Pb(Zr,Ti)03 ceramic thick films for optical device applications

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ABSTRACT

Ferroelectric $Pb_xZr_yTi_{1-y}O_3$ (PZT) has been prepared by chemical solution deposition (CSD) and spin-coating technique, using acetate and alkoxide precursors. Rapid thermal annealing has been employed in order to obtain crystallization in the perovskite phase. Aiming to study the optical properties of the films, PZT was deposited on different glass substrates. Structural characterization of the films was done by X-ray diffraction, morphology was investigated by SEM micrography. Using standard photography analysis, the films were qualified in terms of crack density, their appearance strongly depending on the type of substrate. Using a visible to the near infrared spectrophotometer, the transmittance normal to the surface of the films was studied. Coupling of laser light into the films by the M-lines technique allowed the determination of the refractive index and the thickness of the ferroelectric layer. A waveguiding interferometer structure of Mach-Zehnder type was realized by photolithography and wet chemical etching.

Keywords: PZT, thick films, glass substrate, transparency, M-lines, wet chemical etching, optical waveguide

1. INTRODUCTION

The improvement of optical networks for high bit rate telecommunication is mainly limited by the modulation and amplification stages of the light signal and hence new materials with improved properties are needed. An appropriate material would have a high transparency in the visible and near infrared range, a strong refractive index, a high electro-optic response and a sufficient good long term stability.[1,2] In order to realize a typical multi-layer waveguide structure, integration is necessary which also implies elaboration of the material by thin film techniques. Some ferroelectrics seem to meet this criteria, like lithium niobate ($LiNbO_3$) which is one of the most prominent member of this class of materials. Other perovskite type ferroelectrics, like barium titanate ($BaTiO_3$) or the large family of PLZT solid solutions [$(Pb,La)(Zr,Ti)O_3$] equally exhibit interesting properties for electro-optic applications.[3-7] In the present study, we investigated the optical properties of lead zirconate titanate (PZT) spin-coated on glass and the possibility to realize a Mach-Zehnder interferometer structure. The realization of a PZT waveguide based on the use of glass substrates would allow a future development of low cost devices which is of high interest for telecommunication applications.

2. EXPERIMENTAL TECHNIQUE

The PZT thin films were elaborated by the Chemical Solution Deposition (C.S.D.) technique using a modified MOD Sol-gel process. The precursor solution was prepared at room atmosphere and temperature. In order to obtain PZT (36/64), lead acetate [$Pb(CH_3CO_2)_2,3H_2O$] was dissolved with an acetic acid solvent and an appropriate ratio between zirconium alkoxide [$(Zr(C_3H_7O)_4)$] and titanium n-propoxide [$(Ti(C_3H_7O)_4)$] adjusted. A 20 % lead excess was used in order to prevent losses during the annealing process, and ethylene glycol ($HO-CH_2-CH_2-OH$) was added to the solution in order to reduce cracking of the films.[8] The final solution was filtered with a 200 nm seringe filter and was spin-coated onto the substrates at 2500 rpm during 20 seconds. Subsequently, the films were dried at 120°C and submitted to a rapid thermal annealing (RTA)

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process during one minute. The crystallization behavior of the films was studied for different annealing temperatures, ranging from 520°C to 620°C.

The PZT precursor solution was deposited on glass substrates of 25 x 25 mm² area. Microscope slide glass was used in order to adjust the spin-coating parameters, and four types of glass with different thermal properties were used in order to study the filmability of the material. Depending on the spin-coating velocity, the thickness of one single layer of PZT varied from 450 nm to 550 nm. Thicker films were realized by multiple spin-coating, including drying and RTA heat treatment of each individual coating. The thermal properties of the substrates are shown in Table 1. As PZT has a linear thermal expansion coefficient of $5{,}5.10^{-6}$, glass substrates with bigger and smaller coefficients were available.[9]

Table 1: Thermal properties of the glass substrates used for PZT thin film deposition

Substrate	Schott D263T	Schott AF45	Corning 7059	Corning 1737F
Coefficient of linear thermal expansion	$7{,}2.10^{-6}$ (20°C-300°C)	$4{,}5.10^{-6}$ (20°C-300°C)	$4{,}6.10^{-6}$ (0°C-300°C)	$3{,}76.10^{-6}$ (0°C-300°C)
Strain point	529°C	627°C	565°C	666°C

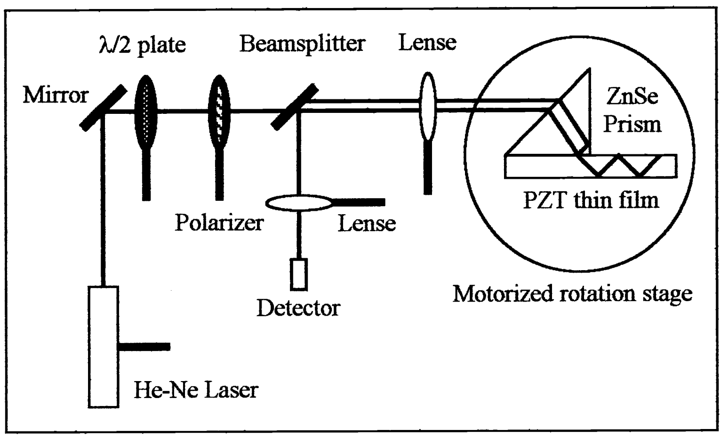

Figure 1: Schema of the m-lines measurement set-up

The structural properties of the PZT films have been determined by X-ray diffraction and Scanning Electron Microscopy. Mesoscopic optical scanning of the films was performed with a MINOLTA Dimage Dual Scan camera. The optical transmittance, normal to the surface of the films, has been determined in a wavelength range between 200 nm and 2 µm with a CARY spectrophotometer.

In order to determine the refractive index of the PZT thin films, a M-lines measurement apparatus was set up which applies the principle of distributed coupling by evanescent fields to the modes of the guiding structure.[10] A ZnSe prism having a refractive index higher than that of the ferroelectric, is pressed on the film (Figure 1) and is separated from it by a small air gap. The incident light is totally reflected at the two sides of the prism, and leaves the prism parallel to the incident direction. For some angles of incidence, phase matching is obtained and coupling into the film due to the evanescent field excited in the gap becomes possible. Determination of these synchronous angles allows to find the characteristic propagation constants of the film.[11-13] The attenuated totally reflected light as a function of the angle of incidence constitutes a dark line spectrum. Variation of the angle of incidence was performed by rotating the ensemble PZT/prism with a remote controlled motorized rotating stage, synchronized to the detector (photo diode). The light source was a He-Ne laser of 632.8 nm wavelength, and the polarization of the incident beam was controlled by a half-wave plate associated to a polarizer.

Classical photolithography and wet chemical etching was employed for the realization of the waveguide structures, using a mixture of 50 ml HCl (37%), 50 ml HNO_3 (69%) et 2 ml HF (48%) diluted to 50%. A detailed study on the etching behavior of PZT ceramic thin films shall be published elsewhere.[14]

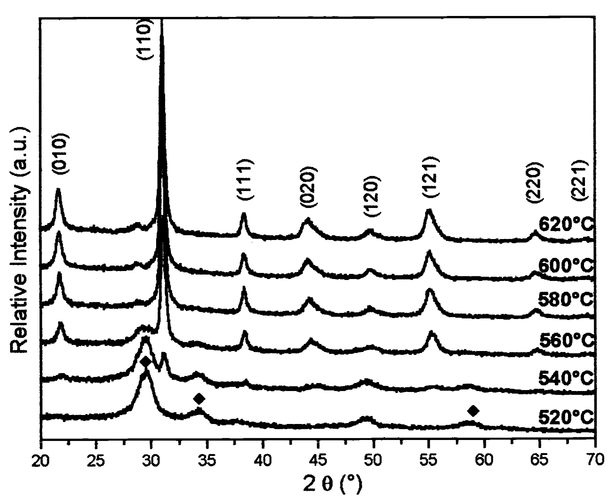

Figure 2: XRD pattern of PZT (36/64) films [♦ pyrochlore phase, (xyz) perovskite phase)]

3. EXPERIMENTAL RESULTS AND DISCUSSION

The development of the X-ray diffraction pattern of a 2 μm thick PZT (36/64) film deposited on a microscope slide glass substrate is shown in Figure 2 as a function of the annealing temperature. At 520°C, only a pyrochlore phase of the PZT can be detected. With increasing annealing temperatures the respective peaks (at $2\theta \approx 29.5°$, 34°, and 59°) decrease and are replaced by the perovskite pattern. At 580°C, the pyrochlore peaks become almost invisible. Starting from 600°C, crystallization in the perovskite phase with a preferential (110) orientation of the film ($2\theta \approx 31°$) was obtained.

The microstructure of the PZT (36/64) films was studied by SEM technique in the normal secondary electron mode and the backscattering mode. Figure 3 shows cross-sections of a 5-layer PZT film annealed at 620°C, resulting in an overall thickness of approximately 2.7 μm. In the normal mode (Figure 3a), the typical PZT grain structure can be seen with the substrate on the right hand side of the photo. As the SEM picture was focussed to the PZT, the substrate does not appear clearly. Figure 3b was taken in the backscattering mode, where the brightness is proportional to the mass of elements. At the surface of the substrate, a brighter region of approximately 500 nm thickness is visible which should correspond to a chemical element heavier than glass. We suppose that diffusion of lead from the PZT to the substrate during the thermal annealing process causes this zone (diffusion layer).[15]

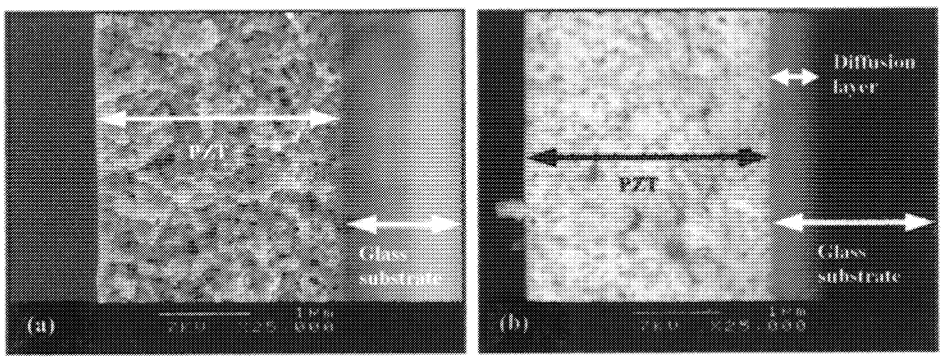

Figure 3: SEM micrographs of a PZT (36/64) film spin-coated on microscope slide glass. Cross-section (a) in the SEM normal mode and (b) in the backscattering mode

The mesoscopic structure of a PZT mono-layer of approximately 450 nm thickness was analyzed using optical photography. In Figure 4, deposition on four different glass substrates is compared. Figures 4a and 4b show the PZT films spin-coated on a Schott D263T and a Corning 7059 glass substrate, presenting a high number of cracks, respectively. In the case of Figures 4c and 4d, Schott AF45 and Corning 1737 glass substrates were used, showing a more homogeneous surface with considerably less cracks. As the cracks appear during drying and annealing of the films, we suppose that the mismatch between the thermal properties of the glass and the PZT film is at the origin of this phenomenon. This may cause desiccation cracks during the drying process and strain cracks during annealing and cooling of the films to room temperature.

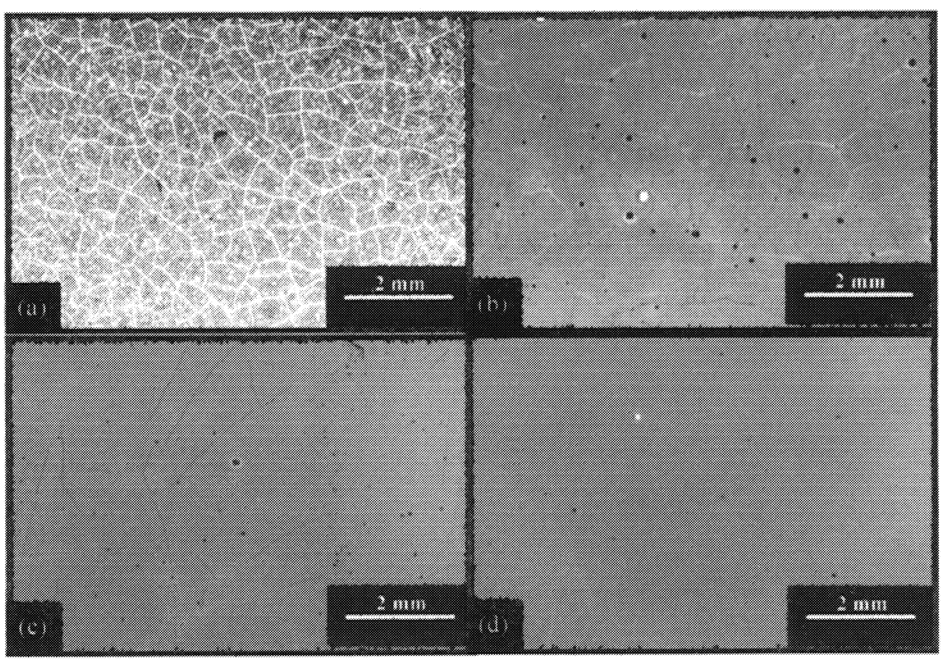

Figure 4: Optical photography of PZT films spin-coated on different glass substrates and annealed at 620°C, (a) Schott D 263, (b) Corning 7059, (c) Schott AF 45 and (d) Corning 1737F.

Unlike the case of metal substrates,[16] deposition on glass resulted in more homogeneous films with less mesoscopic cracks when the thermal expansion coefficient of the substrate is smaller than that of the PZT. This might be explained by the different thermal behavior of the two types of substrate during the annealing process. Glass has a lower thermal conductivity than metal, and the glass substrates used are thicker than the metal substrates (0.7 mm and 0.2 mm). In the case of the glasses investigated, homogeneous and crack-free crystallization of the PZT films was favored by using the substrate with the smallest thermal expansion during the RTA heat treatment process.

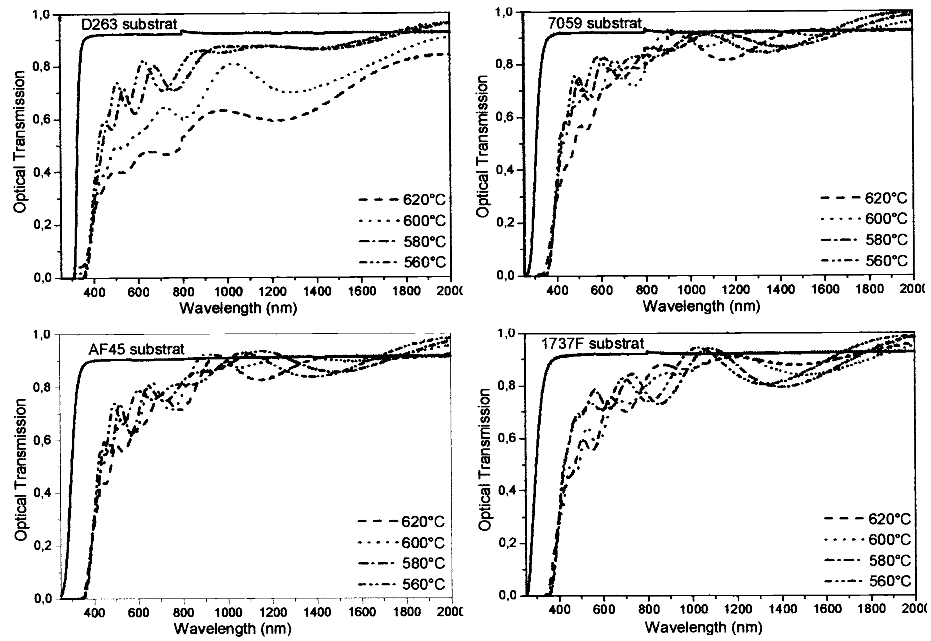

Figure 5: Optical transmission of PZT films prepared on different glass substrates and for different annealing temperature.

Optical transmission of a PZT mono-layer, deposited on the different glass substrates, is shown in Figure 5 for heat treatment temperatures ranging from 560°C to 620°C. Transmission has been found to be between 30% and 80% in the visible wavelength range and up to 90% in the near infrared (2000 nm). In the case of the D263 glass substrate only, a lower transparency was observed for the films crystallized in the perovskite phase (600°C and 620°C). This is supposed to be due to light scattering, as in this case the PZT films show an overall inhomogeneous aspect with many mesoscopic cracks. The higher transparency of the same PZT film in the pyrochlore phase (560°C and 580°C)) where no cracks have been found, confirms this assumption. The transmission spectra of the PZT films deposited on the 7059, AF45 and 1737F glass substrates do not differ significantly. The UV cut off wavelength of the PZT is around 350 nm, respectively, corresponding to a band gap energy of 3.5 eV, which is in accordance with the intrinsic limit of transparency.[17] In the near infrared, and particularly at the "telecommunication wavelength" (1,55 µm), transparency is almost that of the substrate.

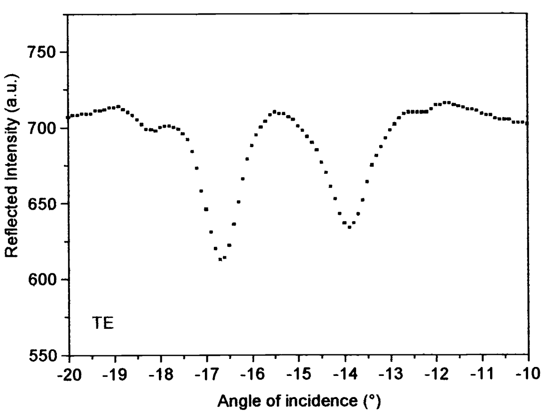

Figure 6: Typical TE dark line spectrum

A typical TE dark line spectrum from the PZT film obtained by the M-lines technique is presented in Figure 6. Two absorption lines appears at an angle of approximately -16.7° and -13.9° and correspond to the excitation of two guided modes in the film.

The refractive index n_1 and the thickness d of the ferroelectric film are related to the synchronous angles θ_{3m} and the mode order m via the dispersion equation of a planar dielectric waveguide[18]

$$d.k_0.\sqrt{n_1^2-(n_3\sin\theta_{3m})^2}-\arctan\ g1^2\left(\sqrt{\frac{(n_3\sin\theta_{3m})^2-n_2^2}{n_1^2-(n_3\sin\theta_{3m})^2}}\right)-\arctan\ g2^2\left(\sqrt{\frac{(n_3\sin\theta_{3m})^2-n_0^2}{n_1^2-(n_3\sin\theta_{3m})^2}}\right)-m\pi=0 \quad (1)$$

where k_0 is the wave vector and n_0, n_2, and n_3 represent the refractive index of the substrate, the air gap, and the prism, respectively. The parameters g1 and g2 are equal to one for TE polarization and equal to n_1/n_2 and n_1/n_0 for TM polarization.

In order to determine n_1 and d, equation (1) was solved numerically using a modified Newton-Raphson method.[19] In the case of the PZT film deposited on the 1737F glass substrate, a refractive index $n_1 = 2.26 \pm 0.03$ and a thickness $d = 2 \pm 0.2$ μm for a wavelength of 632 nm were obtained. The results are in good agreement with measurements at 1.3 μm and 1.55 μm wavelength (n_1 = 2.26 and 2.20, respectively), obtained from the same film with a commercial measurement device.

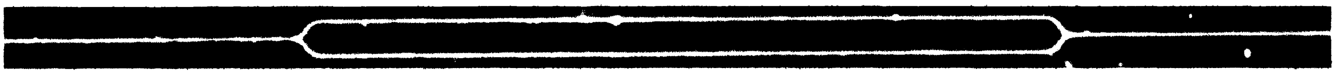

Figure 7: Optical photography of a Mach-Zehnder interferometer structure etched in a 2 μm thick PZT (36/64) film on glass substrate.

In order to study the possibility of using PZT films on glass substrates for waveguide applications, a Mach-Zehnder interferometer structure was realized by photolithography and wet chemical etching, which is shown in Figure 7. A linear waveguide (left hand part of the structure) is split into two parallel branches (central part of the structure), one of which can be supplied with electrodes, in order to induce the electro-optic effects (linear Pockels effect or quadratic Kerr effect). Due to the resulting phase shift of the light with respect to the second branch, interference is obtained where the branches are reunified (right hand part of the structure). The thickness of the PZT film is approximately 2 μm, the overall length of the interferometer structure is 14 mm. A SEM micrograph can be seen in Figure 8, showing the right hand end of the two central branches of the interferometer. The width of the etched structure is approximately 30 μm. Light propagation within the waveguide was observed qualitatively, but could not be recorded as yet.

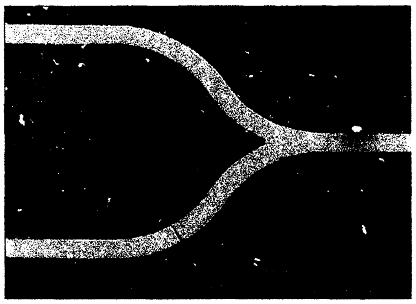

Figure 8: SEM micrograph of part of a Mach-Zehnder interferometer.

4. CONCLUSIONS

PZT (36/64) films were realized by CSD, deposited by spin-coating on glass substrates, and a typical Mach-Zehnder waveguide structure was obtained by wet chemical etching. While the grain structure of the ceramic type PZT thin film does not a priori hinder light propagation, up to now, macroscopic cracks in the ferroelectric layers did not allow a quantitative analysis of the attenuation in the guide. As could be shown, those cracks result from the different thermal behavior of the PZT and the glass substrate during the RTA heat treatment. For certain substrates, however, the PZT elaboration route might be adapted in order to allow homogeneous and crack-free deposition of the films. The results from the optical characterization of the films are encouraging for a future application in electro-optical devices. The transparency normal to the surface is high at the telecommunication wavelength, and light propagation in the film over a few centimeters was observed qualitatively. A M-lines measurement technique was set up which shall allow a more systematic study of the refractive index of the ferroelectric as a function of the material composition and the preparation route parameters. A more profound knowledge on the related phenomena combined with the possibility of tailoring the refractive index of the films will be necessary to obtain monomode light propagation. Preliminary results on a wet chemical etched Mach-Zehnder type interferometer structure show a sufficient good resolution in the micrometer region for a fundamental investigation of light propagation in the PZT films and a future study of the electro-optic linear and non-linear effects.

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