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$Pb(Zr_{0.6},Ti_{0.4})O_3$ (PZT) thin films are grown *in situ* on $LaAlO_3$ substrates by rf magnetron sputtering. The relationship between structural and optical properties is investigated as a function of growth temperature. The ferroelectric films exhibit satisfying crystallization with epitaxial growth from 475 °C. The optical refractive index value is 2.558, in agreement with the bulk value. The films show homogeneous structure and the squarelike shape of the index profile along with the PZT thickness suggests a good interface quality with the substrate. The crystallographic and optical properties measured on our films tend to demonstrate the suitability of *in situ* grown PZT films for optical applications. [DOI: 10.1063/1.1610776]

I. INTRODUCTION

$Pb(Zr_x,Ti_{1-x})O_3$ (PZT) thin films have attracted very much attention due to their high optical index values making them serious candidates for optical applications. In particular, they can be used as waveguides for integrated devices.[1–4]

However, it is now well established that the properties of ferroelectric films are very sensitive both to composition and crystallographic orientation of the films.[5–10] Preparation of PZT thin films suitable for optical waveguiding requires epitaxial growth, high crystalline properties, low surface roughness, and high optical index. Moreover, for a further integration of the optical device, it is preferable to perform growth of the PZT layer at the lowest temperature in order to avoid the interdiffusion mechanism and also the degradation of the neighboring semiconductor layers. For compositions close to the transition between tetragonal and rhomboedral PZT phases, a large dielectric constant and electro-optic coefficients are expected.[11]

The very low refractive index (2.2) of the transparent crystal $LaAlO_3$ (LAO) is essentially favorable for use as a substrate for waveguiding applications. Moreover LAO can be deposited by pulsed laser deposition on Si substrate to serve as an antidiffusion barrier layer and to improve the crystallization of PZT films.[12] Only few works investigate the relationship between both structural and optical characteristics of epitaxial PZT films and growth conditions.[7,11,13–17] Moreover, none of them has been dedicated to PZT growth on LAO substrate. These articles were indeed mainly related to PZT deposition on STO substrate. Also, because the physical properties of PZT films (optical indices, polarization, dielectric constant, etc.) are strongly dependent on the growth temperature, it appears necessary to investigate the optical properties of PZT films as a function of this parameter.

In this article, we report on the influence of deposition temperature on the crystallographic and optical properties of $PbZr_{0.6}Ti_{0.4}O_3$ thin films grown *in situ* on $LaAlO_3$ substrates by rf sputtering.

II. EXPERIMENT

A. Preparation of the PZT films

PZT thin films were grown at different temperatures on single crystalline $LaAlO_3(001)$ substrates by rf magnetron sputtering. The depositions were performed by sputtering a $Pb_{1.1}Zr_{0.6}Ti_{0.4}O_3$ ceramic target with a Pb powder excess of 10% in order to compensate for the Pb deficiency in the films. The target was mounted on a magnetron cathode whose rf power density was kept at 10 W/cm^2. The substrate temperature was changed from 400 °C to 550 °C and the sputtering gas was composed of a mixture of 95% of argon and 5% of oxygen. The total gas pressure was adjusted in order to obtain stoichiometric films in all cases. The films thickness was 500 nm, as determined with a Dektak profilometer. The sputtering conditions are summarized in Table I.

B. Structural and optical characterization

The composition of the films was checked by energy dispersive x-ray analysis. Their crystalline quality and crystallographic orientations were investigated by x-ray diffraction (XRD) analysis using a Philips four-circle diffractometer with a monochromated Cu $K\alpha$ radiation. The lattice parameters were determined from x-ray diffractograms and the epitaxial growth was established from pole figure measurements. Their surface morphology was investigated by atomic force microscopy (AFM).

The optical waveguiding properties were examined by a prism coupling method using a 632.8 nm laser beam.[18–20]

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TABLE I. PZT sputtering conditions.

Sputtering condition	PZT thin films
rf power density	10 W/cm^2
Substrate temperature	400–550 °C
Sputtering gas	$O_2/(Ar+O_2)=0.05$
Gas pressure	0.45–0.65 Pa
Substrate	$LaAlO_3(001)$
Target	$Pb_{1.1}Zr_{0.6}Ti_{0.4}O_3$
Target size	1 in. diameter
Thickness of the film	500 nm

The optical beam was injected in the PZT films though a rutile prism, which is pressed against the film surface. Each optical guide mode propagating inside the film is observed as a dark line on the laser beam reflected by the prism. One, therefore, obtains a guided mode spectrum with successive minima when the incident angle is swept. The optical indices of the films can be estimated from the *m*-lines spectroscopy.

III. RESULTS

A. Structural and crystallographic properties

The PZT films were crystallized with the conditions summarized in Table I. The θ–2θ XRD pattern of a PZT film grown at 500 °C on LAO(001) substrate is shown in Fig. 1. Only the (001) and (002) lines of the perovskite are visible and revealed that the film grew along the *c* axis. The lattice mismatch *M*, given by $(a_s-a_f)/a_s$, where a_s and a_f are the lattice parameters in the plane of the substrate and of the film, respectively, was about −5%. In order to check for the possible presence of *a*-axis oriented grains in the PZT film, ω-scans were performed for different values of the χ angle since it is known that the *a* domains may be tilted from the *c*-axis direction.[7,14,21,22] No peak was found, indicating that the grains fully crystallized into the *c*-axis orientation. The *c* parameter was calculated from the (001) line and the full width at half maximum (FWHM) was systematically measured to check for the crystalline quality.

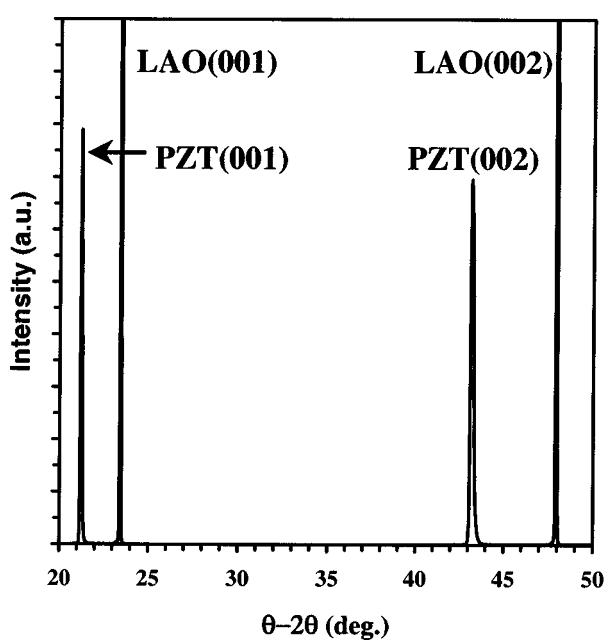

FIG. 1. XRD pattern of the PZT thin film crystallized *in situ* at 500 °C.

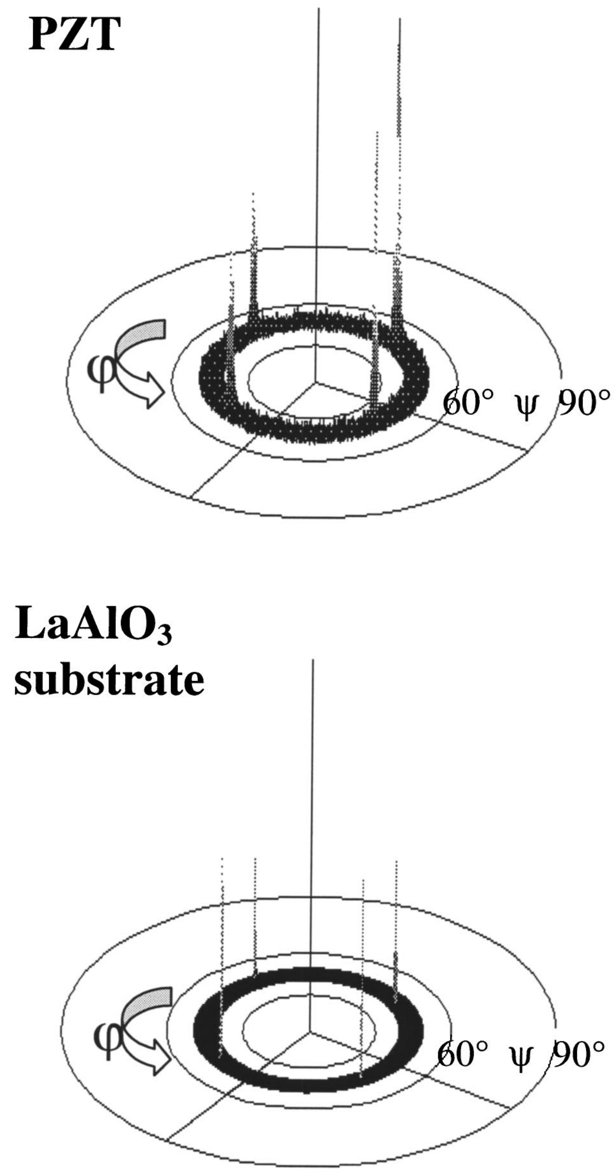

FIG. 2. Pole figures measured on LAO substrate and PZT thin film crystallized *in situ* at 500 °C.

For studying the effect of the substrate temperature on the crystallographic and optical properties, different PZT samples were prepared. For substrate temperatures lower than 400 °C, the perovskite phase did not crystallize as observed on the XRD patterns. For temperatures larger than 550 °C, the Pb content in the film rapidly decreased despite an increase of the sputtering gas pressure. As a consequence, it was not possible to grow PZT without pyrochlore phases beyond 550 °C with our PZT target.

In order to investigate the epitaxial growth of the films on LAO substrates, pole figures of the (101) planes of the *c*-axis oriented PZT grains and of the LAO substrate were recorded. A typical result is presented in the Fig. 2 for a PZT deposition carried out at 500 °C. The Bragg conditions for the PZT (101) and the LAO (101) planes gave for the 2θ

angles, 30.74° and 33.41° respectively. The ϕ scans showed four peaks separated by 90° for PZT and LAO reflections clearly revealing the epitaxial growth of the PZT film. The FWHM of the ϕ lines were 1.1°. Pole figure measurements performed on all the PZT films grown at temperatures ranging from 400 °C to 550 °C indicated that the samples crystallized *in situ* with an epitaxial *c*-axis microstructure. We have previously reported *in situ* epitaxial growth of PZT films on MgO/Pt substrates in the same temperature range.[23]

The crystallographic parameters extracted from XRD measurements are summarized in Figs. 3(a)–3(c). The parameter a was calculated from the 2θ value of the (101) line. Although the PZT films should present a rhombohedral phase, as in bulk, because of their composition, their structure appeared to be tetragonal since the values of a and c parameters were different [see Fig. 3(a)]. Moreover, the [100] and [001] axes were separated by an angle of 90° and the lattice constants deviated from the rhombohedral bulk values.[7] In our case, the morphotropic phase boundary (MPB) seems, therefore, to be shifted toward compositions with Zr-rich content. These changes may arise from epitaxial strains likely to occur in our films and which result from the lattice mismatch between the film and the substrate at the initial stage of the perovskite growth.[24] Since the lattice parameter of the LAO substrate is smaller than the PZT one, one may expect that *c*-axis epitaxial growth of PZT required the lattice to compress in plane. As just mentioned, no *a*-axis oriented grains were found in spite of the thermal expansion mismatch between PZT and LAO. Consequently, the decrease of the a parameter in plane may be sufficient to make the perovskite grow with a tetragonal structure with an increase of the c parameter because the composition of the PZT films is close to the MPB. In the same way, Zhao *et al.*[25] obtained ferroelectric $BaTiO_3$ thin films grown on $SrTiO_3$ substrates with lattices parameters and tetragonality c/a larger than the bulk values.

Also revealed by Fig. 3(a) is a gradual increase of the c parameter and a gradual decrease of the a parameter when the substrate temperature is increased. However, from 475 °C, the values of c and a parameters remained almost constant with $c = 0.418$ nm and $a = 0.399$ nm. Figure 3(b) shows the change in the tetragonality c/a as a function of the substrate temperature. A constant c/a of 1.048 was obtained for temperatures above 475 °C, indicating that the perovskite reached a stable structure. Figure 3(c) displays the FWHM values of the (001) lines, determined from the ω-rocking curves, as a function of the deposition temperature. Beyond 475 °C, the FWHM exhibited values nearly constant and inferior to 0.3° with the best value of 0.23° achieved at 500 °C. These FWHM magnitudes indicated that the films expanded with a very good alignment of the grains along the c axis of the film. The high crystalline quality of these PZT films may probably be related to their structural properties since the changes in the FWHM values closely follow those of both the lattice constants and the tetragonality c/a. Last, the surface of the PZT film crystallized at 500 °C was studied by AFM: The root mean square surface roughness values recorded on $1\ \mu m \times 1\ \mu m$ square areas was 1.5 nm, corresponding to a variation of three or four atomic lattices. It was found that the surface was formed by small rounded grains (about 17.5 nm in diameter) with a dense and smooth morphology. No evidence for rosette or mosaic structures were observed.

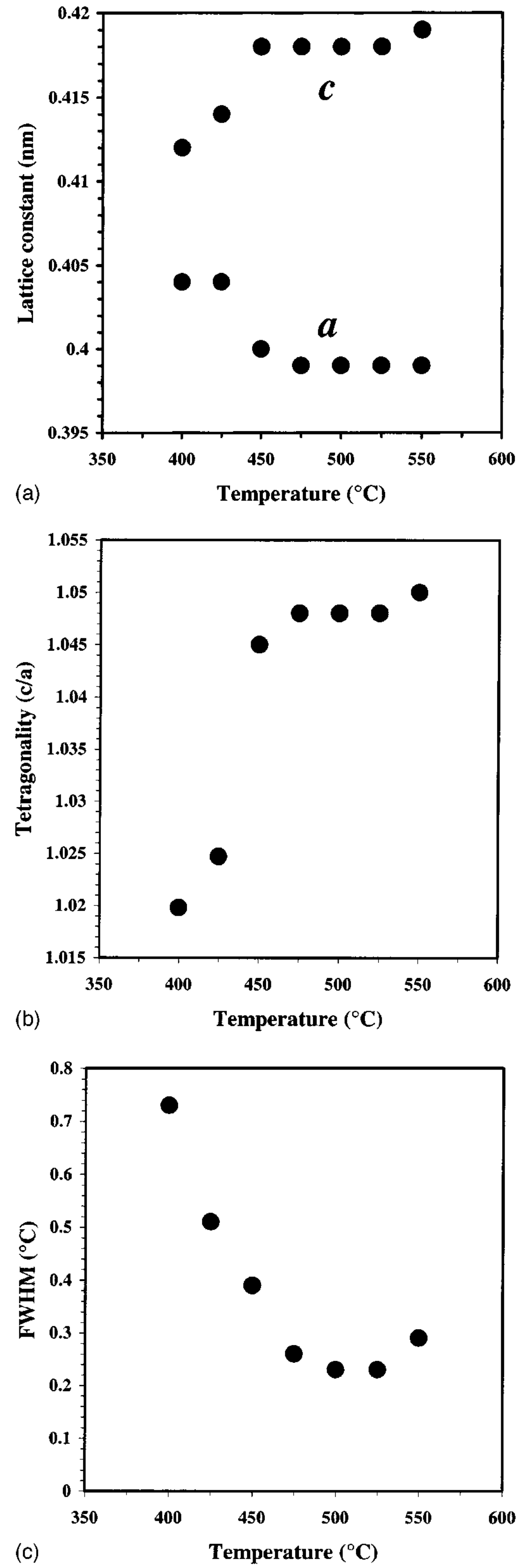

FIG. 3. (a) Variation of the PZT lattice parameters with the growth temperature. (b) Variation of the PZT tetragonality with the growth temperature. (c) Variation with the growth temperature of the FWHM measured on the (001) PZT rocking curve.

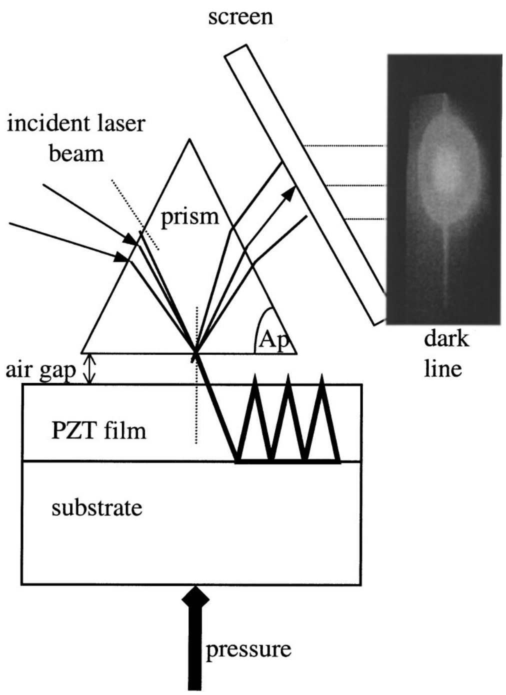

FIG. 4. Diagram of the *m*-lines measurement setup.

B. Optical properties

The experimental setup describing the *m*-lines measurements is presented in Fig. 4. Figure 5 displays the *m*-lines spectrum measured on the PZT film grown at 500 °C. The reflected intensity of the transverse electric modes exhibited successive minima. Because the *m* lines appeared well defined and relatively thin, one may suppose that the optical losses in the film were rather low since the optical losses are related to the FWHM of the *m* lines.[26] The refractive indices were calculated from two successive modes measured on all the PZT films. Figure 6 shows the variation of the refractive index as a function of the deposition temperature. Above 450 °C, the index remained almost constant with an excellent value of 2.56, very close to the bulk one,[27] i.e., 2.57. The packing density "*p*" of the PZT layer calculated by the Bragg and Pippard model[28] is found to be 99% and reflects both higher density and lower porosities in the layer at 450 °C. Generally, this parameter is highly sensitive to a change in the microstructure and crystallinity of the films. One may notice the evolution of the refractive index with a dramatic drop below this temperature. This behavior may, therefore, be directly related to the crystallographic and structural properties investigated herein, which were greatly improved when the growth temperature was above 475 °C. These results also suggested that a crystallization temperature as low as 475 °C may be sufficient to prepare epitaxial PZT films on a LAO substrate with properties suitable for optical applications.

By using the inverse Wentzel–Kramers–Brillouin method, previously described by Dogheche *et al.*,[29] it is possible to determine the index profile along with the thickness of the film. This method only depends on the refractive index

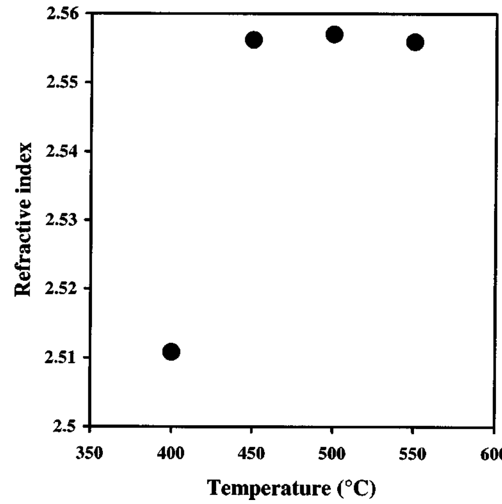

FIG. 6. Variation of the PZT refractive index with the growth temperature.

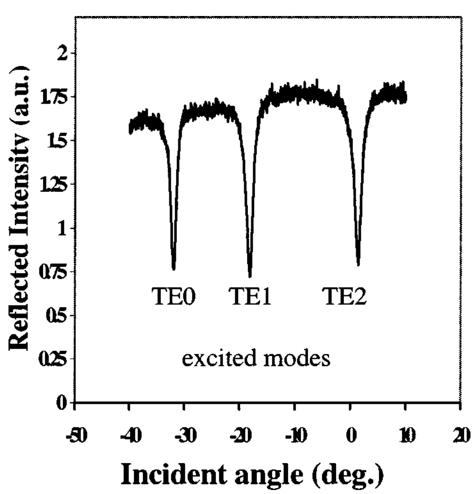

FIG. 5. *m*-lines spectrum of transverse electric modes measured on the PZT thin film crystallized *in situ* at 500 °C.

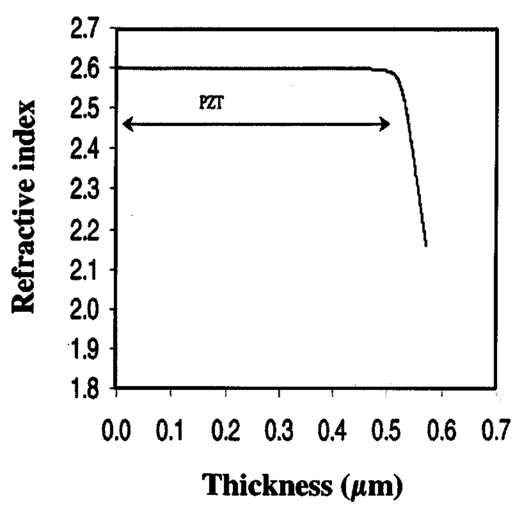

FIG. 7. Variation of the PZT refractive index along the thickness of the PZT thin film crystallized *in situ* at 500 °C. The index profile is plotted starting from the top surface (left-hand side of the thickness axis) to the bottom interface (right-hand side of the axis).

distributions within the guiding layer. This is displayed in Fig. 7 for the PZT film crystallized at 500 °C. The refractive index profiles indicate a step-index variation which is synonymous of a good optical homogeneity along the PZT film thickness. Indeed, the refractive index remains constant within the guiding region and decreases rapidly near the film–substrate interface. Therefore, this result clearly reveals no influence of the substrate on the growth process. The thickness of the PZT layer determined from the index profile was 500 nm, in agreement with the value found with the Dektak profilometer. From these observations, one may assume that our films exhibited a satisfying homogeneity from both the crystallographic and optical properties points of view. However, optical propagation loss measurements must be performed to draw conclusions about these properties. One may also infer *a priori* that these samples presented no defects in the region near the interface between the PZT layer and the substrate. Additional experiments, such as transmission electron microscopy (TEM) observations, are required to confirm this point.

IV. SUMMARY

PZT thin films with *c*-axis epitaxial microstructure were crystallized *in situ* on (001) LAO substrates by rf magnetron sputtering. The epitaxial growth was achieved for a substrate temperature as low as 475 °C. The PZT films prepared in the 475 °C–550 °C temperature range exhibited high crystalline quality with a mozaïcity of 0.23° achieved for a temperature growth of 500 °C. Optical measurements performed on the films by a prism coupling method gave a refractive index value of 2.56 close to the bulk value. Moreover, the optical measurements suggested that the PZT films were homogeneous with no perturbed region near the interface with the substrate.

The correlation between optical, structural, and crystallographic properties was clearly established through growth temperature. Tough additional experiments, such as TEM and optical propagation loss measurements, must be carried out to confirm the aforementioned results, our observations suggest the feasibility to prepare PZT films at relatively low temperature and with a high potential for optical applications.

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