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ABSTRACT

Metalorganic chemical vapor deposition (MOCVD) was used to prepare epitaxial or highly oriented PLT ($Pb_{1-x}La_xTiO_3$) thin films with x values in the range of 0.21 to 0.34. The growth of PLT films resulted in three-dimensional epitaxial heterostructures on a (100) surface of both MgO and $KTaO_3$ substrates. The PLT film grown on a $KTaO_3$ (100) substrate has a significantly lower minimum channeling yield compared to that grown on the MgO (100) substrate because of the smaller lattice mismatch associated with $KTaO_3$. The thickness and refractive indices in the wavelength range of 435 to 1,523 nm were measured by the prism-coupling method. The measured film thickness of 570 nm was in good agreement with that obtained from RBS measurements. The refractive index of the PLT film is smaller than that of $PbTiO_3$, and its difference at λ = 632.8 nm is about 2.5%. The dispersion of the refractive index was well fitted by a Sellmeier dispersion formula.

INTRODUCTION

Ferroelectric thin films are currently of general interest for fabricating novel functional devices. The specific ferroelectric $Pb_{1-x}La_xTiO_3$ (PLT) is a transparent material which results from the addition of La as a chemical modifier to $PbTiO_3$. It is well known that PLT thin films have excellent quadratic electro-optic effects and a linear electro-optic effect for x values of 0.28 and 0.21, respectively[1]. Because of these effects, PLT thin films are expected to be useful in the development of various optoelectronic devices. Applications involving optoelectronic devices based on optical waveguides require epitaxial PLT films with high transparency, and prior work on the preparation of PLT thin films has shown that PLT films possessing good optical properties can be prepared by rf-planar magnetron sputtering[1] and rf-sputtering[2].

In the present work, the MOCVD technique has been applied to the growth of PLT thin films exhibiting full three-dimensional epitaxial orientation on (100)-oriented MgO and $KTaO_3$ single-crystal substrates. We report here on the substrate dependence of the growth phenomena and the optical properties of the resulting epitaxial PLT thin films.

EXPERIMENTAL DETAILS

In all cases, the film deposition was carried out in an inverted vertical, warm-wall reactor vessel using a resistively heated susceptor. The substrate temperature was measured using a type-K thermocouple that was embedded in the susceptor about 1.0 mm from the substrate. The metalorganic precursors employed for each of the components were: tetraethyllead, $Pb(C_2H_5)_4$; lanthanum β- diketonate, $La(C_{11}H_{19}O_2)_3$; and titanium isopropoxide, $Ti(OC_3H_7)_4$. Argon was utilized as the carrier gas, and the carrier-gas flow rates were 1000, 140, and 250 sccm for the Ti, Pb, and La sources, respectively. The temperatures of the Pb and La sources were varied from 9.5 to 11.5°C and 175 to 176.5°C, respectively, and the Ti-source temperature was varied in the range from 17.5 to 22.0°C. The substrate temperature was fixed at 650°C during the deposition process, and the reactor pressure was maintained at 70 torr. An oxygen flow of 50 sccm was used to enhance the pyrolysis process and, more importantly, to eliminate the incorporation of carbon into the film during growth. The film-growth rates were determined to be in the range of 120 to 250 nm/h by Rutherford Backscattering spectroscopy (RBS).

The crystallographic structure of the as-grown PLT thin films was examined by x-ray diffraction methods using a Siemens digitized horizontal diffractometer employing both rotational and rocking capabilities in order to provide statistically correct averaging over the reciprocal lattice points. The in-plane epitaxial relationships between the film and the substrate were examined by pole-figure and ϕ-scan measurements using a Philips X-Pert Materials Research Diffractometer. RBS and RBS/channeling experiments were performed in order to determine the film thickness, composition, and crystallographic perfection. The refractive indices at different wavelengths were obtained by using a Metricon 2010 prism coupler with rutile prism.

RESULTS AND DISCUSSION

Figure 1 shows the θ-2θ scan from 18 to 50° in 2θ for PLT thin films deposited on MgO (100) and $KTaO_3$ (100). For the case of PLT films deposited directly on (100) MgO substrates without an initial TiO_2 layer, a polycrystalline film was grown as shown in Fig. 1(a). However, by first introducing the titanium isopropoxide for a 20 sec time period in order to grow an initial TiO_2 layer, it was possible to deposit three-dimensionally epitaxial PLT films. In Fig. 1(b), the only diffraction peaks observed are from the PLT (100) and (200) and from the MgO (200) planes. This result indicates that the PLT film is oriented with its (100) planes parallel to the (100)-oriented substrate surface. This observation is consistent with the interface stability of perovskite films grown on MgO (100) substrates as reported previously[3]. The lattice parameter of the PLT film on MgO was determined to be 3.900 Å. For the $KTaO_3$ substrate, heteroepitaxy

was achieved without the introduction of TiO_2 as the initial, intervening layer between the PLT film and the substrate. Due to the isostructural nature of the $KTaO_3$ substrate and the PLT film and the good lattice match, the diffraction peaks from the PLT (100) and (200) planes overlap those from the $KTaO_3$ (100) and (200) planes as shown in Fig. 1(c).

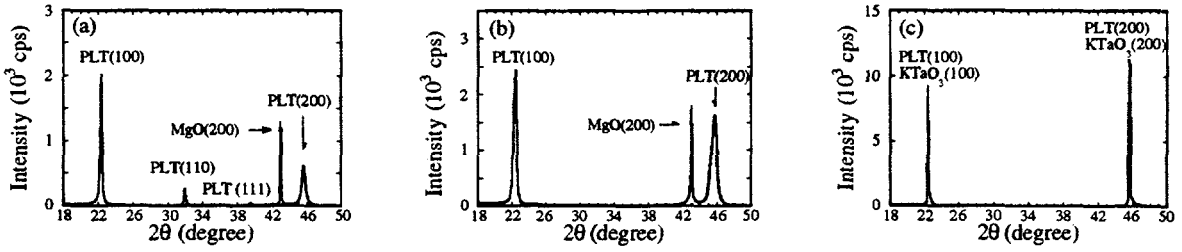

Fig. 1 θ-2θ x-ray diffraction patterns from PLT thin films grown on (a) a MgO (100) substrate without a consideration of the interface stability, (b) a MgO (100) substrate with a consideration of the interface stability, (c) a $KTaO_3$ (100) substrate.

The nature of the three-dimensional epitaxial relationship between the film and the substrate was investigated using ϕ-scan measurements as shown in Fig. 2 (a), which illustrates 360° ϕ-scans around a small circle through the PLT (220) and MgO (220) reflections. In Fig. 2 (b), additional 360° ϕ-scans around a small circle through the PLT (111) and MgO (111) reflections confirm that the PLT (111) and MgO (111) planes are aligned. Figs. 2 (c) and (d) show the ϕ-scans from the (110) and (111) reflections, respectively, of a PLT film grown on a $KTaO_3$ (100) substrate. Only four peaks with a 90° separation are observed, and these reflections represent overlapping contributions from the film and isostructural substrate. These results demonstrate the excellent in-plane epitaxial relationship that is achieved using (100)-oriented $KTaO_3$ substrates.

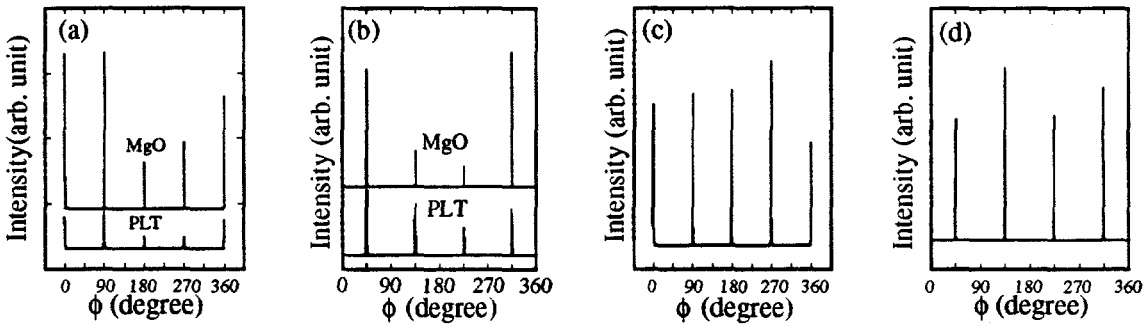

Fig. 2 ϕ-scan x-ray-diffraction patterns from: (a) the PLT (220) and MgO (220) reflections, (b) the PLT (111) and MgO (111) reflections, (c) the PLT (110) and $KTaO_3$ (110) reflections, (d) the PLT (111) and the $KTaO_3$ (111) reflections.

Figures 3 (a) and (b) show the RBS and RBS/channeling spectra for PLT films deposited on $KTaO_3$ (100) and MgO (100) substrates, respectively. The dotted-dashed line represents the simulation of the $Pb_{1-x}La_xTiO_3$ spectra with an x value of 0.28 as determined by using the Rump program[4]; and the solid line shows the experimental data. The dashed line shows the ion-channeling results. The minimum channeling yield χ_{min} along the [100] direction were determined to be 74% and 32% for PLT films on MgO (100) and $KTaO_3$ (100), respectively. From the equilibrium theories of epitaxy[5], misfits smaller than about 7% will be accommodated by uniform elastic strain until a certain film thickness is reached. Above this critical thickness, strain in the film would be partially relieved by misfit dislocations. In spite of the observation of three-dimensional epitaxy for PLT films on MgO substrates, the relatively high χ_{min} value may be due to the presence of misfit dislocations. Because of the smaller lattice mismatch for PLT films on (100) $KTaO_3$ substrates, the observation of a significantly smaller minimum RBS/channeling yield is to be expected.

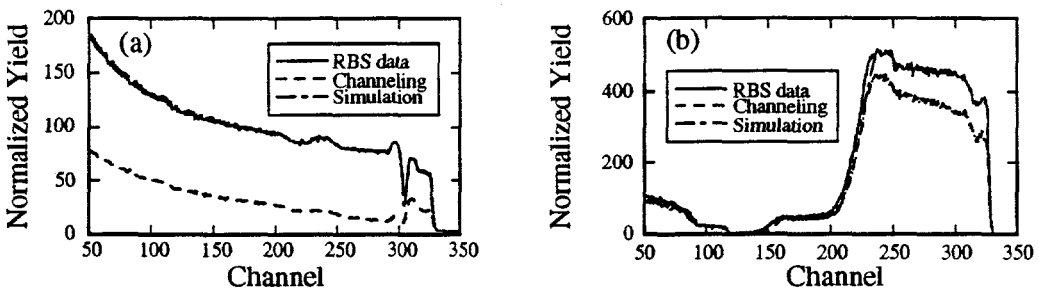

Fig. 3 RBS and ion channeling spectrum from (a) a PLT (100) film on $KTaO_3$ (100), (b) a PLT (100) film on MgO (100) substrates.

In an optical waveguiding system, the important parameters are the refractive index difference between the film and the substrate, and the thickness of the film. The prism coupler can be used for observing so-called *m* lines and from them the mode structure, thickness, and

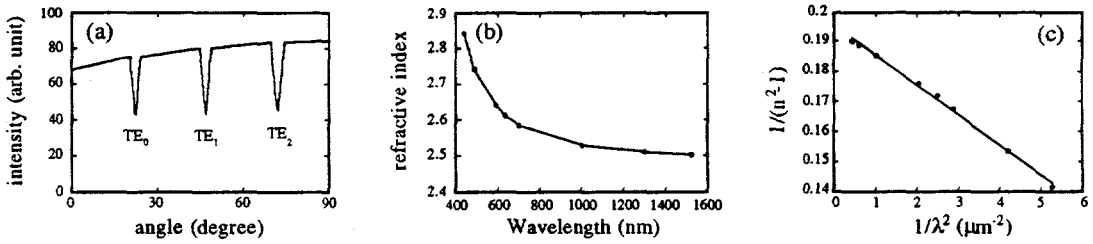

Fig. 4. (a) The coupling curve of the He-Ne (632.8 nm) laser beam into a PLT film using the prism-coupler. (b) The dispersion of the refractive index of the PLT films in the wavelength range of the 435.8 to 1500 nm. (c) a plot of $1/(n^2-1)$ vs. $1/\lambda^2$.

refractive index of the waveguide can be deduced[6]. Fig. 4 (a) shows the coupling curve of the He-Ne (632.8 nm) laser beam into a PLT film using the prism-coupler. The narrow coupling width is indicative of a smooth film with uniform thickness. At the wavelength of 632.8 nm, the refractive index of PLT film was determined to be 2.61, while the measured thickness of 570 nm is in good agreement with that determined by SEM and RBS measurements. The standard deviations of refractive index and thickness obtained by prism-coupling method were 0.0003 and 3 nm, respectively. The refractive index of the PLT film is smaller than that of $PbTiO_3$ by 2.5 %, and greater than that of PLT film with x of 0.14 grown by rf sputtering by about 6.4 % [2]. The different values for the refractive index may originate from the differences in the lanthanum amount and possibly different density of the film due to different synthesis techniques. It has been reported that the refractive index of PLT films grown by rf-planer magnetron sputtering varied with the Pb content in the film and was in the range of 2.4 - 2.7 at 632.8 nm[1].

For the study of the optical dispersion of the PLT film, the refractive index at different wavelength was measured by changing the wavelength of the light and keeping the coupling position fixed. Since the number of guiding modes decreases as the wavelength of the light increases, only one mode was observed when the wavelength was greater than 1000 nm. It was still possible to determine the refractive indices with one observed mode since the thickness of the film could be determined by using smaller wavelengths, at which more than two observed modes exhibited waveguiding. Fig. 4 (b) shows the dispersion of the refractive index of the PLT films in the wavelength range of the 435.8 to 1,523 nm. This dispersion curve is fairly flat above 600 nm and rises rapidly at shorter wavelengths, showing the typical shape of a dispersion curve near an electronic interband transition. Generally, the dispersion of the refractive index for many materials is fitted to the Sellmeier dispersion formula

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - \left(\frac{\lambda_0}{\lambda}\right)^2} \qquad (1)$$

where λ_0 is an average oscillator position and S_0 is an average oscillator strength[7]. As shown in Fig. 4 (c), a plot of $1/(n^2-1)$ vs. $1/\lambda^2$ gives a straight line and fit the Sellmeier dispersion formula with a single electronic oscillator well. By considering the relationship of Sellmeier-oscillator parameters to band structure of oxygen-octahedra ferroelectrics, this behavior originates from the contributions of the oxygen octahedron and an enclosed transition metal ion of titanium, while lead and lanthanum contribute only to higher conduction bands than those given by titanium ions with the oxygen octahedra[7]. Since the slope of the resulting straight line gives $1/S_0$, and the infinite wavelength intercept gives $1/S_0\lambda_0^2$, the values of S_0 and λ_0 could be determined to be 1.012×10^{14} m^{-2} and 0.2251 μm, respectively. The average interband-oscillator energy, E_0 (=

hc/λ_0), is calculated to be 5.52 eV. The refractive index dispersion parameter (E_0/S_0), which depends on the characteristics of the various interband transitions, is found to be 5.5×10^{-14} eV·m^2.

CONCLUSIONS

PLT films exhibiting three-dimensional epitaxy have been successfully grown on MgO (100) and on $KTaO_3$ (100) surfaces. The films exhibited a single-phase perovskite structure with (100) planes parallel to the substrate surface. Due to the smaller lattice mismatch between the film and substrate in the case of PLT growth on (100) $KTaO_3$, low RBS/channeling yields were obtained relative to those determined for PLT films grown on (100) MgO substrates. For the PLT films grown on MgO (100) substrates, the refractive indices in the wavelength range of 435 to 1,523 nm were measured by a prism coupling method. At the wavelength of 632.8 nm, the refractive index of PLT film was determined to be 2.61, while the measured thickness of 570 nm is in good agreement with that determined by SEM and RBS measurements. The dispersion of refractive index fit well to a single-term Sellmeier relation with an average oscillator strength (S_0) of 1.012×10^{14} m^{-2} and an average oscillator position (λ_0) of 0.2251 μm. The refractive index dispersion parameter (E_0/S_0) is found to be 5.5×10^{-14} eV·m^2.

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