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# Substrate Effects on the Structure and Optical Properties of Epitaxial $PbTiO_3$ Thin Films Prepared by Metal-Organic Chemical Vapor Deposition*

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# SUBSTRATE EFFECTS ON THE STRUCTURE AND OPTICAL PROPERTIES OF EPITAXIAL $PbTiO_3$ THIN FILMS PREPARED BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

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## ABSTRACT

Epitaxial $PbTiO_3$ films were prepared by metal-organic chemical vapor deposition (MOCVD) on MgO(001), $SrTiO_3$(001) and $LaAlO_3$(001) surfaces. Four-circle X-ray diffraction and optical waveguiding experiments were performed to characterize the deposited films. The films on all three substrates were single-crystal; however, the domain structure of the films was strongly dependent on the substrate material. Films on MgO and $LaAlO_3$ substrates showed a large amount of 90° domain structures, whereas, the degree of twinning was greatly suppressed for films on $SrTiO_3$. The refractive indices and optical birefringence of the films were measured as a function of wavelength using the film-prism coupling method. We found that for films on $LaAlO_3$(001), the ordinary index and for films on MgO(001) both the ordinary and extraordinary refractive indices were higher than those of bulk single-crystal $PbTiO_3$. For films grown on $SrTiO_3$(001), the ordinary refractive index was very close to that of single crystal $PbTiO_3$. We correlate the increased refractive index and the reduced birefringence to the degree of epitaxial strain and twinning in the samples, respectively.

## INTRODUCTION

Current interest in ferroelectric thin films results from the numerous potential applications for these materials which utilize the unique dielectric, pyroelectric, electro-optic, acousto-optic, and piezo-electric properties of ferroelectrics materials[1]. The synthesis of thin films of the lead-based ferroelectrics, $PbTiO_3$, $Pb(Zr_xTi_{1-x})O_3$ (PZT), $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ (PLZT), etc., using a variety of techniques (e. g., sol-gel, sputtering, laser ablation, MOCVD) and the resulting properties of the films have been studied extensively [1]. For many applications, such as non-volatile dynamic random access memory (DRAM) or electro-optic waveguide modulators, a highly textured microstructure is preferable or essential. Ferroelectric film deposition using MOCVD has been widely reported and has been shown to be able to produce film microstructures from random polycrystalline to highly epitaxial [2].

We have systematically studied the effects of the deposition parameters and the factors controlling the formation of single-phase stoichiometric $PbTiO_3$ films grown by MOCVD [3]. We have also reported the effects of gas phase composition, substrate materials, substrate orientation, and deposition temperature on the phase, composition, crystallinity, morphology and domain structure of epitaxial thin films of $PbTiO_3$ [4]. In this paper, we examine in detail the effect of the choice of substrate materials on the structure and twinning of the $PbTiO_3$ thin films and effect this has on the optical properties of the film determined by waveguiding.

## EXPERIMENTAL

The film depositions were carried out in a low pressure, horizontal, cold wall reactor with a resistive substrate heater. Tetraethyl lead, $Pb(C_2H_5)_4$, and titanium isopropoxide, $Ti(OC_3H_7)_4$ were chosen as the metal ion precursors. A mixture of the organometallic precursor vapor was introduced into the reactor via a high purity nitrogen carrier gas. The temperature of each of the precursor chambers and the flow rate of the carrier gas through the source chambers were controlled individually, and these parameters were used to adjust the film compositions. Pure

oxygen was used as the oxidant and introduced into the reactor via a separate delivery line. The precursor delivery lines, as well as the inlet flange, were heated and maintained at ~100°C which is higher than the highest source evaporation temperature to avoid the condensation of the vapor phase precursors. Epitaxial-grade (001) MgO, (001) $SrTiO_3$, and (001) $LaAlO_3$ (pseudo-cubic) were chosen as substrates. For initial comparison, different types of substrates were placed on the susceptor for simultaneous film deposition, and the effect of the substrate on the crystallinity and orientation of the deposited film was compared. Larger area films for optical waveguiding analysis were subsequently deposited. Immediately prior to deposition, the substrates were cleaned with an acetone and methanol solvent; no further surface treatments were performed. The typical growth conditions are shown in Table I.

Table I. Growth Conditions

| | | | |
|---|---|---|---|
| Substrate temperature | 700-750°C | | |
| Reactor pressure | 10 torr | | |
| OM precursor temperature | $Ti(OC_3H_7)_4$ | - | 28-30 °C |
| | $Pb(C_2H_5)_4$ | - | 20-22 °C |
| Flow rate of reactant gas ($O_2$) | 200 sccm | | |
| Flow rate of OM and carrier gas ($N_2$) | $Ti(OC_3H_7)_4$ | - | 50-80 sccm |
| | $Pb(C_2H_5)_4$ | - | 20-40 sccm |
| Flow rate of background gas ($N_2$) | 250 sccm | | |
| Film thickness | 0.4-1.0 μm | | |
| Film growth rate | 20-50 Å/min. MgO(001), $LaAlO_3$ (001) | | |
| | 50-70 Å/min. $SrTiO_3$ (001) | | |
| Substrates | MgO(001), $SrTiO_3$ (001), $LaAlO_3$ (001) | | |

X-ray θ-2θ diffraction and ω-rocking spectra of the films were obtained using a Rigaku diffractometer and a 10 kW $Cu_{K\alpha}$ rotating anode x-ray source. Crystallographic analysis and off-specular x-ray diffraction was performed using a 12 kW $Cu_{K\alpha}$ rotating anode x-ray source focused by a bent graphite monochromator to the center of a four-circle Huber spectrometer with a two-circle graphite-crystal analyzer stage. The angular resolution of this system is 2θ, θ: 0.17°, ϕ:0.17-0.50°, χ: 0.9-1.5°. A detailed description of this system and its application to the study of epitaxial thin films is given elsewhere [5]. Prism-coupling waveguide experiments were performed with a Metricon 2010 Prism-Film coupler using a tunable HeNe laser (632.8, 612.0, 604.6, 594.1, 543.5 nm) and a Coherent Innova 70 $Ar^+$ Ion Laser (514.5, 501.7, 496.5, 487.9, 476.5, 472.2, 465.8, 457.9 nm). This system has been described elsewhere [6].

## RESULTS AND DISCUSSION

With the growth conditions specified in Table I, the films produced on the three substrates, MgO(001), $SrTiO_3$(001), and $LaAlO_3$(001), were all single-phase perovskite, single-crystalline $PbTiO_3$. For a typical film grown on MgO(001) (thickness ~7900Å), results of four-circle x-ray diffraction analysis are shown in Fig. 1. The specular θ-2θ scan is shown in Fig. 1a. The only Bragg reflections observed in this scan are the MgO (002) and the $PbTiO_3$ (002) reflections. Similarly, for a scan range of 10-70° in 2θ, the only additional observed reflections were $PbTiO_3$ (001) and (003) indicating the film appears to consists of a single (001) growth plane. The θ-rocking curve (ω-scan) of the $PbTiO_3$ (003) reflection is shown in Fig. 1b. This scan clearly indicates that the peak is split in two. The full width at half maximum (FWHM) of the peaks is 0.69°; a similar splitting of the $PbTiO_3$ (003) reflection is observed in the χ-scan. Fig. 1g. is a contour plot of the x-ray intensity in the reciprocal space H-K plane of the $PbTiO_3$ (003) reflection. This plot shows that even though the specular θ-2θ scan indicates that the film consists of a single growth plane, there are actually four variant grain structures in the film, each tilted ~0.6° from the MgO[001] surface normal along the MgO[110], [1$\bar{1}$0], [$\bar{1}$10] and [$\bar{1}\bar{1}$0] directions reflecting the four fold symmetry of the substrate surface. Since the film is grown at a temperature

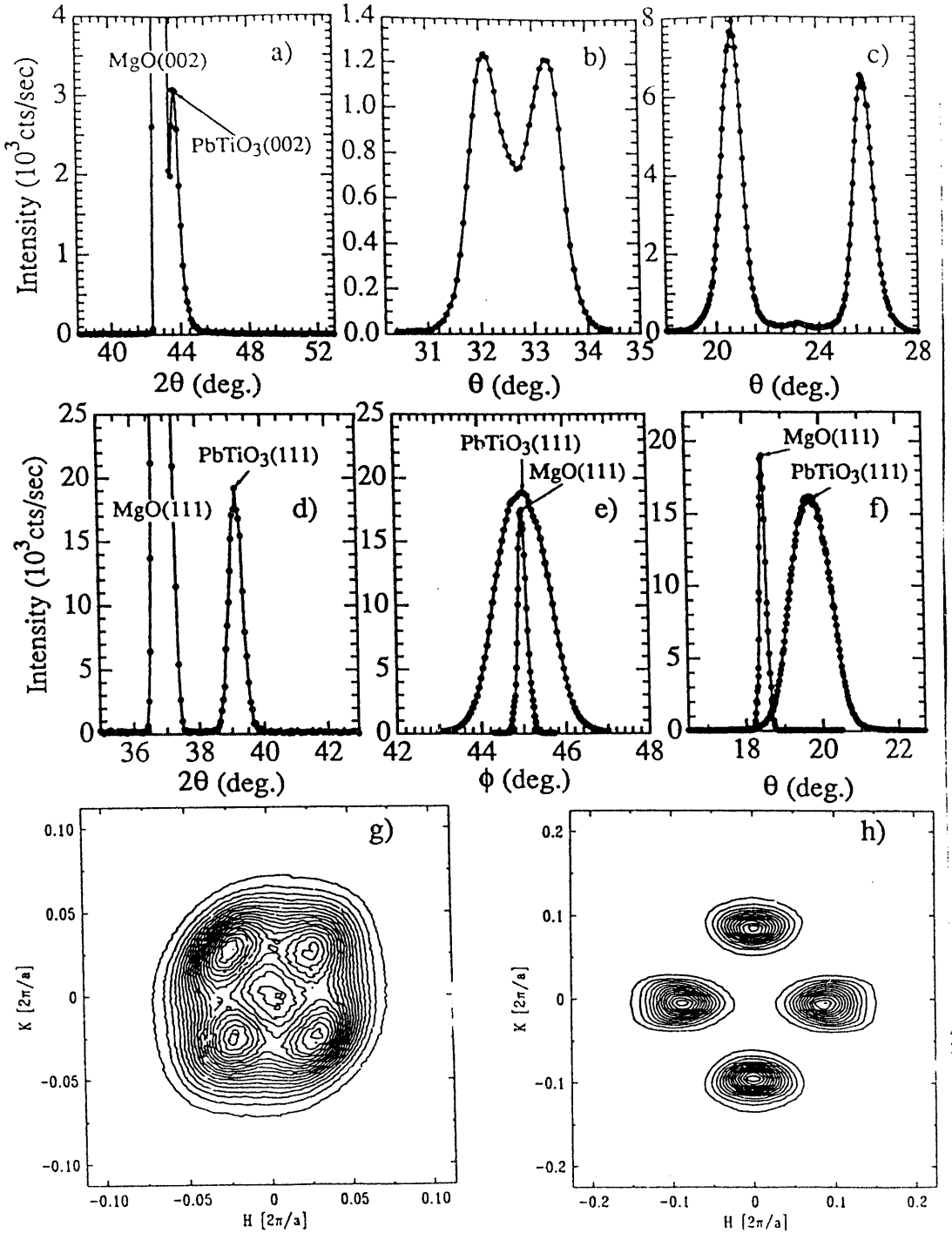


Figure 1. Four circle x-ray diffraction data for $PbTiO_3$ thin film deposited on MgO(100): a) specular θ-2θ scan, b) θ-rocking of $PbTiO_3$ (003), c) θ-rocking of $PbTiO_3$ (200) domains, d) offspecular θ-2θ scan, e) offspecular θ-rocking, f) offspecular ϕ-scan, g) contour plot of $PbTiO_3$ (003), and h) contour plot of $PbTiO_3$ (200) domains.

(~700°C) higher than the Curie temperature (~490°C) of the $PbTiO_3$, it must grow in the cubic phase. We believe that these tilt structures must form during the growth process and represent a relaxation mechanism for relieving the ~6.8% tensile strain arising from the cubic-on-cubic lattice mismatch at the growth temperature. Fig. 1c. shows the specular θ-rocking curve measured at the 2θ angle appropriate for the $PbTiO_3$ (200) reflection. While the θ-2θ scan showed no evidence of

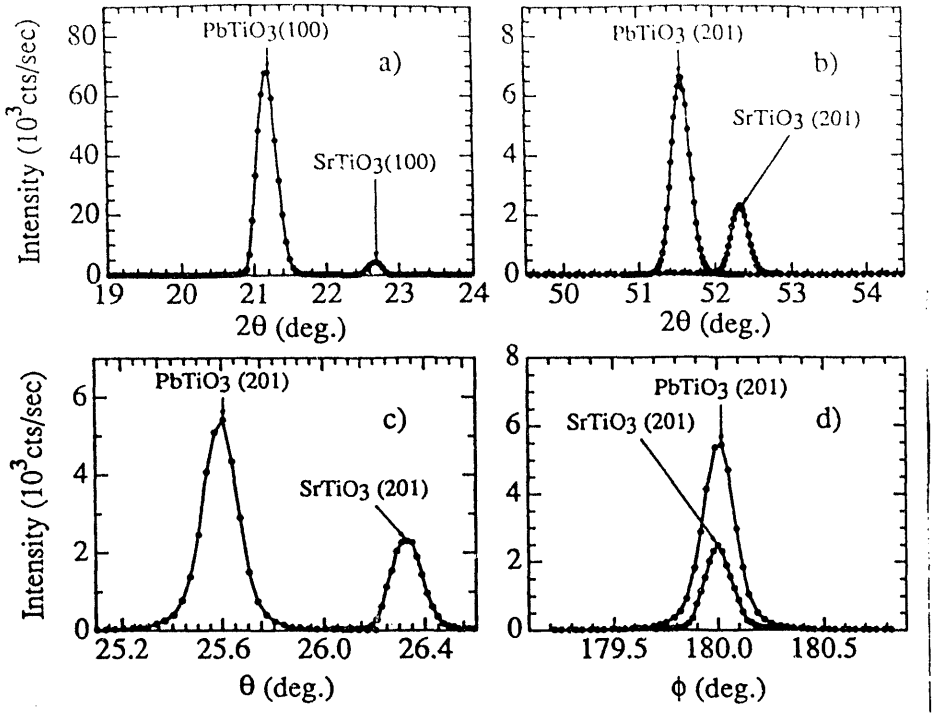


**Figure 2. Four circle x-ray diffraction data for $PbTiO_3$ thin film deposited on $SrTiO_3(100)$: a) specular θ-2θ scan, b) offspecular θ-2θ scan, c) offspecular θ-rocking, d) offspecular ϕ-scan.**

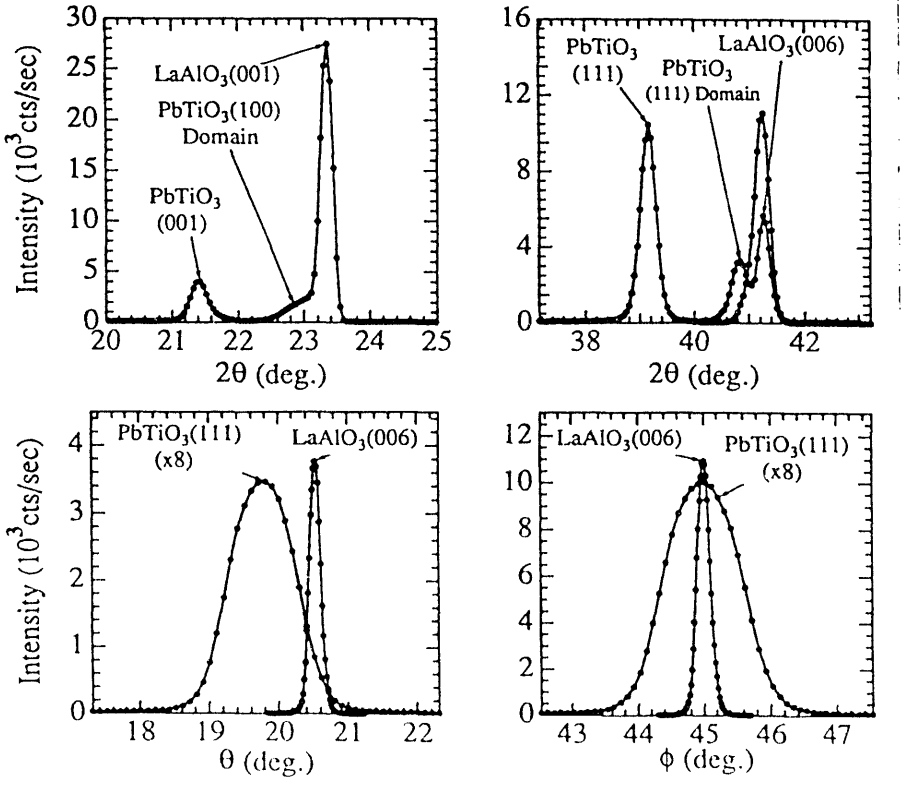


Figure 3. Four circle x-ray diffraction data for $PbTiO_3$ thin film deposited on $LaAlO_3$ (001): a) specular θ-2θ scan, b) offspecular θ-2θ scan, c) offspecular θ-rocking, d) offspecular ϕ-scan.

any specular reflection at this 2θ-value, the θ-rocking curve clearly shows two peaks, each with a FWHM of ~0.7°; in addition, another two peaks are observed in the χ-scan. Fig. 1h. is a contour plot of the x-ray intensity in the reciprocal space H-K plane of the $PbTiO_3$ (200) reflection. This plot clearly shows these four peaks each tilted approximately 2.7° from the MgO[001] surface normal along the MgO [010], [0$\bar{1}$0], [100] and [$\bar{1}$00] directions reflecting the four fold symmetry of the substrate surface. Note that these peaks are rotated by 45° with respect to the splitting observed in the $PbTiO_3$ (003) reflection, and that the magnitude of the splitting is much greater than that of the $PbTiO_3$ (003) peak. We attribute these four reflections to the presence of [101] and [011] type 90° domain structures in the film. These domain structures must form during the cooling process from the growth temperature and represent another relaxation mechanism for relieving the lattice mismatch strain, the thermal expansion mismatch strain and the transformational strains associated with the cubic-to-tetragonal phase transformation. Figs. 1d-1f show the offspecular θ-2θ, θ-rocking, and φ-scans of the MgO(111) and $PbTiO_3$(111) reflections, respectively. The presence of the $PbTiO_3$(111) reflection oriented with respect to the MgO(111) reflection indicates the single crystal nature of the film and determines the in-plane epitaxial relationship between the film and the substrate: MgO(100)//$PbTiO_3$(100). The in-plane crystalline mosaic in the film is determined by the FWHM of the θ-rocking and φ-scans of the $PbTiO_3$(111) as ~1.15°; the θ-rocking and φ-scans of the MgO(111) is shown for reference.

For a typical film grown on $SrTiO_3$ (001) (thickness ~7700Å), results of four-circle x-ray diffraction analysis are shown in Fig. 2. The specular θ-2θ scan is shown in Fig. 2a. The only Bragg reflections observed in this scan are the $SrTiO_3$ (001) and the $PbTiO_3$ (001) reflections. Note that while the thickness of the films grown on $SrTiO_3$ (001) and MgO (100) are similar, the intensity of the $PbTiO_3$ (001) is much stronger relative to the substrate reflection for the film on $SrTiO_3$ (001); this indicates a drastic improvement in film orientation and crystallinity. For a scan range of 10-70° in 2θ, the only additional observed reflections were $SrTiO_3$ (002), $PbTiO_3$ (002) and $PbTiO_3$ (003) indicating the film consists of a single (001) growth plane. Note that The θ-rocking curve (ω-scan) and the χ-scan of the $PbTiO_3$ (002) reflection show only a single peak with a FWHM of 0.12° (instrument resolved). Consequently, there is no tilt variant structures in the film grown on $SrTiO_3$ (001) as seen in films grown on MgO(001). Since the cubic-on-cubic lattice mismatch strain at the growth temperature between $SrTiO_3$ (001) and $PbTiO_3$ (100) is ~1.0%, we conclude that this relaxation mechanism is only active for systems with a lattice mismatch greater than this value. At room temperature the lattice mismatch in between $SrTiO_3$ (100) and $PbTiO_3$ (100) is ~0.02%, representing an almost perfect lattice match. The specular θ-rocking curve measured at the $PbTiO_3$ (100) reflection shows two peaks, similar to the that seen in the film on MgO(001), each with a FWHM of ~0.4° and, similarly, another two peaks are observed in the χ-scan. We again attribute these reflections to the presence of [101] and [011] type 90° domain structures in the film; however, the intensity of these domain peaks is ~0.01 times as intense as those observed for the films grown on MgO(001). Consequently, the formation of 90° domains must result predominantly as a relaxation mechanism for relieving the transformational and lattice mismatch strains, and to a lesser degree, the thermal expansion mismatch strain. Figs. 2b-2d show the offspecular θ-2θ, θ-rocking, and φ-scans of the $SrTiO_3$(201) and $PbTiO_3$(201) reflections, respectively. The presence of the $PbTiO_3$(201) reflection oriented with respect to the $SrTiO_3$(201) reflection indicates the single crystal nature of the film and determines the in-plane epitaxial relationship between the film and the substrate: $SrTiO_3$(100)//$PbTiO_3$(100). Since the linewidths are instrument-resolution limited, we obtain an upper bound of the degree of in-plane crystalline mosaic in the film indicated by the FWHM of the θ-rocking and φ-scans of the $PbTiO_3$(201) as >0.15°, the θ-rocking and φ-scans of the $SrTiO_3$(201) is shown for reference.

For a typical film grown on $LaAlO_3$ (001) (pseudo-cubic) (thickness ~6200Å), results of four-circle x-ray diffraction analysis are shown in Fig. 3. The specular θ-2θ scan is shown in Fig. 2a. The only Bragg reflections observed in this scan are the $SrTiO_3$ (001) and the $PbTiO_3$ (001) reflections and a small component of $PbTiO_3$ (100) associated with 90° domains. The θ-rocking curve and χ-scan of the $PbTiO_3$ (003) reflection both show two peaks (FWHM ~0.62°). A contour plot of the x-ray intensity in the reciprocal space H-K plane of the $PbTiO_3$ (003) reflection shows the same four-fold tilt variant grain structure as in the film grown on MgO(001). These results are quite similar to the case of films grown on MgO(001), even though the lattice mismatch strain at the growth temperature between $LaAlO_3$ (001) and $PbTiO_3$ (100) is smaller

(3.9%) than for MgO(001) substrates (6.8%). Also, the strain is compressive as opposed to tensile. The $LaAlO_3$ (001) pseudo-cubic surface should have only two-fold rotational symmetry; however, the $LaAlO_3$ substrates clearly showed twin structures which yield an effective four-fold surface symmetry. We conclude that the tilt variant grain structures observed in films grown on both MgO(001) and $LaAlO_3$ (001) substrates are a general relaxation mechanism for relieving the cubic-on-cubic lattice mismatch strain (≥3.9%, tensile or compressive) at the growth temperature. The specular θ-rocking curve, χ-scan, and H-K plane contour scan measured at the $PbTiO_3$ (200) domain reflection also shows four reflections associated with the presence of [101] and [011] type 90° domain structures. The intensity of these domain peaks is ~0.10 times as intense as those observed for the films grown on MgO(001). The lattice mismatch strains at just below the approximate Curie temperature (~485°C) of $PbTiO_3$ films grown on MgO(001), $SrTiO_3$(001) and $LaAlO_3$ (001) are 7.2%, -0.07%, and -3.6%, respectively. We conclude that the magnitude of the lattice mismatch strain is the dominant factor in controlling the amount of 90° domain formation in $PbTiO_3$ epitaxial thin films. Figs. 3b-3d show the offspecular θ-2θ, θ-rocking, and ϕ-scans of the $LaAlO_3$(006) and $PbTiO_3$(111) reflections, respectively. The presence of the $PbTiO_3$(111) reflection oriented with respect to the $LaAlO_3$(006) reflection indicates the single crystal nature of the film and determines the in-plane epitaxial relationship between the film and the substrate: (pseudo-cubic) $LaAlO_3$(100)//$PbTiO_3$(100). The in-plane crystalline mosaic in the film is determined by the FWHM of the θ-rocking and ϕ-scans of the $PbTiO_3$(111) as ~1.25°, the θ-rocking and ϕ-scans of the $LaAlO_3$(006) is shown for reference.

In Fig. 4, we show the ordinary refractive index for the $PbTiO_3$ films as a function of wavelength as determined by prism-coupled planar waveguiding. For films grown on $SrTiO_3$(001) the measured ordinary refractive index was equivalent to the literature value for single-crystal $PbTiO_3$ [7] at all wavelengths, whereas for films grown on MgO(001) and $LaAlO_3$(001) the measured ordinary refractive index was consistently higher at all wavelengths. Note that the consistently high refractive index reflects the high quality of the $PbTiO_3$ thin films. We attribute the enhancement of the ordinary index for the films grown on MgO(001) and $LaAlO_3$(001) to residual stresses in the film arising from the constraint of the substrate lattice. We conclude that the bulk-like refractive index and the reduced amount of twinning of films grown on

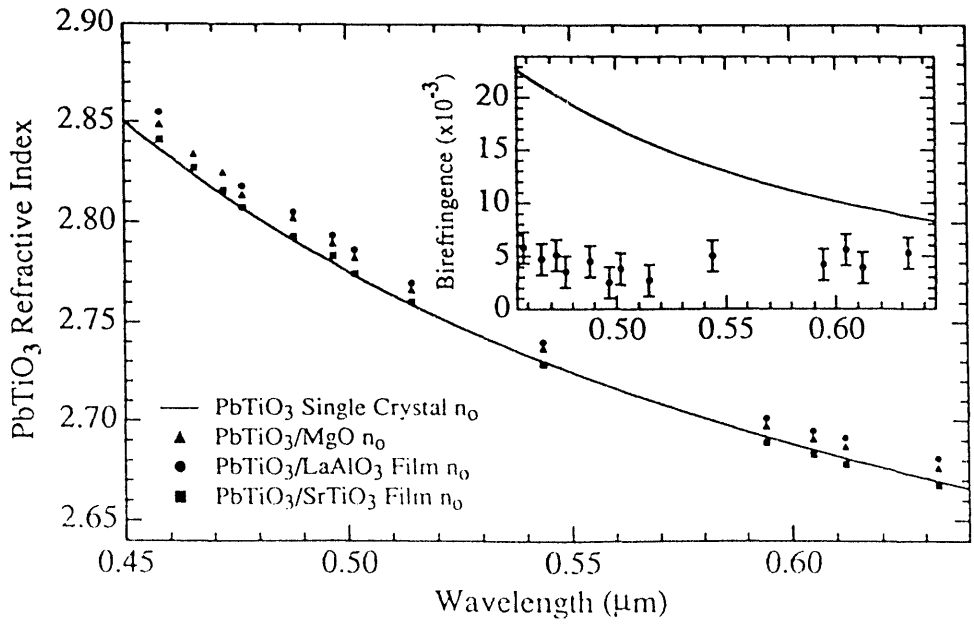


Figure 4: Ordinary refractive index for $PbTiO_3$ thin films grown on MgO(001), $SrTiO_3$(001), and $LaAlO_3$(001) compared to that of single-crystal $PbTiO_3$. The inset show the optical birefringence for $PbTiO_3$ thin films grown on MgO(001) compared to that of single-crystal $PbTiO_3$.

$SrTiO_3(001)$ reflects the low amount of residual stress in these films arising from the almost perfect lattice match for this system. Since extraordinary index data could only be obtained for the film grown on MgO(001) due to prism index limitation (films on $SrTiO_3(001)$ substrates) and substrate twinning-induced roughness (films on $LaAlO_3(001)$ substrates), optical birefringence data, shown as the inset of Fig. 4, was obtained for only the film grown on MgO(001). Note that the birefringence for these films is reduced from that of $PbTiO_3$ single crystals[7]. For a twinned film with a domain size small relative to the wavelength of light, the resulting effective dielectric medium as measured by the waveguiding technique will represent an averaging of true ordinary and extraordinary indices of the film. Such an averaging should lower the effective birefringence of the film. Therefore, since the film grown on MgO(001) contains a substantial fraction of 90° domain volume, the observed reduction in the birefringence is expected.

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