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Ferroelectric (Ba,Sr)TiO_3 and Pb(Zr,Ti)O_3 thin films prepared by pulsed laser deposition

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Abstract

Barium strontium titanate, (Ba, Sr)TiO_3 (BST), and lead zirconium titanate, Pb(Zr, Ti)O_3 (PZT) thin films were synthesized on indium-tin-oxide coated glass substrates using pulsed laser deposition process. Perovskite structure of these materials can be obtained by controlling the substrate temperature at 500–620°C. All the films possess good ferroelectric properties at low frequency regime. When both films were deposited at 500°C and measured at 10 GHz, the dielectric constant is $\varepsilon_\tau \cong 1000$ for (Ba, Sr)TiO_3 thin films and is $\varepsilon_\tau \cong 550$ for Pb(Zr, Ti)O_3 thin films. Optical transmission spectroscopies show that the Pb(Zr, Ti)O_3 thin films exhibit larger refractive index ($(n)_{PZT} = 2.1$–2.8) than the (Ba, Sr)TiO_3 thin films ($(n)_{BST} = 1.95$–2.15), which is ascribed to the heavier mass of the constituents in the Pb(Zr, Ti)O_3 thin films. The (Ba, Sr)TiO_3 thin films also possess much lower absorption coefficient (κ) than the Pb(Zr, Ti)O_3 thin films, which indicates that the (Ba, Sr)TiO_3 thin films contain less intrinsic defects than the Pb(Zr, Ti)O_3 materials.

Keywords: Ceramics; Dielectric properties; Thin films

1. Introduction

Ferroelectric thin films possess overwhelming advantage over bulk materials in several aspects, including (1) lower operation voltage, (2) faster response and nonlinear relationship in dielectric properties.[1–2] Much attention has been paid to the application of ferroelectric thin films, such as (Ba,Sr)TiO_3 (BST), Pb(Zr, Ti)O_3 (PZT), $PbTiO_3$ (PT), and $(Pb_{1-x}La_x)TiO_3$ (PLT) to the fabrication of integrated capacitors for the dynamic random access memories (DRAMs) due to their high dielectric constant, and for nonvolatile memories (NFRAM) because of their large and reversible remanent polarization characteristics.[3–5] Among the ferroelectric ceramics, the BST and PZT materials, which possess a wide range of ferroelectric properties depending on the cationic ratio, have been extensively applied in electro-optic devices. The same desirable dielectric properties are expected in thin film form. Ferroelectric thin films have been successfully synthesized by RF sputtering, activated reactive evaporation, metalorganic chemical vapor deposition, sol–gel and pulsed laser deposition techniques.[6–8] Among these processes, the pulsed laser deposition method is the most superior, for it possesses the following advantages such as: (1) lower synthesized temperature, (2) easiness in controlling the stoichiometry of the films, (3) possibility in depositing oxide films of high melting point and the materials of metastable phase. The PLD technique is thus adopted in this research for synthesizing BST and PZT ferroelectric thin films. Both the deposition parameters and ferroelectric properties of the BST and PZT films are discussed.

2. Experimental procedure

The conventional mixed oxide processes including mixing, calcining, pulverizing, pelletizing and sintering, were utilized, for synthesizing $(Ba_{0.6}Sr_{0.4})TiO_3$, BST, and $Pb_{1.07}(Zr_{0.52}Ti_{0.48})O_3$, PZT, bulk ceramic target. BST ceramics were sintered at 1500°C for 4 h, and PZT ceramics were sintered at 1350°C for 4 h. The $(Ba_{0.6}Sr_{0.4})TiO_3$ (BST) and $Pb_{1.07}(Zr_{0.52}Ti_{0.48})O_3$ (PZT) ferroelectric

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thin films were prepared by the pulsed laser deposition (PLD) technique using a XeCL excimer laser (λ = 308 nm, Lambda Physik) with the energy density of 3 J/m^2. The target to substrate distance was fixed at 3.5 cm and the oxygen pressure of the chamber was maintained at 0.1 mbar. The films were deposited at 500–600°C, followed by 10 min of annealing at the deposition temperature with 1 atm oxygen pressure. The crystal structure of the films was examined using x-ray diffractometer (Rigaku, P/max-IIB). Electric polarization–electric field (*P–E*) ferroelectric hysteresis loops, were measured using Sawyer-Tower circuit, whereas the capacitance–voltage (*C–V*) properties were characterized using HP 4194A impedance analyzer. The optical transmittance of the films was measured in the range from 300 to 800 nm using spectrometer (Hitachi U-3410).

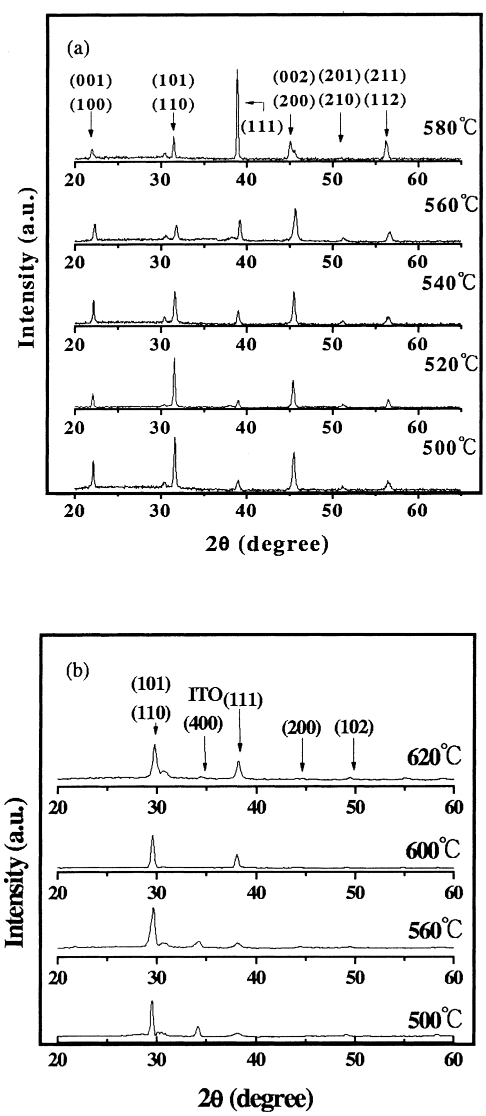

Fig. 1. X-ray diffraction patterns of (a) $(Ba_{0.6}Sr_{0.4})TiO_3$, and (b) $Pb_{1.07}(Zr_{0.52}Ti_{0.48})O_3$ thin films at different substrate temperatures.

3. Results and discussion

X-ray diffraction patterns in Fig. 1a and b for $(Ba_{0.6}Sr_{0.4})TiO_3$, BST, and $Pb_{1.07}(Zr_{0.52}Ti_{0.48})O_3$, PZT, reveal that perovskite phases form easily on $In_{1-x}Sn_xO_2$ (ITO) coated glass substrates for both BST and PZT films. Crystallized films can be obtained for a wide range of deposition temperatures. The BST films crystallize at much lower substrate temperature than the PZT films. Both films exhibit good ferroelectric properties (not shown).

The frequency dependence of dielectric constant measured using impedance analyzer is shown in Fig. 2a and b for BST and PZT films, respectively. The dielectric constant of the films, which is around $\varepsilon_\tau \cong 1000$ (at 10 kHz) for BST and $\varepsilon_\tau \cong 550$ for PZT films deposited at 500°C, decreases as deposition temperature increases. Apparently, this phenomenon can be ascribed to the appreciable interaction between the BST (or PZT) films and the ITO coating (or glass substrate). The dielectric constant for PZT thin films is markedly smaller than the ε_τ value for BST thin films, although the former possess much better ferroelectric properties than the latter. The dielectric constant of the BST (PZT) films decreases with operating frequency (Fig. 2).

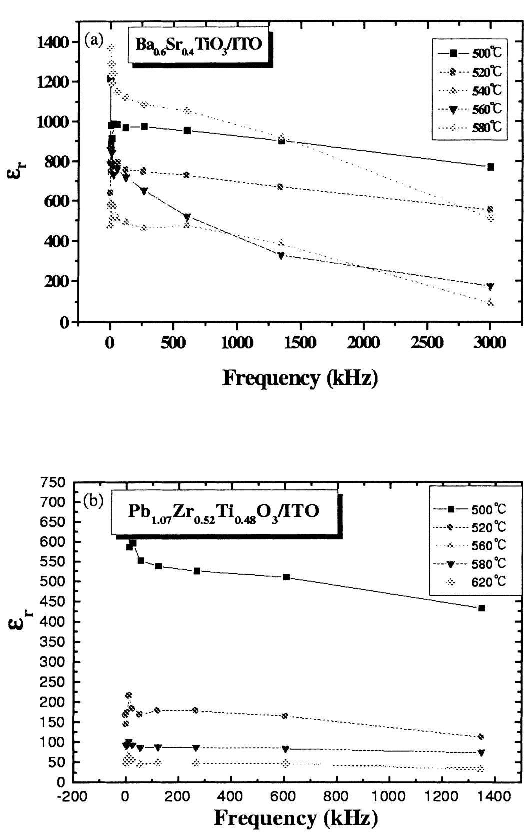

Fig. 2. The frequency dependence of dielectric constants of (a) $(Ba_{0.6}Sr_{0.4})TiO_3$, and (b) $Pb_{1.07}(Zr_{0.52}Ti_{0.48})O_3$ thin films at different substrate temperatures.

Both films own leakage current density smaller than $J_L \leqslant 10^{-5}$ A/cm^2 for an applied field smaller than 50 kV/cm (not shown). The advantage of the ITO electrode layer is due to its transparent characteristics, which make the measurement on optical transmission spectra (OTS) of the BST and PZT films possible. The index of refraction (n), of the films can be estimated from those OTS spectra using the formula,

$$n = \left[N + \left(N^2 - n_0^2 n_1^2\right)^{1/2}\right]^{1/2},$$
$$N = \frac{\left(n_0^2 + n_1^2\right)}{2} + \frac{2n_0 n_1 (T_{\max} - T_{\min})}{T_{\max} T_{\min}}, \quad (1)$$

where n_0 and n_1 are the refractive indices of air and ITO layer, respectively, n is the refractive index of the BST (or PZT) films. $T_{\max}(\lambda)$ and $T_{\min}(\lambda)$ are the maximum and minimum transmittance of the optical transmission spectra. Moreover, the absorption coefficient (κ) of the films can be estimated using the formula:

$$\kappa = -\frac{\ln\alpha}{d},$$
$$\alpha = C_1\left[1 - (T_{\max}/T_{\min})^{1/2}\right]/C_2\left[1 + (T_{\max}/T_{\min})^{1/2}\right], \quad (2)$$

where $d = \lambda_1\lambda_2/2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]$, $C_1 = (n + n_0)(n + n_1)$ and $C_2 = (n - n_0)(n_1 - n)$.

The results of calculation are shown in Fig. 3. The refractive index (n) of PZT films is around $n = 2.8$ for low-temperature deposited films, decreases appreciably for the films deposited at a temperature higher than 580°C, in accompany with the marked increase in absorption coefficient (solid squares, Fig. 3a and b). This is in accord with the decrease in low frequency dielectric constant of the films and can be ascribed to the occurrence of films to substrate (i.e. PZT and ITO) interaction.

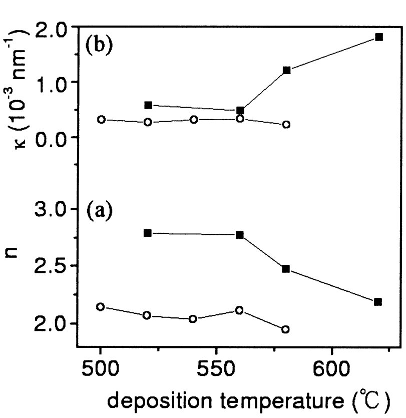

Fig. 3. Varitations of (a) refractive index n and (b) absorption coefficient κ.

The index of refraction (n) for the BST films ($n = 1.95-2.15$, open circles, Fig. 3a and b) is insensitive to the substrate temperature and is pronouncedly smaller than the n values of the PZT films. This is in accord with the phenomenon that the materials containing heavy ions such as Pb species usually possess larger index of refraction. The large difference in index of refraction of the two materials provide a possible optical wave guide structure, in which PZT layer can serve as core materials and BST layer can serve as cladding materials.

4. Conclusion

Ferroelectric and optical properties of BST and PZT thin films were simultaneously measured by using ITO as underlying electrode materials. Perovskite phase was easily synthesized on ITO coated glass substrates by using pulsed laser deposition technique with substrate temperature controlled in the range $T_s = 500$–620°C. Low frequency dielectric constants (ε_τ) of BST thin films measured at room temperature are markedly larger than the ε_τ values of PZT thin films. By constrast, the index of refraction (n) of BST materials is pronouncedly smaller than the n value of the PZT materials, which is owing to the fact that the Pb species are heavier than the cations in BST films.

Acknowledgements

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