Optical properties of Pb(Zr,Ti)O$_3$ thin films on sapphire prepared by metalorganic decomposition process

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Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) thin films were synthesized on a sapphire substrate for application as planar optical waveguide devices using a metalorganic decomposition (MOD) process. Pyrochlore phase, which always forms preferentially when the PZT thin films ($\sim$200 nm) are deposited on a sapphire substrate directly, has been effectively suppressed by using a SrTiO$_3$ (STO) film ($\sim$190 nm) as a buffer layer. The PZT/sapphire thin films have a significantly larger refractive index than the STO/sapphire ones: $n_{PZT}=2.2012$ and $n_{STO}=2.0639$ (at 632.8 nm) by prism coupling measurement and $n'_{PZT}=2.215$ and $n'_{STO}=2.084$ (at 632.8 nm) by optical transmission spectroscopic measurement. The STO layer cannot only serve as buffer layer for enhancing the crystallization kinetics of the subsequently deposited PZT thin films, but can also serve as cladding layer in a ridge-type planar waveguide, which uses PZT thin film as core materials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625428]

Silicon dioxide materials possess marvelous optical properties and have been widely investigated for planar optical waveguide application, which has great potential for miniaturization of planar lightwave circuits employed in optical fiber communication systems.[1–3] These materials are, however, not tunable, which makes the design and fabrication of active components, such as a digital optical switch and an electro-optic modulator, difficult. In contrast, Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) materials, which are ferroelectric, have great potential for fabrication of voltage tunable optical waveguides.[4–6] However, preparation of PZT materials is not straightforward as pure perovskite phase with low optical loss is required for optical waveguide application. Pyrochlore phase always formed preferentially during the heat treatment process, even on sapphire single-crystal substrates.[7]

In this letter, we report the deposition of crack-free transparent PZT films by a metalorganic decomposition (MOD) process on a sapphire substrate utilizing thin-film SrTiO$_3$ (STO) as a buffer layer.[8,9] Optical properties of the films were measured, and the suitability of these materials for optical waveguide application is discussed.

The STO precursors, using Sr(C$_7$H$_{15}$COO)$_2$ and Ti(OC$_2$H$_5$)$_2$(C$_7$H$_{15}$COO)$_2$ as starting materials, were spin-coated on sapphire substrates, followed by heat treatment at 120 °C for 10 min to remove solvent, and were then pre-annealed at 400 °C for 30 min to pyrolyze the organic ligands. The STO films were then post-annealed at 650 °C for 1 h to crystallize the amorphous into perovskite phase. PZT films ($\sim$200 nm) were deposited on the STO ($\sim$190 nm)/sapphire substrates by spin-coating the PZT precursor using Pb(CH$_3$COO)$_2$, Zr(O(CH$_2$)$_2$CH$_3$)$_4$, and Ti(O(CH$_2$)$_2$CH$_3$)$_4$ as starting materials. A similar heat treatment process was employed for the crystallization of the PZT layer. After preparing the PZT/STO/sapphire structure, a wet etching process was utilized for alpha step instrument measurement of the thickness of each layer. Crystallization of STO and PZT films was analyzed by x-ray diffraction (XRD, Rigaku Model Dmmax-B). The top-view and cross-sectional morphology of the films were examined using scanning electron microscopy (SEM, JEOL Model JSM-6330F). Optical properties, such as transmittance and refractive index of the films, were measured by optical transmission spectroscopy (Perkin Elmer Model Lamda 900) and a prism coupling method (Metricon Model 2010).

The XRD pattern shown in Fig. 1(a) indicated that perovskite phase is easily formed in PZT deposited on sapphire substrates. The top-view and cross-sectional SEM micrographs shown in Fig. 2 revealed that the films consist of densely packed grains of equi-axed granular structure for the PZT films post-annealed in air. The deficiency for these films is the coexistence of a large proportion of pyrochlore phase with perovskite phase, regardless of the post-annealing temperature. The probable cause for the presence of pyrochlore is that the lattice mismatch between the substrate and PZT layer hinders the phase transformation process. Post-annealing in O$_2$ atmosphere markedly increases the proportion of perovskite phase, but still cannot completely eliminate the occurrence of pyrochlore phase (not shown). To circumvent such a difficulty, STO materials were utilized as a buffer layer to enhance the formation kinetics for the perovskite phase, since they have perovskite structure similar to that of the PZT material.
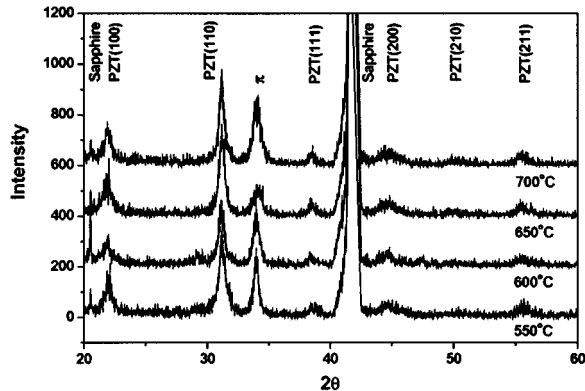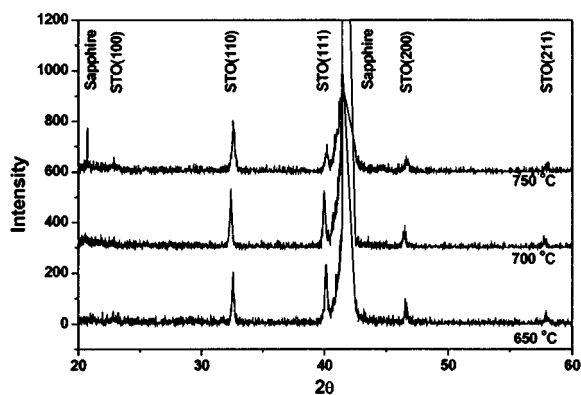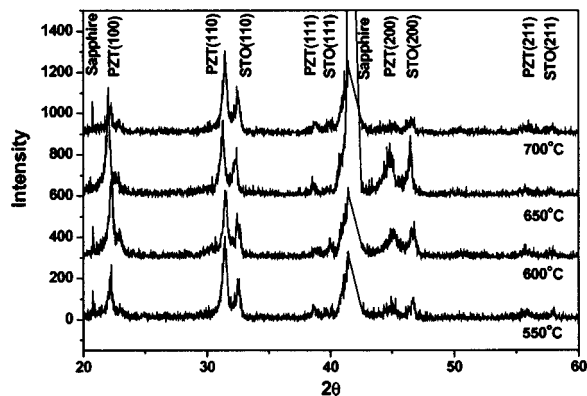

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(a) PZT/ sapphire annealed in Air

(b) STO/ sapphire annealed in Air

(c) PZT/STO/ sapphire annealed in O$_2$

FIG. 1. XRD patterns of (a) PZT/sapphire, (b) STO/sapphire, and (c) PZT/STO/sapphire thin films prepared by the MOD process followed by post-annealing in either air or O$_2$ atmosphere at 550–750 °C for 1 h.

The XRD pattern in Fig. 1(b) shows that STO materials deposited on sapphire substrates readily crystallize, forming perovskite phase, after post-annealing at a temperature higher than 650 °C (1 h). The SEM micrograph in Fig. 3(a) indicated that the STO/sapphire films consisted of uniform grains about 100 nm in size. The surface of the films contains a large proportion of pores. However, using O$_2$ in lieu of air atmosphere in post-annealing, the STO films can effectively eliminate the pores, improving the morphology of the films, which is clearly illustrated in Fig. 3(b).

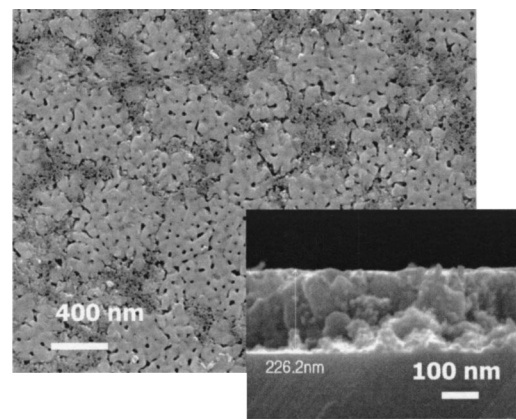Thus obtained STO films markedly improve the crystal-

FIG. 2. SEM top-view and cross-sectional (inset) micrographs of PZT/sapphire thin films prepared by the MOD process followed by post-annealing at 650 °C for 1 h.

lization behavior of the PZT films subsequently deposited. XRD patterns in Fig. 1(c) reveal that perovskite phase was formed on the STO-buffered sapphire substrate without the appearance of pyrochlore phase, by post-annealing the PZT films at 550–700 °C (1 h). The SEM micrograph in Fig. 4 shows that the PZT films inherit the microstructure of the STO buffer, that is, they contain ultrafine grains (about 50 nm in size) that are uniformly distributed. The cross-sectional SEM micrograph in the inset of Fig. 4 clearly exhibits the equi-axed granular structure of the PZT films.

The optical properties of these thin films were measured using a prism coupling technique[10–13] and an optical transmission spectroscopic method,[14,15] which are shown in Figs. 5(a) and 5(b), respectively. It is interesting to observe that, in the prism coupling measurement, the PZT/sapphire thin films possess a significantly larger refractive index than the STO/sapphire ones, that is, $n_{PZT}=2.2012$ and $n_{STO}=2.0639$ (at 632.8 nm). The implication of such a phenomenon is that the STO thin films can serve as cladding materials for the PZT cores in planar waveguides, with a structure illustrated in the inset of Fig. 5(a). Meanwhile, the PZT/sapphire thin films are ferroelectric and the STO/sapphire thin films are paraelectric. The application of an external electric field al-
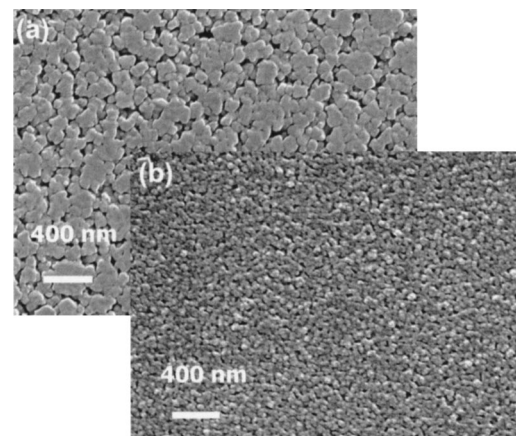

FIG. 3. SEM micrographs of STO/sapphire thin films prepared by the MOD process followed by post-annealing in (a) air and (b) O$_2$ atmosphere at 750 °C for 1 h.
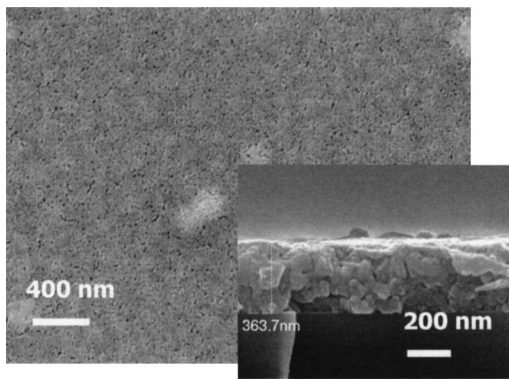
FIG. 4. SEM top-view and cross-sectional (inset) micrographs of PZT/STO/sapphire thin films prepared by the MOD process followed by post-annealing in O_2 atmosphere at 650 °C for 1 h.

ters only the refractive index of the PZT/sapphire films. The PZT/STO/sapphire materials are thus good candidates for tunable planar optical waveguides.

A similar trend was observed when the optical parameters of the films were derived from the optical transmission spectroscopy. The inset in Fig. 5(b) shows that the refractive
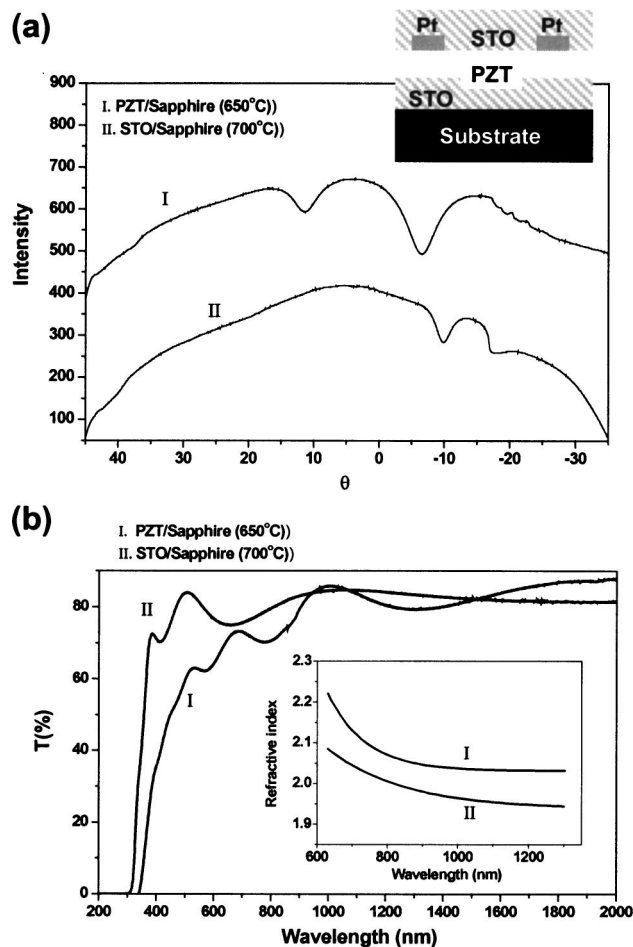

FIG. 5. Optical properties of the PZT/sapphire and STO/sapphire thin films measured by (a) prism coupling technique at 632.8 nm, with the inset showing the structure of proposed ridge-type planar optical waveguide; and (b) optical transmission spectroscopy, with the inset showing the dispersion of refractive index derived from the spectra.

index of the films decreases with the wavelength. More interestingly, the refractive index of the PZT/sapphire thin films is significantly larger than STO/sapphire thin films for all wavelengths: $n'_{PZT}=2.215$ and $n'_{STO}=2.084$ (at 632.8 nm). These results imply that PZT and STO thin films are a good combination for a tunable planar waveguide structure, that is, they can be a core and cladding material, respectively, for the waveguides with a tunable propagation constant.

In conclusion, the characteristics of $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films on sapphire substrates were optimized by systematically adjusting the parameters in metalorganic decomposition process. Using $SrTiO_3$ thin films ($\sim$190 nm) as a buffer layer can effectively suppress the presence of pyrochlore phase, enhancing the formation of perovskite phase. Post-annealing at a temperature higher than 550 °C is sufficient to grow PZT perovskite thin films ($\sim$200 nm) on STO-buffered sapphire substrate. Utilization of O_2 atmosphere in lieu of air in post-treatment process further improves the granular structure of the films. Both prism coupling and optical transmission spectroscopic measurements indicate that the refractive index of PZT films is significantly larger than that of STO films. Moreover, the refractive index of PZT layer is voltage tunable, whereas that of STO layer is not. These results indicate that STO can serve not only as buffer layer, but also as cladding material for an optical waveguide structure using PZT as core materials. The PZT/STO combination can be an excellent material system for tunable optical waveguide devices.

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