

Fabrication and Characterization of Planar and Channel Polymer Waveguides. II. Poly(*p*-phenylene benzobisthiazole) (PBZT) Films

LORA A. CINTAVEY,¹ STEPHEN J. CLARSON,¹ D. MARK HUSBAND,² GREG N. DE BRABANDER,³ JOSEPH T. BOYD³

¹ Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012

² AFRL/MLBP, Wright-Patterson Air Force Base, Dayton, Ohio 45433-6533

³ Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0030

Received 9 September 1998; accepted 11 October 1998

ABSTRACT: Solutions of poly(*p*-phenylene benzobisthiazole) (PBZT) in methane sulfonic acid (MSA) were prepared and studied. Solutions with concentrations less than 0.04 wt % PBZT were characterized by dilute solution viscometry. Planar PBZT waveguides were spin-coated from a 0.5 wt % PBZT solution onto oxidized silicon wafers. The optical attenuation of the resulting polymer waveguides was measured and found to depend on both the thickness of the oxide layer on the silicon substrate and also the wavelength of the incident light. The lowest optical loss recorded for PBZT in this investigation was 4.81 ± 1.39 dB/cm at 834 nm. This work thus demonstrates the successful fabrication of PBZT into thin-film planar waveguides. The PBZT films prepared here also show improved optical characteristics over PBZT films prepared previously by either extrusion or spin coating. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1448–1456, 2000

Key words: poly(*p*-phenylene benzobisthiazole); waveguides; optical loss; polymer thin films

INTRODUCTION

The first rigid-rod polymers were synthesized in the mid-1960s in order to achieve an improvement in the thermal stability over conventional organic materials. Such polymers consisted of fused aromatic rings and they were also found to provide superior mechanical properties and chemical resistance.¹ In the early 1970s, the Air

Force Materials Laboratory at Wright-Patterson Air Force Base, Dayton, Ohio, began researching the synthesis of rigid-rod or ladder polymers for high-temperature applications in the aerospace industry.² In the early 1980s, electrochemical and chemical doping of these polymers was utilized to make them electrically conductive. By the mid-1980s, it had also been demonstrated that rigid-rod polymers could be fabricated into thin films. Within the last 5–10 years, the focus has shifted to the nonlinear optical (NLO) properties of conjugated polymers,¹ and research continues today to enhance the NLO properties and processability of these materials.

Poly(*p*-phenylene benzobisthiazole) (PBZT, Fig. 1) is a rigid-rod polymer that exhibits excellent mechanical properties (high tensile strength

Dedicated to the memory of Bruce A. Reinhardt who is no longer with us in this world. Bruce was a loyal friend and a gifted chemist—we all miss his insight, humor, and company.

Correspondence to: S. J. Clarson.

Contract grant sponsor: RDL/AFOSR; contract grant numbers: 94-0138; 94-0402; 95-0852.

Journal of Applied Polymer Science, Vol. 76, 1448–1456 (2000)
© 2000 John Wiley & Sons, Inc.

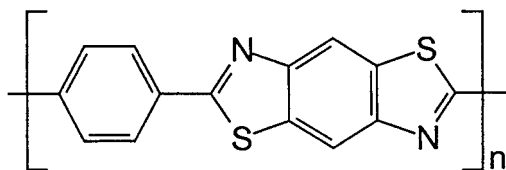


Figure 1 Chemical structure of PBZT.

and modulus) and also has high chemical and thermooxidative resistance.^{3,4} PBZT has also been shown to be a third-order NLO polymer and has been reported to have a $\chi^{(3)} = 4.5 \text{ E-10 esu}$.⁵

A number of attempts have been made previously to obtain PBZT samples of high optical quality and the optical loss values that have been previously reported for PBZT are summarized in Table I.⁶ As can be seen from these data, the optical loss of spin-coated PBZT thin films was not measured because no light streak was identified in previous work.⁶ An out-of-plane optical loss of 1500 dB/cm and in-plane optical losses of 20–60 dB/cm have been reported for extruded and coagulated PBZT films.⁶ Such values are clearly too high for this polymer to be used in optical device configurations.

This investigation describes a dilute solution viscosity analysis of PBZT, the processing of PBZT thin films, and the fabrication of these films into planar waveguides by spin coating. Analysis of the optical quality of the resulting PBZT film waveguides through measurement of their optical losses was an important objective of this work.

EXPERIMENTAL

Materials

The PBZT was supplied by SRI International and was quoted to have a weight-average molecular

weight of 27,000 g/mol.⁷ The solvent, methane sulfonic acid (MSA; $\text{CH}_3\text{SO}_3\text{H}$), was purchased from Aldrich Chemical Co. and had a reported density of 1.481 g/cm³. The substrates used were 2-in.-diameter oxidized silicon wafers. The prime-grade 2-in.-diameter silicon wafers without an oxide layer were acquired from International Wafer Service. They had a $\langle 100 \rangle$ orientation with a standard flat, N-type polarity, a resistivity of 1.0–15.0 ohms cm, and a thickness of 254–305 μm . The 2-in.-diameter oxidized silicon wafers were acquired from Transition Technology International with a $\langle 100 \rangle$ orientation and standard flat, N-type polarity, and a resistivity and thickness of 6.0–12.0 ohms cm and 325–375 μm , respectively. The native SiO_2 thickness was 1.987 μm . The thickness of the in-house-grown oxide layers on the silicon wafers used here were 2, 4.5, 5.7, and 7.3 μm , respectively. The SiO_2 layer was thermally grown on the unoxidized silicon wafers at 1050°C. It took approximately 1 week to build up a 7- μm -thick layer of SiO_2 . Applications for the PBZT films, including waveguiding on the oxidized silicon wafers, will be described below.

Solution Viscosity Measurements

In conducting the dilute solution viscometry experiments, a Ubbelohde 100-mL-capacity viscometer (E 575), dilute solutions of PBZT/MSA, and a temperature bath regulated at 30°C were used. The efflux times of the solvent and polymer solutions were recorded to the hundredth of a second using a digital timer. The three or more readings were averaged and recorded as the efflux time of each solution and also for the pure distilled MSA. A stock 0.05-g/dL PBZT/MSA solution was prepared and vacuum-filtered through a 10–20 μm glass frit. The viscometer was then filled with 10

Table I Summary of the Previous PBZT Optical-loss Results^{1,3}

Material	Substrate Supported or Freestanding	Processing Method	Thickness (μm)	Wavelength (μm)	Optical Loss (dB/cm) min-max
PBZT	Substrate	Extruded	2.87	1.064 1.319	29.8–58.9 15.7–31.0
PBZT	Substrate	Spin-coated	2.0	1.064	No streak seen
PBZT	Free standing	Extruded	2.50	1.064 1.319 1.535	24.1–56.8 12.8–43.9 15.7–58.1
PBZT/nylon	Free standing	Extruded	1.6	1.064 1.319 1.535	15.5–87.3 15.7–51.6 18.8–35.8

mL of this PBZT/MSA solution. Three efflux times were recorded, and 10 mL of pure distilled MSA was added to the solution. Nitrogen gas was gently bubbled through the viscometer in order to mix the pure MSA and the PBZT/MSA solution. Efflux times of this solution concentration were recorded. Four additional amounts of MSA were then added to dilute the solution and efflux times were determined in each case. Viscosities of the PBZT/MSA solutions were thus measured with concentrations ranging from 0.01 to 0.05 g/dL (0.0068 to 0.0337 wt % PBZT). The intrinsic viscosity was then determined by extrapolation to zero concentration; $[\eta] = (\eta_{sp}/c)_{c=0}$.

Cleaning of Substrates

The cleaning solution for the substrates consisted of five parts distilled water (H_2O), one part ammonium hydroxide (NH_4OH , 28–30 wt %) from Ashland Chemical, and one part hydrogen peroxide (H_2O_2 , 30 wt %) from Aldrich Chemical Co. (parts are by volume). Although the initial attempt at cleaning the substrates described here was unsuccessful for our applications, it is important to describe the type of failure and the steps leading to this failure. This will give a better understanding of the importance of cleaning the substrates and emphasize the subtle difference between the successful and unsuccessful cleaning processes. Initially, the distilled water was heated to $70 \pm 5^\circ C$ and then the two solutions were added. The addition of the H_2O_2 caused the solution to bubble and depressed the temperature slightly, but with continued heating, the temperature was recovered. An overshoot of the $70^\circ C$ mark was found to be acceptable up to $85^\circ C$. After the mixture bubbled for approximately 30 s, the substrates were immersed in the solution for 15 min or more, irrespective of the initial temperature depression. The first substrate was removed (at the 15-min mark) and directly rinsed under running distilled water for about 60 s. Immediately after rinsing, the substrate was dried with N_2 gas before any water spots developed. To ensure that no moisture remained on the surface of the substrate, it was then placed in a clean oven at $120^\circ C$ for at least 20 min. Each substrate followed this rinsing and drying process. Visually, the substrate surfaces were spotless, but it was, nevertheless, difficult to get the PBZT films to adhere to the substrates. There was visual shrinkage of the applied PBZT film around the entire outside edges of the substrate immediately

after immersing the resulting film and substrate in the distilled water bath. This shrinkage caused the entire film to delaminate from the substrate and float off into the water bath. Altering the cleaning process as described below resulted in better adhesion between the polymer film and the substrate.

The successful cleaning process started with the same chemicals, but used a different sequence of mixing. The distilled H_2O , H_2O_2 , and NH_4OH were mixed together at room temperature in the proportions given above, covered with paraffin film, and stored overnight. The solution bubbled for several hours after mixing. This solution was then heated to $70^\circ C$, just as the distilled H_2O was heated previously. Additional H_2O_2 was added, equal in volume to the original amount of H_2O_2 , and the heating continued. The remaining steps in the successful cleaning process were identical to the unsuccessful process, starting with submersing the substrates in the solution for at least 15 min and ending with the substrates drying in the oven at $120^\circ C$ for at least 20 min. However, particular attention was paid to the temperature overshoot of the solution. It was extremely important that the temperature of the solution never exceeded $90^\circ C$. If this happened, the films again delaminated from the substrates in the water bath. To avoid this, the temperature was regulated to be between 70 and $85^\circ C$, including removing the cleaning solution from the heat source when the temperature started to increase abruptly.

Processing Challenges for the Spin-coating of PBZT Films

Spin-coating of PBZT onto substrates posed some processing challenges. PBZT is a rigid-rod polymer and the pure polymer exists in solid form as feathery gold flakes. It has been shown that the viscosity of PBZT rigid-rod polymer solutions increases significantly with small increases in the solution concentration.⁷ It was therefore necessary to use relatively dilute solutions in the spin coating, with concentrations ranging from 0.1 to 1.0 wt %. Due to the structure of PBZT, solubility was possible only in aggressive solvents, such as MSA. An acidic solution posed processing challenges in itself. Usually, polymers that are spin-coated are dissolved in volatile solvents—so, almost instantaneously after spin coating, the solvent evaporates and the resulting thin film consists only of the polymer with just traces of the

solvent to be removed. Using MSA as the solvent, the acid had to be removed by soaking the film in distilled water immediately after spinning. Water is a nonsolvent for the PBZT films; therefore, the films were found to shrink when immersed in the water. This dimensional change in the film can lead to adhesion problems between the polymer and various substrates. Another possible cause of poor adhesion was surface contamination of the substrate. After trying several cleaning schemes for the silicon wafers, one particular process resulted in both minimal visual shrinkage of the polymer film and also better adhesion to the substrate.

The nature of a PBZT/MSA solution is that exposure to any moisture, including moisture in the air, causes coagulation upon which the PBZT precipitates out of the solution. Premature coagulation during spinning can result in incomplete spreading which results in a nonuniform film. Therefore, spinning times were restricted to approximately 30 s or less. Any longer exposure to the atmosphere at spin rates around 3000 rpm was found to cause coagulation before the spinning was complete. Preliminary spin-coating studies were conducted on glass slides. PBZT was spin-coated on rectangular glass slides to observe the spreading capabilities, coagulation rates, and adhesion characteristics of different solution concentrations of PBZT in MSA. The concentrations that were found to give the most flexibility in spin coating were the 0.1, 0.25, 0.5, and 1.0 wt % PBZT in MSA. More concentrated solutions did not readily spread onto the glass substrate. Of these solutions, the 0.1- and 0.25-wt % solutions were found to spread well, but only formed films with thicknesses up to several hundred angstroms, which was not thick enough for a PBZT waveguide. The 1.0-wt % solution produced good optical-quality films with thicknesses from approximately 5000 Å up. These films were slightly thicker than desired. The 0.5-wt % solution was thus selected because good optical-quality films were easily spun from this solution with thicknesses from 1500 to 1800 Å, which was comparable to the thickness desired for optical waveguiding, as described below.

Spin-coating Procedures

A coagulation bath was set up which consisted of a large glass Pyrex dish, (9 × 13 in.) containing several smaller 4-in.-diameter Pyrex dishes and filled with distilled water for coagulation of the

films after spinning. The spin coater used here was a Solitec Model 5110-C/T. Spinning of the films took place in two stages: The first stage, called the spread stage, used a relatively slow rate of rotation (usually from potentiometer settings of 100–350 rpm) to coat the substrate thoroughly with the dope. The second stage, called the spin stage, used a faster rate of rotation to spin off excess dope from the substrate and create a uniform thin film. In this work, the spread and spin speeds cited in reference to the PBZT films are given as the potentiometer settings of the spin coater, not the actual spin speeds. A correlation table between the potentiometer setting (dial setting) on the Solitec spin coater and the actual speeds of rotation for the substrates may be found in ref. 7.

Prior to spin coating of the polymer films, the spinning rates and times for each of these stages were set. A 1-in.-diameter chuck was used to support the 2-in.-diameter oxidized silicon wafer. This chuck was removable and was secured to the center rotating rod of the spin coater. To make a PBZT film, a clean substrate was placed on the chuck and the vacuum was activated to secure the substrate to the chuck during spin coating. A pipette was used to dispense approximately 2 mL of the PBZT/MSA solution onto the center of the substrate. This was done carefully to assure that no air bubbles were trapped in the solution. Air bubbles and other foreign objects in the dopant can produce striations in the resulting film. The spin coater was then started and the preset stages run consecutively. After spinning, the vacuum was deactivated and the substrate with the film on it was immediately removed from the chuck and submerged in a distilled water bath. A time lapse in excess of a few seconds between finishing spinning and submersing the film in the water was found to cause undesirable coagulation of the film from moisture in the atmosphere. To produce a clearer film, it is desired to have coagulation occur only in the distilled water. Here, coagulation was a diffusion process where the solvent (MSA) is replaced by a nonsolvent (H₂O). Since H₂O was a nonsolvent, the PBZT then precipitated out of the solution and formed a solid film. The polymer film was observed to turn orange immediately upon contacting the water and coagulating. The films were left in water for 1–2 days in order to remove all the MSA. The neutralized films were seen to be clear with a slight yellow tint. If the films stayed in the distilled water bath for 2 days, the water in the bath was replaced

with clean distilled water after 1 day. Next, the films were then dried in an oven at a temperature of 65°C for 2–3 days.

Film-thickness Determination

The thickness of the film is an important controlling factor in waveguiding for an optical material. Light can propagate through a material in a single mode or in several modes at once. Certain modes may individually produce a larger optical loss than can others or the light may be split between several modes, also increasing the total optical loss of the film. The restriction of the light's path to a single mode is therefore often desirable to maximize its intensity. A particular thickness of the film assures single-mode transmission of the light through the film. This thickness is a function of the film's refractive index and the wavelength of the light used.

Profilometry was used to determine the thickness of the PBZT films. The profilometer (Sloan Dektak IIA) contains a stylus that glides across the film surface while its vertical and horizontal motion is tracked by a chart recorder. The film was first scribed using a metal-tipped object with a width of approximately 0.5 μm . A small portion of the film was carefully removed down to the SiO_2 layer, without scratching the SiO_2 , thus creating a sharp valley in the film. When the stylus encountered this scribe in the film, the chart recorder returned a profile of the valley with a numerical scale corresponding to its depth. This depth, in turn, corresponded to the thickness of the polymer film. Four measurements were taken on each film as per ASTM designation F 399-88 and the average was reported as the film thickness.⁷

Optical Waveguiding Considerations

A basic requirement for optical waveguiding is certain refractive indices for the particular layers of the waveguide in order to confine the light to a desired layer.⁵ Single-mode waveguiding is particularly important for planar and channel waveguiding. For thicker films, multiple modes become active for light transmission. In planar waveguiding, the substrate may be cleaved and the light directed into the cleaved edge of the film parallel to its surface. This is referred to as "end-fire" coupling and is discussed in more detail below. Multiple-mode waveguides are important for assessing the optical loss of each separate mode.

In the case of multiple modes, a prism is placed in the path of the light beam, and if in good contact with the film surface and at the correct angle, light will couple into individual modes.

When light enters the film, some of it is absorbed and some scattered and some transmitted. Absorption may be attributed to either the film itself or to the substrate or to both. A thick oxide layer on the silicon wafer minimizes the absorption of light into the silicon substrate. The refractive index of PBZT has been found to vary from 1.8 to 2.6.⁷ The index varies because PBZT is anisotropic: Different refractive indices result from different orientations of the material. The index also varies due to the degree of orientation in the processed material. For example, an extruded PBZT film has a typical refractive index of 1.80–1.96, whereas a highly ordered PBZT structure can have a refractive index as high as 2.6.⁷ The refractive index of silicon dioxide (SiO_2) is 1.487 and the refractive index of air is approximately 1.0.⁷ As the light travels through the PBZT, it encounters the interface between the PBZT and the SiO_2 and reflects off the interface, back into the PBZT. This is a result of the difference in refractive indices of the two media. Even though most of the light reflects back into the PBZT, some of it transmits through the oxide and is absorbed into the silicon wafer. This occurs because the refractive index of the silicon wafer is 3.49.⁷ This absorption effect by the substrate diminishes with a thicker SiO_2 layer. As mentioned earlier, the oxide thicknesses used here were 2, 4.5, 5.7, and 7.3 μm , respectively.

Inclusions, striations, and even dust in the film act as scattering centers and increase the optical loss. Filtration of the PBZT/MSA dopant can decrease all these effects. Clean and meticulous film-preparation methods also played a big part in decreasing optical loss in the film. The pore size of the filters used here was 10–20, 1.0, and 0.7 μm . These filters had glass microfiber membranes and were purchased from Whatman International Ltd.

Optical-loss Measurements

Optical losses were determined by measuring the relative outscattering intensity as a function of distance along the light streak. The incident light from a 2-mW polarized He:Ne laser ($\lambda = 632.8$ nm) was end-fire coupled into the PBZT films through a 3 \times microscope objective lens. The outscattering intensity perpendicular to the wafer

along the streak was measured using a fiber-optic cable and a photomultiplier tube, as shown in Figure 3 of ref. 8. The measured out-scattering intensity, $I(z)$, as a function distance, z , is plotted on a log scale as a function of z , and the loss is then calculated in dB/cm. From the slopes of the logarithmic intensity versus distance plots, the propagation losses for the various waveguides were thus obtained.

RESULTS AND DISCUSSION

PBZT Dilute Solution Viscometry

Figure 2 shows the results of the dilute solution viscometry study for PBZT in MSA at 30°C. The intrinsic viscosity $[\eta]$ of PBZT in MSA at 30°C was calculated to be 14.4 dL/g using the double extrapolation of the dilute solution viscometry data to $c = 0$ as shown in Figure 2. One plot is the reduced viscosity, η_{red} , versus the concentration and the other is the inherent viscosity, η_{inh} , versus the concentration. The common intercept of these two sets of data gives the intrinsic viscosity, $[\eta]$. The Mark-Houwink relationship reported by Kumar,^{9,10}

$$[\eta] = 1.65 \times 10^{-7} M_w^{1.8}$$

was found to give a molar mass for the polymer of 25,800 g mol⁻¹. This characterization is in good agreement with the molar mass reported by the supplier SRI International of 27,000 g/mol.⁷

Spin Coating and Profilometry Results

The thicknesses of the PBZT thin films spun on glass slides and oxidized silicon wafers for a wide variety of conditions have been reported in detail elsewhere.⁷ From these thickness data, it was difficult to say whether the spread speed or the

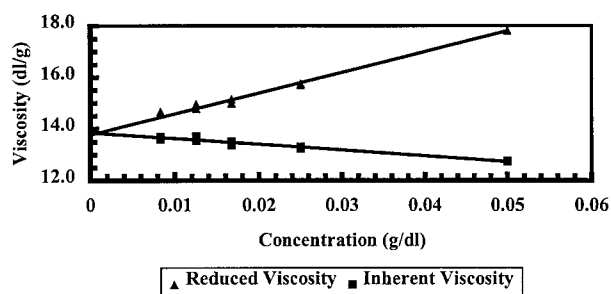


Figure 2 Dilute solution viscometry results for PBZT in MSA at 30°C.

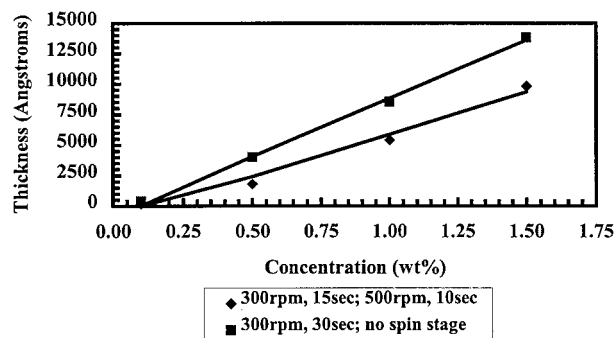


Figure 3 Thickness versus concentration plot for two spin-coating conditions and several solution concentrations of PBZT in MSA.

spin speed was the controlling factor for the thickness of the PBZT films. Correlations were made between two spin-coating conditions and the resulting thicknesses of the PBZT films for a series of solutions of different concentrations. The two conditions were as follows: (i) a spread stage of 300 rpm for 30 s and no spin stage and (ii) a spread stage of 300 rpm for 15 s and a spin stage of 500 rpm for 10 s. This correlation plot is shown in Figure 3.

The thickness of the PBZT film calculated for single-mode light propagation in the TE mode was 1200 Å. This was calculated for a PBZT film with a refractive index of 2.0. The code can also be

Table II Planar Optical Loss of PBZT Films Spin-coated from 0.5 wt % Solutions in MSA (TE Mode, Except Where Indicated)

Dopant Filter (μm)	SiO ₂ Thickness (μm)	Wavelength (nm)	Optical Loss (dB/cm)
None	2.0	632.8	159 ± 2.9
None	2.0	632.8	180 ± 1.3 ^a
None	2.0	834	180 ± 1.9
None	2.0	834	196 ± 1.5 ^a
None	4.5	834	24.7 ± 2.0
None	4.5	834	29.1 ± 1.8
None	5.7	632.8	10.6 ± 0.3
None	5.7	632.8	10.7 ± 0.3
None	5.7	834	18.9 ± 0.7
None	5.7	834	20.0 ± 0.6
None	7.3	632.8	9.62 ± 0.5
None	7.3	632.8	9.41 ± 0.4
None	7.3	834	8.40 ± 1.3
None	7.3	834	4.81 ± 1.4

^a TM mode waveguiding.

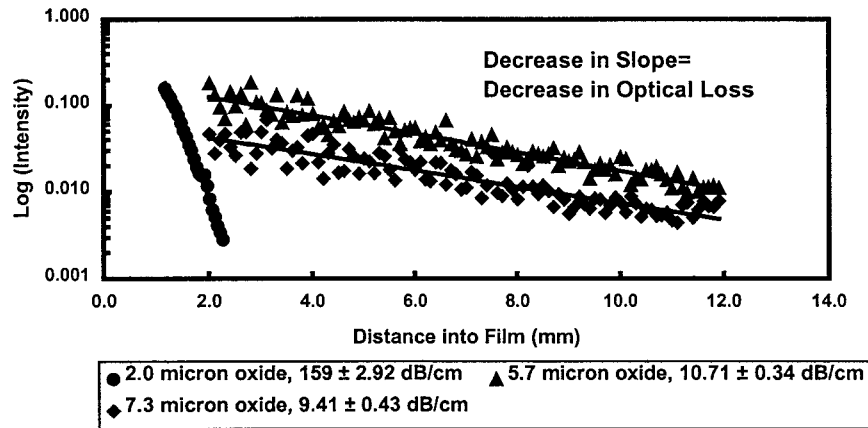


Figure 4 Optical loss dependence on the SiO_2 layer thickness at 632.8 nm for spin-coated PBZT 0.5 wt % in MSA.

used to perform this calculation in the TM mode if desired. Using this information and the data shown in Figure 3, it was possible to obtain single-mode conditions for the polymer films.

Optical Losses of the PBZT Films

The method used to achieve waveguiding was end-fire coupling and a schematic of this technique for waveguiding and collecting optical loss data was presented in Part I of this series.⁸ The planar optical loss data for PBZT spin-coated films are given in Table II. From all the data collected here, the thickness of the SiO_2 between the PBZT and the silicon substrate appeared to be the most significant factor in reducing the optical loss of the PBZT films. As shown in Table II, the thicker the SiO_2 layer, the less the coupling of light into the silicon wafer substrate and, therefore, the lower the optical loss of the films. Fig-

ures 4 and 5 show this effect at wavelengths of 632.8 and 834 nm. It also appears that the observed optical losses were seen to be slightly greater for TM than for the TE mode at both 632.8 and 834 nm in the PBZT films.

The wavelength of the light used in waveguiding also had an effect on the optical loss of the PBZT films. An absorption spectra was taken on a dilute PBZT/MSA solution using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer and wavelengths from 185 to 1600 nm were scanned. The absorption of PBZT was found to decrease at longer wavelengths in transmission. In the waveguide studies, by contrast, the shorter wavelength of 632.8 nm produced slightly lower optical losses for the PBZT films than did the longer wavelength of 834 nm. This effect was seen in the PBZT spin-coated films spun onto silicon wafers with SiO_2 thicknesses of 2.0, 4.5, and 5.7 μm ,

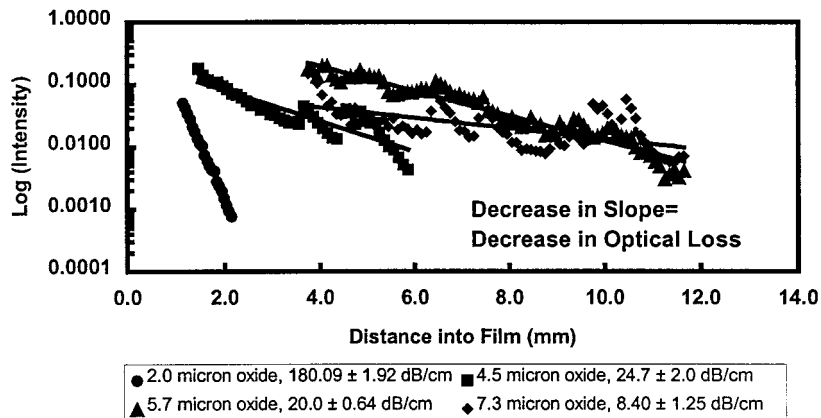


Figure 5 Optical loss dependence on the SiO_2 layer thickness at 834 nm for spin-coated PBZT 0.5 wt % in MSA.

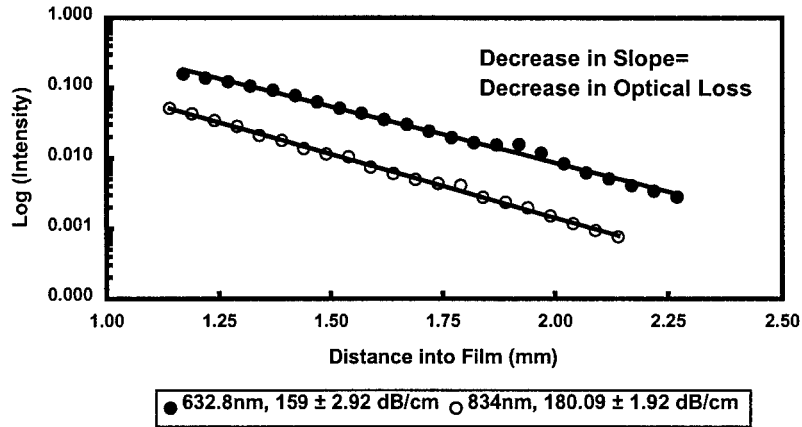


Figure 6 Optical loss dependence on wavelength with SiO_2 thickness = $2.0 \mu\text{m}$ for spin-coated PBZT 0.5 wt % in MSA.

respectively (see Table II and Figs. 6 and 7). PBZT films spun onto silicon wafers with thicker SiO_2 layers ($7.3 \mu\text{m}$) did not show a decrease in optical loss at longer wavelengths (Fig. 8). In this case, the reduction in the optical loss due to the increased thickness in the SiO_2 layer alone resulted in comparable optical losses for the PBZT films at 632.8 and 834 nm.

Previous research has shown some conflicting results for the optical properties of PBZT. Studies on PBZT extruded and free-standing films have shown a decrease in optical loss for longer wavelengths of light. Such results were attributed to the number of modes in the film and not the absorption effects at different wavelengths. For example, Mittler-Neher and colleagues reported that at longer wavelengths light propagated through the PBZT extruded films in a fewer num-

ber of modes, causing the optical loss to decrease.⁶ In other planar waveguide studies, Borland and colleagues reported that the optical loss of silicon oxynitride waveguides on oxidized silicon wafers decreased with decreasing wavelength due to substrate coupling.¹¹ There are several competing factors involved in the optical loss reduction of waveguides as a function of the wavelength of light. These include absorption, multiple-mode propagation, and substrate coupling. Comparing previous results with those obtained in this investigation indicates that substrate coupling and its wavelength dependence had the most influence on the optical loss of the spin-coated PBZT waveguides.

This work thus demonstrates the successful fabrication of PBZT into thin-film planar waveguides. The PBZT films prepared here also

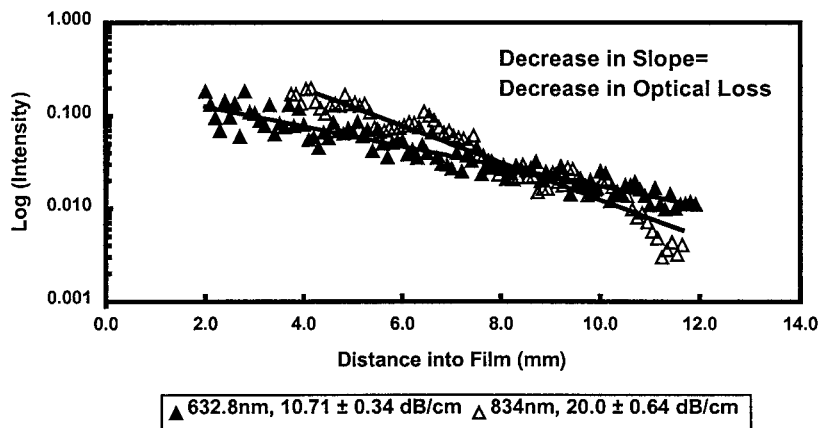


Figure 7 Optical loss dependence on wavelength with SiO_2 thickness = $5.7 \mu\text{m}$ for spin-coated PBZT 0.5 wt % in MSA.

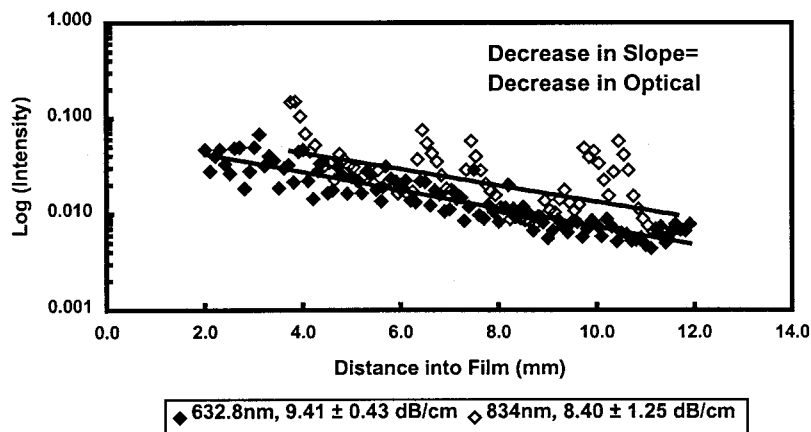


Figure 8 Optical loss dependence on wavelength with SiO_2 thickness = $7.3 \mu\text{m}$ for spin-coated PBZT 0.5 wt % in MSA.

show improved optical characteristics over PBZT films prepared previously by either extrusion or spin coating. Investigations of polymeric thin films, which include PBZT, in waveguide and device configurations are currently being carried out and will be reported later.

The authors find it a pleasure to thank Bruce A. Reinhardt, Lisa R. Denny, and C. S. Wang of MLBP, WPAFB, for a number of helpful discussions. The authors also thank RDL/AFOSR for financial support of this research through a Summer Faculty Research Award (94-0138, to S. J. C.), a Summer Graduate Research Award (94-0402, to L. A. C.), and an SREP grant (95-0852, to S. J. C.). The authors also find it a pleasure to thank Dr. Ted Helminiak and Dr. Bob Evers for their friendly encouragement and kind hospitality during our visits to the Polymer Branch at AFRL/WPAFB, Dayton, Ohio.

REFERENCES

1. Wang, C. S. *TRIP* 1993, 1(7), 199–205.
2. Arnold, F. E. *The Birth of Ordered Polymer Technology for Air Force Applications*; Air Force Materials Laboratory, Wright-Patterson Air Force Base: Dayton, OH 45433-6533; unpublished manuscript.
3. Lee, J. W.; Wang, C. S. *Polymer* 1994, 35, 3673–3678.
4. Arnold, F. E. *Structural Modifications of Rigid-Rod Polymers*; Air Force Materials Laboratory, Wright-Patterson Air Force Base: Dayton, OH 45433-6533; unpublished manuscript.
5. Berry, G. C.; Metzger, P. C.; Venkatramen, S.; Gotts, D. B. *Polym Prepr* 1979, 20(1), 42.
6. Mittler-Neher, S.; Otomo, A.; Stegeman, G. I.; Lee, C. Y.-C.; Mehta, R.; Agrawal, A. K.; Jenekhe, S. A. *Appl Phys Lett* 1993, 62(2), 11.
7. Cintavey, L. A. MS Thesis, University of Cincinnati, 1995.
8. Zeik, D. B.; Dugan, J. R.; Schroeder, D. W.; Baur, J. W.; Clarson, S. J.; De Brabander, G. N.; Boyd, J. T. *J Appl Polym Sci* 1995, 56, 1039–1044.
9. Kumar, S. In *International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH: New York, 1991; Vol. 4, pp 51–74.
10. Wong, C.-P.; Ohnuma, H.; Berry, G. C. *J Polym Sci Polym Symp* 1978, 65, 173.
11. Borland, W. C.; Zelmon, D. E.; Radens, C. J.; Boyd, J. T.; Jackson, H. E. *IEEE J Quantum Elect* 1987, QE-23, 1172–1179.