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Wet Chemical Etching of $Pb(ZrTi)O_3$ Ferroelectric Thin Films for Optical Waveguide Application

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In order to develop optical waveguide structures using $Pb(ZrTi)O_3$ ferroelectric thin films, chemical solution deposition and spin-coating on glass substrates were studied. Classical photolithography and wet chemical etching method were applied for the realization of linear and Mach-Zehnder type waveguide structures, having a width of up to 100 m and a irregularity of the border in the 1 m region for an overall length of 20 mm. Optical characterization allows to qualify the ferroelectric material in terms of use for telecommunication applications, coupling of laser light by the M-lines technique allows to study light propagation and the related propagation losses.

Keywords: PZT; optical waveguide; Mach-Zehnder; M-lines; thin films; wet chemical etching

I. INTRODUCTION

The world spanning development of today's information society considerably depends on the quality of high bit-rate telecommunication techniques. While microwaves and optical fibers are used for transmission over long distances, optical networks will also play a crucial role for the local distribution of high bit-rate information. Since several years, active optical devices, including modulation and amplification functions, stand among the most important elements in this concept and still require research and development effort.

In analogy with electronic integrated circuits, the possibility of combining several optical processing functions on a single miniature platform, make conceivable integrated all optical circuits [1]. Also called Planar Optical Chips or Circuits, this devices incorporate functional optical components like linear or curved waveguides, filter devices (controlling the spectra characteristic as Bragg grating), lenses and mirrors, and electro-optic phase or amplitude modulator waveguides like an Integrated Mach-Zehnder Interferometer.

The use of ferroelectric materials may contribute to the material aspects of this development as their strong refractive index, the transparency in the visible and near infrared range, and the high electro-optic response of certain of them, make them potentially suitable for application to active electro-optic devices [2, 3]. In the present work, we investigate the possibility to use classical photolithography and wet chemical etching of $Pb(ZrTi)O_3$ ferroelectric thin films in order to develop integrated planar optical devices like light modulator structures.

II. EXPERIMENTAL TECHNIQUES

Elaboration of the $Pb(Zr_{0.36}Ti_{0.64})O_3$ (PZT) ferroelectric thin films was based on a modified sol-gel process, using alkoxide precursor components and acetic acid as a solvent. While spin-coating of the solution onto metal substrates results in homogeneous and crack free films [4], deposition on glass appeared to be more difficult. In a very recent study, several substrates had been used in order to better adapt the thermal expansion coefficient of the substrate to that of the PZT [5]. In the present experiments we used Corning 1737 F glass and employed a rapid thermal annealing process, however rather slow cooling down of the samples to room temperature. This allowed us to obtain films with a relative small amount of cracks on the overall area of 25×25 mm^2 of the substrates. Multiple spin-coating was performed in order to obtain films of a thickness up to 2 m, which were used especially for the study of the wet chemical etching process. The transfer of the mask pattern to the PZT thin films was done by classical photolithography process using a positive photo resist (Shipley S1818). Two different mask patterns were used, one for the study of the etching process itself, a second for the realization of the waveguide structures.

Optical characterization was performed normal to the plan of the ferroelectric thin films by transmission spectroscopy and in the plan of the waveguide by M-lines spectroscopy. The latter allows to determine the refractive index and the thickness of the PZT films [6, 7, 8]. The M-lines technique is based on the use of a prism of refractive index higher than that

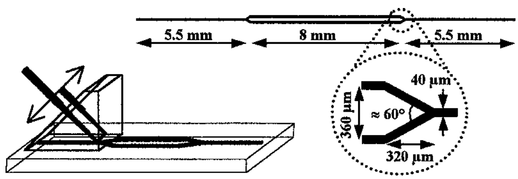
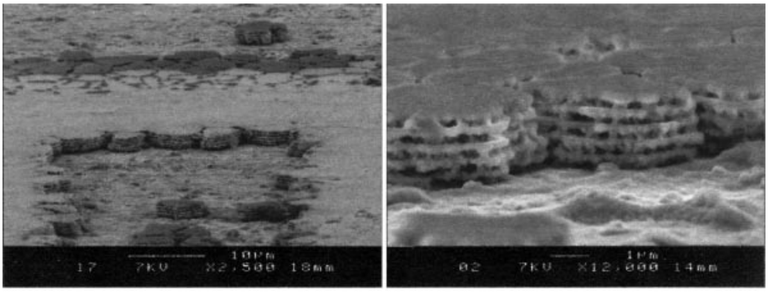


Figure 1. Scheme of the prism-film coupler set-up and typical dimensions of a Mach-Zehnder interferometer waveguide structure.

of the PZT (in our case ZnSe) which is pressed on the thin film (see Fig. 1). Under the base of the prism, an evanescent wave is created by total reflection of the incident laser beam. The prism-film coupler can be rotated in order to change the angle of incidence of the laser beam. For certain angles, which are called synchronous angles, phase matching is obtained between the wavevector of the evanescent wave and that of an eigenmode of propagation of the waveguide. At those synchronous angles, part of the light is coupled into the thin film, and the intensity of the reflected light decreases. Thus, by varying the angle of incidence, a M-lines absorption spectrum or dark line spectrum can be recorded. Knowing the refractive index of the prism, the propagation constants of the eigenmodes of the film can be found from the position of the synchronous angles. By numerical resolving of the modal dispersion equation of the slab waveguide, using a two dimensional Newton-Raphson method, the refractive index and the thickness of the film can be deduced.

The scheme of a Mach-Zehnder type waveguide structure is represented in Fig. 1, too. The motifs have an overall length of 19 mm, the length of the interferometer arms is 8 mm, and the width of the guiding structure is 40 m. The structures were realized by wet chemical etching of the PZT thin films at room temperature. The results of the etching process were analyzed by scanning electron microscopy.

In order to study light propagation in the waveguide structures, the M-lines technique was used as a light coupler, allowing to couple the light of a TE polarized He-Ne laser (632.8 nm) into the PZT thin film. As it can be supposed that the propagation losses are proportional to the intensity of the propagating light, we recorded the light scattered out of the waveguide structures by standard photography. The profile of the propagation losses can be found by digitizing the optical density recorded [9]. Due to a non-linear dependency on the exposure and the development parameters in a standard photography film, in our case, however, an absolute value of the loss coefficient of the waveguide could not be deduced.



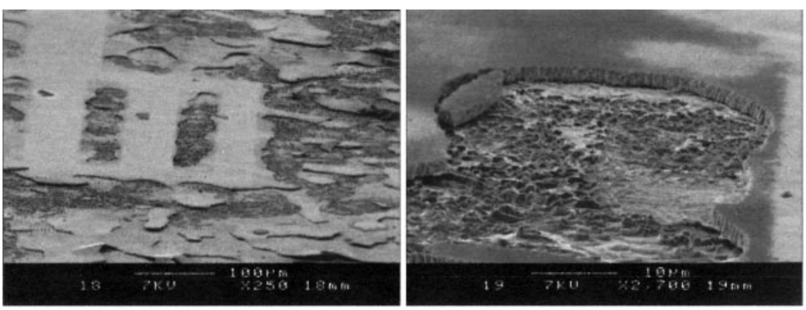
(a) (b)

Figure 2. Wet chemical etching of a PZT thin film with HCl (37%).

III. WET CHEMICAL ETCHING OF THE PZT THIN FILM

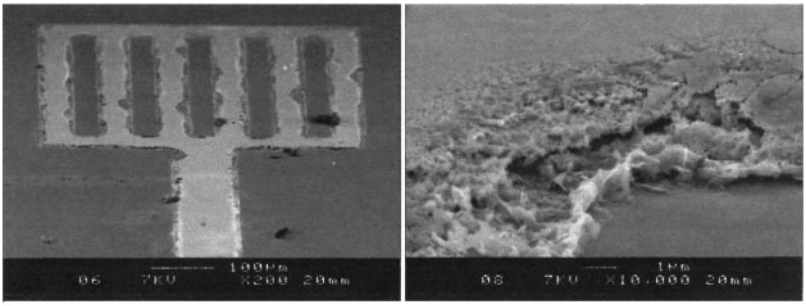
In order to realize the light guiding structures used for the M-lines coupling experiment, wet chemical etching of the PZT films was studied. The etching results are represented in Figs. 2 to 5, where SEM micrographs of different resolution can be seen.

Preliminary tests with pure acids did not result in reasonable etching. Sulfuric acid (H_2SO_4) did not attack the PZT thin films at all, etching with fluorhydric acid (HF) resulted in a too fast attack of the photoresist. Etching with pure chlorhydric acid (HCL, 37%) is shown in Fig. 2. From Fig. 2a it is visible, that etching is selective and results in the separation of the film into individual “islands” having a typical diameter of up to 10 m. Formation of



(a) (b)

Figure 3. Wet chemical etching of a PZT thin film with HNO_3 (69%).

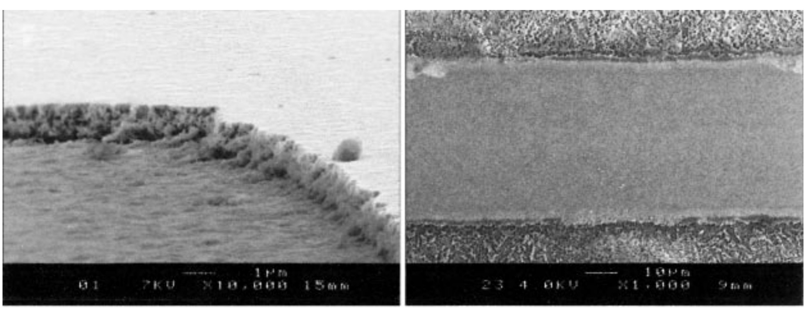


(a) (b)

Figure 4. Wet chemical etching of a PZT thin film with HCl and HNO_3.

"islands" is also well visible in Fig. 2b, where, in addition, the multi-layer structure of the thin film is revealed. Hence it appears that HCL preferentially attacks the interface between the individual PZT layers. In the case of Fig. 2b a 5 layer thin film had been processed; the individual coatings are well visible and have an uniform thickness of approximately 400 nm.

Etching with pure nitric acid (HNO_3, 69%) is represented in Fig. 3. The results are not satisfying, since the PZT thin film gets off in rather large plates (Fig. 3a), not well reproducing the form of the photoresist structure. This peeling off of the ferroelectric seems to be caused rather by mechanical forces than by chemical etching. The magnification of Fig. 3b shows that etching of the PZT does not proceed homogeneously from the surface to the



(a) (b)

Figure 5. Wet chemical etching of a PZT thin film with a mixture of 50 ml HCl (37%), 50 ml HNO_3 (69%), and 2 ml HF (48%).

substrate and the vertical edges appear to be broken. The substrate's surface, however, seems to be attacked. Penetration of the acid to the substrate at some preferable points of the PZT film (cracks, defects, etc.) and a consecutive etching along the interface PZT/substrate might be the reason. In the case of etching with pure HNO_3, neither a PZT surface structure nor the interfaces between the individual PZT coatings are visible.

The effect of etching with a combination of HCL and HNO_3 at a ratio 50/50 is shown in Fig. 4. The mask pattern is reasonably well reproduced, except that the PZT was etched too long and the proceeding lateral etching process underneath the photoresist resulted in considerable irregularities of the border (Fig. 4a). The detail of Fig. 4b shows gradual etching at the border of the PZT thin film, which is consistent with isotropic wet chemical etching. The border, however, is not net and formation of some micro cavities appear.

The etching process could be improved with a mixture of 50 ml HCl (37%), 50 ml HNO_3 (69%), and 2 ml HF (48%) [10]. The etching profile is shown in Fig. 5a, where a considerable steepness of the etching edge can be seen for a PZT thin film of approximately 1 m thickness. In Fig. 5b, a linear structure of 50 m width can be seen in a top view. The irregularity of the border is approximately ± 1 m, sufficiently small in order to allow a preliminary study of light propagation in the waveguides.

IV. OPTICAL CHARACTERIZATION OF THE PZT THIN FILMS

The optical transmission spectrum of a 450 nm thick PZT (36/64) monolayer, deposited on a Corning 1737 F glass substrate, was determined in a wavelength range from the visible to the near infrared (300 nm to 2500 nm). In Fig. 6 we compare transmission for a PZT thin film in its pyrochlore phase (heat treated at 560°C, just below the crystallization temperature) and in the perovskite phase (annealed at 620°C). In both cases, a sharp absorption edge at 350 nm can be seen and interference oscillations occur due to multiple reflections inside the PZT film. The position of the absorption edge is close to that reported for transparent PLZT ceramic bulk material in the perovskite phase [11], and is consistent with the yellow color of the films. In the near infrared, and particularly at the "telecomunication wavelengths" (1.3 m and 1.55 m), the transparency of the PZT is higher than 85%.

A typical dark line spectrum for a TE polarized He-Ne laser beam obtained by the M-lines technique is shown in Fig. 7, allowing to characterize the PZT

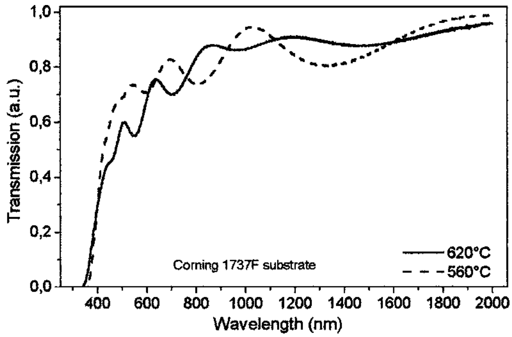


Figure 6. Transmission as a function of the wave length of a PZT thin film.

films in terms of refractive index and thickness. In a first step, resolution of the modal dispersion equation, using an approximated film thickness and refractive index, allows to identify the mode order of the measured absorption peaks. While the peaks m = 0 to m = 3 could be well identified, the existing higher order modes could not be attributed unambiguously and hence are not indexed in the figure.

In a second step, calculation of the refractive index and the thickness of the PZT film was performed by numerically resolving the dispersion equation of a planar dielectric waveguide for two modes. By combining the four identified TE-modes of the dark line spectrum, six mode couples can be formed; the results from the numerical calculations for the refractive index and the film thickness are shown in Table I for the different mode couples, respectively.

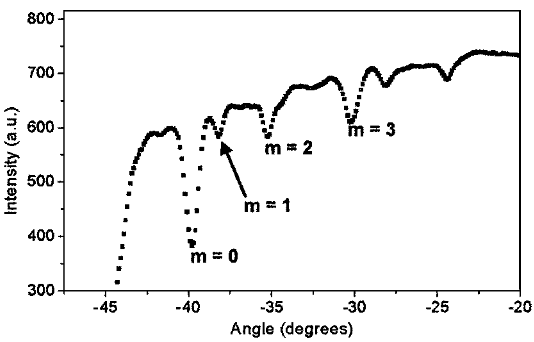


Figure 7. TE dark line spectrum of a PZT thin film.

TABLE I Refractive index and thickness of the PZT thin film calculated for different mode couples from the TE dark line spectrum

Mode couple	0–1	0–2	0–3	1–2	1–3	1–4
Refractive index	2.235	2.236	2.236	2.240	2.240	2.240
Thickness (m)	2.26	2.07	2.02	1.97	1.97	1.97

The positions of the absorption peaks is in accordance with earlier publications [12, 13], as compared to the results from ceramic bulk material [14], however, smaller values of the refractive index were obtained. The results obtained in our studies are also in relatively good accordance with the data from other PZT thin films elaborated by chemical solution deposition processes [15, 16]. Determination of the refractive index and the thickness of our films by the envelop method [17] confirmed the results, however was less precise than the M-lines measurements.

During the angular scan of the PZT thin film, linear light propagation in the plane of the ferroelectric which was extended up to the border of the sample, was observed for the synchronous angles.

V. COUPLING INTO THE WAVEGUIDE

In order to study light propagation in the waveguides prepared by wet chemical etching, the prism-film coupler device was used as a light coupler. Linear and Mach-Zehnder multimode waveguide structures were investigated. In Fig. 8 we show a photograph of the scattered light from the right hand part of an integrated interferometer structure (compare Fig. 1). As the coupling prism had to be posed on the left part of the substrate, only half of the Mach-Zehnder structure can be seen. The visible part of the two parallel interferometer arms and of the right hand side output arm correspond to a length of 55 mm, each, the width of the light guiding structure is 40 m. A decreasing intensity of the scattered light from the left side to the right side can be seen for both of the interferometer arms. At their intersection, the light intensity increases due to the unification of the two arms, but probably

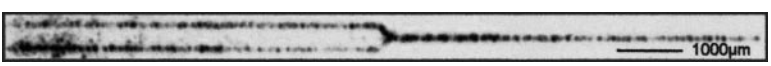


Figure 8. Scattered light from part of a Mach-Zehnder interferometer structure.

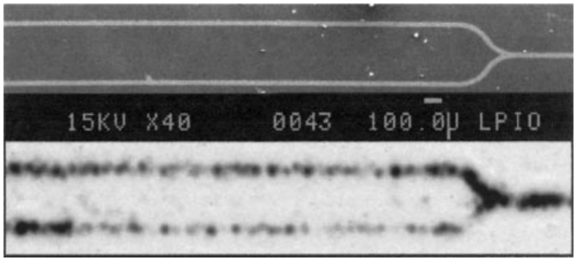


Figure 9. Magnified view of the Mach-Zehnder interferometer, showing a SEM micrograph of the structure (a) and the emission of the scattered light (b).

also due to multiple-reflections as a consequence of the changed geometry. In the output arm of the interferometer, again, the scattered light intensity decreases from the left side to the right side.

The intersection region where the parallel interferometer arms are unified to the output arm of the Mach-Zehnder structure, is shown in a magnified view in Fig. 9. In the upper part, a SEM micrograph can be seen, the lower part of the figure shows the scattered light from the waveguide. The length of the white bar correspond to 100 m for both parts of the figure.

In order to determine the propagation losses in the Mach-Zehnder interferometer, the density of the scattered light has been extracted from the photograph of Fig. 8 for the three linear sections of the PZT waveguide. As an example, we show in Fig. 10 the profile of the scattered light from the interferometer output arm as a function of the propagation distance together

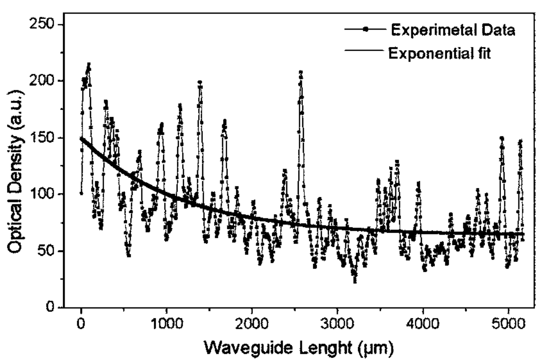


Figure 10. Light density as a function of propagation distance in the output arm of the Mach-Zehnder interferometer waveguide.

with an exponentially decaying function, fitted to the experimental points. The recorded light intensity seems to be composed of an (exponentially decaying) continuous background to which are superposed more or less regularly appearing individual light peaks of high intensity. We suppose that the losses caused by the surface roughness, the irregularity of the etching edges, and the grain structure of the PZT contribute to the background spectrum, whereas the irregular scattering might be due to mesoscopic defects like dust particles at the surface, interface defects, and cracks.

VI. CONCLUSIONS AND PERSPECTIVES

PZT transparent films were realized by chemical solution deposition on glass substrates and wet chemical etching was successfully used for the realization of optical waveguide structures of Mach-Zehnder type. While the etching solution is not yet optimized, an irregularity of the etching edge around ± 1 m was achieved and permitted to realize interferometer structures with a width of 40 m and an overall length of up to 19 mm. From a more systematic study of the PZT wet chemical etching process, and in particular of the etching solution, an improvement can be expected which should allow to considerably reduce the width of the waveguide to only a few micrometers. Alternatively ion beam etching could be employed.

The results from the transmission spectroscopy showed the potential utility of PZT ceramic thin films for light transmission at the telecommunication wavelength. Laser light propagating and guiding at 632 nm in a Mach-Zehnder interferometer structure confirm the interest of PZT for this type of application. The utilization of the M-lines technique allowed to measure the refractive index of the PZT film which shall be of importance for the calculation of an optimum cross-section of the waveguide.

Light confinement in the waveguide structure was achieved, but has still to be improved. From the propagation loss measurements two main conclusions can be drawn: first, there are irregular mesoscopic defects which seem to be responsible for a considerable loss of the light intensity. This should be healed by an improved deposition process of the PZT film. Second, the intersection between the parallel interferometer arms and the output arm is an additional source of losses due to an augmented number of reflections in this region. A detailed study of the geometry will be necessary, varying the angle and eventually the form of the intersection. Finally, integration of the waveguide with its electrodes has to be realized in order to allow a characterization of the ferroelectric waveguide structure in terms of the electro-optic effects.

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