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$BaBiO_3$: A potential absorber for all-oxide photovoltaics

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ABSTRACT

$BaBiO_3$ is presented as a potential absorber for all-oxide solar cells. Thin-films of $BaBiO_3$ were deposited by pulsed laser deposition. As-deposited thin-films were amorphous, but a rapid thermal anneal at 600 °C for 10 min yields polycrystalline thin-films. X-ray photoelectron spectroscopy measurements show that deposited films have Barium in Ba^{+2} state and bismuth in both Bi^{+3} and Bi^{+5} state. UV–Vis spectrophotometer (UV–Vis) shows that $BaBiO_3$ films have direct and indirect bandgap (E_g) of 2.25 eV and 2.02 eV respectively, while ultraviolet photoelectron spectroscopy (UPS) shows that valence band maxima (E_V), conduction band minima (E_C) and work-function (ϕ) of $BaBiO_3$ is at 5.82 eV, 3.8 eV and 4.22 eV respectively. $BaBiO_3$ thin-film devices with a FTO/c-TiO_2/$BaBiO_3$/Au structure show rectifying current–voltage characteristics in dark. Under illumination, a photo response with a J_{light}/J_{dark} ratio of 1.75 is observed.

1. Introduction

Metal-oxide (MO) semiconductors are widely used in photovoltaic devices as transparent conducting oxides (TCO) [1] and carrier transport layers [2,3] but seldom as primary light absorbers [4,5]. In this report we present $BaBiO_3$ (BBO) a potential solar absorber for all-oxides thin-film solar cells. BBO is a well-known material used for high T_c superconductors like $BaK_{1-x}Bi_xO_3$ [6]. Theoretically BBO is predicted to be a metal, however experimentally BBO has been shown to be a semiconductor [7] with reported band-gap of 2.05 eV [8].

2. Experimental section

2.1. Synthesis of $BaBiO_3$

BBO was synthesized by solid state synthesis using $BaCO_3$ and Bi_2O_3. The precursors were grinded in a ball mill for 12 h followed by calcination at 850 °C for 4 hours in a tube furnace. Resulting BBO powder was pressed into a pellet of 5 mm diameter and sintered at 900 °C for 2 h.

2.2. Film deposition and device fabrication

The substrate was commercially sourced FTO-coated glass substrate (Techinstro; 7 ohm/sq.). On the FTO layer, a 40 nm thick compact-TiO_2 (c-TiO_2) was deposited by reactive sputtering using a Ti target. Thin-films of BBO were deposited by pulsed laser deposition (PLD) using a 248 nm Excimer laser in a custom-designed system (Supplementary Information). PLD deposition parameters are as given in Table 1. Diodes with FTO/c-TiO_2/BBO/Au structure were fabricated by depositing 100 nm of gold on top of BBO thin-film using e-beam evaporation (Fig. 3(c)).

3. Results and discussion

X-Ray diffraction (XRD) pattern of the BBO pellet was compared with JCPDF card #07-070-0652 (Fig. 1(a)). All peaks are accounted for, which confirms that the synthesized material is BBO. XRD pattern of as-deposited BBO thin-films show low-intensity peaks corresponding to the underlying FTO/TiO_2 substrate (SnO_2 and TiO_2) but no clear peaks of BBO, probably because as-deposited BBO films are amorphous. For devices, more crystalline films are desirable, so the as-deposited films were annealed for 10 min at 600 °C in O_2. M.S.M-Gonzalez et al have previously reported that high temperature anneals under an oxygen ambient lead to more crystalline BBO thin-films [9]. XRD pattern of annealed films shows

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Table 1
Deposition parameters for $BaBiO_3$ thin-films deposited using PLD.

Deposition Temperature (°C)	500
Base Pressure (mBar)	2×10^{-5}
Deposition Pressure (mBar)	0.1
Target-Substrate Distance (cm)	4
Laser Pulse Frequency (Hz)	5
Oxygen Flow (sccm)	0.55
Laser Energy (mJ)	100
Laser spot area (mm^2)	3

peaks corresponding to (1,1,0), (−1,1,2), (2,2,0) and (1,1,4) (Fig. 1 (b)). Scanning electron microscope (SEM) images (Fig. 1(c and d)) confirm that annealing increases the grain-size of the BBO films: from ~150 nm in the as-deposited film to ~400 nm for annealed films. Energy-dispersive X-ray spectroscopy (EDS) shows that the BBO films are stoichiometric, (Fig. 1(e)).

Reported first-principle band-calculations predict that BBO is metallic [10] but experiments have found BBO to be a semi-conductor [7]. To explain this discrepancy, charge disproportion in bismuth atoms is generally considered.

$$2Bi^{+4} = Bi^{+3} + Bi^{+5} \quad (1)$$

Due to the twin oxidation state, BBO is better represented as $Ba_2Bi^{+3}Bi^{+5}O_6$ [7]. X-ray Photoelectron spectroscopy (XPS) was used to investigate the oxidation states of barium and bismuth in films. To remove surface contamination, BBO films were etched in the XPS chamber using an Ar-ion gun for 100 s. XPS spectra show peaks at 780.3 eV and 795.5 eV, corresponding to Ba^{+2} 3d core levels (Fig. 2(a)). More crucially, peaks at 159.5 eV and 161.4 eV, corresponding to Bi^{+3} 4f and Bi^{+5} 4f, respectively, are observed. The separation between Bi^{+3} and Bi^{+5} peak is ~2 eV, which is larger than the 1 eV separation typically observed between Bi^{+3} 4f and Bi^{+4} 4f or Bi^{+4} 4f and Bi^{+5} 4f core levels. Similar observations have been reported for BBO films by Zalecki et al. [11] Overall, we can confidently state that the deposited films do not have Bi^{+4} impurities and are composed completely of as $Ba_2Bi^{+3}Bi^{+5}O_6$.

UV–Visible spectrophotometer was used to measure optical properties of 1 μm thick BBO films. The Tauc plot shows that BBO has both a direct and an indirect optical bandgap of 2.25 eV and 2.02 eV respectively (Fig. 2(b)), in line with previous reports [8]. Ultra-violet photoelectron spectroscopy was used to characterize band energy levels in BBO films. The UPS signal roll-over at the higher binding energy corresponds to the photoemission cut-off from which the work function (ϕ) of films can be extracted. UPS onset at the lower binding energy corresponds to electrons photo-emitted from the top of the filled states, from which the difference between Fermi level and valence band ($E_F - E_V$) can be extracted. For BBO thin-film the work-function and $E_F - E_V$ were 4.22 eV and 1.6 eV, respectively (Fig. 2(c)). Given the indirect optical bandgap of 2.02 eV, the absolute position of the valence-band maxima (E_V) and conduction-band minima (E_C) in BBO films is found to be at 5.82 eV and 3.8 eV, respectively, below the vacuum level.

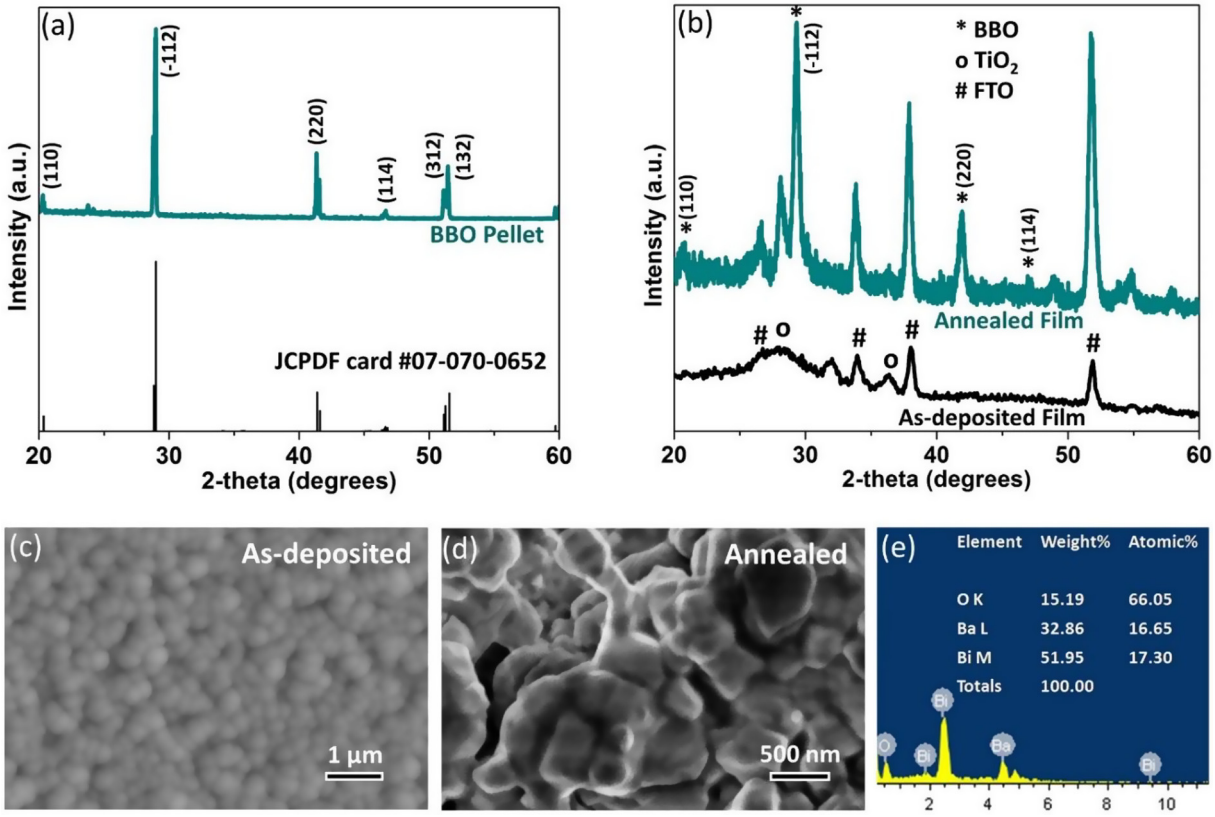

Fig. 1. (a) XRD pattern of phase pure BBO pellet. (b) XRD pattern of BBO thin-film deposited by PLD on TiO_2/FTO Stack, before and after annealing (c) SEM image of as-deposited thin-film (d) SEM image of annealed BBO thin-film (e) EDS spectra for annealed BBO thin-film, showing the expected stoichiometry.