Journal of Electroceramics 2:2, 105–111, 1998

Optical Waveguiding Properties of $(Pb,La)TiO_3/Al_2O_3$ Planar Structures

E. DOGHECHE, B. JABER & D. RÈMIENS
Laboratoire des Matériaux Avancés Céramiques, CRITT Céramiques Fines Techniques, Université de Valenciennes, Le Mont-Houy, BP311 59304, Valenciennes, Cedex-France, email: edoghech@univ-valenciennes.fr

Submitted July 22, 1997; Revised April 7, 1998; Accepted April 10, 1998

Abstract. Thin films of lead lanthanum titanate $(Pb,La)TiO_3$ have been grown by radio-frequency magnetron sputtering on (0001) Al_2O_3 substrates. The structure, the microstructure and the optical properties of the films have been investigated as a function of the postdeposition annealing. Films deposited at low temperatures crystallize to a perovskite phase after the annealing treatment from 500°C to 650°C. X-ray $(\theta - 2\theta)$ diffraction studies have shown that films are crystallized with a strong (111) orientation and the best crystalline structure is reported at 600°C. The optical properties were both demonstrated by spectrophotometry and prism coupling. PLT thin films with a transparency of 80% in the wavelength range 300–2000 nm have exhibited a refractive index of 2.38 @ 632.8 nm representing 97% of the bulk corresponding material. Investigation of optical propagation has been accomplished in a 10 mm long planar optical waveguide using a butt-coupling configuration.

Keywords: lanthanum doped lead titanate, thin films, planar waveguide, optical characterizations

1. Introduction

The need of high speed optoelectronic devices for communication systems has resulted in a great interest in integrated optics. Most projects concerning the development of guided-wave optical devices have been concentrated on the hybrid integration of structures often realized in bulk technology. To make possible the development of novel optical interconnection architectures using miniaturized electronic components, there has been a challenge to develop thin film devices performing the same function as bulk ceramics, taking advantage of geometrical flexibility and integration with semiconductor integrated circuits [1,2]. Due to the high transparency and large electrooptic effects [3,4], lead-based ferroelectric materials have been especially attractive for applications in integrated optics devices such as optical TIR switches and acoustooptic deflectors [5–7] and waveguide modulators [8]. Moreover, epitaxial thin films are required in order to minimize the optical transmission losses [9–11]. The objective is to define high quality thin film optical waveguides that can be used directly as passive connections between components or as a basis for designing other devices. The most used techniques for depositing ferroelectric $(Pb,La),(Zr,Ti)O_3$ thin films include rf sputtering [4,8,12], sol-gel process [13], pulsed laser deposition [14] and metalorganic chemical vapor deposition [10,15]. The aim of this work is to correlate the crystalline structure of the films (that could be controlled by the process conditions) and the optical properties with postdeposition annealing temperatures. In this study, the optimum annealing conditions have been found for obtaining thin films with optical properties close to those of the bulk material.

2. Experimental Procedure

Thin films of lanthanum-doped lead titanate have been successfully grown on (0001) Al_2O_3 substrates by radio-frequency magnetron sputtering from ceramic targets (chemical formula: $Pb_{1-y}La_yTi_{1-y/4}O_3$ where $y = 0.28$). The experimental set-up used for the sputtering deposition has been described previously [16,17]. The parameters have been optimized in order to assure that the composition transfer between the target and the film gives the desired stoichiometry. The sputtering conditions are summarized in Table 1. The substrate temperature reached about 170°C during the deposition (due to species bombardment) and the deposition rate was maintained at about 5 nm/min. In order to crystallize the material, it is necessary to densify the layer with a post-deposition annealing treatment using a conventional furnace anneal. The temperature (550°C to 650°C) and the heat treatment time (2 h) have been optimized to yield a high level of crystallization. This densification process is very important in order to eliminate the porosities which are primarily the main cause of scattering losses. The crystal structure has been analyzed by X-ray diffraction in the $(\theta, 2\theta)$ configuration with monochromatic CuKα radiation. The film morphology was examined using scanning electron microscopy (SEM). The optical properties of PLT thin films have been evaluated from optical transmission measurements using an UV/VIS/NIR spectrophotometer (Perkin-Elmer Lambda 9) in the wavelength range 300 nm to 2000 nm. The light used for transmission was incident normal to the sample surface. The optical properties were calculated using the spectral transmittance based on the envelope technique described by Manifacier et al. [18]. The packing density (p) of the films have been determined by the Bragg-Pippard model [19] using the refractive indices of the film and bulk $(Pb, La)TiO_3$ material at 632.8 nm. The optical waveguiding properties of the PLT thin film have also been obtained using prism coupling [20,21].

Table 1. Deposition conditions for $(Pb,La)TiO_3$ thin films on (0001) Al_2O_3 substrate

Parameters	Conditions
Target composition	Mixing PbO, TiO_2, La_2O_3
RF power (W/cm^2)	2.6
Deposition gas	Ar (100%)
Gas pressure (mTorr)	50
Target diameter (mm)	72.6
Target-subst. spacing (mm)	70
Substrate	Al_2O_3 (0001)
Substrate temperature	unheated
Deposition rate(nm/min)	5

3. Results and Discussion

3.1. Crystal Structure and Microstructure

Figure 1 shows the X-ray diffraction patterns of the PLT thin films deposited on (0001) Al_2O_3 and annealed by a conventional process (from 500°C to 650°C). The X-ray diffraction study shows the enhancement of the degree of the *c*-axis orientation and crystal quality by changing the annealing temperature. The post-deposition annealing influences the crystalline quality of the film, and more precisely the film orientation. The parameter I has been defined by the following relation: $I = I(111)/\Sigma I(h, k, l)$ where $I(111)$ and $I(h, k, l)$

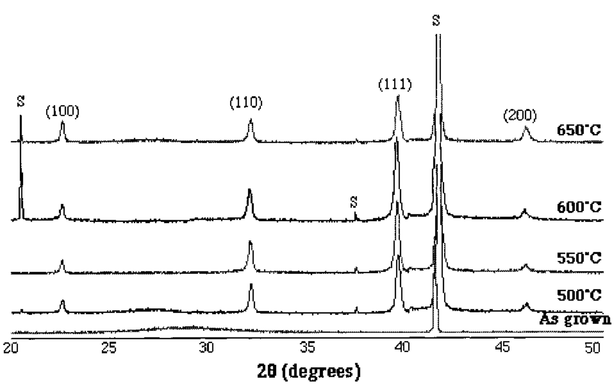

Fig. 1. $(\theta - 2\theta)$ X-ray diffraction patterns of $(Pb, La)TiO_3$ thin films on (0001) Al_2O_3 substrates versus postdeposition annealing temperature ranging from 500°C to 650°C.

represent respectively the intensities of (111) and (h, k, l) peaks of the perovskite structure. Such a parameter can be used to characterize the film.

As observed, the structure is cubic single phase at low temperature (below 500°C). In addition, before the perovskite phase formation, the pyrochlore phase is not observed. The perovskite phase formation is complete at 600°C, the intensity of the (111) peak is maximum with a lattice parameter $a = 3.9286$ Å. Similarly, the intensities of the (100) and (110) peaks increased with increasing the annealing temperature. The crystal quality is found to be optimum at 600°C $(I = 0.65)$. This indicates a higher crystallization of the structure in the (111) direction. When the annealing temperature increased from 600°C to 650°C, the (111) peak of the perovskite phase decreased while the other peaks have a significant change, the parameter I decreases to 0.45.

The morphology of PLT films has been observed with a scanning electron microscopy (SEM). These are highly transparent. After annealing, it has been found that the films have a microstructure with a very fine grain size without porosities suitable for optical waveguide applications. The cross-section photograph shows that the layer is uniform with a thickness of 600 nm.

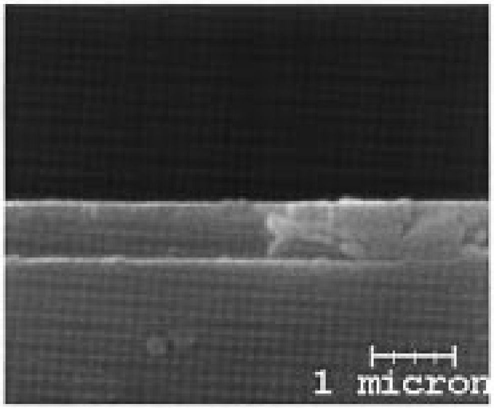

Fig. 2. Cross-section of PLT thin films on (0001) Al_2O_3 annealed at 600°C.

3.2. *Optical Characterizations*

The optical properties have been investigated by optical transmission measurements. Typical spectra T(λ) of sputtered (Pb,La)TiO_3 thin films deposited from 550°C to 650°C on transparent (0001) Al_2O_3 substrates are presented in Fig. 3. A high transmission of 80% can be observed in the PLT thin films with the oscillations due to multiple reflections in the film resulting from constructive and destructive interfer-

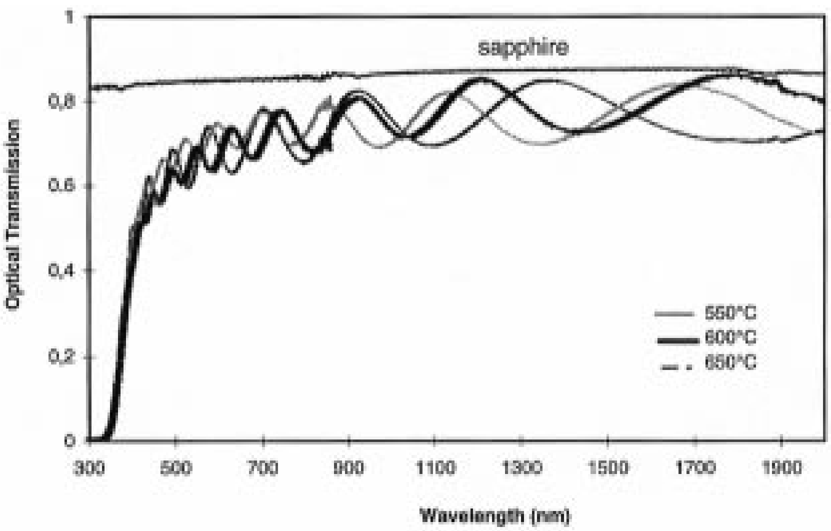

Fig. 3. Optical transmission spectrum of PLT films versus λ for various annealing temperatures.

ences of the transmitted light. The optical transmission coefficient increases with the temperature; the difference observed is certainly due to the evolution of the densification of the layer. The film transmittance drops abruptly at short wavelength (>350 nm). This is related to the fundamental absorption which refers to band-to-band transition, i.e., to the excitation of an electron from the valence band to the conduction band, and the direct band-gap energy (E_g) is estimated as 3.70 eV in agreement with values reported in the literature [22].

In this work, significant changes in optical properties are observed with temperature. At 550°C, the crystallization process is not complete, the index of refraction is found to be 2.11 ± 0.01@632.8 nm. The packing density p is calculated to be about 85% from the model described by Bragg and Pippard. The densification of the layer is obtained at 600°C and the refractive index is 2.38 ± 0.01@632.8 nm. The increase of the refractive index with the annealing temperature is attributed to optimum densification and crystalline orientation. This gives a high packing density p of 97%. In comparison, the refractive index of single crystal (Pb,La)TiO_3 is 2.44 at 632.8 nm [23]. The result obtained at 600°C is in agreement with those reported by authors with a postdeposition annealing process [13,24].

A lower refractive index of 2.24 ± 0.01 is obtained for films annealed at 650°C. The most important cause of the degradation in optical properties comes from the PbO loss, especially due to evaporation during annealing. This transforms the microstructure of the films and this implies porosities inside the layer resulting in a smaller packing density of 91%. This phenomen has been reported previously in PLT thin films [15]. The extinction coefficient ($k = 10^{-3}$ at 600°C) remains constant for a wide wavelength range. This low value illustrates the high transparency of these films and is related to the low surface roughness.

In an optical system, the important parameters determining the waveguiding in a thin film are the refractive index difference between the film and the substrate, the film thickness and the propagation losses. The determination of the optical properties in a planar waveguide is given by the prism coupling (or the m-lines) technique. It consists of measuring the angles (θ) for which dark lines appear in a beam reflected on a rutile prism coupled to the waveguide. With this configuration, the optical axis is perpendicular to the sample surface. By varying the angles, all TE or TM guided-modes for the structure are separately excited. The effective indices (β/κ) can be determined from these angles. Both ordinary indices (n_0) and extraordinary indices (n_e) and film thickness were respectively determined by TE and TM modes excitation. Waveguiding modeling using

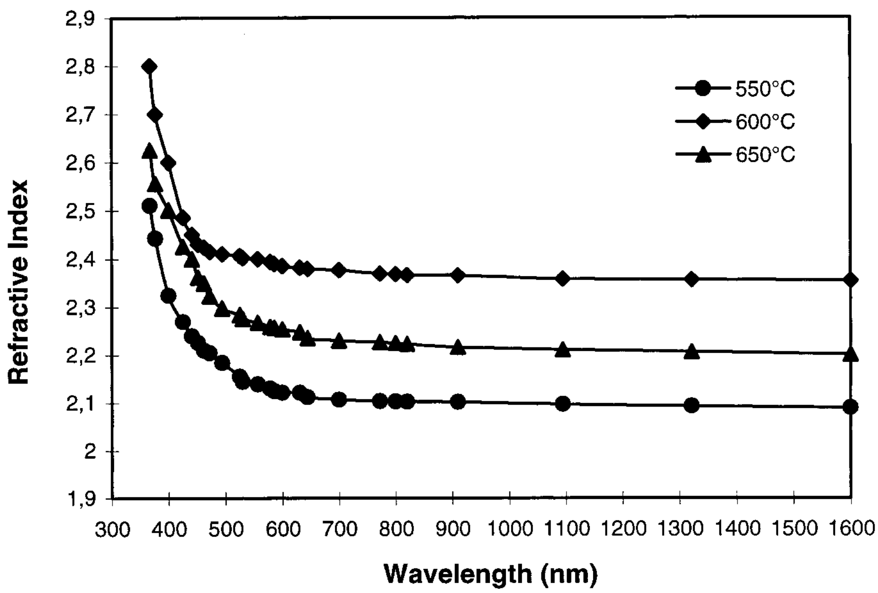

Fig. 4. Dispersion of the refractive index for PLT films annealed at different temperatures.

the dispersion equations predicted three solutions for both TE and TM modes. As example, Fig. 5 represents the calculated TE guided-mode index (β/κ) for the PLT film on Al_2O_3: the number of TE modes increases with increasing film thickness. Three TE modes can be excited for a thickness d of 600 nm. Figure 6 shows the observed m-lines of the waveguiding TE modes for a PLT film. 3 TE modes were excited in the layer of thickness 600 nm: $\theta_{\mathrm{TE2}} = +1.5°$, $\theta_{\mathrm{TE1}} = -19°$ and $\theta_{\mathrm{TE0}} = -33°$. The refractive indices have been calculated by using Snells law: $n_0 = 2.38 \pm 0.001$ for the TE mode and $n_e = 2.27 \pm 0.001$ for the TM mode at 632.8 nm. The refractive indices obtained are similar to those previously reported for films with same composition [5,25,26]. The film thickness obtained from the TE and TM fits is 590 nm ± 10 nm, in agreement with the value defined by the SEM cross-section measurements. We can notice that the narrow coupling width indicates a smooth film with uniform thickness, and a good coupling of the light into the layer. The quite good quality of the film can be proved by these sharp lines for TE and TM modes and the width of half height ($\sim 0.1°$) suggests that optical losses are weaker in the waveguide [9,28].

Measurements by such a guided-wave technique are of considerable interest for studying the anisotropic nature of the film [27]. The optical anisotropy can be determined with the m-lines method by simultaneously using TE and TM polarizations. This can be represented by the birefringence Δn and it is clearly correlated with the microstructure, i.e., the packing density of the film material. At 600°C, PLT films exhibit a denser layer and the anisotropy is very low ($\Delta n \approx 0.11$) in comparison to higher values obtained at 550°C and 650°C.

Furthermore, the refractive index profiles have been analyzed using an inverse WKB method [29]. This method is the common approximation used for planar waveguides index profiles analysis (Fig. 7) and it depends only on the refractive indices distribution in the layer. The ordinary refractive index n_0 remains constant over the film thickness (600 nm) and decreases near the substrate surface. The results revealed a steplike behavior of the films indicating an

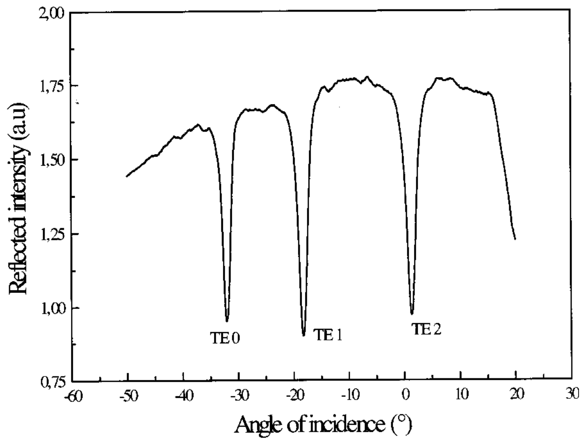

Fig. 6. Coupling curve of the TE guided modes in (Pb,La)TiO_3 thin film annealed at 600°C.

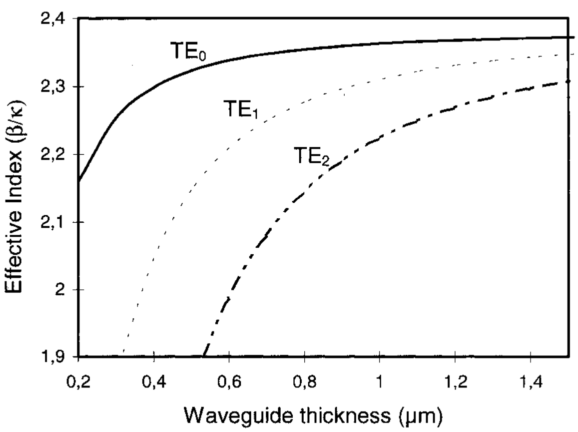

Fig. 5. Theoretical effective index (β/κ) for TE mode excited in PLT films.

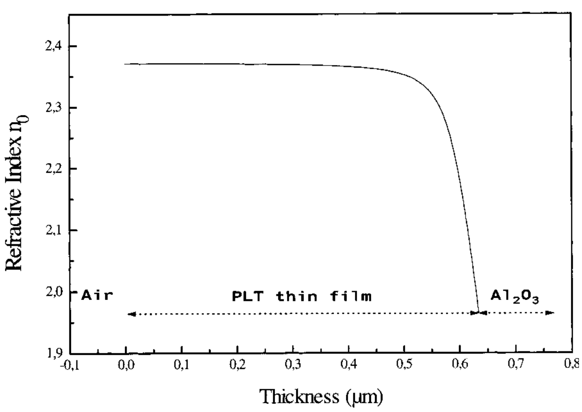

Fig. 7. Index profile reconstruction of PLT film annealed at 600°C by an inverse WKB method.

optical homogeneity along the thickness without film-substrate interaction. In addition, a linear regression fitting of the variation of the square effective mode indices (Nm^2) with the square mode number $(m+1)^2$ can provide thin films parameters (Fig. 8). The variation reported for a step index layer is linear as given by the following relation

$$Nm^2 = n^2 - \lambda/4_d^2(m+1)^2$$

where d and λ are respectively the film thickness and the wavelength. Consequently, this agreement between the measured (from m-lines) and the computed effective index values confirm the homogeneous nature of the PLT layers [30].

The butt-coupling configuration has also been used to observe the propagation of the optical beam inside the PLT planar waveguide. The distinct m-lines indicate that favorable optical waveguiding properties can be expected. We have used transparent PLT films deposited on a sapphire substrate. Both ends of the samples have been cut and optically polished so as to obtain a 10 mm waveguide length. The optical polishing is critical at the edges in order to test this configuration [31,32]. A 10 mW He-Ne laser source was used and micropositioners were used to align the focused beam into the guide as much as possible. This simple technique is relatively easy to use, all that is necessary is to align the optics. The set-up is presented Fig. 9. The high refractive index difference between the film and the substrate provide a good confinement of the light in the waveguide layer. The laser light is coupled into the guide input using an objective lens (Nikon $\times$20) and the light is gathered at the output facet by an objective lens (Nikon $\times$40) which focused the output pattern onto a CDD camera (Sony).

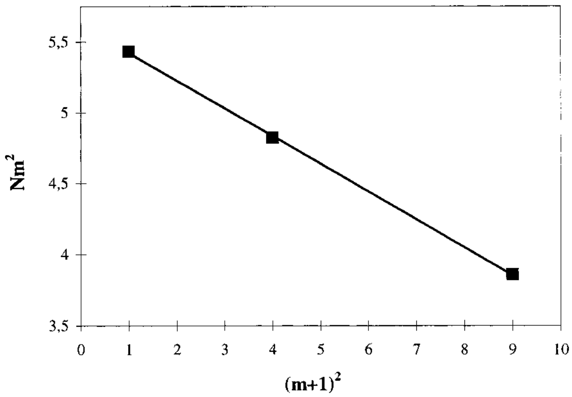

Fig. 8. Square of effective indices Nm^2 versus $(m+1)^2$ for TE mode.

A waveguiding distance of 10 mm was observed for PLT thins films at 600°C. Figure 10 shows the photograph of the light propagation inside the layer. A larger bright light is sent through the guide. This reflects moderate loss in the waveguide as a result of the most important densification of the layer. For samples annealed at 550°C and 650°C, an optical waveguiding has been observed for a lower distance. As the packing density is smaller for films annealed at 550°C and 650°C, the surface roughness is greater. This will probably lead to scattering losses which are the most important mechanism of optical propagation losses in thin films [28]. The evaluation of losses as a function of process parameters are in progress, they will provide more informations about the optical quality of the PLT thin films.

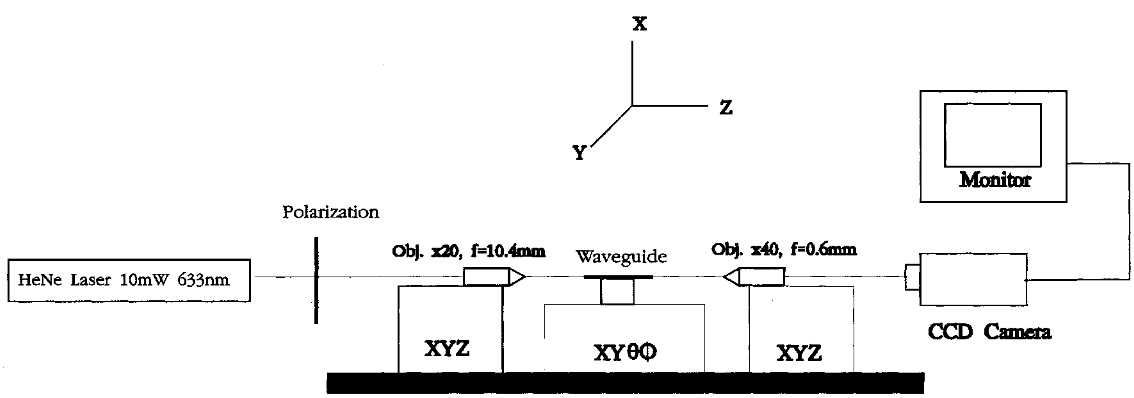

Fig. 9. Experimental set-up for butt-coupling measurements.

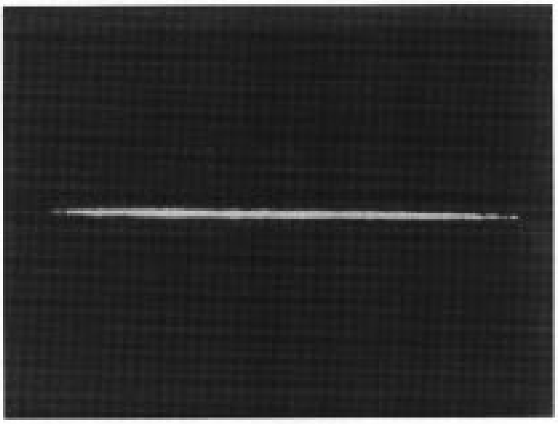

Fig. 10. Photograph of the output near-field of the planar PLT waveguide. The edges were cleaved and polished.

4. Conclusion

In this paper, we have described the growth and the X-ray diffraction analysis of sputtered (Pb,La)TiO_3 thin films on Al_2O_3 substrates. Stoichiometric thin films with a high crystallization in (111) orientation have been obtained by optimizing the post-deposition annealing process. The optical characterizations have been both realized by optical transmission measurements and prism coupling. With the optimum annealing condition of 600°C, a high packing density of 0.97 could be achieved and wide range transparent thin films have exhibited a refractive index of 2.38@632.8 nm close to that of the bulk material. Using an inverse WKB method, a steplike refractive index profile is determined revealing the existance of an homogeneous layer. Optical waveguiding on a distance of 10 mm is observed at 632.8 nm using the butt-coupling configuration. Such optical waveguides can be directly used in integrated photonic circuits or as basis for designing new complex circuits.

Acknowledgments

The authors would like to thank Dr. Boudrioua from CLOES-MOPS for his help.

References

1. R.W. Whatmore, *Ferroelectrics*, **118**, 241 (1991).
2. Y. Watanabe, *Appl. Phys. Lett.*, **66**, 1770 (1995).
3. G.H. Haertling and C.E. Land, *J. Am. Ceram. Soc.*, **54**, 1 (1971).
4. H. Adachi, O. Osamu, and K. Wasa, *J. Appl. Phys.*, **60**, 736 (1986).
5. H. Adachi and K. Wasa, *IEEE Trans. Ultra. Ferroelec. Freq. Cont.*, **38** (1991).
6. K. Wasa, O. Yamazaki, H. Adachi, T. Kawaguchi, and K. Setsune, *J. Ligh. Techn.*, **LT-2**, 710 (1984).
7. T. Kawaguchi, H. Adachi, K. Setsune, O. Yamazaki, and K. Wasa, *Appl. Optics*, **23**, 2187 (1984).
8. A.B. Wegner, S.R. Brueck, and A.Y. Wu, *Ferroelectrics*, **116**, 195 (1991).
9. C.M. Foster, S.K. Chan, H.L. Chang, R.P. Chiarello, T.J. Zhang, J. Guo, and D.J. Lam, *J. Appl. Phys.*, **73**, 7823 (1993).
10. Y. Kim and A. Erbil, *Appl. Phys. Lett.*, **70**(2), 143 (1997).
11. Y.M. Kang, K.S. Lee, and S. Baik, *J. Appl. Phys.*, **78** (1995).
12. H. Adachi, T. Mitsuyu, O. Yamazaki, and K. Wasa, *Jap. J. Appl. Phys.*, **24**, 287 (1985).
13. J. Koo, S.U. Kim, D.S. Yoon, K. No, and B.S. Bae, *J. Mat. Res.*, **12**, 812 (1997).
14. G.M. Rao and S.B. Krupanidhi, *Appl. Phys. Lett.*, **64**, 1591 (1994).
15. A.R. Khan and S.B. Desu, *J. Mat. Res.*, **10**, 2777 (1995).
16. E. Dogheche, B. Jaber, D. Rémiens, and B. Thierry, *Microelectron. Engin.*, **29**, 315 (1995).
17. B. Jaber, D. Rémiens, E. Cattan, and B. Thierry, *Sensors and Actuators*, **A51**, 1 (1995).
18. J.C. Manifacier, J. Gasiot, and J.P. Fillard, *J. Phys. E.: Sci. Instrum.*, **9**, 1002 (1976).
19. W.L. Bragg and A.B. Pippard, *Acta Cryst.*, **6**, 865 (1953).
20. P.K. Tien, R. Ulrich, and R.J. Martin, *Appl. Phys. Lett.*, **14**, 291 (1969).
21. E. Pelletier, F. Flory, and Y. Hu, *Applied Optics*, **28**, 2918 (1989).
22. V.I. Zametin, *Phys. Stat. Sol. (b)*, **124**, 625 (1984).
23. P.D. Thacher, *Appl. Optics*, **16**, 3210 (1977).
24. M. Okuyama, T. Usuki, Y. Hamakawa, and T. Nakagawa, *Appl. Phys.*, **21**, 339 (1980).
25. S.B. Xiong, Z.G. Liu, X.Y. Chen, X.L. Guo, X. Liu, and S.N. Zhu, *Appl. Phys. Lett.*, **67**, 2729 (1995).
26. J. Koo, S.U. Kim, K. No, and S.B. Bae, *J. Mat. Res.*, **12**, 812 (1997).
27. B.G. Potter, Jr. B. Sinclair, and D. Dimos, *Appl. Phys. Lett.*, **63**, 2180 (1993).
28. D.K. Fork, F. Armani-Leplingard, J.J. Kingston, and G.B. Anderson, *MRS. Symp. Proc.*, **392**, 189 (1995).
29. K.S. Chiang, *J. Light. Techn.*, **LT-3**, 385 (1985).
30. R. Th. Kersten, *Opt. Comm.*, **4**, 427 (1973).
31. B.J.H. Stadler and M. Oliveria, *J. Am. Ceram. Soc.*, **78**, 3336 (1995).
32. P.F. Baude, C. Ye, T. Tamagawa, and D.L. Polla, *J. Appl. Phys.*, **73**, 7960 (1992).