

Rational Synthesis of Lead-Free Epitaxial $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ Perovskite Thin Film: A Structure-Property Relationship Study for Emerging Optoelectronic Application

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1. Thesis Title and Abstract

Thesis Title

Rational Synthesis of Lead-Free Epitaxial BiFe_{0.5}Cr_{0.5}O₃ Perovskite Thin Film: A Structure-Property Relationship Study for Emerging Optoelectronic Application

Thesis Abstract

Multiferroic BiFe_{0.5}Cr_{0.5}O₃ (BFCO) in which ferroelectric and magnetic orders coexist has gained research interest owing to its potential applications, e.g., spintronic and resistive random-access memory. Moreover, multiferroics possess a narrower bandgap compared to typical ferroelectrics, extending their application to photovoltaic devices. In contrast to the conventional semiconductors, the polarization-induced electric field facilitates the photoexcited charge separation, leading to an above-bandgap photo voltage in ferroelectrics. Nevertheless, a long-standing issue is the relatively low absorption of visible light. Thus, it is essential but challenging to tune their bandgap without compromising ferroelectricity.

This thesis explores structural phase transition in the epitaxial BFCO films grown on SrRuO₃ buffered (001) SrTiO₃ substrate via Laser Molecular Beam Epitaxy (LMBE). Reciprocal space mapping result shows strain relaxation mechanism is not solely by the formation of misfit dislocation but also by changing the crystal symmetry, transitioning from tetragonal-like to a monoclinically distorted phase as the thickness increases. The crystallographic evolution is also coupled with bandgap modulation, confirming that BFCO structure and its physical properties are strongly intertwined. Using spectroscopic ellipsometry, the slight redshift of the bandgap distinguishes the absorption process of the T-like BFCO layer from that of monoclinically distorted structure, further confirmed by spectral photocurrent measurement via conductive-atomic force microscopy.

The preparation of pure phase BFCO film with a robust polarization is of paramount importance for practical application. Yet, similar to the parental bismuth ferrite, BFCO suffers from poor electrical leakage performance. We report a three-order of magnitude suppression in the leakage current for the BFCO film through judicious adjustment of the growth rate. Scanning probe microscopy (PFM, AFM and c-AFM) results reveal that both microstructure and ferroelectric properties can be tuned by lowering the growth rate, ensuring realization of the room-temperature ferroelectric polarization comparable to the *ab-initio* predicted value. This thesis provides a facile strategy to tailor the structure-property of epitaxial BFCO film and its functional response for emerging optoelectronic devices.

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Rational Synthesis of Lead-Free Epitaxial $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ Perovskite Thin Film: A Structure-Property Relationship Study for Emerging Optoelectronic Application

Mohammadmoein Seyfour

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List of Publications

1. **M.M. Seyfour**i and D. Wang, Recent progress in bismuth ferrite-based thin films as a promising photovoltaic material, *Critical Review in Solid State & Material Science*, 46, 83–108 (2021).
2. **M.M. Seyfour**i, Q. Liu, J. Yang, Y. Sun, J. Shi, D. Wang et al., New insights on the substantially reduced bandgap of bismuth layered perovskite oxide thin films, *Journal of Material Chemistry C*, 9, 3161–3170 (2021).

Articles in preparation:

1. **M.M. Seyfour**i, D. Zhang, C. Menéndez, D. Sando, D. Wang et al., Unfolding the relation between structural distortion and optoelectronic properties of epitaxial $\text{BiF}_{0.5}\text{Cr}_{0.5}\text{O}_3$ thin film
2. **M.M. Seyfour**i, J. Du, Y. Sun, Q. Zhang, S. Chang, D. Wang et al., Enhanced photoferroelectric properties in $\text{BiF}_{0.5}\text{Cr}_{0.5}\text{O}_3$ thin film induced by the growth rate

Conferences (poster presentation):

1. Impact of laser fluence on the room-temperature ferroelectric properties of epitaxial $\text{BiF}_{0.5}\text{Cr}_{0.5}\text{O}_3$ thin film by pulsed laser deposition, CAMS2021-Advancing Materials and Manufacturing, Melbourne Australia

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Symbols and Abbreviations

α	Absorption coefficient
AFM	Atomic force Microscopy
BFO	BiFeO_3
BFCO	$\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$
BPVE	Bulk photovoltaic effect
FWHM	Full width at half maximum
DoS	Density of states
DFT	Density functional theory
E_g	Bandgap
h	Planck constant
$h\nu$	Photon energy
FE	Ferroelectricity
KPFM	Kelvin probe force microscopy
LMBE	Laser molecular beam epitaxy
LSMO	$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
PLD	Pulsed laser deposition
MSE	Mean standard error
n	Refractive index
k	Extinction coefficient
rms	Root mean square
RSM	Reciprocal space mapping
SEM	Scanning electron microscopy
SRO	SrRuO_3
STO	SrTiO_3
SE	Spectroscopic ellipsometry
TM	Transition metal
TEM	Transmission electron microscopy
λ	Wavelength
PFM	Piezoresponse force microscopy
PV	Photovoltaic
PVD	Physical vapor deposition
PCE	Power conversion efficiency
pc	Pseudocubic
P_r	Remnant polarization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectivity
r_i	Ionic radii
σ_d	Dark conductivity
σ_{ph}	Photoconductivity
V_{oc}	Open circuit photovoltage
J_{sc}	Short circuit photocurrent
V_o	Oxygen vacancy

Chapter 1. Introduction

1.1 Motivation

Over the past decades, multiferroic materials have been an interest of research curiosity simply due to the coexistence of multiple ferroic orders.¹ In principle, ferroelectricity and magnetism originate from different microscopic phenomena, i.e., ordering the electric dipole moment versus spin ordering in the ferroelectrics and ferromagnets, respectively. In other words, multiferroicity is rare because of the mere fact that (1) conventional ferroelectricity arises from second-order Jahn-Teller distortion in transition metal ions which necessitates an empty *d*-orbital configuration (2) contrarily, the unpaired *d*-electron in transitional metals are the origin of typical ferromagnetism.² Although there are no restricting physical criteria, the local chemistry would favour one another as described above. Therefore, alternative routes have been used to render the ferroelectricity by introducing off-centring on non-transition metal ions, for instance, stereochemical active lone pair in Bi^{3+} compounds,³ and breaking inversion symmetry through geometrical distortion like hexagonal YMnO_3 ,⁴ coined “improper ferroelectricity”.

In terms of functionality, magnetic materials are pivotal in data storage devices like spintronic memories,⁵ and ferroelectrics are widely used in transducers and sensors owing to the large piezoelectric response.⁶ Hence, multiferroics are increasingly in demand not only to be used in miniaturized nanoelectronics but also because of the intriguing functionalities endowed from the interplay between magnetism and ferroelectricity. Moreover, multiferroics possess a reduced bandgap with respect to the typical ferroelectrics due to the significant *e-e* interaction, extending their application to

photovoltaic (PV) devices. Multiferroic oxides also exhibit intriguing properties, e.g., above bandgap photovoltage and switchable photocurrent,^{7,8} which distinguish them from conventional semiconductors. Besides, most ferroelectric oxides show good resistance to humidity and ultraviolet light, giving them an edge over the highly efficient hybrid perovskite cells, e.g., methylammonium lead iodide.⁹ In particular, the usage of toxic lead has become an arguable topic in this field. Thus, there is a strong tendency for environmentally friendly alternatives in both multiferroic and photovoltaic research communities.

So far, lead-free BiFeO_3 (BFO) based materials have demonstrated a potential to be used as a multifunctional system possessing magnetic, ferroelectric, and optoelectronic properties. Although BFO has a relatively narrow bandgap of ~ 2.8 eV,¹⁰ its photocurrent output is still quite low since a small fraction of sunlight is absorbed (ca. 25%). To enhance the optoelectronic performance of BFO based thin films, one could tune the physical properties of thin film, including optical gap and electrical conductivity, without compromising its ferroelectricity which is often hard to achieve due to the leakage current.¹¹

The physical properties of BFO-based films rely on numerous factors, including but not limited to chemical composition,¹² film thickness,¹³ concentration of defects,¹⁴ substrate-induced strain,¹⁵ and polarisation.¹⁶ In terms of chemical doping, a theoretical study hypothesized that Cr and Mn are favourable transition metal dopants to tune the bandgap of BFO.¹⁷ Therefore, multiferroic $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (BFCO) was opted as a model system since ab-initio studies have also predicted it would be multiferroic with a non-trivial magnetic moment and polarisation at 0 K.² Moreover, recent experimental work has demonstrated a considerable energy conversion efficiency (3.3%) in a single layer

BFCO based PV device, emphasizing the role of growth kinetic on the film properties.¹⁸ While their studies mainly focused on the cation ordering aspect of such compound, there is still a gap in better understanding of other influences that growth parameters can have on the optoelectronic properties of BFCO. To probe the underlying factors, thin epitaxial films were synthesized using laser molecular beam epitaxy in this thesis, which belongs to the physical vapour deposition technique family. LMBE has been widely employed to grow multi-cation oxide thin films,^{19,20} because it offers rigorous control over the growth parameter—pivotal to the objective of this thesis—.

1.2 Thesis Objectives

With an increasing quest for energy-saving and renewable technologies, the research community is exploring new material systems to achieve higher performance in such technologies. The coupling of ferroelectricity with other functionalities like photovoltaic properties provides feasible alternatives for light energy harvesters. In this regard, the overall aim of this thesis is to develop a narrow bandgap eco-friendly multiferroic oxide with robust polarisation, good carrier transport and enhanced visible light absorption. The BFCO perovskite oxide is a promising material of choice due to the relatively narrow bandgap. Therefore, studying the structure-property relationship of BFCO thin film is of importance for fundamental research and promoting new functionalities. The key objectives are outlined as follows:

- 1)** Although exhaustive research has been conducted on synthesizing BFO-based materials, preparing single-phase BFCO with controllable microstructure and functional properties is yet an arduous task. The key step is to not only optimize growth conditions, including temperature, oxygen pressure, etc. but also to understand how

these various conditions influence the structure and phase composition of the BFCO thin film. Therefore:

- a) First, it necessitates obtaining the optimal growth window and establishing a phase diagram.
- b) Once the growth window is known, systematically investigate the impact on the optical and ferroelectric properties along with the charge transport mechanism.

2) Although a large body of literature has focused on the B-site cation ordering in BFCO perovskite, a thorough understanding of structural phase evolution and the related functional properties is still missing. Thus, I intend to:

- a) Systematically study the phase transition of BFCO thin film induced by varying the film thickness.
- b) Examine the optical properties of the epitaxial BFCO thin film with different crystal symmetry.
- c) Ascertain the implication of this crystallographic distortion in the photoresponse of the films.

3) Multiferroic BFCO thin film has gained widespread interest owing to its potential use in optoelectronics. To be used in such technological applications, robust polarisation is essential. Yet, like the parental bismuth ferrite, BFCO suffers from a high electrical leakage current. Therefore, this thesis proposes a facile strategy to obtain epitaxial BFCO thin films with excellent room-temperature ferroelectric properties.

- a) Investigate the effect of growth kinetic on defect formation and the ferroelectric properties.
- b) Study the photocurrent density of BFCO thin film grown at the optimized growth rate.

4) Most photoferroelectrics exhibit unsatisfactory energy conversion efficiency due to the low short circuit photocurrent density, i.e., tens of nA cm^{-2} . Despite all the endeavours in the literature to increase the photocurrent of BFCO films through bandgap engineering, there is still room for enhancement. Thus, this study aims to investigate routes to enhance the photoresponse of BFCO thin film holistically, i.e., charge excitation, separation, and transport. Note that there is a trade-off between conductivity and ferroelectric polarisation in ferroelectric materials, adding another degree of complexity to this study.

- a) The first step is to determine the conduction mechanism in the epitaxial BFCO thin films.
- b) Modify transport mechanism of epitaxial BFCO thin films using novel approaches, e.g., tuning growth rate.

1.3 Thesis Outline

To accomplish the objectives mentioned above, this thesis is organized as follows:

Current chapter (1) states the significance of this thesis and introduces the key objectives.

Chapter 2 describes the fundamental of ferroelectricity and multiferroics. It summarises the prominent theories associated with the ferroelectric-photovoltaic mechanism and provides the most recent progress in thin film devices for solar harvesting application. Emphasis is given to the optoelectronic properties of BiFeO_3 -based material, focusing on the limitations and the practical approaches to overcome this limitation.

Chapter 3 presents the experimental details of this thesis. First, the principles of synthesis methods used to prepare thin film devices are described in detail. Next, the main analytical techniques are highlighted for the characterization of the $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ heterostructure. Due to the intricacy of these methods, only the operating procedures pertinent to our study is discussed

Chapter 4 assesses the deposition condition for obtaining single-phase epitaxial $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ thin films on SrTiO_3 (001) single crystal substrates. Next, the detailed structural characterization of the SrRuO_3 buffer layer is discussed.

Chapter 5 investigates the structural phase transition in the epitaxial (001) $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ film deposited on SrRuO_3 -buffered SrTiO_3 substrate. A thickness-dependent structural evolution from tetragonal-like to a monoclinically distorted phase is observed. More importantly, the correlation between the film structure and its optoelectronic properties is also examined in this chapter. A distinct optical absorption process is identified in the tetragonal phase, which is also manifested in the spectral photoresponse.

Chapter 6 employs a new approach to realize the room-temperature ferroelectric polarisation in BFCO thin film by using the combined effect of epitaxial strain and growth kinetic during the film deposition. A three-order of magnitude suppression in the leakage current is reported through judicious adjustment of the laser fluence. High remnant polarisation, i.e., $2P_r \sim 100 \mu\text{C cm}^{-2}$, was measured for the 200 nm epitaxial BFCO (001) film on SrTiO_3 substrate comparable to the *ab-initio* predicted value. A considerable photocurrent density was also obtained under an external bias of 1 V for the film grown at optimum condition, associated with the effective photoexcited charge separation.

Chapter 7 is a summary of the major experimental findings, accompanied by a conclusion and possible future works. It also presents prospects of BFCO-based thin film for solar energy harvesting and optoelectronic application.

Chapter 2. Literature Review

Note that substantial part of this chapter is formed from an ‘Accepted /Original Manuscript’ of an article²¹ published by Taylor & Francis Group in *Critical Reviews in Solid State and Materials Sciences* on 7 Jan 2020, available online: [10.1080/10408436.2019.1708700](https://doi.org/10.1080/10408436.2019.1708700)

Purpose of this section is to ascertain the promising role of ferroelectric oxide perovskite in solar harvesting applications, with a major focus on lead-free bismuth ferrite-based devices. While photoferroelectrics mostly remained an area of academic research during past decades, this study is expected to motivate researchers from other fields, namely solar engineering, to delve deep into ferroelectrics perovskite to overcome the existing limitations. After a brief introduction on the ferroelectricity in perovskite structure, the status of ferroelectrics as light absorber material is discussed, highlighting their advantages and drawbacks. Then a brief survey of advances in understanding the ferroelectric PV effect is introduced. Different approaches are then delineated to understand strategies to optimize PV effect in BFO-based structures. From this point, the cooperative impact of interfacial effect and oxygen vacancies on the realization of bulk PV effect features (e.g., switchable photocurrent) will be discussed. This is followed by the concept of bandgap tuning in bismuth ferrite to increase the power conversion efficiency.

2.1 Perovskite Structure

Perovskite compounds with an ABX_3 chemical formula are widely investigated due to their versatile physical and chemical properties. The ideal perovskite structure is cubic, where six X anions surround the B-site cation, creating the BX_6 octahedron as shown in

Figure 2-1(a). Goldschmidt's rule determines the probability of forming a perovskite structure by the pairing of ions as follows:²²

$$t = (r_A + r_X) / \sqrt{2}(r_B + r_A) \quad (\text{Equation 2 – 1})$$

where r_i is the ionic radii of ions and t is the tolerance factor, which is close to 1.0 for the stable structure. Note that modification of atomic species leads to a distortion of octahedra accompanied by a tolerance factor alteration. A similar effect can be envisaged by chemical substitution in the A/B-site, resulting in a wide range of properties.

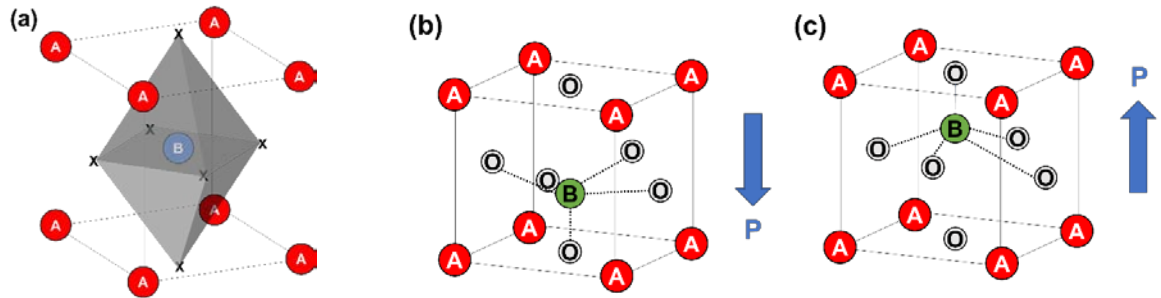


Figure 2-1 Schematic of perovskite structure

(a) Structure of perovskite oxide (x denotes oxygen atom). Ferroelectric phase with (b) downward (c) upward polarisation direction.

2.2 Ferroelectric Oxide Perovskite

Ferroelectricity refers to the ability of a material to display a spontaneous electric polarisation that can be switched upon applying an electric field.²³ In oxide perovskites, the ferroelectric phase appears when perovskite undergoes a structural phase transition from the centrosymmetric cubic phase at higher temperature to the low-symmetry phase below transition temperature also known as the Curie temperature.⁹ Along with this mechanism, cations are also shifted relative to the arrangement of the anions, as shown in Figure 2-1(b, c), causing an electric dipole moment, which is the source of

spontaneous polarisation in the conventional ferroelectric perovskites like BaTiO₃²⁴. Nonetheless, the quest for a novel inversion symmetry breaking mechanism has led to the emergence of the ferroelectricity induced by the lone pair, geometric effect and charge ordering.¹ Ferroelectrics are extensively used as storage media,²⁵ ferroelectric random-access memories,²⁶ and micro-electro-mechanical systems (MEMS).²⁷ With an increasing demand for miniaturization of devices, the coupling of ferroelectricity with other characteristics such as magnetism has led to novel areas of research with the possibility of application in emerging technologies.

2.3 Multiferroics

Multiferroics are a category of materials where at least two ferroic orders, like magnetism and ferroelectricity, are paired. The technological importance of such material is triggered by the possibility of controlling the charges by an external magnetic field and the spin order by the electric field.²⁸ However, multiferroics are very rare because transition metals as B-site cation control the breaking of inversion symmetry and magnetic ordering in the majority of ferroelectrics and magnetic materials, respectively. On the one hand, breaking the centrosymmetry requires the transition metal to possess an empty d orbital to repress the electrostatic repulsion of the adjacent oxygens. On the other hand, transition metal needs to have a partially-filled d orbital enabling the magnetic moment.²⁹ Therefore, the condition for magnetic and ferroelectric order to coexist is restricted in the conventional perovskite materials. In this regard, there are possible routes to integrate both properties into a single compound. One can think of (a) incorporating d^0 TM cation on the centre of octahedral and the magnetic element positioned at the corner of the unit cell,³⁰ or (b) employment of the improper ferroelectricity to induce noncentrosymmetric polar structure combined with a

magnetic behaviour from transition metals with partially-filled *d*-orbital, like Ruddlesden-Popper $\text{Ca}_3\text{Mn}_2\text{O}_7$ compound,³¹ and (c) using stereochemical active cations like Bi^{3+} at A-site to introduce ferroelectricity and magnetic ions as the B-site candidate.¹ The latter has triggered a great research interest in Bi-based perovskite oxide with a host of fascinating properties, where simultaneous ferroelectricity and anti-ferromagnetism has been observed at room temperature.³²

2.4 Multiferroics as Photoactive Materials

Photovoltaic effect refers to the process in which energy of light is directly transformed to electricity by separation of the photoinduced bound excitons. Several mechanisms can induce the electron-hole pair dissociation, such as a built-in electric field in a conventional p-n junction,³³ the heterojunction of inorganic-organic hybrid systems,³⁴ and lacking inversion symmetry in ferroelectric materials.³⁵ There is a considerable amount of literature on PV devices that can be categorized in the crystalline, thin film, and emerging PV technologies, each having their respective drawback towards their future use (see Table 2-1).

Recently, hybrid perovskite solar cells (e.g., methylammonium lead iodide) have spurred interest of the PV community by virtue of rapid power conversion efficiency (PCE) enhancement from 3.9%³⁶ to 22.7%³⁷ in less than a decade. Yet, archetype 3D hybrid perovskites suffer from instability when exposed to moisture, UV light and high temperature.³⁸ On the other hand, the emerging low-dimensional Ruddlesden-Popper perovskites have become a rising star for use in solar harvesting applications due to their remarkable moisture tolerance and photo /and thermal stability.³⁹

Such layered 2D structures with the general formula of $(A_{n-1}A'2M_nX_{3n+1})$ can be achieved by incorporating an organic molecule spacer (A') between the adjacent $[MX_6]^{4-}$ octahedral sheet, bringing about a multiple-quantum-well structure.⁴⁰ The control over stacking of the inorganic layer provides a unique degree of freedom – facile structural flexibility – which endows these types of perovskite with tunable optoelectronic properties.⁴¹ Most recently, a five-layered Ruddlesden-Popper $(MTEA)_2(MA)_4Pb_5I_{16}$ cell with a PCE of 18.06% has been reported along with promising moisture resistance up to 1512 h under 70% humidity and thermal stability for 375 h at 85 °C conditions.³⁹ It is worth noting that the insulating characteristic of the organic spacer in the Ruddlesden-Popper structure diminishes the carrier mobility, which in turn exacerbates radiative recombination losses.⁴⁰ Therefore, regardless of increasing research effort on the Ruddlesden-Popper perovskites, further enhancement in device performance and transport dynamics is required for these types of perovskite to compete with the conventional 3D hybrid counterparts.

Note that apart from the long-term stability issue, an arguable topic in the perovskite solar cells is the usage of toxic lead, a staple component of highly efficient perovskite cells.^{42,43} Lead content in PV cells is dissolvable in water, contaminating the food chain with deleterious consequences on human wellness. According to the hazardous substances directive of the European Union, the upper limit of lead concentration is set to 0.1% in weight in any electronic device.⁴⁴ Unfortunately, all the sufficiently efficient halide perovskites include more than 10% Pb concentration.⁴² Thus, the substitution of lead would increase the likelihood of commercialization for hybrid perovskite solar cells from an environmental and statutory perspective. In this regard, tin perovskite has been extensively studied with the highest-efficiency of 8.12% for mixed-ion mixture of

(FA)_{0.75}(MA)_{0.25}SnI₃.⁴⁵ However, most efforts toward replacement of lead with tin or germanium have exhibited formation of lattice vacancies associated with the oxidation state of Sn (Ge).⁴⁶ This behaviour is correlated with non-stable s pair in isoelectronic s²p² elements, i.e., Sn (Ge) is more stable in +4 oxidation state.⁴³ Therefore, exploring alternatives for lead-free perovskite have resulted in more attention to oxide perovskites, especially ferroelectric oxide perovskite.^{47,48} In ferroelectric perovskites, the charge separation mechanism relies on the bulk PV effect, which is a fascinating phenomenon due to featuring distinctive above-bandgap photovoltage and switchable photocurrent, making ferroelectrics an appealing candidate for next-generation PV devices. In contrast to hybrid halide perovskite, most of the ferroelectric oxide perovskite exhibit good resistance to humidity and ultraviolet light. The variety of attributes in oxide perovskite is linked with ease of accommodating the majority of metallic elements in the periodic table in their crystal structures.⁴⁹

Table 2-1 Photovoltaic technologies and respective technical limits

	Technology	PCE ³⁷ (%)	Drawback to future use
Bulk crystalline	Crystalline Si	26.1	High cost of processing ⁵⁰
	α -Si	14	Short minority carrier diffusion length ⁵¹
Thin film	CdTe	22.1	Toxicity of cadmium ⁵²
	CIGS	22.6	Scarcity of elements, such as indium ⁵³
	CZTS	12.6	High recombination rate at defects and interfaces ⁵¹
Emerging	Dye-sensitized	11.9	Stability and low efficiency ⁵⁴
	Quantum dot	13.4	Marginal photon absorption, and low photovoltage ⁵⁵
	Perovskite	22.7	Stability in different environment and toxicity of Lead ⁴²

The PV effect in bulk of ferroelectric crystals was firstly observed in BaTiO₃ about 60 years ago, showing a steady photocurrent above the Curie temperature.⁵⁶ The photovoltaic effect in ferroelectrics is assumed to be a bulk effect resulting from non-

centrosymmetry nature of crystal where photoinduced charge carriers are dissociated through a homogeneous media.⁸ The working principle of ferroelectric PV devices differs entirely from that of the conventional p-n junction in which the photoexcited electron and holes are separated by built-in electric field at the junction. In the conventional semiconductor, electrons are dislodged from the valence band to the conduction band and leaving holes behind by excitation energy from the absorbed photon. Therefore, the magnitude of photovoltage is limited by the bandgap of the light-absorbing material.⁵⁷ In ferroelectric materials, by contrast, the photovoltage output is anomalously above the bandgap of the material,^{7,58,59} and its value is related to the crystal size in the polarisation direction.⁸ Generally, the binding energy of the electron-hole pair is inversely related to the material's dielectric constant. The dielectric constant of ferroelectric oxide perovskites can range up to 5×10^3 ,⁹ resulting in the relatively smaller binding energy of excitons compared to the inorganic semiconductors. Furthermore, sizable magnitudes of spontaneous polarisation have been reported for ferroelectric. For instance, epitaxial BiFeO₃ (001) films demonstrate polarisation of $60 \mu\text{C cm}^{-2}$,⁶⁰ which is also beneficial to the photoinduced charge separation mechanism.

To date, the PV effect has been investigated in various ferroelectric oxide perovskites, including LiNbO₃ (LNO),^{59,61} BaTiO₃ (BTO),⁵⁸ Pb(Zr,Ti)O₃ (PZT),^{62,63} and BiFeO₃ (BFO).^{8,64} Figure 2-2 depicts the chronological advancement of thin film ferroelectric oxides in terms of device efficiency.

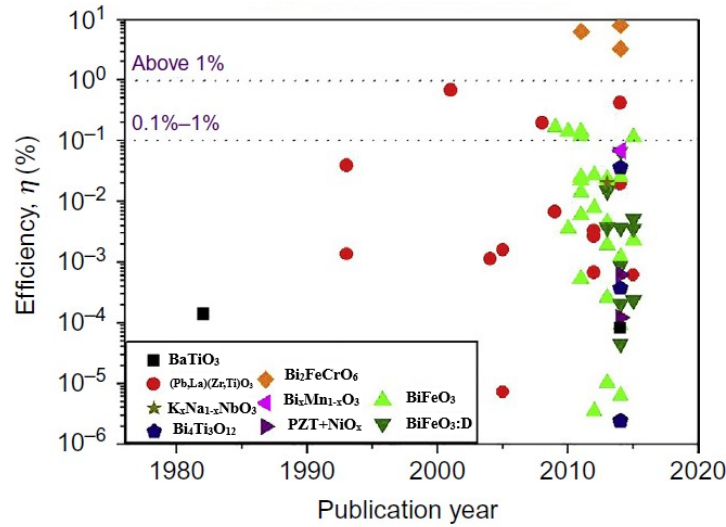


Figure 2-2 Power conversion efficiency

PCE of the ferroelectric oxide films plotted based on publication year. (Reprinted with permission from Ref.⁶⁵)

Note that most ferroelectric materials have a bandgap greater than 3 eV and hence, the absorption of visible light declines, resulting in a low photocurrent output. The B-site cations in oxide perovskite are generally transition metal ions. The considerable electronegativity difference between the conventional transition metal ions and oxygen is deemed to be the main reason for possessing a wide bandgap. As shown in Figure 2-2, the majority of reported efficiencies fall below 0.1% which considerably hampered industrial acceptance of ferroelectric based PV devices. However, the field of ferroelectric PV went through a resurgence in recent years because of the ability to engineer high-quality thin films with tuned properties.

2.4.1 BiFeO₃ Structure and Properties

As a lead-free intrinsic multiferroic oxide perovskite, bismuth ferrite has gained interest in the PV research by virtue of having a rather low bandgap compared to other ferroelectric oxides. BFO has a distorted rhombohedral perovskite structure related to R3c space group with lattice parameter of $a_{rh} = 3.965 \text{ \AA}$ and $\alpha_{rh} = 89.3^\circ$ (Figure 2-3(a)).

The distorted Fe-O octahedra resulting from mismatched ionic sizes is of paramount importance in controlling the magnetic ordering and orbital overlap between Fe and O in BFO crystal.³ The unit cell has also been reported as hexagonal structure with a lattice parameter of $a_{\text{hex}} = 5.58 \text{ \AA}$ and $c_{\text{hex}} = 13.90 \text{ \AA}$, having direction of $[001]_{\text{hexagonal}}$ parallel to $[111]_{\text{pseudocubic}}$ (see Figure 2-3(b)). Bismuth ferrite exhibits ferroelectricity and G-type anti-ferromagnetism at high transition temperature of $T_c \approx 1100 \text{ K}$ and $T_N \approx 640 \text{ K}$, respectively. In general, the condition of coupling between ferroelectric and magnetic order is stringent due to their different origins, considering the subtle role of transition metal *d*-electrons. In bismuth ferrite, however, asymmetry resulted from lone pair electrons of Bi provides the possibility for concomitant ferroic orders regardless of the occupancy level of *d*-orbital of magnetic Fe^{+3} .²⁹ From optical perspective, BFO turns out to possess a direct bandgap ranging from 2.3-2.8 eV,³ and to demonstrate non-trivial bulk photovoltaic effect.⁸ These prominent attributes endow BFO-based devices with remarkable functionalities in the field of ferroelectrics, magnetic and next-generation photovoltaics.

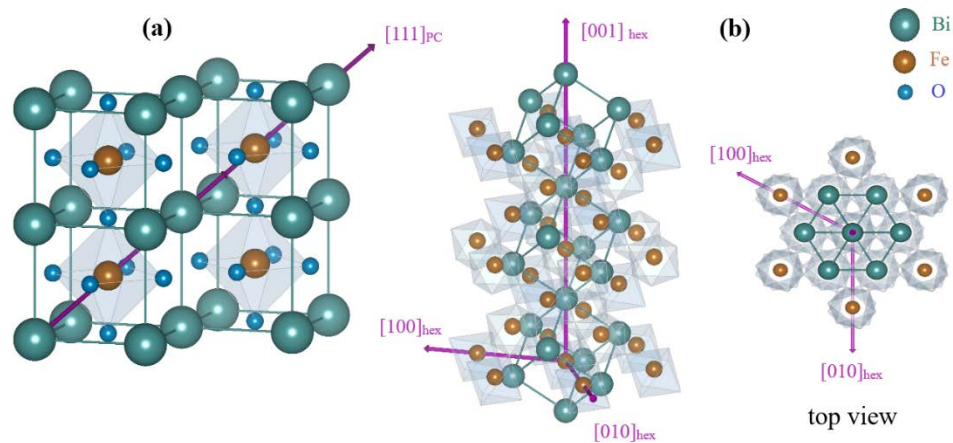


Figure 2-3 Crystal structure of BFO

(a) rhombohedral and (b) hexagonal frame (VESTA was used to model the structure.⁶⁶)

The photoresponse of BFO-based devices relies on various factors, including chemical composition,¹² film thickness,¹³ concentration of defects,^{14,67} substrate-induced strain,¹⁵ intensity and wavelength of incident light,⁶⁸ polarisation⁶⁹ and film/electrode interface characteristics.⁷⁰ In addition, the way in which oxide perovskite is fabricated also influences its properties. Thus, many studies have been conducted to synthesize BFO-based thin film using different growth techniques, such as chemical solution deposition and physical vapour deposition. Notwithstanding the flexibility and cost-effectiveness of chemical solution deposition processes, physical vapour deposition can yield very good quality complex oxide thin films for research purposes. It has been claimed that PVD offers high control over the growth and properties of thin film.⁷¹ In this perspective, we have opted to outline the recent progress about photovoltaic effect of the BFO-based thin films deposited solely by physical vapor deposition methods, including rf magnetron sputtering, pulsed laser deposition and molecular beam epitaxy.

2.5 Advances in Understanding Photovoltaic Effect in Ferroelectric BiFeO₃

2.5.1 Bulk Photovoltaic Effect

In general, PV effect originates from the spatial nonuniformities caused by either crystal inhomogeneity like conventional p-n junction or nonuniform illumination known as the Dember effect.³⁵ Nevertheless, in the late 1960s, lacking a centre of symmetry in a medium was also reported to contribute to generation of the photocurrent.⁷² Note that contrary to the former origins of the photovoltaic effect, the latter was observed in a homogeneous crystal and under uniform illumination. The appearance of a steady photocurrent in a non-centrosymmetric homogeneous media is coined “bulk photovoltaic effect” (BPVE).⁷³ The BPVE current has polarisation dependency and it

can be termed by third rank tensor under linearly-polarized illumination since it exhibits a second-order nonlinear optical response. Hence, the contribution of BPVE to the photocurrent and its dependency on the light wave polarisation vector can be written as

$$J_{sc} = \beta_{ijk}^L E_j E_k^* I \quad (\text{Equation 2 – 2})$$

where β_{ijk}^L is BPVE third rank tensor for linearly-polarized light, E_n denotes polarisation vector in direction n and I is the intensity of light.⁷² Assuming a steady photocurrent, the open-circuit photovoltage V_{oc} arising from photocurrent is proportional to electrode spacing (d), dark and photo-conductivity (σ_d , σ_{ph}) by:

$$V_{oc} = \frac{d}{\sigma_d + \sigma_{ph}} J_{sc} \quad (\text{Equation 2 – 3})$$

From Equation 2-2, one can simply infer the symmetry requirement for having a non-zero photoresponse. Furthermore, it is evident that the value and sign of BPVE current also vary with crystal orientation with reference to the angle of the light polarisation vector. Recently, Bhatnagar et al. showed the angular-dependency feature of BPVE in BFO thin films as photocurrent fitted the sinusoidal function of light polarisation angle with respect to in-plane direction of sample (Figure 2-4).⁷⁴ Similarly, strong oscillation of short-circuit photocurrent with polarisation direction of light was observed in Mn, Zn co-substituted BFO film grown epitaxially on vicinal STO substrate, suggesting the BPVE is the most probable origin of photovoltaic effect.⁷⁵ An enhanced photovoltage was also obtained in co-doped BFO films compared to that of pristine films due to the lowered photoconductivity induced by co-doping in compliance with Equation 2-3.

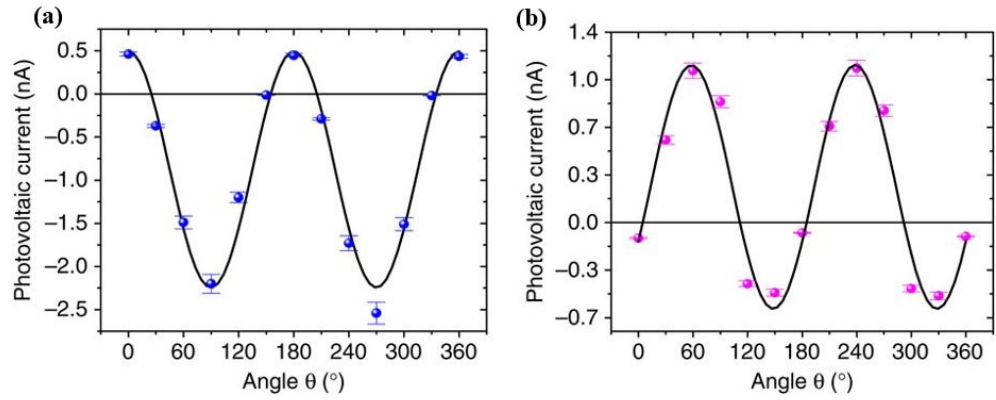


Figure 2-4 Oscillation of PV current in BFO thin film with 71° domain walls

For configuration of electrodes (a) parallel to domain walls (b) perpendicular to domain walls. (Reprinted with permission from Ref.⁷⁴)

From a microscopic perspective, BPVE mechanism stems from the absence of symmetry in velocity or density of non-thermalized carriers in momentum and real space, correspondingly.⁷⁶ On one hand, asymmetric distribution of photoexcited carriers in momentum space generates a local net current in non-centrosymmetric systems, known as “ballistic current”. The ballistic contribution to BPVE current is related to the breakdown of the detailed balancing for nonequilibrium carriers, which arises from asymmetrical scattering sites (Figure 2-5(a)), anisotropic potential well at the absorbing centres (Figure 2-5(b)) and bands splitting by spin-orbit coupling in gyrotropic crystals (Figure 2-5(c)).³⁵

It is important to realize that breaking inversion symmetry is the key requisite for ballistic contribution to BPVE current; and also worth mentioning that this current is ephemeral and relies on the mean free path of photogenerated carrier which is approximated to be less than 100 nm.⁷² The mean free path dependency of photocurrent, also stipulated in earlier Glass’ model,⁵⁹ emphasizes possibility of enhancing BPVE at nanoscopic scale. Following this concept, a six-fold increment in the photocurrent density was observed by decreasing thickness of BFO film fabricated on STO from 450

nm to 40 nm under the illumination of violet monochromatic light with intensity of 20 mW cm^{-2} .⁷⁷ Nonetheless, contradictory thickness-dependence of photocurrent has been reported by Nakashima et al., claiming short-circuit photocurrent decreases with reducing BFO (111) film thickness in PV cells with Pt coplanar electrodes since photoconductance of STO substrate diminishes the photocurrent more effectively as BFO films become thinner.⁷⁸ Although both studies considered BPVE theory as the main mechanism of abnormal photovoltaic effect, the latter had also taken the effect of photon absorption into account.

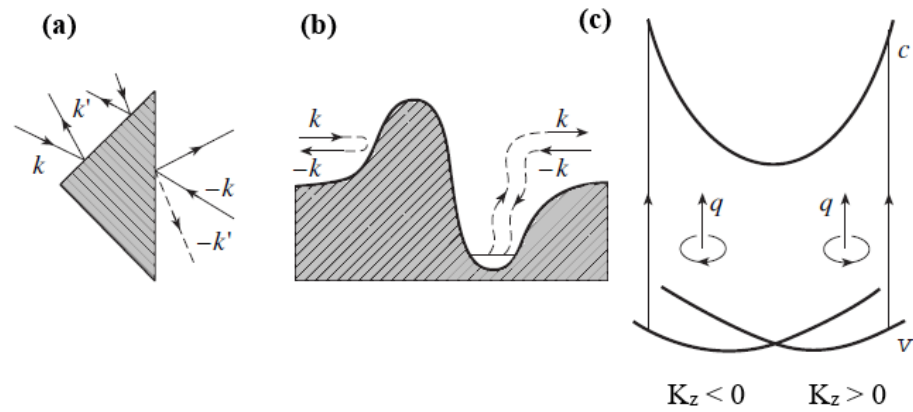


Figure 2-5 Breakdown of the detailed balancing for nonequilibrium carriers

(a) asymmetric scattering sites (b) asymmetric potential well at absorbing centre (c) valance band maximum splitting in gyrotropic crystal due to relativistic spin-orbit coupling. (Reprinted with permission from Ref.³⁵)

On the other hand, a net current termed “shift current” arises from asymmetrical shift in density of photogenerated carriers in real space when excited from one band to another. At first, Von Baltz and Kraut proposed the shift current theory to justify BPVE in barium titanate.⁷⁹ Afterwards, it was derived within the theoretical model of the Green function and nonlinear optics.^{80,81} Later on, the shift current theory was improved by

Young and Rappe, who provided first-principles calculation which was in agreement with experimental data of ferroelectric materials for the first time.⁸²

Here, the excitation mechanism of nonequilibrium carriers is governed by the consistent evolution of electron-hole wave functions that are well expressed by the time-sensitive perturbative framework. The shift current is thus associated to electromagnetic field as follows:⁸²

$$J_q = \sigma_{rsq} E_r E_s \quad (\text{Equation 2 – 4})$$

$$\sigma_{rsq}(\omega) = e \sum_{n', n''} \int dK I_{rs}(n', n'', K; \omega) R_q(n', n'', K)$$

where σ_{rsq} is a second-order response function of crystalline material integrated across the Brillouin zone, and I_{rs} , R_q indicating transition intensity and shift vector between the band n' and n'' , respectively. Upon excitation, shift current carriers quickly transmit to the collecting electrodes, making energy losses originated from inelastic scattering insignificant compared to the drift-diffusive mechanism in p-n junction. Thus, the degree of delocalization of bands state can highly influence shift current via aiding coherent evolution of carriers.⁸³ The shift current phenomenon has been studied both experimentally,^{84,85} and theoretically.^{82,86} However, its relationship with the physical properties of materials, namely ferroelectricity, has not been assertively elaborated. It is denotive that shift current relies on the attributes of the electronic wavefunction,⁸⁷ and it has no direct mutual relation with the polarisation of material, except both phenomena necessitate breaking inversion symmetry.⁸⁶ A comprehensive survey of design strategies to optimise the shift current can be found elsewhere.⁸³

2.5.2 Depolarisation Field Effect

Since early attempts to fabricate ferroelectric thin films, their poor retention capability has been associated with the depolarisation field. If not completely screened by compensation charges in the electrodes, polarisation charges distributed at the surface of the ferroelectric material sandwiched between electrodes can induce an electric field with an opposite direction to polarisation vector, suppressing the amplitude of polarisation.⁸⁸ As the depolarisation field is inversely related to the distance between charged surfaces, its effect is more significant in ferroelectric thin film (<100 nm) than bulk counterparts,⁸⁹ and in the worst case, the ferroelectric polarisation would completely vanish in ultrathin films below a critical thickness.⁹⁰ Note that surface charges are inevitably screened partially because the centre of the polarisation charges and electrode mobile carriers is not the same.⁸⁸ Therefore, a non-vanishing electric field as large as 300 MV cm^{-1} can exist over the entire film,⁹¹ that is reportedly believed to play a significant role in the separation of the photoinduced charge carriers.^{9,92} In 1969, Chen noticed a photocurrent in the direction opposite to the spontaneous polarisation in single-crystal LiNbO_3 under UV illumination and considered an unidentified internal electric field to be the source,⁹³ that was later specified as depolarisation field. This sparked further investigation on the depolarisation-induced PV effect mechanism. In 2009, Qin et al. established a detailed model in which ferroelectric material and contacting electrodes were taken into account as a whole.⁷⁰ Theoretical results shown in Figure 2-6(a) reveal that electrodes with large dielectric constant, e.g., conductive oxides such as $(\text{La, Sr})\text{MnO}_3$, induce higher photocurrent by virtue of weakening the polarization screening effect. Additionally, the authors predicted that minimizing the screening effect gives rise to higher power conversion efficiency up to 19.5% in

ultrathin PLZT films, ca. 1.2 nm. However, one can raise a question on the validity of their prediction since insufficient compensation of polarisation charges compromises intrinsic polarisation in ferroelectric film.^{94,95}

Regardless of all uncertainties, the depolarisation-induced charge separation mechanism can clearly explain the switchable photovoltaic effect by studying the polarity of PV output. For example, Katiyar et al. grew polycrystalline co-substituted BFO thin films and ascribed the observed switchable J_{sc} and V_{oc} after flipping polarisation (shown in Figure 2-6(b)) to the depolarisation field.^{96,97} Section 2.6.1 is devoted to understand further the effect of film/electrode interface on depolarisation field and energy barrier modulation.

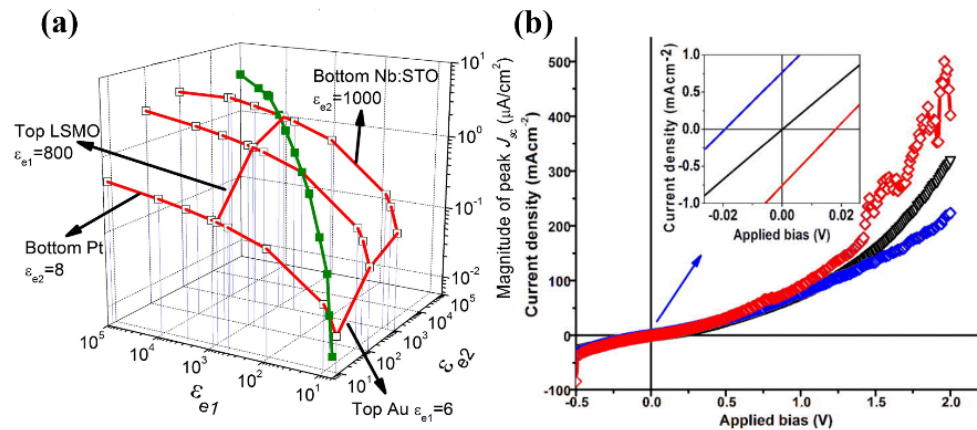


Figure 2-6 Investigating impact of depolarisation field on the photocurrent density

(a) Calculated results showing effect of dielectric constant on peak of photocurrent density. (Reprinted with permission from Ref.⁷⁰) (b) I-V curve for Al-doped ZnO/Bi_{0.9}La_{0.1}Fe_{0.97}Ti_{0.02}Zr_{0.01}O₃/Pt under illumination of 1 kW m⁻² (blue, red and black lines indicate positive, negative and no poling situation, respectively). (Reprinted with permission from Ref.⁹⁷)

2.5.3 Schottky Barrier Effect

In a situation that a metal with high work function and ferroelectric semiconductors are brought into contact, a photovoltage is generated by the built-in electrical field near the metal/ferroelectric interface, where photoexcited charge carriers are separated. The magnitude of the photovoltage is commensurate with the Schottky barrier height and width of the depletion region.⁹⁸ Consequently, PV effect derived from Schottky barrier is limited to the bandgap of ferroelectric material, and it cannot describe the PV effect in bulk ferroelectrics as the observed photovoltage is much larger than the bandgap. However, this effect is more apparent in the ferroelectric thin film due to the comparability of the film thickness and width of the depletion layer. Provided that either ferroelectric polarisation charges^{16,70} or charged defects^{14,99} can adjust the Schottky barrier height, switchability of the PV effect can be elaborated by the Schottky barrier effect. In a ferroelectric-based PV device with the ferroelectric film sandwiched between two electrodes, both direction and value of PV response is determined by the difference between Schottky barrier at electrode/ferroelectric interfaces.⁷⁰ Therefore, having asymmetric electrode/ferroelectric interfaces may be essential to observe contribution of Schottky barrier into PV effect.⁹² Otherwise, PV response from similar Schottky junction would cancel out each other due to running in opposite direction.

A simple model was proposed by Zheng et al.¹⁰⁰ to differentiate the contribution of Schottky barrier and depolarisation on PV effect of Pt electroded PZT films by calculating values of $(I_{up}+I_{down})/2$ and $(I_{up}-I_{down})/2$ which represent short-circuit photocurrent derived from built-in field of Schottky barrier and depolarisation field, respectively. One can readily measure the photocurrent in up-poled (I_{up}) and down-poled (I_{down}) films to estimate aforementioned values. The authors disregarded the

polarisation-dependence behaviour of Schottky barrier height as they assumed the Schottky junction effect is conversely proportional to the film thickness and not affected by changing polarisation. This is a baffling issue on which the following sections further shed light.

2.5.4 Domain Wall Effect

No significant breakthrough had been made regarding the exact photovoltaic mechanism in ferroelectrics until late 2000s when Yang et al.⁷ unfurled a new mechanism based on the electrostatic potential steps at the ferroelectric domain walls. They observed above bandgap photovoltage of 16 V and photocurrent density of 0.12 mA cm⁻² in BFO films possessing arrays of either 71° or 109° domains with the orientation of the electrodes parallel to the domain walls, while no PV effect was detected for perpendicular configuration of the electrodes with respect to the domain walls. Of note, samples having no domain wall between electrodes exhibited insignificant photovoltage, which further corroborates the authors' postulation regarding the eminent role of domain walls over the non-centrosymmetric nature of crystal in photovoltaic effect.

In domain wall effect, the photoexcited electron-hole pairs are separated by high electric field (of the order of 5 kV cm⁻¹) resulting from potential drops at the domain walls. These potential steps are originated from the component of polarisation orthogonal to the domain walls as shown in Figure 2-7.¹⁰¹

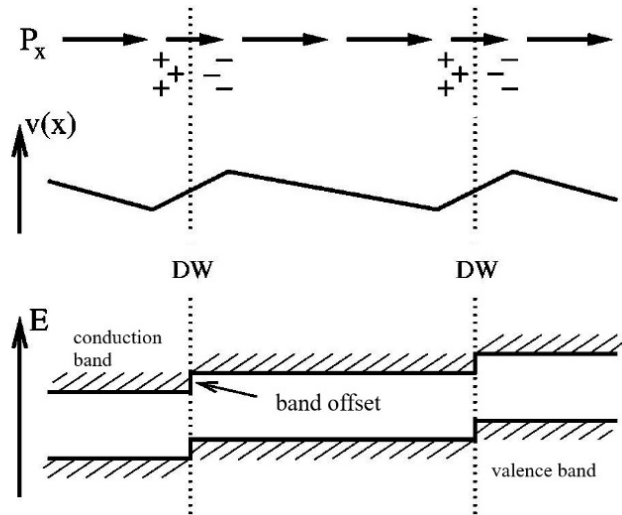


Figure 2-7 Domain wall effect

Schematic of polarisation component orthogonal to DWs and corresponding electrostatic potential ($v(x)$) and band diagram. (Reprinted with permission Ref.¹⁰¹)

Yang et al.⁷ assumed that the excitons tend to recombine rapidly and become localized within the domains, and on the contrary, they are more effectively dissociated near the domain wall because of the significantly large electric field. Thus, the charge carriers pile up on different sides of the domain wall, and this unequal distribution of charge carriers in the vicinity of the domain walls, which acts like a depletion layer, results in the energy band alignment. In this way, a net photovoltage is produced throughout the whole sample.

Nevertheless, domain wall effect has been questioned based on subsequent experimental findings. Alexe and Hesse¹⁰² cast doubt on the main assumption of domain wall theory, i.e., rapid recombination in domains. Employing photoelectric AFM not only refuted massive recombination of photoexcited carriers within domains compared to the vicinity of domain walls, but also proved that AFM tip effectively scaled up the photocurrent density and quantum efficiency by seven-order of magnitude. Furthermore, the role of domain walls has been elucidated by Bhatnagar and co-workers

who studied PV properties of BiFeO₃ thin films as a function of the temperature.⁷⁴ They asserted that the shift current is the origin of the abnormal photovoltaic effect since large photovoltage was measured irrespective of domain wall type and geometry of the electrodes with decreasing temperature to 80 K (see Figure 2-8).

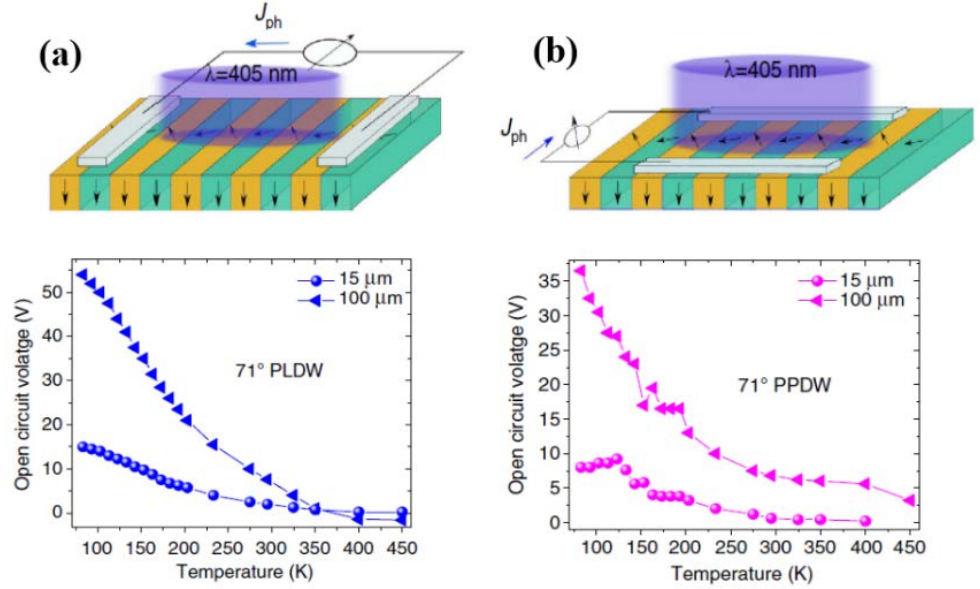


Figure 2-8 Temperature-dependent photovoltages in BFO thin films

For different configurations of surface electrodes (a) parallel and (b) perpendicular to array of 71° DWs. Two electrodes spacing i.e., 15 μm and 100 μm , were adopted for the measurements. (Reprinted with permission from Ref.⁷⁴)

Considering the enhanced conductivity of the domain walls compared to the bulk of BFO, and taking Equation 2-3 into account, one can simply elaborate the role of domain wall in the temperature-dependent behaviour of V_{oc} . In the same fashion, Yang's observation can be explained, such that domain walls act rather as an electrical shunt in case of electrodes placed perpendicular to the domain walls, as a result of high dark and photoconductivity of domain wall. This enhanced conductivity is likely due to release of free carriers from localized defects near the domain walls.¹⁰³

More studies have been conducted on the effect of domain walls on PV effect. For instance, Nakashima et al.¹⁰⁴ have grown BiFeO₃ thin films on STO (113) substrate and notwithstanding the single-domain structure, BFO films still showed above-bandgap photovoltage of 26 V when electrodes are running perpendicular to the in-plane polarisation vector. Similar to Bhatnagar et al.,⁷⁴ they also considered shift current model as the origin of abnormal V_{oc} value. More recently, a thorough investigation on the effect of domain wall, namely 71° domain structure, on PV effect showed that apart from inducing electrostatic potential steps as reported by Yang et al.,⁷ an additional PV component derived from strong local ferroelastic lattice distortion, is also present at the domain wall region that is superimposed onto the bulk PV effect.¹⁰⁵ Experimentally, they have shown that 71° striped-domain films exhibited superior photovoltage compared to that of single-domain films although the former had higher photoconductivity (0.9 $\mu\text{S cm}^{-1}$). Their observation contradicted the finding of Bhatnagar et al.,⁷⁴ and implied a considerable contribution of domain walls to the PV effect.

Given the intricate function of domain walls in the ferroelectric PV effect, there is still room to shed light on its true mechanism. Yet, a plethora of surprising properties can be provided by different domain structures. As an example of how domain engineering can be utilized to enhance photovoltaic properties, BFO films were epitaxially deposited on vicinal STO substrate with varying miscut angles (Figure 2-9).¹⁰⁶ It turns out that photocurrent scaled up with decreasing miscut angle, while photovoltage, measured by SKPM, remained constant. The photocurrent enhancement was attributed to the larger number of domain walls favoured by smaller miscut angles, at which photoexcited carriers can readily move due to higher conductivity.

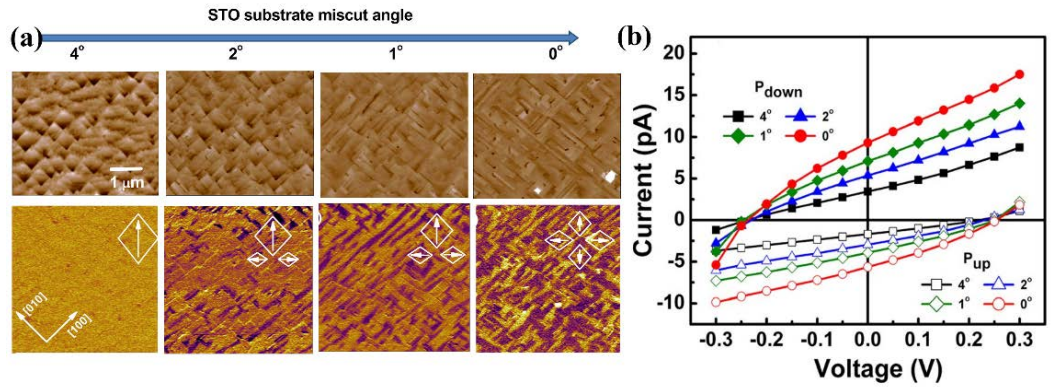


Figure 2-9 Effect of vicinal substrate on photoresponse of BFO films

(a) Topography (top row) and in-plane PFM (bottom row) images of BFO film on STO with different miscut angle [inset arrows illustrate the in-plane polarisation variant] (b) Corresponding I-V curve under illumination of halogen lamp with energy density of 20 mW cm^{-2} . (Reprinted with permission from Ref.¹⁰⁶)

2.5.5 Nanoscale Excitonic Photovoltaic Mechanism

As discussed above, the domain wall effect assumes that charge separation is localized at the domain wall, which is wholly counterpointed to the conventional belief that charge separation is uniform through the sample due to non-centrosymmetric nature of bismuth ferrite crystal. However, none of these studies provided compelling evidence regarding the dynamic of photoexcited carriers.

Taking advantage of transient optical spectroscopy and time-resolved X-ray diffraction (TRXRD) method with nanoscale spatial resolution, Li and co-workers studied optically-stimulated dynamic strain gradient in epitaxial BFO (001) thin films.¹⁰⁷ The authors found a nanoscale relation holds between the optical absorption from photocarrier dynamic and the piezoelectric response arising from photovoltaic field. Thus, they proposed nanoscale excitonic mechanism, suggesting photoexcited carrier remain charge-neutral, i.e., exciton, in the bulk of the film and become separated by local band bending at the interface (see Figure 2-10). Subsequently, the free carriers

may remain or move to the other side depending on the local polarisation and the screening field. Such localized dissociation of exciton agrees well with the interfacial and domain wall effects mentioned earlier. However, note that the nanoscale excitonic mechanism cannot be detected directly for bulk samples because of short diffusion length of excitons.

In addition, this mechanism can be clearly linked to the origin of photostriction effect, a coalescence of photovoltaic and inverse piezoelectric effects in bismuth ferrite thin films,¹⁰⁸ which demonstrate photoinduced strain gradient lasting up to a few nanoseconds.¹⁰⁹ Coupling light to the lattice dynamic in multiferroic bismuth ferrite bestow promising horizons, including but not limited to optically controlled non-volatile ferroelectric memory¹¹⁰ and polarisation tuning via the flexoelectric effect.¹⁰⁹

To gain a better understanding of microscopic mechanism of ferroelectric PV effect, more fundamental studies on the charge carrier dynamic is required. Among the scarce studies, using femtosecond optical spectroscopy, Sheu et al. detected relaxation time of the photoinduced electrons to be within a few picoseconds in BFO (*100*) single crystal.¹¹¹ Moreover, employing novel scanning probe microscopy technique, Alexe found the generation and recombination processes in (*100*)-oriented BFO single-crystal occur in the range of few tens of microseconds,¹¹² which is markedly longer than values reported earlier.¹¹³ The author associated the longer generation lifetime with shallow trapping levels. Yet, many factors of carrier dynamics like mobility and diffusion length are still difficult to be evaluated due to the relatively insulating characteristic of ferroelectric materials. Further research on the carrier dynamic can lead to new design strategies for ferroelectric photovoltaic devices.

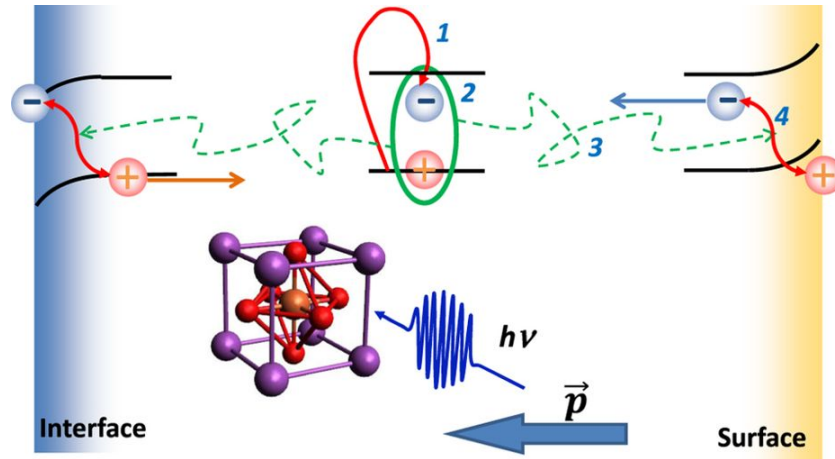


Figure 2-10 Schematic of nanoscale carrier dynamic

- (1) electrons excitation (2) formation of excitons (3) diffusion of excitons to the interface
 (4) separation caused by local band bending. (Reprinted with permission from Ref.¹⁰⁹)

2.6 Engineering Ferroelectrics for Harvesting Solar Energy

Several options are theoretically available to enhance the photoresponse of BFO based thin films. One solution is to modulate the Schottky barrier height the way in which the interfacial effect synergistically enhances the BPVE. Another avenue is to adjust the physical properties of thin film, including optical bandgap and electrical conductivity, whilst still maintaining its ferroelectricity which is often hard to achieve due to the leakage current.¹¹ Having described the feasible methods, a detailed discussion of each strategy will be presented as follows.

2.6.1 Modulating Schottky Barrier Height

2.6.1.1 Interface and Electrode Effect

Engineering of Schottky barrier height can be successfully realized by selecting the appropriate electrodes for the ferroelectric materials. The ideal design for achieving an enhanced photovoltaic effect is an asymmetric structure, consisting of one Schottky contact, while the other has ohmic behaviour.¹¹⁴ As shown in Figure 2-11, the structure

of the capacitor has to be attentively designed so that the built-in electric field at the Schottky contact is along the bulk depolarisation field.¹¹

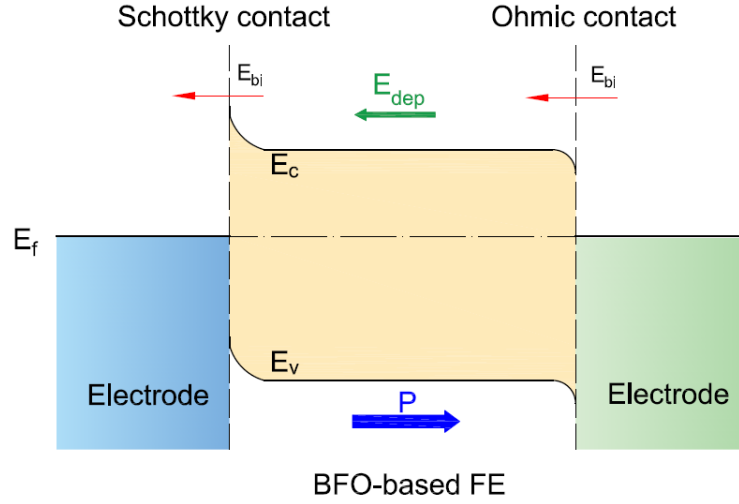


Figure 2-11 Energy band diagram of an ideal capacitor for PV effect

It is well-known that barrier height of the Schottky contact can be modulated via altering polarisation in the ferroelectric material. The polarisation-induced variation of Schottky barrier height is thus quantified by:

$$\Delta\phi_P = \pm \frac{P\delta}{\epsilon_0\epsilon_{FE}} \quad (\text{Equation 2 – 5})$$

where P , ϵ_0 , ϵ_{FE} and δ are switchable ferroelectric polarisation (P towards the electrode has a minus sign and vice versa), dielectric permittivity of free space, dielectric permittivity of ferroelectric and thickness of interfacial region, respectively.¹¹⁵ In fact, one can expect devices with relatively high Schottky barrier height compared to $\Delta\phi_P$, do not show switchable photovoltaic effect. For instance, Yang et al.⁴⁷ reported considerable increment (about one order of magnitude) in short-circuit photocurrent after flipping polarisation of (111)-oriented BFO films grown on SrRuO₃ bottom electrode, while no substantial changes were found to that of (001)-oriented BFO thin

film. The authors attributed their finding to the larger polarisation-induced change of Schottky barrier height for (111)-oriented BFO film compared to (001)-oriented BFO thin film. In another study, large V_{oc} of about 0.6 V and five-fold improvement in efficiency was also observed in negatively poled ITO/BiFe_{0.6}Sc_{0.4}O₃/LaNiO₃ heterostructure due to polarisation tuning of Schottky barrier height at FE/LNO interface.¹¹ This polarisation-induced modulation leads to an adjustable Schottky to ohmic contact at BiFe_{0.6}Sc_{0.4}O₃/LNO interface, producing switchable high and low-resistivity states. They also ruled out the effect of Sc-doping as major contributors in the enhancement of PV effect in terms of tuning both bandgap and magnitude of polarisation. However, they claimed that Sc-substitution effect is to adjust the band structure of bismuth ferrite near the interfacial region by changing the surface states.

Other works studied PV effect of ITO/ZnO/BFO/Pt multilayer polycrystalline films and obtained a considerably higher photocurrent compared to that of ITO/BFO/Pt heterostructure under monochromatic illumination with wavelength of 435 nm.¹¹⁶ By comparing results of I-V measurement for ITO/ZnO/Pt, ITO/BFO/Pt multilayers, the significant increase of the photocurrent density up to 340 $\mu\text{A cm}^{-2}$ in ITO/ZnO/BFO/Pt films was related to the contribution of zinc oxide as a major site for electron-hole generation. On the other hand, ITO/ZnO/BFO/Pt films exhibited a comparable open-circuit voltage to that of ITO/BFO/Pt, whilst ITO/ZnO/Pt showed insignificant open-circuit voltage, indicating formation of two constructive built-in field at ZnO/BFO and BFO/Pt interfaces acting as n^+-n and Schottky contact, respectively (see Figure 2-12(a)). It is to remind that authors assumed minor effect of depolarisation field on photovoltaic effect, due to insignificant polarisation-dependent PV behaviour as shown in Figure 2-12(b), which was associated to considerably smaller switchable polarisation of

ITO/ZnO/BFO/Pt originating from depression of Schottky barrier between ITO and BFO by integration of ZnO layer.

In contrast, the PV properties for ITO/bilayer BiFeO₃-BiMnO₃/Nb:STO structure with different polarisation directions demonstrated a sizable enhancement of both V_{oc} from 0.35 to 0.56 V and J_{sc} from 0.7 to 3.5 mA cm⁻² in downward and upward polarisation, respectively (Figure 2-12(d)).¹¹⁷ Consequently, for the up-polarized bilayer of BiFeO₃-BiMnO₃, a markedly large PCE of 1.43% with a high fill factor of 0.72 was measured under AM1.5 G illumination exceeds the values reported earlier for BFO-based devices. Contrary to the Fan and co-workers' assumption,¹¹⁶ authors of this study concluded that net depolarisation field developing from the self-generated polarisation of bilayer not only influenced the Schottky barrier at FE/electrode, but also gave rise to further band bending at the bilayer interfaces, enhancing the photocurrent to a greater extent for the more favourable energy band alignment at the junction (Figure 2-12(c)).

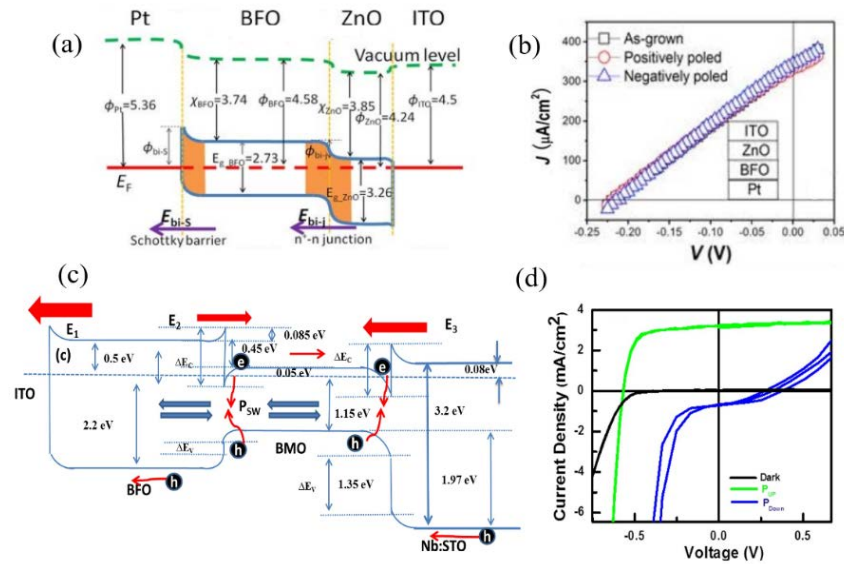


Figure 2-12 Schematic energy band alignment and PV characteristic curve

(a, b) ITO/ZnO/BFO/Pt (Reprinted with permission from Ref.¹¹⁶) and (c, d) ITO/Bilayer BFO-BMO/Nb:STO (Reprinted with permission from Ref.¹¹⁷)

Further study of interface-induced PV effect in polycrystalline BFO thin films deposited on Pt/Ti/SiO₂/Si(001) shows that degradation of interface state, stimulated by high-temperature thermal treatment, for both symmetric¹¹⁸ and asymmetric cells¹¹⁹ would be detrimental to the photovoltaic output.

The effect of electrodes and interfaces on photovoltaic attributes of ferroelectrics is of a two-sided trait. Not only can electrodes form an interfacial built-in field, but they influence the depolarisation field as well. The internal electric field in the ferroelectric capacitor may arise from electrode/ferroelectric contact, defects within the ferroelectric layer and the depolarisation field. According to Mehta et al.⁸⁸ the depolarisation field is expressed as:

$$E_{dep} = \frac{P}{\epsilon_{FE}} \frac{2\epsilon_{FE}/l}{2\epsilon_{FE}/l + \epsilon_e/l_s} \quad \text{(Equation 2 – 6)}$$

where P is the polarisation, ϵ_{FE} the dielectric permittivity, l the thickness of the ferroelectric film. ϵ_e and l_s denote dielectric permittivity and screening length of the electrode, respectively. It is evident from Equation 2-6 that depolarisation field is clearly contingent on the electrode characteristics, i.e., screening length and dielectric permittivity.

In this regard, oxide electrodes are theoretically expected to yield a larger depolarisation field compared to metal top electrodes.⁷⁰ Ding et al.¹²⁰ investigated the effect of Ag and ITO top electrodes on photovoltaic properties of polycrystalline BFO-based solar cell. Higher V_{oc} and J_{sc} were observed when using ITO as top electrode. In their study, the contribution of larger transmittance of ITO compared to that of Ag on enhanced PV response was ignored as samples were illuminated from bottom through ITO-coated

glass. Thus, noticeable enhancement of open-circuit voltage and short-circuit current were primarily ascribed to the greater screen length of ITO compared to that of Ag electrode, as a result of having comparatively smaller carrier density. Equation 2-6 also confirms their finding for the reason that larger screening length will induce larger depolarisation field.

Fang and co-workers¹⁶ systematically investigated the Schottky barrier-induced field and depolarisation field's contribution to the photovoltaic response of BFO thin films with symmetric and asymmetric heterostructures. Interestingly, they obtained a significantly greater magnitude of PV response in Pt/BFO/LSMO epitaxially grown on STO relative to LSMO/BFO/LSMO samples, which contradicts the observation of Qin et al.⁷⁰ mentioned above. In the latter study, the authors attributed larger PV response to the weaker screening effect of LSMO. However, in Fang's work, the independency of V_{oc} and J_{sc} on the thickness of LSMO electrode distinctly revealed that the intensified PV response largely originated from the polarisation-modulated Schottky barrier at Pt/BFO interface with a minor share of bulk depolarisation field. Otherwise, thinner LSMO as bottom electrode would yield greater PV response due to the larger depolarisation field. Note should be taken that contribution of photo-emitted electrons from metal electrodes to the photocurrent, as discussed by Zhang et al.,⁹⁸ is not considered in the above studies.

It is readily apparent that the underlying principles of switchable PV response in ferroelectrics is of uncertain nature, as the Schottky barrier at the interface can be modulated by either the impact of electrodes and polarisation flipping or the effect of charged defects, e.g., oxygen vacancies. It has been reported that the migration of oxygen vacancies upon applying an electric field in leaky ferroelectrics like bismuth

ferrite would determine the switchable PV behaviour and also decline the stability of generated photocurrent throughout more cycles.¹²¹ Therefore, to exclusively study the impact of Schottky barrier modulation by polarisation, one must carefully avoid the presence of charged defects as much as possible. Agarwal et al.¹²² employed co-substitution of Samarium and Hafnium in A-site and B-site of BFO, respectively, to minimize the formation of charged defects. The rectangular shape of P-E loop with a small leakage current along with no degradation in the transient measurement of photocurrent, confirmed successful suppression of oxygen vacancy (see Figure 2-13). Poled $(\text{Bi}_{0.9}\text{Sm}_{0.1})(\text{Fe}_{0.97}\text{Hf}_{0.03})\text{O}_3$ film sandwiched between Pt and LaNiO_3 electrodes exhibited switchable V_{oc} -0.32 (0.26) V and J_{sc} 308 (-222) $\mu\text{A cm}^{-2}$ with upward (downward) polarisation direction. Here, the modulation of Schottky barrier induced by polarisation at $\text{Pt}/(\text{Bi}_{0.9}\text{Sm}_{0.1})(\text{Fe}_{0.97}\text{Hf}_{0.03})\text{O}_3$ interface is the prevailing factor to delineate the switchable photoresponse, whereas contribution of oxygen vacancies has been ruled out from the experimental results.

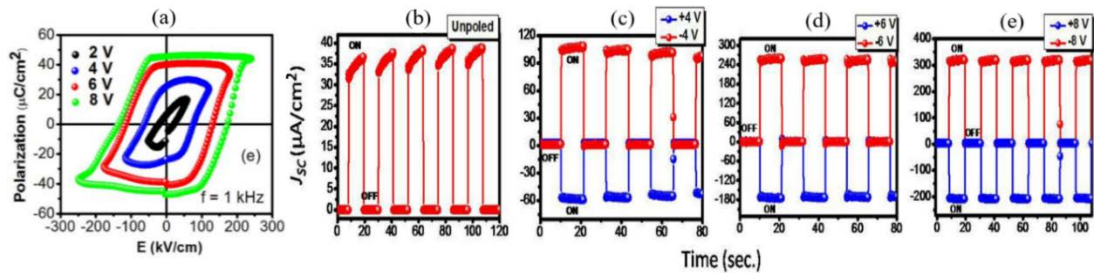


Figure 2-13 Switchable photoresponse in Pt/BSHFO/LNO structure

(a) P-E loop (b-e) time dependent photocurrent under various applied bias. (Reprinted with Permission from Ref.¹²²)

As mentioned earlier, oxygen vacancies as charged defects have been proved to cause a built-in field at interfaces, and their migration has affected switchability of

photocurrent.¹⁴ In the next section, the function of oxygen vacancies will be highlighted in more detail.

2.6.1.2 Effect of Oxygen Vacancies

It has been postulated earlier that aggregation of oxygen vacancies at the interface would deleteriously influence the ferroelectric properties, especially demonstrating detrimental effects on the long-term reliability of the ferroelectric random access memories, like fatigue¹²³ and imprint.¹²⁴ Notwithstanding these early findings, recent studies have disclosed the additional level of control of PV effect provided by the oxygen vacancies.

Besides polarisation-induced modulation, the barrier height can be alternatively adjusted through heavily doping of the electrode/ferroelectric interfaces. Owing to the considerably low formation energies of charged defects, oxide materials possess oxygen vacancies even if synthesized under high oxygen pressure.¹²⁵ Likewise, bismuth ferrite has been reported to be n-type semiconductor due to the inevitable formation of oxygen vacancies during the synthesis process. Presuming that oxygen vacancies are positively charged defects and can move towards negative electrodes in the presence of an external electric field, the electromigration of oxygen vacancies stimulates the formation of a heavily doped n^+ layer at the interface.¹⁴ Consequently, insertion of n^+ doping layer near the n-type semiconductor interface can lower the barrier height.¹²⁶ To further elucidate this idea, Guo and co-workers⁹⁹ have studied the PV behaviour of epitaxial $\text{Bi}_{0.9}\text{Sr}_{0.1}\text{FeO}_{(3-\delta)}$ thin films with large oxygen vacancy content and concluded that, regardless of direction of polarisation, the sign of photocurrent would change by applying voltages well below the coercive field of highly defective $\text{Bi}_{0.9}\text{Sr}_{0.1}\text{FeO}_{(3-\delta)}$,

when the energy band bending driven by oxygen vacancies suffices to balance out the impact of polarisation on the energy band.

From the mounting evidence in the literature, unravelling whether the ferroelectric polarisation or the presence of oxygen vacancies or even both impact the switchable PV effect is rather a baffling task. A great deal of work has employed energy band diagrams to explicate the direction of photocurrent via migration of oxygen vacancy and the polarisation flipping. Gao et al.¹²¹ established energy band diagrams and clarified the impact of oxygen vacancies on PV effect in Ag/ Bi_{0.9}La_{0.1}FeO₃/LSMO capacitor. Irrespective of the polarisation flipping, they observed non-switchable photocurrent when polarisation switching was conducted at low temperature (50 K). In contrast, the capacitor exhibited a switchable photocurrent after applying pulse voltages to manipulate the distribution of oxygen vacancies. After such treatment, the direction of polarisation has not been switched because the direction of pulses was the same as the poled state in all events. They interpreted their result by changes of the diffusion current as well as modulation of the energy band at Ag/Bi_{0.9}La_{0.1}FeO₃ interface caused by the oxygen vacancies.

Gao et al. further investigated the effect of oxygen vacancy density and distribution controlled by the partial pressure of oxygen during cooling, on the PV effect of a similar BFO-based capacitor to their previous study.⁶⁷ The crucial influence of oxygen vacancy on PV effect was evident as both V_{oc} and J_{sc} deteriorated when the oxygen pressure during cooling increased. Distinct switchable PV effect (V_{oc} of 0.18 V and J_{sc} of 80 $\mu A\ cm^{-2}$) was detected for the unpoled sample with a high concentration of oxygen vacancy. The virgin-state samples maintained good stability of short-circuit photocurrent throughout multiple on-off cycles regardless of different oxygen pressure during

cooling. However, poled sample exhibited poor retention as the partial oxygen pressure decreased during cooling (i.e., concentration of V_o increased). According to their proposed energy band model, the switchability of PV effect in the poled samples resulted from the cooperative effect of oxygen vacancies and the ferroelectric polarisation. In addition, the unstable PV effect in the poled samples was explained by diffusion and redistribution of oxygen vacancies as well as the recombination of oxygen vacancies with hopping electrons.

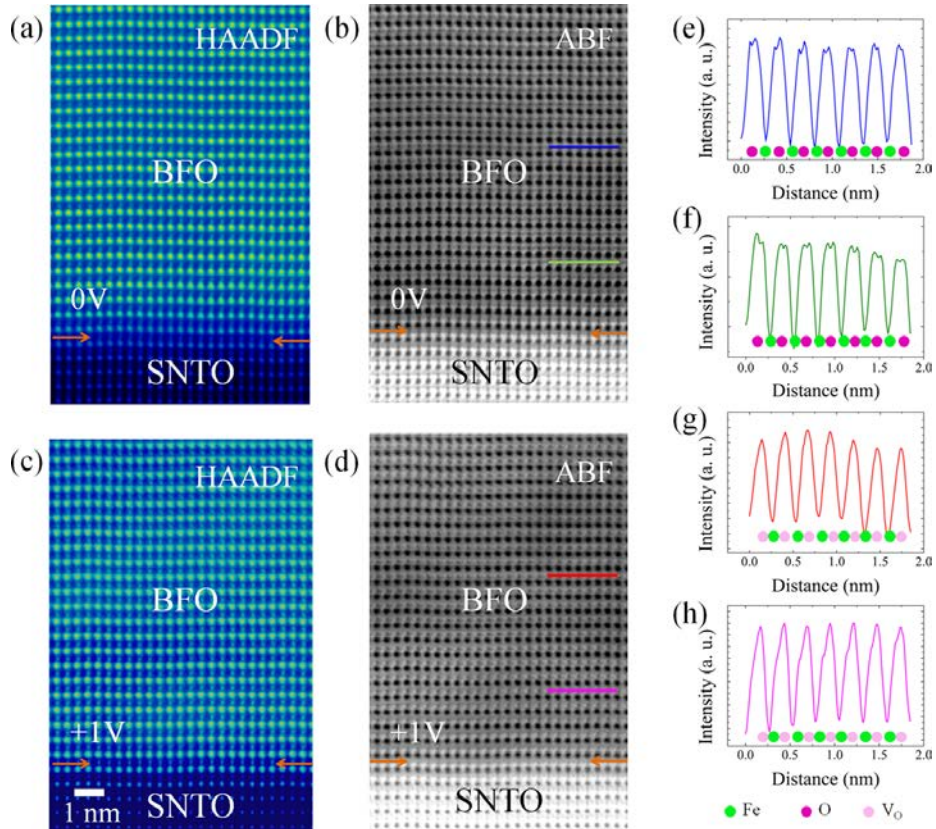


Figure 2-14 switchable PV effect by field-driven migration of oxygen vacancy HAADF and ABE graphs of (a, b) pristine and (c, d) poled BFO/Nb:STO heterostructure, respectively (darker spots denote Bi site and brighter spots are oxygen in the ABE graphs whilst contrast is reversed in HAADF images). (e-h) line profile of Fe-O-Fe corresponding to colour bars as marked in ABE graphs confirms diffusion of the oxygen vacancies toward BFO/Nb:STO interface upon applying positive bias as the valleys of O sites get shallower. (Reprinted with permission from Ref.¹⁹)

Ge and co-workers also studied the switchable PV effect via field-driven migration of mobile oxygen vacancies in both ferroelectric BFO and paraelectric STO perovskite oxide films synthesized via Laser MBE.¹⁹ In their work, contribution of the Schottky barrier at the interface and ferroelectric polarisation on PV effect was disregarded firstly by choosing chromium as the electrode, whose work function is smaller than that of both BFO and STO, to form ohmic contact and applying electric field below the coercivity for BFO samples. Intriguingly, externally polarized STO films demonstrated better PV performance, showing almost similar V_{oc} around 150 mV, while providing a three-fold enhancement in the absolute value of J_{sc} ($173 \mu A cm^{-2}$).

Considering the same values of V_{oc} , it was concluded that the impact of oxygen vacancies was dominant compared to that of polarisation switching in BFO samples. Moreover, the larger photocurrent for STO-based devices was ascribed to its intrinsically higher carrier mobility.¹²⁷ They have also investigated the temperature dependence of the vacancy-induced PV effect to corroborate their findings; and observed that both V_{oc} and J_{sc} became larger with raising the temperature. Using aberration-corrected STEM characterization with in-situ biasing (see Figure 2-14), the relying mechanism of this phenomenon was instantly attributed to the field-induced ionic migration of the oxygen vacancies that is also enhanced at the elevated temperature. The nonuniform distribution of oxygen vacancies creates a built-in electric field opposite to the direction of applied bias, leading to the flipping of the band diagram upon switching the direction of polarisation.

Nevertheless, other study on the temperature-dependent behaviour of PV effect in ITO/BFO/LSMO heterojunction showed somehow different results.¹²⁸ By increasing temperature from 20 °C to 130 °C, the I_{sc} escalated from 180 nA to 404 nA at the

expense of diminishing V_{oc} by 50%. Oxygen vacancies are considered to provide one or two electrons to the conduction band, acting as an electron donor.¹²⁹ Hence, Yang et al. have postulated that the density of free electrons was raised because oxygen vacancies release more electrons at the elevated temperature, narrowing the width of the depletion region at the electrode/ferroelectric junction.¹²⁸ This mechanism would justify the increase in short-circuit photocurrent by raising the temperature at the cost of lower open-circuit photovoltage. The conflicting results in the abovementioned studies can be elucidated via disparate mechanisms controlling the PV effect in the devices solely based on the ionic degree of freedom similar to the former study and the structures having Schottky interface in the latter study.

Figure 2-15 shows the impact of electrical training on the PV response of symmetrical SrRuO₃/BFO/SrRuO₃ capacitor, in which the oxygen vacancies can be electrically redistributed.

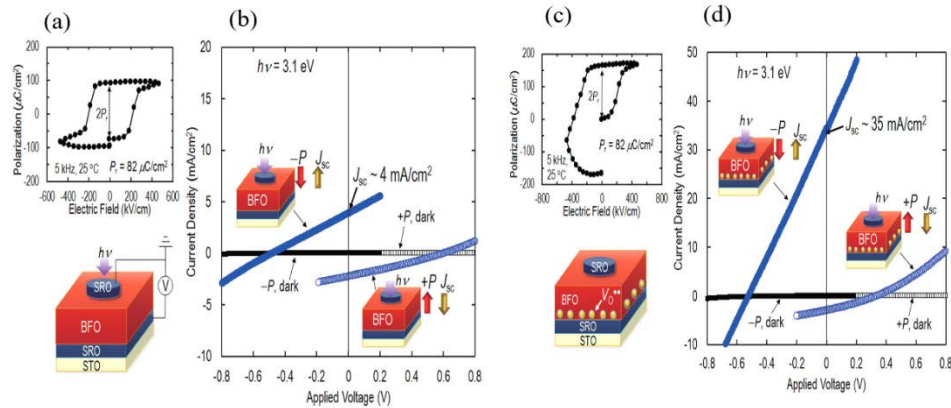


Figure 2-15 Polarisation and PV characteristic curves for BFO capacitor

(a, b) with electrical training and (c, d) without electrical training. (Reprinted with permission from Ref.¹³⁰)

Approximately nine times higher J_{sc} for BFO capacitor without electrical training (34.6 mA cm^{-2}) was obtained compared to that of the samples with electrical training (4 mA

cm^{-2}).¹³⁰ Given that both type of capacitors exhibited similar remanent polarisation, the enhancement of PV output by redistribution of V_o charged defects implies the cooperative impact of polarisation induced charges and the oxygen vacancy-rich layer at the interface on modifying the energy band.

Given the above explanations, it is evident that the PV effect in a highly defective bismuth ferrite-based capacitor (i.e., having high concentration of oxygen vacancies) is not only induced by the polarisation, either via modulation of the Schottky barrier or bulk effect, but it also strongly depends on the distribution of oxygen vacancies. Therefore, defect engineering seems to play a significant role in tailoring PV response for energy harvesting applications. Previous studies of epitaxial BFO films pointed out the fact that defect states and their distributions are highly contingent on the synthesis method, process condition, stoichiometry and epitaxial strain.¹³¹ For instance, MBE-deposited films are believed to have a higher concentration of oxygen vacancies due to difficulty maintaining oxygen stoichiometry during film deposition. Thus, careful control of the abovementioned parameters would determine the properties of the BFO thin films.

2.6.2 Modifying Electrical Conductivity

Study of the charge transport in BFO thin films is of paramount importance, especially when an external voltage is applied to the samples to measure ferroelectric and photovoltaic properties. In general, the possible conduction mechanisms are either (1) bulk limited including ohmic conduction, space charge limited current, and Pool-Frenkel emission or (2) interface limited comprising Schottky emission, and Fowler-Nordheim tunnelling.¹³² Having a sound knowledge of the conduction mechanism is essential to improve photoexcited charge transport through a trade-off between

ferroelectricity and conductivity of BFO thin films. Therefore, the electrical conductivity of BFO-based devices can be modified depending on the dominant conduction mechanism. For instance, chemical substitution can improve the limited bulk conductivity and thus increase the photocurrent.¹¹

Different conduction mechanisms have been reported for BFO thin films. Although highly textured BFO thin films were under investigation, one study found the conduction mechanism in asymmetric Pt/BFO/SRO structure to be space charge limited conduction via oxygen vacancies as deep traps;¹³³ whilst the other study on symmetric SRO/BFO/SRO structure suggested the dominant transport mechanism as Pool-Frenkel emission with Fe^{2+} acting as trap centres.¹³⁴ In both studies, the charge transport process was associated with vacancies regardless of a different mechanism. Moreover, a comparison between the outcomes of these studies further confirms the role of electrode selection on the charge transport mechanism. As mentioned earlier, considering the enhanced conductivity of domain walls compared to the domains, an additional conduction mechanism can also be surmised in BFO thin films, which offers a promising tool to manipulate photoexcited charge transport via engineering the pattern and orientation of domain walls.^{113,135}

2.6.3 Bandgap Tuning

To be an ideal candidate for any kind of photovoltaic device, the ferroelectric material should have a bandgap in the vicinity of the solar spectrum maxima, i.e., ~ 1.4 eV. Most ferroelectrics have bandgaps placed in the UV region of the sunlight spectral. This wide-bandgap is associated with the electronic structure of ferroelectric oxide perovskites, forming by oxygen 2p orbital-derived valance band maximum and transition metal d orbital-derived conduction band minimum.¹³⁶ However, BFO has

recently gained widespread interest for energy harvesting applications as it was found to have a relatively narrow bandgap in range of 2.65-2.82 eV for its rhombohedral thin films.¹³⁷ Yet, BFO absorbs sunlight in the blue region of the visible range, which is speculatively around 25% of the solar energy. Thus, several approaches have been adopted to engineer the BFO bandgap while maintaining its intrinsic properties.

An instinctive method is to modify the chemical composition through doping with materials having a narrow bandgap.⁴⁸ Xu et al. have demonstrated bandgap tunability of Bi(Fe, Mn)O₃ films with varying Mn concentrations.¹² Figure 2-16(a) shows that the bandgap can be narrowed to 1.1 eV with increasing Mn content from 0 to 100%. It is worth mentioning that the complete substitution of B-site cations by manganese (BiMnO₃) will result in thin films with no spontaneous polarisation.¹³⁸ Notwithstanding such a considerable decrease in the bandgap, the compromise between narrowing bandgap and polarisation magnitude, as the main charge separation mechanism, seems to be a limiting factor when incorporating manganese in BFO lattice. Another study investigated the effect of Mn doping on PV performance of Bi(Fe,Mn)O₃ films epitaxially grown on Nb:STO.¹³⁹ Their results exhibit a significantly enhanced power output of 175 times larger for 30% Mn-doped BFO capacitor compared to that of pristine BFO films. This enhancement was ascribed to the bandgap engineering by incorporating Mn dopant up to the point that ferroelectric behaviour is retained (See Figure 2-16(b)). Their results also demonstrate that Mn element doping would greatly reduce leakage current. Another theoretical study also hypothesized that both Cr and Mn are favourable transition metal dopants to tune the bandgap of BFO.¹⁷ In particular, manganese is preferred for practical improvement of the PV effect due to its efficient solubility in BFO without deteriorating the polarisation up to 50% of Mn content.¹⁴⁰ In

fact, the authors found that remnant polarisation remains constant around $80 \mu\text{C cm}^{-2}$ in $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ films with Mn content ranging in $0 < x < 0.1$, while substituting even half of B-site cations by Mn element would decrease the saturation polarisation by relatively small value of $13 \mu\text{C cm}^{-2}$. It should be noted that although other elements, e.g., titanium, cerium and sodium, have been used as dopants, further discussion is out of scope of this study due to utilizing solution-based deposition technique, but relevant results can be found elsewhere.^{141–143}

The ultimate purpose with bandgap tuning of photovoltaic materials is to absorb more energy from sunlight. However, as mentioned above, bandgap reduction via doping is limited by the loss of ferroelectric polarisation. Multi-layered structures have been reported to offer an enhanced photovoltaic response,^{117,144,145} and provide superior ferroelectric characteristics simultaneously.^{146,147} Thus, this strategy can be employed to deal with the trade-off between polarisation and bandgap reduction. In a similar way, it was shown by Sharma et al. that five-layered BFO/BTO structures possessed improved photovoltaic output with $J_{\text{sc}} = 0.318 \text{ mA cm}^{-2}$, $V_{\text{oc}} = -1.25 \text{ V}$ and $\text{PCE} = 0.067\%$ under violet laser illumination.¹⁴⁵ The obtained result was ascribed to relatively large remnant polarisation of $45.71 \mu\text{C cm}^{-2}$ for multi-layered structure much closer to that of BTO single layer, yielding more effective depolarisation field, accompanied with narrow bandgap of 2.87 eV , which is remarkably lower in comparison to pure BTO, but identical to that of BFO films (Figure 2-16(c)).

Physical attributes of a material are closely related to its structure, and one may surmise strain engineering method, that is utilizing epitaxial strain imparted from substrates crystal to induce the structural modification in thin films, can bestow possibility of modulating the optical properties, e.g., bandgap. The influence of the substrate on

optical properties of BFO thin film has been studied by Himcinschi et al. who reported the bandgap of films deposited on Nb:STO to be 50 meV wider than that of films on DSO substrate (Figure 2-16(d)).¹⁴⁸ As confirmed by high-resolution XRD, the presence of a larger compressive strain for films on STO compared to DSO substrate due to higher lattice misfit of the former contributed to the shift of optical bandgap. In fact, epitaxial strain can not only affect the polar distortion but also impact oxygen octahedra rotation in BFO film, inducing new structure and functional phases.¹⁴⁹

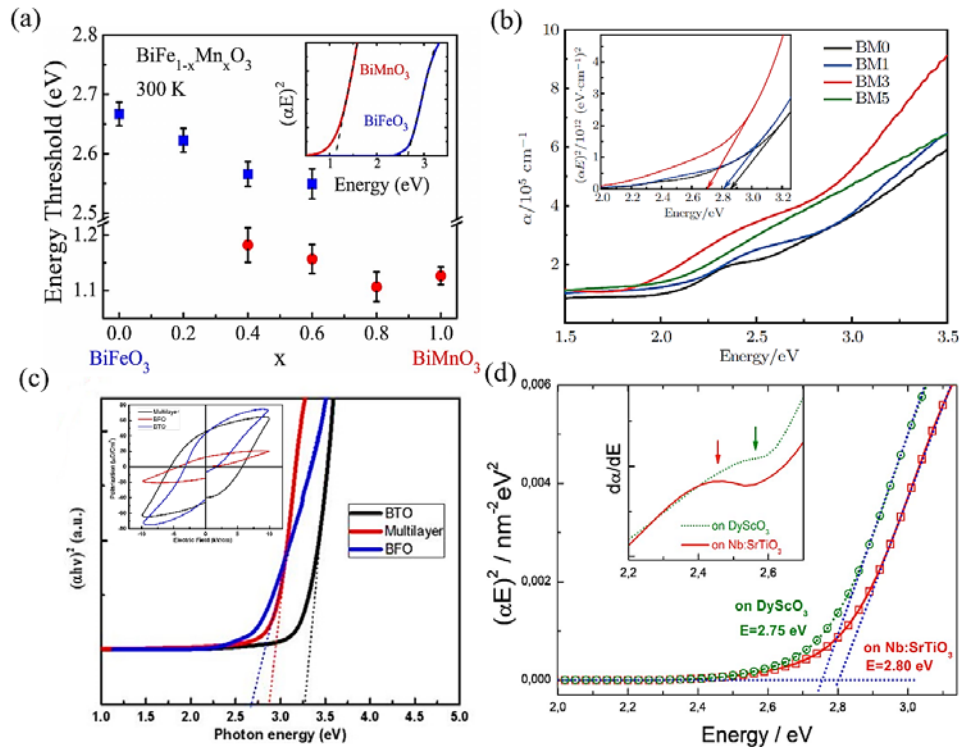


Figure 2-16 Optical properties of modified-BFO structures

(a) Bandgap threshold at room temperature for $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ thin films. (Reprinted with permission from Ref.¹²) (b) Absorption coefficient as function photon energy for BFO film with varying Mn content of 0, 10, 30 and 50 mol%. (Reprinted with permission from Ref.¹³⁹) (c) Tauc plot of BTO, BFO single layers and BTO/BFO multilayered structure (the inset shows ferroelectric polarisation P - E loop). (Reprinted with permission from Ref.¹⁴⁵) (d) direct optical transition for BFO thin films on DSO and Nb:STO substrates. (Reprinted with permission from Ref.¹⁴⁸)

Using first-principle calculation, Wang and co-workers proposed a bandgap modulation route through rhombohedral to tetragonal phase transition since the rhombohedral phase of several perovskite structures was systematically wider than their tetragonal equivalent.¹⁵⁰ On the other hand, BFO films appears to present a contradictory behaviour as the optical bandgap of the tetragonal phase was found to be higher than that of the rhombohedral counterpart.^{149,151} Care must be taken when comparing reported values of the bandgap in literature since the discrepancies are most likely arose from different measurement techniques. Excluding the homogeneous strain from consideration, the bandgap of epitaxial BFO films has been statistically shown not to be susceptible to inhomogeneous strain and out-of-plane lattice constant but somewhat depends on film thickness and surface roughness.¹³⁷

Controlling the chemical ordering of material, with invariant chemistry, is another effective way of bandgap engineering. DFT calculation has shown that layered B-site cation arrangement coupled with high degree of tetragonality in perovskite material like $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$, can notably lower the bandgap and affect the carrier mobility concurrently.¹⁵² Using such a strategy, tailoring the Fe/Cr cationic order in double perovskite BFCO thin film showed efficient reduction as high as 1.4 eV in the bandgap through alteration of the Jahn-teller distortion of $\text{FeO}_6/\text{CrO}_6$ octahedra (see Figure 2-17).¹⁸ By optimising the growth rate, Nechache et al. achieved the unprecedented photovoltaic outputs of $J_{\text{sc}} = 11.7 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.79 \text{ V}$, $\text{PCE} = 3.3\%$ and $J_{\text{sc}} = 20.6 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.84 \text{ V}$, $\text{PCE} = 8.1\%$ under 1 sun illumination for single and multi-layered structures with each layer harvesting specific region of solar spectrum, respectively. So, controlling the growth condition proved to be an effective way of modulating the bandgap of the BFCO double perovskite structure. For instance, tuning of the optical

bandgap of epitaxial BFCO films grown by PLD can be achieved by changing laser frequency during deposition.¹⁵³

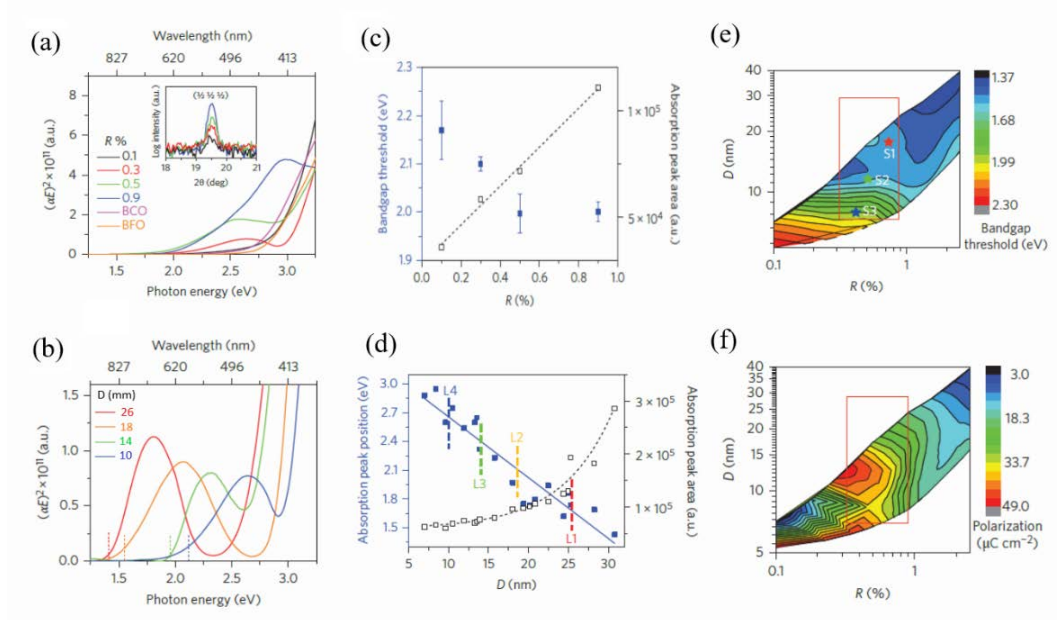


Figure 2-17 Bandgap modulation via cation ordering in BFCO thin film

(a, b) Impact of Fe/Cr cationic ordering characteristics on direct optical transition (R is ratio of $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ superstructure reflection intensity to that of main (111) perovskite peak, and D represents width of superlattice peak) (c, d) Bandgap threshold at various R and D . (e) Mapping of bandgap threshold and (f) ferroelectric polarisation with respect to cationic ordering parameters. (Reprinted with permission from Ref.¹⁸)

As shown in Figure 2-18, the laser repetition rate has a strong impact on the structural and optical properties, as well as the saturation magnetization, whilst no clear relation was observed for concentration of antisite defects, quantified from the ratio of intensities of superstructure peak and main peak of the double perovskite. Thus, Quattropiani et al. suggested that, in contrast to the previously reported study,¹⁸ superstructure peaks may not be an authentic parameter of cation ordering.¹⁵³ It is believed that antiferromagnetic interactions in the double perovskite system, i.e., Fe/Cr cationic disorder, would lessen the saturation magnetization.¹⁵⁴ Therefore, modulation

of the saturation magnetization has been investigated to extract more accurate information on the Fe/Cr cation ordering promoted by different laser repetition rate.

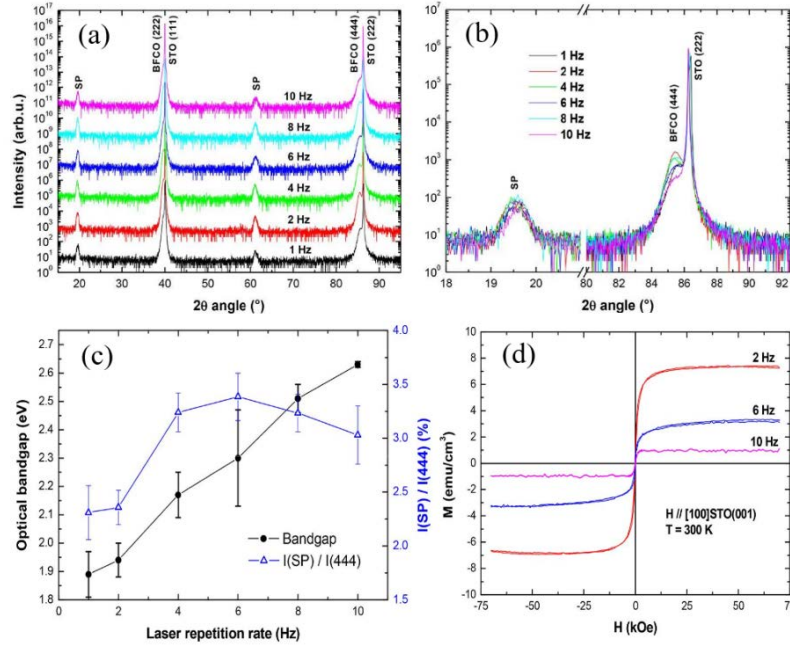


Figure 2-18 Effect of laser repetition rate on properties of BFCO films

(a) XRD scan along [111] direction of BFCO film to confirm presence of superstructure peak (b) Closer look on superstructure and main peak along pseudocubic [111] direction. (c) impact of laser frequency on optical bandgap and cation order parameter and (d) Evolution of magnetization hysteresis loop at different laser repetition rates. (Reprinted with permission from Ref.¹⁵³)

Subsequent work also demonstrated the possibility of incorporating BFCO as the top cell in tandem silicon solar cells.¹⁵⁵ Despite a large lattice mismatch between BFCO and Si, ordered growth of epitaxial BFCO on (100)-oriented Si substrate was achieved via the integration of MgO buffer layer. Such device yielded a power conversion efficiency of 2.65% with values of J_{sc} and V_{oc} around 14 mA cm^{-2} and 0.5 V, respectively. The lower photovoltage compared to the formerly reported value¹⁸ was associated with in-plane ferroelectric domain orientation in BFCO thin layer as confirmed by PFM, giving rise to inadequate polarisation-induced charge dissociation process.

2.7 Summary

A thorough survey of bismuth ferrite-based thin films for photovoltaic applications is delineated in a comparative way. Ferroelectric BFO-based materials have exhibited intriguing photovoltaic properties, including switchable photocurrent, anomalous above-band photovoltage and charge separation at nanoscale domain walls. Yet, photoferroic processes still require significant enhancement regarding the low photocurrent density as summarized in Table 2-2. Low photocurrent in ferroelectric oxide perovskites stems from intrinsic bulk properties, which is highly susceptible to unit cell structure and ionic substitution. Thus, continuous improvement of bulk properties of bismuth ferrite, particularly light absorption, carrier lifetime and electrical conductivity, is imperative for photovoltaic applications. This has led to approaches like bandgap engineering and compositional modification, which were highlighted in this section. Using a multi-layered structure coupled with cation ordering has been found to be another feasible path to enhance power conversion efficiency. Therefore, chemical/charge ordering on the optical properties of double perovskite thin film is worthy of scrutinising.

Surprising photoelectronic properties can be anticipated through defect engineering while minding its concurrent influence on ferroelectric properties. The prospect of BFO thin film for photovoltaics will be tied in closely with a better understanding of the interplay between polar structure and photoexcitation properties. As a ferroelectric material, properties of BFO-based films are expected to be dependent on phase transition, domain structure and strain, which their impact on photoinduced characteristics can also trigger new findings.

Table 2-2 PV properties of various BiFO₃-based structure

Structure of cell	Substrate	Growth method	PV characteristic		Light source	
			V _{oc} (V)	J _{sc} (μA/cm ²)	WVL (nm)	Intensity (mW/cm ²)
Pt/ BFO/Pt Coplanar ⁷⁴	TSO	PLD	7.6	-	405	80 (mW)
Pt/BF_{0.9}Mn_{0.05}Zn_{0.05}O₃/Pt Coplanar ⁷⁵	STO	RF Sputtering	145	0.055 (nA)	405	62 (mW)
Pt/ BFO /Pt Coplanar ⁷⁸	STO	RF Sputtering	~29	~0.11 (nA)	405	62 (mW)
ITO/ BFO /SRO ⁸⁵	STO	RF Sputtering	~ 0.3	~0.3	435	0.75
ZnO:Al/BLFTO/ Pt ⁹⁶	Pt/TiO ₂ /Si O ₂ /Si	PLD	0.2	1350	visible	100
ZnO:Al/BLFTZO/Pt ⁹⁷	Pt/TiO ₂ /Si O ₂ /Si	PLD	0.022	650	visible	100
Pt/ BFO / LSMO ¹⁶	STO	PLD	~ 0.2	~0.001 (nA)	Halogen lamp	20
Pt/ BFO /Pt Coplanar ¹⁰⁴	STO	RF Sputtering	29	0.76 (nA)	405	380,000
Multi-domain BiFeO₃ ¹⁰⁵	STO	PLD	7.7	180	405	250
ITO/BFSO/LiNbO₃ ¹¹	NdCaAlO ₄	RF Sputtering	0.6	~6.5	435	22.3
ITO/ZnO/ BFO /Pt ¹¹⁶	Pt/TiO ₂ /Si O ₂ /Si	RF Sputtering	0.225	340	435	22.3
Pt/ BFO /Pt ¹¹⁸	Pt/TiO ₂ /Si O ₂ /Si	RF Sputtering	0.33	71.2	405	5
ITO/ BFO /Pt ¹¹⁹	Pt/TiO ₂ /Si O ₂ /Si	RF Sputtering	0.28	3.2	405	5
ITO/ BFO /ITO ¹²⁰	ITO coated glass	RF Sputtering	~0.33	28	visible	100
Au/ BFO /LSMO ²⁰	STO	L-MBE	0.75	170 (nA)	375	840
Ag/Bi_{0.9}La_{0.1}FeO₃ /LSMO ¹²¹	STO	PLD	-	7.5 (nA)	532	100
Pt/(Bi_{0.9}Sm_{0.1})(Fe_{0.97}Hf_{0.03})O₃/ LNO ¹²²	Si	PLD	0.32	303	Visible	100
Au/BFO/Au coplanar ¹⁵⁶	STO	PLD	0.2	660	405	24.25 (mW)
Ag/Bi_{0.9}La_{0.1}FeO₃/LSMO ⁶⁷	STO	PLD	0.18	80	532	100
Cr/BFO/Cr coplanar ¹⁹	STO	LMBE	0.15	67	375	1,000
SRO/ BFO /SRO ¹³⁰	STO	PLD	~0.53	34,600	405	5,000
ITO/Bi(Fe_{0.7}Mn_{0.3})O₃/Nb:STO ¹³⁹	STO	PLD	0.33	1.81	Xenon	8.5
Bi(Fe_{0.95}Mn_{0.05})O₃ ¹⁷	STO	PLD	3.1	15	515	2,500
ITO/ BFO/BiMnO₃ / Nb:STO ¹¹⁷	STO	PLD	0.56	3,500	white	100
ITO/ BFO /BiCrO₃/ CRO ¹⁴⁴	LAO	PLD	~1.2	~10	white	100
Au/ BFO/BTO/Pt ¹⁴⁵	Pt/TiO ₂ /Si O ₂ /Si	PLD	1.25	~320	405	160
ITO/BFCO/ SRO ¹⁸	STO	PLD	0.79	11,700	white	100
ITO/BFCO/SRO ¹⁵⁵	MgO buffered Si	PLD	0.5	13,800	white	100

Chapter 3. Experimental Methods

This chapter outlines the principles of fabrication and characterization techniques employed in our work. The BFCO films were deposited in a laser molecular beam epitaxy chamber (LMBE), using a home-made ceramic target. Hence, details of the target fabrication for the growth of the BFCO films are also delineated. To prepare the heterostructure device for the photocurrent and electromechanical measurement, bottom and top electrodes were grown via in-situ LMBE and lithography, respectively. A variety of techniques have been utilized to study structural-functional properties, including but not limited to, X-ray diffraction (XRD), atomic force microscopy (AFM), piezoelectric force microscopy (PFM), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry, scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) and transmission electron microscopy (TEM). Due to the intricacy of these methods, solely operating procedures pertinent to this research will be discussed.

3.1 Thin Film Heterostructure Preparation

3.1.1 Synthesis of Ceramic Targets

To deposit BFCO thin films, a highly dense and homogenous ceramic target was prepared by conventional solid-state reaction using Bi_2O_3 , Fe_2O_3 and Cr_2O_3 oxide powders as specified in Table (3-1). Excess bismuth oxide was added to the stoichiometric mixture to compensate for the loss of volatile Bi during target and thin film preparation.

Table 3-1 List of raw materials for BFCO target synthesis

Chemical	Formula	Purity (%)	Manufacturer
Bismuth oxide	Bi_2O_3	99.9	Sigma Aldrich
Iron oxide	Fe_2O_3	99.995	Sigma Aldrich
Chromium oxide	Cr_2O_3	99.9	Sigma Aldrich

Numerous studies have suggested using excess bismuth oxide in their ceramic targets for physical vapour deposition.^{157,158} In this project, a 20 wt% . excess bismuth is incorporated in the target due to the high synthesis temperature. Figure 3-1 schematically presents the preparation procedure of the ceramic targets. Then, thin films were prepared by ablation of this home-made target using LMBE technique which will be elaborated in the next section.

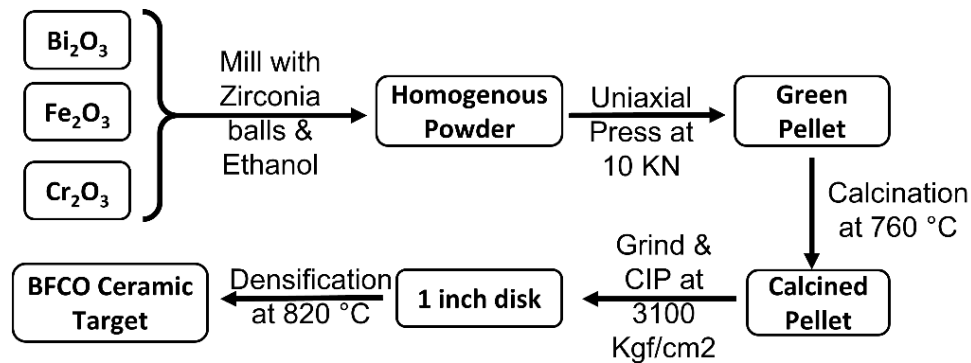


Figure 3-1 Flowchart of BFCO ceramic target preparation

3.1.2 Laser Molecular Beam Epitaxy

The quest for novel functional materials has led to the development of various thin film growth techniques, such as chemical solution deposition (CSD) and physical vapour deposition (PVD). Regardless of the flexibility and cost-effectiveness of CSD processes, high-quality complex oxide thin films can be achieved by PVD method. Of all, laser molecular beam epitaxy, similar to pulsed laser deposition, is a widely used physical vapour deposition technique due to its ability to grow multi-cation complex

oxide thin films in which rigorous control over stoichiometry is required.¹⁵⁹ As shown in Figure 3-2, the deposition process is carried out by ablation of the target via a nanosecond-width pulsed laser with sufficiently high energy and under a high vacuum. The ablated material is then transferred to the substrate within a radiant plasma plume expanded away from the target.

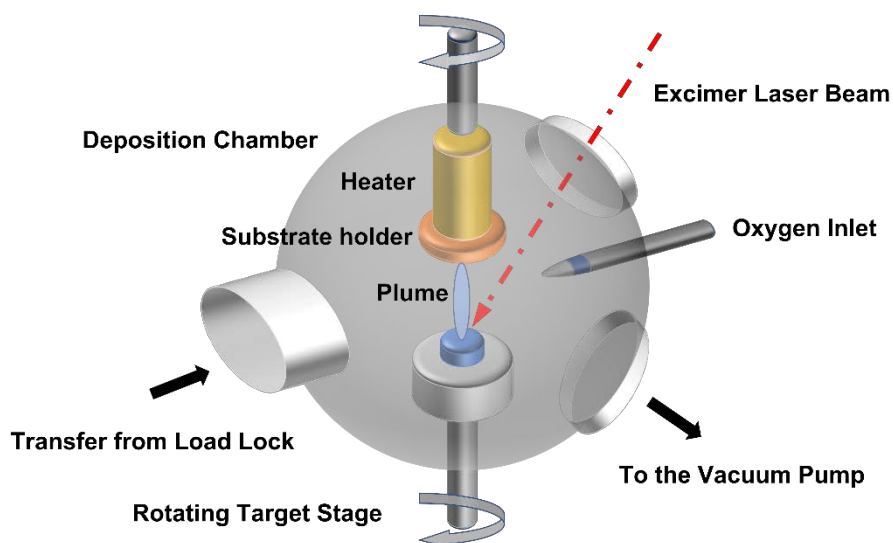


Figure 3-2 Schematic of LMBE apparatus

In the laser ablation, material removal from the target is induced by absorption of incident photon energy which is initially converted to electronic excitation and subsequently to thermal energy.¹⁶⁰ The laser-matter interaction is contingent on the characteristics of the laser. Efficient ablation of material from the target requires high absorption of laser energy within the surface layer, which highly depends on the penetration depth of the laser determined by its wavelength. This can be readily achieved by short-wavelength lasers such as KrF excimer or Nd:YAG working in the ultraviolet spectrum.¹⁵⁹ Moreover, the laser energy density (fluence) should surpass a certain threshold for optimal material ablation from the target surface. Typically, energy

densities ranging from $1\text{--}5\text{ J cm}^{-2}$ have been utilized for excimer laser (248 nm, and 20–35 ns pulse duration).¹⁶¹

As mentioned above, the main advantage of PLD is the stoichiometric transfer of elements from a single multi-component target. Here, a small-scale of material receives sufficiently high energy once the ablation threshold is reached, leading to local vaporization of target species independent of their vapour pressure that originates from the nonequilibrium characteristic of this process.¹⁵⁹ Note should be taken that the stoichiometric transfer of target compound does not necessarily yield stoichiometric film at high temperature, especially for cations having high vapour pressure, e.g., Pb, Bi, K, Na, etc. Therefore, utilizing targets rich in the volatile cation are numerous reported for compensation of the volatile element.^{157,158} Another feature of PLD is the ability to grow almost any complex oxide material that requires a reactive element during synthesis. Molecular oxygen can be introduced as background gas functioning in two ways. First, it facilitates the phase formation from the thermodynamic perspective; second, the background gas interacts with expanded plume, and hence, it can moderate the kinetic energy of the ablated materials.¹⁵⁹

Furthermore, PLD offers a great degree of control for growth rate and mode, which is crucial when a multilayer structure is required, as deposition rate per pulse can be tuned precisely. In-situ reflection high energy electron diffraction (RHEED) provides a tool to evaluate the growth mode, crystallinity and surface quality film during the deposition.¹⁶² The so-called "Laser MBE" has been used interchangeably with PLD systems in which growth mode can be monitored in real-time by RHEED under ultra-high vacuum. However, this term is imprecise, as pulsed laser plasma plume always includes ions, electrons, and neutral particles altogether, hence, it is not precisely molecular beam.¹⁶¹

The application of multilayer structure in electronic devices requires atomically smooth interfaces that necessitate controlling the surface morphology throughout thin layer growth. From a thermodynamic perspective, growth mode is determined by the balance between the free energies of the surface for the film, substrate, and the interface thereof. Layer-by-layer growth (Frank-Van der Merwe) is achieved if the total surface energy of film and substrate/film is lower than that of bare substrate.

In contrast, island growth mode (Volmer-Weber) occurs if wetting the substrate raises the total surface energy. During heteroepitaxial layer deposition, the growth mechanism transitions from layer by layer to island mode coined as Stranski-Krastanov growth mode.¹⁶³ This transition is due to the formation of elastic energy caused by a considerable lattice mismatch between substrate and the film, which will be relieved through misfit dislocations. It is worth noting that film nucleation and growth process in PLD, similar to many vapour deposition techniques, do not occur in thermodynamic equilibrium and thus, kinetics influences the growth mode predominantly.¹⁶³ The time interval between deposition and growth endows PLD to optimize film surface quality via kinetic parameters at different growth conditions, which will be discussed in Chapter 6 in more detail.

3.1.3 Preparation of the Top Electrode

To successfully measure the ferroelectric properties of the samples, squared Au/Cr electrode pads (edge length $\leq 45 \mu\text{m}$) were patterned on the surface of BFCO thin films via photolithography followed by metal thermal evaporation. These methods are proved to be efficient in preparing relatively small electrodes, which is highly desirable for polarisation measurement of bismuth ferrite based thin films due to the high leakage current. For this reason, it was opted to deposit $21 \times 21 \mu\text{m}^2$ electrodes for thinner films

(<130 nm) as shown in Figure 3-3, whilst larger pads, i.e., $45 \times 45 \mu\text{m}^2$, were used for films with thickness larger than 130 nm.

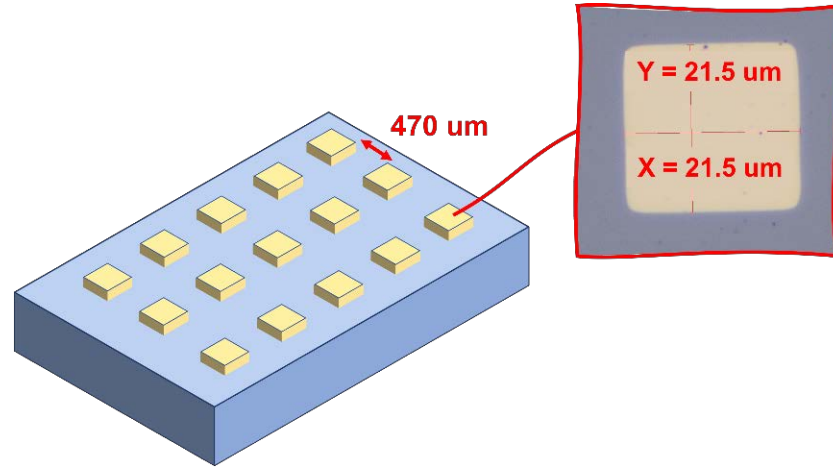


Figure 3-3 Top electrodes layout for ferroelectric characterization
(zoom-in image of a single pad under optical microscope)

The negative photoresist layer, nLOF 2020, was spin-coated on the samples at 3000 rpm for 30s followed by a heat treatment at 110°C to remove the excessive solvent. A direct-write MLA100 system (Heidelberg) was then used to pattern the top electrodes. The samples were then rinsed in the AZ726 developer solution and went through post-baking at 110°C. To deposit 10/50 nm of Cr/Au, A Lesker thermal evaporator (Kurt J. Lesker Company) was used at the base pressure of less than 2×10^{-6} Torr followed by lift-off in acetone for several minutes to dissolve the photoresist. The samples were finally cleaned in IPA and completely dried using compressed nitrogen.

3.2 Analytical Methods

3.2.1 X-ray Diffraction (XRD)

XRD method is commonly used to non-destructively probe the structural properties of crystalline materials owing to the comparative simplicity of X-ray production and compatibility of its characteristic wavelength with respect to the atomic distance in a

crystalline material.¹⁶⁴ Versatile thin film characterizations can be conducted using available laboratory XRD equipment, including but not limited to identification of phase, lattice parameter, crystal symmetry, epitaxial relation with substrate and film thickness/roughness. The incident X-ray on the surface of a crystalline sample is scattered when interacting with the crystal lattice. This phenomenon is described mathematically by Bragg's law

$$2d_{hkl} \sin\theta = n\lambda \quad (\text{Equation 3 – 1})$$

Where d , θ , and λ are the interplanar distance of diffracting planes ((hkl) denotes miller indices), the angle of incidence and the X-ray wavelength, respectively. As seen in Figure 3-4(a), diffracted waves constructively interfere when the angle of incidence is such that the extra path travelled by the diffracted wave from the lower plane is the product of incident X-ray wavelength by an integer.

X-ray diffraction was an essential part of this study to explore the structural changes of the deposited thin films. PANalytical X'pert MRD Pro (Philips, Netherland) equipped with a four-circle diffractometer and a 2-bounce Single-crystal Ge-220 monochromator was employed to conduct 2θ - ω coupled scan, Reciprocal Space Mapping (RSM), and Phi-scan/pole figure measurement. The four-circle configuration allows a thorough structural characterization of the thin films by modifying the four angles, as shown in Figure 3-4(b).

All diffraction patterns were collected using Copper $K\alpha$ radiation with a characteristic wavelength of 1.54056 Å generated at 45 kV/40 mA. SmartLab Rigaku diffractometer featuring a 2-bounce Ge-220 monochromator and a 9 kW turbo Cu $K\alpha$ rotating anode at the working condition of 45 kV/200 mA was also used to conduct high-resolution 2θ - ω

coupled scan and X-ray Reflectometry (XRR) for the determination of thickness and surface roughness of the fabricated thin films.

All samples were fixed on a glass slide using double-sided tape and mounted on the XRD stage. First, direct beam and then crystal orientation alignment was performed for all samples to adjust the goniometer to (1) place the sample surface parallel to the incident beam while it cuts the beam into half (2) place the crystal plane of interest, which is the preferred orientation of the commercial substrate here, perpendicular to the scattering plane. Further refinement was also taken via phi-scan to align the in-plane orientation of the substrate prior to any asymmetric scan. In contrast to symmetric configuration, diffraction in asymmetric geometry signifies the collection of diffraction patterns when $\omega \neq \theta$ and/or Psi is not equal to zero. This configuration is tremendously valuable for probing the planes that are not parallel to the sample surface and in-plane attributes of crystal structure. Hereunder, the typical measurement techniques for thin film application are delineated.

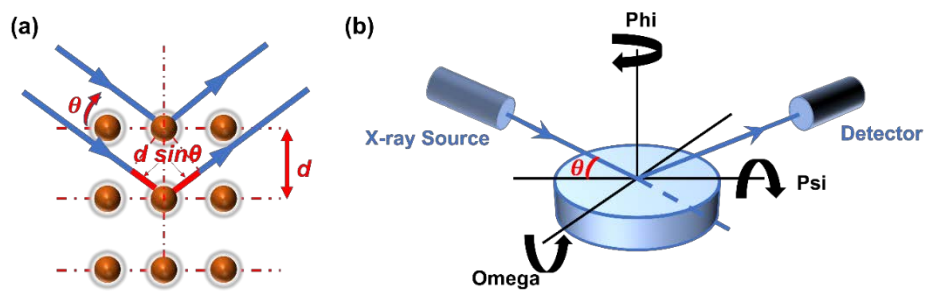


Figure 3-4 X-ray diffraction method

(a) Representation of the Bragg's law (b) schematic diagram of 4-circle diffractometer where ω is the angle of the incident beam with respect to the sample surface, 2θ is the angle of the incident beam, and the diffracted beam, Φ (Phi) denotes the angle of sample rotation around its axis orthogonal to the surface, and ψ (Psi) refers to the angle between the diffraction plane and the axis orthogonal to the sample surface.

The 2θ - ω coupled scan is the most widely used measurement method to acquire information on the out-of-plane lattice constant, phase identification and verification of epitaxial growth. This scan measures the diffraction pattern from the planes oriented parallel to the sample surface by rotating the sample and detector axis simultaneously whilst maintaining the $\omega = \theta$ relationship.

The rocking curve (omega-scan) measures the spread of diffraction intensity at a given reflection angle (2θ) through scanning the omega-axis in the vicinity of $\omega = \theta$. Here, as shown in Figure 2-5, the degree of out-of-plane texture (mosaicity) of thin film is expressed by the full width at half maximum (FWHM), which is very narrow for a nearly perfect crystal. Thus, having smaller FWHM has become a quality factor for the crystallinity of fabricated thin films. In addition, the in-plane texture of thin films can be studied by measuring the diffraction intensity distribution by scanning Phi-axis in the range of $\phi = 0$ to 360° around an asymmetric reflection peak of interest. In this setting, 2θ and ω are set to achieve Bragg's diffraction condition as Psi-axis is tilted to place the normal vector of the plane under the study in the scattering plane, i.e., plane formed by the incident and diffracted beams. The phi-scan of a highly oriented thin film will exhibit as many diffraction peaks as the order of rotational symmetry of the sample. Therefore, in contrast to a randomly oriented sample, the diffraction intensity does not uniformly spread over the full range of the phi-axis. Besides, the epitaxial relation between the thin film and the substrate can be further studied by comparing the angular position of the diffracted peaks in the phi-scan for the thin film and substrate. For instance, if the diffraction angles of both film and substrate coincide in the phi-scan, the so-called cube-on-cube epitaxial growth is fulfilled.

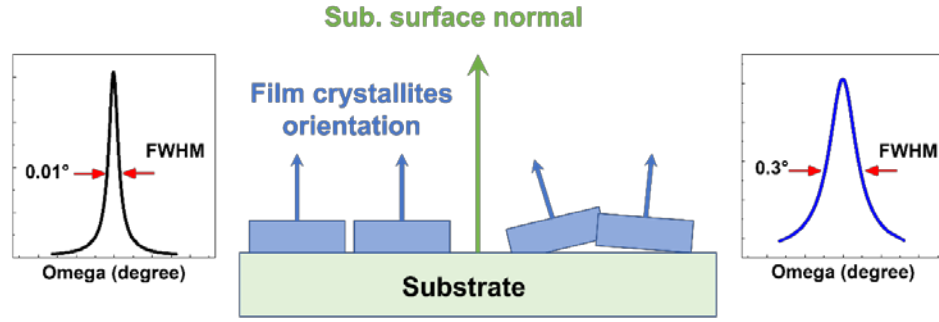


Figure 3-5 Out-of-plane texture of epitaxial thin film

Corresponding rocking curve for (left) the highly-oriented and (right) mosaic textured films

A reciprocal lattice is conceptualized in two-dimensional projection through the Fourier transformation of real space to clarify the relationship between various lattice planes in three-dimensional space more effectively. The crystal lattice plane (hkl) is presented by the reciprocal lattice vector, which can be quantified by its length, i.e., the reciprocal of d -spacing of (hkl) planes, and a direction that is orthogonal to the (hkl) planes. The terminus of the reciprocal lattice vector is identified as the reciprocal lattice point of the (hkl) planes. Hence, the length of the reciprocal lattice vector can be expressed by Equation 3-2 as follows,

$$|q| = 1/d = 2/\lambda \sin \theta \quad (\text{Equation 3 - 2})$$

where the nomenclatures are like Bragg's formula. Reciprocal space mapping (RSM) is a commonly used technique to acquire in-depth information on the crystal structure, crystallinity, strain level, and orientation relationships.¹⁶⁵ The RSM measures diffraction intensity distributions around the desired reciprocal lattice point (part of a projected Ewald sphere) by performing successive scan of 2θ - ω while changing ω step by step. To interpret the data, it is helpful to depict the position and shape of reciprocal lattice points in the q -coordinates instead of measurement axes. The orthogonal vectors

of this Cartesian coordinates (q_x , q_z) are related to the angular position (θ , ω) by the following formulas:

$$q_x = \frac{2}{\lambda} \sin \theta \sin(\theta - \omega)$$

(Equation 3-3)

$$q_z = \frac{2}{\lambda} \sin \theta \cos(\theta - \omega)$$

In this way, both in-plane and out-of-plane lattice parameters of thin film and substrate can be readily deduced from RSM measurement around an asymmetric reflection point. In addition, the degree of lattice relaxation can be determined by comparing the position of reciprocal lattice points of the epitaxial film and the substrate, as schematically shown in Figure 3-6. For instance, the film lattice is fully strained to the substrate lattice if the reciprocal lattice point of the substrate and film are aligned in q_z direction (i.e., having equal q_x values).

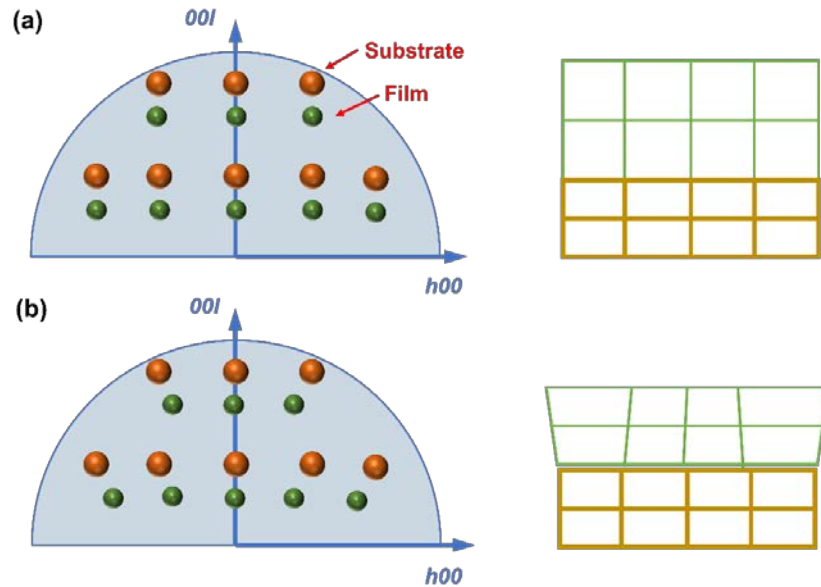


Figure 3-6 Schematic of reciprocal space mapping

(a) fully strained and (b) relaxed epitaxial thin film

All the abovementioned X-ray measurement techniques are used to obtain crystallographic information based on the diffraction process. In contrast, X-ray reflectivity (XRR) measurement is used to evaluate thin film parameters through an x-ray reflection pattern yielded from a grazing incident beam. XRR measurement is a non-contact technique to non-destructively determine the thickness and surface or interface roughness of the thin film.¹⁶⁶ As depicted in Figure 3-7(a), the X-ray beam experiences total reflection at the incident angles below a critical value (θ_c) determined by electron density of the material. Beyond the critical angle, the incident X-ray beam penetrates the thin layer through the refraction governed by Snell's law at the film/air interface. The transmitted part of the beam also undergoes an additional reflection and transmittance at the film/substrate interface due to dissimilar electron densities of materials, resulting in an interference pattern being contingent on the optical path difference corresponding to the thickness of the film. The XRR measurement is customarily carried out by a coupled 2θ - ω scan up to $2\theta = 6-8^\circ$ depending on the nominal film thickness, typically more extended range is required for thinner films. Figure 3-7(b) illustrates a typical XRR spectrum of 70 nm BFCO film, showing an oscillating pattern with an acceptable dynamic range of intensity in which the period of oscillation is used to estimate the thickness of the film. In practice, a powerful tool for multilayer heterostructure is a simulation/modelling process that provides a comprehensive set of information on each layer's thickness and surface/interface roughness. In this case, the quality of interfaces is considerably influential on the outcome pattern and accessibility of data since the intensity counts diminish more rapidly if a significant interface roughness is present.

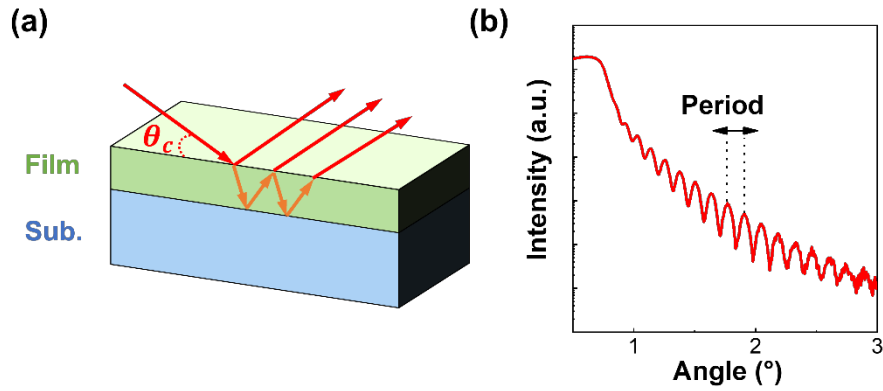


Figure 3-7 X-ray reflectometry

(a) X-ray reflection of incident beam at grazing angles (b) representative XRR spectrum of 70 nm BFCO thin film using Rigaku Smartlab XRD.

3.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface-sensitive quantitative technique to examine the chemistry of the sample. Monochromatic photons are employed to excite electrons of atoms within the surface layer, i.e., top ~10 nm, to a higher energy state. Provided the energy of incident photons suffices, electrons may escape from the surface and get screened by an energy analyser before their intensity for a defined energy level is recorded by a detector. The resultant energy spectra include peaks representing electronic structure features of atoms present at the sample surface. The number of detected electrons is quantified as a function of their kinetic energy, which is automatically converted to binding energy by the data measurement software as follows:

$$E_K = h\nu - E_B - \varphi \quad \text{(Equation 3 – 4)}$$

Where $h\nu$, φ are X-ray energy and the work function of solid, respectively. In addition, since the local chemical environment and nominal oxidation state of atoms influence the binding energy peaks, the valence of elements in the sample can also be specified.

XPS spectra were acquired using Escalab 250xi (Thermo Scientific, UK) equipped with a monochromatic aluminium K_{α} x-ray source (1486.68 eV). Pass energy of 100 eV and 20 eV was used for survey and region scans, respectively. The binding energy of C-1s (284.8 eV) for adventitious hydrocarbon was taken as the reference.

3.2.3 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a well-established method to study the film thickness and spectral optical function ranging from several micrometres thick down to a few atomic surface coverages. The alteration of the polarisation state is measured upon the reflection of an elliptically polarised light beam from the sample of interest. SE directly measures the ratio of amplitudes (Psi, ψ) and phase shift (delta, Δ) of the orthogonal components of the reflected polarized light as shown in Figure 3-8.¹⁶⁷ Regression analysis is then performed to find the best fit for a proposed optical model that relates the ellipsometry quantities to the thickness and optical properties of the sample under study.

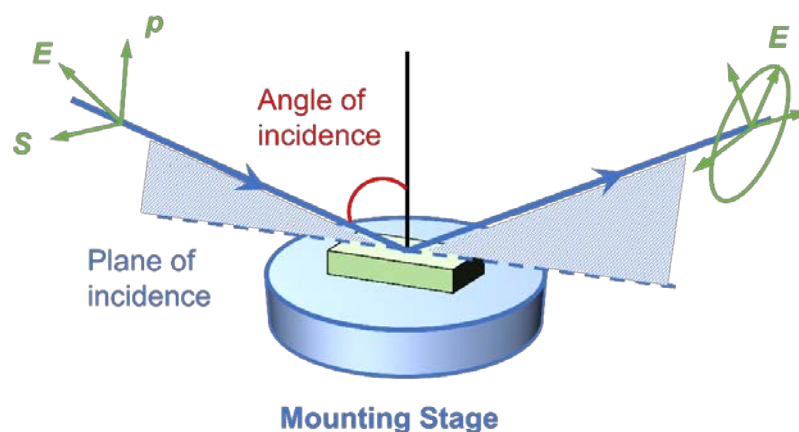


Figure 3-8 Interaction between sample and polarized light in SE

P and S are the orthogonal components of a linearly polarized light.

A VASE ellipsometer system (J.A. Woollam M-200 DI) was used to examine the optical absorption of the thin films in the photon energy range 1.24–3.2 eV at a variable angle of incidence. The choice of the incident angle depends on the magnitude of change in acquired data, which usually is most significant near the Brewster angle, particularly for the extremely thin layers. Nonetheless, advanced ellipsometers can obtain precise data using a broad range of angles. Thus, due to the small size of samples, the incidence angle was limited to 45–75 degrees to avoid spillover of the beam spot on the mounting stage. SE data analysis procedure consists of (i) measuring ellipsometry data, (ii) representing the sample with an accurate model, (iii) comparing the generated and experimental data to find the unknown parameters through the fitting process, (iv) and lastly assessing the results.

A well-constructed optical model is a prerequisite for data analysis. This model should describe the structure of all materials/and interfaces with which light interacts during measurement. In this work, a multilayer model composed of ambient, thin film, buffer layer and substrate were adopted whilst the surface/interfacial roughness was also considered to enhance the goodness-of-fit within reason. An ellipsometric response is generated based on the thickness and optical function of each material. The known parameters are fixed in this step, while an initial but educated guess estimates the unknowns. Data fitting is then performed between the model-generated and experimental data via the analysis software (WVASE 32). The variable parameters are adjusted iteratively in regression analysis until the mean squared error (MSE) function is minimized. The low MSE value is sometimes considered as the Figure of Merit in the fitting procedure. However, care should be taken that the analysis algorithm has not

fallen into a local minimum. After finding the best fit, these results should be assessed on the basis of uniqueness, sensitivity to each parameter and its physical validity.

3.2.4 Photocurrent Characterization

The photocurrent measurement of the films was performed with a standardized set-up composed of a tuneable light source generated from a 300 W Xenon lamp (TLS55-X300, ScienceTech Inc.), a source meter (Keithley 4200A) with a probe station for sourcing and measurement. Photocurrent density (J) was measured between in capacitor-like structure, top Au/Cr and bottom SrRuO₃ electrodes (Figure 3-9).

A calibrated reference silicon detector (SSIVIT-REF, ScienceTech Inc.) attached to a handheld solar power meter is utilized to measure the incident light intensity. The white light intensity was estimated to be around 20 mW cm⁻².

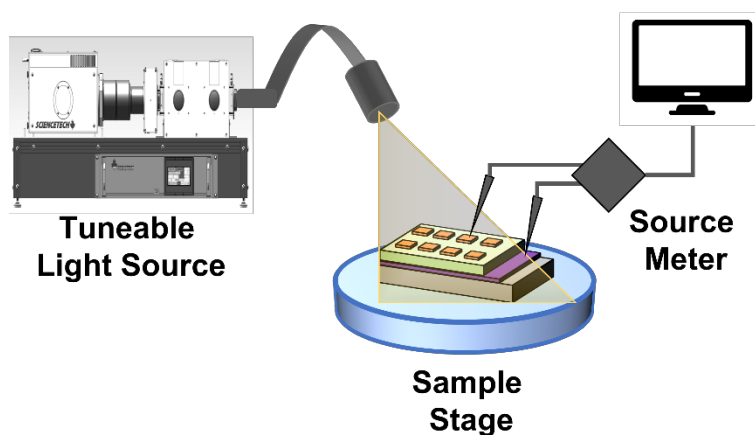


Figure 3-9 Photocurrent measurement setup

3.2.5 Electron Microscopy

Electron microscopy has revolutionized the growth of nanotechnologies over the past decades. Unlike optical microscopy, an electron beam is directed to the sample by an electromagnetic lens. Thus, the intrinsic resolution limit due to the larger wavelength of visible light is quashed in electron microscopy.¹⁶⁸ As shown in Figure 3-10, different

types of electron-sample interaction are envisaged when the primary electrons strike on the specimen.¹⁶⁹ The emitted signals from the sample are collected through the detector to render an image on a monitor or Fluorescence screen. This study uses scanning electron and transmission electron microscopy techniques, which will be discussed in detail.

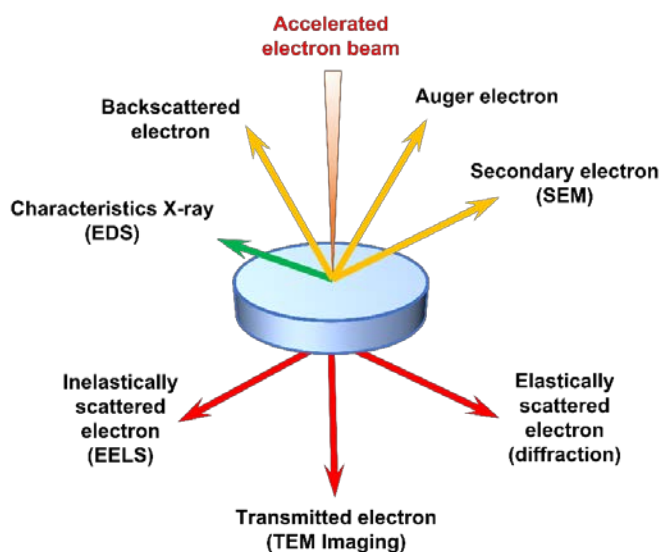


Figure 3-10 Schematic diagram of the electron-matter interaction

3.2.5.1 Scanning Electron Microscopy (SEM)

In SEM, a focused beam of accelerated electrons hits the sample, resulting in emission of signals that are then detected from a high-magnification image of the specimen. A typical SEM includes an electron source, electromagnetic lens, high vacuum chamber and a mixture of the detector to pile up the emitted signals.¹⁷⁰ During the scan across the surface of a sample, the electron-sample interaction leads to emission of the secondary electron, backscattered electron, and characteristic X-rays in the form of photons from which information on the morphology and composition of the sample can be extracted, respectively.

We used a field-emission electron microscope (Nova Nano SEM 230, FEI) equipped with an SDD-EDS Bruker detector to acquire microanalysis data on the BFCO heterostructure. Energy Dispersive X-ray Spectroscopy (EDS) is a valuable technique to identify elements present in the sample under study (qualitative) and their ratios (quantitative). The characteristic X-ray is detected by the detector, which then turns the signal into a spectrum. The concentration of each element can be deduced from the intensity of characteristic peaks, through spectral processing using standardized or semi-quantitative analysis. Considering the spatial resolution of SEM-EDS analysis,¹⁷¹ a semi-quantitative data was obtained for the thicker films (> 200 nm).

3.2.5.2 Transmission Electron Microscopy (TEM)

TEM is a versatile technique to characterize the microstructure of materials at the atomic level. It utilizes a high-energy electron beam in a high vacuum to obtain data about the crystal structure, defects, e.g., dislocation and elemental mapping. A significantly high-resolution image is then formed from the transmitted electron. Therefore, the TEM specimen needs to be ultra-thin to satisfy the condition of being electron transparent.¹⁶⁸ Figure 3-11 shows the primal components of a typical TEM system. Depending on the path of transmitted electrons via post-specimen lenses, aperture, and sensors,¹⁷² there is a variety of analytical modes in TEM, permitting the utmost information to be obtained from the sample. In the bright-field mode, an image is established from non-scattered electrons. Thus those regions that scatter more electrons, i.e., microstructural features like grain boundaries, dislocation, and segregation of heavier elements, show darker contrast.¹⁶⁸ On the contrary, if the objective aperture is placed behind the focal plane, blocking the non-scattering electron, the dark-field image is formed.

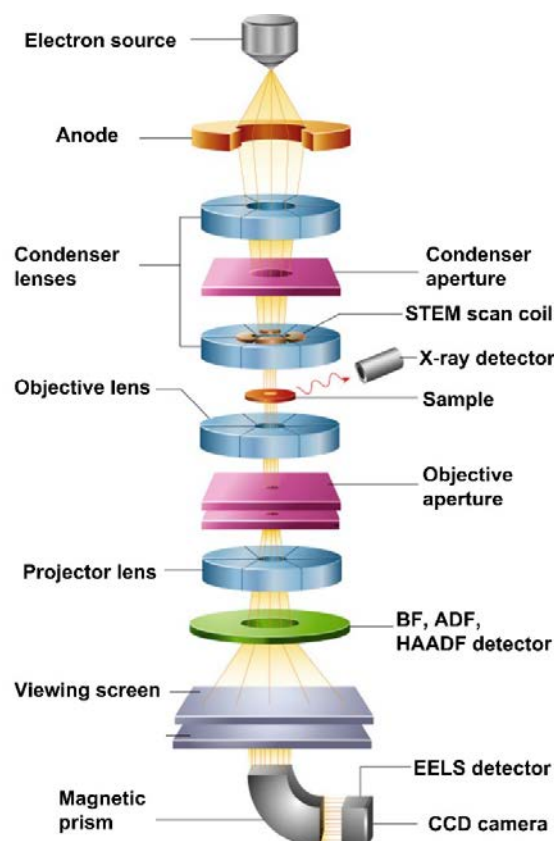


Figure 3-11 Typical TEM components (Reprinted with permission from Ref.¹⁶⁸)

Another frequently used analysis is the electron diffraction mode, in which the diffraction pattern is generated from the interference of elastically scattered electrons in the rear focal plane of the objective lens.¹⁷³ The electron diffraction mode can elaborately determine structural information, including but not limited to the lattice type, constants, and symmetry.

Scanning TEM (STEM) mode is another immensely valuable technique to conduct the chemical analysis of the specimen at the atomic scale. In this mode, the condenser lens focuses the beam spot (sub-0.1 nm in diameter) on the sample that can scan across the specimen via scan coils.¹⁶⁸ depending on the placement of the detector in the path of scattered electrons, bright/dark field image can be obtained in STEM mode.

In this study, a cold field emission gun scanning transmission electron microscope (JEM-F200, JOEL) was used at the operating voltage of 200 kV. The lattice resolution is about 0.16 nm and 0.1 nm in the annular dark-field STEM and TEM mode, respectively. As explained above, samples are required to be sufficiently thin, allowing the electrons to pass through. Thus, the TEM specimens with sub-100 nm thickness were prepared by the focused ion beam (FIB) method, using Helios G4 PFIB DualBeam system (ThermoFisher) and Nova Nanolab 200 (FEI).

3.2.6 Atomic Force Microscopy (AFM)

AFM is a well-established surface characterization technique based on scanning probe microscopy, which allows acquiring high-resolution three-dimensional surface images. Figure 3-12 shows the schematic representation of the AFM apparatus. A typical device consists of a sharp tip attached to the end of a cantilever, laser source and photodiode detector. During a scan, the interaction between the tip and the sample surface causes deflection of the cantilever due to the short-range forces that is detected by the photodiode detector through the change in reflection angle of the laser point. This deflection change is then translated to the topography of the sample surface.

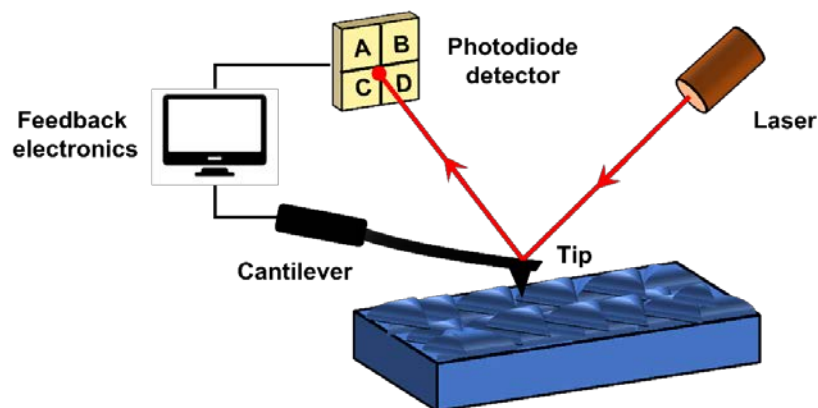


Figure 3-12 Illustration of detection system in AFM measurement

In this thesis, a Bruker Dimension Icon SPM was used to obtain surface roughness and topography of samples. This set-up is equipped with SCANASYST-AIR probe having a silicon nitride cantilever with a nominal tip radius of about 2 nm. The small spring constant of 0.4 N m^{-1} and resonance frequency of 70 kHz for the cantilever intensifies the deflection signals. The resultant digital information was then rendered using Nanoscope software (Ver. 1.7). Apart from topographical information, the measured root mean square (rms) surface roughness of the film has been taken to account when building the optical model for ellipsometry analysis.

3.2.7 Conductive Atomic Force Microscopy (C-AFM)

C-AFM is another mode of atomic force microscopy technique to study the conductivity of a sample. In this study, a conductive tip probes the sample surface while an external bias is applied to the sample from the bottom electrode (unless mentioned otherwise). The charge carriers conducted within the sample are then collected by the conductive tip, enabling a current map image to be obtained on the microscopic scale. In this study, the Asylum AFM instrument in ORCA mode fitted with a Pt/Cr-coated tip was used, which has an average radius of $<25 \text{ nm}$.

3.2.8 Piezoresponse Force Microscopy (PFM)

The local polarisation state and domain structure of ferroelectric materials can be investigated if the AFM measurement is conducted in contact mode under the application of an alternating current (AC) bias to the conductive probe tip.¹⁷⁴ The working principle of the piezoresponse force microscopy (PFM) is based on the converse piezoelectric effect, meaning that the applied bias stimulates vibrations of ferroelectric samples since all ferroelectric materials are piezoelectric as well, and this mechanical deformation is then imparted to the cantilever, which subsequently is

converted to the electrical signals. This yields the PFM amplitude and phase images which map the piezoelectric deformation and piezoresponse direction under an applied bias, respectively. Asylum Cypher AFM system equipped with Pt/Cr-coated probes (ElectriMulti 75G, Budget Sensors, Bulgaria) was used in this study.

3.2.8.1 Domain Switching Demonstration

Utilizing the PFM method, the domain switching of the ferroelectric sample can be performed under external DC bias greater than coercive voltage. In most cases, a square area is written on the thin film sample when a positive DC bias is applied to the probe tip during the scan, accompanied by writing another square within the former by applying negative DC bias. By this operation, also known as box-in-box DC writing, all domains in the larger square are initially aligned downward, whereas those within the inner square are switched back upward (see Figure 3-13). In this way, the switching of domains under an external electric field can be locally performed, confirming the ferroelectric characteristics of the sample.

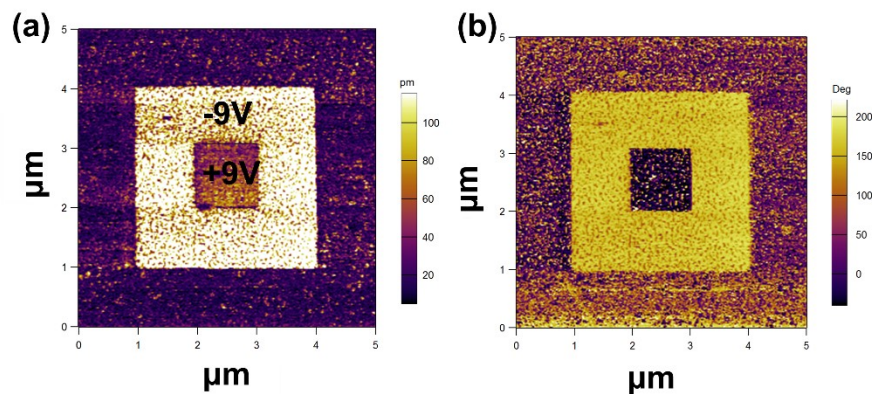


Figure 3-13 Ferroelectric domain switching

(a) amplitude (b) phase graph of (001) BFCO films under ± 9 V external bias

3.2.8.2 Kelvin Probe Force Microscopy (KPFM)

KPFM were performed to probe the surface potential and space charge distribution in the BFCO thin film. All measurements were conducted using a commercial AFM system (AIST-NT Smart SPM 1000) under ambient atmosphere. Platinum-coated tips (Mikromasch HQ: NSC35/Pt) with a force constant of ~ 5 N/m and a tip radius less than 30 nm have been used for all imaging modes. Moreover, the variation in surface potential of the film was also measured under UV laser illumination (405 nm) and in the dark. An external tunable illumination source (FemtoPower 1060) was used to illuminate the samples at an angle of 30° to the surface to avoid shading from the probe tip.

3.2.9 Macroscale Ferroelectric Polarisation Measurement

Global ferroelectric characterization is typically performed using hysteresis loop measurement, i.e., polarisation versus electric field (P-E). An external ac bias is applied across the film through the electrodes to obtain the ferroelectric characteristic. A Radiant Precision Multiferroic testing system fitted with a probe workstation was utilized to acquire the P-E loop via triangular voltage function. The frequency and range of applied AC bias, the film thickness, and the electrode area are submitted in the testing program prior to the measurement.

3.3 Summary

The fundamentals of fabrication and characterization techniques that are used in the subsequent chapters were highlighted. The process of preparing BFCO ceramic target for deposition of BFCO thin film via LMBE was elaborated. Moreover, the device fabrication procedure for the electrical measurement was described, including preparing

top Au/Cr electrodes employing lithography and metal evaporation. The analytical techniques for the characterisation of epitaxial BFCO heterostructures are summarised in Table 3-2.

Table 3-2 Measurement techniques used in this thesis

Analytical Technique		Information obtained	Chapter
XRD	2 θ - ω scan	• Out-of-plane lattice parameter • Qualitative phase analysis	4,5,6
	Rocking curve (Omega scan)	• Crystalline quality	4,5,6
	Pole figure (Phi Scan)	• Crystal preferred orientation	5,6
	XRR	• Film thickness • Surface/interfacial roughness	4,5,6
	RSM	• In-plane lattice parameter • Epitaxial relation (Strain state)	4,5,6
SEM/EDS		• Compositional analysis	6
TEM		• Cross-section imaging • Compositional analysis	6
XPS		• Elemental analysis • Ion composition & oxidation state	4,6
AFM		• Surface morphology • Surface roughness	4,5,6
C-AFM		• Local electrical conductivity	5,6
PFM		• Out-of-plane piezoelectric response • Ferroelectric domain switching	5,6
KPFM		• Surface potential measurement	5
I-V	Dark	• Leakage current • Charge transport mechanism	6
	Illumination	• Photocurrent density	6
Ferroelectric testing system		• Macroscale polarisation hysteresis loop	6

Chapter 4. Single-phase $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ Thin Film Stabilisation

Due to exhibiting intriguing properties, the complex oxides consisting of multiple transition metals has spurred the interest of the research community. Recent progress in thin film technologies has also made the synthesis of such complex oxides possible. Formation of single-phase BFO-based perovskite with high crystal quality and outstanding functionality is of interest to this thesis. It demands a painstaking empirical process due to the presence of volatile bismuth for which the phase stabilization depends on desorption and reaction rates simultaneously.¹⁷⁵ Bulk perovskite $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$, in particular, forms only in an extremely high pressure/high-temperature regime via solid-state synthesis, i.e., under 6 GPa at 1000 °C,¹⁷⁶ while conventional sintering of bismuth oxide, iron oxide and chromium oxide in ambient pressure leads to the formation of a mixed-phase dominated by nonstoichiometric bismuth chromate, e.g., $\text{Bi}_{7.38}\text{Cr}_{0.62}\text{O}_{12+x}$.¹⁷⁷ Alternatively, the high mechanical pressure can be replaced by the epitaxial strain imposed from the suitable lattice-mismatched substrate to stabilize such complex oxide regardless of the thermodynamic instability of their bulk counterparts. In this approach, both the kinetic and thermodynamic aspects of the synthesis process greatly influence the composition of the deposited film. For instance, phase and structure of the thin films deposited via LMBE can be modified via growth parameters such as temperature, oxygen partial pressure and laser characteristics which determine the kinetic and thermodynamic of process.

In this chapter, first, the deposition condition for obtaining single-phase epitaxial BFCO thin film on STO (001) will be assessed. Next, the structural characterization of the

SrRuO₃ buffer layer will be discussed since it is used as the bottom electrode for all electrical measurements. Finally, the optical dispersion of the SRO buffer layer is obtained using spectroscopic ellipsometry.

4.1 Optimization of Deposition Parameter

BFCO films with a nominal thickness of 70 nm were deposited using a Pascal Mobile-Combi Laser MBE (MC-LMBE-KA6LSM0E4) with a KrF excimer laser (248 nm wavelength, 25 ns pulse duration). Laser fluence was measured via a power meter and kept constant at $\sim 2 \text{ J cm}^{-2}$ based on a laser spot size of 1.6 mm^2 . The distance between the target and substrate was fixed at 5 cm. The growth rate is approximated to be $\sim 0.12 \text{ \AA}$ per pulse under these conditions. Note that growth rate slightly varies by changing the deposition temperature and oxygen pressure; however, this variation is trivial within the narrow growth window in this thesis.

The growth chamber was initially pumped down to the base pressure of $\sim 10^{-8}$ Torr and the substrate was heated up to the deposition temperature at the ramp rate of $40^\circ/\text{min}$. Once substrate reached the desired temperature, background oxygen gas was introduced to the chamber by regulating the gas flow controllers. The target surface was pre-ablated at a high laser repetition rate prior to each deposition to remove any contaminants and obtain a steady-state condition at the surface. During the film growth, the substrate was rotated continuously while rastering the laser beam over the target in order to produce consistent film coverage over the substrate. The samples were cooled down at $10^\circ/\text{min}$ rate under similar oxygen pressure as the deposition pressure.

Due to the high volatility of bismuth, the phase structure of bismuth compounds is susceptible to growth conditions. Therefore, finding the growth window for the pure-

phase BFCO thin film is of great importance. In this chapter, the influence of the deposition temperature (T_s), oxygen partial pressure (P_{O_2}) and laser repetition rate on the phase stability of BFCO films has been studied. Whilst the oxygen pressure is often correlated with oxygen content in the perovskite oxides, it also affects the cation stoichiometry, leading to different functional properties.¹⁷⁸ Not only does the deposition temperature determine the crystallinity of the grown film, but it also influences the phase structure.¹⁷⁹ Finally, varying the laser repetition rate during growth has been reported to strongly impact the structure and functional properties of double perovskite BFCO films.^{18,153}

4.1.1 Influence of Deposition Temperature

The BFCO films were initially grown at 10 mTorr and the laser repetition rate of 5 Hz while changing the substrate temperature (500-750 °C). Figure 4-1(a) presents the impact of deposition temperature on the phase stability of films.

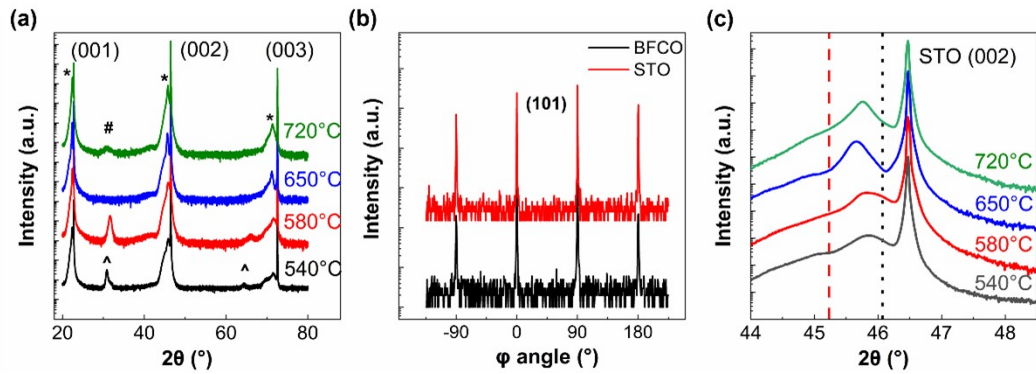


Figure 4-1 Structural study of BFCO film grown at various temperatures

(a) XRD spectra of BFCO film grown under 10 mTorr P_{O_2} . Asterisks correspond to BFCO film, # and ^ represent Fe/Cr rich and Bi-rich parasitic phases, respectively. (b) Phi scan recorded around (101), confirming cube-on-cube growth of BFCO film on the substrate (c) zoom around (002) peak, black dotted and red dashed line represents relaxed and fully strained OP lattice constant, respectively.

It can be seen that film grown at 650 °C shows no parasitic phases within the resolution of XRD technique. For the optimum deposition temperature, only (00l) reflections associated with the STO substrate and the BFCO layer are observed in the XRD scan, confirming the growth of *c*-axis oriented films. It is also noted that the out-of-plane lattice constant varies with deposition temperature. As shown in Figure 4-1(c), the (002)_{pc} peak for BFCO films shifts to higher angles, i.e., toward bulk lattice constant, for the lower growth temperature, exhibiting the largest OP lattice constant (~3.97 Å) at the optimum temperature. The phi-scan further establishes the cube-on-cube epitaxial relation between the substrate and the layer (See Figure 4-1(b)). On the contrary, those films deposited at the lower or higher temperature present additional reflections that correspondingly can be assigned to Bi-rich and Bi-deficient secondary phases. These secondary phases were identified to be Bi₂O₃ and Bi₂(Fe,Cr)₄O₉, respectively. The difference in the prevalent parasitic phase within the film gives evidence of variation in the Bi content resulting from the high volatility of metallic bismuth. The films prepared at a lower temperature than the optimal condition exhibit Bi-rich phase reflections associated with tetragonal β or cubic δ Bi₂O₃ structure or an assortment of them.¹⁸⁰ On the other hand, the Bi-deficient phase with a similar structure to the orthorhombic Bi₂Fe₄O₉ (ICSD:238979) was present at the elevated temperature. To the best of my knowledge, no XRD pattern has been indexed for Bi₂(Fe,Cr)₄O₉ in the crystallographic databases. However, the Bi₂(Fe,Cr)₄O₉ compound, as reported earlier,¹⁸⁰ may also resemble layered bismuth metal oxides like Bi₂Fe_{4-x}Ga_xO₉, exhibiting an antiferromagnetic order below room temperature.

Distinguishing between these parasitic phases solely from diffraction patterns is difficult due to the overlapping XRD peaks. Intriguingly, it is found that the surface

morphology of film changes as deposition temperature deviates from the optimum condition. For instance, Figure 4-2(b) shows that the film surface comprises elongated structures when deposition temperature exceeds 700 °C. The presence of such a structure is previously attributed to the outgrowth of secondary phases like $\text{Bi}_2\text{Fe}_4\text{O}_9$ -like compounds as explained above.¹⁸⁰ Hence, XPS is used to investigate the surface chemical composition of the films grown at different temperatures. First, the representative Fe-2p XPS spectra show a clear $2p_{3/2}$ satellite at 719 eV that is the signature of Fe^{3+} ions,¹⁸⁰ whilst no feature is present at 715 eV (Figure 4-2(c)).

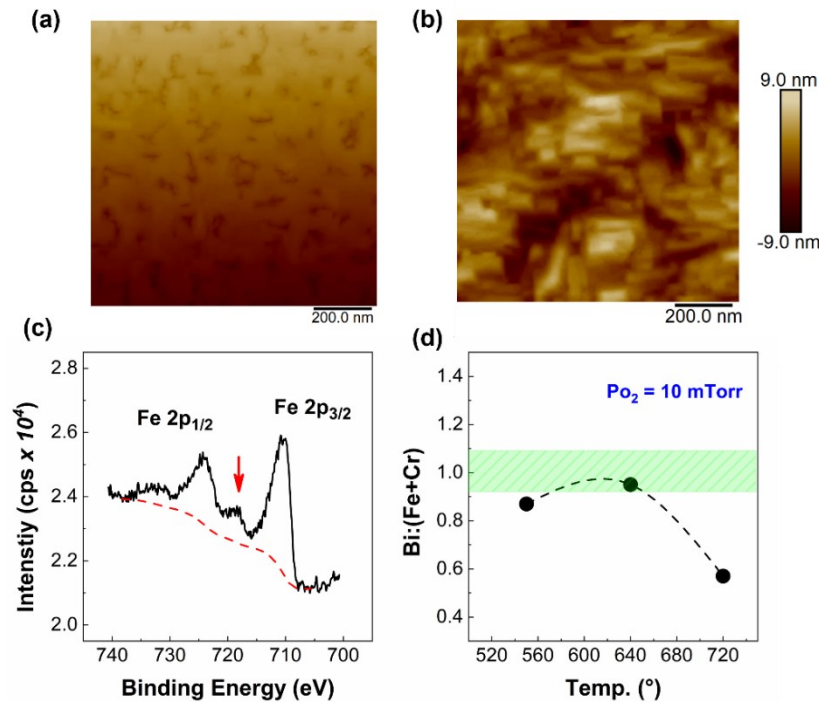


Figure 4-2 Surface analysis of BFCO film grown at various temperatures

- (a,b) AFM images for films deposited at optimal and elevated temperatures, respectively.
(c) XPS spectrum for Fe 2p core level. The red arrow points toward the $2p_{3/2}$ satellite at 719 eV. (d) Cation ratio for BFCO film deposited at different temperatures. The green hashed box is only for the guide.

Thus, it is conferred that majority of Fe cations are in +3 oxidation state. Deconvolution of cations core level will be discussed in more detail in Chapter 6. Furthermore, Figure

4-2(d) reveals that bismuth content is close to the nominal stoichiometric value only when the corresponding XRD spectrum did not exhibit additional peaks (raw XPS data is summarized in Table 4-1). More importantly, the outgrowth of the Bi-deficient phase for the sample deposited at 720 °C is confirmed since the $Bi:(Fe+Cr)$ atomic ratio is considerably decreased by elevating the substrate temperature.

Table 4-1 XPS peak area for BFCO film grown at different temperatures

T_s (°)	Element	Peak BE (eV)	FWHM (eV)	Area (CPS.eV)	Atomic (%)
540	O1s	529.56	1.2	43338.61	60.02
	Bi4f	158.74	1.05	185564.4	18.60
	Cr2p	576.07	2.42	28116.23	9.60
	Fe2p	710.44	3.46	40869.24	11.78
650	O1s	529.5	1.19	38921.64	60.10
	Bi4f	158.68	1.05	174048.1	19.46
	Cr2p	576.07	2.38	24753.37	9.43
	Fe2p	710.4	3.64	34280.79	11.00
720	O1s	529.61	1.22	38509.13	56.95
	Bi4f	158.77	1.11	146329.9	15.66
	Cr2p	576.35	2.54	33786.58	12.33
	Fe2p	710.64	3.87	48994.03	15.07

4.1.2 Influence of Oxygen Pressure

To better understand the influence of processing conditions on the BFCO phase, the oxygen pressure during deposition was varied at a constant substrate temperature of 620 °C. It is evident that a slight change in the P_{O_2} significantly impacts the phase stability of the BFCO film. As presented in Figure 4-3(a), the XRD spectra appeared to be single-phase for the sample grown at 4 mTorr and did not show any additional reflection except those corresponding to the BFCO layer and STO substrate. Similar to Nechache et al. study,¹⁸⁰ we also could not detect any BFCO peaks when films were deposited at oxygen pressure lower than 0.1 mTorr. This observation may indicate that

the phase formation under a high vacuum is significantly inhibited. In addition, a mixture of BFCO and preferentially Bi-rich phases is observed in the films grown under high oxygen pressure. The presence of each phase highly depends on the bismuth content as the incorporation of Bi increases in the film with the judicious increment of P_{O_2} .

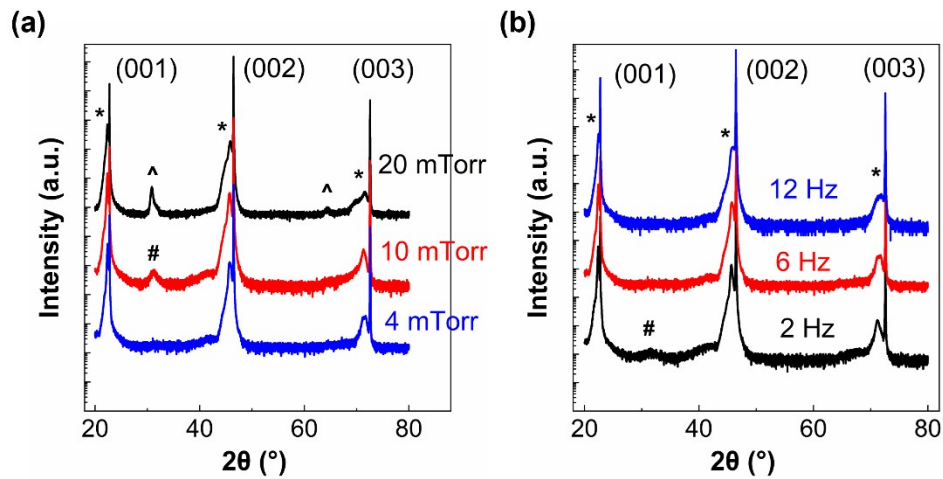


Figure 4-3 Structural study of BFCO film grown at various oxygen pressures
XRD pattern of BFCO films grown at constant substrate temperature of 620 °C (a) under different oxygen pressures and (b) at different laser frequencies

4.1.3 Influence of Laser Repetition Rate

In the PLD-grown films, the laser repetition rate is deemed to tune the defect concentration, namely anti-sites, resulting in modification of the structural and functional properties.¹⁵³ Moreover, the impact of laser repetition rate on the bandgap of BFCO thin films has been widely studied due to possible modulation of the transition metal cation ordering.^{18,155,181} Here, the laser repetition rate is changed ranging from 2-20 Hz while maintaining the laser fluence, and in turn, the impact of growth time on the phase and structure of BFCO films is probed. The effect of laser repetition rate on the phase stability of BFCO films has been initially examined. From Figure 4-3(b), It is evident

that changing the growth time can result in the presence of mixed phases in the films. The lower the growth rate, the likelihood of BFCO film tending to bismuth deficiency is more significant. In particular, Fe-rich phase like $\text{Bi}_2(\text{Fe,Cr})_4\text{O}_9$,¹⁸⁰ appears in the XRD spectra of the sample grown at 2 Hz frequency. The Bi:(Fe+Cr) cation ratio was also quantified using XPS and found out the ratio is reduced from 0.95 to 0.77 when laser repetition is dialled down to 2 Hz. This observation further corroborates the XRD results. It could be inferred that more bismuth desorbs at a lower laser repetition rate during growth given that the film is exposed to high temperature for an extended time.¹⁵⁸

In addition, the impact of the laser fluence on the cationic long-range order was also investigated. As a general rule in ABO_3 perovskite, it is well-known that the difference in the oxidation state of B-site cations is the main factor influencing the cation ordering when B-site is composed of two different atoms.¹⁸² The ordered arrangement is favoured if this difference is larger than two; contrarily, disorder arrangement is preferred. For $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$, the latter case is more plausible since Fe^{3+} and Cr^{3+} have identical oxidation states and very similar ionic radii. Nonetheless, both kinetics and thermodynamics can influence the long-range ordering,¹⁸³ and previous studies have shown a tunable degree of Fe/Cr ordering in the BFCO thin films can be achieved by adjusting the growth rate.¹⁸

Asymmetric XRD scans were performed along the $[111]_{\text{pc}}$ BFCO direction to probe the presence of the superstructure peaks in the representative XRD spectrum. As seen in Figure 4-4(a), two small peaks at 19.5 and 61.1° appear for samples grown at 650 °C, suggesting doubling the unit cell along $[111]$ direction. From peak analysis (Figure 4-4(b, c)), it can be inferred that the normalized intensity of the superstructure reflection

$(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ is at its maximum for the lowest laser frequency, which can be correlated to the more extensive Fe/Cr cation ordering.¹⁷⁵ In addition, Figure 4-4 (d) presents a cross-sectional TEM image of (001)-oriented BFCO film taken along the [010] direction. As shown in the Fast Fourier Transform (FFT) graph corresponding to the ordered domain, superlattice spots $(\frac{1}{4} 0 \frac{1}{4})$ are visible parallel to the $[\bar{1}01]$ direction, further corroborating the presence of superstructure peaks in XRD measurements.

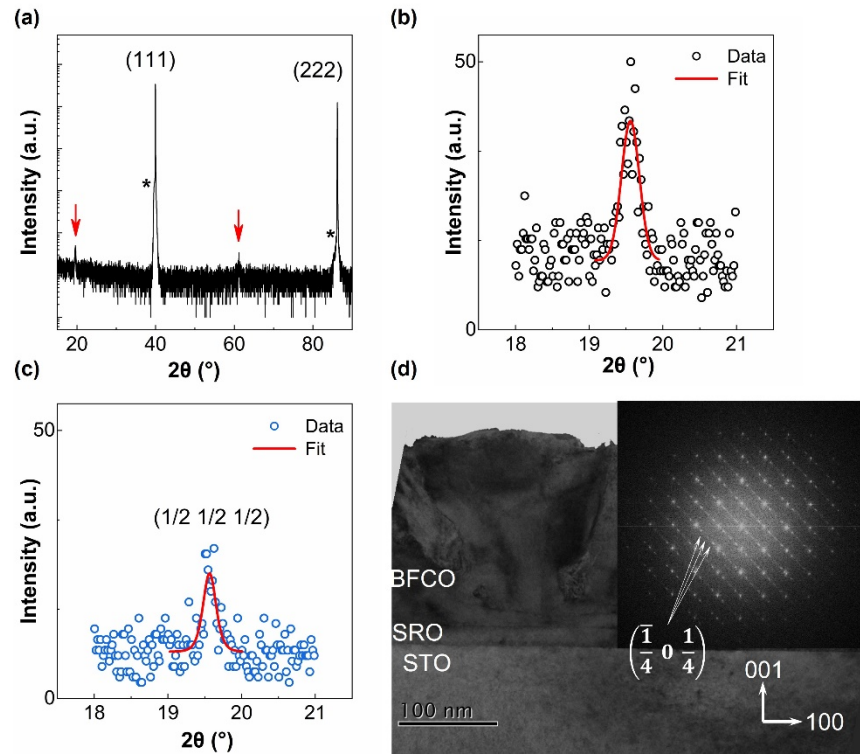


Figure 4-4 Effect of laser repetition rate on the superstructure peak

(a) Asymmetric XRD pattern along [111] direction for BFCO film deposited on STO (001) substrate. The asterisk and arrow represent the BFCO main and superstructure peak, respectively. Zoom on the superstructure $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ corresponding to BFCO film deposited at (b) 2 Hz (c) 12 Hz laser frequency - plotted on the same scale. (d) Cross-sectional TEM image with FFT pattern corresponding to BFCO ordered regions

It is expected that a longer annealing time provides B-site cations with enough kinetic energy to be placed at their preferential site, increasing the probability of chemical ordering in double perovskites.¹⁸⁴ Of note, although the correlation between

superstructure peak and chemical ordering is widely reported,^{185,186} other factors such as cation displacement can also produce such peaks in double perovskites.¹⁵⁴ In these cases, a combination of XRD and neutron powder diffraction (NPD) can be used to detect cation ordering indirectly via oxygen position.¹⁸² Further investigation on the laser repetition rate, is not the scope of this thesis as comprehensive studies can be found elsewhere.^{18,153} Considering the trade-off between phase purity and presence of superstructure peak, the laser repetition rate was fixed at the optimum value of 4 Hz for all samples studied in the following chapters. Above investigation on phase formation under different processing parameters is schematically delineated in Figure 4-5.

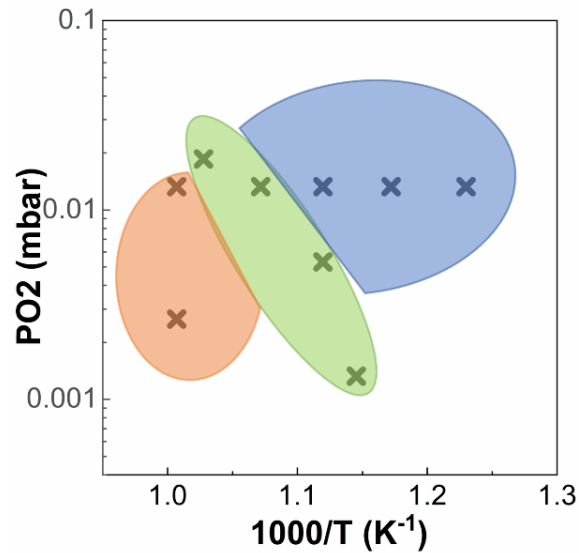


Figure 4-5 P-T phase diagram of epitaxial BFCO thin films

The 70 nm -thick films were deposited at a constant laser fluence of 2 J cm^{-2} . The green ellipse represents the narrow window for single-phase BFCO films deposition while blue and amber area demonstrates Bi-rich and -deficient phase, respectively.

As expected, the stabilization of pure Bi-based oxide has been a painstaking task. Yet, it was shown that the formation of the metastable BFCO phase could be realized in a very narrow deposition window. Either high substrate temperature or low oxygen would lead to the formation of Fe/Cr-rich phase combined with the BFCO phase. One can explain

this observation via evaporation of metallic bismuth or decomposition of bismuth oxide at elevated temperatures.¹⁸⁰ On the other hand, the formation of Bi-rich phases is favoured under a low temperature or high oxygen pressure regime. Note that the obtained phase diagram highly depends on other factors such as target stoichiometry, substrate-target distance, and laser configuration.

4.2 Deposition of SrRuO₃ Bottom Electrode

By far, SrRuO₃ has been widely used as a bottom electrode in the all-oxide heterostructure due to its conductive properties with no further need for doping.¹⁸⁷ SRO demonstrates orthorhombic symmetry in the bulk form with a perovskite structure having lattice parameters $a = 5.57 \text{ \AA}$, $b = 5.53 \text{ \AA}$ and $c = 7.84 \text{ \AA}$.¹⁸⁸ The pseudocubic lattice constant is estimated to be $a_{pc} = 3.93 \text{ \AA}$,¹⁸⁷ which has a good lattice match with both BFCO and STO. Hence, SRO is incorporated as a buffer layer between BFCO thin film and STO, serving as the bottom electrode for the transport and ferroelectric measurement.

The SRO thin films were deposited on STO (001) substrate from a stoichiometric target at 700 °C under an oxygen pressure of 100 mTorr. Depending on the desired thickness, total number of 1500-3000 pulses were used, with a laser fluence of 2.8 J cm^{-2} at a frequency of 4 Hz. Subsequently, the thin films cooled down to room temperature at the rate of 10 °C per minute in the same oxygen environment as during growth.

X-ray diffraction pattern confirms that SRO thin film is single phase and epitaxially grown on STO substrate. Figure 4-6(a) shows the high-resolution ω -2 θ scan of SRO film around (002) peak, from which the thickness of the film was estimated using the interference fringes as expressed by:¹⁸⁹

$$t = \frac{\lambda}{2\Delta\omega \cos(\theta)} \quad (\text{Equation 4 - 1})$$

where t and λ are the layer thickness and X-ray wavelength, respectively, and $\Delta\omega$ represents the difference between two adjacent fringes in radians. From Equation 4-1, the growth rate was calculated to be 0.08 Å per pulse under the optimized processing condition. Moreover, the out-of-plane lattice parameter of SRO film was estimated to be 3.96 Å, exhibiting 0.76% expansion compared with the bulk pseudocubic constant.

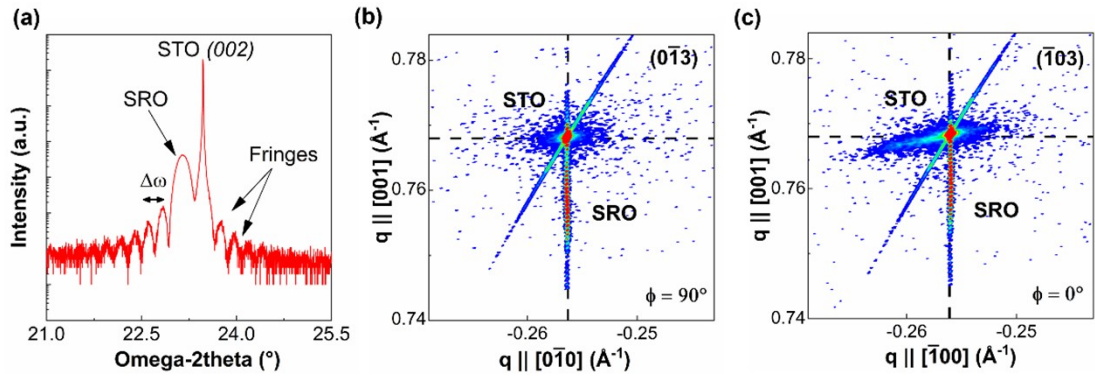


Figure 4-6 Structural characterisation of the SRO layer

(a) Omega-2theta around symmetric (002) peak (b, c) RSM around asymmetric (103) plane family

RSM scans around (103) diffraction planes clearly confirms that the film is grown coherently and has the same in-plane lattice constants as the substrate, i.e., ~3.905 Å. As presented in Figure 4-6(b, c), the reciprocal spot for the SRO layer stretches out vertically due to the finite thickness effect. Further examination of the peak position along out-of-plane direction reveals that 12-nm SRO film possesses a tetragonal structure since both (103) and (013) diffraction peaks have a similar value of $q \parallel [001]$.

The surface morphology of the SRO thin films was studied by AFM. As shown in Figure 4-7(a), no features corresponding to the secondary phases is seen, and the deposited film mimics the overall stepped structures of STO substrate.

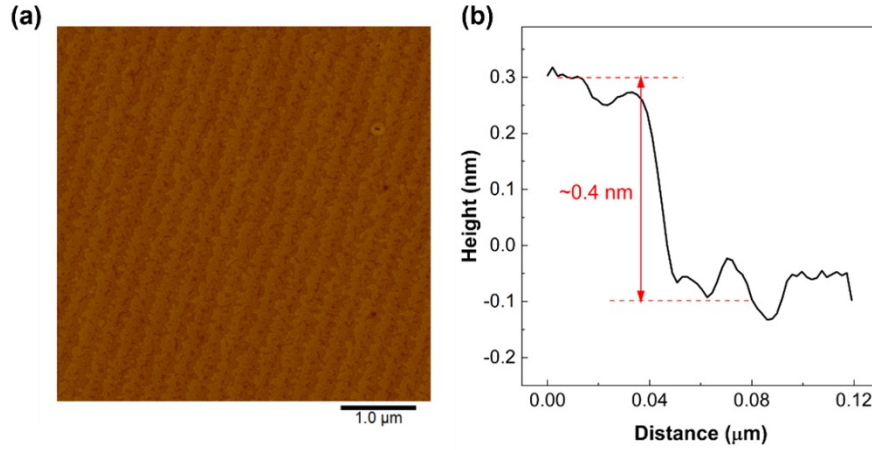


Figure 4-7 Surface analysis of the SRO bottom electrode

(a) AFM image of 12 nm-thick SRO buffer layer (b) Step line profile extracted from AFM image using NanoScope software

The height of the terrace is estimated to be ~ 0.4 nm compatible with the unit cell of SRO, i.e., 0.393 nm (see Figure 4-7(b)). It is known that SRO thin film follows a step-flow growth mechanism,¹⁹⁰ which makes the deposition of a very smooth layer possible at the optimized condition. The 12 nm-thick SRO film demonstrates an atomically smooth surface with rms of ~ 0.3 nm across $5 \times 5 \mu\text{m}^2$, which fulfils the smooth interfacial condition prior to the BFCO deposition. To ascertain the conductive nature of our SRO films, we simply measured the resistance across the substrate length, i.e., 5 mm, before and after deposition. Using a handheld digital multimeter (Fluke 12E+), the SRO films exhibited resistance in the range of 300-500 k Ω , which is acceptable as the bottom electrode.

Later in chapters 5 and 6, the measured ellipsometry spectra of heterostructures will be fitted to an optical model consisting of substrate/SRO bottom electrode/BFCO layer/surface roughness. Thus, obtaining the optical dielectric function of the SRO layer epitaxially grown on the (001) single crystal STO is a crucial step. In this way, the number of unknown variables is significantly reduced during the fitting procedure,

leading to valid and physically justifiable results. Of note, apart from serving as the bottom electrode, SRO thin film is deemed to act as a buffer layer to manipulate the nanoscale domain structure,¹⁹¹ or to tune the preferred direction of polarization in the top layer.¹⁹² Possible influence of the SRO thin layer on ferroelectric properties of BFCO film will be further discussed in section 6.2.4.

The dielectric function of the SRO layer is derived from the ellipsometry data, using a three-layer optical model, which includes semi-infinite STO substrate, SRO layer and ambient. A surface roughness layer was included, but it did not improve the figure-of-merit of the fitting process due to the very low surface roughness of film confirmed by AFM. Utmost care should be taken, as the SRO layer is absorbing over the entire measurement range, i.e., 200-1000 nm; therefore, a Drude and two Lorentz oscillators were used to parametrize the optical function of the SRO layer. The fitted ellipsometry data is presented in Figure 4-8 with a reasonable MSE value.

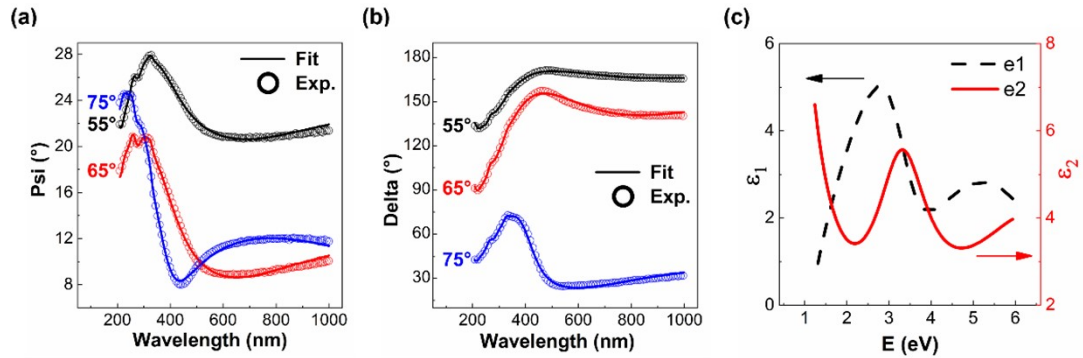


Figure 4-8 Ellipsometry data of the SRO thin layer

(a) Ψ (b) Δ measured and fitted at three angles of incidence (c) Dielectric function of SRO buffer layer

The Drude oscillator is chosen to represent the Drude-like behaviour at the very low photon energies correlated with the SRO electrical properties.¹⁹³ The Lorentz oscillators' centre energies are ~ 3.4 and 6.9 eV, which agree with the prominent optical excitation

reported earlier.¹⁹³ The parameters representing these oscillators are shown in Table 4-2, yielding a comparable thickness to that measured by the X-ray technique.

Table 4-2 Detail of the oscillators for the ellipsometry fitting procedure

MSE	ϵ 1. offset	Drude.Osc		Lorentz. Osc.1			Lorentz. Osc.2		
		Br.	Amp.	Br.	En.	Amp.	Br.	En.	Amp.
7.8	1.97 (± 0.03)	1.28 (± 0.007)	14.31 (± 0.07)	1.50 (± 0.01)	3.39 (± 0.003)	3.84 (± 0.04)	4.54 (± 0.15)	6.92 (± 0.04)	3.77 (± 0.03)

4.3 Summary

This chapter explored the influence of deposition parameters, i.e., temperature, oxygen pressure and laser frequency, on epitaxial growth of the BFCO films on STO (001) substrate. This chapter revealed that the pure BFCO phase could be grown within a very narrow deposition window, showing much higher sensitivity to the growth conditions compared to Bi-Fe-O tertiary system. It was shown that the formation of the BFCO phase is favoured when the processing conditions are limited to a narrow range of $T_s = 600-700$ °C and $P_{O_2} = 1-15$ mTorr. For the oxygen pressure and substrate temperature outside the optimum range, either Bi-rich or Fe-rich parasitic phases are formed coupled with the destabilization of the BFCO phase. It was demonstrated that Fe^{3+} is the prevalent chemical state of iron in the single-phase BFCO films within the resolution limit of the XPS technique.

Following stabilization of the BFCO films, the processing condition for high-quality SRO bottom electrode was also optimized. An atomically flat conductive SRO film was deposited on STO (001) substrate via LMBE under the heating condition of 700 °C in 100 mTorr O_2 . The in-depth XRD investigation suggests that SRO films, up to the thickness of about 20 nm, are fully strained to the underlying substrate due to the

moderate lattice mismatch. This optimized SRO thin film will be incorporated as the bottom electrode in the all-oxide heteroepitaxial BFCO structure in Chapters 5 and 6.

Chapter 5. Structural Phase Evolution in BFCO Thin Films

5.1 Introduction

In this chapter, the thickness-dependent structural phase transition of the BFCO thin films will be explored. Pure phase BFCO thin films were prepared on the SRO-buffered STO (001) substrate at the substrate temperature of 620 °C under a dynamic oxygen pressure of 4 mTorr. The laser fluence was kept constant at about 2 J cm⁻². To perform SPM measurements, SRO bottom electrode with a nominal thickness of ~12 nm was deposited in-situ on the substrate at 680 °C in 100 mTorr of oxygen before growing the BFCO layer. The structural characterisations show the strain imposed by the substrate changes the symmetry of thin film, transitioning from T-like to an R-like phase as the thickness of film increases. Spectroscopic ellipsometry results combined with density functional theory (DFT) suggest that the bandgap can be tuned through a structural phase transition. Photoresponse measurement using wavelength-resolved conductive atomic force microscopy demonstrates that the onset of optical absorption is also redshifted for the T-like BFCO film.

5.2 Result and Discussion

5.2.1 Structural Characterisation

The coupled θ - 2θ scans demonstrate all the BFCO heterostructures with a nominal thickness of 30, 70 and 130 nm are grown with out-of-plane direction oriented parallel to the (00l) plane of the substrate (Figure 5-1(a, b)). No secondary phases can be detected within the resolution limit of XRD measurement. The Laue fringes, albite less pronounced around the higher orders, attest to smooth interface and high coherency of

the film layers.¹³⁷ For 30 nm-thick BFCO film, as shown in the zoom-in image around (001) reflection, multiple diffraction events are present on both sides of the main peak, where the larger oscillation period corresponds to the SRO, and the shorter ones are from the BFCO thin layer. As expected, the Laue fringes associated with the BFCO layer gradually disappear by increasing the film thickness.

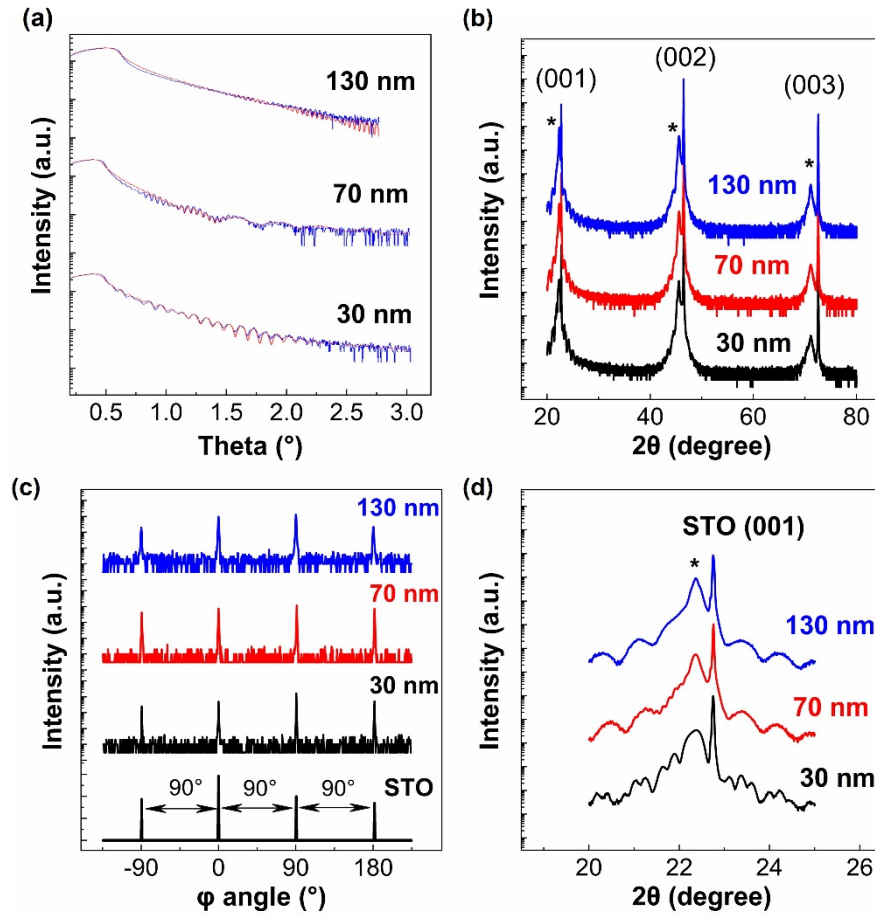


Figure 5-1 Structural study of BFCO films with different thickness

(a) X-ray reflectometry pattern (red line represent the fitted spectrum). (b) Coupled θ - 2θ scan of three representative samples. The asterisks identify the BFCO peak at the left side of STO reflections. (c) Phi scan recorded around (101) peak, highlighting the epitaxial growth of BFCO film on the substrate. (d) zoom around (001) reflection

In addition, the phi-scan of the (101) BFCO film (see Figure 5-1(c)) shows four peaks separated by 90° at the same angle as the substrate, confirming the cube-on-cube

epitaxial relation. Intriguingly, a closer look at (002) diffraction peak for the thinnest and thickest films reveals that the out-of-plane expansion of the films is nearly the same, showing the lattice constant of epitaxial films along *c*-axis remains unchanged regardless of the increase in the thickness. This is in stark contrast to the fact that lattice expansion is deemed to decrease with thickness.¹⁹⁴ Nevertheless, similar behaviour is also observed previously for both strained BFO and BFCO films which exhibited constant lattice parameters below 90 nm, a rather confusing result.^{195,196} The narrow full width at half maximum (FWHM) of omega scan around (002) reflection, as shown in Figure 5-2, confirms the high crystalline quality of all three samples. Note that the thicker films exhibited slightly larger FWHM—by a factor of two—compared to 30 nm samples that can be associated with the larger mosaicity of the film.¹⁹⁷

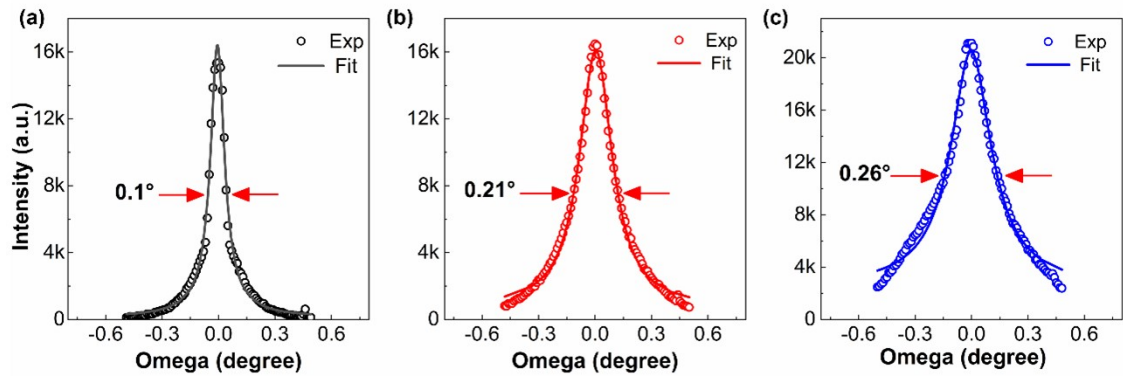


Figure 5-2 Rocking curves of BFCO films with different thickness

Scan around BFCO (002)_{pc} peak for (a) 30 (b) 70 and (c) 130 nm-thick films.

XRR measurement provides further evidence on the quality of interfaces and information about the thickness of layers. All samples exhibited a multitude of oscillations depending on the thickness of the layer. Fitting the reflectometry data using a genetic algorithm yielded the thickness of layers, as presented in Table 5-1.

Table 5-1 Calculated thickness from fitted XRR measurement

Sample	Thickness of layer (nm)	
	SRO	BFCO
1	11.50	31.30
2	11.80	71.20
3	11.40	130.00

Confidence of results was confirmed by monitoring the Error analysis. A representative image of such analysis is shown in Figure 5-3 for the 30 nm-thick film, pointing out that the fitting process is optimised by the global solution, which minimises the absolute square root difference function.

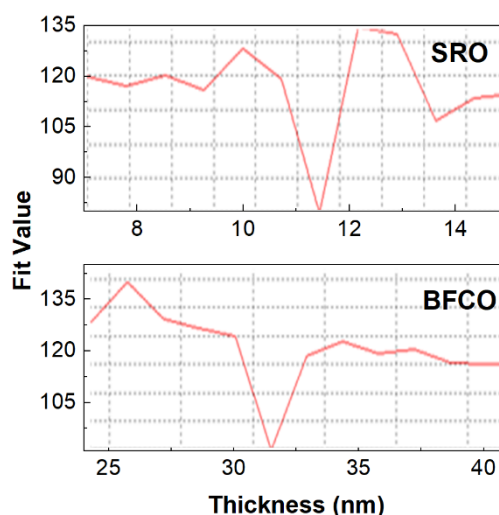


Figure 5-3 Regression error analysis for thickness calculation

X'Pert Reflectivity software Ver. 1.1 is used to fit the XRR data.

5.2.2 Surface Analysis of the BFCO Films

5.2.2.1 Valence State of Cations

High-resolution XPS region scans were obtained to qualitatively investigate the valence state of the cations within the surface of BFCO film. The C-1s signal of adventitious carbon (284.8 eV) is used for the charge correction. As shown in Figure 5-4(a), the binding energy of the Bi-4f core level appears at 158.7 and 164.1 eV for the 4f_{7/2} and

4f_{5/2}, respectively. The Bi-4f spin-orbit doublets are apart by 5.4 eV, implying an oxidation state of 3+ for bismuth.¹⁹⁸ Figure 5-4(b) clearly shows a distinctive satellite feature at the binding energy of 719.4 eV, which is the fingerprint of Fe³⁺ ions.¹⁸⁰ In addition, separation of 14 eV between 2p_{3/2} and 2p_{1/2} further corroborates the prevalence of Fe³⁺ cations.¹⁹⁹ Nonetheless, the presence of minority Fe²⁺ states cannot be ruled out due to relatively low oxygen pressure during growth, but further investigation is not the scope of this study.

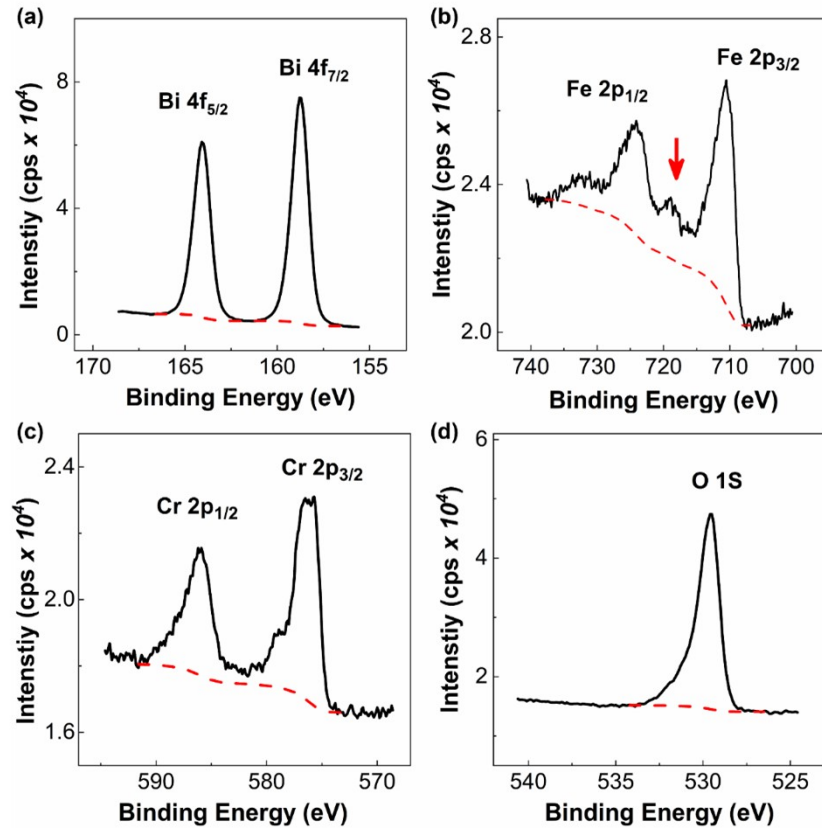


Figure 5-4 Representative XPS spectrum of the BFCO thin film

High-resolution XPS region scan for (a) Bi 4f (b) Fe 2p (c) Cr 2p (d) O 1s core levels

The region scan around the Cr-2p spectrum, as shown in Figure 5-4(c), exhibits 2p_{1/2} and 2p_{3/2} components at binding energies of 576.3 eV and 586.3, respectively, consistent with a single-peak fitted trivalent Cr spectrum.²⁰⁰ These observations

unambiguously corroborate the assumption in Section 5.2.4 regarding the nominal valance state of cations. Furthermore, the sharp peak at 529.6 eV in the O-1s spectrum is associated with transition metal-oxygen species in agreement with the photoelectron line position of metal oxides.²⁰¹ Table 5-2 summarised the centre of gravity for core-level photoemission peaks as described above.

Table 5-2 Binding energies of XPS peak extracted from the core level spectrum as shown in Figure 5-4

Elements	O (-2)	Bi (3+)		Cr (3+)		Fe (3+)		
Peak	1S	4f _{7/2}	4f _{5/2}	2p _{3/2}	2p _{1/3}	2p _{3/2}	2p _{1/3}	Sat. 2p _{3/2}
BE (eV)	529.6	158.7	164.1	576.3	586.3	710.8	724.8	719.4

5.2.2.2 Surface Morphology and Growth Mode

The growth mode of the epitaxial BFCO film was inferred by observing the surface morphology. The SRO buffer layer demonstrates an atomically smooth surface (rms=0.3 nm) and preserves the overall structure of the as-received STO stepped substrate as shown in Chapter 4. In contrast, the AFM images for BFCO heterostructure (Figure 5-5) exhibit a corrugated surface where terraces are hardly visible for the 30 nm thin layer and they completely fade for the thicker films. With increasing thickness, the surface of bilayer BFCO/SRO became rougher, with roughness varying from 1.65 nm to 2 nm, which is still much smoother than high-quality BFCO films reported earlier with similar thickness.^{181,202}

All BFCO layers exhibited an island-like morphology consistent with 3D growth mode, which persists throughout the thickness ranging from 30 to 130 nm. This result indicates that BFCO might follow the island mode from the very early growth stage due to the high nucleation density, or the 2D layer-by-layer (LBL) growth occurs up to a certain

thickness before transitioning to 3D island mode. The latter behaviour is more plausible since LBL growth of coherent ultrathin BFCO films only up to a few nm was reported earlier, where stringent processing conditions had to be applied, e.g., judicious choice of vicinal substrate.²⁰³ Therefore, one can assume that the BFCO/SRO/STO heteroepitaxy can be a representative case of Stranski-Krastanov growth, for which the corresponding surface roughening is due to the elastic forces imparted by the underlying substrate.²⁰⁴

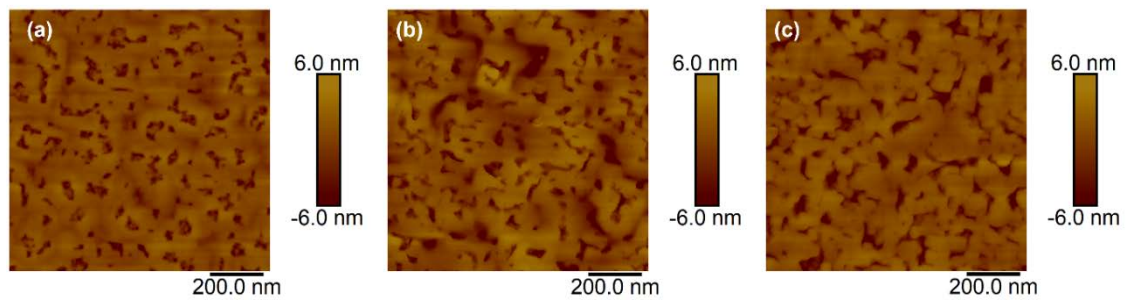


Figure 5-5 Surface morphology of the BFCO films with different thickness

AFM images of (a) 30 nm (b) 70 nm (c) 130 nm -thick BFCO films grown on SRO-buffered STO

5.2.3 Structural Evolution of the BFCO Film

5.2.3.1 Critical Thickness Calculation

Bulk BFCO showed rhombohedral crystal structure once stabilised at extremely high pressure.¹⁷⁶ Thus, regardless of a relatively small lattice mismatch with the cubic (001) STO, the epitaxial synthesis of the BFCO on top of a cubic substrate becomes more perplexed than simply elongation of c axis to adapt the pseudomorphic epitaxy.²⁰⁵ Besides, in epitaxial layers, relaxation of the strain imposed by the substrate is often more evident as the film becomes thicker. So, it is crucial to unfold the strain relieving mechanism as thickness increases.

The first step is to find the thickness beyond which strain relaxation takes place. For the pseudomorphic epitaxy, the modified Matthews-Blakeslee (MB) model (given in ref.²⁰⁶) can predict the critical thickness for thin films where strain relaxation occurs by the misfit dislocation.

$$\frac{t_c}{b} = \frac{1}{8\pi(1+\nu)\epsilon} \left(\ln \left(\alpha \frac{t_c}{b} \right) \right) \quad (\text{Equation 5 – 1})$$

where b is the Burgers vector, ν is Poisson's ratio, ϵ and α denotes misfit strain and cut-off parameter representing the continuum energy of the dislocation core, respectively. The Poisson's ratio was presumed to be 0.3, a typical value for BFO-based thin film on STO (001) substrate,²⁰⁷ and α was set to 4.²⁰⁶ Solving Equation 5-1 numerically, the critical thickness is estimated to be about 6 nm, above which the formation of the misfit dislocation becomes energetically favourable, and strain relaxation initiates through the presence of dislocation.

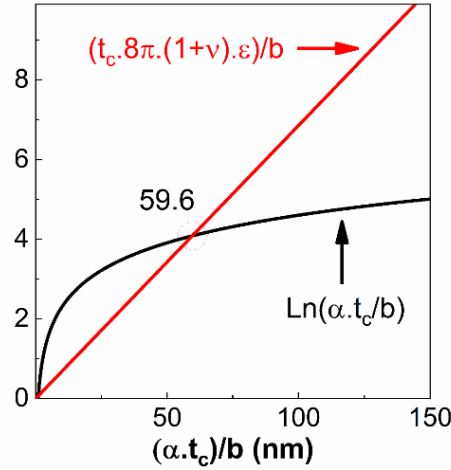


Figure 5-6 Numerical solution for Matthews-Blakeslee (MB) equation

Note that the growth kinetic can considerably extend this range; however, the thickness of the epitaxial film needs to be constrained to just a few factors larger than the MB

critical thickness to achieve an utterly commensurate film with the minimum dislocation density.²⁰⁸

5.2.3.2 Inhomogeneous Strain Distribution

Since the thinnest film in this study is at least five times beyond MB critical thickness, it is not unreasonable to expect misfit dislocation in the film. It has been reported that lattice parameters are more altered in the vicinity of dislocation,²⁰⁹ ensuing an inhomogeneous strain distribution. In particular, this nonuniformity makes the thickness-dependent studies of perovskite thin films a gruelling task.²⁰⁸ Hence, to quantitatively investigate the inhomogeneous strain, the diffraction line broadening was analysed as a function of film thickness, using Williamson-Hall relation:^{197,210}

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon_i \sin \theta \quad (\text{Equation 5 – 2})$$

where θ and β are the angle and breadth of diffraction peak, respectively, and D denotes the coherence length along the scattering vector. As shown in Figure 5-7, the inhomogeneous strain (ε_i) was obtained from the slope of linear fit for (00 l) BFCO reflections — up to $l=4$ — by plotting $\beta \cos(\theta)$ versus $4 \sin(\theta)$. The XRD peak broadening is mainly due to the finite size, inhomogeneous strain, and the diffractometer resolution as expressed by $\beta = \beta_{size} + \beta_{strain} + \beta_{instrument}$.²¹¹ In this study, the instrumental contribution was approximated by subtracting the line width of the corresponding substrate peak. Note should be taken that the described quantitative analysis heavily depends on the approach taken to separate the contribution of size and strain in the linewidth broadening. Therefore, it is better to use such analysis for comparison per se.

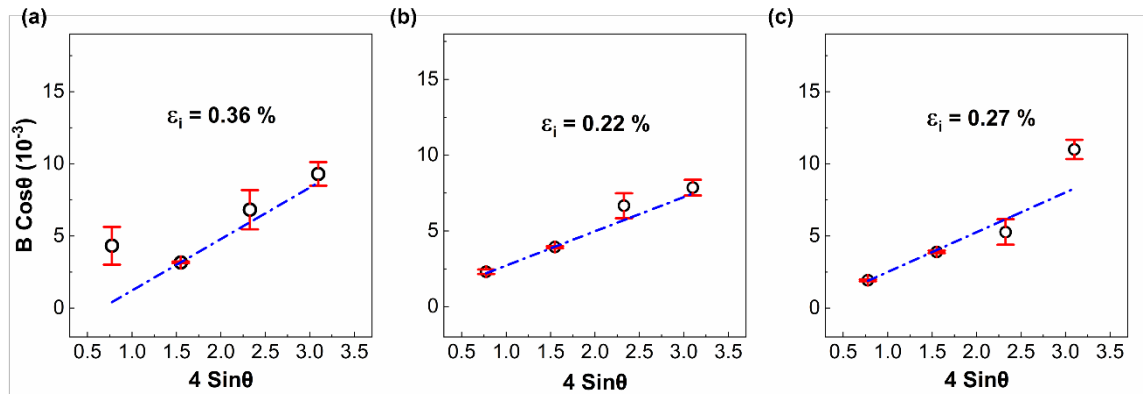


Figure 5-7 Williamson-Hall analysis of BFCO films with different thickness

Slope of linear fit is calculated for (a) 30 (b) 70 and (c) 130 nm films.

Remarkably, it is observed that the inhomogeneous strain for the 30 nm thin film exceeds that of the thicker films. Note that the density of dislocation is rapidly increasing in the vicinity of the critical thickness before it saturates,²¹¹ leading to a higher inhomogeneous strain from dispersion of the lattice parameters in a substantial fraction of the film thickness. Moreover, we presume the strain relaxation mechanism is not solely by the formation of misfit dislocation.

5.2.3.3 Investigation of Crystallographic Symmetry

To obtain a complete picture of the strain relieving as a function of film thickness, the crystallographic evolution is investigated using reciprocal space mapping. It is possible to determine the low symmetry phases by performing diffraction measurement in the scattering zones with a fixed (001) crystallographic axis. In other words, the highly oriented epitaxial (001) film simplifies the interpretation of the result as the splitting of the peak is associated with the axis perpendicular to the fixed one.²¹² For instance, splitting of Bragg peak in the H0L and HHL scattering planes that are geometrically accessible in most diffractometers is commonly utilised to resolve the monoclinic distortion.^{192,213}

Figure 5-8 presents contour plots of the RSMs around substrate (003), (203) and (113) reflections for the (001)-oriented films with different thicknesses. The coincidence of the horizontal line in the symmetric (003) scans further confirms the earlier observation regarding the unchanged OP lattice parameter for the film thickness range in this study.

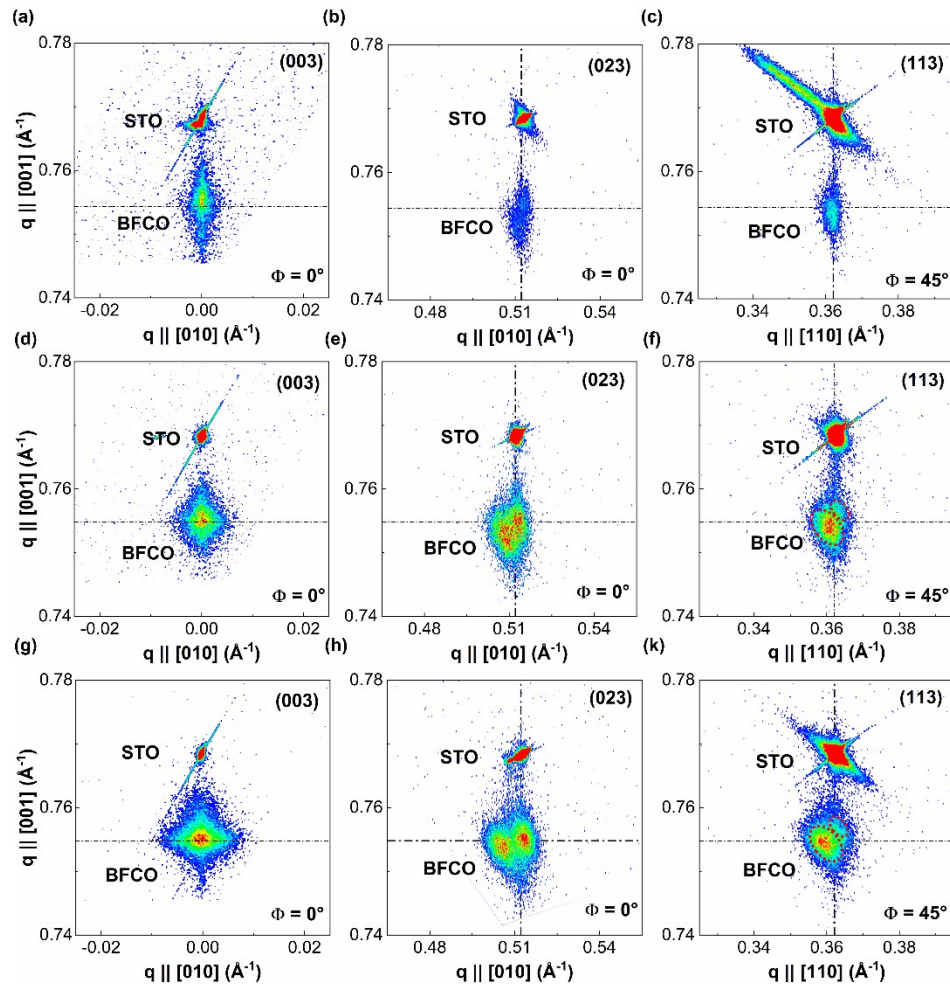


Figure 5-8 XRD reciprocal space maps of the films with different thickness

RSM plot for (a-c) 30 nm (d-f) 70 nm (g-k) 130 nm BFCO film. Peak splitting is less pronounced in the (113) graph due to the limited resolution of the diffractometer.

However, the asymmetric diffraction peaks develop from a unique spot for the 30 nm-thick film, although it spreads out in the OP direction due to finite thickness, to two separated peaks for 70 and 130 nm films. This observation clearly indicates that multiple crystallographic domains are developed as the film thickness increases.^{212,214}

Note that the twofold asymmetric reflections are slanted away from the q_z ($\parallel$ [001]) of the (003) spot, implying these films have adopted a monoclinically distorted structure while the 30 nm-thick film has a tetragonal-like symmetry. The disappearance of the splitting pattern for the 30 nm-thick film indicates transitioning to tetragonal symmetry, where BFCO film is fully clamped by the substrate with equal in-plane lattice constants resembling that of STO without structural twinning within the resolution of the diffractometer used herein.

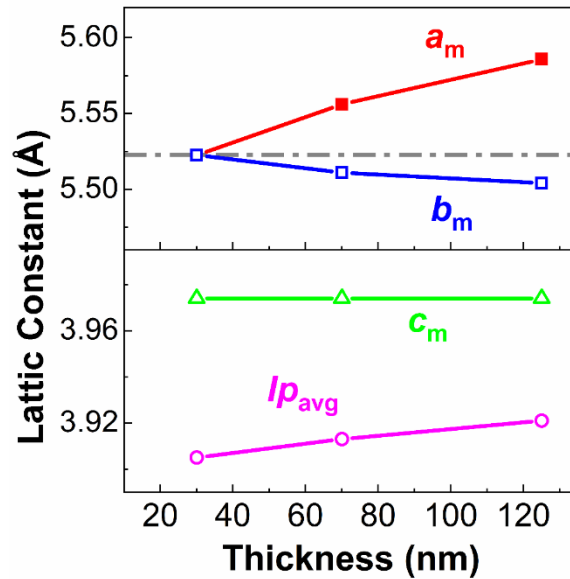


Figure 5-9 Thickness-dependent lattice constant

$l_{p_{avg}}$ represents the average in-plane constant in pseudocubic notation.

The lattice parameters of the distorted phase were extracted from the RSM scan of 130 nm-thick film as follows: $a_m = 5.59$ Å, $b_m = 5.50$ Å and $c_m = 7.94$ Å with distortion angle value of $\sim 0.15^\circ$. To obtain more useful information, the average in-plane lattice parameter was also estimated using $0.5 \times \sqrt{a_m^2 + b_m^2}$ Formula.²¹² Several points can be deduced from Figure 5-9; firstly, the out-of-plane parameter (c_m) is almost constant as mentioned before. Next, the average in-plane lattice parameter increases with the

thickness. The thicker films exhibit a larger IP constant, yet not exceeding the pseudocubic bulk value of 3.937 Å,¹⁹⁶ which confirms the residual strain due to the clamping effect of the substrate. Moreover, the (003) RSM plots recorded with the X-ray beam along the [010] and [110] directions reveal different patterns. Figure 5-10 shows an apparent splitting along [110] direction ($\phi = 45^\circ$) for 130 nm thin film, implying tilting of the (00l) planes.^{197,214,215} Of note, this behaviour appears to be thickness dependent since the tilting did not occur for the sample below 100 nm.

Based on these findings, it can be inferred that beyond a certain thickness, tilting of the domains comes to play as an additional mechanism to release the epitaxial stress imposed by the substrate partially. The evolution of crystallographic distortion manifests that the perovskite BFCO thin film grown epitaxially on (001)-oriented cubic substrate adopts a low symmetry regardless of the minor lattice mismatch.^{214,216} Note that the remainder of this chapter only focuses on the thinnest and thickest samples named T-like and R-like structures, respectively.

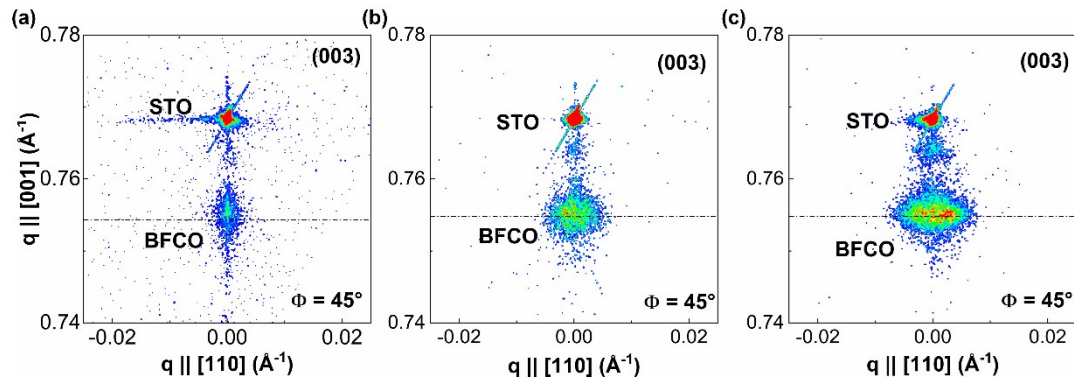


Figure 5-10 Symmetric x-ray reciprocal space mapping around (003) STO peak recorded along [110]

RSM for (a) 30 nm (b) 70 nm (c) 130 nm BFCO films

5.2.4 First-principles Calculation

Changes in the strain states or in the crystallographic symmetry induce complex interatomic interaction and thus affecting the electronic structure of the material.²¹⁷ First-principles calculations can assist in gaining insight into how the observed crystallographic distortion affects the electronic structure when the system transitions from rhombohedral to tetragonal symmetry.

For all the geometry optimisations, first-principles spin-polarised calculations based on density functional theory (DFT) were performed with the generalised gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) as implemented in the VASP package.^{218,219} The Hubbard-U scheme derived by Dudarev *et al.*²²⁰ was employed to deal with the 3d electrons in Cr and Fe ions (3.7 and 5.0 eV, respectively). The projected augmented wave method²²¹ was used with the following ions (and valence electrons): Cr ($3s^23p^64s^13d^5$), Fe ($3p^64s^13d^7$), Bi ($6s^25d^{10}6p^3$), and O ($2s^22p^4$). All relaxations were performed on a $2\sqrt{2}\times 2\sqrt{2}$ supercell containing 20 atoms (4 formula units). The k-point grid used was $4\times 6\times 6$ and Γ -centred. Energy cut-off was truncated at 800 eV, and forces between ions were expected to relax below 0.01 eV/Å. The vibrational stability of each phase was checked with the calculation of phonons at Γ . The polarisation was estimated with the Born effective charges method,²²² and the HSE06 hybrid functional was used to compute the density of states.²²³

The theoretical study was started by performing a complete structural characterisation of BFCO in the bulk system. Starting from different seeds based on usual geometries found in similar perovskites, the experimental rhombohedral and tetragonal structures could be identified as represented in Figure 5-11(a). Slight distortions in both phases can be assigned to the effect of the chemical disorder of the solid solution. The

predicted c/a ratio for tetragonal BFCO (~ 1.05) is also smaller than similar perovskites like BFO or BiCoO₃, where DFT-calculated values can reach close to 1.30.^{224,225}

The calculation of the polarisation confirmed that both phases are polar with value of $\sim 90 \mu\text{C cm}^{-2}$ along the [111] pseudocubic direction for the rhombohedral structure, and along the [001] direction for the tetragonal phase. On a side note, a third stable and competitive orthorhombic phase was also found at high compressive strain. This phase, with symmetry derived from the $Pnma$ space group, was identified as centrosymmetric and hence, non-polar active.

To overcome the size limitations in the DFT calculations, one can reproduce the physics experienced by the film in the experimental study with the computational approach represented in Figure 5-11(b). The strain experienced by the BFCO film when the thickness is increased from 30 nm to 130 nm can be modelled by modifying the in-plane lattice parameter. The a and b lattice parameters were constrained to a fixed value called a_{in} , and the out-of-plane lattice parameter c was left unconstrained and free to relax. The in-plane lattice parameter a_{in} was then subsequently increased from 3.88 Å, to reproduce the thinnest film, to 3.98 Å, which represents a thick enough film that shares physical properties with the rhombohedral-like BFCO. The bandgap was calculated for both phases at 3.88, 3.94 and 3.98 Å (Figure 5-11(c)). It was found that the tetragonal-like phase has a slightly smaller bandgap than the rhombohedral-like. We could discard any critical role of the lattice strain on the narrowing of the bandgap, and the bandgap difference can be assigned almost entirely to structural differences between the tetragonal and rhombohedral phases.

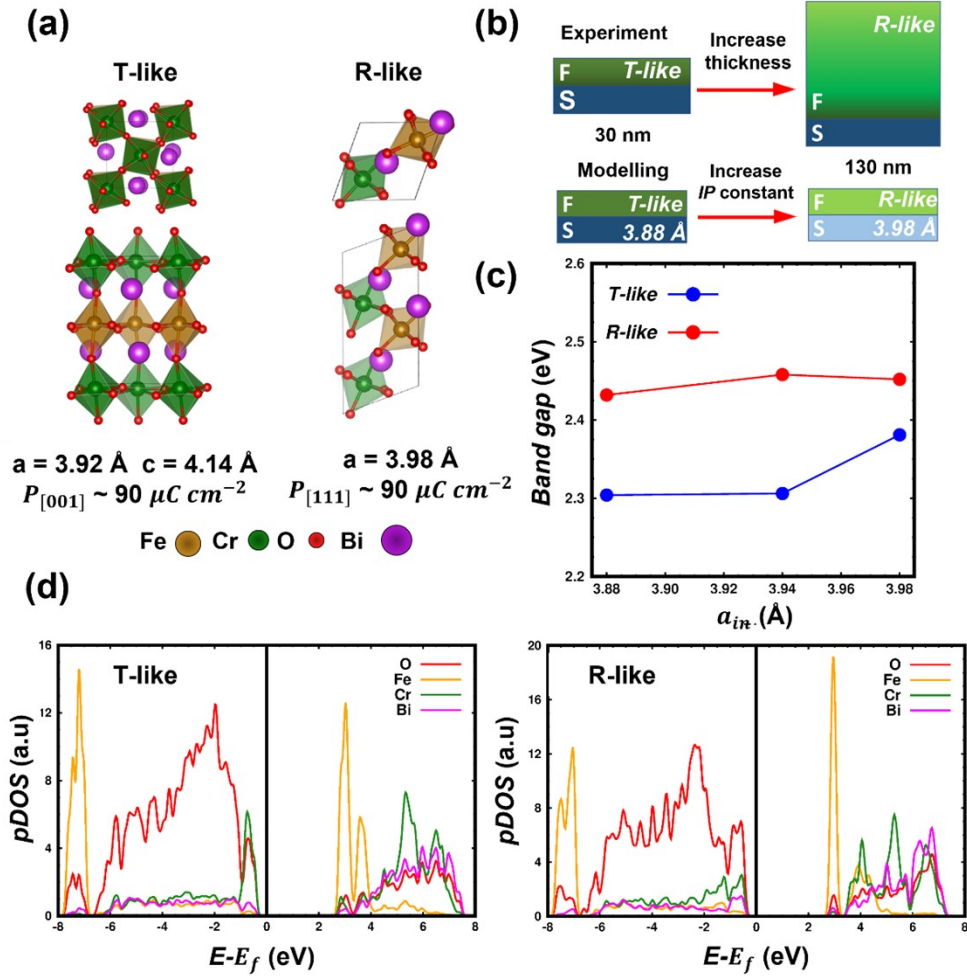


Figure 5-11 First-principles calculations results for two structural variants

(a) Crystal structure of BFCO, note that the lattice constant is optimised within DFT calculation (b) Schematic diagram showing the modelling process (c) Predicted bandgap modulation (d) Electronic density of states for two structural variants

The partial density of states (pDOS) of both structures, presented in Figure 5-11(d), revealed little but critical differences that explain the nature of the bandgap in the BFCO. It shows that the electronic bandgap is lower for the tetragonal phase than the rhombohedral-like counterpart. In both structures, the conduction band minimum (CBM) is dominated by Fe 3d empty states. Below the Fermi level, oxygen 2p states dominate the valence band with intermixing of Cr 3d state at the top edge, which is more pronounced in the tetragonal-like structure. Like the parental BFO, the occupied

Fe d states appear at very low energy, far from the VBM. Hence, the Cr d states at the top of the valence band are responsible for narrowing the bandgap in BFCO compared to BFO.¹⁴⁹ When projected on the individual d -orbitals (Figure 5-12), the pDOS also confirmed the presence of Fe³⁺ and Cr³⁺ species in both structures. For both R- and T-like structures, Cr atoms conserved the stable octahedral electron configuration $t_{2g}^3e_g^0$. In contrast, it was noticed that iron ions transition from an electron configuration compatible with square-based pyramid coordination in the tetragonal phase ($b_{2g}^1e_g^2a_{1g}^1b_{1g}^1$) to an electron configuration compatible with octahedral coordination in the rhombohedral system ($t_{2g}^3e_g^2$). This further splitting of the $3d$ orbitals in the tetragonal structure is understood to bring the CBM towards the Fermi level and hence, narrows the bandgap.¹⁵¹

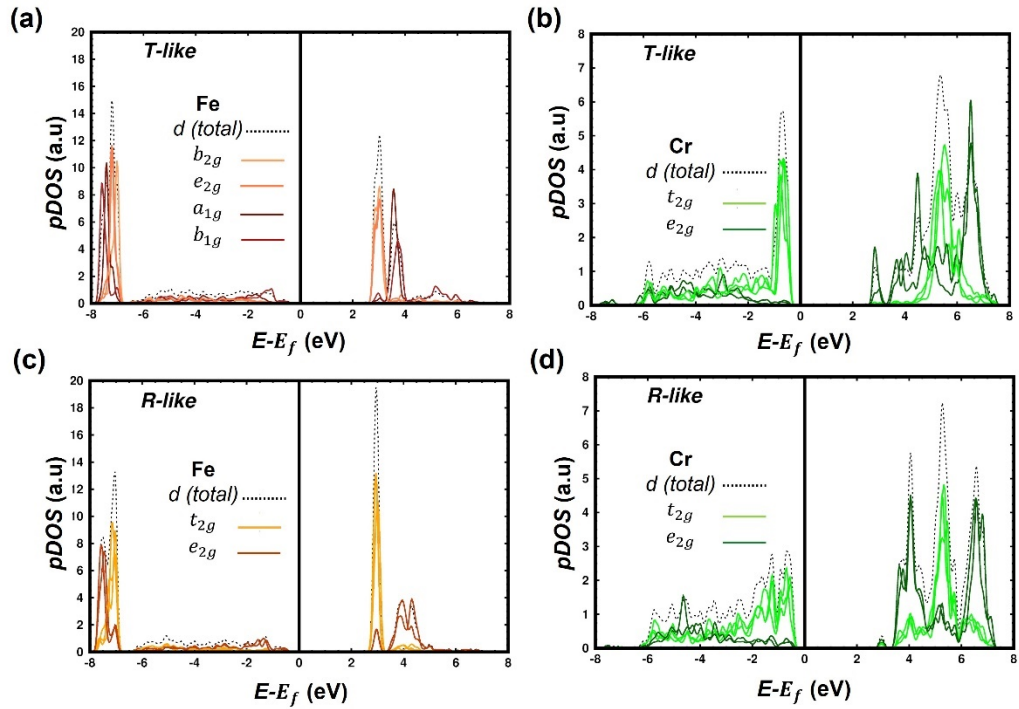


Figure 5-12 Projected density of states on individual d -orbitals
pDOS of (a, b) Tetragonal-like (c, d) Rhombohedral-like structure

Comparing the electronic structure of different crystallographic symmetries, it is noted the band structure of T-like BFCO slightly differs – specifically at the top of the valance band – from that of the R-like structure. For the latter, the lowest energy charge transfer (CT) is between the unoccupied Fe states and the hybridised oxygen orbitals with cations, while a Mott-Hubbard transition between Cr and Fe can be envisaged for the former in addition to the CT mentioned above. A similar electronic structure has also been reported for the Cr-related oxides previously.²²⁶ Having established both the electronic and crystallographic structure of the BFCO films, the ferroelectric properties of BFCO/SRO/STO heterostructure will be now investigated.

5.2.5 Investigation of the Photoferroelectric Properties

The ferroelectric nature of the BFCO films is affirmed through observing the domain switching under an external electric field. Figure 5-13(a, d) shows a clear indication of ferroelectric switching where ferroelectric domains are switched in the inner $1.5 \times 1.5 \mu\text{m}^2$ box by applying +10 V from the tip. The T-like BFCO films also exhibit similar domain switching under an external bias (+5 V); however, a severe polarisation back switching to the initial state was observed. In epitaxial ferroelectric films, polarisation relaxation may arise from incomplete screening at ferroelectric/electrode interface (depolarisation field),²²⁷ non-switchable interfacial layers,²²⁸ defect dipoles²²⁹ and the built-in electric field near ferroelectric/electrode interface.²³⁰ From the polarisation switching observation, it seems the interfacial electric field is becoming more dominant as the thickness of film decreases. This field is pointing toward the bottom electrode, which promotes the formation of upward polarisation domains adjacent to the interface, initiating the backswitching.²³¹

As it can be seen from the scale bar of the phase image, the phase difference is about 180° between brown and bright yellow in the upper half of Figure 5-13(a), but it flips to -180° (black) in the lower half. This observation confirms a complete phase switching occurs regardless of UV illumination, although a contrast change is observed. During measurement, it was noticed that turning on the laser source had changed the contact resonance frequency between the tip and sample, thus causing a phase shift from 180 to -180 degrees. This observation is quite common when there is an external vibration /or fluctuation source during PFM measurements. As for standard PFM imaging, the resonance frequency of the tip-sample contact is first optimised and then is fixed to enhance the PFM response, assuming the resonance frequency remains constant. However, considering a rough sample surface along with the extra noise from the laser source, this is not the case here.

KPFM was performed to probe the surface potential and space charge distribution in the BFCO thin film. Moreover, variation in the surface potential of the film was also measured under UV illumination (405 nm) and in the dark. Here, the photoexcited carriers are dissociated due to the built-in field in BFCO films, leading to a surface potential difference that represents the local spatial photovoltage.^{106,232} In this measurement, the bottom half of the image was recorded in the dark, while the top half represents the measurement during exposure to the laser source. The photoinduced surface potential is evident in the outer region (upward polarisation) as shown in Figure 5-13(b), implying the separation of photoexcited carriers and the non-trivial impact of the polarisation direction.

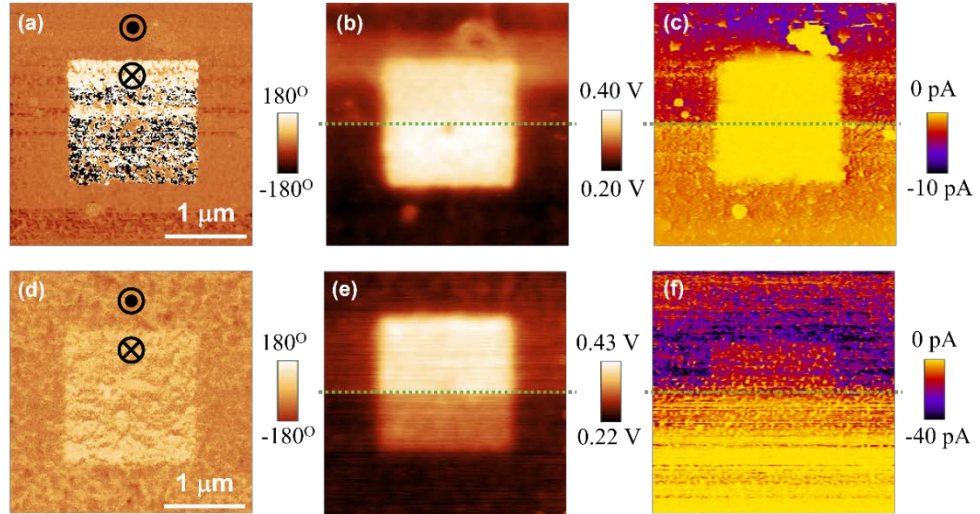


Figure 5-13 Photoferroelectric properties of the BFCO structural variants

PFM phase, KPFM and C-AFM mapping for (a-c) R-like (d-f) T-like BFCO film, respectively. (Top half is under UV illumination (405 nm) and the bottom half is at dark)

Figure 5-13(c, f) presents the C-AFM image under the bias of -2 V, where a clear contrast for the upward and downward polarisation state is evident because the conductivity of the former region is clearly enhanced. Furthermore, the current mapping under UV illumination reveals that light absorption (photon energy of 3 eV) yields mobile carriers contributing to a measurable photocurrent. Of note, the upward polarisation (outer region) appears to allow the photoinduced charge transport since a significant contrast is discernible in the upper half of Figure 5-13(c), suggesting a rectifying behaviour. As explained earlier, this difference was extremely difficult to capture in the T-like structure due to the severe polarisation back switching.

5.2.6 Optical Transitions in the BFCO Thin Film

To ascertain the bandgap reduction deduced from DFT results, spectroscopic ellipsometry was employed to extract the optical dispersion law of the epitaxial BFCO films. First, the optical data for the STO substrate and SRO bottom electrode was acquired. The bandgap of STO substrate was extracted to be 3.2 eV (see Figure 5-14),

which is in agreement with that in the literature.¹³⁷ Therefore, all the BFCO optical data were constrained to 3.2 eV, due to the substantial interference from the underlying substrate.

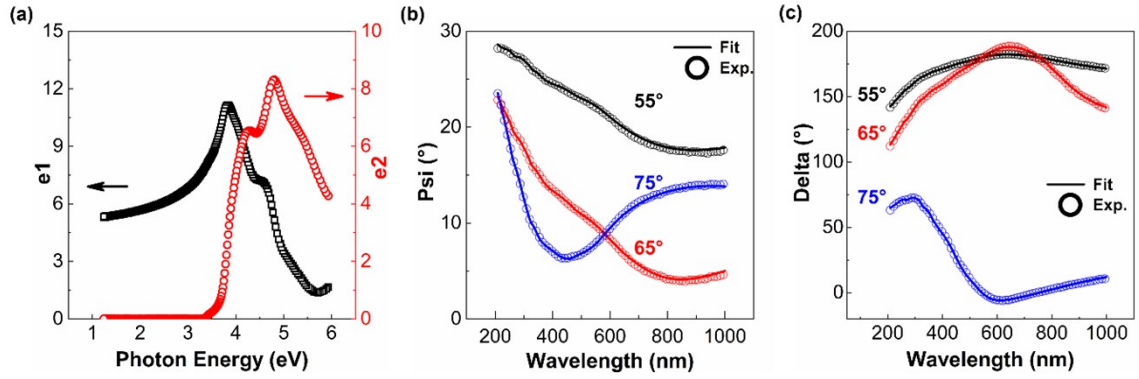


Figure 5-14 Ellipsometry data of the representative heterostructure

(a) Dielectric function of STO substrate. (b, c) Raw ellipsometry parameter of the 30 nm-thick BFCO film measured at three different angles.

Figure 5-15(a) shows the optical absorption coefficient, together with the Tauc plots of the R-like and T-like films in the range of 1.4-3.2 eV. Despite the complexities associated with bandgap estimation in such oxide due to strongly correlated d electrons, the experimental result perfectly matches the DFT calculation. Tauc plot illustrates the direct bandgap for T-like BFCO narrowed down by about 150 meV. On a similar note, larger octahedral tilting has promoted a wider bandgap in the hybrid halide perovskite.²³³

To better understand the optical transition in BFCO thin film, the wavelength-resolved photocurrent has been acquired. The spectral photocurrent measurement reveals that absorption onset is below the fundamental direct gap for both structures, in agreement with previous studies on BFO.²³⁴ Transition metal oxides, in contrast to conventional semiconductors, do not exhibit a sharp absorption edge. Thus, an accurate estimation of E_g from experimental data, i.e., ellipsometry or UV-Vis spectrometry, is not free from

ambiguity.²³⁵ The significant finding in Figure 5-15(b, c) is that the absorption threshold is redshifted for the T-like sample, implying the photon energies of ~ 1.6 eV (800 nm) can be absorbed. Figure 5-15(d) unambiguously distinguishes the T-like photoresponse since, in contrast to the R-like sample, the photo-to-dark current ratio of the T-like structure is greater than unity at the wavelength larger than 700 nm. The redshift of absorption threshold can be correlated to the higher crystallographic symmetry of the T-like structure, which tunes the *d-d* charge transfer. Note that the photoresponse of T-like structure for photon energies below 2 eV might seem to be larger in magnitude. Upon a profound examination, it appears that the photoresponse of T-like structure initially decreases by increasing the light source wavelength (see blue arrows in Figure 5-15(c)), and it then tends to grow as a function of time. The time-dependent photoresponse observed in T-like structure can be explained by photoinduced ionic conductivity since such time-dependency was not detected in the dark-current measurement.²³⁶

Furthermore, both structures demonstrate a photocurrent maximum at the laser wavelength of 500 nm (~ 2.48 eV), which is close to the estimated direct bandgap. Time-dependent photoresponse at different laser wavelengths was also measured one at a time (not showing), ensuring modulation of photon energy is the main contributor to the observed result. One could also find that photocurrent surprisingly decreases for the above-bandgap photon energies. This observation can be explained by the surface recombination effect, implying that although more carriers are excited as the wavelength of light decreases, these photoexcited carriers recombine rapidly via surface states and do not contribute to the photocurrent.²³⁷

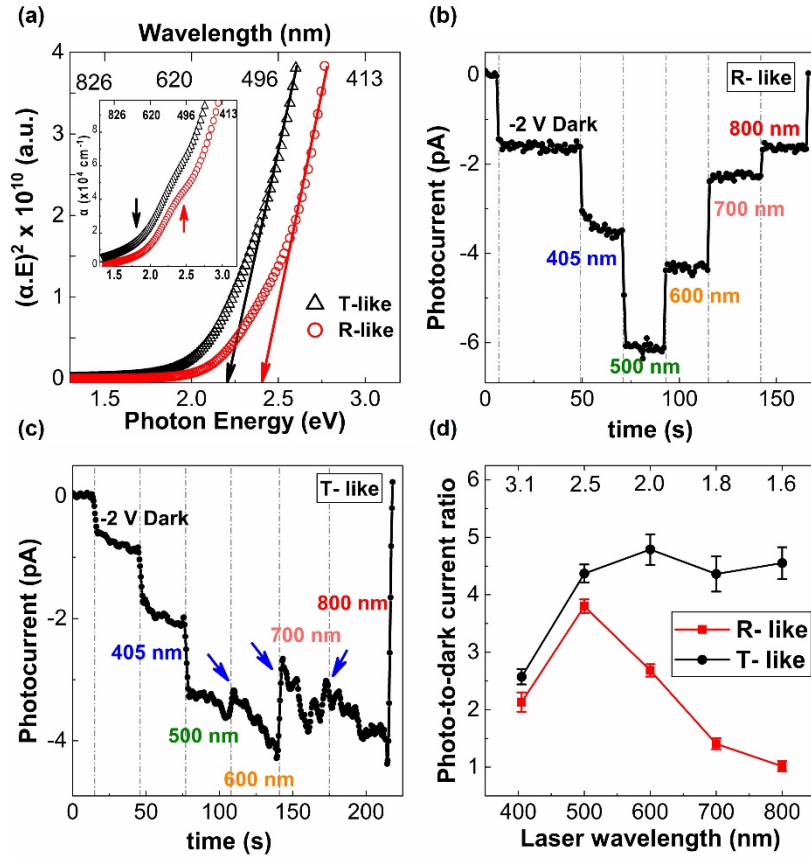


Figure 5-15 Optical properties and photoresponse of two structural variants

(a) $(\alpha E)^2$ plot as a function of photon energy for two structural variants (inset shows UV-Vis absorption spectrum) (b, c) Wavelength resolved photocurrent for R-like and T-like BFCO structure, respectively. (d) Photo-to-dark current ratio of both sample at different laser wavelengths

It is tempting to assign the absorption onset below the fundamental bandgap with charge transfer instabilities associated with self-trapping of excitons.^{234,235} However, the energy difference is not reasonable for the excitonic effect. Moreover, defects like oxygen vacancies have been reported to create in-gap states below the conduction band, resulting in the sub-bandgap optical absorption.²³⁸ Note that no reliable method was available to us to quantify the oxygen vacancy concentration. Given the spectral photocurrent measurement demonstrates dependency on the crystallographic symmetry,

we propose the early absorption onset is linked to the *d-d* charge transfer, which can be tuned by adopting a higher symmetry phase.

Taking a closer look at the absorption coefficient extracted for the BFCO films (inset of Figure 5-15(a)), a clear peak structure appears around 2.4 eV along with less pronounced features below 2 eV, which can only be seen once the absorption spectra is deconvoluted. Note that nuances in spectral features can be disregarded when employing parameterised functions, e.g., ellipsometry data analysis, in agreement with the fact that absorption values vary significantly within the photon energies of 1-6 eV in BFO based compounds.²³⁹ These results indicate the optical transition in BFCO within the visible range originates from the complex charge transfers between $O \rightarrow Fe$, $O \rightarrow Cr$, $Cr \rightarrow Fe$ and $Cr \rightarrow Cr$, consistent with the Fe-Cr-O compounds in earlier studies.^{18,240,241}

The lowest energy excitation is associated with the *d-d* charge transfer between metal, e.g., from occupied Cr *3d t_{2g}* state to unoccupied Fe (or Cr) *3d t_{2g}*. Such transition has been previously reported to be separated into sub-bands peaking at ~1.8 and 2.4 eV,²⁴¹ in excellent agreement with the result presented in this chapter. The analogous LaFe_{1-x}Cr_xO₃ perovskite system also presented an absorption peak located at ~2.4 eV photon energy.²⁴⁰ Although triggered by changing the laser repetition rate during film growth, a similar feature in the optical absorption of BFCO film was observed earlier.¹⁸ However, their interpretation of results regarding the superstructure peak was questioned later.¹⁵⁴ Although this effect does not seem to have an impact on the results of this study, the presence of superstructure peaks was probed by performing asymmetric XRD scans through tilting the samples by 54.7° (Psi angle). Both R-like and T-like structures showed a weak signal at ~19.5° and 61.1°, implying the possible local cation ordering

along the $[111]_{\text{pc}}$ BFCO direction. The intensity of $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ superstructure peak, as shown in Figure 5-16, is slightly higher for the R-like BFCO. To factor in the impact of thickness on the peak intensity, the main $(222)_{\text{pc}}$ BFCO peak was also measured as a reference. It confirmed that the thickness difference is not the main contributor to the observed intensity variation. Of note, the sample with the lower superstructure intensity possesses a narrower bandgap consistent with the previous studies.^{18,153}

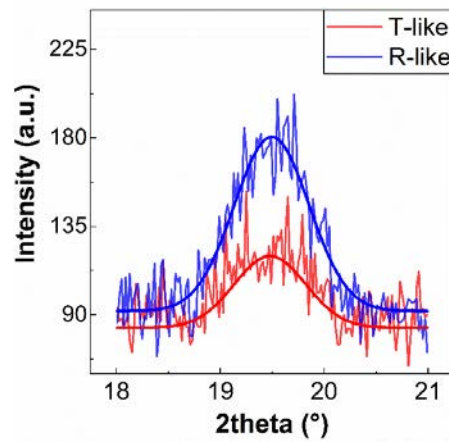


Figure 5-16 XRD scan of $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ superstructure peak for both structures

The straight line represents the fitting of the experimental data.

From the space group symmetry perspective, the out-of-phase octahedral tilting gives rise to (odd-odd-odd) superstructure reflection.²⁴² On a similar note, the cation ordering in the double perovskites also produces identical reflection in the X-ray diffraction pattern, if there is a sizable difference between scattering power (atomic form factor) of B-site cations.²⁴² Therefore, the contribution from each factor is difficult to ascertain when a combined effect of the octahedral distortion and cation ordering is at play simultaneously. One can presume the intensity of superstructure peak observed in skew-symmetric XRD scan, i.e., along $[111]_{\text{pc}}$, is a combined effect of both processes because the local order of B-site cations cannot be neglected even in the non-distorted structure.

5.3 Summary

In summary, the thickness-dependent crystallographic evolution was investigated in the epitaxial BFCO thin film on SRO-buffered (001) STO substrate. In-depth X-ray reciprocal space mapping provides insight into the complex strain relaxation mechanism, transitioning to a lower symmetry coupled with the tilt of domains as thickness increases. The present study demonstrates a practical strategy to tune the optical and electronic properties of the BFCO thin film through the structural phase transition. Using first-principles calculation and spectroscopic ellipsometry, a practical mechanism was identified to tune the BFCO bandgap, which can also be deployed in other oxide perovskites. The tetragonal-like BFCO film exhibits a narrower bandgap, and its absorption onset appears about 150 eV lower than in the R-like phase, confirmed by the wavelength-resolved photoresponse measurement. The enhanced charge transfer in T-like structure also shows the potential use of Mott multiferroic BFCO in emerging all-oxide optoelectronic devices. It is hoped these results provide the impetus for further research to complete the jigsaw pieces of the structure/properties relationship in the bismuth-based perovskites.

Chapter 6. Effect of Growth Kinetic on Photoferroelectric Properties of BFCO Thin Films

6.1 Introduction

Recent progress in thin film technologies has enabled the fabrication of high-quality ferroelectric films with tunable properties. This includes but is not limited to the strain-induced stabilisation of metastable BFO polymorphs,²¹⁶ or cation ordering triggered by laser frequency modulation in the epitaxial BFCO film.¹⁷⁵ The latter has gained widespread interest owing to its potential use in technological applications, like photovoltaic¹⁵⁵ and resistive random-access memory.²⁴³ To be used in such devices, robust polarisation is essential. Yet, similar to the parental bismuth ferrite, BFCO suffers from unsatisfactory electrical leakage performance. While there is mounting evidence in the literature to alleviate this problem via the chemical substitution,²⁴⁴ here, a three-order of magnitude suppression in the leakage current is reported for the LMBE-grown BFCO film through judicious adjustment of the laser fluence during the deposition. The defect formation and its coupling with the growth condition is also investigated. Our results reveal that both microstructure and ferroelectric properties can be tuned by lowering the laser fluence, ensuing the room-temperature ferroelectric polarisation that is comparable to the *ab-initio* predicted value. This facile strategy offers great opportunities for tailoring the electronic properties of other ferroelectric oxides, facilitating their implementation in practical application. Details of the growth parameters for 200 nm-thick samples are shown in Table 6-1. The lone difference in the growth conditions is the laser fluence, i.e., energy density, leading to a significant

variation in the growth rate. This alteration influences the structural properties of the films as will be discussed later.

Table 6-1 Sample deposition parameters by LMBE

Sample	Laser		Growth rate (Å per pulse)	Substrate temperature (°C)	Oxygen pressure (mTorr)
	Fluence (J cm ⁻²)	Frequency (Hz)			
R-BFCO	5.2	4	0.3	680	10
S-BFCO	1.9	4	0.1	680	10
SRO bottom electrode	2.8	4	0.1	700	100

6.2 Result and Discussion

6.2.1 Structural Characterisation

6.2.1.1 Effect of Laser Fluence on Crystal Structure

The crystallographic structure and phase purity of the BFCO thin films on SRO-buffered STO (001) substrate are examined under different deposition conditions. Figure 6-1(a) shows coupled θ -2 θ XRD scan of as-deposited films. For both samples, only the (001) pseudocubic reflections of the films and the substrate appear, confirming the highly oriented growth of heterostructure along *c*-axis with no parasitic phases within the detection limit of X-ray diffraction technique.

The rocking curve measurement around (002) reflection with an FWHM of ~ 0.3 , as shown in Figure 6-1(c), confirms the high crystalline quality of both films. The out-of-plane (OP) lattice parameter was calculated to be ~ 3.970 Å and 3.965 Å for S-BFCO and R-BFCO films, respectively, as demonstrated by a slight (002) peak shift toward higher angle in Figure 6-1(b)). This value is larger than the reported pseudocubic bulk parameter for BFCO,¹⁵³ indicating both films are expanded along [001] direction.

The overall feature of these two samples, as indicated on XRD patterns, are also rather different. As shown in Figure 6-1(d), the Laue fringes associated with finite thickness of the SRO bottom electrode are clearly present on both sides of the S-BFCO (001) peak, manifesting a smooth interface between two layers. On the contrary, these oscillations are considerably obstructed in the R-BFCO film, despite the identical SRO buffer layer in both samples.

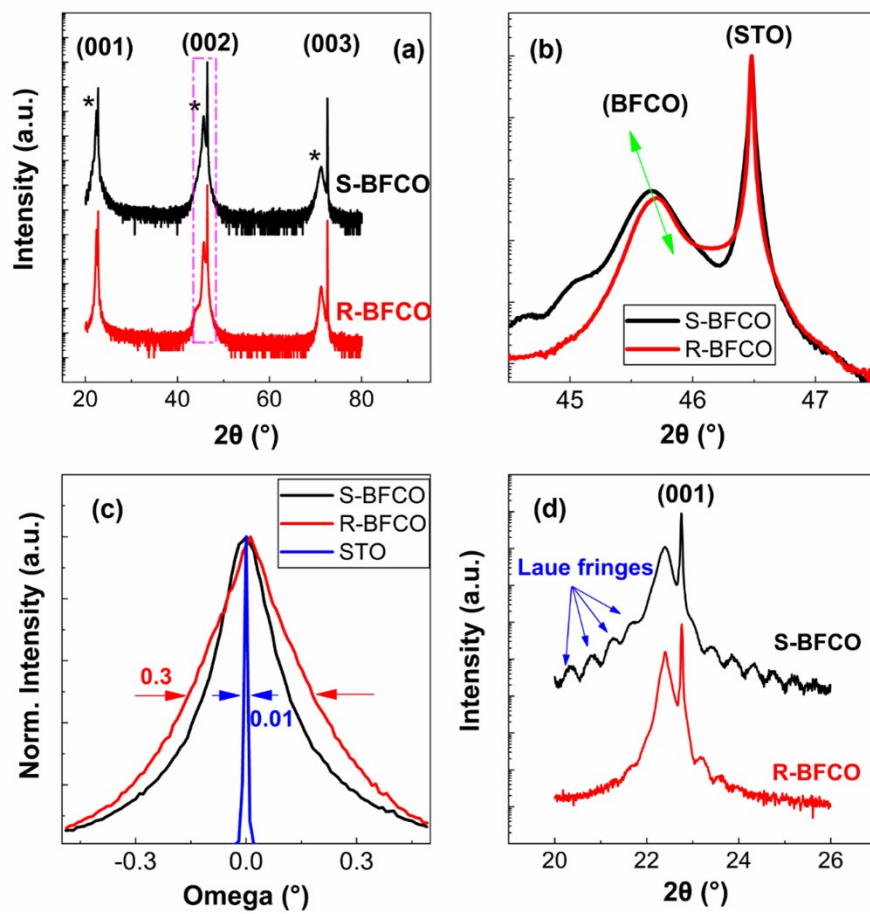


Figure 6-1 Structural study of BFCO films grown under different laser fluence

(a) Coupled θ - 2θ scans. The asterisks denote the BFCO peak at the left side of STO reflections. (b) zoom around (002) reflection. (c) Rocking curve around (002) peak, highlighting the crystalline quality of BFCO films. (d) zoom around (001) peak.

To gain detailed information on the in-plane strain state, reciprocal space mapping of the films around symmetric (003) and asymmetric {103} family of STO reflections were used as illustrated in Figure 6-2. The asymmetric BFCO peak of two samples along the in-plane reciprocal axis, albeit having similar thickness, are positioned differently with respect to the vertical dotted line that represents the lattice parameter of bulk STO.

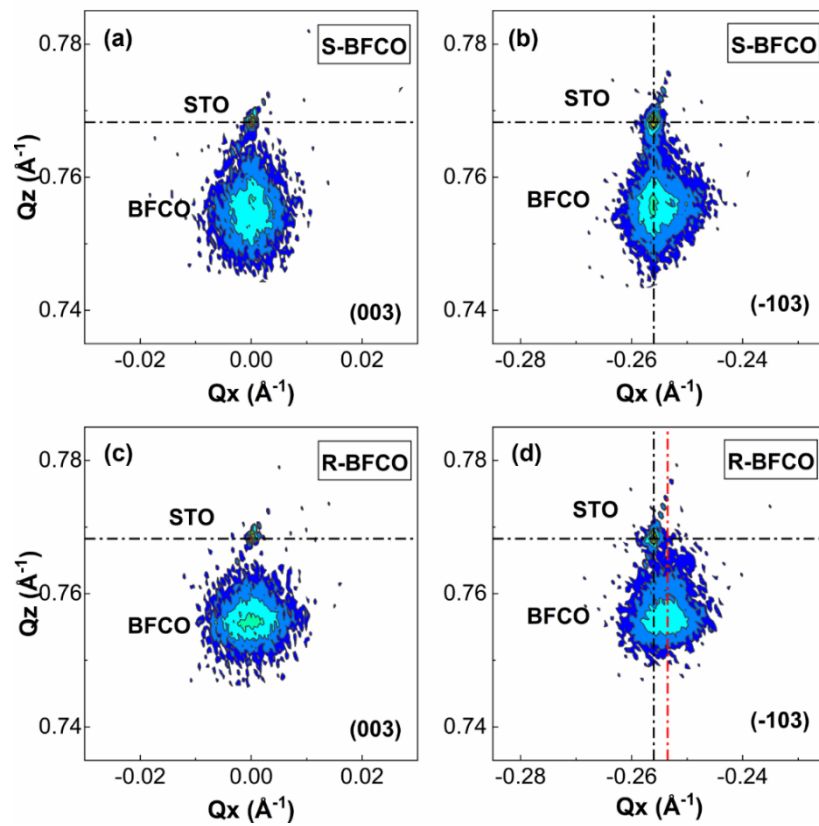


Figure 6-2 XRD reciprocal space maps around symmetric (003) and asymmetric (103) peak

(a, b) S-BFCO (c, d) R-BFCO. The black dashed line denotes the in-plane and out-of-plane constant of STO substrate in reciprocal space.

The film grown at higher laser fluence is partially relaxed as its reciprocal spot is very close to the in-plane lattice parameter of bulk BFCO. The in-plane (IP) lattice parameter was calculated to be ~ 3.906 Å and 3.933 Å for S-BFCO and R-BFCO films,

respectively. A single diffraction spot is observed for both structures, while they seem to be deformed. Although there is no clear splitting similar to was observed for the samples in chapter 5, this observation reveals that a monoclinic/rhombohedral distortion exists, suggesting the films present a tetragonal distorted perovskite structure with an OP pseudocubic lattice constant slightly larger than the IP parameter. Note that similar reciprocal maps around {103} reflection family were recorded by rotating the sample by 90 degrees about its normal axis, which excludes orthorhombic distortion.

It is also known that the shape of reciprocal lattice points can provide qualitative information. The symmetric (003) spot spreads vertically for the S-BFCO, confirming the d-spacing variation of the film. In contrast, the reciprocal lattice point of R-BFCO diffused along in-plane direction, which can be attributed to the mosaicity consistent with the slightly wider FWHM in the rocking curve measurement. For the R-BFCO film, the fact that the measured in-plane lattice parameter coincides with that of bulk lattice parameter indicates a lack of substantial strain along [100] direction. However, the out-of-plane lattice constant is markedly different compared to the bulk form. It is noted that the OP lattice parameter of the R-BFCO expanded by about 0.7% compared to the value expected from in-plane relaxation (see Figure 6-2(d)). The high concentration of point defects, like oxygen and bismuth vacancies or deviation from cation ratio stoichiometry in the R-BFCO film can possibly explain this observation based on the widely accepted defect-stimulated chemical expansion in the complex oxides.²⁴⁵

6.2.1.2 Effect of Laser Fluence on Morphology of Thin Films

As shown in Figure 6-3(a, b), the formation of 3D islands is distinctly detectable for both films, exhibiting the growth of BFCO films is governed by the Volmer-Weber

mode. The AFM measurement conducted on both samples exhibited a relatively smooth surface with a root mean square of below 6.2 nm over $1 \times 1 \mu\text{m}^2$ area, comparable to the previous studies.²⁰² Most importantly, for the higher laser energy, the lateral length of the R-BFCO grains is almost three times smaller compared to that of the S-BFCO film, which can be explained by correlation of the grain aspect ratio and strain relaxation.²¹⁰ Thus, a systematic variation of the grain size was observed by changing the laser fluence, which its impact on the film properties will be discussed later.

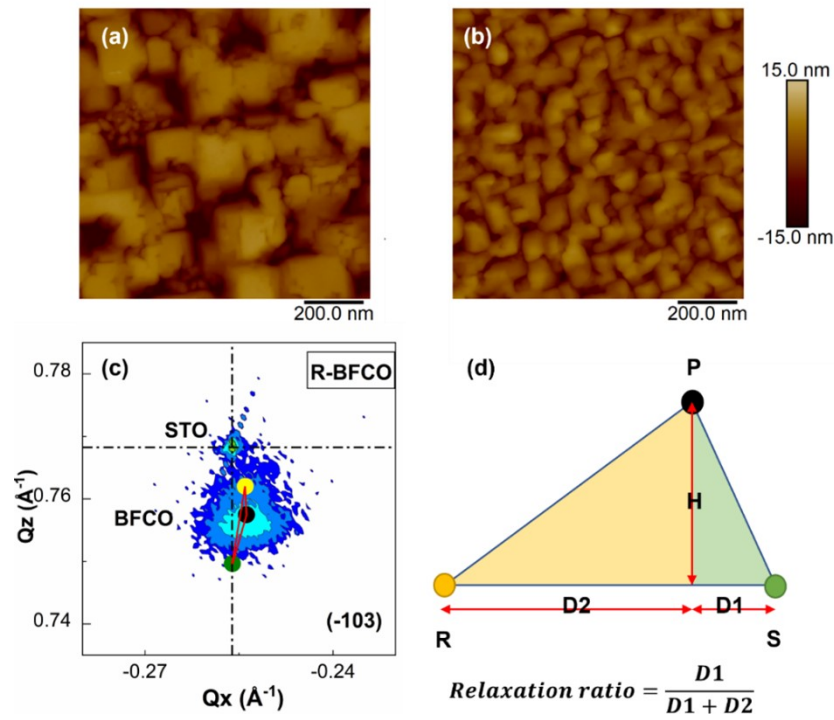


Figure 6-3 Surface morphology and strain relaxation in the BFCO films

AFM images of (a) S-BFCO (rms = 6.2 nm) (b) R-BFCO (rms = 3.4 nm) films grown on SRO-buffered STO. (c) RSM around (103) reflection for R-BFCO film, yellow and green spots represent the bulk (fully relaxed) and coherently strained peak position for BFCO, respectively. (d) Schematic illustrating the calculation procedure for the relaxation percentage.

Bulk BFCO has rhombohedral perovskite structure as does its parental BFO crystal; thus, the epitaxial synthesis of the rhombohedrally distorted BFCO on the cubic STO

imposes an extra shear strain, irrespective of the small in-plane misfit between the film and substrate. The shear strain due to the symmetry mismatch impedes the in-plane growth, i.e., layer by layer, ensuing a small grain size as it can also be inferred from AFM image. This shear strain can be accommodated by a twist distortion along c -axis,²⁰⁵ which makes out of plane growth relatively more favoured consistent with 3D-island formation. In fact, the highly energetic flux of atoms exacerbates this effect as the arrival time of atoms becomes shorter than the diffusion time.¹⁶¹ Hence, for the high growth regime, atoms accumulate more rapidly on the top of island regions. However, it is possible to sustain the strain state in the epitaxial BFCO film through lowering the deposition rate. At this regime, adatoms have sufficient diffusion time to adopt the substrate lattice.²⁴⁶ The effect of growth rate on the interfacial quality will be investigated in the next section, using high-resolution STEM images.

6.2.2 Stabilisation of Metastable Single-phase BFCO and Strain State

The correlation between the strain state and presence of possible Bi-deficiency is of great relevance to this study. The epitaxial strain imposed by the substrate plays a critical role in stabilising the pure phase formation for complex oxide showing the coexistence of multiple phases.¹⁷⁹ Bulk BFCO perovskite is known to form only under extremely high-pressure conditions (~ 6 GPa)¹⁷⁶. Nevertheless, synthesis of this otherwise unstable compound in the form of thin film has proved the practicality of epitaxial growth.²⁴⁷ Although growth of the BFCO thin films has been carried out under the processing conditions relatively far from those of the bulk counterpart, yet we cannot be conclusive to exclude neither of the kinetic nor thermodynamic factors. In fact, the phase stabilisation in epitaxial growth can occur due to the synergetic effect of both thermodynamic and kinetic grounds. Here, we shed light on how the joining strain

state and growth rate promote the formation of pure metastable BFCO phase from a thermodynamic perspective. In this respect, epitaxial stabilisation can be explained by addressing the minimisation of free energy. In theory, the difference of formation energy between the stable (incoherent) (s) and metastable (m) phase is expressed as:²⁴⁸

$$\Delta E = t \left[(\Delta g_s - \Delta g_m) - \left(\frac{\mu}{1 - \nu} \right) \epsilon^2 \right] + (\zeta_s^I - \zeta_m^I) \quad (\text{Equation 6 - 1})$$

where Δg and ζ^I are the energy of phase formation and the interface energies, respectively. In addition, ϵ , μ and ν represent strain, shear coefficient and Poisson's ratio, in the given order. One can readily notice that the first term in Equation 6-1 is negative in every case, whilst the sign of second term is positive provided the interface between stable phase and substrate is not coherent, knowing that the solid-solid interfacial energy of noncoherent interfaces is considerably large.²⁴⁸ Thus, the overall sign of ΔE is largely intertwined with the cooperative effect of film thickness and interfacial energy of corresponding phases. It is worth mentioning that in contrast to the previous study of BFO-based thin films in which no definite conclusion has been made due to the different thickness of films,²⁴⁹ in our case, both films have the same thickness, ruling out direct impact of the film thickness.

The percentage of relaxation is estimated in both films by quantitatively analysing the position of weighted-mean (103) RSM peak with respect to the theoretical value of the fully strained and relaxed layer. The weighted-mean diffraction peak position for each RSM point is calculated by²⁵⁰

$$2\theta_{mean} = \frac{\sum 2\theta \log I}{\sum \log I} \quad (\text{Equation 6 - 2})$$

$$\omega_{mean} = \frac{\sum \omega \log I}{\sum \log I}$$

The residual strain is then estimated from the proportion of the projected length of the mean diffraction spot on the line connecting the strained and relaxed position, as depicted in Figure 6-3(c, d). The percentage of relaxation is calculated to be ~65% for the R-BFCO films. The smaller relaxation in S-BFCO film (~40%), which is mainly coming from the OP component, shows that the lower laser fluence promoted the film to be more coherently strained to the substrate irrespective of the relatively large thickness of film.

Considering that the structural relaxation would increase the interface energy of metastable BFCO phase,²⁴⁹ It can be assumed that higher interfacial energy would favour the formation of bismuth deficiency due to its high vapour pressure, which may not be easily detectable via diffraction characterisation. On the other hand, the metastable BFCO phase is stabilised due to the lower interface energy induced by the strained state, which throws Equation 6-1 out of balance via the enhanced coherency between the film and underlying layer. The smoother interface between S-BFCO and SRO-buffered STO is evident from clear Laue fringes in diffraction studies and TEM images, as shown in Figure 6-4, supporting this hypothesis.

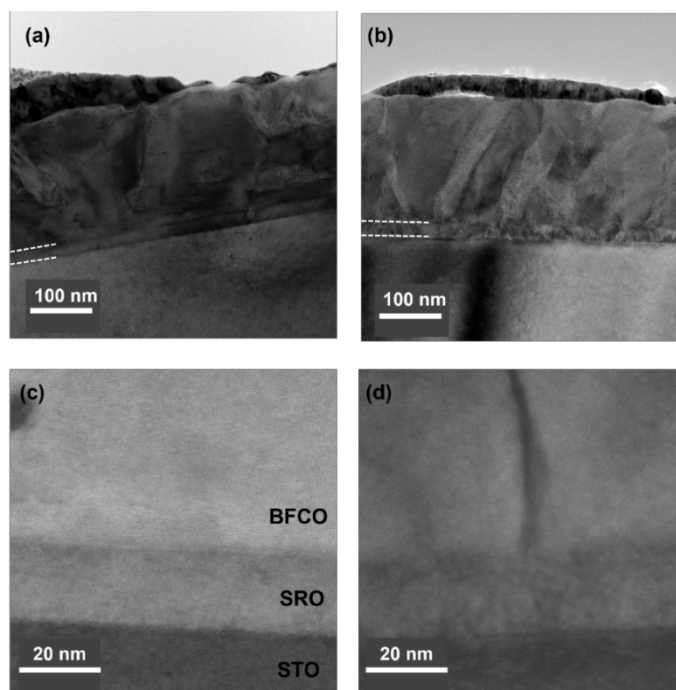


Figure 6-4 High magnification cross-sectional TEM image

(a) S-BFCO (b) R-BFCO film, the white dashed lines mark the interface. High-resolution dark field STEM image at the interface (c) S-BFCO (d) R-BFCO

6.2.3 Chemical State Analysis of the Elements in BFCO Thin Films

The C-1s signal of adventitious carbon (284.8 eV) is used for the charge correction. As shown in Figure 6-5(a), a sharp main peak associated to C-C or C-H is observed without any other structure at lower binding energies. Further high energy features are detected in the spectra, which can be ascribed to C-(OH), C=O and O-C=O functionalities at 1.5, 3 and 3.6 eV above the binding energy of the main peak, respectively. The Bi-4f core level exhibits two symmetric peaks positioned around 158.8 and 164.1 eV corresponding to the binding energies of $4f_{7/2}$ and $4f_{5/2}$, respectively (Figure 6-5(b)). The separation of spin-orbit doublets by 5.3 eV affirms the trivalent oxidation state of bismuth.^{251,252}

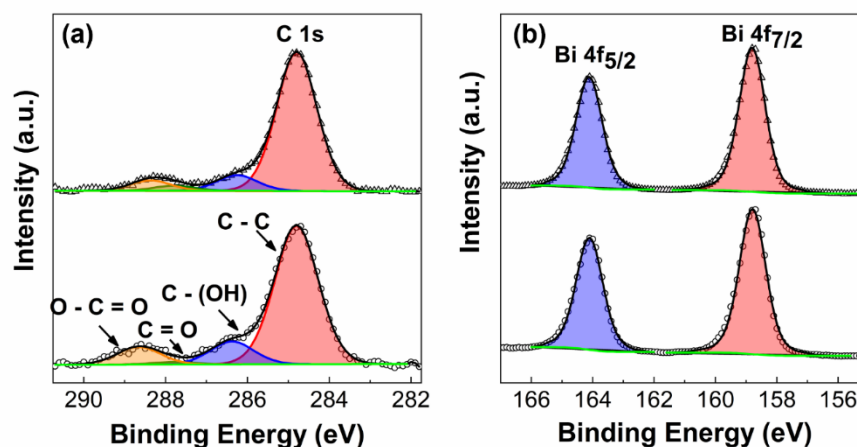


Figure 6-5 XPS spectrum for (a) C 1s (b) Bi 4f core levels.

Top and bottom panels represent S-BFCO and R-BFCO, respectively.

The electronic state of some transition metals produces notable components in their 2p spectra, which are not considered in many studies. During photoionisation process, if the atom under study comprises unpaired electrons in the core level, they can pair off with the unpaired electron in the outer shell, creating a couple of final states in the photoelectron spectrum – known as multiplet splitting.²⁰¹ Therefore, it should be expected to observe multiplet splitting in the Fe^{3+} and Cr^{3+} species due to presence of unpaired d-electron, which introduces distinctive complexities during the chemical state analysis. The spin-orbit split components of the 2p spectrum for both iron and chromium are well-separated, so the fitting is performed only on the intense $2p_{3/2}$ peak within good reason. For the fitting purpose, a standard Shirley background covering the $2p_{3/2}$ component is used.

As shown in Figure 6-6(a), the Fe-2p core level consists of two main features that are ascribed to Fe-O bond at ~711 eV ($2p_{3/2}$) and 724.5 eV ($2p_{1/2}$) with their corresponding satellite peaks. The position and intensity of satellite features in the Fe-2p spectra are often used as fingerprints to confirm the iron chemical state. The presence of satellite peak at binding energy of 719 eV and separation of 14 eV between $2p_{3/2}$ and $2p_{1/2}$

confirms the prevalence of Fe^{3+} cations.^{199,253} Although, iron is deemed to be in a mixed-valence state in the PLD-grown thin films under relatively low oxygen pressure, interestingly, no feature is observed in the deconvoluted line shapes for the binding energies ranging from 715-716 eV that can be assigned to the Fe^{2+} $2p_{3/2}$ satellite peak.²⁵³

The $\text{Fe-}2p_{3/2}$ peak is deconvoluted to further examine the chemical state of iron. Compared to the other transition metals, the $\text{Fe-}2p$ spectra is generally arduous to analyse due to the broadened nature of line shape as there are many distinct spectral characteristics, e.g., multiplet splitting, surface structure and multiple valence state, overlapping in the photoemission spectra.²⁵⁴ Thus, the utmost care should be taken to not misinterpret the oxidation state. Here, the $\text{Fe-}2p_{3/2}$ spectrum is accurately reproduced by a set of peaks representing the multiplet splitting and a surface structure. Figure 6-6(a) shows that multiplet components for both samples are consistent with the spectra of the high-spin Fe^{3+} oxides species in which all iron cations are octahedrally coordinated.²⁵³ The experimental energy-intensity distribution resembles the predicted multiplet splitting structure of core p-vacancy level.²⁵⁵ The slightly broader lineshape compared to those reported in the literature,^{253,256} is to accommodate the lower resolution setting, i.e., pass energy of 20 eV, used in this study. To fit the remainder of the $\text{Fe-}2p_{3/2}$ envelop, a high binding energy tail is added at ~ 714 eV, representing the surface structure of the Fe^{3+} ions. Due to the dangling bond at the surface termination, the Fe cations in the outermost layer possess a lower symmetry compared to the octahedral symmetry in bulk.²⁵⁴ This change in the crystal-field energy for the Fe cations at surface and bulk would introduce a final state in higher binding energy.^{253,254} The existence of the minority divalent iron on the film surface was also investigated by including the multiplet components for the high-spin Fe^{2+} state along the trivalent iron

peaks. Nevertheless, the fitting process did not converge, reassuring the predominancy of trivalent iron in both samples. Of course, a very minor concentration related to Fe^{2+} state cannot be disregarded within the data analysis accuracy. The suppression of the valence change for Fe ions can be linked to the presence of stable Cr^{3+} ions consistent with earlier studies on the B-site substituted BFO thin films.²⁵⁷

Therefore, it is of interest to determine the chemical state of chromium ions in the BFCO lattice. Numerous studies have used a single peak of either symmetric or asymmetric line-shape to fit the Cr-2p spectra,^{258,259} which led to misinterpretation of its oxidation state. Of great relevance to our investigation is the fact the widely-used binding energies of 575.2 and 576.3 eV ascribed to Cr^{4+} and Cr^{3+} , respectively, contradict the chemical shift theory, which indicates the higher oxidation state of chromium should be located at higher binding energies.²⁵⁶ In this regard, we employed the approach described in Ref.^{200,256,260}; as shown in Figure 6-6(b), the XPS spectrum of Cr-2p confirm that the oxidation state is Cr^{3+} since the deconvolution of the $2p_{3/2}$ core level is perfectly in line with the discrete multiplet structure described above.

The sharp peak at 529.5 eV of O-1s spectrum corresponds to the signal from the transition metal-oxygen species,²⁰¹ confirming the majority of oxygen is in the oxide lattice. The other clear features at the higher energy side of main peak can be associated with the absorbed oxygen in hydroxyl (530.9 eV), and the surface carbonyl group (532.2 eV).²⁶¹ A key observation here is the chemisorbed hydroxyl feature, underpinning the observed Fe-terminated surface structure in the Fe- $2p_{3/2}$ spectra. The surface hydroxylation process of Fe^{3+} cations with dangling bonds clearly explains the appearance of hydroxyl derived features as reported previously for the high vacuum deposition systems at the threshold pressure of 0.1 mTorr.²⁶²

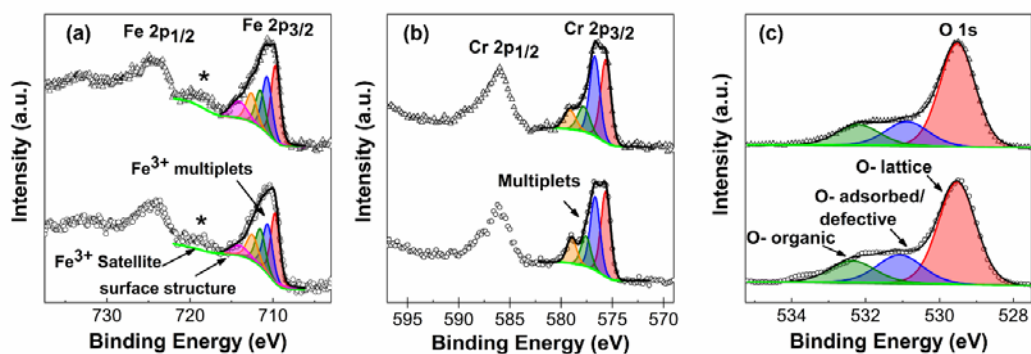


Figure 6-6 XPS spectrum for (a) Fe 2p (b) Cr 2p (c) O 1s core levels.

Top and bottom panels represent S-BFCO and R-BFCO, respectively. A standard Shirley background (green line) is used to fit the spectrum.

The phase diagram of BFCO is exceedingly intricate due to the high volatility of bismuth, leading to possible formation of Bi-rich phase, e.g., Bi_2O_3 , and Fe/Cr-rich phase such as $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$, upon the modest deviation from the optimal processing condition. Formation of these parasitic phases has a drastic influence on the functionality of BFO-based thin films.²⁶³ Therefore, the presence of secondary phases is further examined using the above XPS data. The starting point is to investigate the outgrowth of Bi-rich phases. The nominal compositions are expected to be Bi_2O_3 or tetragonal Cr-doped Bi_2O_3 structures ($\text{Bi}_{14}\text{CrO}_{24}$ or nonstoichiometric $\text{Bi}_{7.38}\text{Cr}_{0.62}\text{O}_{12+x}$).^{177,180} Presence of any Bi-rich phases can be simply ruled out as the oxidation state of chromium is deemed to be mainly 6+ in these structures,^{264,265} while the Cr^{3+} species are solely detected in this study. Moreover, the $\text{Bi}_{7.38}\text{Cr}_{0.62}\text{O}_{12+x}$ unit cell can be referred to as the tetragonal $\beta\text{-Bi}_2\text{O}_3$ structure showing a signature peak at a diffraction angle of 27.7° (JCPDS no. 50-0373)^{177,265}, but neither of the heterostructures exhibits such signals within the resolution limit of the diffractometer. AFM images of the films deposited at different growth regimes also corroborate the absence of bismuth-rich phases since no related outgrowth is present on the film surface.^{196,263} Now, impact

of the laser fluence on the ferroelectric and optoelectronic properties of the BFCO films will be investigated.

6.2.4 Ferroelectric Properties of BFCO Thin Films

6.2.4.1 Effect of Laser Fluence on the Local Piezoelectric Response

Figure 6-7 shows the local ferroelectric polarisation of the BFCO thin films at nanoscale. The virgin domain structure in both BFCO films shows dependency on the grain structure. The OP phase image of the S-BFCO film demonstrated more homogeneous upward polarisation direction, whilst the R-BFCO layer showed marginally a mixed polarisation direction.

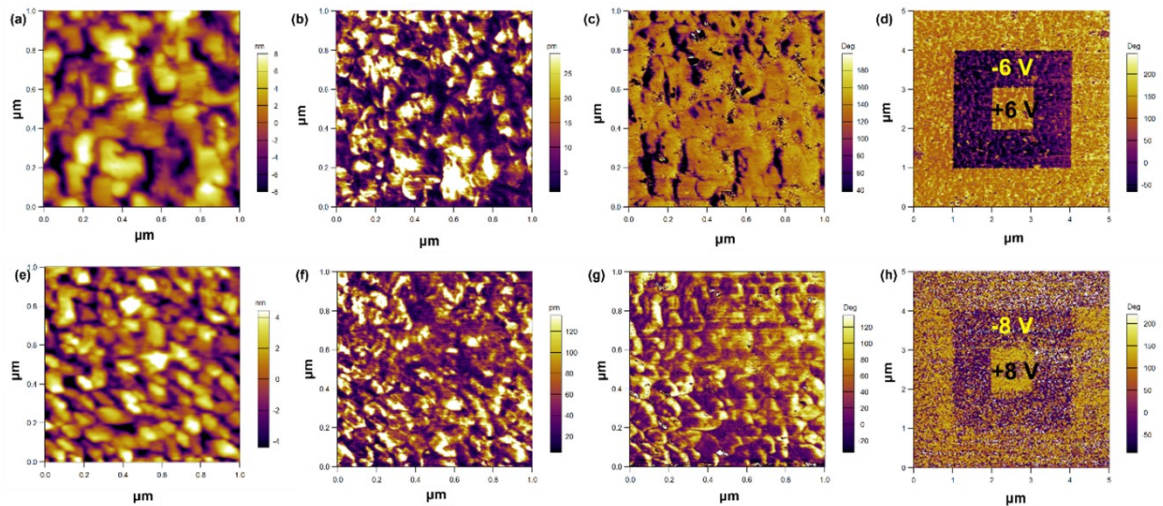


Figure 6-7 Local piezoelectric response of BFCO films grown under different laser fluence

Top panel: (a) $1 \times 1 \mu\text{m}^2$ AFM image of S-BFCO film on SRO/STO substrate. Out-of-plane PFM (b) amplitude (c) phase image in the same scan region. (d) $5 \times 5 \mu\text{m}^2$ polarisation domain switching image, the outer square (dark region) is downward polarisation, and the inner square (bright region) is upward direction. Bottom panel: (e-h) same as above for R-BFCO sample.

The so-called box-in-box pattern was written by first applying a negative DC bias using conductive tip over a $3 \times 3 \mu\text{m}^2$ area, followed by a positive DC bias in a $1 \times 1 \mu\text{m}^2$ inside

the larger square region. The PFM phase images clearly exhibit bright and dark contrast, confirming the ferroelectric domain switching behaviour for both heterostructures.

For both samples, the square-like phase loop confirms the typical ferroelectric characteristic with a 180° phase change at the coercive voltage, as shown in Figure 6-8. In addition, the average local coercive field ($2E_C$) was estimated to be 7 V and 5 V for R-BFCO and S-BFCO, respectively where the corresponding amplitude loop displays its minima. More interestingly, it is noted that S-BFCO thin film underwent substantial domain switching even at a lower switching voltage of 6 V. On the other hand, R-BFCO thin film showed slightly more difficult domain switching, i.e., there are still some domains resisting to 180° switching despite a higher applied bias (8 V). From the PFM switching experiment, it can be deduced that a low density of defect is beneficial for domain modification.

Furthermore, Figure 6-8 exhibits an opposite direction of the imprint for the BFCO samples. A slight difference in preferred polarisation can be observed when comparing the vertical PFM phase images, as shown in Figures 6-7 (c, g). Both samples exhibit upward polarization in the as-grown state. However, the bright yellow colour (poled-up) is significantly more dominant in the S-BFCO film, while the dark violet tone (poled-down) also appears in the PFM phase image of the R-FBCO film. Therefore, the slight negative shift of the S-SBFCO hysteresis loop is in accord with the prevailing preferred polarization direction. The offset of hysteresis loops can be associated with the built-in electric field within the film.²⁶⁶

One can assume that the competing sources of the internal field in the epitaxial BFCO film on SRO-buffered STO substrate are: (1) an upward electric field arose from the flexoelectric effect (2) a downward electric field originated from the interfacial effect.²¹⁰

Due to the different strain states observed in the films, a strain gradient can be envisaged along the direction of film thickness. Its value is estimated to be $0.51 \times 10^5 \text{ m}^{-1}$ and $0.29 \times 10^5 \text{ m}^{-1}$ for R-BFCO and S-BFCO, respectively (refer to Appendix A.1 for calculation). Note that the interfacial effect is more or less the same for both heterostructures. Considering the preferred upward polarization direction and smaller flexoelectric field of the S-BFCO film, it is reasonable to presume that the interfacial effect is more prevailing here. Moreover, defect-dipole complexes also induce an internal electric field, which can influence the direction of polarization within the ferroelectric domains.²⁶⁷ Such defect dipoles can be formed via coupling of the $V_{Bi}'' - V_O^{\circ\circ}$ defects (evidence of these point defect is given in section 6.2.6.1 for the R-BFCO film). The dipole-induced field can also influence the hysteresis loop imprint, and the magnitude of offset depends on the defect-dipole concentration.²¹⁰ Given the confirmed non-stoichiometric point defect in the R-BFCO film, it can be inferred that the high concentration of the defect-dipoles coupled with the larger flexoelectric field could promote the opposite imprint direction (positive shift) for this sample.

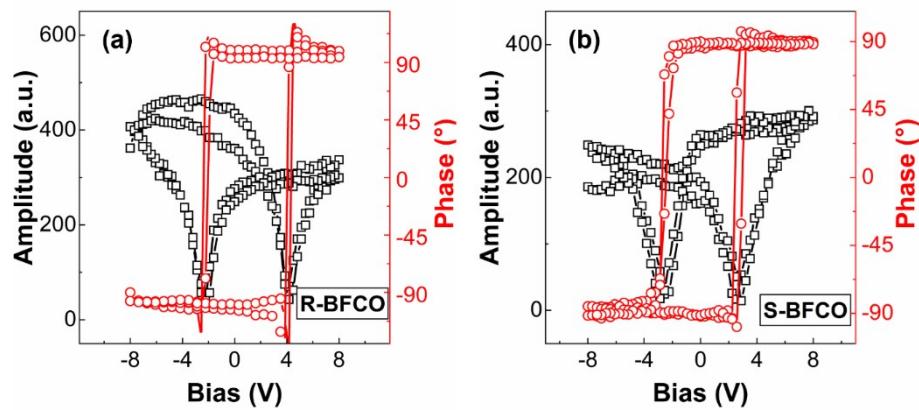


Figure 6-8 PFM amplitude (black square) and phase loop (red circle)
(a) R-BFCO (b) S-BFCO films measured within the applied bias range of ± 8 V.

6.2.4.2 Effect of Laser Fluence on Macroscopic Ferroelectric Hysteresis Loop

To probe impact of the growth rate on the macroscopic ferroelectric response, the P-E hysteresis loops of the same capacitor heterostructures was measured at room temperature (RT). As shown in Figure 6-9, two films exhibit strikingly different P-E performances. The R-BFCO exhibits an inferior hysteresis loop due to large contribution of the leakage current to the polarisation. In contrast, P-E loop of the S-BFCO film is markedly enhanced in which its overall features are less susceptible to the frequency (Figure 6-9(c)). The square-like shape of the loop corroborates the substantial domain switching that is also observed in the PFM result.

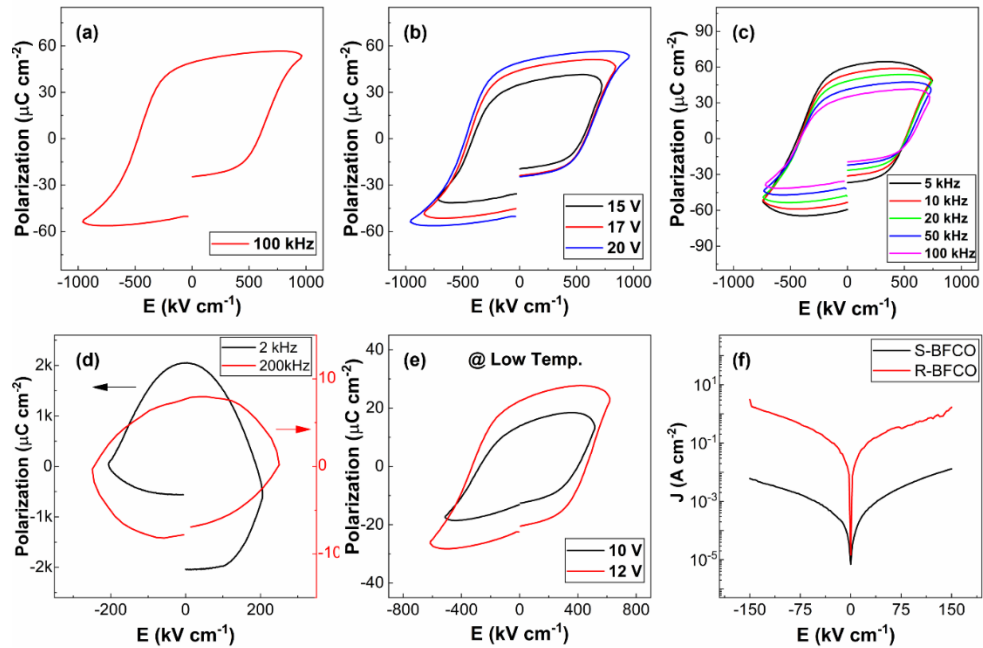


Figure 6-9 Ferroelectric polarisation hysteresis loop

PE loop of S-BFCO measured at room temperature at (a) 100 kHz (b) different bias at 100 kHz (c) different frequency and that of R-BFCO measured at (d) room temperature (e) low temperature, 100° K. (f) Dark I-V curve of both samples.

To ascertain the ferroelectric nature of the R-BFCO sample, low temperature (LT) P-E measurement was carried out at 100° K. Unsurprisingly, the P-E loop shape improved

significantly, as seen in Figure 6-9(e). Yet, the slanted shape of LT loop of R-BFCO compared to the RT S-BFCO loop, indicates nonuniformity of its domains wherein different coercivity of each domain does not allow the complete polarisation switching. This difference is also manifested in the coercive voltage trend observed in the PFM results, which agrees well with the domain pinning effect due to the non-stoichiometric point defect.¹⁵⁸

6.2.5 Current Leakage Mechanism in BFCO Thin Films Grown at Different Growth Rates

To understand the nature of leakage current, the J-E curve for the Au/Cr/BFCO/SRO/STO heterostructures was measured. Here, the external bias was applied from the top electrode to the BFCO thin film while the SRO bottom electrode was grounded. Note that during the macroscopic current-voltage test, the local joule heating effect became considerable for DC voltage exceeding ± 8 V, resulting in unrecoverable behaviour in our film. Yet, pulsed high voltage (up to 18 V) can be applied to measure the polarisation as described earlier. A significant reduction in leakage current density is observed for sample deposited under the lower laser fluence. The S-BFCO film exhibits leakage current density of $3 \times 10^{-3} \text{ A cm}^{-2}$ at 100 kV cm^{-1} which is comparable to previously reported value for BFO-based films.²⁶⁸ The leakage current of S-BFCO is reduced by two order of magnitude compared to that of R-BFCO heterostructure.

The commonly reported conduction routes in BFO-based thin films are governed by either (i) bulk-limited mechanism including ohmic, space-charge limited (SCLC) and Poole-Frenkel emission or (ii) Interface-limited conduction, namely Schottky emission.^{21,134} Detailed analysis through plotting the leakage data as a function of

applied voltage in different arrangements provides insight into the dominant charge transport mechanism inside the BFCO heterostructure.

The first potential mechanism is Schottky emission that describes a carrier transport route determined by the difference in Fermi level at the electrode/film interface. Due to this energy difference, a Schottky barrier is created that must be overcome by charge carriers. The current density is, hence, characterised by²⁶⁹

$$J_S = AT^2 \exp \left[-\frac{\phi}{\kappa_B T} + \frac{1}{\kappa_B T} \left(\frac{q^3 V}{4\pi\epsilon_0 K d} \right)^{0.5} \right] \quad (\text{Equation 6 – 3})$$

where A is the Richardson constant, ϕ are Schottky barrier height, ϵ_0 is vacuum permittivity, and K is the dielectric constant of the thin film. One can conclude the leakage mechanism is governed by Schottky emission if the $\ln(J/T^2)$ vs $V^{0.5}$ plot exhibits linear fit to the data. Then, the estimated dielectric constant from the slope of straight-line fit should match the actual values for the BFCO thin film.

On the other hand, space charge limited conduction is a bulk-limited mechanism characterised by the electrical properties of the semiconductor thin film. A limiting space charge is created when the charge injection from the electrodes occurs at a higher rate than they can move within the bulk of the film. In such case, the current density is described by²⁷⁰

$$J_{SCLC} = \frac{9\mu\epsilon_0 K}{8d^3} V^2 \quad (\text{Equation 6 – 4})$$

where μ denotes carrier mobility. When the typical J-V characteristic is represented in double-log scale, we may conclude whether the conduction is ohmic or dominated by

trap-controlled space charge limited current if the derivative of current density versus applied voltage is near unity or two, correspondingly.

Finally, Poole-Frenkel emission is another bulk-limited mechanism characterised by thermally or field-triggered emission from ionised trap states. Depending on the complexity of trap states, the conductivity for classical or modified Poole-Frenkel equation is expressed as²⁷¹

$$\sigma_{P-F} = c \exp \left[-\frac{E_1}{\kappa_B T} + \frac{1}{r \kappa_B T} \left(\frac{q^3 V}{\pi \epsilon_0 K d} \right)^{0.5} \right] \quad (\text{Equation 6 – 5})$$

where c is a constant, E_1 is the ionisation energy of trap states, and the compensation constant “ r ” equals 1 or 2 corresponding to the classical or modified equation. Similar to the analysis described for Schottky emission, the K value for the film under study is estimated from the slope of linear fit for the $\ln(\sigma)$ vs. $V^{0.5}$ plot. It can then be used as a figure of merit to confirm the dominant conduction mechanism.

The analysis of leakage current data provides some significant observations. Most importantly, neither of the samples is governed by the Schottky emission mechanism, ruling out the interface-limited conduction triggered by the electrodes. Even though some regions can be fitted with a straight line, but a dielectric constant of 1.5-2.7 is extracted, which is smaller than the reported dielectric constant of $K=6.76$ for multiferroic BFCO.²⁷² This observation is of great importance as it assures the electrical behaviour in different heterostructures arises from the bulk of thin film itself.

For the film deposited at a high growth rate, the symmetrical shape of leakage current data indicates alike mechanism for both positive and negative bias. Accordingly, as shown in Figure 6-10, the ohmic conduction is found to be the sole charge transport

mechanism in the measured voltage range with an excellent linear fitting of $\ln(J)$ versus $\ln(V)$ with a slope of ~ 1 at both sides. In contrast, a slight asymmetry is observed for the film grown at a low flux regime, suggesting different mechanisms may dictate the charge transport under positive and negative bias.

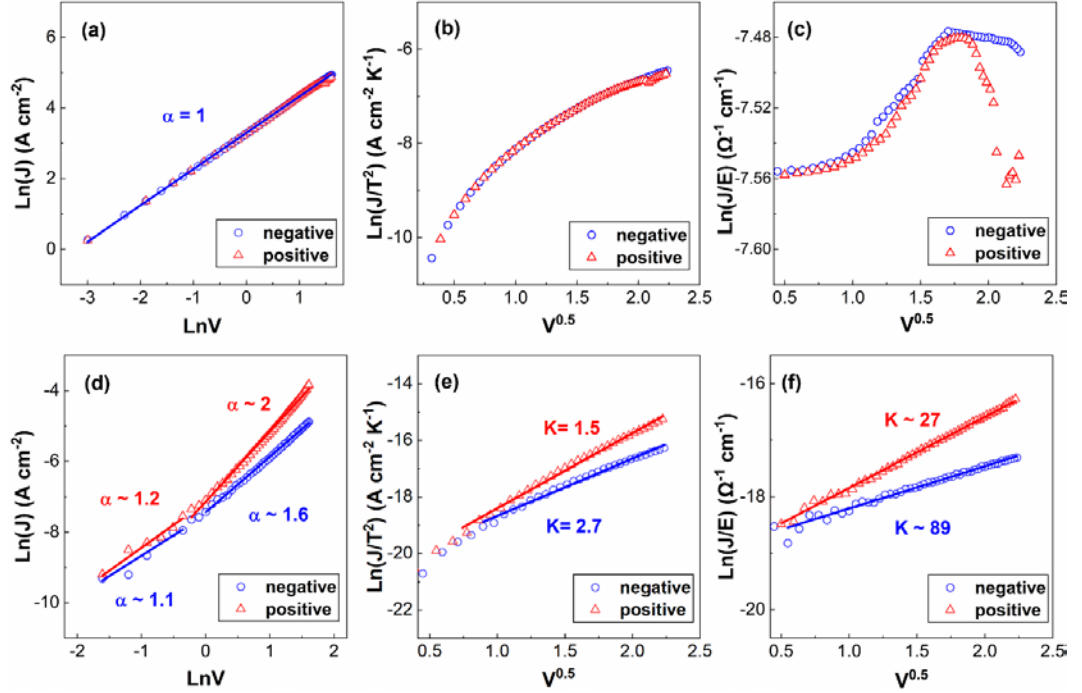


Figure 6-10 Leakage data fitting to determine transport mechanism

Top panel for R-BFCO: (a) Ohmic (b) Schottky emission (c) Poole-Frenkel and bottom panel for S-BFCO: (d) Space charge-limited (e) Schottky emission (f) Poole-Frenkel

Study of best fit for the film deposited at a low growth rate reveals a more complicated evolution. For both positive and negative bias, ohmic conduction is the dominant charge transport route up to voltage < 1 V, while the conduction mechanism alters to the trap-controlled SCLC in the higher electric fields. Note that the slope of linear fit slightly differs for the positive and negative bias strands. The moderate slope of negative bias compared to the expected value of ~ 2 for the SCLS conduction can be associated with the gradual transition to the trap-filled region.²⁷³ At low applied voltages, the thermally generated free carriers outnumber the injected carriers, which corresponds to the

dominance of ohmic conduction. Upon increasing the applied voltage, the onset of SCLC mechanism occurs when carrier transport time becomes comparable to that of the dielectric relaxation, i.e., the time required for redistribution of charges in the dielectric.²⁷⁴ Thus, the injected carriers become dominant as applied voltage further increases and fill up the traps eventually; thus, SCLC mode governs the carrier transport inside the film.

A thorough investigation of J-V characteristics implies that conduction route for carriers inside both films is bulk-limited, although the dominant mode is ohmic and space charge limited for the partially relaxed and strained epitaxial BFCO film, respectively.

6.2.6 Possible Mechanism for Increased Leakage Current

In the light of these findings, we surmise that non-stoichiometric point defects and the large volume of grain boundaries—both triggered by the growth kinetic—play a major role in the significant increase of leakage current.

6.2.6.1 Non-Stoichiometric Point Defects

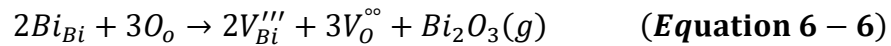
First, the formation of non-stoichiometric point defects, i.e., bismuth and oxygen vacancies, can provide an explanation for the enhanced leakage current density with increasing the laser fluence. Defects can establish an extra energy state into the bandgap, resulting in the defect-mediated change of the electronic structure in complex oxides.²⁷⁵ In general, the conduction band minimum (CBM) of perovskite oxide is derived from outer shell *d*-orbital of B-site cation, e.g., transition metals, whereas hybridisation of oxygen 2*p*-orbital with the filled *d*-orbital of transition metal determines the valance band maximum (VBM).²⁷⁶ Thus, a range of impacts on the electronic properties can be envisaged depending on the type and energy position of

defect state with regard to CB/VB. For instance, when defect states with holes (electron) are introduced into the valence band (conduction band), they can provide additional carriers and enhance the conductivity. Similar effect can also be realised if empty (filled) defect states are located near VBM (CBM) functioning as shallow acceptors (donors) upon excitation.

Although stoichiometric transfer of material gives the LMBE technique an edge over the other deposition routes for the fabrication of complex oxide materials, the simultaneous arrival of the atom from a multicomponent target on the substrate cannot assure a stoichiometric film growth. In fact, various competing processes take place throughout different stages of the pulsed laser deposition of which their judicious control bestow a wealth of modified structure and functional properties in the deposited film. The very first stage of the pulsed laser deposition process is governed by the laser-solid interaction, resulting in the ejection of the atom, ions, and electron from the solid target.²⁷⁷ In the BFCO multicomponent target, the magnitude of ablation yield varies from one component to another depending on the energy needed to discharge an atom from the solid, i.e., cohesive energy.²⁷⁸ Here, the volatile bismuth possesses an ablation yield of about 10^{16} atom/pulse, which is approximately an order of magnitude larger than that of the transition metals.²⁷⁹ Therefore, variation of the laser energy density may result in non-stoichiometric behaviour of ablation process, particularly in the case of preferential evaporation of bismuth with low cohesive energy. Moreover, the heavy atoms of bismuth propagate preferentially along the direction of the target surface normal during the plume expansion, which further leads to a nonuniform diffusive flow of Bi atoms towards the substrate.²⁷⁸ Up to this stage, the higher energy of laser appears to be advantageous to alleviate the common loss of bismuth during high-temperature

synthesis. However, it can be shown that the physical issue in this scenario is primarily associated with the sputtering of growing film by the highly energetic ablated atoms, which is induced by the high laser fluence of 5 J cm^{-2} .²⁸⁰ In this study, the re-sputtering prevalently occurs for the volatile bismuth as well as the light oxygen atoms. In other words, significant re-sputtering causes depletion of the bismuth atom due to the large nuclear stopping force, i.e., the breaking power on the incident ion from the collision with the atoms in solid, which is most crucial for the heaviest atom in the film.²⁷⁸ This can clearly elucidate the immediate effect of the high laser energy on the film growth as the kinetic energy of ablated atoms substantially increases with the fluence, ensuing in the loss of bismuth on a microscopic scale.

Bi-deficiency would be accompanied by the oxygen vacancies to compensate for cation non-stoichiometry and preserving the charge neutrality that can be expressed by the Kröger-Vink defect equation as follows:^{281,282}



As evidenced from the XPS results, the charge compensation through valance change of iron cations is largely suppressed. Here, ionisation of V_o provides electrons to compensate hole carriers introduced by bismuth vacancies, sustaining the nominal valance state of irons.²⁸³

(a) Direct Evidence of Non-Stoichiometric Defects

More detailed information relating to the atomic weight percent (at%) of the cations were obtained from Energy Dispersive X-ray (EDX) analysis. All the elements, including those of the substrate, are detected and homogenously distributed in the sample (Figure 6-11). Despite being single-phase with nearly ideal stoichiometric

chemistry, EDX analysis shows the average ratio of Bi:Fe slightly decreases from 2.0 to 1.9 with increasing the laser fluence, while the average Fe:Cr ratio remained constant ~1.1 in both samples. This variation in the Bi-content conclusively confirms our hypothesis regarding differences in the electrical leakage and conduction mechanism induced by the growth kinetic during the film synthesis.

Table 6-2 Representative EDX data for S-BFCO acquired at magnification of x 5k using an accelerating voltage of 20 kV

Element	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]
Oxygen	K-series	11724	2.440	2.440	12.574
Bismuth	M-series	119883	39.110	39.110	15.433
Chromium	K-series	19338	4.379	4.379	6.945
Iron	K-series	18872	5.139	5.139	7.589
Titanium	K-series	76203	15.096	15.096	25.999
Ruthenium	L-series	11793	3.062	3.062	2.499
Strontium	L-series	137010	30.773	30.773	28.962
Sum			100	100	100

Table 6-3 Representative EDX data for R-BFCO acquired at magnification of x 5k using an accelerating voltage of 20 kV

Element	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]
Bismuth	M-series	110815	37.577	37.577	14.595
Iron	K-series	19059	5.395	5.395	7.841
Chromium	K-series	18647	4.389	4.389	6.852
Titanium	K-series	75160	15.477	15.477	26.237
Strontium	L-series	135655	31.670	31.670	29.338
Ruthenium	L-series	11040	2.980	2.980	2.393
Oxygen	K-series	11615	2.512	2.512	12.744
Sum			100	100	100

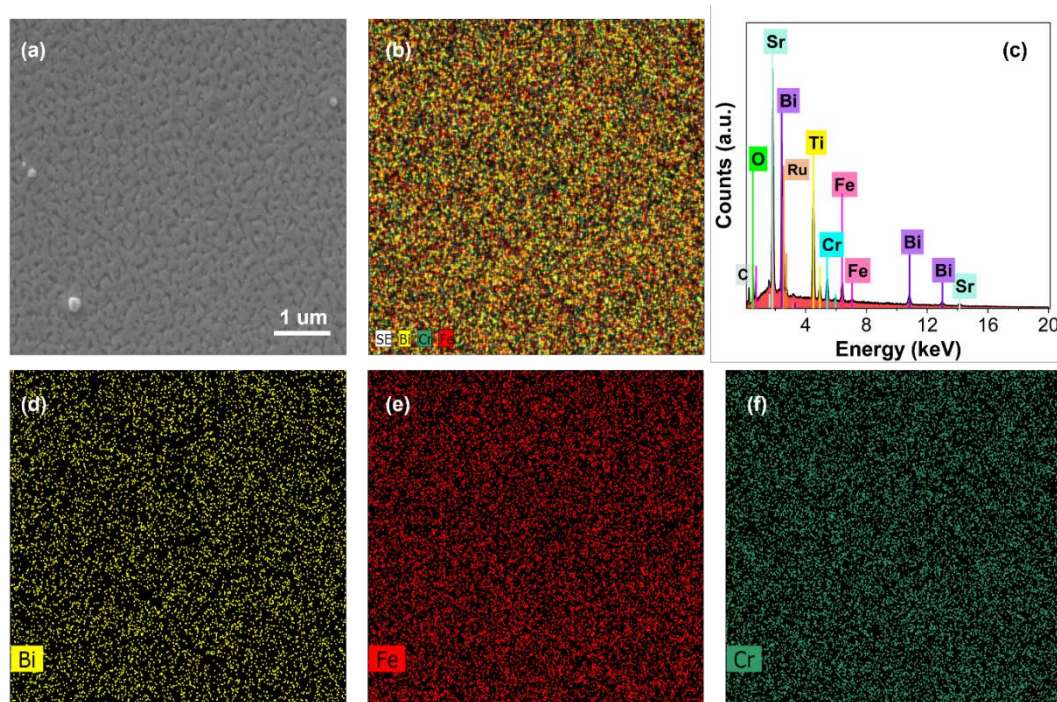


Figure 6-11 Energy Dispersive X-ray analysis of representative BFCO film
 (a) SEM image in $6 \times 6 \mu\text{m}^2$ area at the magnification of 5000x. (b) Superimpose image of elemental EDX mapping (c) Elemental peaks in EDX spectrum of BFCO film grown on SRO-buffered STO substrate. Elemental mapping of (d) Bi (e) Fe (f) Cr in the same scan region

For all heterostructure, the microscope operating configuration was maintained and both mapping and spectrum acquisition were performed at least over three different regions under the optimised count and dead time. The wavelength-dispersive spectrum was acquired using an accelerating voltage of 20 kV, which result in the generation of the X-ray lines for all elements in the heterostructure. For this study, only the spectrum of cations, i.e., excluding oxygen, was semi-quantitatively processed, using the TEM PB-ZAF models in Bruker Esprit software. The atomic ratio of Sr/Ti pertaining to the substrate was used as a figure of merit to assess the quality of our analysis. Note that a similar trend is observed for the normalised atomic ratios regardless of the chosen quantification model.

Table 6-4 Average at% over three different area

Sample	Bi:Fe (at%)		Fe:Cr (at%)	
	TEM PB-ZAF	Error (±)	TEM PB-ZAF	Error (±)
S-BFCO	2.0	0.01	1.1	0.005
R-BFCO	1.9	0.02	1.1	0.01

(b) Indirect Evidence of Non-Stoichiometric Defects

The Bi-deficiency can unambiguously explain the observed I-V characteristic of R-BFCO. The work function value of Cr is 4.5 eV,¹³² while that of the bottom electrode SRO is 5.2 eV,¹⁸ which shows reasonable conductivity. Moreover, the electron affinity of BFCO is approximated to be 3.6(8) eV.^{18,181} Taking the bandgap of BFCO film from ellipsometry measurement into account, the valence band maximum (E_c) can be around 5.6(8) eV. Based on the absence of rectification effect for the R-BFCO during the I-V test, which indicates no Schottky barrier is formed at neither of the interfaces, we speculated the Bi-deficiency confers p-type features to the R-BFCO thin film. Interestingly, a noticeable modulation of resistance state is also observed for R-BFCO during cyclic current-voltage measurement, consistent with earlier reports on the resistive switching (RS) effect in the p-type BFO-based semiconductor.¹⁵⁷ As shown in Figure 6-12, the leakage current characteristics clearly exhibits a hysteresis behaviour, suggesting a variation in the resistance state. Of note, it was found that the switching sequence is different from the diode-like switching behaviour reported earlier.^{284,285} Here, the switching of resistance state follows HRS $\rightarrow$ HRS $\rightarrow$ LRS $\rightarrow$ LRS $\rightarrow$ HRS order as the voltage sweeps from -3 to +3 V and then back to the initial value (Figure 6-12(a)). Thus, in contrast to the diode-like switching where resistance state changes at

$V=0$, switching for R-BFCO film is governed by a defect-mediated charge trapping process at a positive (negative) voltage.²²⁷

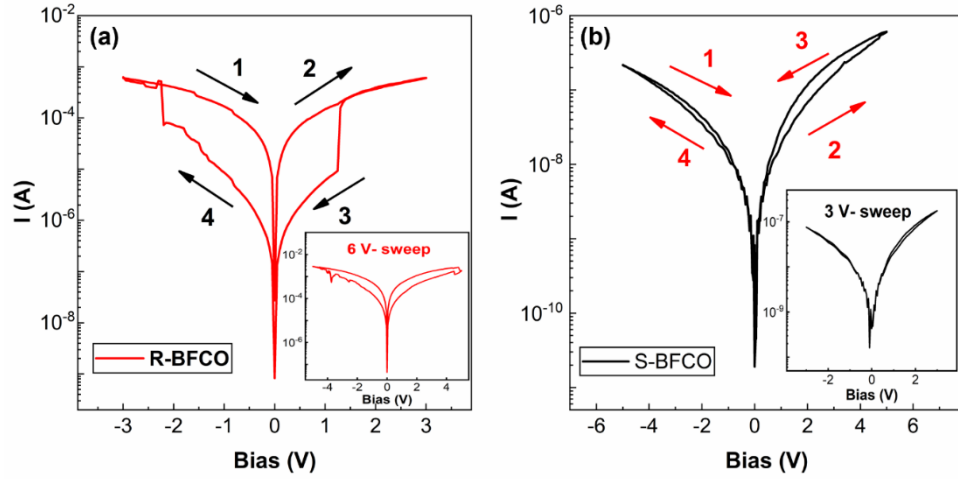


Figure 6-12 Dark I-V curves showing the resistance state modulation

- (a) R-BFCO heterostructure, the inset shows the curve when swept range increased to ± 6 V. (b) S-BFCO heterostructure, the inset represents the curve when swept range decreased to ± 3 V.

This hysteresis effect becomes less pronounced in the S-BFCO film, which can be associated with the lower concentration of point defects. Contrary to the observed defect-mediated RS characteristic of R-BFCO film, Figure 6-12(b) shows that the LRS $\rightarrow$ HRS switching of S-BFCO heterostructure occurs when crossing the zero voltage, i.e., changing the polarity of sweeping voltage. Although not very strong, it suggests a slight rectifying behaviour, indicating the formation of a small Schottky barrier only at the S-BFCO/SRO interface, which can be modulated by the polarisation.

This hysteric nature of I-V curve can be of interest for the resistive random-access memory (ReRAM) application. In other words, the ON/OFF state is represented by alternating between two different currents at the same voltage. Further discussion is out of the scope of current study; however, it is worth investigating in future works. Unlike

preceding studies on the resistive switching behaviour of the BFCO thin film in which n-type characteristics was assumed for the films,^{243,284} findings of this thesis suggest that ferroelectricity and resistive switching can be realised in the BFCO films irrespective of the majority carrier or defect type.

6.2.6.2 Leakage Path through Grain Boundaries

Next, a considerable reduction in the leakage current density can be associated with the lower density of grain boundaries in S-BFCO. It is possible that the grain boundaries also act as leakage paths, providing a secondary explanation to the observed trend. To investigate this hypothesis, the effect of grain boundaries on the electrical properties of BFCO films was probed using C-AFM measurement. As shown in Figure 6-13, despite relatively similar current signals in both samples, the number of bright areas is considerably larger in the R-BFCO heterostructure. Of great relevance to our prediction is that more conductive areas superpose the proximity of grain boundaries.

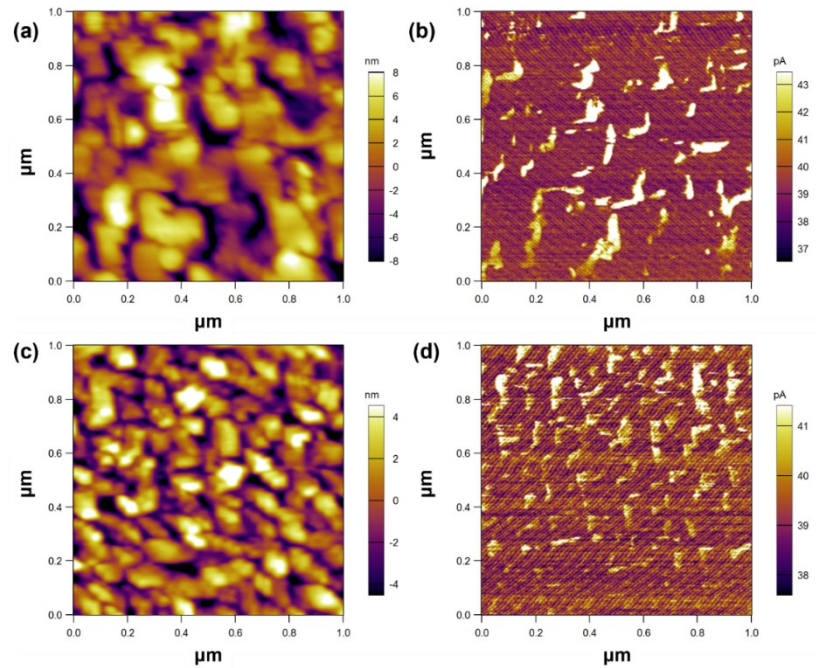


Figure 6-13 Evidence of leakage path through grain boundaries

AFM image (a) S-BFCO (b) R-BFCO. Conductive-AFM current mapping in the same scan area for (c) S-BFCO (d) R-BFCO

In perovskite oxides, grain boundaries tend to be largely charged due to the preferred accumulation of non-stoichiometric point defects, e.g., charged vacancies, giving rise to distinctive conduction properties.²⁷⁵ Using EDX/TEM, elemental mapping around grain boundaries clearly corroborates the bismuth deficiency in these regions (Figure 6-14). Therefore, those grain boundaries that are parallel to the applied electric field enhance the leakage current as schematically presented in Figure 6-14(h). Moreover, it is widely accepted that polarisation switching is either obstructed or ferroelastic switching occurs with a high coercive field around grain boundaries.²⁸⁶ Such effect is also clearly seen in the PFM domain switching images wherein polarisation direction around domain boundaries is resisting the switching mechanism upon flipping the external bias. Considering the higher local coercive field required in R-BFCO (Figure 6-8), the leaky nature of P-E hysteresis loop for the R-BFCO film can be explained now. At high electric fields, the leakage current through grain boundaries prevails, impeding the complete switching at room temperature. However, this adverse effect is alleviated during low-temperature measurement.

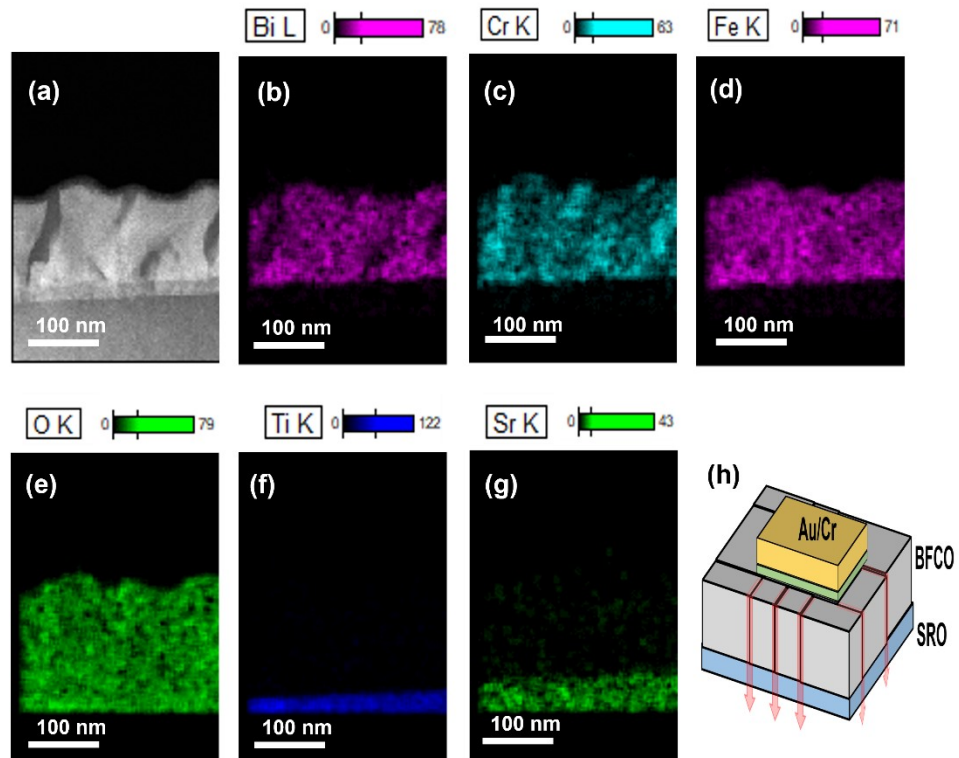


Figure 6-14 EDX/TEM elemental mapping of R-BFCO

(a) Dark-field STEM image (b) Bi-L α (c) Cr-K α (d) Fe-K α (e) O-K α (f) Sr-K α (g) Ti-K α , showing clear Bi-deficiency at the vicinity of grain boundaries. (h) Schematic showing the possible leakage path in Au-Cr/BFCO/SRO/STO heterostructure.

6.2.7 Enhanced Photoresponse in the BFCO Film Grown in Low Growth Rate Regime

Despite the fact that functional oxides are often deposited directly on the bottom electrode layer for the purpose of electronic and ferroelectric studies, the optical properties are usually reported based on the data measured on the bare underlying substrate.²⁸⁷ Hence, the optical properties of BFCO films grown on the SRO-buffered substrate is investigated in this section. A four-medium optical model composed of STO substrate/SRO bottom electrode/BFCO film/surface roughness layer was adopted to analyse the ellipsometry data. The roughness layer is represented by Bruggeman effective medium approximation, consisting of 50% void and 50% bulk of the film.¹⁶⁷

The dielectric function of SRO and STO were obtained separately, as explained in Chapter 4 and 5. Thus, the free parameters include the complex dielectric function of BFCO layer along with the thickness of each layer. A GenOsc function consisting of three Gaussian oscillators was employed to parametrise the dielectric function of the BFCO films within the wavelength ranging from 200 to 1000 nm. Figure 6-15 exhibits the uniqueness of fit as the figure of merit to assess the reliability of our model, in which the iterative Marquardt-Levenberg algorithm was used to minimise the Mean Square Error (MSE).

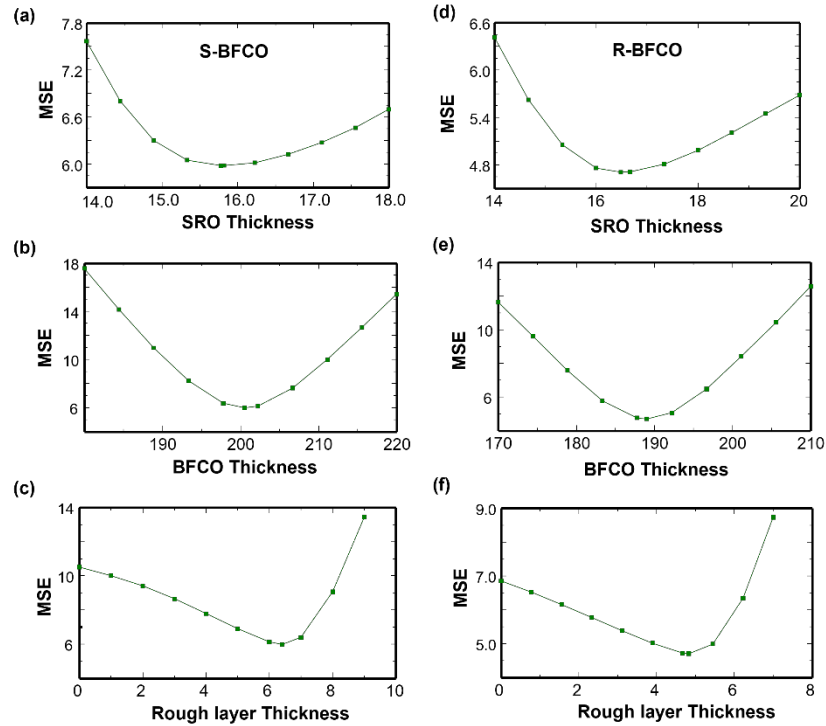


Figure 6-15 Goodness of Fit for ellipsometry analysis

(a) Bottom electrode thickness (b) Film thickness (c) Surface roughness of S-BFCO. (d-f) the same for R-BFOC

In the mathematical model representing the dielectric function of BFCO, the central energy of oscillators were 2.2, 4.2 and 6.5 eV, which agree with the prominent charge transition centres of the related ferrites.²³⁵ Table 6-5 presents the result of the fitting

process, yielding the thickness of layers in accord with the cross-section TEM and AFM results.

Table 6-5 Detail of the oscillators for the ellipsometry fitting procedure

Sample	MSE	Gauss.1						Gauss.2						Gauss.3					
		Br		En		Amp		Br		En		Amp		Br		En		Amp	
		value	±	value	±	value	±	value	±	value	±	value	±	value	±	value	±	value	±
R-BFCO	4.70	0.29	0.01	2.18	0.01	0.44	0.02	2.00	0.06	4.07	0.03	2.58	0.24	3.39	0.07	6.14	0.05	8.32	0.05
S-BFCO	5.98	0.37	0.03	2.29	0.01	0.23	0.02	2.04	0.05	4.23	0.03	2.29	0.18	3.68	0.05	6.50	0.05	9.38	0.08

As shown in Figure 6-16(a), the optical transition of both BFCO films consists of two linear segments, implying two threshold gaps exist within the visible spectra. The higher energy threshold gap is assigned to the p - d transition associated with O $2p$ -TM $3d$ charge transfer.²³⁵ The band transition around 2 eV is associated with the d -orbital Mott-Hubbard charge transfer between chromium and iron cations.²⁸⁸ Nechache et al. attributed similar absorption peaks and positions to the effect of Fe/Cr cation ordering modified by the laser repetition rate during the film deposition.¹⁸ Moreover, the $\epsilon_1(E)$ graph shows very similar characteristics for both films within the visible region spectra (inset of Figure 6-16(a)). Of note, the value of optical dielectric constant used for the determination of the leakage mechanism agrees well with ϵ_1 magnitude at the infrared region.

To study the photoresponse properties of Au/Cr/BFCO/SRO heterostructures, the I-V characteristic was obtained at a low applied voltage (below 1V) under dark and white light illumination (Figure 6-16(b)). Electric poling was performed by a ± 8 pulsed DC voltage (pulse width ~ 50 μ s) to macroscopically flip the polarisation direction of the

BFCO films. Comparison of dark and light I-V characteristics implies a jump in conductivity of the poled heterostructures at the non-zero applied field.

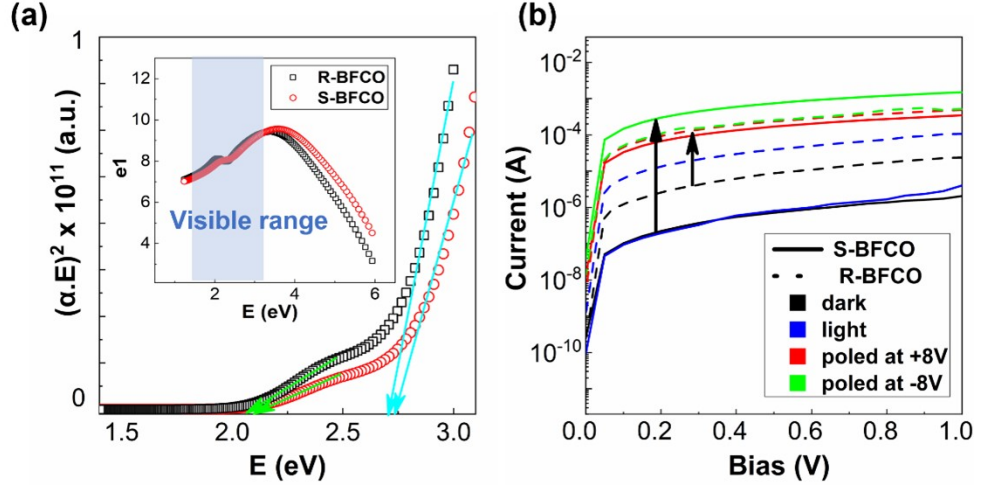


Figure 6-16 Optical properties and photoresponse of BFCO films

(a) Direct optical transition, inset: real part of optical dielectric function obtained from ellipsometry. The blue region marks the visible spectrum. (b) I-V curve for both films under white light illumination by solar simulator (300 W) at different polarisation direction.

The most prominent observation is a remarkable enhancement of photo-to-dark current ratio in the S-BFCO sample. The photoresponse increases by three-order of magnitudes when S-BFCO is poled at -8 V, while an approximately 20-fold enhancement is realised for that of R-BFCO under the same condition. A narrow bandgap, substantial visible light absorption and effective e-h separation are prerequisites for the photoferroelectrics.²⁸⁹ With the knowledge that the absorption spectrum is quite similar for both samples, it is concluded that enhanced ferroelectric characteristic of the S-BFCO film efficiently separates the photoexcited e-h pairs as expected in ferroelectric oxides, leading to a higher photo-to-dark current ratio. In other words, the total current in BFCO can be expressed by⁹²

$$J = J_{sc} + (\sigma_d + \sigma_{ph})E \quad (\text{Equation 6 - 7})$$

where σ_d , σ_{ph} are dark and photo conductivity, respectively, and E denotes the applied electric field. Thus, the superior photoresponse of S-BFCO indicates the effective transport of the photoexcited carriers induced by the intrinsic polarisation, since the photoconductivity component of S-BFCO film changes significantly upon reorientation of the ferroelectric domain by electrical poling. Using Equation 6-4, the carrier mobility of S-BFCO heterostructure is approximated to be in the range of $3.59 \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, consistent with the high polar order of ferroelectrics as explained elsewhere.¹³² Hence, the polarisation switching is crucial to facilitate the transport of photoexcited carriers. On a similar note, the photovoltaic properties of the PZT-based perovskite solar cell were enhanced considerably upon careful optimisation of electrical poling, wherein insulating PZT transformed to an effective electron transport layer.²⁹⁰

6.3 Summary

This chapter explored the relationship between kinetic growth parameters and ferroelectric properties in the BFCO thin film. It is demonstrated that the growth rate can be utilised to not only reduce the leakage current but to control the extent of strain relaxation. The latter observation is intriguing as neither the thickness nor the deposition temperature has been changed. It should be noted that growth parameters have been used previously to control the defect density in complex oxides.²⁹¹ However, our results also imply the possibility of the unit cell modification triggered by lowering the laser fluence during the growth. This approach may enable the crafting of unexplored structural variants with no need to alter the underlying substrate.

Additionally, a considerable change was also observed in the transport mechanism. The space charge-limited and ohmic conduction was found to be the primary conduction

mechanism in the sample grown under low and high laser fluence, respectively. The remnant polarisation of $2P_r \sim 100 \mu\text{C cm}^{-2}$ was measured for the 200 nm-thick BFCO film grown at the low growth rate regime. A three-order of magnitude increase in the photo-to-dark current ratio was also observed concomitant with the realisation of room-temperature ferroelectric in the reduced leakage current sample.

Chapter 7. Conclusions and Future Work

Note that some section of this chapter is part of an ‘Accepted /Original Manuscript’ of an article published by Taylor & Francis Group in *Critical Reviews in Solid State and Materials Sciences* on 7 Jan 2020, available online: [10.1080/10408436.2019.1708700](https://doi.org/10.1080/10408436.2019.1708700)

7.1 Thesis Conclusions

Ferroelectric perovskite oxides are promising candidates for emerging optoelectronic devices. However, the wide bandgap of ferroelectrics has yet to be addressed, enabling their practical use as photoactive materials. Over the past few years, multiferroic BFCO thin film in which ferroelectric and magnetic orders coexist has gained widespread interest owing to its relatively narrow bandgap. The existing body of literature has focused on the bandgap engineering of BFCO via B-site cation ordering. Nonetheless, a thorough understanding of structural evolution and the associated functional properties is still lacking. Moreover, to be used in such devices, it is crucial to demonstrate a robust polarisation in BFCO thin films. Yet, like the parental bismuth ferrite, BFCO also suffers from an unsatisfactory level of electrical leakage current.

To address the abovementioned issues and understand the structure-property relationship in BFCO thin film, high-quality epitaxial BFCO thin films were synthesized on single-crystal STO (001) substrates using the LMBE method. This thesis comprised a systemic investigation of the deposition conditions and phase stabilisation. After determining the optimal growth window for developing pure-phase BFCO thin films, a comprehensive structural, optical, and ferroelectric characterisation was performed. The key outcomes of this thesis are outlined as follows:

1) The influence of deposition parameters on the epitaxial growth of the BFCO films on STO (001) substrate was systematically investigated. The results revealed that the pure BFCO phase could be grown within a very narrow temperature, oxygen pressure and laser frequency window, being more susceptible to the growth conditions compared to the Bi-Fe-O system. It was shown that the formation of the BFCO phase is favoured when the processing conditions are confined to a range of $T_s = 600\text{-}700\text{ }^\circ\text{C}$ and $P_{O_2} = 1\text{-}15\text{ mTorr}$.

2) The thickness-dependent structural phase transition was explored in the epitaxial BFCO thin films and the impact of such crystallographic distortion on the photoresponse was ascertained. The results show the strain imposed by the substrate changes the crystal symmetry, transitioning from tetragonal-like to rhombohedral-like with a rather complex relaxation mechanism as the thickness of film increases. The evolution of crystallographic distortion is also coupled with the modulation of the BFCO bandgap. Optical characterisation via spectroscopic ellipsometry clearly confirms the possibility of bandgap tuning ($\sim 150\text{ meV}$) upon this phase transition. Moreover, wavelength-resolved photocurrent measurement reveals that absorption onset is redshifted for the tetragonal-like structure, implying light wavelengths up to 800 nm can be absorbed. First-principles calculation shed further light on the symmetry-induced changes in the electronic structure of the BFCO films. Crystallographic symmetry proved to be a decisive factor in modifying the characteristics of valence band maximum and conduction band minimum intrinsically, opening doors to a new type of Mott multiferroic system. These results provide a strategy – depending on the structural phase transition – to further engineer the optoelectronic properties of the multiferroic oxide perovskite.

3) It was demonstrated that both microstructure and ferroelectric properties could be tuned by lowering the laser fluence during deposition, ensuing realisation of the decent room-temperature ferroelectric polarisation. A three-order of magnitude suppression in the leakage current is reported for the LMBE-grown BFCO film through judicious adjustment of the growth rate. A thorough investigation of J-V characteristics implied that the conduction route for carriers inside both films is bulk-limited. However, the dominant mode changes from the ohmic to space charge limited upon reducing the growth rate. Moreover, it was demonstrated that non-stoichiometric point defects and a large volume of grain boundaries—both triggered by the growth kinetic—play a major role in the significant increase of leakage current. More importantly, the poling history dependence of photoelectric characterisation sheds light on the role of ferroelectric polarisation on the photoexcited charge separation in the BFCO films. This facile strategy offers great opportunities for tailoring the electronic properties of other ferroelectric oxides, facilitating their implementation in practical application.

There are still opportunities available for further circumventing the intrinsic limitations. The photocarrier generation and recombination mechanism at ultrafast time scales should be further studied to proceed the photoferroelectrics a step forward. It is promising to integrate BFO-based perovskite into other solar harvesting devices such as organic solar cells or organohalide perovskite to enhance conversion efficiency. For instance, in a typical organic solar cell, photo-induced charge carriers cannot be separated by the weak internal electric field resulting from high binding energy in organic materials. In this case, the functionality of ferroelectric material to provide the driving force for the dissociation of excitons would be advantageous. Another possibility is to incorporate BFO-based perovskite in monolithic tandem silicon solar

cells, whereas the counterpart halide perovskite/silicon system has been reported to be a promising route to achieve a cost-effective multijunction.²⁹² Growing a thin layer of modified BFO-based perovskite with a relatively wide bandgap might not only aid in diminishing the thermalisation losses but also in absorbing a wider solar spectrum beyond the bandgap of crystalline silicon subcell. A monolithic tandem solar cell will produce a voltage on par with the sum of those of the subcell. However, a major constraint with this design is that subcell must yield a similar photocurrent.

For the successful commercialisation of BFO-based devices, scaling-up technologies are to be developed. So much effort has been put into preparing high-quality thin films through complex deposition techniques, while from the industrial perspective, simple and low-cost manufacturing processes are highly desirable. In this regard, further work needs to be done to investigate the adoption of less-complicated techniques, such as printing which is proved to be viable in the case of the halide perovskite solar cell family.^{293,294} Finally, to answer the question “How can we fabricate a BFO-based photovoltaic device that is comparable with Silicon solar cells?”, expertise from various fields, e.g., thin film technology, ferroelectric community and photovoltaic engineering, is required for fruitful breakthroughs.

7.2 Future Work

7.2.1 Impact of the Strain Gradient

In Chapter 6, it was shown that lowering the growth rate promoted modulation of the in-plane lattice parameter. This may yield different strain profiles in the films, resulting in a notable strain gradient, as presented in the preliminary results below. Considering that strain gradient has a reciprocal relation with material dimension, the flexoelectric effect

(the interplay between polarisation and strain gradient) can be non-trivial in the complex oxide thin films, and thus its impact on the physical properties.²⁹⁵ Previous studies have shown flexoelectric effect may be beneficial for energy harvesting applications.^{296,297} Therefore, it is worth further investigating the potential of such effect in the BFCO nanoelectronics structures in future studies. Following the procedure explained in Appendix A.1, the strain gradient along the [001] and [010] directions are $0.29 \times 10^5 \text{ m}^{-1}$ and $0.46 \times 10^5 \text{ m}^{-1}$, respectively for S-BFCO heterostructure. Although the assumption of exponential strain profile is reasonable and has been employed in several studies,^{211,298} note should be taken that the described quantitative analysis heavily depends on the selected strain profile as well as the calculated inhomogeneous and average strain. Therefore, it is better to use such analysis for comparison per se.

7.2.2 A-Site Substituted BFCO Thin Film

Laser molecular beam epitaxy, like pulsed laser deposition, is widely used due to its ability to grow multi-cation complex oxide thin films in which rigorous control over stoichiometry is needed. This indicates a great potential to incorporate suitable cations on the A/B-sites simultaneously. As mentioned throughout this thesis, large polarisation magnitude enhances the photoexcited charge separation in the ferroelectric oxide perovskite. Lanthanum substitution in the Bi-based multiferroics has been reported to improve dielectric response,²⁹⁹ and enhance the charge carrier mobility in BFO when co-substituted with Mn.³⁰⁰ Moreover, computational studies predicted a possible bandgap reduction in La-doped BFCO due to modification of the local Bi-O environment and its impact on the oxygen 2p and TM *d*-orbital overlapping.³⁰¹ Our preliminary study demonstrated that 10% of bismuth could be readily substituted with lanthanum without the formation of the secondary phases in BFCO films. In addition,

the epitaxial growth of doped and undoped-BFCO films on (111)-oriented STO substrate revealed an intriguing result. From the shape of asymmetric RSM scan, as shown in Appendix A.2, structural distortion appears to become less pronounced by changing the substrate orientation. More interestingly, although the deposition condition was kept unchanged, the so-called superstructure peaks disappeared for the La-doped BFCO sample (see Appendix A.2). Although the film surface morphology slightly changes upon doping, it is worth cross-checking if lanthanum substitution influences the leakage mechanism. On that note, the impact of A site-substitution, specifically lanthanoid series, on the optical and multiferroic properties of the BFCO thin film can be investigated in future studies.

7.2.3 BFCO/(Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃ (BNBT) Bilayer Structure

As highlighted in Chapter 2, multi-layered structures such as BiFeO₃/BaTiO₃¹⁴⁵ or BiFO₃/BiCrO₃¹⁴⁴ have been reported to offer an enhanced photoresponse and superior ferroelectric characteristics simultaneously. Therefore, this strategy can be utilised to address the adverse effect of bandgap reduction on the spontaneous polarisation of photoferroelectrics. We have initiated the growth of the BFCO/BNBT bilayer structure. After a painstaking optimisation process, the initial XRD analysis presents that high-quality interface is formed with no evidence of parasitic phase segregation within the diffractometer resolution limits (shown in Appendix A.3). Our group has previously reported a large saturation polarisation for BNBT thin films (80 $\mu\text{C cm}^{-2}$) stable at the elevated temperature,³⁰² which may not only yield the driving force for separation of photoexcited charges but can also extend the UV absorption region. Therefore, it is worth exploring the impact of different BNBT thicknesses on the overall performance of the bilayer structure in terms of optical/ferroelectric properties.

Appendix

A.1 Impact of the Strain Gradient

Figure A-1 shows the out-of-plane inhomogeneous strain extracted from the diffraction line broadening analysis as described in Chapter 5.

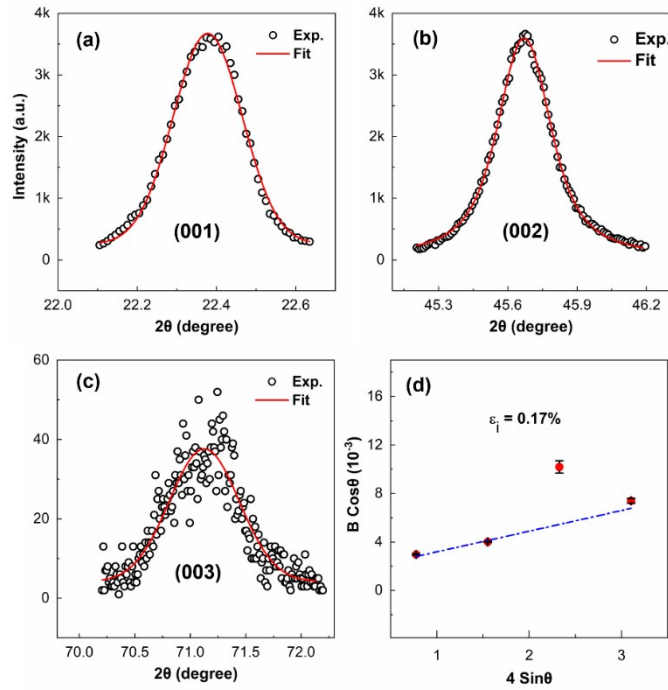


Figure A- 1 Williamson-Hall analysis for S-BFCO thin film

Experimental and fitted x-ray pattern around (a) (001) (b) (002) (c) (003) reflections, peaks are fitted using Voigt function. Note that (004) reflection is not shown here. (d) W-H plot showing the inhomogeneous strain for S-BFCO sample

Subsequently, the internal strain profile can be resolved from the integral expressions for the average and inhomogeneous strain²¹¹

$$\bar{\epsilon}(t) = \frac{\int_0^t \epsilon(z) dz}{t} \quad (\text{Equation A - 1})$$

$$\epsilon_i^2(t) = \frac{\int_0^t (\epsilon^2(z) - \bar{\epsilon}^2) dz}{t} \quad (\text{Equation A - 2})$$

To solve the above equations, we presume an exponential function for the strain profile $\epsilon(z)$, which is not contingent on the relaxation mechanism³⁰³

$$\epsilon(z) = \epsilon_0 e^{-z/\delta} \quad (\text{Equation A - 3})$$

where ϵ_0 and δ refer to strain at the interface and the strain penetration depth, respectively. The value of δ can be obtained by rearranging the Equation A-1 and 2 which yields²¹¹

$$\frac{t}{2\delta} \frac{\bar{\epsilon}^2}{(\epsilon_t^2 + \bar{\epsilon}^2)} = \tanh \frac{t}{2\delta} \quad (\text{Equation A - 4})$$

and then finding the value of ϵ_0 accordingly. Once all variables are known, the average strain gradient can be estimated using Equation A-3.

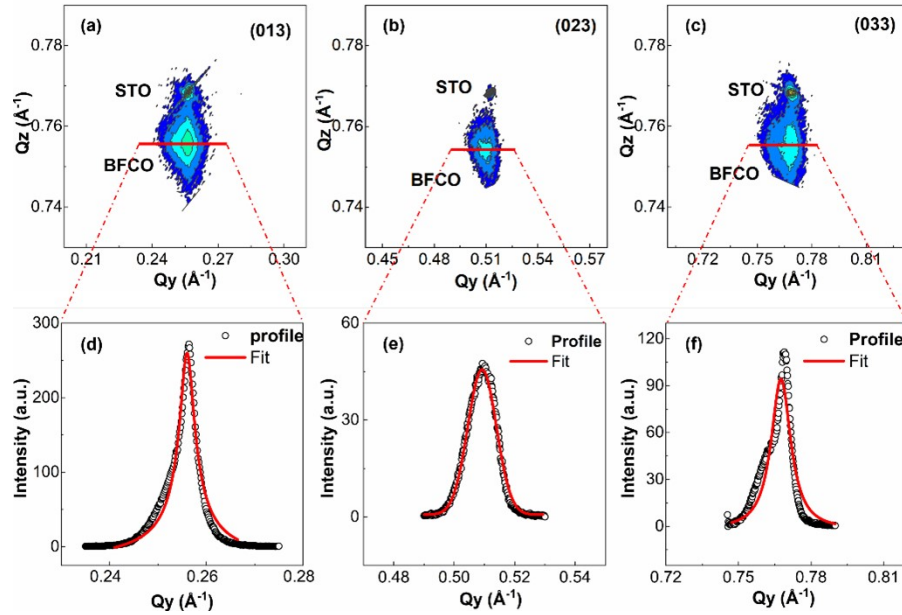


Figure A- 2 RSM scan around asymmetric S-BFCO reflection

(a) (013) (b) (023) (c) (033) S-BFCO reflections. (d-f) Corresponding line profiles, fitted using Pearson IIV function.

Using similar methodology, the in-plane inhomogeneous strain along [010] direction was obtained from the extracted line width of the asymmetric (013), (023) and (033) RSM peaks (Figure A-2).²¹⁰

Following the above-mentioned steps, the in-plane strain gradient was approximated over the terrace width of STO substrate (250 nm), as summarized in Table A-1.

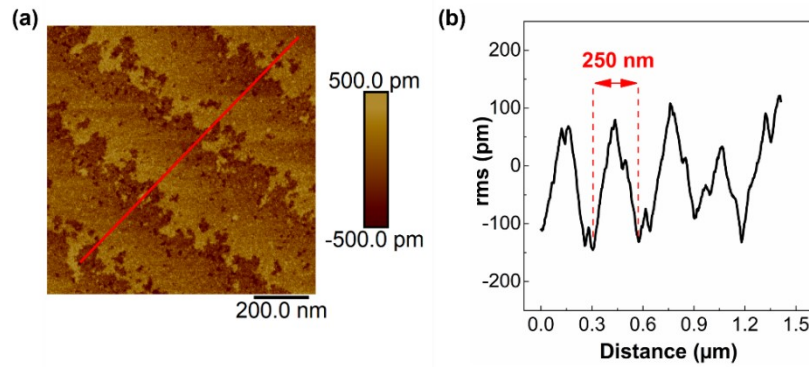


Figure A- 3 Surface topography of STO substrate

(a) AFM image of bare STO substrate (b) Width of terraces

Table A- 1 Details of strain gradient parameter calculated for S-BFCO

Direction	$\bar{\epsilon}$	ϵ_i	δ	ϵ_0	$\frac{\partial \epsilon}{\partial z(x)}$
Out-of-Plane (OP)	+0.0084	0.0017	283.58	0.012	0.29E+5
In-Plane (IP)	-0.0079	0.0033	171.35	0.015	0.46E+5

A.2 A-Site Substituted BFCO Thin Film

Figure A-4 demonstrates a topographic AFM image of La-modified BFCO film ($\text{Bi}_{0.9}\text{Li}_{0.1}\text{Fe}_{0.5}\text{Cr}_{0.5}\text{O}_3$). The island growth mode is consistent with the undoped BFCO film as described in Chapter 5 and 6. Comparison of XRD scan for BFCO and LBFCO grown on the STO (111) substrate also shows disappearance of superstructure peak upon La-substitution.

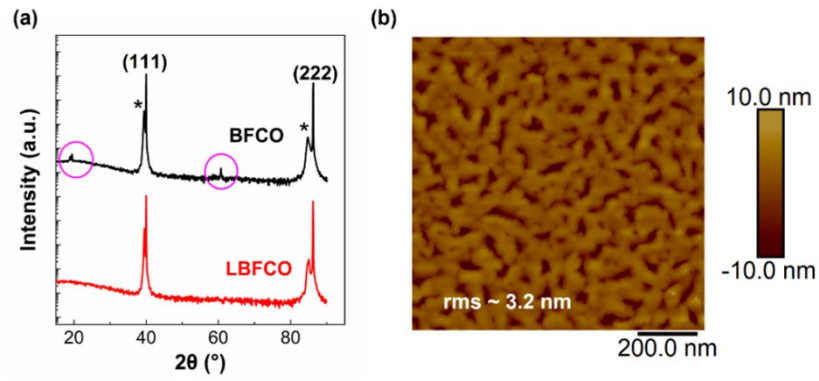


Figure A- 4 Microstructural characterisation of 10% La-doped BFCO

(a) XRD of LBFCO film on STO (111) substrate, circles and asterisks denote the half-order and main BFCO reflections, respectively. (b) AFM image of 70 nm-thick LBFCO.

Figure A-5 shows the asymmetric contour map around (103) and (312) film reflections prepared on STO (001) and (111) substrate, respectively. Both doped and pristine BFCO films exhibited more pronounced structural distortion when deposited on STO (001) substrate.

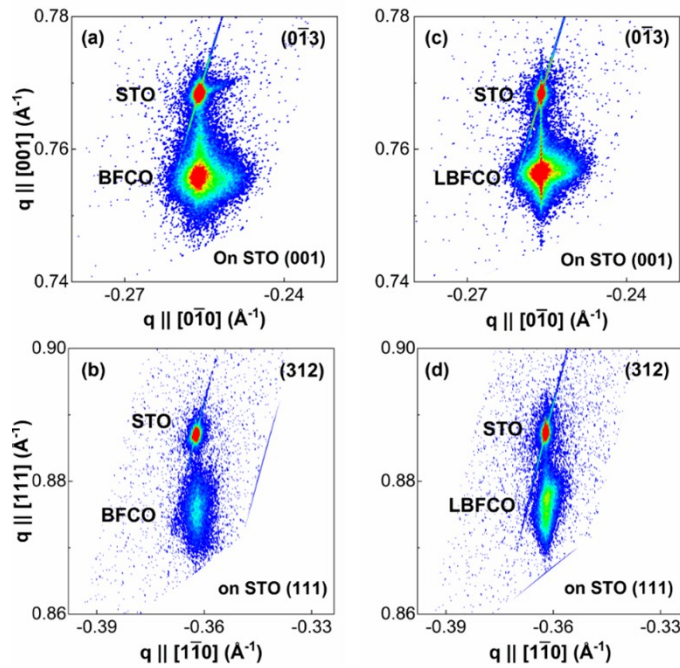


Figure A- 5 Asymmetric RSM plot for 70 nm-thick films

(a, b) BFCO (c, d) LBFCO films on the (001) and (111)-oriented STO substrates

A.3 BFCO/(Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃ (BNBT) Bilayer Structure

Figure A-6 provides preliminary results for the successful growth of the BFCO (70 nm)/BNBT (30 nm) bilayer structure. The coupled θ - 2θ scan shows only the (00 l) reflections of film and the substrate, confirming the growth of highly oriented heterostructure along the c -axis with no parasitic phases.

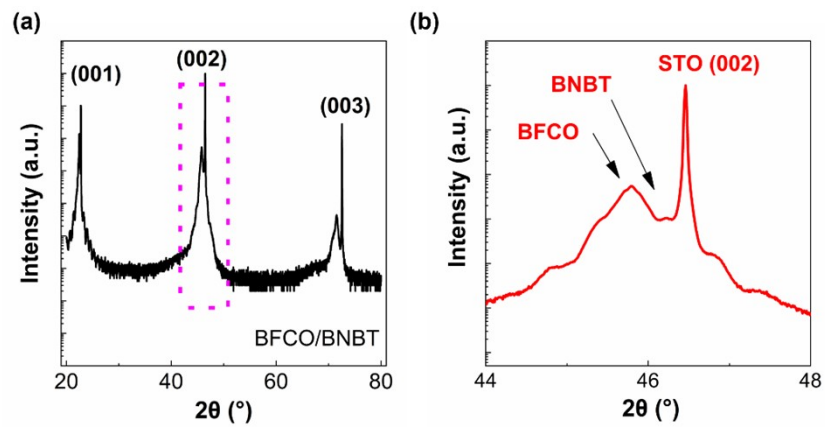


Figure A- 6 Structural characterisation of BFCO/BNBT bilayer.

(a) Coupled θ - 2θ scans BFCO/BNBT bilayer. (b) zoom around (002) reflection

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