LOW-TEMPERATURE MOCVD GROWTH OF ORIENTED $PbZr_xTi_{1-x}O_3$ THIN FILMS ON Si SUBSTRATES*

Nan Chen,† G. R. Bai,† C. M. Foster,† O. H. Auciello,†
M. J. Brukman, and M. T. Lanagan
Energy Technology Division
†Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

April 1998

Paper to be presented at the 100th Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 3-6, 1998.

*Work supported by Argonne National Laboratory's Directed Research and Development Program, with funding from the U.S. Department of Energy.

DISCLAIMER

LOW-TEMPERATURE MOCVD GROWTH OF ORIENTED $PbZr_xTi_{1-x}O_3$ THIN FILMS ON Si SUBSTRATES

Nan Chen,* G. R. Bai, C. M. Foster, O. H. Auciello, Materials Science Division, M. J. Brukman and M. T. Lanagan, Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439–4838

ABSTRACT

Polycrystalline $Pb(Zr_{0.6}Ti_{0.4})O_3$ (PZT) thin films, 3000–6000 Å thick, have been grown by metal–organic chemical vapor deposition (MOCVD) on (111)Pt/Ti/SiO_2/Si substrates at temperatures as low as 450–525°C. Random and (111)-oriented, or occasionally (100)-oriented, PZT films can be deposited directly on (111)Pt/Ti/SiO_2/Si. In addition, highly (100)-oriented films can be deposited consistently by using 150–250 Å thick (100)-oriented $PbTiO_3$ (PT) or TiO_2 as a template. Films were characterized by X-ray diffraction, electron microscopy, and electrical measurements. The as-grown (100)-oriented films on (111)Pt/TiSiO_2/Si substrates exhibited dielectric constants (ε_r) of up to 600, remnant polarization (P_r) of 40 $\mu C/cm^2$, coercive field of 55 kV/cm, and breakdown field of 2–6 x 10^7 V/m.

INTRODUCTION

Ferroelectric materials such as PZT offer considerable potential for applications such as capacitors,[1] nonvolatile memory devices,[2] surface-acoustic-wave devices,[3] and electro-optic devices.[4] Processing of PZT thin films by MOCVD has been widely pursued in recent years because MOCVD is believed to offer great advantages for application of ferroelectric materials to ULSI-scale technologies. Good quality, highly oriented PZT films with excellent ferroelectric properties (e.g., P_r = 40–60 $\mu C/cm^2$, ε_r = 300–600) have been reportedly grown on substrates such as (100)$SrRuO_3$/(100)$SrTiO_3$,[5] (100)Pt/(100)MgO,[6,7] and (111)Pt/Ti/SiO_2/Si[8] at the relatively high temperature of ≈700°C. Highly (100)-oriented PZT films recently grown on (100)RuO/SiO_2/Si at 525°C also showed good ferroelectic properties without annealing.[9] Other studies have reported the feasibility of growing oriented or nonoriented PZT films on commercially available substrates, such as (111)Pt/Ti/SiO_2/Si, at temperatures of 450–600°C.[10-14]

For PZT film processing to be incorporated into large-scale processing, low-temperature growth on Si substrates presents great advantages. In this study, the goal was to grow high-quality films with good electrical properties on Si substrates at low temperatures without the need for annealing at higher temperatures later.

EXPERIMENTAL DETAILS

Preparation of PZT films

PT and PZT film depositions were carried out in a low-pressure, horizontal-flow, cold-wall reactor that contained a resistive substrate heater. Tetraethyl lead ($Pb(C_2H_5)_4$), zirconium t-butoxide ($Zr[OC(CH_3)_3]_4$), and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) were used as the metal-ion precursors. The growth conditions are shown in Table I. Because the rate at which Pb deposition diminishes as substrate temperature decreases is much faster than for either Zr or Ti deposition rates, we had to increase the Pb precursor temperature to 40°C from 36° when changing growth temperature from 525°C to 450°C while the carrier-gas flow rate was maintained at ≈20 standard cm^3/min (sccm). When grown under optimal conditions, the films exhibited a shiny, smooth surface.

Table 1. Growth conditions for PZT films on (111)Pt/Ti/SiO_2/Si.

Variable		Value
Substrate temperature		450–525°C
Reactor pressure		20–40 Torr
Organometallic (OM) precursor temperature	$Ti(OC_3H_7)_4$	40°C
	$Zr[OC(CH_3)_3]_4$	45°C
	$Pb(C_2H_5)_4$	32–38°C
OM precursor pressure	$Ti(OC_3H_7)_4$	100 Torr
	$Zr[OC(CH_3)_3]_4$	150 Torr
	$Pb(C_2H_5)_4$	400 Torr
Flow rate of reactant gas (O_2)		400 sccm
Flow rate of OM precursor and carrier gas (N_2)	$Ti(OC_3H_7)_4$	30 sccm
	$Zr[OC(CH_3)_3]_4$	25 sccm
	$Pb(C_2H_5)_4$	20 sccm
Flow rate of background gas (N_2)		600 sccm
Film thickness		0.2–0.7 μm
Film grown rate		50-70 Å/min

Characterization methods

X-ray θ and 2θ diffraction (XRD) scans were obtained with a Rigaku diffractometer and a 3 kW Cu Kα X-ray source. The film thickness was measured by Rutherford backscattering; results were confirmed by an optical wave-guide method.[15] Film surface roughness, grain structure, and cross section were characterized by scanning electron microscopy (SEM) and film compositions were determined by energy dispersive X-ray spectroscopy.

For electrical measurements, Ag top electrodes were electron-beam evaporated through a paterned mask to form capacitor structures with contact areas of 2×10^{-3} – 1×10^{-5} cm^2. Ferroelectrtic hysteresis loops were obtained with a Radiant

Technologies RT6000HVS test system. Dielectric-breakdown strengths were measured with a Keithley 237 source measurement unit. Dielectric constants and loss tangents at 1 kHz were obtained with a Hewlett-Packard HP4192A impedance analyzer.

RESULTS AND DISCUSSION

Growth of PZT on (111)Pt/Ti/SiO_2/Si

PZT films with various orientations could be grown on (111)Pt/Ti/SiO_2/Si, as shown in Fig. 1; however, the film reproducibility was poor. Growth of films with the desired (100) orientation occurred only randomly and could not be controlled systematically and reproducibly. It appeared that slight changes in the gas-phase Pb/(Zr+Ti) ratio led to changes in PZT film orientation, while a single phase was maintained. Within the window of a gas-phase Pb/(Zr+Ti) ratio in which a single phase was obtained, higher Pb/(Zr+Ti) ratios favored growth of randomly oriented films, lower ratios favored growth of (111)-oriented films, and the median ratio favored growth of (100)-oriented films.

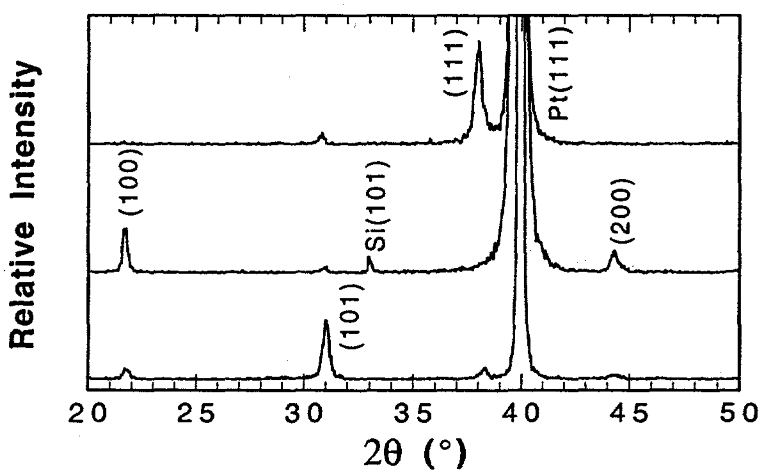

Fig 1. XRD 2θ scans of (111) (top), (100) (center), and randomly (bottom) oriented PZT films grown on (111)Pt/Ti/SiO_2/Si at 525°C.

It is speculated that nucleation and growth of certain orientations were probably affected by gas-phase stoichiometry and the initial growth rate. Figure 2 shows XRD 2θ scans of PZT films grown at a substrate temperature of 450–475°C. At 475°C, no impurity phase was detected by XRD on the as-grown films. When the substrate temperature was reduced to 450°C, impurity phases appeared (at $2\theta \approx 29°$). These impurities persisted for all films grown at 450°C, even for those of optimal Pb/(Zr+Ti) ratio. The impurity phases appeared to be PbO and $PbTi_3O_7$ (pyrochlore). Besides the presence of impurity phases, at the lower growth temperatures of 475 and 450°C, only randomly oriented films could be obtained on (111)Pt/Ti/SiO_2/Si.

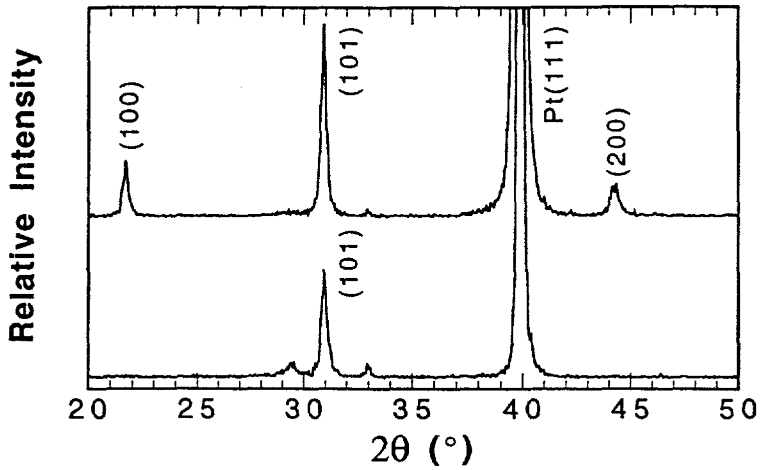

Fig. 2. XRD scans of PZT films grown on (111)Pt/Ti/SiO_2/Si at 475 (top) and 450°C (bottom).

Growth of PZT on (111)Pt/Ti/SiO_2/Si with PT and TiO_2 as buffer layer

As discussed above, growth of (100)-oriented PZT films on (111)Pt/Ti/SiO_2/Si could not be achieved reproducibly. To circumvent this problem, ≈200 Å thick PT films were initially grown on (111)Pt/Ti/SiO_2/Si at 475°C. The substrate temperature was then adjusted to the desired temperature for PZT growth. The growth conditions for PZT were essentially the same as those for growth of PZT directly on (111)Pt/Ti/SiO_2/Si. With PT as a template, the PZT films were highly oriented (Fig. 2), and the reproducibility of growing (100)-oriented films was much better than that of films grown directly on (111)Pt/Ti/SiO_2/Si. Furthermore, (100)-oriented films were also obtained at a substrate temperature of 450°C, in contrast to the randomly oriented films without a PT template.

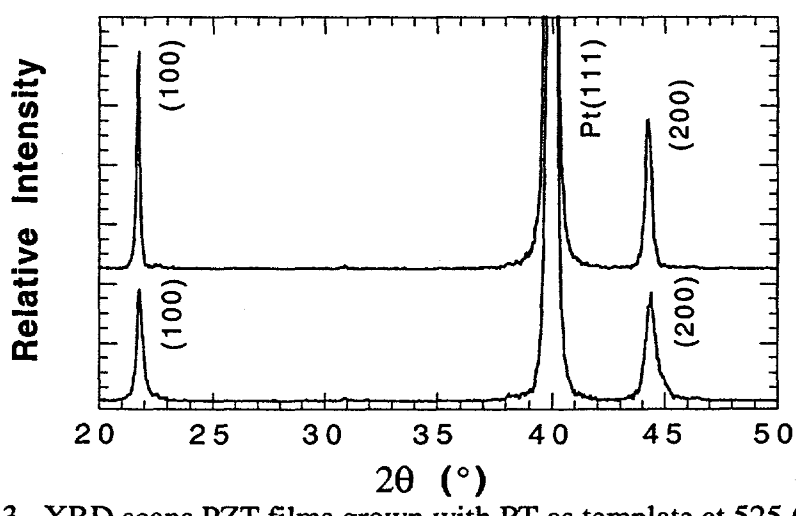

Fig. 3. XRD scans PZT films grown with PT as template at 525 (top) and 450°C (bottom).

Highly oriented (100)-PZT films were also obtained on TiO_2 templates (Fig. 4). In the case of TiO_2 templates, film reproducibility was extremely good. Variations up to 10% in carrier gas ratio of Pb/(Zr+Ti) still resulted in growth of (100)-oriented films.

The improved PZT film orientation with use of a PT buffer layer is probably related to the fact that (100)-oriented PT provides a very good lattice match with PZT. The origin of the greatly improved orientation with use of TiO_2 templates is not yet clear, however.

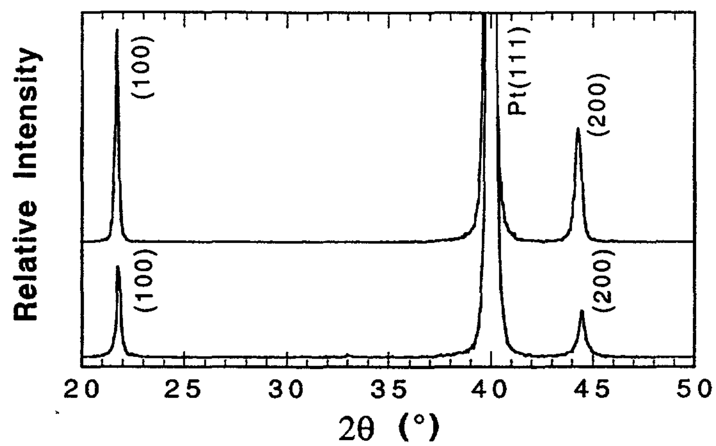

Fig. 4. XRD scans of PZT films grown with TiO_2 as template at 525 (top) and at 450°C.

Microstructure and Electric Characterization

Figure 5 shows SEM photomicrographs of the surface morphology of PZT films grown on (111)Pt/Ti/SiO_2/Si with and without template layers. When grown without templates, film morphology appeared coarser, with an identifiable island structure of fine grains. With template layers, the films exhibit uniform fine-grained structures.

Dielectric constant values of PZT films obtained in this study ranged from 360 to 600. The value of the dielectric constant seemed independent of films orientation, but was strongly influenced by the presence of film flaws, such as pinholes. The breakdown fields were between 2 and 6 $\times 10^7$ V/m.

Figure 6 shows the polarization-versus-electric-field hysteresis (P-E) loops for Ag/PZT/Pt and Ag/PZT/PT/Pt thin-film capacitors of various crystallographic orientation. The loops showed a dependence of ferroelectric behavior on grain orientation. For Ag/PZT/Pt thin film capacitors, the film with (100) orientation exhibited higher P_r and lower E_c than those of films with random orientation (P_r = 30 vs. 20 μC/cm^2, and E_c = 100 vs. 115 kV/cm). The film with a (111) orientation showed very little polarization at electric fields to 575 kV/cm, which is the equivalent of 20 V, the limit of the RT6000HVS test system. A (111)

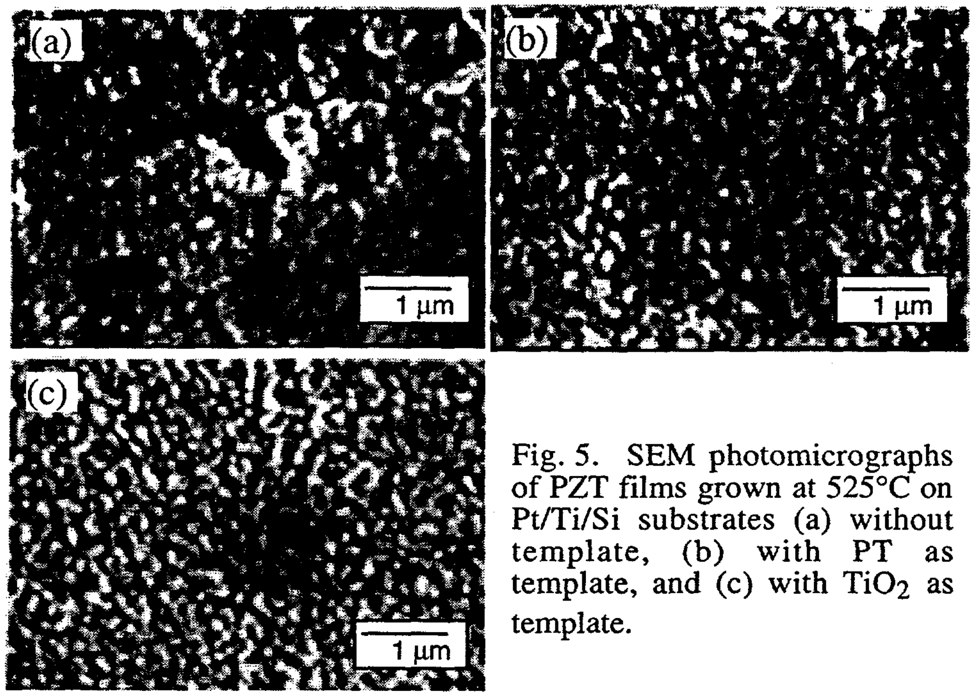

Fig. 5. SEM photomicrographs of PZT films grown at 525°C on Pt/Ti/Si substrates (a) without template, (b) with PT as template, and (c) with TiO_2 as template.

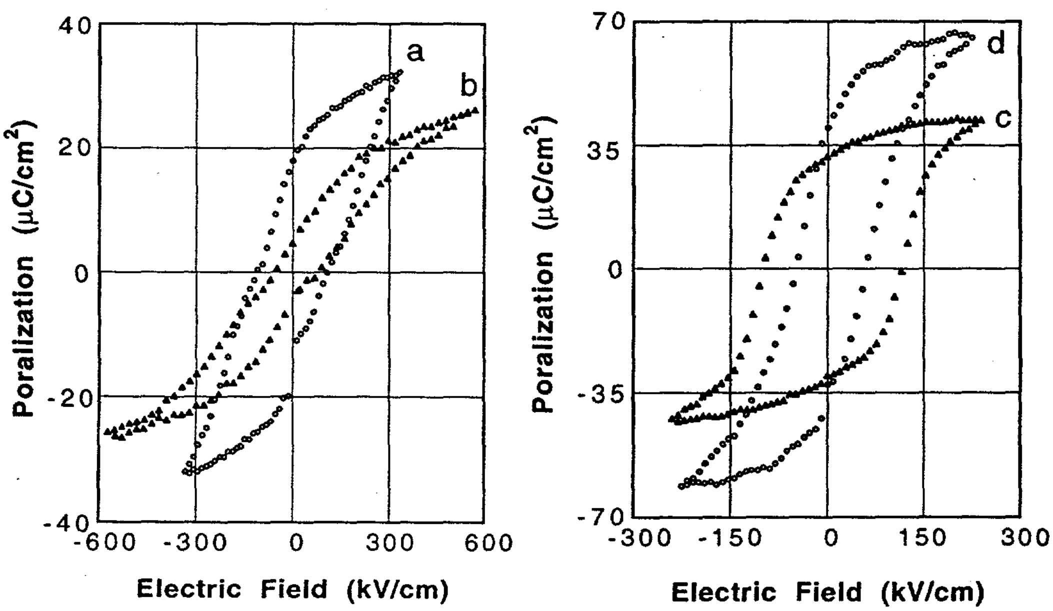

Fig. 6. P-E hystereses of (a) randomly oriented, (b) (111)-oriented, (c) (100)-oriented PZT films on Pt/Ti/Si, and (d) (100)-oriented film with PT as template.

orientation in PZT, which is an unfavorable polarization direction, probably would need higher electric field to exhibit reasonable loops. Highly (100)-oriented PZT films grown with a PT template showed better ferroelectrc properties ($Pr \approx 40\ \mu C/cm^2$, and $E_c \approx 55$ kV/cm) than the partially (100)-oriented PZT films grown without a template.

SUMMARY

It was demonstrated that single-phase PZT films with various orientations could be grown directly on (111)Pt/Ti/SiO_2/Si substrates at 525°C. Randomly oriented PZT films could be grown on (111)Pt/TiSiO2/Si at temperatures as low as 450°C. Highly oriented PZT films could be grown consistently at temperature as low as 450°C on (111)Pt/Ti/SiO_2/Si substrates by using 150–200 Å thick template layers of either PT or TiO_2. P-E hysteresis measurements showed that ferroelectric behavior was influenced by grain orientation. PZT grown on PT templates exhibited the best ferroelectric properties. Further study is needed to understand the growth mechanism of PZT films

ACKNOWLEDGMENTS

This work was supported by Argonne National Laboratory's Directed Research and Development Program, with funding from the U.S. Department of Energy.

REFERENCES

[1]B. Jaffe, W. Cook, and H. Jaffe, Ferroelecric Ceramics (Academic Press, London, 1971) p. 136.

[2]J. C. Crawford and F. L. English, "Ceramic Ferroelectric Field Effect Studies," IEEE Trans. Electron. Devices, **ED-16**, 525-32 (1969).

[3]K. Suzuki and M. Nishikawa, "Poling Dependence of the Surface-Wave Frequency-Generation on PZT," Jpn. J. Appl. Phys. **13**, 240-43 (1974).

[4]C. E. Land, P. D. Thacher, and G. H. Haertling, "Electrooptic Ceramics," Appl. Solid State Sci. **4**, 137-233 (1974).

[5]C. M. Foster, G. R. Bai, R. Csencstis, J. Vetrone, R. Jammy, L. A. Wills, E. Carr, and J. Amano, "Single-Crystal $Pb(Zr_xTi_{1-x})O_3$ Thin Films Prepared by Metal-Organic Chemical Vapor Deposition: Systematic Compositional Variation of Electronic and Optical Properties," J. Appl. Phys. **81**, 2349-57 (1997).

[6]A. Sakurai, K. Shiratsuyu, H. Takagi, and Y. Sakabe, "Preparation and Characterization of Epitaxial Lead Zirconate Titanate Films on Pt/MgO Substrates by Metalorganic Chemical Vapor Deposition," Jpn. J. Appl. Phys. **36**, 5812-14 (1997).

[7]Y. Sakashita, T. Ono, H. Segawa, K. Tominnaga, and M. Okada, "Preparation and Electrical Properties of MOCVD-deposited PZT Thin Films," J. Appl. Phys. **69**, 8352-57 (1991).

[8]G. J. M. Dormans, M. de Keijser, and P. J. van Veldhoven, "Ferroelectric $Pb(Zr_xTi_{1-x})O_3$ Thin Films Grown by Organometallic Chemical Vapor Deposition," Mater. Res. Soc. Symp. Proc. **243**, 203-12 (1992).

[9]G. R. Bai, I. F. Tsu, A. Wang, C. M. Foster, C. E. Murray, and V. P. Dravid, "In-Situ Growth of Highly Oriented $Pb(Zr_{0.5}Ti_{0.5})O_3$ Thin Films by Low-Temperature Metal-Organic Chemical Vapor Deposition," Appl. Phys. Lett., in press.

[10]T. Asakura, K. Ishikawa, A. Sato, and M. Okada, "Preparation and Pyroelectric Characteristics of $Pb(Zr,Ti)O_3$ Thin Films Grown by Metalorganic Chemical Vapor Deposition," Jpn. J. Appl. Phys. **35**, 4886-89 (1996).

[11]C. H. Peng and S. B. Desu, "Metalorganic Chemical Vapor Deposition of Ferroelectric $Pb(Zr,Ti)O_3$," J. Am. Ceram. Soc. **77**, 1799-812 (1994).

[12]P. Lu, H. Li, Y. M. Wang, S. Sun, and B. Tuttle, "Growth Characteristics of $PbTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$ Thin Films by Novel Single-Solid-Source Metalorganic Chemical Vapor Processing," J. Crystal Growth **181**, 374-81 (1997).

[13]M. Shimizu, M. Sugiyama, H. Fujisawa, and T. Shiosaki, "Control of Orientation of $Pb(Zr,Ti)O_3$ Thin Films Using $PbTiO_3$ Buffer Layer," Jpn. J. Appl. Phys. **33**, 5167-71 (1994).

[14]Y. M. Kim, W. J. Lee, and H. G.Kim, "Deposition of PZT Films by MOCVD at Low Temperature and Their Change in Properties with Annealing Temperature and Zr/Ti Ratio," Thin Solid Films **279**, 140-44 (1996).

[15]C. M. Foster, S. K. Chan, M. Chang, R. P. Chiarello, T. J. Zhang, J. Guo, and D. J. Lam, "Electromagnetic Modes and Prism-Film Coupling in Anisotropic Planar Waveguides of Epitaxial (101) Rutile Thin Films," J. Appl. Phys. **73**, 7823-30 (1993).