO) buffered SrTiO<sub>3</sub> (001) (STO)) and compressive [BCO on SRO buffered NdGaO<sub>3</sub> (NGO)] strain. Such films were investigated using high resolution X-Ray diffraction, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and transmission electron microscopy (TEM) analysis. Our results pointed out that both the in-plane tensile strained (BCO on SRO/STO) and compressive

strained (BCO on SRO/NGO) films exhibit different crystallographic structures at RT. In addition, we find that the in-plane tensile strained BCO epilayers exhibit structural heterogeneity similar to polytypes and local microstructural modification with respect to its layer thickness.

## II. EXPERIMENTAL

Highly oriented and epitaxial BCO thin films were fabricated using the pulsed laser deposition (PLD) with a KrF excimer laser ( $\lambda \sim 248$  nm) having the laser fluence of approx. 2 Joules/cm<sup>2</sup>. The BCO films were grown under the optimised growth conditions of (i) substrate temperature ( $T_s$ )  $\sim 650$  to  $700^\circ\text{C}$ ; (ii) oxygen partial pressure ( $p_{\text{O}_2}$ )  $\sim 10$  to  $20$  mTorr and (iii) laser frequency of 3 to 5 Hz. The BCO films were fabricated on oriented single crystalline substrate that can impose different strained conditions such as, (i) in-plane tensile strain: SRO buffered STO (001) [BCO<sub>STO</sub>] and (ii) in-plane compressive strain: SRO-buffered NGO (110) [BCO<sub>NGO</sub>], both under the same growth conditions. The atomically flat SRO buffer layers had thicknesses between 15 and 25 nm and can act as a bottom electrode for electrical characterization. The number line depicted in Fig. 1 shows the pseudocubic in-plane lattice constants ( $a_{\text{pc}}$ ) values (in Å) for BCO (above the number line), NGO (110) and STO (001) substrates (below the number line)<sup>[2,22]</sup>. The (110) oriented orthorhombic NGO [along pseudocubic NGO<sub>pc</sub> (001) with  $a_{\text{pc}} \sim 3.867$  Å] substrate imposes an in-plane compressive strain of approx.  $-1.08$  % whereas, the STO (001) ( $a_c \sim 3.905$  Å) imposes an in-plane tensile strain ( $+0.64$  %) on BCO. Both the substrates were subjected to certain surface pre-treatments like thermal annealing [ $1000^\circ\text{C}(2\text{h})$ ] for NGO (110) and in case of STO (001) substrate, chemically etching using  $\text{NH}_4\text{OH}$  buffered HF solution followed by thermally annealing ( $950$  to  $1000^\circ\text{C}$  for 2h), in order to achieve an atomically flat terraces having a single unit cell step height [Fig. 1b]. The AFM morphology of the

SRO-buffer layer fabricated on STO (001) also revealed a step and terrace growth structures [Fig. 1 c]. The crystallinity and the epitaxial growth nature of the BCO films were analysed using high resolution XRD studies (Philips X' Pert MRD, Cu K $\alpha$  radiation). Surface morphology of the films was investigated using the AFM (CP Research, Veeco) operating in the tapping mode. A VG Scientific 220 i-XL ESCALAB spectrometer was used for the surface analysis with a monochromatized AlK $\alpha$  source ( $h\nu=1486,6\text{eV}$ ) at 70 W. The spot size was about 180  $\mu\text{m}$  in diameter. A pressure of  $10^{-7}$  Pa was maintained in the chamber during analysis. The full spectra (0-1350eV) were obtained with a constant pass energy of 150eV and high resolution spectra with a constant pass energy of 40eV. Depth profiles were then obtained through Ar $^{+}$  sputtering. High resolution spectra could have been fitted and quantified using the AVANTAGE software provided by ThermoFischer Scientific.. In-depth XPS was performed by sputtering the layers as a function of the depth using Ar ion etching, until the STO substrate surface was reached, obtained mainly by high Sr and Ti core level signals. Microstructural details and crystal structure data of the fabricated BCO<sub>STO</sub> and BCO<sub>NGO</sub> epilayers were investigated by TEM, using a JEOL 4010 at 400 kV and scanning TEM (STEM) by high angular annular dark field (HAADF) imaging acquired on a C<sub>s</sub>-corrected FEI-TITAN 80 - 300 microscope at 300 kV. Both cross-sectional and plan-view TEM samples were prepared by the standard mechanical and ion beam polishing procedures.<sup>[23]</sup>

### III.RESULTS

The representative XRD analysis of the in-plane tensile strained BCO<sub>STO</sub> and in-plane compressively strained BCO<sub>NGO</sub> epitaxial films is displayed in Fig. 2a and b respectively. Phase pure and highly oriented epitaxial growth could be envisaged for both the films,

without any minor secondary phases of  $\text{Bi}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ , etc. In contrast to  $\text{BCO}_{\text{NGO}}$ , the  $\text{BCO}_{\text{STO}}$  heterostructure, do not exhibit a distinct and separate peak corresponding to the BCO layer due to the close lattice constant matching of BCO, SRO and STO (001) substrate [Fig. 2a & b]. The (003) reflection is enlarged in Fig 2(a) inset to clearly reveal the splitting of the BCO, SRO and STO peaks, which indicates an oriented growth with its c-axis normal to STO (001). The out-of-plane lattice constant for both  $\text{BCO}_{\text{STO}}$  and  $\text{BCO}_{\text{NGO}}$  from the  $\theta/2\theta$  XRD scan is  $\sim 3.88 \text{ \AA}$  and  $3.89 \text{ \AA}$  respectively, in agreement with the reported values of BCO epilayers [Fig. 2 a & b].<sup>[18]</sup> The rocking curve analysis performed along (004) for  $\text{BCO}_{\text{STO}}$  and  $\text{BCO}_{\text{NGO}}$  films showed a full width at half maxima (FWHM) of approx.  $0.2^\circ$ , indicating a highly textured growth nature for all BCO films fabricated on STO (001) and NGO (110) substrates. The epitaxial nature of these BCO films were further confirmed using the conventional phi-scan ( $\Phi$ -scan) analysis, that clearly indicated a cube-on-cube growth of BCO and SRO buffer layer onto the substrates.

Fig. 2 shows the reciprocal space mapping (RSM) analyses for  $\text{BCO}_{\text{STO}}$  and  $\text{BCO}_{\text{NGO}}$  films along the asymmetric (203) reflection. The RSM analysis reveals the nature of lattice misfit growth strain and the in-plane and out-of-plane lattice constants [ ]. The RSMs for  $\text{BCO}_{\text{STO}}$ , do not exhibit a distinct or separate (203) peak for BCO [Fig. 2c]. Instead, the BCO (203) exhibits as a broad peak that is closely surrounded with that of STO (203) peak, thus revealing a strong lattice constant matching with that of STO. The intensity and the broadness of BCO (203) reflection decreased with layer thickness [Fig. ---]. Coherent and strained growth of the BCO layer at lower thicknesses [figure not shown] for layer thickness ...-nm. Further, the nearly circular peak above the STO reflection in Fig. 2(c) corresponds to SRO, that indicates a strained and coherent growth of the SRO buffer layer. In The typical RSM analysis of compressively strained  $\text{BCO}_{\text{NGO}}$  films [Fig. 2(d)] clearly display two peaks that correspond to the monoclinic splitting of the BCO phase. Infact, the RSM of

compressively strained BiFeO<sub>3</sub> epitaxial thin films are previously reported to exhibit such monoclinic splitting of (203) reflection.<sup>[24]</sup> Both, the  $\omega/2\theta$  XRD scan and RSM studies revealed that the out-of-plane and in-plane lattice constants for all BCO<sub>NGO</sub> films adopt a pseudocubic values of approx. 3.906 Å and 3.87 Å respectively. The RSM also revealed a partial strain relaxation for the studied BCO<sub>NGO</sub> (160 nm thick) film [Fig. 2(d)].

Atomic force microscopy (AFM) was employed to analyze the surface morphology of BCO films [Fig. 3]. The BCO<sub>STO</sub> showed a smooth and dense surface morphology with a roughness (RMS) value below 0.7 nm without any pore or crack formations [Fig. 3(a)] However, AFM indicated an interesting surface structure that revealed a micron sized rectangular blocks or roofs (or blocks with roofs) having two different azimuthal orientations of 90° difference. Inside these rectangular blocks, striped features were seen that could be due to the texture-like growth morphology. Infact, the size of these rectangular blocks decreased with thickness of BCO<sub>STO</sub> layer. In contrast, the AFM of BCO<sub>NGO</sub> do not indicate a step-flow growth and revealed a dense and grainy morphological growth features [Fig. 3(b)] with RMS roughness below 0.8 nm.

The XPS analysis was carried out on the surface and as a function of depth across the thickness to analyse the chemical valence of cations and oxygen stoichiometry of the ions. Figs. 4(a) and 4(b) show the O *1s* and Cr *2p* core level spectra recorded at the surface of the BCO<sub>STO</sub> film. The obtained core level spectra were carefully analyzed after the curve fitting in order to estimate the peak position and the asymmetric nature, if any, present in the spectrum. The binding energy (B.E) for O *1s* appears at approximately 530.40 eV [Fig. 4(a)], while the Cr *2p* spectra displays two peaks at 577.04 eV and 586.5eV, corresponding to the *2p*<sub>3/2</sub> and *2p*<sub>1/2</sub> excitation levels, respectively [Fig. 4(b)]. The obtained peak positions



for the Cr 2*p* level could be correlated with the B.E values for Cr<sup>3+</sup> reported in rare-earth perovskite chromites like LaCrO<sub>3</sub>,<sup>[25]</sup> (Pr<sub>1-x</sub>Ca<sub>x</sub>)CrO<sub>3</sub><sup>[26]</sup> and (La<sub>1-x</sub>Sr<sub>x</sub>)CrO<sub>3</sub>.<sup>[27]</sup> The latter strongly suggest that all the Cr ions are in +3 states in BCO. The in-depth XPS analysis showed that the intensity and the peak positions corresponding to O 1*s* and Cr 2*p* spectrum remained the same throughout the depth of the film, hence indicating a homogeneous distribution of the oxygen content and oxidation states for Cr and Bi ions. Several of the O 1*s* XPS lines with respect to the various depths from the surface to the substrate (after a given Ar etching rate) were recorded and analyzed. The analysis showed a constant ratio between the Bi and Cr cation intensity and the anion spectrum, strongly suggesting a homogeneous distribution of cations and anions throughout the BCO layer, including at the BCO/SRO interface [Fig. 4(c)] thus confirming the unaltered valence state (+3) within the BCO layer.

The TEM analysis was carried out for BCO<sub>STO</sub> films and is displayed in Fig. 5. The bright field (BF) image of 130 nm thick BCO<sub>STO</sub> [Fig. 5(a)] clearly revealed the presence of local structural regions with varying brightness contrast inherent to the BCO layer. This indicates a strained or defective area as enclosed by white box. The selected area electron diffraction (SAED), acquired for BCO<sub>STO</sub> heterostructure along the [001]<sub>STO</sub> zone axis, shown in the inset marks the epitaxial/coherent growth nature of BCO<sub>STO</sub>. Analysis of the main SAED spots revealed that the BCO<sub>STO</sub> film adopts an orthorhombic crystal structure having pseudo-cubic lattice constants of  $a \approx c \approx 3.80 \text{ \AA}$  and  $b \approx 3.78 \text{ \AA}$ . The estimated lattice constants revealed that the BCO<sub>STO</sub>, experiences an in-plane lattice tensile strain of approx. 2.7% on STO (001). The epitaxial relationship is (100)STO || (100)SRO || (101)BCO<sub>ortho</sub> and [001]STO || [001]SRO || [010]BCO<sub>ortho</sub>, indicating a coherent “cube on cube” growth of the BCO layer on SRO-buffered STO. Hence, the macroscopic phase purity of BCO<sub>STO</sub> thin

films could be envisaged from TEM analysis, which is, in correlation with high resolution XRD data. Furthermore, the HAADF imaging was used to characterise the origin of defective regions around the BCO-SRO interface. From the overview of the BCO<sub>STO</sub> film [Fig. 5(b)] the strain contrast variation observed previously in cross-sectional TEM analysis [Fig. 5(a)] were not present. However, the BCO<sub>STO</sub> exhibits edge-type dislocation lines near the SRO/BCO interface within the regions highlighted by white box. Fig. 5(c) displays the zoomed image of the area 1 in Fig. 5(b) which clearly reveals that the dislocation line is actually formed by four edge-type dislocations originating from the SRO/BCO interface. Fig. 5(d) is a high-resolution HAADF image of the top dislocation in Fig. 5(c), having the Burgers circuit with a vector of  $b = a[200]$ . The edge-type dislocation displayed in Fig. 5(d) is the representative for all dislocations observed in different areas of BCO<sub>STO</sub> layer, since the same Burgers vector was observed for all of them. To further analyse the defective regions as highlighted by white box in Fig. 5(a), several high-resolution TEM (HREM) images were acquired and analysed from the defective regions [Fig. 6(a)]. From the HREM lattice image, the Fast Fourier transform (FFT) patterns were calculated. Fig. 6(b) and 6(c) displays the differences in the FFT patterns acquired from the highlighted areas 1 and 2 respectively. Fig. 6(b) shows the main orthorhombic [010] unit mesh with  $\frac{1}{2}$  superlattice reflections (indicated by arrows) along  $\langle 100 \rangle$ . The presence of such  $\frac{1}{2}$  superlattice reflections indicates a possible cell doubling with a supercell parameter of 7.8 Å. Fig. 6(c) indicates the [010] main orthorhombic unit mesh, similar to that of Fig. 6(b), but with  $\frac{1}{4}$  satellite reflections appearing at a diagonal ( $45^\circ$ ) with respect to the perovskite mesh along  $\langle 101 \rangle$  (as marked by arrows). The FFT patterns having  $45^\circ$  oriented  $\frac{1}{2}$  and  $\frac{1}{4}$  superlattice reflections strongly indicated the possibilities of structural heterogeneity within the main orthorhombic phase for 130 nm thick BCO<sub>STO</sub> film. Plan-view TEM analysis were further carried out for BCO<sub>STO</sub> films. An overview BF image of BCO<sub>STO</sub> displayed in Fig. 7(a),

clearly shows the  $90^\circ$  oriented texture-like growth features whose size is in correlation with size of the  $90^\circ$  rectangular blocks seen in AFM images . The HRTEM image in Fig. 7(b) and FFT analysis showed that although majority of the areas investigated showed the orthorhombic perovskite structure, some other areas appear to have some sort of  $45^\circ$  cell doubling, as shown in the area enclosed by white box. Its SAED pattern in Fig. 7(c), shows the **square** perovskite structure and superlattice reflections in more than one direction, suggesting also the presence of twinning.

The cross-sectional TEM analysis suggest regions with different structural modulation. In order to unravel this mystery a detailed analysis using HAADF imaging was performed on the cross-sectional and planar view samples (not shown) of the 130 nm thick  $\text{BCO}_{\text{STO}}$  film. Fig. 8 (a) shows a high-resolution HAADF image of the top of the  $\text{BCO}_{\text{STO}}$  layer that has no apparent structural differences and its corresponding FFT pattern as inset, presenting  $45^\circ$  superlattice reflections. Though the HAADF parameters were set to reach Z-contrast, contributions from the B-site (Cr) ions could not be observed in the BF image, possibly due to the large difference in atomic numbers of Cr and Bi, and large thickness ( $> 100\text{nm}$ ) of studied  $\text{BCO}_{\text{STO}}$  film. Furthermore, the BF image was processed using Digital Micrograph software to filter and create two high resolution lattice images by using (i) the main reflections as marked by red circle and (ii)  $45^\circ$  superlattice reflections as marked by blue circles. The resulting HR image is displayed in Figs. 8(b) and 8(c), respectively, both with their corresponding enlarged area as an inset. In Fig. 8(b), a cubic structure is observed, similar to the original HAADF image which arises from the A site ion. However, Fig. 8(c) reveals a hexagonal-like lattice image pattern for all its structure. Further, these two HR lattice images were combined to obtain a false colored image, as shown in Fig. 8(d) wherein, the red colour is assigned to the main diffraction spots and blue for the extra

superlattice reflections. From the HAADF analysis, we confirm that the HR image main diffraction spots and superlattice reflections do not superimpose to form single lattice image pattern and they occupy a different lattice positions within the BCO<sub>STO</sub> layer . Since no structural change is observed in the HAADF image, it is suggested that within the orthorhombic BCO<sub>STO</sub> phase there exists a modulated hexagonal-like lattice pattern (blue) that could possibly arise from the Cr-O sublattice and such a structural modulation gives rise to the 45° oriented ½ and ¼ superlattice reflections. The latter could be considered as an intergrowth or modulated structure, a stacking variation arising from the regular perovskite structure, similar to those seen for polytypes. Moreover, it will explain why no structural change is clearly observed in the HAADF images. Polytypes are building up of stacking layers with identical crystal structure and no change in the overall composition<sup>[24]</sup> and have been reported in several other perovskites like BaCrO<sub>3</sub>,<sup>[28]</sup> BaRuO<sub>3</sub>, etc.<sup>[29,30]</sup>. Furthermore, there have been ample evidences, wherein, the polytypes, give rise to an extra superlattice reflections and/or streak formations in the SAED pattern.<sup>[31]</sup>

The strain relaxation in epitaxial thin films has been reported to occur as a function of layer thicknesses.<sup>[23]</sup> In order to study the polytype formation in thinner samples, thickness dependent microstructural modification were carried out for BCO<sub>STO</sub> films grown with thicknesses between 10 to 130 nm(Fig. 9). The thickness dependent microstructural modifications of BCO<sub>STO</sub>, leading to defective strained regions. Fig. 9(a) - 9(c) shows the comparison of BCO<sub>STO</sub> films with 85 and 25 nm, wherein, the 85 nm thick BCO<sub>STO</sub> exhibits several dark contrast, strained regions (marked by circles) in addition to the presence of edge-type dislocation (Burger's vector,  $b = a [200]$ ) that originates at the BCO/SRO interface [Fig. 8(a)]. Whereas, all the BCO<sub>STO</sub> films grown with thickness below approx. 50 nm do not exhibit any evidences of edge-type dislocations. Infact, a coherent growth and

sharp BCO/SRO interfacial regions without any presence of dark contrast regions were observed for all these films. For example, BF image of 25 nm thick BCO<sub>STO</sub> film is displayed in Fig. 8 (d).

The analysis of SAED patterns (in accordance with FFT analysis) strongly suggested the polytypes formation only for BCO<sub>STO</sub> films of thicknesses ~ 50 nm that are strain relaxed (Fig. 8(b) inset). Whereas, BCO<sub>STO</sub> below 50 nm, exhibited a homogeneous orthorhombic crystal structure in all regions of the film without any evidences of structural modulations or polytypes (as shown for 25nm thick BCO<sub>STO</sub> film in Fig. 8 (d)). It was found that the samples with BCO<sub>STO</sub> thickness of 50 nm and above possessed regions with strained regions whose FFT pattern indicated a structural modulation (marked by circles in Fig. 8(a) for 85 nm thick BCO). Further, the presence of edge-type dislocations (marked by arrows) was also observed for all these films, similar to those seen for 130 nm BCO<sub>STO</sub>. However, on decreasing the thickness of BCO<sub>STO</sub> below 50 nm, the strained regions become extinct and the edge-type dislocations density considerably decreased. The thickness dependent studies of BCO clearly pointed out the structural heterogeneity sets only in strain relaxed BCo films induced by the STO (001), thus implying the critical role played by substrate induced tensile strain in stabilizing the structurally inhomogeneities. Strain in the epilayers can be modified by appropriately varying the substrate.<sup>[2]</sup> Infact, earlier reports on epitaxial BCO epilayers exhibiting structural heterogeneities, suggested the role of an inhomogeneous strain distributions and/or oxygen non-stoichiometry.<sup>[21]</sup> Both the strain distribution/relaxation as well as the oxygen vacancy defects are process dependent phenomenon that can be altered by the growth conditions, substrate chosen and film thicknesses. Hence, the BCO<sub>STO</sub> films studied here were subjected to post deposition

annealing treatments at higher oxygen partial pressures. However, no significant change in the microstructure was observed.

Therefore, the role of substrate was studied by (i) varying the  $\text{BCO}_{\text{STO}}$  layer thickness and (ii) utilizing a different substrate:  $\text{NdGaO}_3$  (110) [NGO], both with and without the SRO buffer layer. Fig. 10 display the data set for the case where the substrate is changed, the BCO/SRO/NGO heterostructure. The 160 nm thick BCO film was grown on a 15 nm thick SRO-buffered/NGO, under the similar growth conditions adopted for BCO films grown on SRO/STO. This large thickness was chosen to verify whether the growth strain relaxing in  $\text{BCO}_{\text{NGO}}$  film stabilises the structural modulation. We observed  $\text{BCO}_{\text{NGO}}$  films (up to 160 nm) do not exhibit any presence of misfit or twinned edge type dislocations. The compositional homogeneity of  $\text{BCO}_{\text{NGO}}$  films was further confirmed by EDX analysis in STEM, across the films that showed the constant ratio of Bi and Cr ions. Fig. 10 display the STEM data obtained for this sample. The HAADF image in Fig. 10(a) shows an overview of the sample where both interfaces appear to be smooth. High-resolution HAADF [Fig. 10(b)] clearly demonstrated that the interfaces present in the heterostructure are atomically sharp and coherent. The image clearly indicates the absence of any misfit and edge-type dislocations as observed in the  $\text{BCO}_{\text{STO}}$  films. Fig. 10(c) is the SAED pattern of  $\text{BCO}_{\text{NGO}}$ , films which, indicates the epitaxial nature of this heterostructure. The epitaxial relationship is  $(110)\text{NGO} \parallel (100)\text{SRO/BCO}$  and  $[011]\text{NGO} \parallel [001]\text{SRO/BCO}$ , where BCO showed a monoclinic crystal symmetry . In the  $\text{BCO}_{\text{NGO}}$  films grown with varying thicknesses shows no structural heterogeneity among the film as observed in  $\text{BCO}_{\text{STO}}$  epilayers of thicknesses  $\geq 50\text{nm}$ . In addition the presence of SRO layer (thickness  $\leq 20\text{nm}$ ) plays insignificant role in altering the substrate induced strain on the BCO epilayers in both STO and NGO substrates. Further, BCO films of thicknesses  $\sim 200$  nm were fabricated on NGO substrate without

SRO-buffer layer. The TEM analysis of BCO<sub>NGO</sub> without SRO buffer layer exhibited monoclinic symmetry with no additional structural heterogeneity.

#### IV. DISCUSSION

The present work focuses on the effect of substrate induced in-plane tensile [STO (001)] or compressive strain [NGO (110)] -----, on the microstructural modification of the BCO epitaxial thin films fabricated using the PLD technique. . The detailed structural analysis BCO<sub>STO</sub> and BCO<sub>NGO</sub> epilayers were performed utilizing TEM, high resolution XRD ( $\omega/2\theta$  ,  $\Phi$ -scan) and RSM analysis. The TEM investigations of tensile strained BCO<sub>STO</sub> films clearly revealed the cube-on-cube growth in the SAED pattern, thus indicating macroscopic phase purity of heterostructure. These films also exhibited simultaneous presence of  $\frac{1}{2}$  superlattice reflections along  $\langle 100 \rangle$  and  $\frac{1}{4}$  satellite reflections along  $\langle 101 \rangle$  that indicate the structurally modulated lattice planes within the main orthorhombic phase. Structural modulation were further confirmed using detailed cross-sectional and planar view TEM and Our results pointed out that presence of extra superlattice reflections for BCO<sub>STO</sub> epilayers, could arise due to the presence of lattice modulations. The HAADF-STEM (Z-contrast imaging) investigations suggested that such superlattice reflection is due to the presence of lattice modulation similar to those seen in polytype structures<sup>[29-32]</sup>, It is worth mentioning that in the case of the bulk BCO polycrystalline ceramics, orthorhombic symmetry stabilizes only above  $\sim 420$  K<sup>[13]</sup> and hence, we emphasise that substrate induced in-plane tensile strain plays a crucial role in stabilizing this high temperature orthorhombic phase at room temperature<sup>[13]</sup>. All the fabricated BCO<sub>STO</sub> films on exhibited a typical texture-like growth morphology having azimuthal  $90^\circ$  recatangular blocks from AFM and planar view TEM for all thicknesses studied. Both surface and in-depth XPS analysis clearly revealed a homogeneous cationic distribution without any oxygen inhomogeniety throughout the cross-sectional regions of the BCO layer and at the interfaces of the heterostructure., thus revealing that the structural modulation or polytype do not induce any compositional inhomogeniety. In order to confirm the role of in-plane strain induced structural modifications several BCO<sub>STO</sub> epilayers of different thicknesses were grown . Our studies showed that BCO<sub>STO</sub> epilayers of thicknesses  $\leq 50$ nm could be to fabricated without any misfit dislocations

and do not possess any local structural heterogeneity. Our XRD, RSM and high resolution TEM analysis clearly showed that the  $\text{BCO}_{\text{STO}}$  films below  $\leq 50\text{nm}$  are fully strained and coherent and hence crystallize in a phase pure high temperature orthorhombic phase. On increasing the thickness beyond 50 nm, the  $\text{BCO}_{\text{STO}}$  layers undergo an in-plane strain relaxation that leads to the formation of local structural heterogeneity or polytype formations. However, in order to exploit the strain induced structural stabilization of BCO phase, compressively strained BCO films were fabricated on to  $\text{NGO}(110)$  substrate with and without the SRO-buffer layer.

Further the BCO thin films of varying thicknesses were grown on  $\text{NGO}(110)$  substrates with and without SRO buffer layer. The detailed microstructural analysis from High resolution XRD ( $\omega/2\theta$ ,  $\Phi$ -scan), RSM and TEM analysis showed that phase pure and highly oriented epitaxial growth could be achieved on  $\text{NGO}(110)$  substrates. The TEM analysis shown in Fig. xx clearly establishes that the in-plane compressively strained,  $\text{BCO}_{\text{NGO}}$  layer stabilizes under a monoclinic crystal structure without any structurally defective regions like misfit or edge type dislocations as observed in tensile strained  $\text{BCO}_{\text{STO}}$ . Such a homogeneous monoclinic phase that is free from process defects could be achieved to thicknesses even up to 200 nm for  $\text{BCO}_{\text{NGO}}$  films. It is worth mentioning that the bulk BCO ceramics though a high pressure stabilized phase, it crystallizes in monoclinic symmetry when synthesized as bulk ceramic.

Growing larger thickness of BCO thin films having homogeneous crystal structure without the presence of process defects is very crucial and inevitable to study the FE properties of BCO with least contributions from the thickness and defects dependent leakage currents. Moreover, our results showed that the role of in-plane strain through the appropriate choice of substrate plays a crucial role in stabilizing the orthorhombic and monoclinic crystal structure in BCO thin films. Such a control to obtain a desired crystal structure could be a potential outcome to fabricate superlattices or heterostructures of similar structures like  $\text{BiFeO}_3$ ,  $\text{BiMnO}_3$  in a desired configuration comprising BCO film and to study B-site ordering and enhanced multiferroic property<sup>[20]</sup>.



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## FIGURE CAPTIONS

**Fig. 1:** (a) The 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] . **include the AFM for STO and SRO**

**FIG. 2.** (a) AFM topography of etched and annealed SrTiO<sub>3</sub>(110) substrate with the corresponding line scan as the inset. AFM surface morphology of (b)15 nm thick SrRuO<sub>3</sub> films grown on STO and (c) BCO/BFO bilayer heterostructures grown on SrRuO<sub>3</sub>/SrTiO<sub>3</sub>.

**Fig. 2:** (a) The XRD scan for (a) BCO<sub>STO</sub> and (b) BCO<sub>NGO</sub> films; the (003) reflection is enlarged and shown as an inset. (c) and (d) displays the RSM analysis along (203) for BCO<sub>STO</sub> and BCO<sub>NGO</sub> films respectively.

**Fig. 3:** AFM morphology of epitaxial BiCrO<sub>3</sub> films grown on SrRuO<sub>3</sub> buffered (a) SrTiO<sub>3</sub> (001) [BCO<sub>STO</sub>] (RMS roughness: ----) and (b) a) NdGaO<sub>3</sub> (110) [BCO<sub>NGO</sub>] (RMS roughness: -----). All the images are 4 x 4 μm<sup>2</sup>. The scale for both the images is 10 nm.

**Fig. 4:** X-ray photoelectron spectra for a) O 1s core level and b) Cr 2p core level for BCO film c) In-depth XPS along the depth of the BCO layer.

**Fig. 5:** (a) BF image of a 130 nm thick BCO<sub>STO</sub> and its corresponding SAED pattern (inset), (b) Overview HAADF image indicating two dislocation lines enclosed in the white boxes and (c) High-resolution HAADF image **taken** from the dislocation line marked as 1 in (b) and (d) High-resolution HAADF image from the dislocation enclosed in the box in (c) showing a edge-type dislocation and its Burgers circuit .

**Fig. 6:** (a) HRTEM image from area enclosed by the white box of Fig. 5(a), two areas are marked as 1 and 2 by white boxes, (b) and (c) FFT patterns from areas 1 and 2, respectively. The extra superlattice reflections marked by the arrows.

**Fig. 7:** Plan-view data set for the 130 nm thick BCO<sub>STO</sub> film. (a) BF image, (b) HREM image, and (c) SAED pattern.

**Fig. 8:** (a) HAADF image of BCO<sub>STO</sub> film with its corresponding FFT pattern as an inset, indicating the main reflections in a red circle and the extra reflections in 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), red and blue, respectively.

**Fig. 9:** BF images for  $\text{BCO}_{\text{STO}}$  films with different thicknesses: (a) 85 nm, and (c) 34 nm and (d) 25 nm. The SAED pattern for BCO film of (b) 85 nm and (d) 25 nm respectively.

**Fig. 10:** (a) sample overview, (b) high-resolution HAADF image and (c) SAED pattern of 160 nm thick  $\text{BCO}_{\text{NGO}}$  film

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