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Deposition and dielectric study as function of thickness of perovskite oxynitride $SrTaO_2N$ thin films elaborated by reactive sputtering

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ABSTRACT

The present study concerns the deposition of perovskite oxynitride $SrTaO_2N$ films and their dielectric characterization at low frequencies. Those radio frequency sputtered thin films have been obtained under a reactive plasma (92.3 vol.% Ar/7.7 vol.% N_2) for substrate temperatures ranging from 600 to 900 °C. As shown by X-rays diffraction and band-gap measurements, the deposition temperature (T_S) determines the film structure and leads to films with band-gap and cell volume approaching the ones of the $SrTaO_2N$ bulk material with increased T_S. The dielectric study has been performed on polycrystalline, textured and epitaxial $SrTaO_2N$ layers deposited on conductive niobium doped $SrTiO_3$ substrates and thickness of films ranging from 30 to 900 nm. The related permittivities vary from 66.5 to 90 (@10 kHz, room temperature). These low values do not point out an effect of the crystallographic strain of films, due to their thickness, on the permittivity values. The latter remains irrespective of the frequency up to 100 kHz and does not vary upon the application of an external DC voltage.

1. Introduction

The family of perovskite compounds contains numerous dielectric and ferroelectric materials suitable for integration in electronic and telecommunication devices. The wide variety of their compositions is the result of a broad range of cationic substitutions. In this way, the modulation of the formulation helps to adjust the electronic properties of the material, as for example for the ferroelectric $Ba_{1-x}Sr_xTiO_3$ (BST) having a Curie temperature shifting with the Ba/Sr ratio [1]. Perovskite oxynitride materials are obtained by cross-substitution of cations and anions [2], with the requirement of the electroneutrality of the compound. Several reports have underlined the original properties of the perovskite oxynitrides compared to their parent oxides. In particular, the AMO_2N materials (with M = Ti, Nb, Ta and A = lanthanide, alkaline or alkaline earth ions) present an absorption in the visible region, with potential use as pigment [3,4] and/or photocatalyst, for example in visible overall water splitting [5]. The anionic substitution also influences the electrical properties of the resulting structures. Some reports have emphasized high permittivity values of several thousands for this class of materials [6–8], as well as local ferroelectric behaviors [9,10]. To address these unusual properties, different structural models, based on a nitride anion ordering, have been proposed. Crystal structure refinement and first-principles calculations show that the stable cis-configuration of the nitrogen atoms in the MO_4N_2 octahedra [11,12] gives rise to a large tilting of the latter [13,14] inducing permanent polarizations and high permittivities. An alternative trans-type model has been recently exposed by Oka et al. on $SrTaO_2N$ thin films deposited by nitrogen-plasma-assisted laser ablation [9]. The alignment of the N atoms along the *c*-axis of films was assumed to be stabilized by the epitaxial growth of samples. The latter also gave rise to a tetragonal distortion of the perovskite cells, with high *c*/*a* ratios, as for example $c/a = 1.013$ for a 290 nm thick $SrTaO_2N$ film (with *c*, the out-of-plane axis parameter, and *a*, the in-plane axis parameter of films assuming a pseudo-cubic cell for the oxynitride compound) (on bulk, $c/a \approx 1.002$ [10]). This distortion was associated with very high permittivity values, for example $\kappa \sim 2000$ (@10 kHz, room temperature (RT)) for the 290 nm thick film.

The present article falls within the scope of the dielectric properties of oxynitride perovskite compounds since this is still an open debate whether or not these compounds have unusual properties. Our aim is to provide experimental data and compare them to the current models. The present work is based upon our experience on the reactive sputtering deposition of $LaTiO_2N$ [15,16] and $(Sr_{1-x}La_x)_2(Ta_{1-x}Ti_x)_2O_2N$ [17,18] oxynitride films. Here, our objective is to deposit $SrTaO_2N$ films and study the influence of their crystallographic strain on their permittivity. First part of the article is devoted to the optimization of the reactive sputtering deposition of $SrTaO_2N$ films by varying the substrate temperature; the second part presents the dielectric characterization at low frequencies of films of different thicknesses and so, different crystallographic strains.

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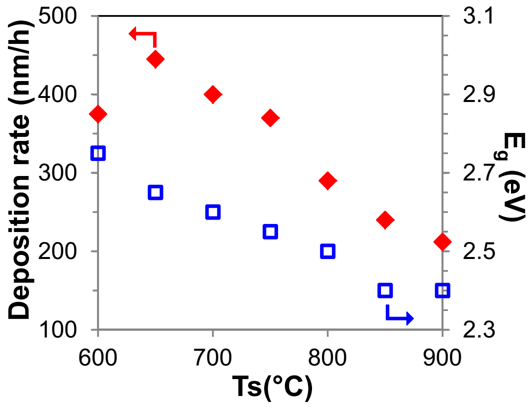

Fig. 1. Evolution as function of the substrate temperature (T_S) of the deposition rate and of the band gap (E_g) of $SrTaO_2N$ films deposited on MgO substrate by reactive sputtering.

2. Materials and methods

$SrTaO_2N$ films were synthesized by rf magnetron sputtering at high temperature using a reactive Ar + N_2 plasma gas. A 2 mm thick sputtering target was formed by cold pressing $Sr_2Ta_2O_7$ oxide powder, under 80 MPa, into a 75 mm-diameter disk. The powder material for the target has been synthesized by solid state route. Stoichiometric amounts of $SrCO_3$ and Ta_2O_5 were mixed in isopropanol in an agate mortar for 30 min and dried at 80 °C for 1 h. The sample was then pelletized, calcined at 1000 °C for 15 h, finely ground and further calcined at 1400 °C for 15 h. The powdered product was clearly identified as $Sr_2Ta_2O_7$ (orthorhombic, S.G. = Cmcm (no. 63) with $a = 3.947$ Å, $b = 27.193$ Å and $c = 5.690$ Å) by X-ray diffraction (XRD) in agreement with the JCPDS #70-0248 datasheet (see diffractogram in Supplementary Data 1).

The oxide target, located 5 cm from the substrate, was sputtered with an input power of 2.05 $W\cdot cm^{-2}$ (90 W). The chamber was pumped down to a base pressure of 10^{-5} Pa; during depositions, the dynamic pressure was maintained at 5.35 Pa. Depositions were performed at substrate temperatures (T_S) ranging from 600 to 900 °C, and the plasma nitrogen content (N_2 plasma vol.%) was set at 7.7%, the optimal condition leading to a stoichiometric oxynitride material, as determined in a previous study [17]. Deposition time was fixed at 135 min for the first series of films and adjusted to the required thickness for the second. Films were deposited on two types of single-crystal substrates obtained from Crystal GmbH (Berlin, Germany): MgO(001) and conductive niobium-doped (1.4 at.%) $SrTiO_3$(001) (Nb-$SrTiO_3$). The latter has been used as substrate and bottom electrode for the dielectric characterization. Both MgO and $SrTiO_3$ substrates have a small crystallographic mismatch with the $SrTaO_2N$ perovskite (respectively, −4.07 and +3.44%), promoting a textured or epitaxial growth of films.

X-ray diffraction patterns were obtained using a Seifert 3003 PTS diffractometer (Cu $K_{\alpha 1}$ radiation). Conventional θ–2θ patterns were recorded at 0.01° intervals with a 2 s count time at each step. In order to quantify the thin film orientation, the Lotgering factor (F_L) was used. This factor compares the orientation of a thin film versus a randomly oriented material (i.e. powder) and is able to vary from 0 for a non-oriented layer to 1 for a fully oriented layer. The Lotgering factor is calculated using the following relations, considering a (00l) orientation of films [19]:

$$\mathrm{F_L} = \frac{P_{001} - P_{0(001)}}{1 - P_{0(001)}} \text{ with } P_{(00l)} = \frac{\sum I_{(00l)}}{\sum I_{(hkl)}}$$

where (hkl) are used for all families of planes, I(00l) and I(hkl) are the intensities of the (00l) and (hkl) indexed peaks, respectively, and the subscript 0 is relative to the powder reference diffractogram (JCPDS data). φ-Scan measurements were also done at a tilt angle $\chi = 45°$, corresponding to the pseudo-cubic (110) plane of the oxynitride compound, in order to evaluate a possible epitaxial growth of films.

Additional X-ray diffraction analysis was performed using a SmartLab Rigaku diffractometer in an in-plane θ–θ configuration, available on this apparatus by the existence of a fifth axis of rotation of the goniometer that enables to rotate the detector in a plane parallel to the surface sample [20]. The use of a highly parallel linear X-ray beam after a CBO (Cross Beam Optics) mirror [21] and the possibility of adjusting a parallel slit collimator [20] allows to vary the horizontal divergence of the incident beam from 0.1° to 1° (angle α, with a critical angle of full

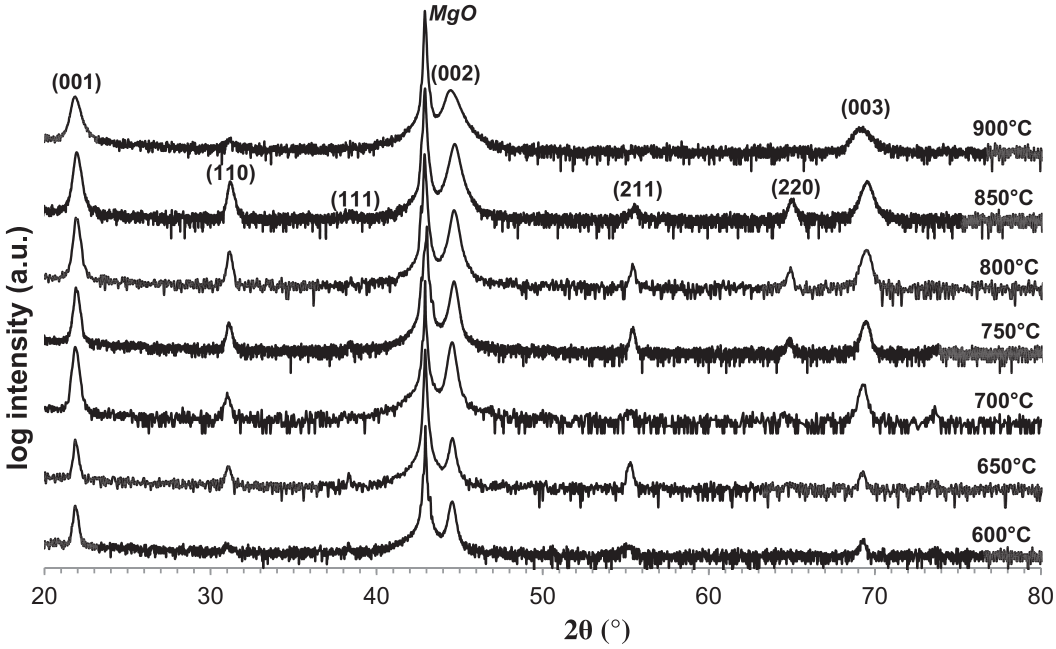

Fig. 2. θ–2θ diffractogramms of $SrTaO_2N$ films deposited on MgO(001) substrate by reactive sputtering at various substrate temperatures. Indexation is made according to a pseudo-cubic cell of $SrTaO_2N$.

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