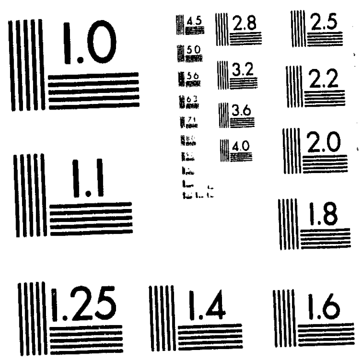
1.0
2.8
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Peter Green

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Electrooptical and Optical Evaluation of $Pb(Zr, Ti)O_3$ Thin Films Using Waveguide Refractometry

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Abstract

Prism-coupled, waveguide refractometry was utilized to independently monitor electric field-induced changes in the extraordinary and ordinary refractive indices of a $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT 53/47) thin film. Under an electric field, applied normal to the film plane and corresponding to saturation of the electric polarization, the ratio of the extraordinary to ordinary refractive index change ($\Delta n_e/\Delta n_o$) is found to be -4/1, contributing to a net birefringence change ($\Delta(n_e-n_o)$) of -0.021. The technique, thus, accesses both diagonal and off-diagonal elements of the electrooptic response tensor describing the macroscopic behavior of the polycrystalline film. In addition, the widths of waveguide mode reflectivity minima were sensitive to variation in the microstructure of several PZT (40/60) films indicating that the refractometry technique can provide information helpful in evaluating optical quality in these films.

1. Introduction

Optical phenomena in ferroelectric oxide materials based on the lead zirconate titanate system (PZT) have been the focus of intense interest in recent years. With advances in the fabrication of high quality, polycrystalline films exhibiting enhanced electrical and ferroelectrical properties over more conventionally produced bulk ceramics, the opportunity to use these materials in applications requiring high device areal densities and integrability of active elements now exists. Indeed, non-volatile, optical memories based on electro-optic and photosensitive processes in these materials are being pursued extensively. PZT films to be used for optical memories, for example, must provide a sufficient change in birefringence with electric field modulation to facilitate reliable read-out of the device state after writing. In addition, the optical quality of the thin films, e.g. optical loss and property homogeneity, must be carefully controlled. Characterization of the optical and electrooptic properties of these films is, therefore, extremely important in providing feedback for optimization of film composition and synthesis for a given application.

Previous measurements of the electrooptic properties of ferroelectric thin films demonstrated behavior comparable to bulk $(Pb,La)(Zr,Ti)O_3$ (PLZT) ceramics [1–4]. These studies utilized ellipsometric techniques to monitor changes in the material birefringence, $\Delta(n_e - n_o)$, under the application of a low-frequency bias field. A major limitation of these methods is the inability to separately measure field-induced refractive index changes along the principal optic axes of the material and, thus, their contributions to the total birefringence change. This precludes a determination of diagonal and off-diagonal elements in the electrooptic tensor describing the material response which is essential in developing an understanding of the microscopic mechanisms contributing to the behavior.

Refractometry, based on prism coupling into thin-film waveguide modes, is an alternative measurement technique which allows the individual contributions to the total, field-induced birefringence change to be determined. This approach has been used previously to obtain ferroelectric oxide film refractive indices under conditions of zero electric field [5,6]. Measurements performed using both transverse electric (TE) and transverse magnetic (TM) polarizations allow electric field induced changes in the ordinary (n_o) and extraordinary (n_e) refractive indices to be independently accessed.

In the present work, a waveguide refractometry technique was used to independently determine field-induced refractive index changes along the principal optic axes of a polycrystalline, PZT thin film. Initial investigations within the waveguiding geometry also indicate that the relative optical quality of a film (taken to correspond to the degree of scattering) may be evaluated.

2. Electrooptic Measurement

The waveguide refractometry technique was used to determine the electrooptic response of sol-gel derived $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT 53/47) films. The films were deposited on Pt-coated silicon substrates ($Pt/Ti/SiO_2/Si$) and were roughly 800 nm thick. A detailed discussion of the sol-gel fabrication process has been presented previously [7]. These samples were single-phase perovskite and exhibited a columnar microstructure with a lateral grain size of 100-150 nm.

Figure 1a depicts the general sample configuration used in this study. The top electrodes consisted of semi-transparent, evaporated Ag films (thickness = 10.5 nm) which define the Ag/PZT/Pt capacitive elements used for evaluation. The sample was clamped to the hypotenuse of a right-angle rutile prism with the top electrode (Ag) in optical contact with the prism. The beam from a HeNe laser (632.8 nm) was focused through the prism onto the coupling spot. TE and TM incident polarization states were used, allowing measurements to be performed with polarization oriented perpendicular to and in the plane containing the applied electric field.

As shown in the refractometer schematic of Figure 1b, the sample/prism arrangement was then mounted onto a computer-controlled rotation stage to allow the angle of incidence to be varied. A Si photodiode (PD2) monitored the reflected beam intensity as function of incidence angle. A mechanical chopper/lock-in amplifier arrangement provided phase-sensitive detection of the reflected signal. The retro-reflected beam intensity, measured at PD1, was used to determine the zero incidence angle position before scanning. Reflectivity scans were collected under various applied-field conditions. Polarization saturation of these PZT films was achieved with a dc voltage of ± 10 V ($E \approx 125$ kV/cm).

Sharp minima in the reflected intensity were associated with waveguiding modes in the PZT/electrode film stack. The angular positions of these minima are determined by the optical constants and layer geometry present in the sample and can, thus, be used to find the refractive indices and thickness of the PZT film. Using known optical constants and thicknesses for the Pt, Ag and prism [8,9], the reflectivity response can be modeled for various PZT indices and thicknesses [10]. An iterative procedure was adopted to fit the observed reflectivity minima positions to those calculated using the unknown PZT refractive index and thickness as adjustable parameters. The deviation between the calculated and experimental reflectivity minima positions was minimized by visual inspection of the reflectivity curves, with refractive index and thickness intervals as small as 0.001 and 1 nm, respectively, causing discernible changes in the degree of fit. Where possible, at least 3 modes were used during the process in an effort to overconstrain the problem and generate a unique fit to the data. This requirement necessitated the examination of films with thicknesses of 700 to 800 nm.

3. Results and Discussion

Figures 2 and 3 contain reflectivity data obtained in both TE and TM polarizations, respectively, for samples with and without an applied electric field. Note that the x-axis values correspond to incidence angles within the prism.

At zero remanent polarization ($P_r \approx 0$), the refractive indices parallel and perpendicular to the film plane were found to be 2.544 and 2.547, respectively. These values indicate that the film was nearly optically isotropic prior to poling. The zero polarization state was achieved by applying an appropriate voltage to give the film a remanent polarization halfway between the positive and negative saturation values. The initial indices were determined using both electroded and non-electroded areas of the sample, with good agreement obtained for both sets of measurements. The film thicknesses obtained from the TE and TM fits, which were 0.828 and 0.825 μm, respectively, were in good agreement with the thickness determined using a Dektak stylus profilometer: $t = 0.81 \pm 0.01$ μm. The refractive indices obtained are also similar to those previously reported for films of this composition [5,6].

Under an applied electric field, a polycrystalline ferroelectric oxide will behave, macroscopically, as an optically uniaxial material with the optic axis aligned along the field direction. With the present geometry, the extraordinary index (n_e), which is perpendicular to the film plane (parallel to the applied field) decreased by 0.017 from 2.547 to 2.530. At the same time, the ordinary index (n_o), which is parallel to the film plane, increased by 0.004 from 2.544 to 2.548. Consequently, the applied field caused the film to become negatively birefringent, as expected for an ABO_3, perovskite-type material [11]. The measured field-induced change in birefringence of $\Delta(n_e-n_o)$ = -0.021 is also similar to values recently reported for other PZT and PLZT films [4]. In a polycrystalline, multi-domain film, the observed index changes correspond to changes in the macroscopic polarization of the sample and, thus, the indices measure the average alignment of domains due to the applied field. As such, the measured birefringence at saturation is less than the birefringence of a single domain region.

In addition, the waveguide measurement indicates that the ratio of $\Delta n_e/\Delta n_o$ is roughly -4/1. A theoretical expression for this ratio may be obtained by considering the electric-field-induced reorientations of the individual domains and by assuming each domain exhibits single crystal birefringence. In the unpoled state, the domains are assumed to be randomly oriented leading to optically isotropic behavior. Electric field poling tends to align the domains parallel to the electric field which results in negative birefringence at remanence, with $\Delta n_e/\Delta n_o$= -2/1 [12]. In the present case, however, the measurement of refractive index is made under an applied field which is likely to modify the ratio due to the linear electrooptic effect characteristic of the individual domains. In addition, strain-optic effects are also likely to affect the ratio, particularly under low frequency applied fields. Thus, measurements of this type can provide information about the contribution to the electrooptic response by mechanisms other than simple domain reorientation.

Since the accuracy of the refractive index and thickness values determined for a PZT film depend on the values of the optical constants and thicknesses of the other layers in the film stack, the sensitivity of the fit to variations in these parameters was examined. It was found that the values of n_o, n_e, and t derived for a PZT film were only slightly dependent on a precise knowledge of the electrode parameters. For example, with changes of ±10% in both n and k of the Ag and Pt, a change of <0.2% was obtained for the optical constants of the PZT film. More importantly, the values of Δn_e and Δn_o are even less sensitive to comparable uncertainties in the electrode parameters, which lends even greater confidence to the values obtained for the field-induced index changes.

Optical hysteresis effects were also observed by rotating the sample stage to the inflection point on the low angle side of the center TE mode (Fig. 2) and applying a 10V, sawtooth voltage (30 Hz). The modulation in the reflected intensity at that incidence angle, corresponding to a shift in coupling angle for the waveguide mode, was monitored using an oscilloscope. The variation in n_o with applied field, obtained using TE polarized light, is given in Figure 4. The maximum change in n_o due to the ac field was within 0.0005 of that observed in the dc measurement. A similar response was also exhibited using TM polarization, although the effect is somewhat reduced due to the broader reflectivity curves observed.

The hysteresis in the n_o–E curve is consistent with the electrical (P–E) hysteresis exhibited by the sample. In fact, previous studies have shown that the birefringence and, thus, Δn_e and Δn_o are essentially single-valued functions of the electrical polarization, where $\Delta(n_e-n_o) \propto P^2$ [13]. Consequently, the optical index vs applied field response can be used as an alternate way of characterizing the hysteresis of PZT films. The slight asymmetry in Fig. 4 can, therefore, be interpreted as a slight reduction in the saturation polarization for a negative bias as compared to a positive one. This type of asymmetry could not be determined simply by measuring the electrical polarization vs applied field response, since these measurements do not determine the absolute value of the polarization.

Since the optical indices provide an absolute measure of the polarization state, electrooptic characterization may also be very useful for evaluating phenomena such as fatigue and polarization-state imprinting.

4. Optical Quality

The widths of the waveguide modes observed in Figures 2 and 3 are dependent upon a number of factors, including: waveguide coupling conditions, guiding and boundary layer optical constants and geometry, and optical scattering within the film stack caused by both interfacial and volume scattering sources originating from the PZT microstructure. Waveguide mode widths, therefore, can provide information regarding the relative degree of optical scattering within the film stack when care is taken to minimize the influence of the other contributions.

In the present case, although coupling conditions can be controlled during the measurement, the presence and identity of high extinction coefficient boundary layers, i.e. the metallic electrodes, can have a large effect on the width of the waveguide modes observed. For example, Figures 5 and 6 depict model reflectivity curves calculated using appropriate material optical constants for a PZT film on MgO (a low extinction coefficient dielectric) with and without a Pt base electrode for both TE and TM polarizations. It can be seen that, when the high extinction coefficient Pt layer is included, the overall mode width is increased, with lower angle (higher order) modes exhibiting broader widths due to increased interaction with the metal boundary layer. The effect is particularly dramatic for TM polarization where optical field penetration into the Pt will be even greater. An increased sensitivity to the effects of optical scattering on mode widths is therefore expected in samples which are free from metallic electroding layers.

Consequently, several $Pb(Zr_{0.40}Ti_{0.60})O_3$ (PZT 40/60) samples, deposited directly on a (100) MgO substrate, were subjected to different annealing schedules after spin-coating in an effort to examine the effect of microstructural evolution on waveguide mode widths. The films were approximately 0.5 μm thick and samples were cut from the same MgO substrate after deposition. Figure 7 shows reflectivity scans from samples in an as-deposited state (dried to 300 C), after rapid thermal processing (RTP) at 650 C for 10 minutes and after a furnace anneal at 650 C for 30 minutes. Immediately evident in the data is a significant increase in mode width after any post-deposition anneal compared to the as-deposited, amorphous film. (The accompanying changes in the angular positions of the modes are associated with the change in film refractive index as crystallization occurs.) Given the presence of a low extinction coefficient boundary layer, the MgO, and the insensitivity of the mode width to extinction coefficient changes in the PZT, the width increase with thermal treatment is most likely attributable to increased scattering resulting from the evolving PZT microstructure. Crystallization of the film introduces discontinuities in refractive index at grain boundaries, inclusions and pores as well as increased surface and interfacial roughness thus forming scattering centers in the film stack. Preliminary scanning electron microscopy (SEM) analyses of the RTP and furnace annealed specimens, in fact, reveal an abnormally high degree of cracking with significantly rougher surface topography in the furnace annealed sample when compared with the characteristic microstructure of the RTP sample. This tends to support a microstructural explanation for the broader mode widths observed in the furnace annealed sample. It is apparent, therefore, that mode width can be sensitive to changes in film microstructure, enabling this aspect of the refractometry data to furnish information important in evaluating the relative optical quality of a film.

5. Conclusion

The optical constants and electrooptical responses of PZT thin films have been determined using waveguide refractometry. Through proper choice of polarization conditions and use of a waveguide coupling geometry, the unknown film refractive index and thickness values were determined with information regarding only the incidence angle dependence of the amplitude of the reflected optical field. This contrasts ellipsometric approaches in which the relative amplitude and phase of the reflected polarization components must be measured to uniquely determine the optical constants of the film.

The refractometry technique has been used to independently determine electric-field-induced changes in the refractive indices, both parallel and perpendicular to the applied field in a PZT 53/47 film. In the unpoled state, the film is nearly optically isotropic while under an electric field sufficient to induce polarization saturation, a negative uniaxial birefringence of $\Delta(n_e-n_o) = -0.021$ is produced. In addition, the ratio of the extraordinary to ordinary refractive index change ($\Delta n_e/\Delta n_o$) is found to be roughly -4/1, which implies that mechanisms other than simple domain reorientation contribute to the electrooptic response. Since the optical indices are single-valued functions of the electric polarization, electrooptic characterization may also be very useful for evaluating a variety of polarization related phenomena in ferroelectric films.

In addition, using a sample configuration free of metallic boundary layers, the widths of the waveguide modes have been associated with variations in the microstructural attributes of PZT 40/60 films subjected to different post-deposition thermal anneals. This illustrates the utility of the refractometry technique in an initial evaluation of thin film optical quality.

Acknowledgements

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FIGURE CAPTIONS

Figure 1. Sample configuration (a.) and experimental apparatus (b.) for waveguide refractometry.

Figure 2. Reflectivity data obtained under TE polarization conditions with and without an applied dc electric field.

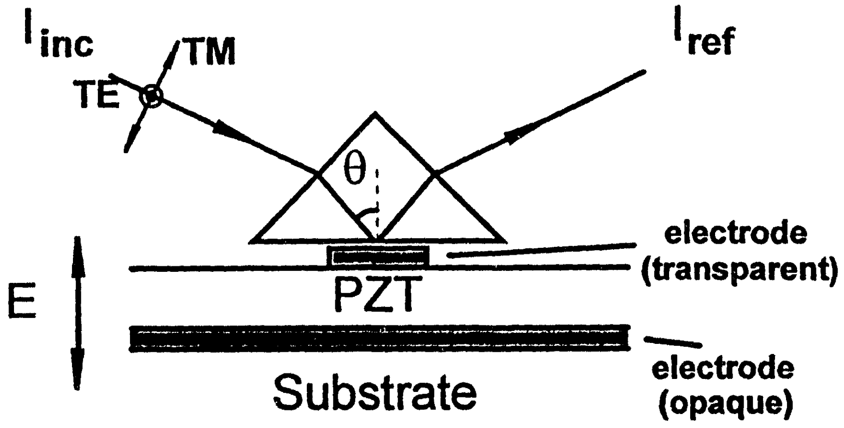
Figure 3. Reflectivity data obtained under TM polarization conditions with and without an applied dc electric field.

Figure 4. Optical hysteresis observed in the PZT film refractive index under an applied ac field at 30 Hz. The y-axis refers to the ordinary refractive index, in the film plane.

Figure 5. Calculated reflectivity under TE polarization conditions for PZT on MgO with and without a Pt base electrode.

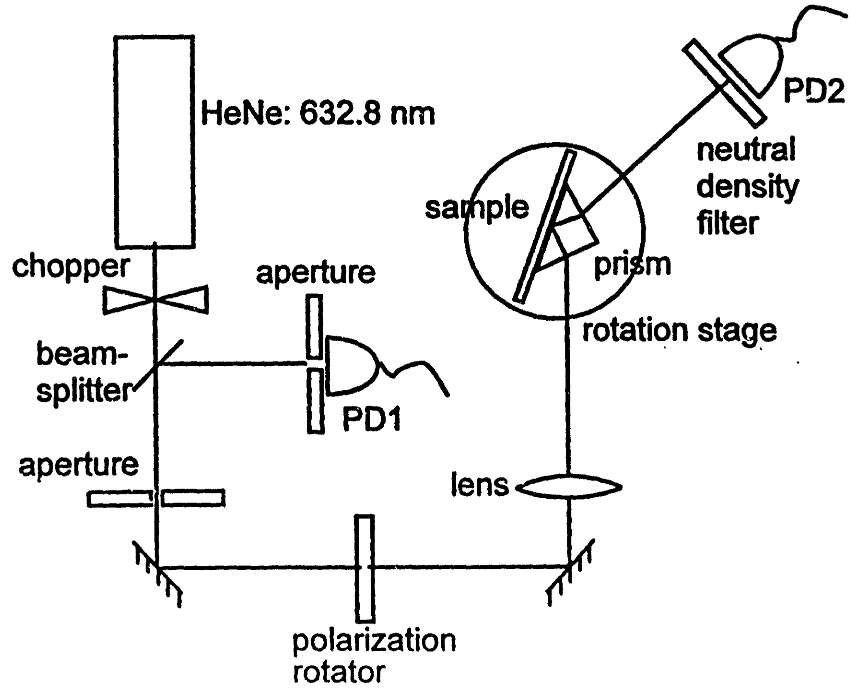
Figure 6. Calculated reflectivity under TM polarization conditions for PZT on MgO with and without a Pt base electrode.

Figure 7. Reflectivity data obtained under TE polarization conditions for PZT (40/60) films on MgO both in the as-deposited condition and after two different post-deposition thermal treatments.



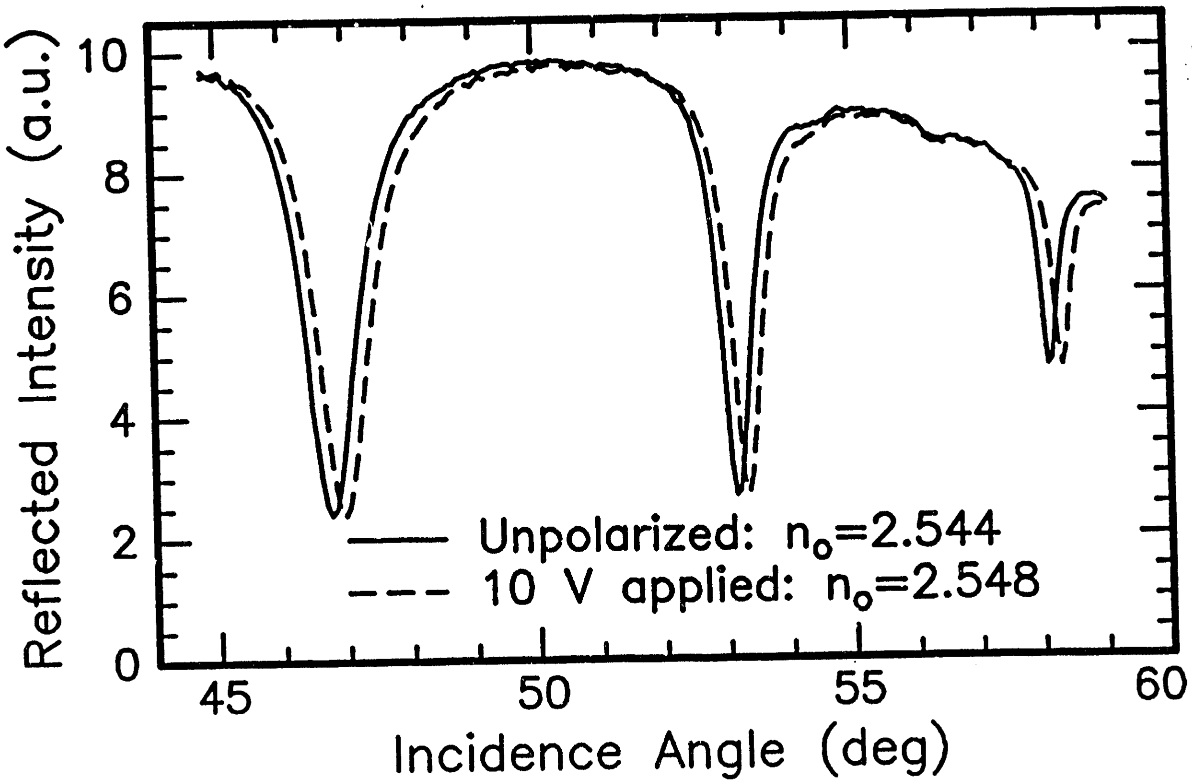
I_{inc}
TM
TE
I_{ref}
θ
electrode
(transparent)
E
PZT
electrode
(opaque)
Substrate

(a.)

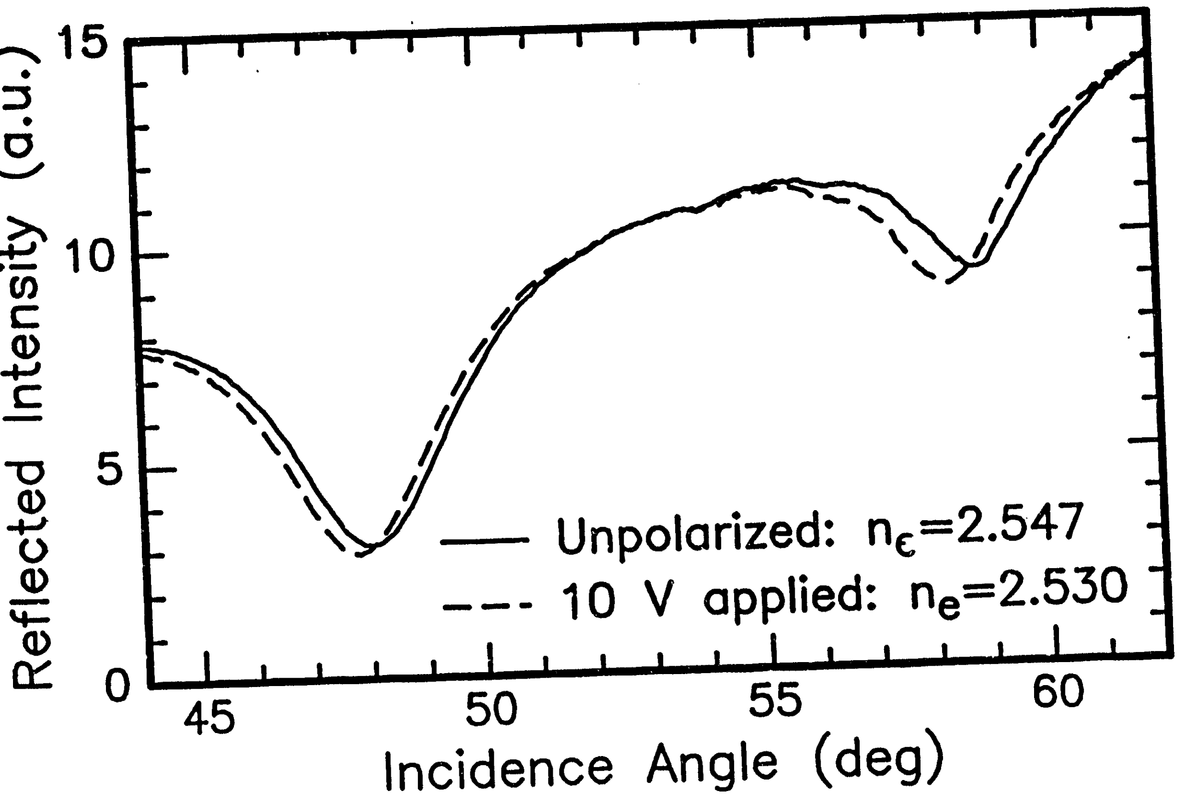


HeNe: 632.8 nm
PD2
neutral
density
filter
sample
prism
rotation stage
chopper
aperture
beam-
splitter
PD1
aperture
lens
polarization
rotator

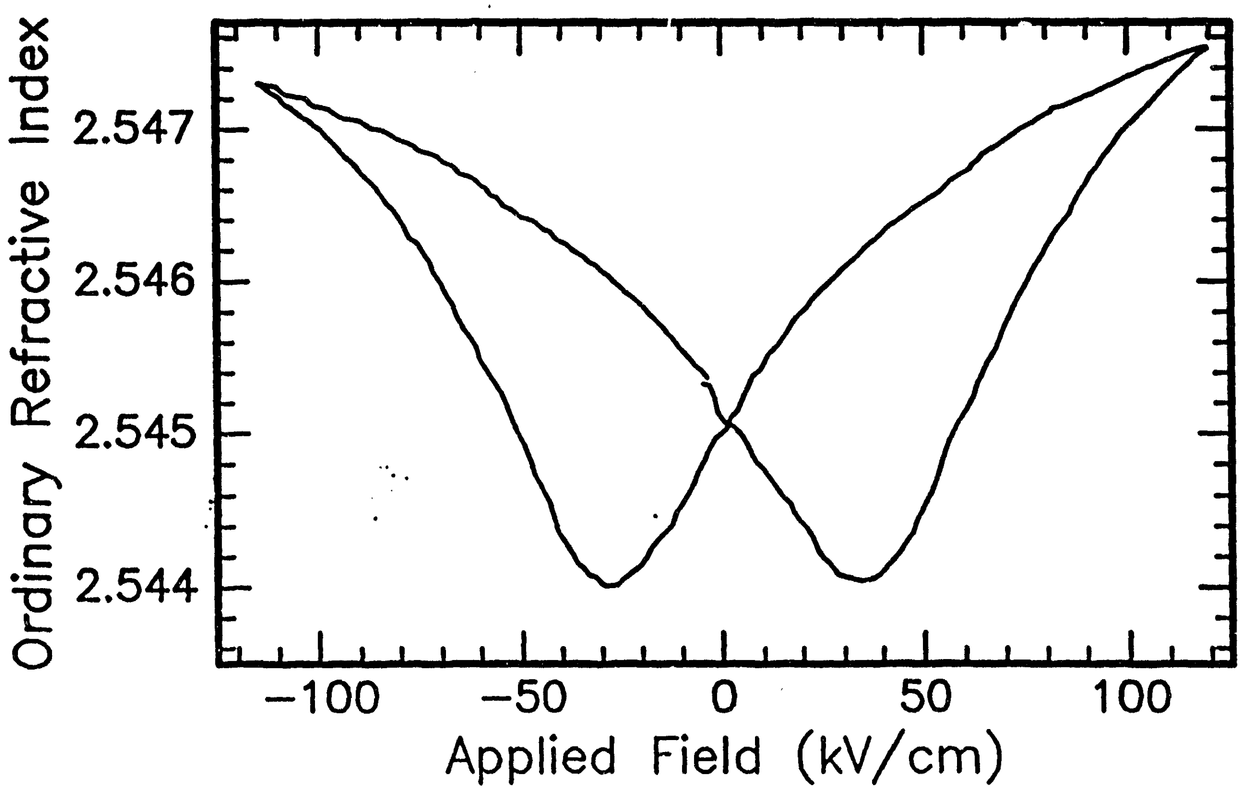
(b.)



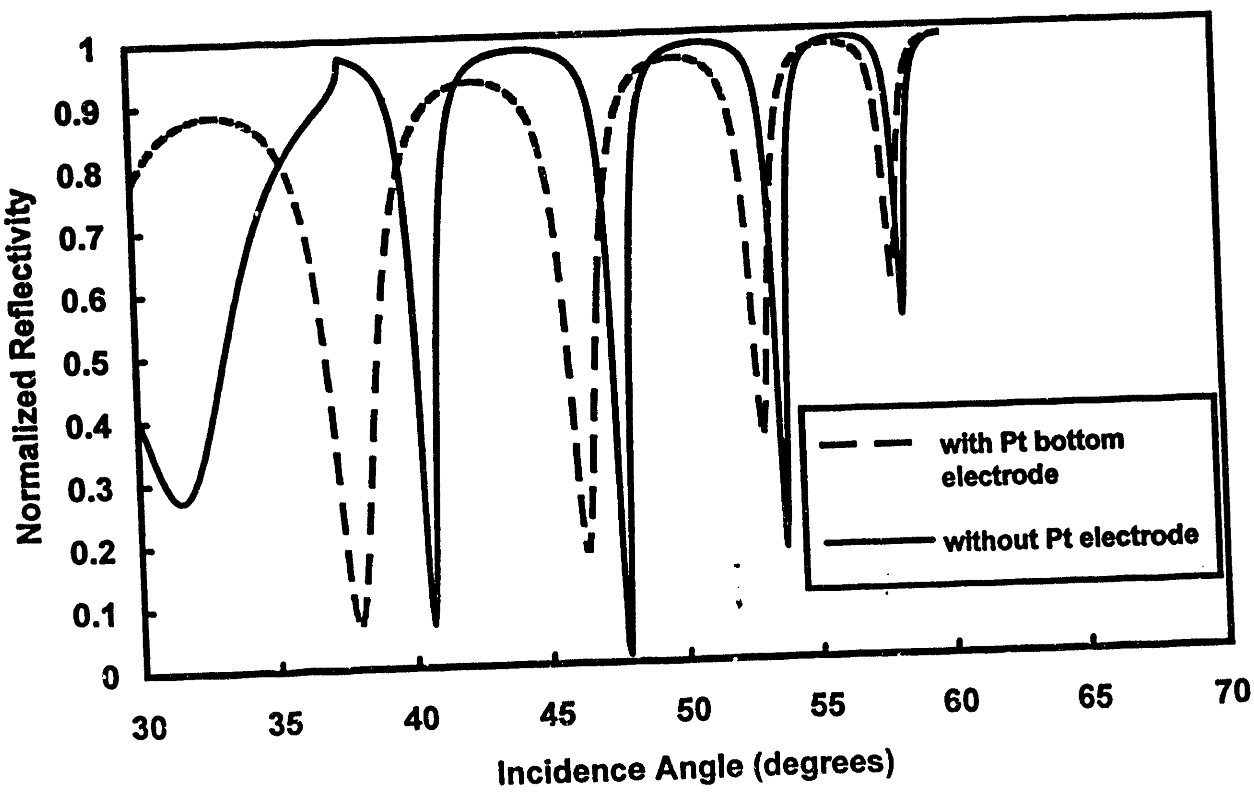
Reflected Intensity (a.u.)
0
2
4
6
8
10
45
50
55
60
Incidence Angle (deg)
Unpolarized: n_o=2.544
10 V applied: n_o=2.548



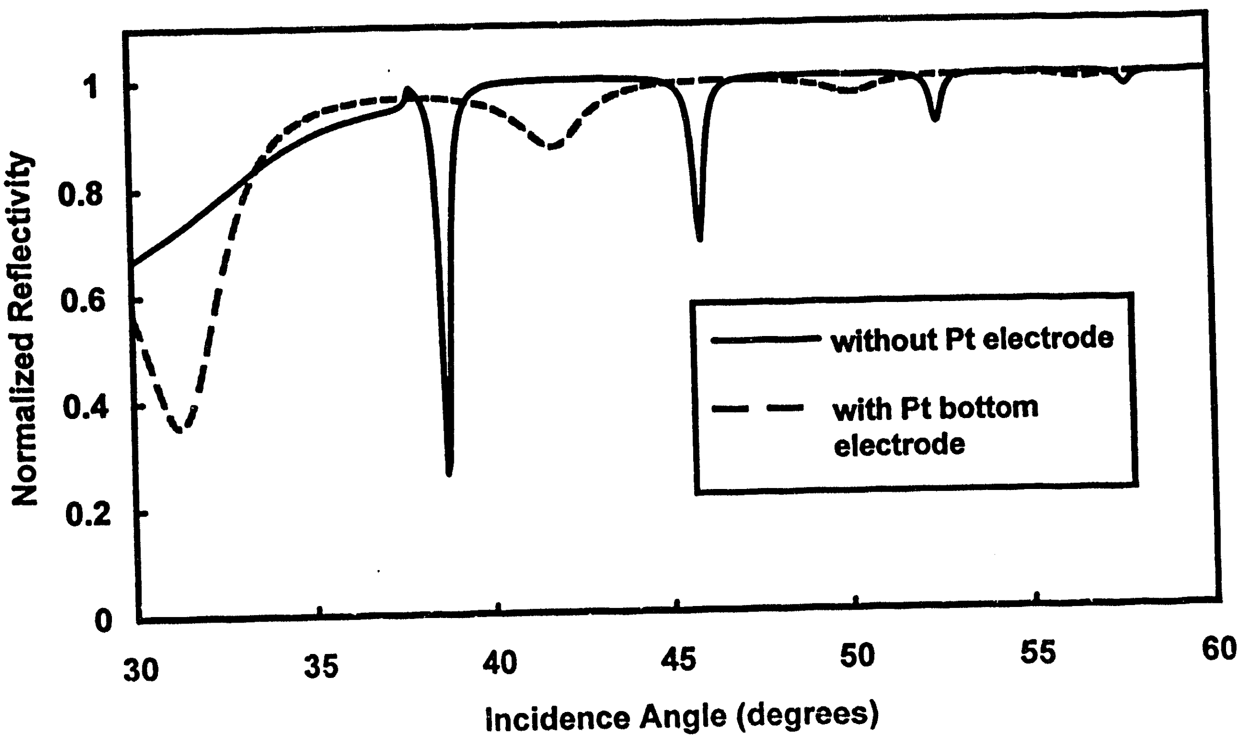
15
10
5
0
Reflected Intensity (a.u.)
45
50
55
60
Incidence Angle (deg)
Unpolarized: n_ϵ=2.547
10 V applied: n_e=2.530



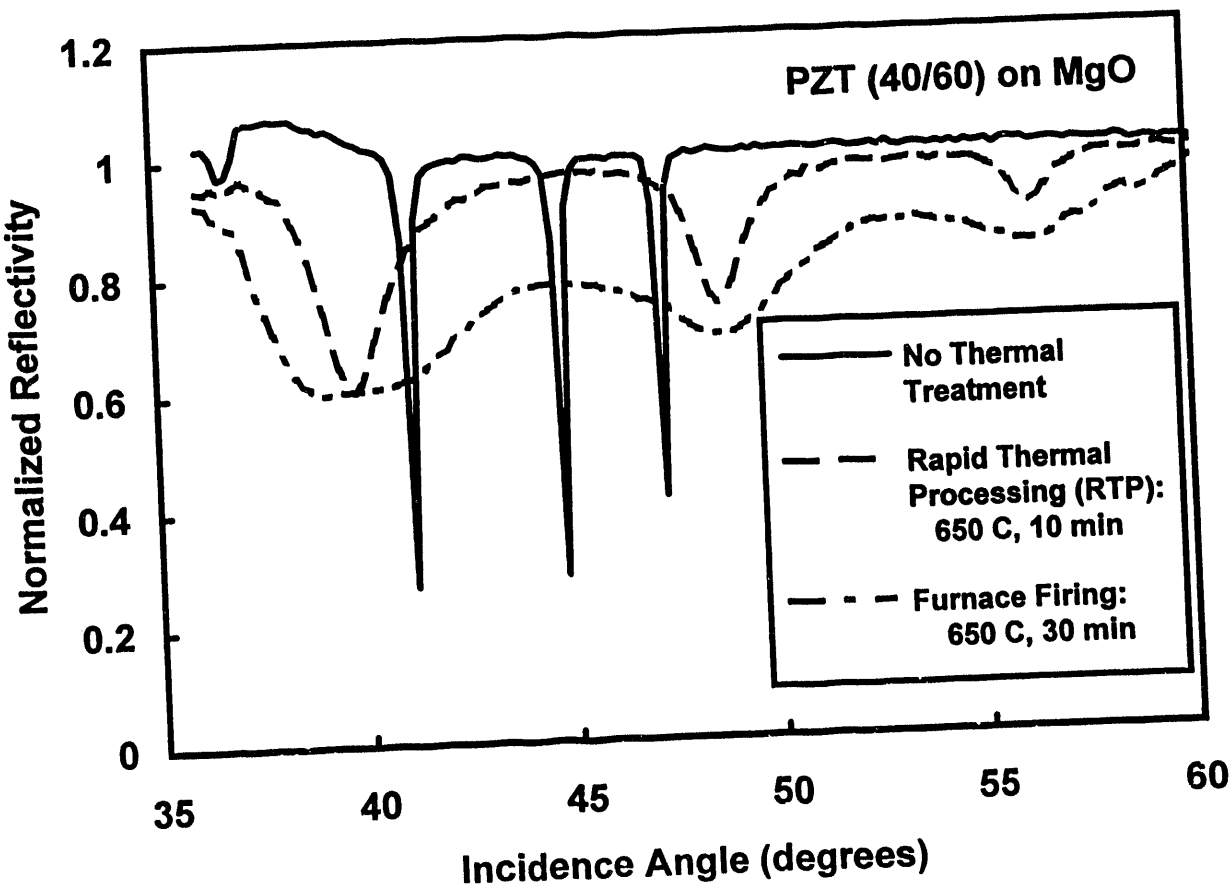
Ordinary Refractive Index
2.547
2.546
2.545
2.544
−100
−50
0
50
100
Applied Field (kV/cm)



Normalized Reflectivity
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
30
35
40
45
50
55
60
65
70
Incidence Angle (degrees)
with Pt bottom electrode
without Pt electrode



Normalized Reflectivity
0
0.2
0.4
0.6
0.8
1
30
35
40
45
50
55
60
Incidence Angle (degrees)
without Pt electrode
with Pt bottom electrode



PZT (40/60) on MgO
Normalized Reflectivity
1.2
1
0.8
0.6
0.4
0.2
0
35
40
45
50
55
60
Incidence Angle (degrees)
No Thermal Treatment
Rapid Thermal Processing (RTP): 650 C, 10 min
Furnace Firing: 650 C, 30 min

DATE

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END