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Lanthanum titanium oxynitride thin films

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Abstract. Using RF-magnetron sputtering, we grew $LaTiO_xN_y$ oxynitride thin films on (001) strontium titanate and glass substrates, starting from an homemade oxide target. The microwave dielectric properties of $La_2Ti_2O_7$ ceramic have been investigated in order to have a reference for further studies. The coatings were characterized using X-ray diffraction and scanning electron microscopy. Films deposited on perovskite oxide substrate in a reactive plasma (N_2, Ar) at 800°C present a textured structure and a smooth surface. A pre-study of laser etching of $LaTiO_xN_y$ material is also reported.

Introduction

In recent years, a considerable amount of research has been focused on the growth and the device fabrication of perovskite-type thin films because of their application into microelectronic as dielectric or ferroelectric materials for example. In many cases, their physical properties are determined by their cationic sublattice composition. That way, lead [1], lead-calcium [2] or strontium [3] lanthanum titanate can be understood as modifications of the initial $LaTiO_{3+x}$ oxide. The difficulty is then to ensure a good transfer of such cationic composition during the process of deposition.

Using a thin film approach can make the control of the electronic behaviour easier by doping the anionic sublattice. Thus, the nitrogen introduction in a reactive plasma can present a good improvement for electronic and especially microwave devices [4,5].

$LaTiO_{3+x}$ exhibits, depending on this x value, a semi-conducting, a ferroelectric or even a metallic behaviour. Controlling the composition by the O_2/Ar ratio during the sputtering, a multilayer thin film, including a metal-insulating transition directly integrated on a ferroelectric film, could be made [6,7].

Likewise, but depending on x and y values in the case of our $LaTiO_xN_y$ materials, semi-conducting, maybe even ferroelectric or Hi-ε_r dielectric properties are expected. We are also able to prepare different $LnTiO_2N$ targets (with Ln = La, Ce, Pr, Nd or $La_{1-x}Ba_x$) to adjust our materials electronic properties [8].

Our primary objective was to show the feasibility of such oxynitride thin films. In this article, we report our work on oxide powder synthesis, target sintering, thin films preparation, characterization and etching. Moreover, dielectric properties of bulk materials have been tested in order to get a comparison point for further analysis.

Experimental details

Powder synthesis. $La_2Ti_2O_7$ was prepared by molten salt synthesis [9]. La_2O_3 and TiO_2 precursors were mixed in a 1:2 ratio. A salt consisting of 50 mol% NaCl / 50 mol% KCl was then added, constituting 50 wt% of the total reaction mixture. The corresponding mixture was heated at 1000°C for 15 h. The resulting product was washed using distilled water and clearly identified, as $La_2Ti_2O_7$, by X-ray diffraction.

Target preparation. The sintering of the target was carried out by hot pressing (HP) in order to control the diameter of the ceramic part. Oxide sample was hot pressed under 15 MPa during 2 hours at 1200°C. Resulting pellet was polished in order to eliminate the boron nitride used as a lubricant in the preceding stage. A re-oxidation step (800°C – 10 hours – static air) led to the target of the requested dimension (∅ = 40 mm).

Dielectric properties measurement. Small dense oxide pellets (∅ = 3 mm) were prepared by pressure-less sintering at 1400°C for 3 hours under air. Gold-palladium electrodes were sputtered on either side of the sintered pellets. The following devices have been used : an HP4284A LCR bridge from 20 Hz to 1 MHz, an HP4291A LCR bridge from 1 MHz to 1.8 GHz and an ANRITSU 37369A vectorial analyser from 40 MHz to 40 GHz. We have made a specific support for the pellets which can be used with all our measurement systems.

Thin films deposition. Oxide $LaTiO_x$ and oxynitride $LaTiO_xN_y$ films have been deposited by reactive r.f. magnetron sputtering using the $La_2Ti_2O_7$ oxide target. Corning glass substrates were used for substrate temperature Ts < 600°C and single-crystalline (100) $SrTiO_3$ (STO) for Ts > 600°C. Prior to deposition, glass and single-crystalline substrates were cleaned, respectively, in dilute detergent at 60°C and in acetone, and dried by N_2 gas. In the sputtering apparatus, the substrate temperature (Ts) was measured by a thermocouple on the opposite side of the substrate holder. The base pressure in sputtering chamber was around 10^{-7} mbar.

Oxide films were deposited from the oxide target in pure argon, with a total pressure of 1.33 10^{-2} mbar. Depositions were made with Ts varying from 25 to 800°C. Oxynitride films were deposited from the oxide target in a reactive plasma made of argon and nitrogen. Rates were controlled by two mass flow meters. One set of films was made at Ts = 25 °C by varying the nitrogen ratio $R_N = P_{N2} / (P_{N2} + P_{Ar})$ where P_{N2} and P_{Ar} are the nitrogen and argon partial pressures. Total pressure was then comprised between 1.33 10^{-2} mbar and 2.40 10^{-2} mbar. Another set of films was made at R_N = 50% with the substrate temperature Ts varying from 25 to 800°C. Total pressure was 2.13 10^{-2} mbar. In all deposition, the power on the target was kept at 19 W. Deposition conditions are presented in table 1.

Etching. The laser workstation used (Optec S.A.) is equipped with an excimer laser (Lambda Physik LPX 240-I-cc). This XeCl laser provides near U.V. emission at 308 nm with pulse duration of 14 ns. An energy attenuator allows control of the fluence. Then, the laser beam lightens an adjustable square mask. A zoom projector focuses its image (600 x 600 μm^2) on the film that undergoes ablation at fluence of about 1.5 J/cm^2. Computer controlled x-y tables (Aerotech 2000) move the substrate under the lens so that the next pulse ablate a square spot, merging it in the former, and so on in order to obtain a line. Separate spots have been made too with a variation of the number of pulses. Overall positioning accuracy is 3 µm, with a travel range of 100 x 100 mm^2.

Characterization. Crystallization of targets and thin films was analysed by X-Ray diffraction using a Seiffert 3003 PTS diffractometer ($CuK\alpha_{1,}\alpha_2$).

Surface morphology characterization was made by Scanning Electron Microscopy (SEM) using a Jeol JSM-5600 apparatus with classical tungsten filament. To ensure a limitation in the charge effect, samples were coated with gold-palladium. Voltages of 5, 10 and 15 kV were used. External Everhart-Thornley detector was used for imaging. Cross-section observations were also performed at 2 kV to measure the film thickness. In this case, resolution is around 10 nm. In order to control the chemical composition of films, Energy Dispersive Spectrometry (EDS) was performed on an Oxford microprobe coupled to the Jeol SEM. Voltages of 10 and 20 kV were used. The analysis was semi-quantitative.

Table 1. Rf magnetron sputtering parameters

Films	Power [W]	Total pressure [mbar]	R_N [%]	*Ts [°C]*
Oxide	19	$1.33\ 10^{-2}$	0	*25*
				400
				600
				700
				800
Oxy-nitride	19	$1.33\ 10^{-2}$	10	*25*
		$1.47\ 10^{-2}$	20	
		$1.73\ 10^{-2}$	33	
		$1.87\ 10^{-2}$	42	
		$2.14\ 10^{-2}$	50	
		$2.40\ 10^{-2}$	56	
		$2.13\ 10^{-2}$	50	*25*
				200
				400
				600
				700
				800

Thermogravimetric analysis (TGA) were done on a SDT 2960 (TA Instruments) under static air at a heating rate of $7°C.min^{-1}$.

Results and discussion

Target. Due to the reducing character of the HP atmosphere (N_2, C), the oxide phase obtained at the end of the sintering is slightly non-stoichiometric. After polishing and crushing, its thermogravimetric analysis indicates a weight gain of 0.31 % resulting, at 800°C, to pure $La_2Ti_2O_7$ (Fig. 1). The non-stoichiometric oxide can be formulated : $LaTiO_{3.45}$. We verified by XRD and TGA on a sacrificed pellet that the long re-oxidation step at 800°C leads to an homogeneous and pure oxide target. This mechanically robust ceramic sample presents a quite low apparent density (65% of the theoretical density) that facilitates the re-oxidation stage.

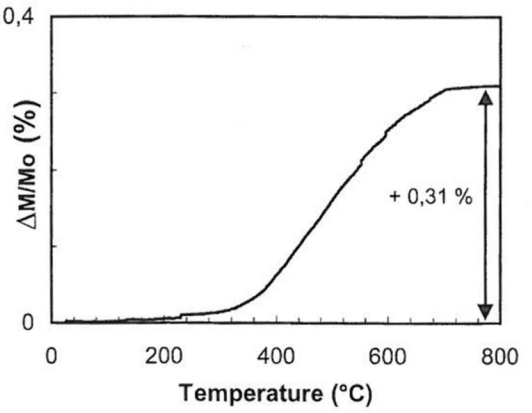

Fig.1 : TGA curve of the non-stoichiometric oxide obtained by hot-pressing.

Dielectric measurements. Fig. 2 shows the ε' permittivity versus frequency in the range 100 Hz - 10 GHz for the $La_2Ti_2O_7$ ceramic. The ε' value is about 57 up to 100 MHz at ambient temperature. This value is close to those seen in the literature and which lie between 45 and 54 [9,10]. This slight difference can be related to the density or to the grain size distribution of our ceramic part. The values obtained in the various ranges of measurement overlap correctly, which validates the procedures of calibration of the two bridges and of the analyser.

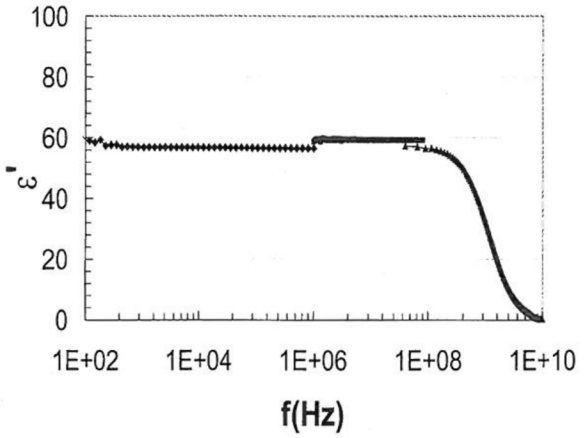

Fig. 2: ε' versus frequency in the range [100 Hz - 10 GHz] at 297K for the $La_2Ti_2O_7$ pellet.

From 200 MHz, a significant decrease of ε' is observed, which hints at the existence of a relaxation domain. The loss tangent is given in Fig. 3 where tgδ remains lower than 0.01 up to 40 MHz with intermediate values which are : 1.8 10^{-3} at 100 kHz and 2.75 10^{-3} at 10 MHz. The increase of the tgδ value starting from 10 MHz can be due to a relaxation domain.

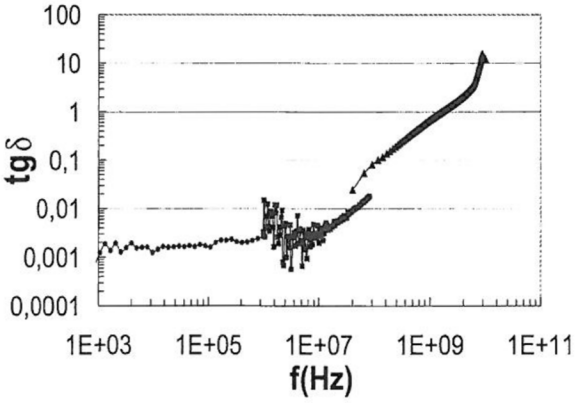

Fig. 3 : Tgδ versus frequency at 297 K for the $La_2Ti_2O_7$ pellet.

The shift between the curves resulting from the bridge of impedances and the analyser can be explained by an electrical contact of insufficient quality. To check the existence of a relaxation domain beyond 200 MHz, complementary measurements were carried out.

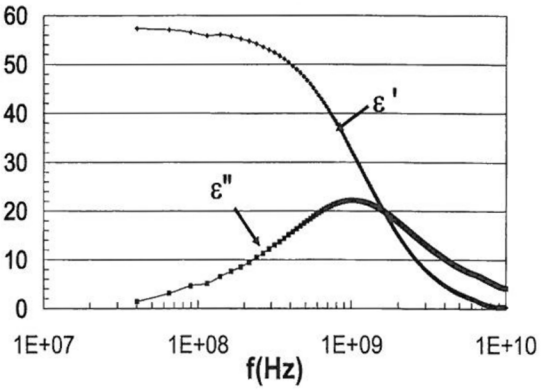

Fig. 4 : ε' and ε" versus frequency in the range [40MHz-10GHz] at 297K for the $La_2Ti_2O_7$ pellet.

The evolution of ε' and ε" in Fig. 4 confirms this dielectric relaxation with a critical frequency Fc = 1 GHz.

The results obtained are promising in the view of applications in electronics, in particular in microwaves on $La_2Ti_2O_7$ materials deposited in thin layers. Indeed, the results found in literature only treat relative permittivity extracted from the quality coefficient of a resonator and the resonance frequency. We did not see, to our knowledge, results of characterization with large frequency range on $La_2Ti_2O_7$ ceramics.

Thin films. The thickness of the films was measured using cross-section SEM observations. From these values, deposition rates were calculated : they were around 2 nm/min for the oxides and 1 nm/min for the oxynitrides. X-Ray analysis has shown that oxide and oxynitride films deposited at ambient substrate temperature are not crystallized (Fig. 5). SEM surface observation showed very smooth surfaces. For oxynitride films, depositions at ambient substrate temperature with increasing nitrogen content (0 – 56 %) have not lead to any modification in crystallization or surface morphology. When increasing the substrate temperature up to 800°C, no variation in crystallization was observed for the oxide films. Oxynitride films remained amorphous until Ts = 700°C (Fig. 6). At Ts = 800°C, on $SrTiO_3$ substrate, a peak at 2θ = 22.331(5)° was observed (indicated by

an arrow on Fig. 6). As such peak did not appear in oxide film deposited at same temperature, one can consider that this peak may mark the crystallization of the oxynitride compound. In this case, the peak could correspond to the (10-1) Miller plan of the triclinic $LaTiO_2N$ distorted perovkite [11]. It could also correspond to the (-210) orientation of a nitrided pyrochlore $La_2Ti_2O_{7-\varepsilon}N_\delta$ isotypical to $La_2Ti_2O_7$. Indeed, $La_2Ti_2O_7$ thin films obtained by pulsed-laser deposition on STO substrates at 970°C present such a shoulder peak at $2\theta = 21.148°$ [7] and are determined to be in the (-210) orientation of the $La_2Ti_2O_7$ layered perovskite. The shift in θ - 2θ position of the shoulder peak is correlated with the introduction of nitrogen into the film. Moreover, the higher-index peaks of the film are not seen for a scan aligned on axis with the STO substrate. This is consistent with the small crystallographic angle existing between the orientation of the film and the substrate.

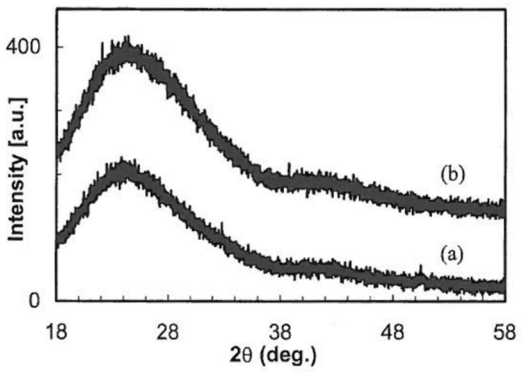

Fig.5 : θ - 2θ X-ray diffraction scans for films deposited on glass at room temperature with (curve a) or without (curve b) nitrogen.

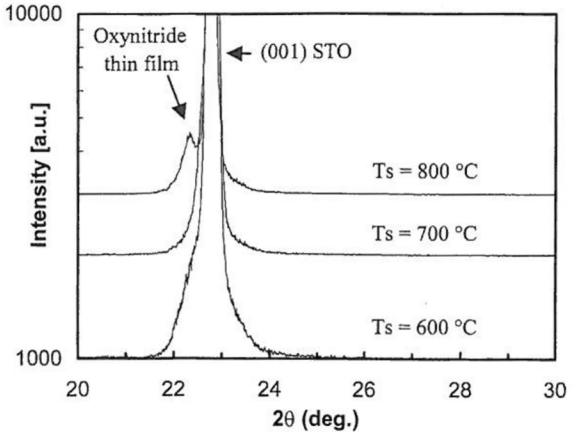

Fig.6 : θ - 2θ X-ray diffraction scans for oxynitride films deposited on (001) $SrTiO_3$ substrates using a reactive plasma (R_N = 50%) at 600, 700 or 800°C.

The SEM observation of the film deposited at Ts = 800°C showed smooth surface, with the existence of big white grains (Fig.7). The grains can reach several ten microns in dimension. Comparative semi-quantitative EDS analysis have been done on the surface and on the grains. Nitrogen is clearly present in both cases.

Since substrate is visible when analysing the thin surface of the film (thickness around 200 nm), no clear conclusion can be drawn as to the composition of the film surface. On the contrary, on micrometric big grains, results are more significant. They showed that the grains are close to the stoichiometric nitride ratios : on one hand, %at. N = 21.0 and %at O = 50.7, and on the other hand, %at Ti = 10.7 and %at. La = 11.5. Quantitative WDS spectrometry is now planned to clarify the overall composition.

With the moderate resolution of the SEM microscope used here, no conclusion can be drawn either, whether the film surface is actually smooth or not. The use of higher-resolution SEM or AFM has to be done. It could show that the film is composed of small nanometric grains. In this case, the crystallization, observed by X-Ray analysis, will concern the entire film.

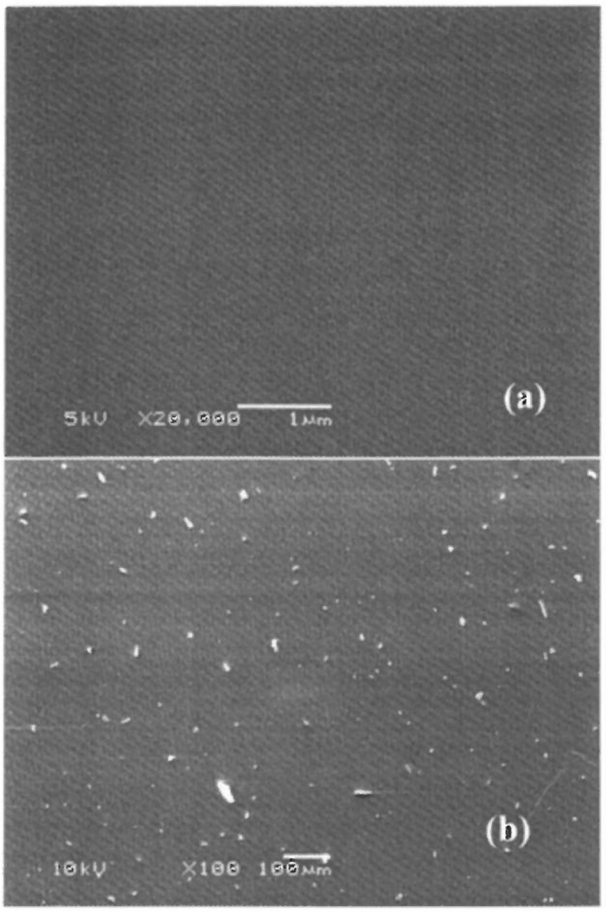

Fig.7 : SEM observation of the $LaTiO_xN_y$ film deposited at Ts = 800°C : (a) smooth film surface and (b) surface showing big grains.

Laser etching. In view of future application in microwaves, our films need to be etched. Since no chemical etching solution for the oxynitride $LaTiO_2N$ is known, physical etching has to be considered. Laser etching is now a reliable and efficient method for surface treatment and etching of thin films [12]. We have used such method and present here the preliminary results.

Square areas of the oxynitride film deposited at Ts = 600°C on glass have been etched. A general SEM view of plots can be seen in figure 8a. They distinguish from each other by the number of runs of the laser ablating beam. Whatever the number of pulses, we have observed two important facts. On the one hand, the surface of laser etched plots is extremely smooth and seems to have been melted. Even with one run, the oxynitride film seems to be ablated. With the fluence used here, a melt of the Corning glass substrate can be envisaged.

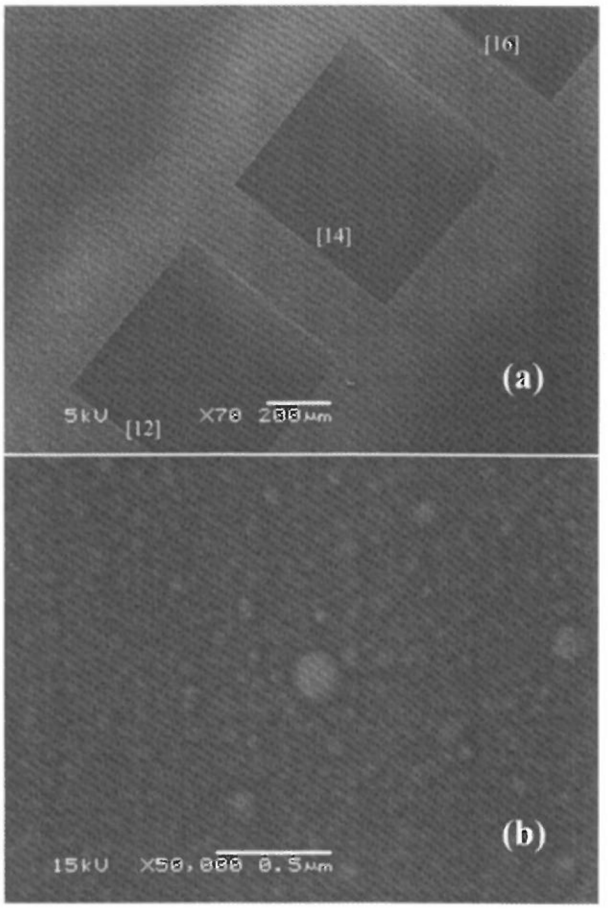

Fig.8 : SEM observation of the $LaTiO_xN_y$ film deposited at Ts = 600°C : (a) general view of the etched plots (number of pulses given in square brackets) and (b) recristallized area.

On the other hand, a contrast is seen between the white area surrounding the laser plots and the grey outer film. Local SEM observations have established that this contrast is a relief contrast. It is due to a recrystallization of the oxynitride film in the vicinity of the laser plot. On figure 8b, one can clearly see granular film. This has to be compared to the smooth surface observed on figure 4a for an as-deposited film. White particles are also observed. They can be attributed to melted material ejection consecutive to the laser ablation.

Conclusion

Lanthanum titanium oxynitride thin films were prepared by r.f. magnetron sputtering technique using a reactive plasma and an oxide target. According to the microwave dielectric measurements done on dense $La_2Ti_2O_7$ ceramic, electronic applications as capacitor are possible. The results of the structure analysis of $LaTiO_xN_y$ thin films indicate that the one deposited on strontium titanate substrate at 800°C is textured and presents a smooth surface. Possibility of laser etching of oxynitride films in view of their micro-machining has been shown.

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