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Current Perspectives

(110)-Textured Ca-doped $BiFeO_3$ film on refined Pt(111) electrode layer on glass substrate at reduced temperature

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ABSTRACT

Multiferroic and photovoltaic properties of polycrystalline $Bi_{0.85}Ca_{0.15}FeO_3$ (BCFO) film on refined Pt(111) electrode buffered glass substrate have been studied. Optimized Pt(111) electrode layer having large grain size and smooth morphology enables the development of highly (110)-textured BCFO film at a temperature as low as 450 °C. The prepared BCFO film has dense microstructure, fine grain size, and smooth surface morphology. Good ferroelectric properties with the remanent polarization ($2P_r$) of 108 μC/cm^2 and electrical coercive field of 405 kV/cm are achieved. Improved ferromagnetic properties with magnetization of 9.2 emu/cm^3 and coercivity of 1250 Oe are also attained. Significant PV properties with open-circuit photovoltage of 0.49 V and the short-circuit photocurrent of 67.4 μA/cm^2 at illumination intensity of 228 mW/cm^2 are observed, which are comparable to BCFO ceramics or BFO epitaxial films.

1. Introduction

$BiFeO_3$ (BFO) perovskite showing outstanding multiferroic (MF) properties at room temperature (RT) and significant photovoltaic (PV) effect under visible light illumination has attracted much attention due to their interesting physics and immense potential for new multifunctional applications [1–26]. High ferroelectric (FE) (Curie temperature ~810 °C) and magnetic (Neel temperature ~370 °C) transition temperatures allow the potential applications for magnetoelectric (ME) devices [4–7]. BFO has a G-type antiferromagnetic (AF) order with a spatially modulated spin structure, which results in very small net magnetization, leading to difficulties in manipulating the ME coupling in bulk form [8–9]. BFO also has significant PV effect originated from the narrower direct energy band gap of ~2.2–2.8 eV as comparing to other FE perovskite oxides [10–14]. This feature opens additional probabilities in the design of the optoelectronic and magneto-optical devices.

The substitution of different valence elements for Bi in BFO provskite phase is a pronounced way to control various physical properties [15–21]. The magnetization enhancement was found in A-doped BFO ceramics and films (A = Ca, Sr, Ba, and Pb) due to the suppressed spiral spin configuration of BFO [15–18]. Among the BFO ceramics with various substituents, $Bi_{1-x}Ca_xFeO_3$ (BCFO) was reported showing interesting structural, magnetic, and electrical evolutions and a significant PV effect [15–21]. It was also reported having a converse ME effect in bulk form [17]. Nevertheless, very low electrical remanent polarization ($2P_r$) of 1.6–8 μC/cm^2 is prohibitive for application. Although the investigation on BCFO ceramics is extensive, limited report on BCFO polycrystalline films is available [22].

However, MF properties including electrical polarization and endurance of BFO films highly depend on its crystal orientation [2,23–28]. Texture and formation temperature of perovskite phase are also sensitive to substrate and interface structure [23–28]. The optimized formation temperature for BFO films grown on single crystal substrates is around 650–700 °C [2,23–27]; in contrast, it is about 150 °C lower when a metal intermediate Pt layer was inserted [28]. In non-epitaxial polycrystalline BFO thin films, metal underlayer also lowered the formation temperature [29–31]. In this study, we report that high-quality (110)-textured BCFO film can be formed on a 20-nm-thick (111)-textured Pt underlayer on glass substrate by pulsed laser deposition (PLD) at reduced temperature of 450 °C. Structural, FE, magnetic, and PV characterizations of BCFO films are presented.

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2. Experiment

Bilayer sample of $Bi_{0.85}Ca_{0.15}FeO_3$/Pt(111) was prepared on Corning 1737 glass substrates. Firstly, a 20-nm-thick Pt bottom electrode was deposited at room temperature (RT) by rf magnetron sputtering. A rapid thermal process (RTA) at 450 °C was then followed for Pt(111) layer optimization. Subsequently, 200-nm-thick BCFO films were grown on Pt(111) buffer by PLD using a solid-state Nd:YAG laser with wavelength of 355 nm. The substrate temperature was 450 °C, the oxygen pressure was 25 mtorr, and the laser repetition rate was 2 Hz. $Bi_{0.85}Ca_{0.15}FeO_3$ target was prepared by the solid state reaction method, and the detailed process was described elsewhere [21]. The composition of the film was identified by a calibrated energy dispersive x-ray analysis and double checked by x-ray fluorescence analysis. Crystallographic structure was identified by x-ray diffractometry (XRD) with Cu K_α radiation. Surface morphology was observed by a scanning electron microscopy (SEM) and an atomic force microscopy (AFM). Magnetic properties at RT were measured by a vibration sample magnetometer. For electric property measurement, circular Pt top electrodes of 200 μm in diameter were sputtered onto the film surface using a shadow mask. The FE properties and leakage current at RT were measured by TF 2000 Analyzer (axiACCT Co.) ferroelectric test system. Before the photovoltaic measurement, the transparent conductive films of indium tin oxide (ITO) electrode with 100 nm in thickness were sputtered onto BFO films. A laser with wavelength of 405 nm was incident normal to the film surface for photo-excitation. No external electric field was applied previously or during the measurement. The details of the photovoltaic measurement were described elsewhere [21].

3. Results and discussion

Fig. 1(a) shows XRD patterns of 200-nm-thick BCFO film on Pt/glass substrate at 450 °C. Strong Pt(111) peak surrounded by Laue fringes is obtained, indicating that the underlayer has a strong (111) texture very flat surface. SEM and AFM analysis [Fig.1(b) and (c)] further confirm that the 20-nm-thick Pt layer has grain size in the range of 100–300 nm and small root-mean-square surface roughness (R) of 0.4 nm. Large and flat Pt(111) grain surface is beneficial for the following growth of BCFO film.

Besides, perovskite structure of the BCFO film with (110) texture is observed, and the diffraction peaks correspond to the

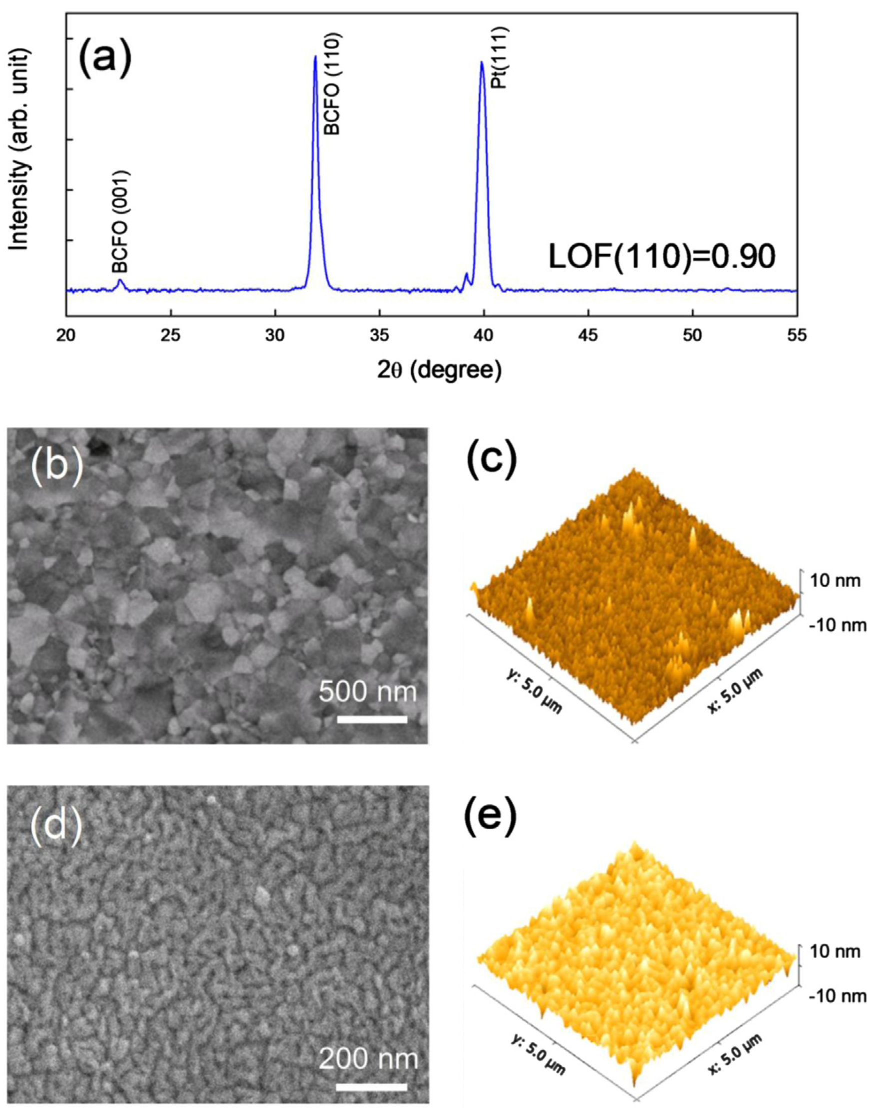

Fig. 1. (a) XRD pattern of BCFO film grown on 20-nm-thick Pt buffered glass substrates at 450 °C; (b) SEM image and (c) AFM image of Pt layer on glass substrates post-annealed at 450 °C; (d) SEM image and (e) AFM image of BCFO film.