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Ferroelectric and dielectric study of strontium tantalum based perovskite oxynitride films deposited by reactive rf magnetron sputtering

C. Le Paven[a,*], R. Benzerga[a], A. Ferri[b], D. Fasquelle[c], V. Laur[d], L. Le Gendre[a], F. Marlec[a], F. Tessier[e], F. Cheviré[e], R. Desfeux[b], S. Saitzek[b], X. Castel[a], A. Sharaiha[a]

[a] Institut d'Electronique et de Télécommunications de Rennes (IETR), Equipe Matériaux Fonctionnels, IUT Saint-Brieuc, Université de Rennes 1, F-22000 Saint Brieuc, France
[b] Unité de Catalyse et Chimie du Solide (UCCS), Université Artois, CNRS, Centrale Lille, ENSCL, Université Lille, F-62300 Lens, France
[c] Unité de Dynamique et Structure des Matériaux Moléculaires (UDSMM), Université du Littoral Côte d'Opale-Université de Lille 1, F-62100 Calais, France
[d] Laboratoire des Sciences et Techniques de l'Information, de la Communication et de la Connaissance (LABSTICC), Pôle Micro-ondes et Matériaux, Université de Bretagne Occidentale, F-29 000 Brest, France
[e] Institut des Sciences Chimiques de Rennes (ISCR), Equipe Verres et Céramiques, Université de Rennes 1, F-35000 Rennes, France

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ABSTRACT

Strontium and tantalum based oxynitride perovskite thin films were deposited by reactive magnetron sputtering. Epitaxial films deposited on Nb-$SrTiO_3$ substrates show smooth surfaces with roughness values from 1.5 to 3.6 nm for a thickness of films in the range 20–1600 nm. The samples are yellow with band gap values around 2.35 eV. Piezo-force microscopy characterization pointed out the local piezoelectric and ferroelectric behavior of the oxynitride perovskite films. In the low frequency range, the 1600 nm-thick film exhibits a permittivity of 175 at 10 kHz, with dielectric losses of 0.055. Permittivity is lowered in high frequencies with a value around 65 obtained on a 1520 nm-thick film deposited on MgO substrate, which is textured with a preferential c-axis orientation. No accordability of the permittivity was highlighted at a macroscopic scale. The moderate crystallographic strain evidenced in the 20 nm thin film does not induce a high permittivity.

1. Introduction

The perovskite oxynitride compounds have received much attention in recent years due to their original properties compared to their oxide parents. For example, the decrease of the band-gap consecutive of the nitrogen substitution for oxygen in the perovskite structure leads to an absorption in the visible domain, with potential applications as pigments [1,2] and visible photo-catalysts, for instance, in overall water splitting reactions [3]. Moreover, high permittivities have been reported. For the $SrTaO_2N$ compound, closest reported material for comparison with our results as explained hereafter, Kim et al. first reported a permittivity $\kappa = 2800$ @1 MHz,RT on 55% dense ceramics [4]. Zhang et al. confirmed this trend with $\kappa = 10000$ @1 MHz,RT on a 90% dense ceramic post-annealed in ammonia [5]. Recently, Sun et al. reported $\kappa = 355$ @1 MHz,RT for a 84% dense pellet densified with $SrCO_3$ and post annealed in ammonia [6]; no drastic change of permittivity was observed in the temperature range 20–160 °C. On thin films, data are dramatically scarce. Oka et al. reported a permittivity close to 2000 @10 kHz,RT for a 290 nm-thick epitaxial film [7]; no significant change was observed upon cooling the films down to 50 K and varying frequency from 20 Hz to 100 kHz. The high values of permittivity observed on perovskite oxynitrides are currently assigned to a possible local oxygen/nitrogen ordering with a cis-type configuration of the nitrogen atom in the MO_4N_2 octaedra (M: transition metal, lanthanide) [8,9]. A local ferroelectric behavior has been demonstrated on $SrTaO_2N$, as bulk [10] and thin films [7].

The aim of our research is to provide experimental data on the oxynitride perovskite compounds, especially on their dielectric and ferroelectric properties. Moreover, we are looking for high permittivity materials for integration in miniaturized/agile devices such as antennas. Given the great difficulty of densifying oxynitrides ceramics, our approach has turned to the synthesis

* Corresponding author.
E-mail address: claire.lepaven@univ-rennes1.fr (C. Le Paven).

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of these compounds in the form of thin films, as reported in other studies [11,12]. We have conducted research on $LaTiO_2N$ films deposited by reactive sputtering from oxynitride $LaTiO_2N$ [13] and oxide $La_2Ti_2O_7$ [14] targets. Recently, our interest has been focused on the deposition of films from the solid solution (1-x) $Sr_2Ta_2O_7$, $xLa_2Ti_2O_7$ [15]. The oxide precursors are both ferroelectric materials with Curie temperatures of −107 °C for $Sr_2Ta_2O_7$ [16] and 1500 °C for $La_2Ti_2O_7$ [17]. According to the results of Nanamatsu [16], it is expected that the $(Sr_{0.99}La_{0.01})_2(Ta_{0.99}Ti_{0.01})_2O_7$) oxide is ferroelectric with a Curie temperature close to room temperature. We have shown that in reactive $Ar + O_2 + N_2$ plasmas, oxide films are obtained for plasmas containing dioxygen and dinitrogen whereas oxynitride $(Sr_{0.99}La_{0.01})(Ta_{0.99}Ti_{0.01})O_2N$ (SLTTON) films are produced only in $Ar + N_2$ plasmas, that is without O_2 [18].

The purpose of the present contribution is to provide a complete dielectric and ferroelectric characterization of oxynitride SLTTON perovskite films. The first series of films is composed of oxynitride samples deposited on conducting Nb-doped $SrTiO_3$ substrates for the nanoscale Piezoelectric Force Microscopy (PFM) analysis and for the low frequency dielectric characterization using Metal Insulating Metal (MIM) structures. This series also concerns films with different thickness in order to evaluate the effect of a possible crystallographic strain on the dielectric properties of oxynitride films. The second series contains samples deposited on MgO substrates for the high frequency dielectric characterization, using metallic transmission lines and a resonant cavity.

2. Materials and methods

Film deposition was carried out using radio frequency (rf) reactive magnetron sputtering in a Plassys MP450S reactor using a homemade $(Sr_{0.99},La_{0.01})_2(Ta_{0.99},Ti_{0.01})_2O_7$ (SLTTO) target. This one, 75 mm in diameter, was obtained by uniaxial compaction of SLTTO powder under 80 MPa. The oxide powder was synthetized by solid state chemical route from stoichiometric amounts of $SrCO_3$, Ta_2O_5, La_2O_3 and TiO_2 heated under air at 1400 °C during 30 h. X-ray diffraction (XRD) analysis confirms the crystallization of the powder according to a $Sr_2Ta_2O_7$ analogue (see Supplementary data 1).

For the sputtering deposition, the plasma gas mixture contained 92.3 vol.% of argon and 7.7 vol.% of dinitrogen, with a total pressure $p_T = 40$ mTorr. The rf power was fixed at $P_{rf} = 90$ W (2.04 W/cm^2) with a target-substrate distance d = 5 cm. The substrate temperature was maintained at $T_S = 750$ °C. Before deposition, a pre-sputtering of the target was performed during 30 min under the reactive gas mixture. The films were cooled under the same gas mixture than deposition at 10°/min; no post-annealing was performed. Films of the present study were deposited using the same sputtering conditions, except the duration of depositions in order to access different thickness of samples. Two series of SLTTON samples were prepared: a first one for the Piezo-force microscopy measurements and for the dielectric characterization in the low frequency range, a second one for the dielectric characterization in the high frequency range.

The first series contains three films with thickness t = 20; 300; 1600 nm. There were deposited on conducting niobium doped (001) Nb:$SrTiO_3$ substrates, acting as bottom electrodes in the MIM structures. Twin films deposited on (001) MgO substrates have served for the UV–vis transmittance characterization of samples giving the band gap of materials, as well for the thickness measurement by scanning electronic microscopy (SEM). SLTTON films of the first series are named relatively to their thickness.

The second series contains two films of the same thickness (1520 nm) deposited on (001) MgO substrates for the high frequency dielectric characterization. SLTTON-Hf1 was measured as function of frequency using transmission lines, whereas SLTTON-Hf2 was used for the precise determination of the dielectric losses via a measurement at a fixed frequency in a resonant cavity. SLTTON-Hf2 is a special sample, divided in two

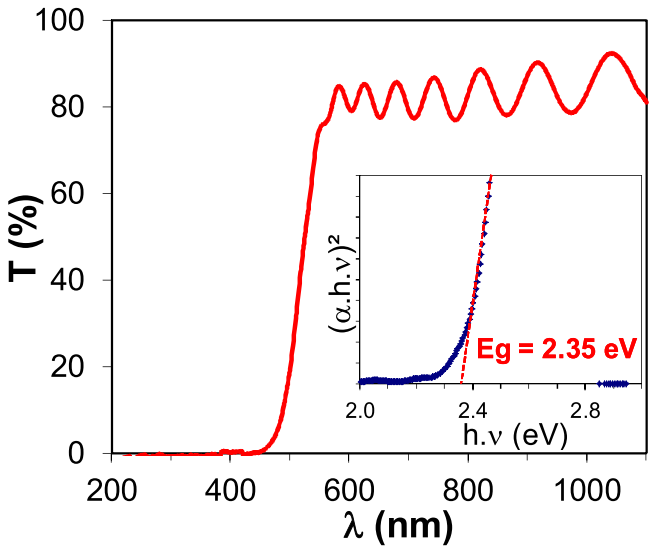

Fig. 1. UV–vis transmittance spectrum of the twin film (deposited on MgO substrate) of the SLTTON-1600 nm sample. The extrapolation, giving the band gap, is shown in insert.

Table 1
Characteristics of oxynitride SLTTON films deposited by reactive rf magnetron sputtering on conducting Nb doped $SrTiO_3$ and insulating MgO substrates depending on the measurement frequency range of the dielectric characterization.

Film	Substrate	Thickness (nm)	Band gap (eV)	10 kHz	
				κ	tanδ
SLTTON-1600 nm	Nb-STO	1600	2.35	175	0.015
SLTTON-300 nm		300	2.55	55	0.055
SLTTON-20 nm		20	2.05	30	0.040
				6.72 GHz	
SLTTON-Hf1	MgO	1520	2.25	65[a]	–
SLTTON-Hf2		1520	2.25	–	0.012[b]

[a] Transmission line.
[b] Resonant cavity.

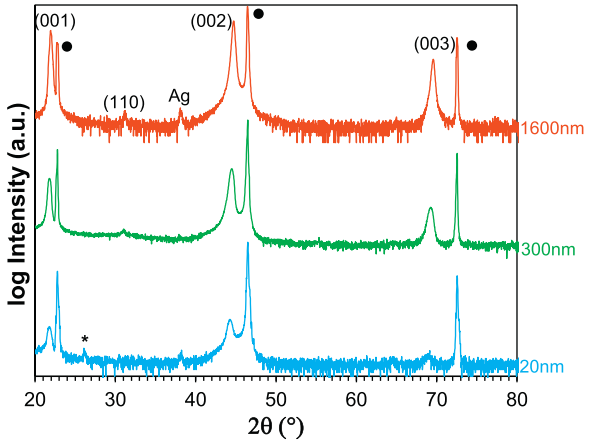

Fig. 2. θ–2θ diffractogramms of SLTTON films deposited on Nb-(001)$SrTiO_3$ substrates by reactive sputtering with different thickness. Indexation is made according to a pseudo-cubic cell of SLTTON, with (Ag) related to the metallization for MIM measurements, (●) to the substrate and (*) to the sample holder.

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