Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Light controlled resistive switching and photovoltaic effects in ferroelectric $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ thin films

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ARTICLE INFO

Article history:
Received 21 April 2016
Received in revised form 6 September 2016
Accepted 16 September 2016
Available online xxx

Keywords:
Light controlled resistive switching
Photovoltaic effect
Ferroelectricity
(0.5BZT-0.5BCT) thin films

ABSTRACT

In this work, the structural and ferroelectric properties of $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (0.5BZT-0.5BCT) thin films deposited at different pulse repetition rates were studied. The films deposited at pulse repetition rate of 1 Hz display the optimum values of ferroelectric polarization and dielectric permittivity and are chosen for the investigation of resistive switching and photovoltaic studies. The Pt/0.5BZT-0.5BCT/ITO capacitors show the electroforming free resistive switching (RS) and is explained based on the polarization modulation of the Schottky barrier at the 0.5BZT-0.5BCT/ITO interface. Furthermore, it is shown that the RS ratio and switching voltage can be tuned with white light illumination. The capacitors display photovoltaic effect with the open circuit voltage ≈0.8 V and the short circuit current density ≈72.6 μAcm^{-2}. The photovoltaic efficiency is found to be ≈0.010% and is greater than that of other perovskite ferroelectric thin films. The underlying mechanism for enhanced RS and photovoltaic effects is highlighted.

1. Introduction

Ferroelectric materials are considered as promising candidates for resistive random access memories (RRAMs), photo-sensitive and energy-related devices, and other integrated technologies [1,2]. Resistive switching (RS), where the resistance can be modulated between the high resistance state (HRS) and low resistance state (LRS) by an external electric field, is the phenomenon behind RRAMs [1]. Recently, it is shown that light can be used as an additional parameter to control RS effect, and thus the resistance can be switched both by voltage pulse and light [3].

On another hand, the ferroelectric photovoltaic (PV) effect exhibits outstanding advantages over the conventional *p-n* junction based PV devices, such as high output voltage and polarization controlled PV response [4,5]. However, the photovoltaic efficiency of polycrystalline films is usually smaller than that of epitaxial films [2]. Besides, the ferroelectric polarization role on RS and PV effects is still under debate and devices concurrently taking advantages of both RS and PV characteristics constitute a modern research topic, since they show potential for light controlled non-volatile memory and energy related applications.

The most widely used ferroelectric materials are lead-based $Pb(Zr,Ti)O_3$ (PZT). However, lead is toxic and its use is legally restricted for many applications [6], thus much attention has been focused on the development of lead-free ferro/piezoelectric materials. In the past decade, great efforts have been made to identify high performance lead-free materials. Potassium sodium niobate $K_{1-x}Na_xNbO_3$ (KNN), bismuth sodium titanate $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) and $(K,Na)NbO_3$-$LiTaO_3$ (KNN-LT) have been subjected to studies [7–9]. However, the main drawback of these materials is the presence of highly volatile elements such as Bi, Na and K, which prevents them from possibly replacing PZT [10].

Recently, $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (0.5BZT-0.5BCT) ceramics are considered as the most promising materials due to their excellent ferro/piezoelectric properties similar to

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.011
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Please cite this article in press as: J.P.B. Silva, et al., Light controlled resistive switching and photovoltaic effects in ferroelectric $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ thin films, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.011

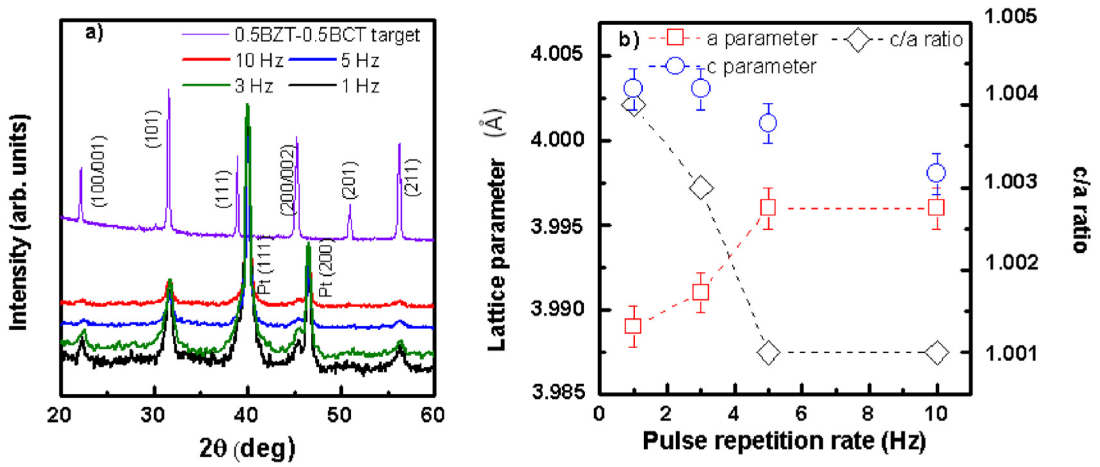

Fig. 1. (a) XRD patterns of the 0.5BZT-0.5BCT target and films deposited at different pulse repetition rates; (b) a and c lattice parameters, and *c/a* ratio as a function pulse repetition rate.

PZT system, owing to its morphotropic phase boundary (MPB) nature [6,11]. However, there are still limited reports regarding the fabrication of 0.5BZT–0.5BCT thin films and most of the reports focus on the ferroelectric and piezoelectric properties [12–15]. Also, there are no studies on light controlled resistive switching and photovoltaic characteristics of 0.5BZT–0.5BCT thin films.

In this work, we aim to study the light controlled resistive switching and photovoltaic characteristics of polycrystalline 0.5BZT-0.5BCT thin films grown on Pt/TiO_2/SiO_2/Si substrates using the pulsed laser deposition technique. In order to enhance those properties, the ferroelectric properties were optimized by depositing the 0.5BZT-0.5BCT thin films at different pulse repetition rates. The relation between the ferroelectric polarization and the RS and PV effects were investigated and the mechanisms underlying the both effects are highlighted.

2. Experimental procedure

0.5BZT-0.5BCT target was prepared by the solid state reaction as reported in Ref. [6] and has been used for the source of thin films. The corresponding films with a thickness of $\approx 300 \pm 10$ nm were grown at the different pulse repetition rates of 1, 3, 5 and 10 Hz on Pt/TiO_2/SiO_2/Si(100) at a temperature (T_s) of 750 °C by pulsed laser deposition. A 248 nm line of an excimer laser with energy of 300 mJ was focused on the target and all the films were grown in presence of an oxygen partial pressure of 0.1 mbar. After the deposition, the films were cooled down to room temperature in an oxygen partial pressure of 0.1 mbar. The x-ray diffraction (XRD) patterns were measured by Siemens D5000 powder diffractometer with monochromatized CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å) and the surface morphology of 0.5BZT-0.5BCT films was scanned with a commercial Multimode 8 Nanoscope Veeco AFM system in peak force tapping mode. Scanning electron microscopy (SEM) was performed using an Electroscan JSM-54 10 with an energy dispersive x-ray (EDS) detector Link ISIS 300. Photoluminescence (PL) spectra were recorded on a Spex Fluorolog spectrometer in front-face geometry in the spectral range of 475 – 600 nm under a 330 nm excitation from a xenon lamp. For the electrical characterization, indium tin oxide (ITO) electrodes with the diameter of 1 mm were deposited by ion-beam sputtering deposition (IBSD) technique on the upper surface of the 0.5BZT-0.5BCT films using a commercially available (Kurt J. Lesker, 99.99%) 90 wt% In_2O_3–10 wt% SnO (ITO) target. During the deposition, the substrate was kept at a temperature of 100 °C and the gas pressure inside the chamber was kept constant at 3.4×10^{-4} mbar. A gas flow of 7.7 ml/min of Ar + 0.3 ml/min of O_2 was introduced into the ion beam gun and the atoms were ionized in the ion source with RF-power of 50 W. Electrical properties of 0.5BZT-0.5BCT thin films were obtained by investigating the capacitors of Pt/0.5BZT-0.5BCT/ITO. The ferroelectric hysteresis loops (P-E) were measured with a modified Sawyer-Tower circuit using a sinusoidal signal at a frequency of 1 kHz. The capacitance–voltage (C–V) characteristics were measured using a precision LCR meter (Agilent E4980A) at an ac voltage of 50 mV, at a frequency of 100 kHz. The current-voltage (I–V) characteristics of ITO/0.5BZT-0.5BCT/Pt capacitors were measured using a Keithley 617 programmable electrometer in the dark and under white-light illumination. A 100 W halogen lamp was used as a light source.

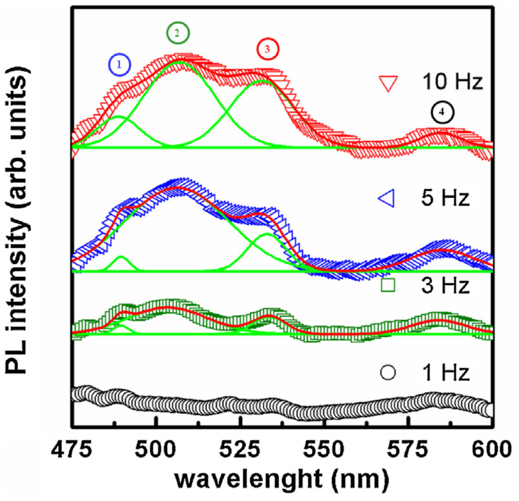

Fig. 2. PL spectra and de-convolution of peaks for the 0.5BZT-0.5BCT films deposited at different pulse repetition rates.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of 0.5BZT-0.5BCT films deposited at different pulse repetition rates, along with the XRD pattern of the used target. All the films show the reflections corresponding to 0.5BZT-0.5BCT polycrystalline perovskite phase, with no preferred orientation. No traces of possible secondary phases were found [13]. Crystallographic planes of the observed reflections were assigned according to JCPDS file n° 27–0530. Compared to the