MORPHOLOGICAL AND OPTICAL INVESTIGATION OF LEAD ZIRCONATE TITANATE (20/80) ULTRA-THIN FILMS

Iulian Boerasu[1], Bernard Enrico Watts[2] and Fabrizzio Leccabue[2]

[1]National Institute of Materials Physics, Bucharest, Romania

[2]Istituto IMEM/CNR, Parma, Italy

Abstract: Ultra-thin (<20 nm) lead zirconate-titanate films with Zr/Ti ratio of 20/ 80 have been deposited on single crystal MgO substrates by sol-gel techniques. Atomic force microscopy reveals a smooth surface consisting of pyramids or domes. The surface morphology is discussed in terms of a double-step growth process: epitaxial growth in the early stages followed by growth on screw dislocations.

Measurements of the optical extinction spectra for the PZT (20/80) ultra-thin films are reported and modelled to extract the data on the energy gap.

Morfološke in optične raziskave ultratankih plasti PZT (20/80)

Izvleček: Nanesli smo ultratanke plasti (<20 nm)zirkonijevega titanata z razmerjem Zr/Ti 20/80 na podlage iz kristalnega MgO s tehniko sol-gel. Preiskava z AFM mikroskopijo pokaže gladko površino sestavljeno iz piramidastih ali kupolastih struktur. Površinsko morfologijo razložimo z dvostopenj-skim procesom rasti : začetna epitaksijalna rast, ki ji sledi rast na vijačnih dislokacijah.

Prikažemo tudi meritve optičnega ekstinkcijskega spektra ultratankih plasti PZT (20/80), ki jih uporabimo pri modeliranju in izračunu vrednosti za energij-sko režo.

1. Introduction

Lead zirconate titanate, $Pb(ZrTi)O_3$ (PZT), ceramics have excellent ferroelectric and optical properties that make them useful for various electronic and optoelectronic applications /1/. Due to the refractive index dispersion n (λ), the low optical loss, high transmittance, together with the strong electro-optic Kerr effect, PZT thin films could also be used for optical and electro-optical applications, e.g. optical shutters and modulators /2/. Ultra-thin films (<20 nm) are particularly interesting in this respect since non-linear effects become important if light can be confined within the film. Moreover, surface roughness becomes an important parameter to control if one seeks to fabricate thin films with optimal optical properties. Recently, new devices have been proposed composed of arrays of ferro-electric nano-capacitors made by self-patterned ultra-thin films /3, 4/.

Fundamental studies on ferroelectric properties show that the grain size and film thickness are important for the limit of ferroelectricity /5, 6, 7/. A number of papers /8-12/ have appeared recently covering different optical properties of ferroelectric PZT bulk ceramics and thin films. There is a lack of information on optical properties of PZT ultra-thin films. Generally, transmission (T) and reflection (R) spectra are used to determine the optical properties i.e. the absorption coefficient (n), the extinction coefficient (k) and the energy band gap (E_g) of thin films. Modelling of these spectra is very sensitive to errors, especially because different experimental set-ups are used. Usually, two methods are used for calculating the optical properties: the Swanepoel's method /11/ and transfer matrix formalism /12/. However, different characteristic values of the optical properties are obtained by applying these methods to the same sample /11, 12/. This difference is coming mainly from the "resolution" method. The basics of the Swanepoel's method consist in solving the equations for T and R of the light with wavelength λ. The system of equations for T and R has more than one solution, since T and R values vary to a great extent with λ. The problem of guaranteeing that the system has a singular solution is solved using the maxima and minima of the transmission spectrum. Considering the Swanepoel's approach /11/ the experimental transmission spectrum is enclosed by the envelope function of the transmittance maxima (T_M) and by the envelope function of the transmittance minima (T_m) which are function of the wavelength λ (Figure 1). The strong drawback of this method it is that it induces errors when one draws the envelopes.

Recently, an alternative method has been proposed in order to determine the optical properties of ferroelectric thin films /12/. The key of the method consists of applying the transfer matrix formalism on modelling the complex dielectric function. The strong drawback of this procedure comes from the difficulty of the mathematical calculus that is rather complex and very sensitive to errors.

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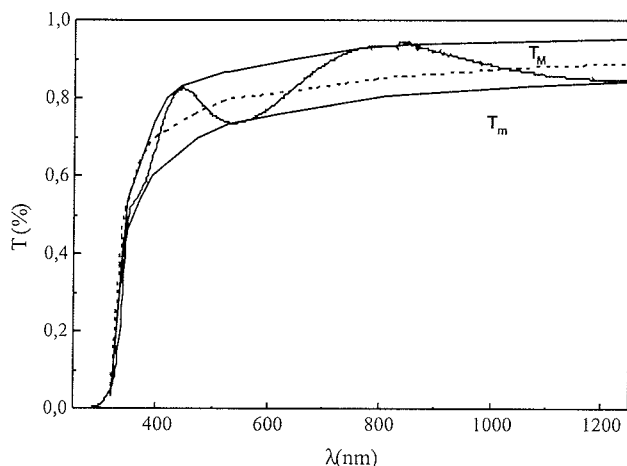

Figure 1.   The T_M and T_m envelope of the
             experimental transmission spectra,
             according to Swanepoel's approach /11/.

In this work, optical extinction measurements are proposed as a quality check of the films of $PbZr_{0.20}Ti_{0.80}O_3$ as thin as 15 nm. Band gap energies (E_g) and the extinction coefficient (k) for these films are reported under the assumption of a direct band-to-band transition.

2.   Experimental

Stoichiometric $PbZr_{0.20}Ti_{0.80}O_3$ films were prepared from the sols derived from methoxyethanol solutions. Lead acetate was dehydrated under vacuum (49 mbar) at room temperature for 15 hours. A 1M stock solution of Pb was obtained by mixing the anhydrous $Pb(CH_3COO)_2$ with 2-methoxyethanol followed by two vacuum distillations (60 mbar at 60 °C each) and dilutions with the solvent. Ti isopropoxide and Zr n-propoxide were mixed with 2-methoxyethanol, followed by two vacuum distillations (66 mbar at 80 °C each). The resultant solution was mixed with the Pb stock solution and 2-methoxyethanol. Two vacuum distillations (66 mbar at 90°C) were again performed to complete the reaction and remove any remaining reaction by-products. The Pb/Zr/Ti solution was partially hydrolysed with an equal volume of a 1 M water mixture in 2-methoxyethanol to obtain a 0.25 M sol.

The films were deposited on MgO (001) single crystal substrates by spin-coating. Prior to deposition, the substrate was thermally treated at 1100 °C for 1 hr to obtain well-defined vicinal surfaces and a reproducible surface finish /13/.

The sol was syringed through a 0.2 μm filter onto the substrate and spun at 6000 rpm/ 60 s. A two-step hot plate treatment was then used at 95 °C and 300 °C for 5 min each. Finally, the amorphous film was placed in an inverse-crucible configuration, together with some lead oxide powder to provide a lead oxide-rich atmosphere, and heated in a chamber furnace to 750 °C.

The surface microstructure of the films was characterized with Atomic Force Microscopy (AFM; Nanoscope IIIa). The equipment allowed the determination of the average surface roughness for selected areas and line scans to determine peak to trough height differences.

The optical extinction spectra were recorded at room temperature using a Carry 17D PC double beam UV-VIS-NIR scanning spectrophotometer.

3.   Results and discussion

3.1.   Atomic Force Microscopy

The AFM images of the ultra-thin $PbZr_{0.2}Ti_{0.8}O_3$ film, in Figure 2, reveal faceted structures that are either pyramids or domes /14/. The density of the pyramids is low, but these are very well defined, with a wide square base and four facets. The surface profiles indicate that the typical height of the pyramids is about 120 nm. The domes, which cover the majority of the substrate, are closely packed and have a square base top surface, and four faces. The film surface is smooth; the average root mean square (rms) roughness is 5 nm, calculated from the AFM data. The height of the domes and equivalently the thickness of the film were estimated at 15 nm. This was measured using a step, made during the sample processing.

Three different structures, domes, super-domes and pyramids, were observed on tetragonal PZT (52/48) films deposited on Nb doped $SrTiO_3$ substrates /15, 16/. The morphology depended on the dilution of the precursor solutions and the crystallisation temperatures. In our work, only pyramids and domes were observed. As depicted in Figure 2, some of the domes resemble "super-domes" /16/, but this could be an artefact; the angle of the tip used for the AFM analysis is about 8°, which could blur the real profile /17/. A similar morphology to that seen in the present work has been reported for germanium grown on silicon by Metalorganic Chemical Vapour Deposition (MOCVD) /18, 19/.
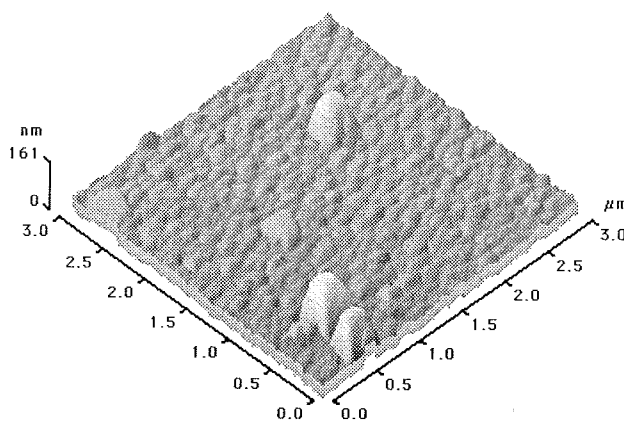

Figure 2.   Atomic force microscope image of the
             surface of the $PbZr_{0.2}Ti_{0.8}O_3$ film,
             deposited on single crystal MgO.

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It was mentioned that AFM revealed closely-packed domes having no holes or empty space in between them. The kinetic model, presented by Srolovitz /20, 21, 22/, explains the formation and evolution of holes in a continuous film as the direct result of volume diffusion and surface evaporation/ condensation. Lead diffuses readily from the bulk of the film to its surface in Pb(Zr,Ti)O$_3$. These phenomena lead to compositional inhomogeneities, due to segregation and evaporation. Additionally, this diffusion promotes the formation of capillary holes through the film thickness. Hence, the suppression of lead oxide surface evaporation by using lead oxide rich atmosphere also reduces the initiation of capillary holes and their further evolution.

The very low roughness of the film could be explained by the following model of nucleation and growth. The base of the domes is wider than their height, suggesting that lateral growth preferentially takes place. In the early stages of crystallisation, the first 2 to 6 monolayers, perovskite nuclei having stoichiometric composition, form on the MgO surface /23/. These nuclei spread laterally and coalesce, due to the very good lattice match between the MgO (a_{MgO} = 0,421 nm) and PZT (a_{PZT} = 0,414 nm), forming an epitaxial film. As the temperature increases, the film acts as a site for uniform growth in three dimensions, either perpendicular or horizontal to the substrate surface /23, 24/; in turn, large dome structures will grow. Strain induced dislocations are present not only at the film-substrate interface, but also develop in the growing epitaxial film. The dislocation periodicity decreases as the film thickness increases, due to the greater stress relaxation. At higher temperatures, the greater surface mobility increases the rate of growth on imperfections leading to a low density of large faceted pyramids resulting in smooth PZT film /25/.

3.2. Optical characterisation

Optical extinction (E) spectra were recorded to characterise the optical properties and to determine the band transition energy of the ultra-thin film. Given the low density of pyramids, one can assume that the optical extinction is measured on a film, about 15 nm thick, composed of domes. An MgO substrate, heat treated at 1100 °C for 1 hour, was used as the reference body. The spectra are presented in Figure 3. A local maximum is present between 3 5 - 3.6 eV (Fig. 2).

According to the Beer-Lambert law, the absorption coefficient (a) is related by the optical extinction (E) and film thickness (d) by the following relationship:

$$\alpha = E/d \qquad (1).$$

The extinction coefficient (k) is directly connected with the absorption coefficient by the relation /10/:

$$\alpha = 4\pi k/\lambda \qquad (2),$$

where λ is the wavelength. Thus, the equation (1) and (2) could be used to obtain the dispersion relationships for k
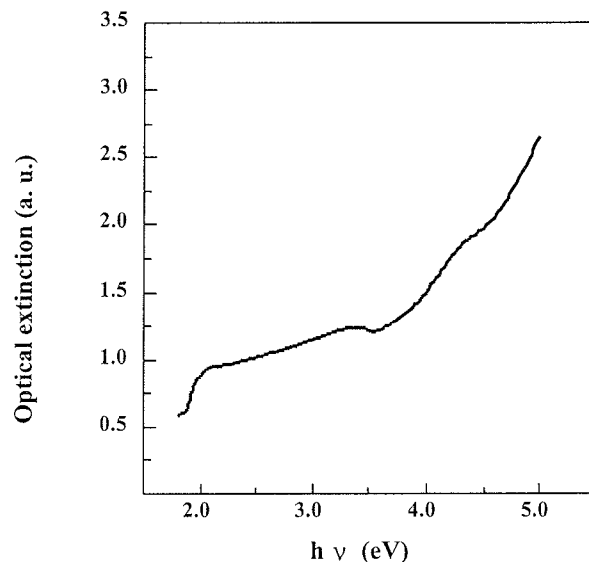

Figure 3. Optical extinction spectrum of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film on MgO.

versus wavelength. To our knowledge, this is the first report for k of ultra-thin PZT films. The latter is shown in Figure 4.
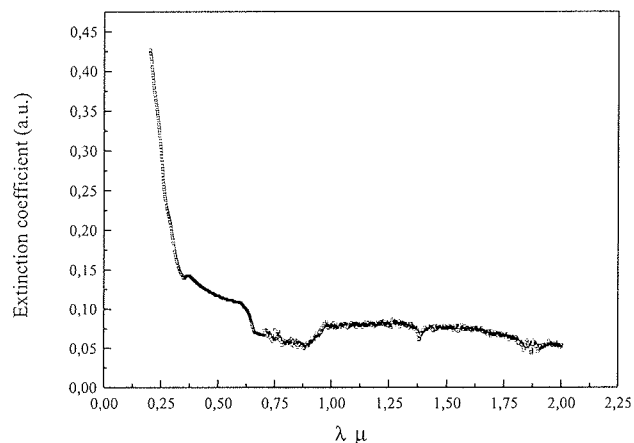

Figure 4. The extinction coefficient k of PZT (20/80) ultra-thin film on MgO as a function of the wavelength.

The extinction coefficient of the film is nearly constant (k ≈ 0,08) for λ > 1 μm and rapidly increases for shorter wavelengths. This increase is related to an interband absorption in PZT (20/80).

Moreover, for a direct band gap material, the absorption coefficient can be expressed as a function of the incident photon energy (hn):

$$\alpha = (\tilde{A} \, h\nu)(h\nu - E_g)^{1/2} \qquad (3)$$

where A is a constant and E_g is the band gap /10/.

Thus, the plot $d(\ln(\alpha h\nu))/d(h\nu)$ vs. hv in Figure 5, will have a divergence at hv = E_g /26/, which corresponds to a transition energy of 3.52 eV. This is in reasonable agreement
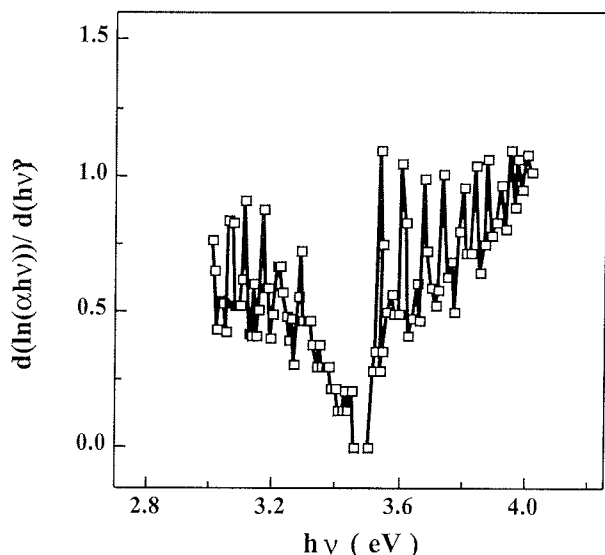
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Figure 5. *Plot of d(ln(αhv))/ d(hv) vs. hv. The observed divergence at hv = 3,52 eV is attributed to a band transition.*

with the value reported in the literature for the band gap energy (E_g) of PZT (20/80) thin films /10, 26, 27/.

Figure 6 is the plot of $(\alpha hv)^2$ vs. hv where a linear behaviour can be seen at high photon energies. Such behaviour has been observed for PZT materials and attributed to a direct band transition /10, 28/.
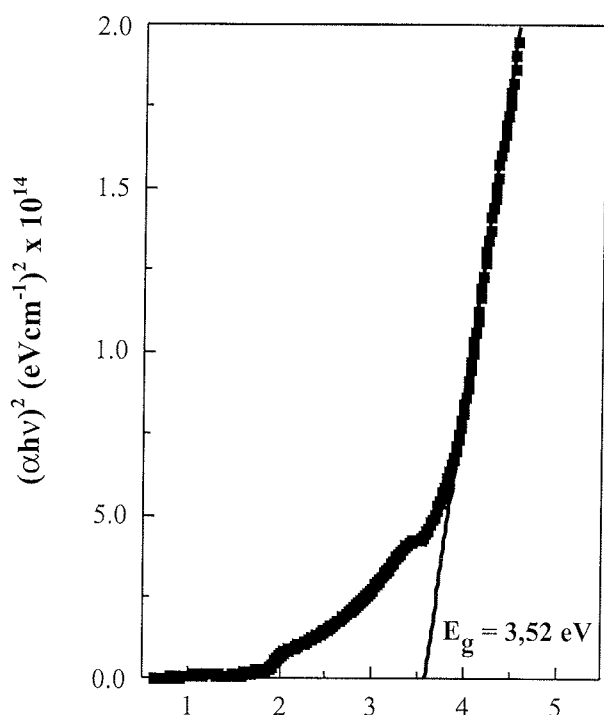

Figure 6. *Plot of $(\alpha hv)^2$ vs. hv for the $PbZr_{0.2}Ti_{0.8}O_3$ film.*

4. Conclusions

PZT (20/80) ultra-thin films have been deposited on MgO (001) substrate by sol-gel techniques. Dilute solutions and high rotation rates were utilized to obtain films approximately 15 nm thick. The surface morphology of the film was analyzed by AFM techniques, which evidenced a complex structure, consisting of pyramids and domes. The density of pyramids is low; however, the domes are closely packed and completely cover the substrate. This leads to a relatively smooth film.

Optical extinction spectra permit the calculation of band transition energy equal to 3.52 eV. Linear behaviour at high incident photon energy indicates a direct band-to-band transition in PZT ultra-thin films.

5. Acknowledgements

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Dr. Iulian Boerasu, National Institute of Materials Physics, Bucharest-Magurele. P.O.Box MG-7, Romania boerasu@infim.ro

Dr. Bernard Enrico Watts, Istituto IMEM/CNR, Area delle Scienze 37/A I-443010 Fontanini, Parma, Italy watts@imem.cnr.it

Dr. Fabrizzio Leccabue, Istituto IMEM/CNR, Area delle Scienze 37/A I-443010 Fontanini, Parma, Italy leccabue@imem.cnr.it