OPTICAL WAVEGUIDING AND ELECTRO-OPTIC PROPERTIES OF SOL-GEL Pb(Zr,Ti)O₃ FILMS

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ABSTRACT

Direct integration of active optical waveguide devices on semiconductor substrates has substantial potential advantages over discrete crystal-based devices. As a first step toward this goal, our research has focused on evaluating the waveguiding and electro-optic properties of Pb(Zr,Ti)O₃ films on SrTiO₃ substrates. We have demonstrated that sol-gel Pb(Zr,Ti)O₃ (PZT) films crystallize epitaxially during annealing when they are deposited on crystalline, lattice-matched and isostructural SrTiO₃ substrates. Using prism coupling techniques, we have measured refractive indices and propagation loss on these PZT films. Refractive index values of \( n \approx 2.55 \) at \( \lambda = 633 \text{ nm} \) were achieved in PZT films on SrTiO₃ substrates, with propagation loss values as low as 6-7 dB/cm for the TE₀ and TE₁ modes at wavelengths between 633 and 1060 nm. The propagation loss appears to be limited by film thickness variations and the nature of the film/substrate interface. Using the method of Bragg diffraction, a linear electro-optic effect with \( r \geq 50 \text{ pm/V} \) was demonstrated in an epitaxial PZT waveguide. This paper describes the current status of our research and outlines approaches for developing integrated thin-film waveguide devices.

INTRODUCTION

Optical waveguide devices will be used in a variety of future optical systems for telecommunications, computing, and signal processing applications. Currently, discrete devices (e.g., modulators, phase shifters, and directional couplers) are produced by modifying the surface of electro-optic lithium niobate single-crystal wafers. Recent developments [1-2] in ferroelectric film technology suggest a promising alternative technology. Deposition of device-quality electro-optic (ferroelectric) films on semiconductor substrates will allow the direct integration of active waveguide devices, such as modulators, switches and frequency shifters, with sources, detectors and passive guiding components. Since many ferroelectric materials have large electro-optic coefficients compared to other materials, considerable past and present research has been focused on the development of ferroelectric films for electro-optic waveguide devices [3-7].
A plausible approach for the fabrication of hybrid monolithic devices based on ferroelectric waveguides integrated on silicon or other semiconductor substrates involves the initial deposition of an interlayer material to act as the low-refractive-index cladding layer for the optical waveguide device, followed by the deposition of a ferroelectric film to act as the waveguide layer. Some preliminary research in this direction already has been conducted [8-14]. The primary requirements of a ferroelectric thin-film waveguide are good optical transparency at the operating wavelength, a high refractive index compared to the cladding or interlayer materials, and a high degree of crystallographic orientation that allows a large electro-optic coefficient to be achieved. Until recently, the deposition technology for waveguide-quality ferroelectric films has not been suitable for achieving useful devices. However, the introduction of sol-gel processes, advanced sputtering methods, and MOCVD techniques have improved the quality of ferroelectric films to the extent that useful hybrid monolithic waveguide devices are now feasible. We have shown that epitaxial Pb(Zr,Ti)O₃ (PZT) films on crystalline SrTiO₃ substrates can be prepared by sol-gel processing [15]. This paper describes optical waveguiding and electro-optic properties of such epitaxial PZT films [15,16].

**FILM PREPARATION AND CHARACTERIZATION**

The sol-gel process used to prepare epitaxial Pb(Zr₀.₅₃Ti₀.₄₇)O₃ films, as described elsewhere [15,17], involves two basic steps: (1) the preparation of a homogeneous methoxyethanol-based precursor solution; and (2) film deposition by spin coating and annealing. Precursors included Pb acetate, Ti-isopropoxide, and Zr-propoxide; solution preparation involves several refluxing and distillation operations. After spin coating, amorphous films are annealed using a rapid thermal annealing system to remove organics and to densify and crystallize the film. Maximum annealing temperatures were in the range of 700 to 750°C. Each sol-gel deposition and annealing cycle provides a film thickness of 60 to 70 nm; thus multiple cycles were required to grow films with the desired thickness of 500 to 600 nm. The crystalline SrTiO₃ substrates used in this study were obtained from Commercial Crystals and from Nikon, where substrates were carefully polished to a surface roughness of 3-4 Å. X-ray diffraction patterns of sol-gel PZT films on crystalline SrTiO₃ substrates, indicating strong crystallographic orientation, are shown in Figure 1. Electron diffraction studies at North Carolina State University confirmed the epitaxial nature of similarly prepared PZT films.

![Figure 1. XRD patterns of Pb(Zr,Ti)O₃ films on SrTiO₃ substrates of different crystalline orientations.](image)

**EVALUATION OF OPTICAL PROPERTIES**

Optical characterization of the epitaxial PZT films included: (1) determination of film thickness and refractive index using a single-prism waveguide method; (2) propagation loss measurements using two prisms or scattered light; and (3) electro-optic measurements using the method of Bragg diffraction of waveguided light. Single-prism waveguide measurements provided refractive index values ranging from 2.52 to 2.56 at a wavelength of 633 nm, consistent with expected values for PZT-based ferroelectrics [15]. Propagation loss in most samples was measured at Battelle by coupling laser light into the PZT film from
one (input) prism and measuring the transmitted light intensity at a second (output) prism, with various prism separation distances. These measurements were conducted as a function of mode (TE₀ or TE₁) at a wavelength of 633 nm, and at several wavelengths (between 633 nm and 1060 nm) for the TE₀ mode. The results are presented in Figure 2, as plots of output light intensity versus prism separation distance. This particular film sample exhibited a substantial reduction in propagation loss, from 15 dB/cm to 6 dB/cm, as the wavelength was increased from 633 nm to 783 nm. For this sample, the propagation loss for the TE₀ mode (15 dB/cm) was considerably larger than that for the TE₁ mode (7 dB/cm) at a wavelength of 633 nm. A different PZT film sample, prepared on a more carefully polished substrate, indicated the reverse effect, where the propagation loss of the TE₀ mode (6 dB/cm) exhibited lower propagation loss than that of the TE₁ mode (9 dB/cm) at a wavelength of 633 nm. These latter measurements were made at Nikon using the scattered light (CCD camera) method. The double-prism and light-scattering methods should give results of comparable accuracy, but specific cross checking has been inconclusive due to the observed variation in attenuation from region to region in some films. In any event, these results suggest that the interface between the substrate and the film has a strong influence on propagation loss, as will be discussed later.

Electro-optic measurements were performed using the method of diffraction by an induced Bragg grating [16]. An interdigital grating transducer was deposited on a 0.5-µm thick PZT film, with an intermediate silica buffer (0.2 µm thick) layer to minimize charging effects. Modulation of light of 633 nm wavelength propagating in the TE₁ mode was achieved by applying a triangular-wave voltage to the interdigital transducer. This experiment confirmed that the PZT film exhibited the linear electro-optic effect; a Pockels coefficient of r ≥ 50 pm/V was calculated. This value compares favorably with values obtained for bulk LiNbO₃, and is comparable with values obtained in previous optical measurements on PZT and PLZT films. This magnitude of electro-optic coefficient certainly is large enough for integrated optic device applications.

DISCUSSION OF RESULTS

Propagation loss values of 6 dB/cm, achieved in this work, are low compared to those of many previously reported PZT-based ferroelectric films, but losses need to be reduced further, to the 1 dB/cm level, for practical applications. One approach to reducing losses might be to modify the PZT composition, perhaps through La additions, to improve the intrinsic transparency of the ferroelectric material. However, our results suggest that improving the smoothness of the film/substrate interface may hold the key to reducing propagation losses to the required level. If we suppose that there may be a region of increased scattering at the film-substrate interface, and if we further assume that this region does not affect the modal properties of the waveguide but simply causes scattering proportional to the guided-wave intensity in that region, then it is not difficult to show that circumstances may arise where either the TE₀ or the TE₁ mode is more strongly attenuated. However, evidence for the existence of such a layer, or for any other sources
of the observed scattering, is not easily obtained from guided-wave measurements alone. The previously mentioned variations in attenuation within a given sample, as well as variations in thickness as evidenced by occasional failure of the TE\textsubscript{1} mode to propagate in parts of the film, when combined with film-to-film changes both intentional and otherwise, make any specific interpretation dubious at best. We presently are undertaking some spectroscopic ellipsometry measurements (in collaboration with Pennsylvania State University) in the hope that this characterization method will provide information regarding the refractive index homogeneity through the depth of the deposited PZT films and, possibly, provide some experimental evidence to support the existence of a scattering layer at the film-substrate interface.

In addition to optimizing waveguiding performance and electro-optic properties of ferroelectric films, a significant amount of research still is required before hybrid monolithic devices, incorporating ferroelectric waveguides on semiconductor substrates, can be produced. Specifically, interlayer technology needs to be developed that allows the deposition of a transparent, epitaxial interlayer material that also fosters epitaxial growth of the ferroelectric film. In this case, lattice match and/or similarity of crystal structure are important. Our research has focused on the potential of SrTiO\textsubscript{3} as an interlayer material for integrated PZT waveguides. Other candidate interlayer materials include CaF\textsubscript{2}, MgAl\textsubscript{2}O\textsubscript{4}, and MgO, all of which have been evaluated to some extent during the past several years [8,9,12-14]. As it is developed, interlayer technology for high-Tc superconductors [18-20], which possess similar perovskite structures, may be applied to integrated optic devices as well.

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