Journal of Alloys and Compounds 509 (2011) 6561–6566

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

High tunability of pulsed laser deposited $Ba_{0.7}Sr_{0.3}TiO_3$ thin films on perovskite oxide electrode

R. Reshmi [a], A.S. Asha [a], P.S. Krishnaprasad [a], M.K. Jayaraj [a,*], M.T. Sebastian [b]

[a] Nanophotonic and Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi, Kerala 682022, India
[b] National Institute of Interdisciplinary Science and Technology, Thiruvananthapuram, Kerala 695019, India

ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form 16 February 2011
Accepted 16 February 2011
Available online 9 March 2011

PACS:
81.15Fg
77.55.fe
73.50.−h

Keywords:
Pulsed laser deposition
Ferroelectrics

ABSTRACT

Ferroelectric thin films such as BST, PZT and PLZT are extensively being studied for the fabrication of DRAMS since they have high dielectric constant. The large and reversible remnant polarization of these materials makes it attractive for nonvolatile ferroelectric RAM application. In this paper we report the characterization of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films grown by pulsed laser ablation on oxide electrodes. The structural and electrical properties of the fabricated devices were studied. Growth of crystalline BST films was observed on $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin film electrodes at relatively low substrate temperature compared to BST grown on PtSi substrates. Electrical characterization was carried out by fabricating PtSi/LSCO/BST/LSCO heterostructures. The leakage current of the heterostructure is studied and a band structure is modeled based on the transport properties of the heterostructure. The dielectric constant of the BST film is found to be 630 at 100 kHz with a loss tangent of 0.04. The capacitance voltage characteristics show high tunability for BST thin films.

1. Introduction

Ferroelectric oxide thin films with perovskite structure are of great technological interest. The tunable devices such as varactors, filters, oscillators, and phase shifters make use of the nonlinearity of the internal electrical polarization, of ferroelectric materials, steerable by an external electric field [1–4]. Compared to the popular tuning elements such as p–i–n diodes, GaAs Schottky diodes or ferromagnetics, ferroelectric components offer the advantages of continuous, quick, low power tunability up to gigahertz frequencies [5,6].

Barium strontium titanate ($Ba_xSr_{(1-x)}TiO_3$) (BST), an environment friendly lead-free ferroelectric material, is an attractive candidate for microelectronic devices and optoelectronic applications. The perovskite thin film of (Ba,Sr)TiO_3 (BST) exhibits high relative dielectric constant, low dielectric dissipation factor, low leakage current, and strong tunability under an external dc electric field. BST can be integrated to the existing semiconductor processing technology for next generation of gigabyte dynamic random access memories (DRAMs), microwave tunable devices, field effect transistors (FETs), and electrooptic devices [7–13].

For the ABO_3 perovskite, different A site and B site dopants (where A = Ca, Sr, La; B = Nb, Ta, Zr) are used to modify the electrical properties of $BaTiO_3$ based compositions [1–3,14]. $Ba_xSr_{(1-x)}TiO_3$ is the solid solution between barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$) and can be formed in the entire range of composition. The dielectric and ferroelectric properties of $Ba_xSr_{(1-x)}TiO_3$ depend on Sr content. At room temperature $Ba_xSr_{(1-x)}TiO_3$ is ferroelectric, for low Sr content, that is x is in the range of 0.7–1 and is paraelectric when x is in the range 0–0.7 [15]. As a result the electrical and optical properties of BST can be tailored over a broad range for various electronic applications [16].

Ferroelectric thin films have been successfully deposited by rf sputtering [17–19], metal organic chemical vapor deposition [17], sol gel [8,9,12,17] and pulsed laser deposition (PLD) [7,17,20–24]. Among these processes the PLD technique is superior since it possesses the advantages viz., lower synthesis temperature, easy to control the stoichiometry of thin films, possibility of depositing oxides of high melting point and materials of metastable phase [17].

Leakage current characteristics of BST films are influenced by the electrode and film electrode interface characteristics. Deposition conditions, composition and electrode structure play the most significant role in leakage current characteristics. Understanding the current transport mechanism is crucial and most of the knowledge is based on the transport across the interfacial potential barrier at the cathode when thermoionic emission, thermoionic field emission, or a combination of these is dominant. The leakage current

* Corresponding author. Tel.: +91 484 2577404.
E-mail address: mkj@cusat.ac.in (M.K. Jayaraj).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.02.074

density J increases with increasing temperature leading to the increased probability for the electrons to overcome or to tunnel the barrier either at the interface or in the bulk due to higher thermal energy [25].

The oxygen vacancies play an important role in perovskite ferroelectrics. Though the oxygen ambient is used to prevent the formation of oxygen vacancies in the deposited film, it has been shown that oxide films grown using PLD at high oxygen ambient pressure are still oxygen deficient [21,22,26,27]. The lattice of an O_2 deficient BST film expands beyond the size than that for the corresponding bulk ceramics [22,26,27]. One of the main technological challenges is to find a suitable electrode material with low electrical resistivity, good thermal stability, high resistance to oxidation and good adhesion both to substrate and the ferroelectric film. The interfacial defect layers may originate from accumulation of oxygen vacancies. Under the electric field oxygen vacancies migrate towards the electrode and aggregate near the electrode interface. The use of conducting oxide electrodes or aqueous solution electrodes helps to compensate the oxygen vacancies in the electrode–film interface [28] thereby inhibiting the accumulation of oxygen vacancies at the interface. As a result no interfacial defect layer is formed at ferroelectric–electrode interface [28]. Perovskite conducting oxide $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) is obtained from ABO_3 perovskite $LaCoO_3$ by partial substitution of La^{3+} by Sr^{2+} [29,30]. The crystal structure of LSCO is same as that of the perovskite ferroelectrics which makes it a potential candidate as electrode for ferroelectric memory devices. The LSCO which is a conductive oxide electrode act as oxygen vacancy sink for the BST capacitors thereby reducing the fatigue problem usually encountered while using conventional platinum electrode [7,31–35]. The similar crystal structure of LSCO and perovskite ferroelectrics facilitates the easy growth of ferroelectrics over textured or epitaxially grown LSCO layer [36,37].

Some problems of porosity and poor adhesion are often reported for BST films and very high temperature thermal treatment is generally required to achieve well-crystallized BST films. Such a high temperature process could limit drastically the application of these BST films in integrated circuits [5,16]. A low processing temperature is crucial for application of these thin film materials in integrated electronic devices. With an oxide buffer or electrode layer the deposition temperature can be reduced.

In this paper we report the study of the growth of ferroelectric (BST) $Ba_{0.7}Sr_{0.3}TiO_3$ films on $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) oxide electrode at relatively low temperature without any post deposition heat treatment. The electrical properties of the PtSi/LSCO/BST/LSCO structure were carried out and a band structure is proposed to explain the leakage current mechanisms. The multilayer oxide structure exhibits ferroelectric nature with a good remnant polarization and low coercive field.

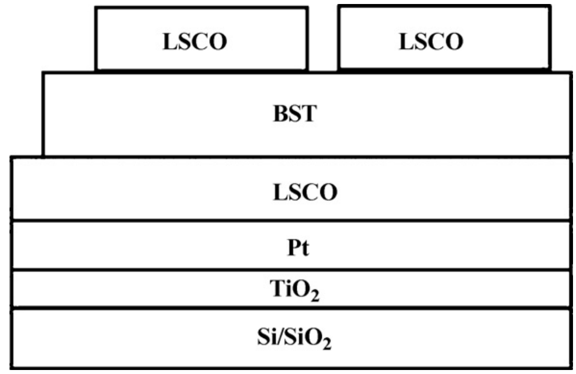

Fig. 1. Schematic diagram of the heterostructure used in the study.

2. Experimental

The target for PLD was prepared by solid state reaction of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$). The mixture was pressed and sintered at 1450 °C for 5 h to obtain $Ba_{0.7}Sr_{0.3}TiO_3$ (BST). The fourth harmonics of Q-switched Nd:YAG laser (266 nm) was used for ablation. The repetition frequency was 10 Hz with a pulse width of 6–7 ns. The laser fluence was kept at 2 J/cm^2. The target to substrate distance was kept at 3.5 cm. The substrate temperature (T_s) was kept at 500 °C and oxygen partial pressure in the chamber was maintained at 0.15 mbar.

The crystallinity of thin films was determined by X-ray diffraction (XRD, Rigaku DMax – C) with CuKα radiation (λ = 1.541 Å). The surface morphology was analysed by scanning electron microscope (SEM, JEOL JSM 5600). The composition was analysed using energy dispersive X-ray (EDX; JEOL JSM 5600). Thickness of the films was measured using Dektak 6M surface profiler. Electrical characterization was carried out using Keithly source measure unit SMU236. The dielectric constant was calculated from the capacitance measured with LCR meter (HP-4192A) by sweeping the voltage as well as the frequency.

Commercial Si/SiO_2/Pt wafers were used as the substrate for deposition. The structure of discrete capacitors is shown in Fig. 1. Both the top and bottom LSCO electrodes were deposited by rf magnetron sputtering. The sputtering power was kept at 100 W with an argon gas pressure of 0.003 mbar at 600 °C. The films were crystalline and had a thickness of about 400 nm. The resistivity of all the samples was of the order 10^{-5} Ω cm. The growth and characterization of LSCO thin films has been reported elsewhere [38].

3. Results and discussion

3.1. Structural and compositional analysis

The crystallinity of BST thin films deposited at substrate temperature of 500 °C and at a pressure of 0.15 mbar have been studied by X-ray diffraction. The XRD pattern of the heterostructure PtSi/LSCO/BST/LSCO is shown in Fig. 2a. The BST perovskite film was

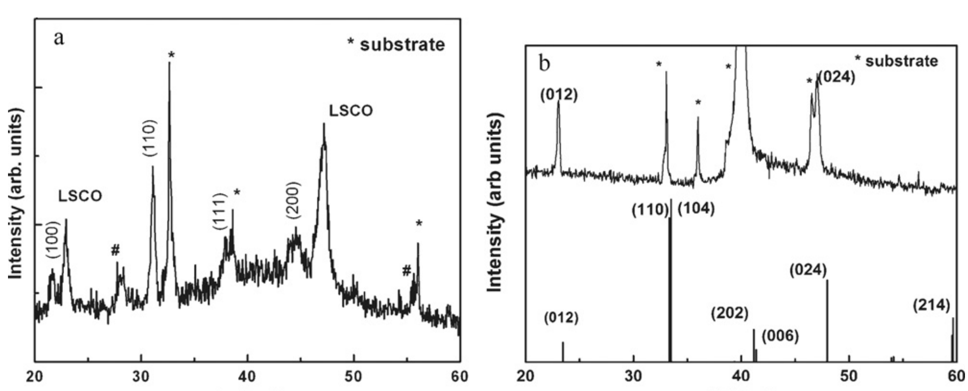

Fig. 2. (a) The XRD pattern of PtSi/LSCO/BST/LSCO grown at 500 °C at 0.15 mbar (# represents pyrochlore phases of BST). (b) The XRD pattern of PtSi/LSCO deposited by rf sputtering.