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Ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films on a conductive $Sr_4Ru_2O_9$ electrode obtained by pulsed laser deposition

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Abstract

Strontium ruthenate and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) layers were grown on Si(100) substrate using pulsed laser deposition technique. Starting from a Sr_2RuO_4 target, we obtained single phase films composed of $Sr_4Ru_2O_9$; on these strontium ruthenate electrodes, textured and non-textured BLT were grown at 700 °C. Structural characterizations of these double layers were done by X-ray diffraction, scanning electron microscopy, normal and high-resolution transmission electron microscopy. The Van der Pauw's resistivity measurements indicate that $Sr_4Ru_2O_9$ can be used as a back electrode. The temperature dependence of the resistivity at low temperatures is $\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/2}$, which corresponds to a variable-range hopping mechanism.

Keywords: Pulsed laser deposition; FeRAM; Ferroelectric thin films; $Bi_{3.25}La_{0.75}Ti_3O_{12}$; $Sr_4Ru_2O_9$; Electron microscopy

1. Introduction

Today, the main potential application field for ferroelectric thin films is the ferroelectric random access memory (FeRAM). Their ability to retain two polarization states forms the basis for memory or logic circuitry. Requirements for ferroelectric films used in FeRAM are mainly high remnant polarization and consistent polarization over many cycles of the applied electric field (ideally over 10^{12} cycles). The active material in commercial FeRAM is lead zirconate–titanate (PZT); PZT has a large polarization and is easy to synthesize, but degradation of its switching properties occurs after 10^6 to 10^8 cycles. Moreover, lead is an important pollutant. Thus, new materials are investigated in order to replace PZT. Lanthanum-substituted bismuth titanate, $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), has already shown interesting fatigue characteristics, over 10^{10} cycles [1–4]. From a structural point of view, the polarization axis should be perpendicular to the thin film plane, and the ferroelectric thin films should be built with crystallites as small as possible, in order to increase the density of polarization domains. Many attempts were already done in order to obtain thin films of BLT with a polarization axis perpendicular to the film [5,6]. Unfortunately, the polarization direction of BLT is not along the easy growth direction; one way to influence the crystallographic orientation of the BLT thin films would be to find an adequate substrate, like an oxide substrate. Furthermore, it has been shown for PZT ferroelectric films that mobile oxygen vacancies lead to domain pinning, hence to a weakened fatigue characteristic [7,8]. Using a conductive oxide substrate as back electrode could prevent this phenomenon, by supplying oxygen vacancies. Sr_2RuO_4 is already used as conductive electrode for superconducting devices. It was shown that crystals of this material have low metallic resistivity in the *a–b* plane, single crystals being even superconductors [9]. On the contrary, polycrystalline samples show a rather semi-conducting behaviour [10].

The Sr_2RuO_4 phase as a single crystal is not easy to obtain; it belongs to a Ruddelsen Popper series, and several phases exist, with small changes in the [Sr]/[Ru] ratio. More than that, another phase exists with the same [Sr]/[Ru] = 2 ratio, namely $Sr_4Ru_2O_9$. Several methods were used, in order to grow epitaxial thin films. Using pulsed laser deposition, thin films were successfully grown when low oxygen pressure and high substrate temperatures were used, typically 2.7×10^{-4} to $\times 10^{-1}$ Pa and 1000 °C, respectively. The use of lower substrate temperatures and higher

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oxygen partial pressures favours the $SrRuO_3$ phase [11]. Other parameters than substrate temperature and oxygen partial pressure may influence the deposition process: the wavelength of the laser, the energy density of the target, the distance between target and substrate. In this work, we present our attempts to grow a bilayer of BLT on Sr_2RuO_4, by pulsed laser deposition. For various deposition conditions, the obtained phases and the crystallographic orientations of the thin films, their microstructure, were investigated by X-ray diffraction analyses, scanning electron microscopy and transmission electron microscopy. The stoichiometry of thin films and targets were checked by energy dispersive spectroscopy (EDS). The conductive properties of the oxide substrate were studied by the Van der Pauw method.

2. Experimental procedure

2.1. Deposition procedure

The samples were obtained by pulsed laser deposition (PLD) techniques on a Si(100) substrate, roughly 1 cm^2. The Sr_2RuO_4 and BLT targets for PLD were prepared by conventional solid state reaction. For the Sr_2RuO_4 target, the starting powders $SrCO_3$ and RuO_2 were mixed with an excess of RuO_2, leading to a ratio [Sr]/[Ru]=1.95. The mixed powders were compacted and sintered at 1150 °C for 24 h. After grinding, the final pellet of Sr_2RuO_4 was compacted at 140 MPa and sintered at 1300 °C. For the BLT target, powders of La_2O_3, TiO_2 and Bi_2O_3 were mixed in a stoichiometric ratio. A solid state reaction was operated at 900 °C for 12 h, and the final pellet of BLT was sintered at 1000 °C for 2 h. X-ray diffraction diagrams confirm that the targets correspond to Sr_2RuO_4 and $Bi_{3.25}La_{0.75}Bi_3O_{12}$ phases.

An excimer laser (KrF, λ=248 nm, COMPex 301, Lambda Physik), working with a pulse duration of 30 ns was employed for deposition. The focused laser beam (size 2×5 mm^2) on the target had a fluency of 1.5 J cm^{-2}. The films were deposited in two oxygen partial pressures of 40 Pa (300 mTorr) and 7 Pa (50 mTorr) at 700 °C. Two repetition rates, 5 and 10 Hz, and two different number of laser pulses, 8000 and 12 000, were used. The distance between target and substrate was also changed from 65 mm to 45 mm. In order to observe the strontium ruthenate layer by SEM, one part of it was kept free of BLT.

2.2. Characterization methods

2.2.1. Structure and morphology

The crystallographic structures of the thin films, and of the targets, were investigated by X-ray diffraction and transmission electron microscopy. The microstructure and the morphology of the thin films were studied by electron microscopy. X-ray diffraction was performed on a D5000 Siemens–Bruker equipment operating with a Cu cathode (λ=0.15406 nm), a secondary monochromator, working in a classical θ–2θ mode. The diffraction pattern were recorded from 2θ=6° to 70°, with a 2θ step of 0.04°, 40 s per step. Although this equipment is not really suited for thin films, information about the phases and the texture of the films could be obtained.

Scanning electron microscopy images were obtained on a high-resolution JEOL JSM-6320F, operating at low tension, thus avoiding the usual gold or carbon coating of the thin films. The microstructural homogeneity, as well as the chemical composition of the deposited films, were investigated and the lateral sizes of the grains were measured.

Transmission electron microscopy observations were done on a Tecnai G2 operating at 200 kV, with a LaB_6 source. Images as well as diffractions patterns were recorded on a 1 k×1 k CCD camera. Cross sectional samples were prepared in a conventional way: two 2.5×6 mm^2 pieces were glued face to face, and put in a brass rod. The composite was sliced into 250-μm-thick slabs, which were mechanically thinned to 100 μm, dimpled on one face down to 20 μm. The ion milling was carried out at low angles +4° and − 6°; the tension used was 5 kV at the beginning, and was progressively decreased. A final clean up of the specimen was done at high angle (10°) and low tension (2 kV). TEM images as well as electron diffraction patterns were related to the chemical composition obtained by EDS.

2.2.2. Conductivity properties of the oxide substrate

The oxide substrate being a thin film, we used the well-known Van der Pauw method to determine the resistivity of the oxide substrate. Four silver paint electrodes were put on the thin film. The current was nearly continuous (frequency 7.5 Hz), several values were tested, but resistivity values did not significantly changed. Measurements were done with a tension

Table 1
For different $Bi_{3.25}La_{0.75}Ti_3O_{12}/Sr_4Ru_2O_9$/Si(100) bilayers, the PLD conditions are given, with the layer thicknesses, determined on cross-sectional TEM images, and the mean lateral grain sizes, determined on SEM images for both $Bi_{3.25}La_{0.75}Ti_3O_{12}$ and $Sr_4Ru_2O_9$

Label		Frequency (Hz)	Target–substrate distance (mm)	Number of pulses	Oxygen pressure (Pa)	Thickness, t (nm)	Lateral size (nm) [Size dispersion (nm)]
7	SR	5	65	8000	40	50	80 [20]
8	SR	5	65	12 000	40	120	75 [30]
	BLT	5	65	12 000	40	200	160 [40]
							70 [15]
9	SR	5	65	8000	7	190	95 [20]
	BLT	5	65	12 000	40	190	120 [30]
							60 [25]
10	SR	5	65	12 000	7	230	90 [20]
11	SR	5	45	12 000	40	1500	175 [45]
	BLT	10	45	12 000	40	1400	200 [65]

Size dispersions are indicated in brackets. In case of elongated grains, the length and the width of the grains are given.