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$La_{0.7}Sr_{0.3}MnO_3$ thin films on $Bi_4Ti_3O_{12}/CeO_2$/yttria-stabilised-zirconia buffered Si(0 0 1) substrates: Electrical, magnetic and 1/f noise properties

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Abstract

The remarkable electronic and magnetic properties of manganites have raised lot of interests for applications. Together with room temperature operation, depositing epitaxial films onto Si substrates is one of the main concerns for their future breakthrough. This paper presents the structural, magnetic and electrical properties of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films deposited on $Bi_4Ti_3O_{12}$ (BTO)/CeO_2/yttria-stabilised-zirconia (YSZ) buffered Si(0 0 1) substrates. A comprehensive X-ray diffraction study was performed in order to investigate the epitaxial quality. The temperature of maximum resistance and the Curie temperature was 390 and 350 K, respectively, for the 50 nm thick films. Preliminary low frequency noise measurements were performed. The normalized Hooge parameter was in the range 10^{-27} to 10^{-28} m^3, which make these films already competitive for uncooled bolometer applications, even if the noise is about one or two orders of magnitude higher than what we typically measured in the best LSMO films deposited on (0 0 1) $SrTiO_3$ substrates. LSMO films deposited on BTO/CeO_2/YSZ buffered silicon substrates were of overall good quality and suitable for use in device fabrication.

Keywords: Epitaxial growth; Buffer layers; Oxide; Silicon; Manganites

1. Introduction

Among rare-earth manganese oxides, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is attracting considerable interest because of its Curie temperature (T_C) above 300 K (namely 360 K), thus potentially leading to devices operated at room temperature [1,2]. In addition to their use in magnetic recording and related applications, their large change of the resistance at the metal-to-insulator transition make them promising materials for uncooled bolometers. A bolometer is a thermal detector, in which the temperature rise due to the absorption of heat from the surroundings causes a change in its resistance and consequently in the voltage across it. It typically consists of an absorber and a thermometer of heat capacity C, connected by a small thermal conductance G, to a heat sink held at a fixed temperature. The thermometer is therefore made of a material that ideally has a large change in resistivity for a small change in temperature, i.e. large temperature coefficient of the resistance (TCR), defined as the relative resistance derivative $(1/R) \times (dR/dT)$. The bolometer design also has to be optimized in order to lower G. The latter condition is fulfilled by the fabrication of membrane-type detectors. This can be technologically achieved by the widely used silicon micromachining techniques, and therefore requires the use of silicon substrates. More generally, depositing epitaxial LSMO films onto Si substrates is the first step towards their integration with conventional electronics.

Around 300 K, LSMO presents typical TCR values of about 0.02, which is of the order or even higher than those of actual materials used for the fabrication of uncooled resistive bolometers, such as amorphous semiconductors, polycrystalline SiGe, semiconducting $YBa_2Cu_3O_7$ (YBCO), VO_2 and VO_x [3,4]. In addition to large TCR, and low G, one also has to consider the intrinsic noise in the thin films since it obviously sets the limit to the device performances. This was detailed in our previous papers [5,6]. Continuous efforts have to be produced in order to fabricate thin films on silicon with high epitaxial quality and consequently to reduce the noise-to-signal ratio.

LSMO thin films have shown optimal properties when grown epitaxially on well lattice matched single crystal substrates, such as $SrTiO_3$ (STO), $LaAlO_3$ or $NdGaO_3$. The epitaxial growth of

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Table 1
Non-exhaustive list of possible buffer layers for the epitaxial growth of LSMO on silicon substrates

Material	Structure	Lattice parameter (nm)			δ with LSMO (%)
		a	*b*	*c*	
Si	Cubic	0.543			−0.7
YSZ	Cubic	0.514			−6.4
CeO_2	Cubic	0.542			−0.9
$Bi_4Ti_3O_{12}$ (BTO)	Orthorhombic	0.541	0.549	3.28	−1.1
$SrTiO_3$ (STO)	Cubic	0.3905 ($a\sqrt{2} = 0.552$)			0.9
$La_{0.7}Sr_{0.3}MnO_3$ (LSMO)	Pseudo-cubic	0.387 ($a\sqrt{2} = 0.547$)			0

$\delta = (a_{\text{Substrate}} - a_{\text{Film}})/a_{\text{Substrate}}$ is the lattice mismatch with LSMO.

LSMO (and many of the multicomponent oxides of interest) with silicon require big efforts, since three major problems occur:

(i) Chemical reaction between Si and LSMO.
(ii) Large difference in the thermal expansion coefficient between Si and LSMO (in the order of 2×10^{-6} to $10 \times 10^{-6}\,K^{-1}$, respectively).
(iii) Amorphous native oxide at the Si surface.

Buffer and template layers are therefore required, in order to achieve both diffusion barrier and lattice matching. Table 1 presents a non-exhaustive list of possible buffer layers for the epitaxial growth of LSMO. The smallest lattice mismatch $\delta = (a_{\text{Substrate}} - a_{\text{Film}})/a_{\text{Substrate}}$ is achieved by using STO or CeO_2. STO layers were grown epitaxially on Si(0 0 1) by McKee et al. using molecular beam epitaxy (MBE) with perfect control of the interface [7]. (0 0 1)-oriented STO films were also obtained on Si(0 0 1) by laser-MBE [8]. In contrast, polycrystalline or partly oriented STO films were obtained by other techniques, like metalorganic chemical deposition and magnetron sputtering [9,10].

A summary of literature data is given in Table 2. Like most of the groups we decided to use a standard pulsed laser deposition (PLD) chamber, which is an easier technique compared to molecular beam epitaxy (MBE) techniques. The latter enables to reach high vacuum (~10^{-8} mbar) and very high deposition temperatures (~850 °C), which is known as fundamental to treat the silicon surface but it is not suitable to meet the requirement of semiconductor industry indeed. Polycrystalline LSMO films were obtained if deposited on Si without buffer layer [11], on SiO_2/Si [12] or on YSZ (yttria-stabilised-zirconia)/Si [13]. Two sets of in-plane orientations were found in 1000 nm thick LSMO films deposited on YBCO/YSZ/Si [13]. Full in-plane epitaxy of LSMO was achieved on STO/Si [14,15] and YSZ-based buffer layers [16–20]. The best results (highest T_C, highest temperature of the maximal resistance T_P and lower resistivity) were obtained using $Bi_4Ti_3O_{12}$ (BTO)/CeO_2/YSZ/Si by Kim and co-workers [16–18].

YSZ is commonly used to start the epitaxial growth on silicon substrate, because its reducing properties can be used to remove the native amorphous oxide at the Si surface, without the need of ultra-high vacuum and particular etching of the Si substrate when adapted deposition conditions are used (low pressure in the first stage of growth) [21,22]. We therefore chose to optimize YSZ-based buffers and, in this paper, we will show our results for BTO/CeO_2/YSZ buffer layers, which will be named in the following BTO-based buffer layers. In Section 2 we will present the deposition conditions of BTO on CeO_2/YSZ buffer layers onto Si(0 0 1) substrates. Sections 3 and 4 will give the electrical, magnetic and 1/f noise properties of LSMO layers deposited onto the BTO-based buffer layers on silicon for various LSMO thicknesses.

2. Deposition conditions

Buffer and LSMO layers were deposited by PLD from stoichiometric targets onto Si(0 0 1) substrates. The PLD chamber is equipped with a multistage rotating carousel on which it is possible to mount up to five different targets. The base pressure is about 10^{-6} mbar and the maximum temperature reached by the radiative heater is 750 °C. For all materials the laser energy density was 1–2 J/cm^2 (250 mJ), the target-to-substrate distance was 50 mm, the beam frequency was fixed at 3 Hz, and the spot size on the target was 2 mm × 1 mm.

Table 2
Examples of literature data showing LSMO deposition on Si(0 0 1) using various buffer layers and deposition techniques

	Buffer materials	Deposition technique	T_C (K)	T_P (K)	ρ at 300 K (mΩ cm)
Liu et al. [11]	None	Spin coater	357	260	300
Bergenti et al. [12]	SiO_2	Pulsed plasma deposition	325	235	?
Goh et al. [13]	YBCO/YSZ	PLD	?	>300	0.9
	YSZ	PLD	?	230	3
Pradhan et al. [14,15]	$SrTiO_3$	PLD	330	335	2
Kim and co-workers [16–18]	BTO/CeO_2/YSZ	PLD	?	390	1.14
Fontcuberta et al. [19]	STO/CeO_2/YSZ	PLD	350	200	20
Trajanovic et al. [20]	BTO/YSZ	PLD	340	390	0.90

T_C is the Curie temperature, T_P is the temperature of the maximal resistance, and ρ is the resistivity of the LSMO layer.