

STRUCTURAL AND OPTICAL CHARACTERIZATION OF NB-DOPED PZT 65/35 THIN FILMS GROWN BY SOL-GEL AND LASER ABLATION TECHNIQUES

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Nb-doped PZT 65/35 thin films were deposited on silicon and sapphire substrates using the sol-gel and laser ablation techniques. The structure and the morphology of the films were investigated by X-ray diffraction and scanning electron microscopy respectively. The refractive index and absorption coefficient were obtained by means of transmittance and reflectance measurements in the wavelength range of 200 to 2500 nm. Band gap energies for these films are reported under the assumption of a direct band-to-band transition. The influence of Nb doped concentration, thickness of the films and the technique of deposition on the structural and optical properties of the films are also investigated in this work.

Keywords: PZTN - Sol-gel deposition, Pulsed laser ablation, Optical properties

1. Introduction

Ferroelectric thin films have received much recent attention for applications including non-volatile memory, piezoelectric devices, optical switches... [1] Lead based perovskite materials such as Lead Zirconate Titanate (PZT) or Lead Lanthanum Zirconate Titanate (PLZT) solid solutions have been extensively investigated due to the possibility of composition control to obtain desirable electro-optical properties [2].

Ferroelectric thin films of PZT have been produced mainly by r.f. sputtering [3], laser ablation [4] and sol-gel [5] processes. Recently, pulsed laser ablation deposition (PLAD) has been successfully employed to grow high quality thin films (homogeneous, with epitaxial orientation). On the other hand, sol-gel technique is able to produce films with exact stoichiometric composition. The later route can easily achieve doping of the PZT compositions. In the present paper, thin films based on PZT and PZTN, i.e. Nb-doped PZT, were obtained using as deposition technique either sol-gel, either pulsed laser ablation. These films were deposited on various kinds of oriented substrates (Si(111), Pt coated Si (100) and c-sapphire (0001)). For each film, the refractive index, extinction coefficient and its thickness were calculated using both transmission and reflection spectra. The results from structural characterization and optical properties are then reported.

2. Experimental

2.1 Theoretical background

PZT and PZTN materials deposited on sapphire substrate by sol-gel technique were first used for optical characterization. Transmittance and reflectance measurements were performed in order to determine the complex refractive index $N = n - j k$ [6], where n is the refractive index and k the extinction coefficient.

The real part of complex refractive index can to be related with the measured transmission spectra (T) and the reflection one (R), which are also correlated with the band structure [6]:

$$T = (1 - R)^2 \exp [-\alpha t] \quad (1) \quad R = \left(\frac{n-1}{n+1} \right)^2 \quad (\text{with } k \ll n - 1) \quad (2)$$

where t is the thickness of the thin film, and α the film absorption coefficient.

The imaginary part of the refractive index k is directly connected with the absorption coefficient by the relation $\alpha = 4 \pi k / \lambda$ (where λ is the wavelength).

The reflectance and transmittance spectra depend on 3 unknown quantities, n , k and t . Among these, the refractive index coefficients n and k are wavelength dependent. For a film on a transparent substrate, one can obtain the different quantities considering the Swanepoel's approach [7]: using the envelope equations given by the extremes of the interference fringes T_M and T_m , which are functions of the wavelength λ , and thus of $n(\lambda)$.

The theoretical transmission spectra can be typically separated into three different parts: A) the transparent region, B) the weak and medium absorption region and, C) the strong absorption region. According to Swanepoel [7], the refractive index can be approximated in these 3 regions, with good accuracy, using the following equations :

A) In the transparent region ($\alpha = 0$),

$$n = \sqrt{\frac{2n_1}{T_m} - \frac{n_1^2 + 1}{2}} + \sqrt{\left(\frac{2n_1}{T_m} - \frac{n_1^2 + 1}{2} \right)^2 - n_1^2} \quad (3)$$

where T_m is one minimum from the measured spectrum, n_1 is the refractive index of the substrate;

B) In the weak and medium absorption region,

$$n = \sqrt{2n_1 \frac{T_M - T_m}{T_M T_m} + \frac{n_1^2 + 1}{2}} + \sqrt{\left(2n_1 \frac{T_M - T_m}{T_M T_m} + \frac{n_1^2 + 1}{2} \right)^2 - n_1^2} \quad (4)$$

where T_M is one maximum from the measured spectrum and T_m is its corresponding value in the minima envelope curve at constant λ .

C) In the maximum absorption region

$$n = \sqrt{H + \sqrt{H^2 - n_1^2}} \quad \text{where } H = \frac{4n_1^2 + 1}{(n_1^2 + 1)T_0^2} - \frac{n_1^2 + 1}{2} \quad (5)$$

In these equation, $T_0 = (T_M T_m)^{0,5}$

In order to calculate the thickness for film, we used the following equation:

$$2 n t = m \lambda \quad (6)$$

where m is the order number, i.e. an integer for maxima and a half integer for minima.

At short wavelength, the transmittance drops abruptly, then the band gap energy E_g for the perovskite materials can be obtained from the variation of the absorption coefficient in this region. For allowed direct transitions, the relation between α and the incident photon energy $h\nu$ can be written as: $\alpha = B \sqrt{h\nu - E_g}$ (7)

By plotting α^2 versus incident photon energy, the energy gap could be estimated.

2.2 Sample preparation and characterization

** The sol-gel technique*

Using the general formula $\text{Pb}_{1-x/2}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{1-x}\text{Nb}_x\text{O}_3$ + 5% mole Pb excess, where $x=0$ and $x=0.04$, two precursor solutions of PZT 65/35 and PZTN (65/35/4) (in Landbölt-Bornstein notation) were prepared from lead acetate trihydrate, Zr n-butoxide and Ti isopropoxide.

Deposition of the sol-gel coatings was accomplished with a spinner. The spinning condition was 6000 rpm for 30 s. Coatings were dried at 200°C to remove solvent. Then, the produced films were pyrolyzed at 400°C for 5 min for removal of residual organic species and for densification of the gel. The sequence spin-on deposition/ pyrolysis was repeated five times. Using this technique, PZT and PZTN thin films ($t < 1\mu\text{m}$) were deposited on Pt/ TiO_2 / SiO_2 / Si (100) and c-sapphire (0001) in order to check the influence of the substrate on the produced film. The as-produced amorphous film was then heat treated at 650°C to enhance the crystallization of the perovskite phase.

** The pulsed laser deposition technique*

To prepare PZTN thin films, a target prepared by conventional ceramic method, with nominal composition PZTN 1/65/35, i.e. $\text{Pb}_{0.995}(\text{Zr}_{0.6435}\text{Ti}_{0.3465}\text{Nb}_{0.01})\text{O}_3$ was irradiated using a focused Nd:YAG laser (Surelite-Continuum) operating at a pulse repetition rate of 10 Hz with a 7 ns pulse width. For the present study, the 3rd harmonic (355nm) wavelength was used, with maximum energy output of 58 mJ focused to a 1mm diameter (energy density about 7,4J/cm²). The working pressure inside the PLAD chamber during film deposition was 10⁻⁶ mbar. The laser beam was set-up at 45° with respect to the target surface. The target underwent a rotary displacement with a 60 rpm step-motor while the target to substrate distance was kept at 49 mm. n-Silicon(111) wafers were used as substrates, which were previously chemically cleaned and mounted parallel to the target on a stainless steel substrate holder heated up to a maximum temperature of 550°C.

** Characterization techniques*

The X-ray diffraction (XRD) patterns were recorded by a Philips (PW 1710) X-ray diffractometer, using Ni filtered CuK_α radiation. The measurement ranged from 10° to 70° with a step size of 0.02° and time constant 1s. The cell parameters were calculated by adjusting theoretical positions of the lattice planes with the experimental spectra by least-squares method.

The transmission and reflection spectra measurements were performed using a Shimadzu ISR-3100 double beam UV-VIS-NIR scanning spectrophotometer. We measured specular spectra (collimated light incident, collimated transmission or reflection measured).

The morphology of the films was investigated by Scanning Electron Microscopy (SEM) using a Philips WDX-3PC microscope.

3. Results

3.1 Structural analysis of the film

The X-Ray Diffraction (XRD) analyses were performed for all the samples in order to determine the crystal structure, the orientation and the lattice constants. The results are presented in Fig. 1.

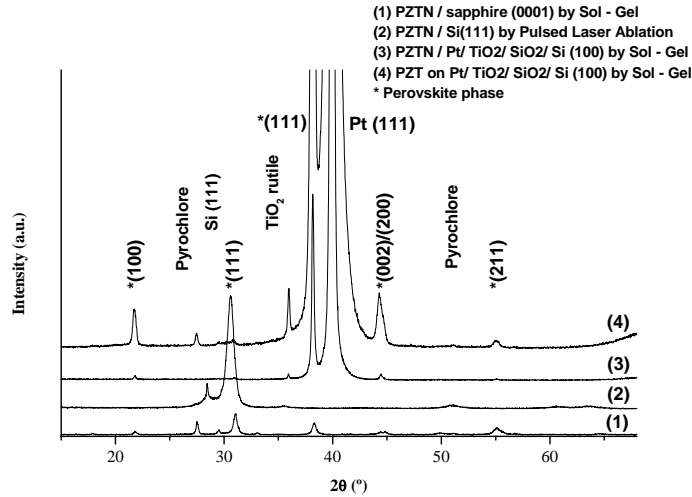


Fig. 1. The X-Ray Diffraction (XRD) analyses.

All the spectra present intense peaks corresponding to perovskite rhombohedral phase. In the case of sol-gel thin films, one peak around 29° can be attributed to pyrochlore phase.

In Table 1, the cell parameters calculated for each film is given. The set of diffracting planes used is imposed by the rhombohedral structure of the PZT 65/35 and PZTN 65/35/4.

The lattice parameters calculated are presented in table I.

Table 1. Cell parameters versus composition, deposition technique and kind of substrate.

Compound	Deposition technique	Substrate	a (Å)	α (°)
PZT (65/35)	Sol-gel	Pt/ TiO ₂ / SiO ₂ / Si	4.0839	89.81
PZTN (65/35/4)	Sol-gel	Pt/ TiO ₂ / SiO ₂ / Si	4.0774	89.86
PZTN (65/35/4)	Sol-gel	Sapphire	4.0694	90.02
PZTN (65/35/1)	PLAD	Si	4.1701	90.64

3.2 Optical analysis

In order to characterize the optical properties of PZT and PZTN thin films deposited by sol-gel and pulsed laser ablation, the transmission and the reflection spectra were measured and presented in Fig. 3. The transmission spectra were performed using an uncoated sapphire substrate as reference body. The bumpy aspect in the 500-2500nm and 300-600nm wavelength ranges in transmittance and reflectance spectra respectively were attributed to interference phenomena. In these conditions, equations (3)-(5) based on Swanepoel's work could be used: the region in the range 900-2500nm is considered as the weak absorption region, while, from 500 to 900nm is the medium absorption region and up to 500nm is the strong absorption region.

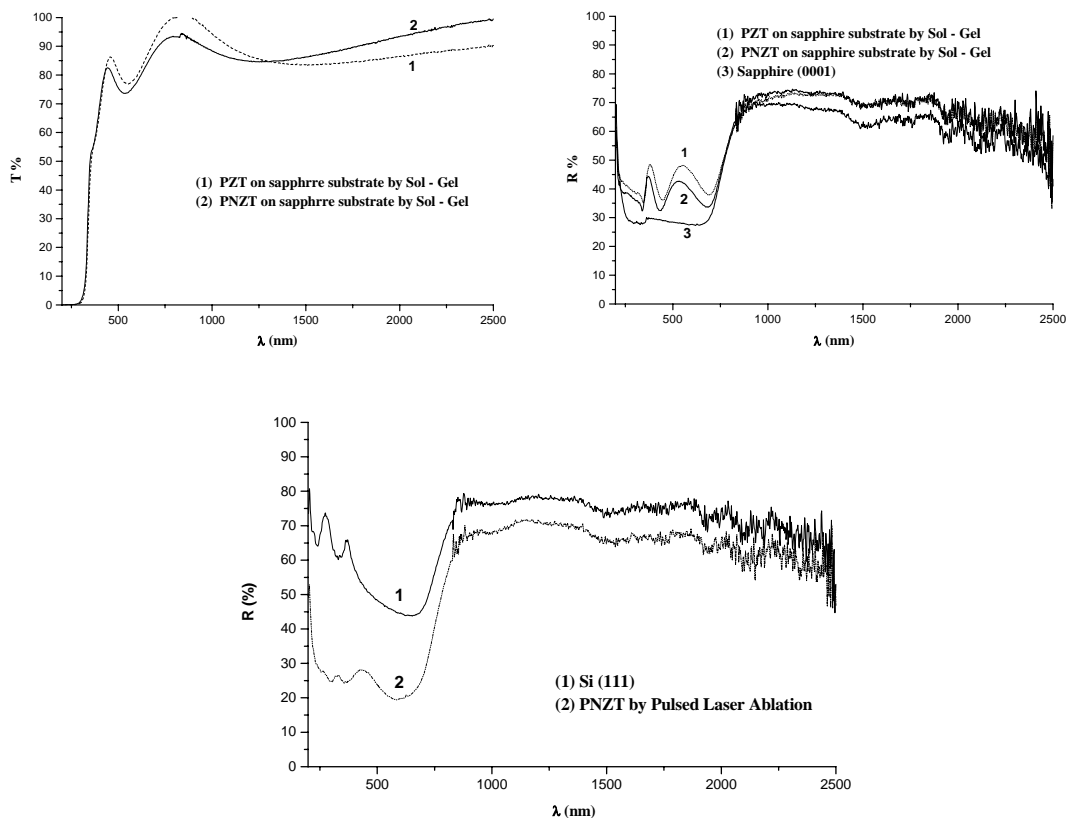


Fig. 2. The transmission and the reflection spectra for PZT and PNZT thin films deposited by sol-gel and pulsed laser ablation.

The n value for PZT decrease from 3.5 at 330 nm to 1.96 at near infrared range, while for PZTN (65/35/4), it decreases from 3,9 to 2,15, in the same wavelength range. For the sample obtained by pulsed laser ablation, the refractive index calculated from eq. (2) was found to be 2.6172, at $\lambda=624\text{nm}$.

Using the obtained function $n(\lambda)$ and the eq. (6), the thickness of PZT films was found to be $0.25\mu\text{m}$ and $0.23\mu\text{m}$ for PZT and PZTN(65/35/4) thin films respectively.

In the further step, the coefficient of absorption was estimated from eq. (1). Fig. 3 presents a plot α^2 versus incident photon energy. At high α values, this curve presents linear behaviour.

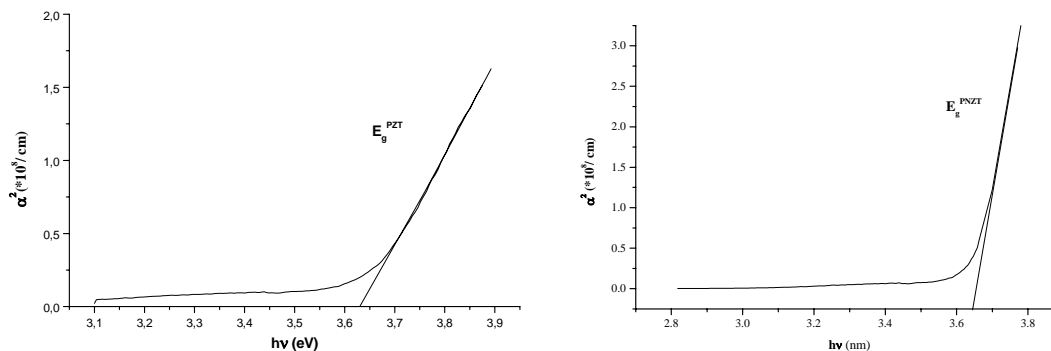


Fig. 3. α^2 versus incident photon energy ($h\nu$).

4. Discussion

4.1 Structural analysis of the thin films

Using the same kind of oriented substrates, Pt/ TiO₂/ SiO₂/ Si(100), the PZT and PZTN thin films exhibits preferred orientation according the (111) perovskite plane. For the same process conditions, the niobium doping of PZT gives rise to a decrease in the pyrochlore phase formation. In comparison, using Si(111), the PZTN perovskite deposited by PLAD grows preferentially according to the (110) plane. Also, the use of c-sapphire (0001) as substrate results in a polycrystalline thin film. Moreover, the broaden shape of different peaks shows the small dimension of the crystallite. This effect is probably due to the presence of higher quantity of pyrochlore phase that is commonly stable at intermediary temperatures (400-550°C).

The cell parameter obtained for PZT 65/35 is slightly lower from the one of the bulk material ($a=4.096\text{\AA}$), estimated from the results of Fushimi et al. [8]. The resulting strain on the crystalline cell is about -0,3%, as a result of a little compressive stress on the film. In the films produced by sol-gel, doping with niobium leads to a decrease of the original cell whatever is the kind of substrate; the compressive stress is not only due to thermal effect but also to inhibition of crystal growth due to the pyrochlore phase presence. In bulk materials PZTN (65/35/x), a progressive substitution of Ti/Zr by Nb in the crystal leads to an increase of the cell parameters and thus of the cell volume [9]. For films produced by laser, there is a sharp increase since there is no pyrochlore blocking phase; but here, the exaggerated cell expansion is certainly due to a high difference between thermal expansion coefficient of Si and PZTN (65/35/1), since, after deposition, these films didn't received post-annealing for stress relaxation.

4.2 Optical analysis of the thin films

The different values of refractive index of films and bulk materials that could be estimated are reported in Fig. 4, considering $\lambda=624\text{nm}$, i.e. in low absorption conditions.

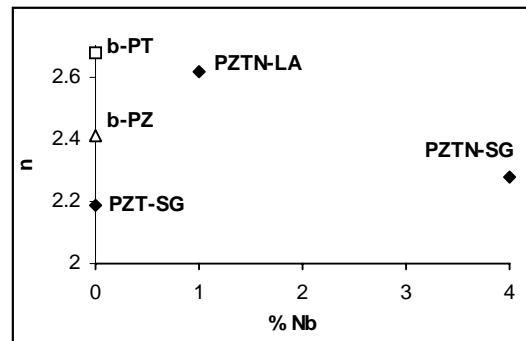


Fig. 4. Refractive index measured at 624nm in the case of films PZT and PZTN produced by sol-gel (SG) and Pulsed Laser Ablation (LA), and in the case of bulk PbTiO₃ (b-PT) and PbZrO₃ (b-PZ).

At 624 nm, we can calculate the refractive index value for the PZT (65/35) starting from the $n(624\text{nm})$ values of PbTiO₃ and PbZrO₃ reported in the literature [10], 2.6733 and 2.4133 respectively. The calculated $n(624\text{nm})$ for PZT (65/35) is about 2.5051, which is much higher than the value for film, i.e. 2.1846. This difference could be due to the film stress, to the presence of pyrochlore phase (with low refractive index), or to low density of the films. Since, in PZT film the compressive stress is light and the quantity of pyrochlore is low, the main factor that affects the n value is the packing density. Using the effective medium approximation, the packing density of the PZT (65/35) film could be estimated equal to 0.79.

Whatever is the deposition technique, the substrate, it seems that the refractive index increases if niobium is introduced in the perovskite structure.

Peng et al. reported that dopants like La and Nd do not affect the refractive index of PZT films [10]. Based on this, we can assume that, by sol-gel technique, PZTN films present higher packing density than the undoped films.

In the case of PZTN produced by PLAD, the main effect changing the refractive index is the stress resulting from the film processing, as it was shown above; The crystallographic results show that films produced by PLAD are submitted to important tensile stress.

In order to validate all the optical calculation, a thin film was characterized by SEM.

The observation of the cross-section of a PZTN film deposited on Pt/ TiO₂/ SiO₂/ Si(100), Fig. 5, shows that the thickness is about 0.23-0.28 μm, i.e. similar to the value obtained by optical measurements. It can be seen also that the surface of the film is homogeneous and smooth; the film itself is also homogeneous, fine grained and, apparently without pores or bubbles. On the contrary, the Pt layer consists mainly in a close packing of nearly spherical grains.

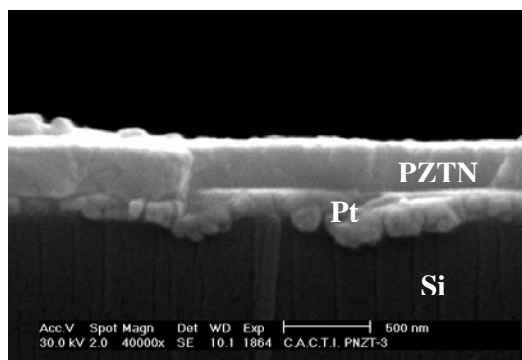


Fig. 5. SEM micrograph of the fracture surface of the film PZTN produced by sol-gel on Pt/ TiO₂/ SiO₂/ Si (100) substrate.

In Fig. 5, we confirm that PZT and PZTN behave as direct band gap materials. The band gap energy, E_g , for PZT and PZTN were determined and correspond to 3.6359eV and to 3.665eV respectively. Using the data of the E_g for PbTiO₃ and PbZrO₃ in a bulk form, i.e. 3.39eV and 3.826eV respectively, the value of E_g for PZT (65/35) is 3.6734eV, which is equivalent to the experimental one. Also, by increasing E_g , the Nb-doping enhances lightly the insulator character of the PZT thin films.

5. Conclusions

In this paper, two techniques were used for thin film deposition: sol-gel and Pulsed Laser Ablation deposition. With these means, it is possible to deposit homogeneous thin films based on the perovskite structure, PZT and PZTN. Using substrates like Pt/ TiO₂/ SiO₂/ Si(100) or Si(111), the films produced have preferred growth along a selected direction.

The films produced by sol-gel can be considered as under low compressive stress, on the contrary by PLAD, the films have important tensile stress.

The addition of niobium gives films with higher packing density and higher band gap energy.

The approximate method based on the Swanepoel's one in order to determine the optical characteristics n and k gives accurate results since the thickness of the films calculated from the spectra is of the same order as the observed one by SEM.

Also, this method is precise enough to determine the band gap energy and the kind of optical transitions (direct or indirect).

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