Tuning of Light-Harvesting Properties in Ferroelectric Bi_2FeCrO_6 Thin Films for Photovoltaics

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The photon energy conversion is driven by the increasing need for efficient, sustainable, and affordable clean energy. Ferroelectric (FE) oxides with low bandgaps hold significant promise for novel optoelectronic (OE) devices due to the spontaneous electric polarization, which can induce electron-hole separation and allows large open-circuit voltages (V_{OC}) [1-2]. The FE double perovskite Bi_2FeCrO_6 (BFCO), obtained by replacing half of Fe atoms with Cr atoms in the $BiFeO_3$ parent compound, shows a reduced bandgap of 1.4 - 1.9 eV [2-3], making it highly suitable for visible light absorption. However, achieving precise control over its functional properties requires a deeper understanding of how synthesis conditions influence the structure and further their performances. Indeed, the growth parameter window used during the pulsed laser deposition (PLD) growth of single phase BFCO is narrow (substrate temperature between 620 and 720 °C, oxygen pressure: ~ 0.01 mbar [4]). Even within this window, the high-vacuum PLD environment promotes oxygen-deficient induced secondary phases, critically altering the FE and OE properties of the film.

This study systematically maps the evolution of structural, morphological, FE and OE properties in epitaxial BFCO thin films grown using PLD at different temperatures and oxygen pressures. A 20 nm Nb-doped $SrTiO_3$ (Nb:STO) conductive layer was deposited between BFCO and $SrTiO_3$ (STO) substrate in order to allow electrical measurements. Structural, morphological and optical characterizations were carried out using X-ray diffraction (XRD), atomic force microscopy (AFM) and UV-Vis spectroscopy. Piezoresponse force microscopy (PFM) and conductive atomic force microscopy (CAFM) coupled with a laser beam enabled to investigate the FE and OE properties of BFCO thin films in darkness and under illumination. Local Kelvin probe force microscopy (KPFM) allowed obtaining the surface photovoltage of BFCO thin films. We found that, within the deposition window, higher temperatures promote a conductive secondary phase, which shows weak ferroelectric properties but generates a strong localized photocurrent. These "hotspots" show an opposite response to oxidizing/reducing annealing when compared to the main BFCO film due to differing dominant defects (Bi vs. oxygen vacancies). Thus, the optimal oxygen pressure balances the oxygen vacancies and the generation of secondary phase during the growth, that consequently modulates the OE properties of the films. By mapping the phase diagram of BFCO, we elucidate a direct correlation between the deposition conditions and the OE properties of BFCO films. Understanding how growth conditions control the formation and properties of defects and secondary phases, allows for better design and engineering of BFCO-based heterostructures with optimized optoelectronic performances, particularly important in devices such as photovoltaic solar cells.

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