



# Lanthanum titanium perovskite compound: Thin film deposition and high frequency dielectric characterization



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## ABSTRACT

Perovskite lanthanum titanium oxide thin films were deposited on (001) MgO, (001) LaAlO<sub>3</sub> and Pt(111)/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si substrates by RF magnetron sputtering, using a La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> homemade target sputtered under oxygen reactive plasma. The films deposited at 800 °C display a crystalline growth different than those reported on monoclinic ferroelectric La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films. X-ray photoelectron spectroscopy analysis shows the presence of titanium as Ti<sup>4+</sup> ions, with no trace of Ti<sup>3+</sup>, and provides a La/Ti ratio of 1.02. The depositions being performed from a La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> target under oxygen rich plasma, the same composition (La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) is proposed for the deposited films, with an unusual orthorhombic cell and Cmc<sub>21</sub> space group. The films have a textured growth on MgO and Pt/Si substrates, and are epitaxially grown on LaAlO<sub>3</sub> substrate. The dielectric characterization displays stable values of the dielectric constant and of the losses in the frequency range [0.1–20] GHz. No variation of the dielectric constant has been observed when a DC electric field up to 250 kV/cm was applied, which does not match a classical ferroelectric behavior at high frequencies and room temperature for the proposed La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> orthorhombic phase. At 10 GHz and room temperature, the dielectric constant of the obtained La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> films is  $\epsilon \sim 60$  and the losses are low ( $\tan\delta < 0.02$ ).

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## 1. Introduction

With a view to integrate functional materials in miniaturized agile microwave antennas, our interest was focused on the perovskite lanthanum titanium LaTiO<sub>3+δ</sub> oxides. They show a broad spectrum of electronic properties depending on their oxygen content (3 + δ), the latter being modulated by appropriate experimental conditions. The resultant Ti oxidation number imposes electronic properties shifting from metallic (LaTiO<sub>3</sub>, Ti<sup>3+</sup>) to semiconducting (LaTiO<sub>3.4</sub>, mixed Ti<sup>3+</sup>/Ti<sup>4+</sup>) and insulating (LaTiO<sub>3.5</sub>, Ti<sup>4+</sup>) materials [1]. La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (i.e. LaTiO<sub>3.5</sub>) is presented as piezoelectric [2] and ferroelectric with T<sub>C</sub> = 1461 °C [3,4]. This ferroelectric material has motivated our study because, used as a substrate for a planar antenna, it can change the antenna resonant frequency by the variation of its dielectric constant under the application of a DC electric field [5,6]. At room temperature, La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> crystallizes in a monoclinic cell with a P2<sub>1</sub> space group; a crystalline transition to an orthorhombic symmetry with Cmc<sub>21</sub> space group is reported at 780 °C [7]. The compound becomes paraelectric at T<sub>C</sub> and adopts an orthorhombic structure with a Cmc<sub>m</sub> space group [7].

The objective of this study was to synthesize the ferroelectric La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound. As detailed hereafter, our depositions lead to an

unusual lanthanum titanium perovskite oxide phase. This paper is dedicated to the study of this material: deposition by reactive magnetron sputtering and chemical, morphological, crystalline and high frequency dielectric characterizations. Phase identification will be proposed for the deposited films.

## 2. Experimental section

Thin film depositions were performed by radio frequency reactive magnetron sputtering (Plassys MP450S) using a homemade La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> target, prepared by molten salt synthesis [8]. X-ray diffraction confirmed that the powder was the La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound with a monoclinic cell, with a part of the powder remaining amorphous.

The films (noted LTO) were deposited with the same sputtering deposition conditions on different single crystalline substrates. The used substrates were (001) MgO, (001) LaAlO<sub>3</sub> and Pt(111)/TiO<sub>2</sub>/SiO<sub>2</sub>/(001)Si, heated at T<sub>S</sub> = 800 °C. The depositions were performed using reactive plasma composed of 75 vol.% Ar and 25 vol.% O<sub>2</sub>. The gases were introduced in the chamber after the base pressure had reached a value of 10<sup>-3</sup> Pa. During deposition, the total pressure was kept equal to 3.6 Pa. The input RF power on the target was 100 W (2.26 W/cm<sup>2</sup>). The substrate to target distance was fixed at 50 mm. After deposition, cooling was performed at 10 °C·min<sup>-1</sup> under the same gas mixture as

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used for the deposition. No post treatment of the films was made. Table 1 details the films studied in this work, their deposition conditions and characteristics.

UV–visible transmittance spectra were carried out by a Perkin-Elmer Lambda 20 spectrometer operating in the range 200–1100 nm. The band-gap of the material ( $E_g$ ) was extracted using the Kubelka–Munk formalism [9] considering a direct band gap for the lanthanum titanium deposited material; the error on the  $E_g$  value is estimated at 0.05 eV. Surface and cross-section observations were conducted using a JEOL 5440 Scanning Electron Microscope (SEM); error on thickness value is estimated as being 50 nm. The chemical composition of samples was determined by semi-quantitative Energy Dispersive Spectrometry (EDS) in a JEOL 5440 SEM operating at 10 kV and by X-ray Photoelectron Spectrometry (XPS) in an apparatus described in [10]. In the latter case, the samples were ex-situ coated by 5 nm of gold just after their deposition in order to protect them from too much contamination before analysis. X-ray diffraction (XRD) analyses were performed on a Seifert 3003 PTS diffractometer ( $\text{CuK}\alpha_1$  radiation).

The dielectric characteristics of LTO films were obtained in the frequency range [0.1–20] GHz in two ways. On insulating MgO substrate, the dielectric constant ( $\epsilon_r$ ) and dielectric losses ( $\tan\delta$ ) of the LTO film were extracted, using a conformal mapping method [11], from the measurement of the coefficients of reflection  $S_{11}$  and transmission  $S_{21}$  of a coplanar metallic transmission line performed upon the LTO sample. A coplanar resonator structure was used to investigate the variation of its resonant frequency under external DC electric field; this measurement was conducted to determine if the dielectric constant of the LTO film varied with DC bias. The transmission line and the resonator were obtained by standard photolithography and wet etching of a metallic layer (2  $\mu\text{m}$  Ag/5 nm Ti) deposited by sputtering on the LTO film. On platinized silicon substrate, a MIM (Metal–Insulator–Metal) capacitor structure was used, the bottom conducting electrode being the platinum layer and the top electrodes being formed of concentric silver metallic disks obtained by standard photolithography and wet etching. The MIM structure corresponds to two capacitances in series with a floating inferior electrode [12]; this structure could be DC biased. In both measures, a HP8510C network analyzer associated to a H100 Signatone probe station was used. A Keithley 2400 Source Meter provided DC electric fields.

### 3. Results and discussion

The LTO-1 sample, deposited on a two-side polished MgO substrate, is transparent, which is in accordance with its transmittance spectrum showing an absorption in the UV region (Fig. 1). The calculation gave a band-gap value  $E_g = 3.90$  eV, close to the published values for  $\text{La}_2\text{Ti}_2\text{O}_7$  (for example, 3.82 eV in [13]). The cross-section SEM observation gave a film thickness of 1200 nm. The EDS analysis gives a ratio La/Ti = 1.07 for LTO-1 film (La = 19.1 at.%, Ti = 17.9 at.%, O = 63.0 at.%) to be compared to the ratio La/Ti = 1 for  $\text{La}_2\text{Ti}_2\text{O}_7$  (La = 18.2 at.%, Ti = 18.2 at.%, O = 63.6 at.%). The EDS results showing a small deviation from stoichiometry, additional chemical composition analysis by XPS was performed on the LTO-2 film deposited on a (001)  $\text{LaAlO}_3$  substrate in the same conditions as the LTO-1 sample. Fig. 2 presents the XPS spectra related to the La(4p) and Ti(2p) contributions of this film compared to a reference which consists of the  $\text{La}_2\text{Ti}_2\text{O}_7$  synthesized

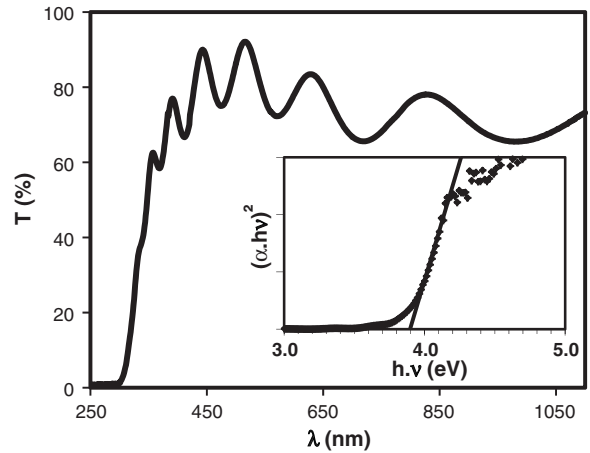


Fig. 1. UV–visible transmittance spectrum of the LTO-1 film deposited on (001) MgO substrate by reactive magnetron sputtering at  $T_s = 800$  °C and  $\%O_2 = 25$ . In the inset is plotted the  $(\alpha E)^2$  versus photoenergy for determining the direct band gap of the sample ( $\alpha$  is the absorption coefficient defined as  $\alpha = (1/t)\ln T$ , with  $t$ , the measured film thickness and  $T$ , the measured transmittance).

powder used to manufacture the sputtering target. The XPS shapes of the La peaks are nearly identical for the film and the reference; the same remark can be done for the Ti peaks. Indeed, considering a La/Ti ratio equal to 1 for the powder reference, the XPS analysis gives a ratio La/Ti = 1.02 for the LTO-2 sample. Moreover, the Ti 2p<sub>3/2</sub> peaks are both centered at 458.7 eV, characteristic of a  $\text{Ti}^{4+}$  contribution [14]. No trace of shoulder at lower values corresponding to  $\text{Ti}^{3+}$  ions can be observed. Remembering that the sputtering deposition was performed using a stoichiometric  $\text{La}_2\text{Ti}_2\text{O}_7$  target under oxygen reactive plasma, one can support that the present LTO films are fully oxidized. The sputtering yields of La and Ti atoms are similar (respectively, 0.57 and 0.52 for 400 eV energetic sputtering argon ions [15]), so that the La/Ti ratios close to 1 measured by XPS and EDS can be considered as valid. As a result, a  $\text{La}_2\text{Ti}_2\text{O}_7$  chemical composition is proposed for the films studied here.

The characterization by X-ray diffraction was conducted on the LTO-1 and LTO-2 films and on the LTO-3 sample deposited on a Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate. The  $\theta$ – $2\theta$  diffractograms of LTO-1 and LTO-2, presented in Fig. 3a, show intense peaks in addition to those of substrates; some peaks are similar for both films. The experimental  $2\theta$  film positions do not correspond to the listed values of the monoclinic  $\text{La}_2\text{Ti}_2\text{O}_7$  compound (JCPDS 81-1066). In fact, no match can be found with the  $\text{La}_2\text{Ti}_2\text{O}_7$  films studied in literature [16–18], in particular with monoclinic (012) oriented films deposited on (001)  $\text{SrTiO}_3$  substrates [19]. A valuable match could be found with the cubic  $\text{LaTiO}_3$  compound (JCPDS 75-0267), but its oxygen content and the conducting nature of the reported thin films [20,21], generally obtained under extremely low oxygen partial pressures, prevented us to identify the present LTO films as this material. In fact, the X-ray diffraction responses of LTO-1 and LTO-2 films match an unusual  $\text{La}_2\text{Ti}_2\text{O}_7$  phase with an orthorhombic cell and a Cmc2<sub>1</sub> space group as proposed by Ishizawa et al. [7] ( $a = 3.954$  Å,  $b = 5.607$  Å and  $c = 25.952$  Å). No JCPDS file exists for this phase, but one exists for the strontium tantalate analog, the orthorhombic  $\text{Sr}_2\text{Ta}_2\text{O}_7$  phase with Cmc2<sub>1</sub> space group (JCPDS 72-0921). From the latter file, all diffracted peaks of LTO-1 can be indexed (Fig. 3a), revealing that the peaks can be separated in two groups, corresponding, on one hand, to a (101) orientation and, on another hand, to a (022) orientation. The rocking-curves performed on the more intense peaks of each group (Fig. 3b) are broader than  $2^\circ$  which denotes a fairly high mosaic spread of the crystallites along the directions of orientation. Indeed, the mismatch of the proposed orthorhombic  $\text{La}_2\text{Ti}_2\text{O}_7$  phase with the cubic MgO substrate ( $a_{\text{MgO}} = 4.121$  Å) is 5.1% for the  $\langle 101 \rangle$  direction and 6.0% for the  $\langle 022 \rangle$  direction. These values are close to each other and explain the observed mixed

Table 1  
Deposition conditions and characteristics of LTO films deposited by reactive RF magnetron sputtering using a  $\text{La}_2\text{Ti}_2\text{O}_7$  target.

| Film  | Substrate                                 | RF power (W) | $T_s$ (°C) | Reactive gas      | Thickness (nm) | $\epsilon_r$ | $\tan\delta$ (10 GHz) |
|-------|---|--------------|------------|-------------------|----------------|--------------|-----------------------|
| LTO-1 | MgO                                       | 100          | 800        | 25%O <sub>2</sub> | 1200           | 59           | 0.021                 |
| LTO-2 | LaAlO <sub>3</sub>                        |              |            |                   | 560            | –            | –                     |
| LTO-3 | Pt/TiO <sub>2</sub> /SiO <sub>2</sub> /Si |              |            |                   | 800            | 62           | 0.011                 |

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