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Dielectric and optical properties of electroceramic PBZNZT thin films prepared by pulsed laser deposition process

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Abstract

The $0.6[0.94Pb(Zn_{1/3}Nb_{2/3})O_3 + 0.06BaTiO_3] + 0.4[0.48(PbZrO_3) + 0.52(PbTiO_3)]$, PBZNZT, thin films were synthesized by pulsed laser deposition (PLD) process. The PBZNZT films possess higher insulating characteristics than the PZT (or PLZT) series materials due to the suppressed formation of defects, therefore, thin-film forms of these materials are expected to exhibit superior ferroelectric properties as compared with the PZT (or PLZT)-series thin films. Moreover, the $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin film of perovskite structure was used as buffer layer to reduce the substrate temperature necessary for growing the perovskite phase PBZNZT thin films. The PBZNZT thin films of good ferroelectric and dielectric properties (remanent polarization $P_r = 26.0\ \mu C/cm^2$, coercive field $E_c = 399$ kV/cm, dielectric constant $K = 737$) were achieved by PLD at 400 °C. Such a low substrate temperature technique makes this process compatible with silicon device process. Moreover, thus obtained PBZNZT thin films also possess good optical properties (about 75% transmittance at 800 nm). These results imply that PBZNZT thin films have potential in photonic device applications.

Keywords: Films; Dielectric properties; Ferroelectric properties; Optical properties; Perovskites; Pulsed laser deposition

1. Introduction

Lead-based ferroelectric thin-film materials, $Pb(Zr_{1-x}Ti_x)O_3$, PZT, possessing high remanent polarization and large piezoelectric coefficient, have been found to have tremendous opportunities in device applications, such as ferroelectric non-volatile random access memories.[1,2] These materials also possess marvelous piezoelectric properties and are thus suitable for synthesizing micro-sensors and micro-actuators, the most critical components in microelectromechanical systems (MEMS).[3] The thin-film form of these materials favors their direct integration in semiconductor technology for these applications. It is desired to optimize the capacity for displacement and force through improving the performance of the materials by adjusting the device geometry.[4] Therefore, the techniques used for fabricating high-quality films have been of special interest.[5] Although the $Pb(Zr_{1-x}Ti_x)O_3$ thin films can be easily deposited on Si-based substrates by the conventional thin-film deposition technique, such as sputtering, sol–gel or metal–organic decomposition (MOD) and the laser-ablation process,[6–8] the processing temperature is too high to be compatible with the Si-based device process. To solve such kind of problems, we utilized a functional layer material, $Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, between the substrate and the PZT-series films to act as a seeding layer during the growth of the PZT films.[9]

Moreover, the drawback of PZT material is the high susceptibility in forming the cationic vacancies, which degrades the ferroelectric properties, especially the fatigue properties, of the thin films. The dielectric property of the ternary compound, such as PMN-PZ-PT, is known to be much superior to the binary compound (PZ-PT). However, the synthesis of ternary compound perovskite is extremely difficult due to the complicated composition. In this study, we attempt to deposit a ternary compound $x(0.94Pb(Zn_{1/3}Nb_{2/3})O_3 + 0.06BaTiO_3)(1-x)(0.48\ PbZrO_3 + 0.52\ PbTiO_3)$, $x = 0.6$, thin films, designated as PBZNZT, by using pulsed laser deposition (PLD) process. In addition, we utilize $Ba(Mg_{1/3}Ta_{2/3})O_3$ material as buffer layer to facilitate the

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formation of pervoskite phase. The effects of processing parameters on the characteristics of thus obtained thin films have been discussed.

2. Experimental details

$x(0.94Pb(Zn_{1/3}Nb_{2/3})O_3 + 0.06BaTiO_3) + (1-x)(0.48(PbZrO_3) + 0.52(PbTiO_3))$, $x = 0.6$, abbreviated as PBZNZT thin films were prepared by pulsed laser deposition (PLD) process, using the bulk materials of the same composition as target materials.[10] The substrate materials are either Pt-coated silicon substrates (Pt/300 nm)/Ti(100 nm/SiO_2/Si), MgO or quartz. The 248 nm laser beams (KrF, Thin Film Star v 2.0) were focused to 1 mm × 1 mm on the target with the laser fluence of 1.50 J/cm^2. The substrate was placed at 4.5 cm away from the target and was heated at 400 °C. The ambient atmosphere (air) was controlled at 0.15–0.55 mbar. $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films were used as buffer layers, which were also deposited by PLD process with similar conditions.

The crystalline structure of the PBZNZT thin films was examined using X-ray diffractometer (Panalytical, X'Pert PRO) and morphology of the films was examined using scanning electron microscope (VEGA YS 5136LS). The laser-ejected plume was monitored by optical emission spectroscope (Ocean Optics, HR4000). The Au-dot about 100 μm in size was deposited on top of PBZNZT/Pt(Si) thin films by using a shadow mask to serve as top electrode. The electric polarization–electric field (*P–E*) hysteresis properties of the films was measured by a *P–E* tracer (Aixact Technology, TF Analyzer 2000), whereas dielectric properties of the films were measured by H.P. 4294A Impedance Analyzer. The optical properties of PBZNZT/MgO (or PBZNZT/quartz) thin films were measured by an optical transmittance spectroscope (Jasco V-570).

3. Results and discussion

Contrary to the phenomenon that PZT or PLZT series materials readily form perovskite phase when deposited on Pt-coated Si-substrates, the crystallization of PBZNZT material, which is a complicated multi-component perovskite material, is very difficult. Fig. 1(a) shows that the pyrochlore phase (π phase) predominates when directly deposit the PBZNZT materials on Pt-coated Si-substrates. Fortunately, deposition of a thin layer of BMT film as buffer layer markedly enhances the crystallization of PBZNZT materials such that pyrochlore-free thin films can be formed (Fig. 1(b)). Fig. 1(b) reveals that it requires only 400 °C substrate temperature to form perovskite. The presence of BMT buffer layer markedly lowers the substrate temperature needed to form perovskite phase. The obtained films contain uniform grains of the typical size around 150 nm.

It is interesting to notice that although the preparation of pure BMT materials is very difficult, the crystallization of BMT thin films is relatively easy. It usually needs high sintering temperature (~1600 °C) and long soaking time (~12 h) to sinter the materials to a high enough density, but perovskite BMT films can be obtained at 375–475 °C substrate temperature. The crystal structure and lattice parameter of the BMT materials are very

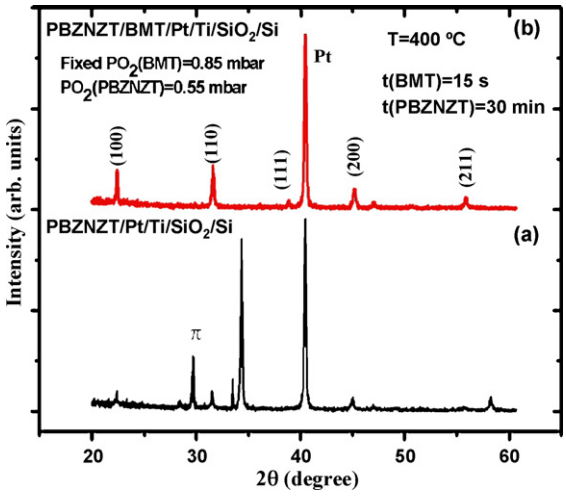

Fig. 1. X-ray diffraction patterns of PBZNZT thin films deposited on Pt-coated silicon substrates (a) without and (b) with the BMT buffer layer.

close to those of the PBZNZT materials such that the crystallization of PBZNZT materials is greatly enhanced at the presence of BMT buffer layer (cf. Fig. 1(a and b)).

The other factors can alter the ferroelectricity of PBZNZT thin films as well as the perfectness in crystallinity of the films. Fig. 2(a) and (b) illustrate, respectively, the variation of the XRD crystallinity and *P–E* characteristics of the PBZNZT films deposited under variable chamber pressures (PO_2 = 0.45–0.55 mbar) in PLD process. Although all the PBZNZT films show crystalline perovskite structure with very good crystallinity, the remanent polarization (P_r) of the films decreases monotonously and the coercive filed (E_c) is not quite sensitive with the oxygen pressure (PO_2) used for growing the films as shown in Fig. 2(c). The possible mechanism causing the decrease of P_r-value with the increase in PO_2-value is the presence of non-crystalline phase, which, in turn, is resulted from low kinetic energy of the species ejected by laser in high-PO_2 environment. To confirm such a phenomenon, the optical emission spectra (OES) of the laser-induced plumes were examined. Fig. 3(a) illustrates the drastic increase in OES peak intensity with decrease of the oxygen partial pressure. To facilitate the comparison, the plasma temperature (T_p) of the Pb-species was calculated from the relative intensity of (Pb I)$_1$ and (Pb I)$_2$ peaks using the Boltzmann plot,[11] viz.

$$\frac{I_1}{I_2} = \frac{\lambda_1}{\lambda_2}\left(\frac{g_1 A_1}{g_2 A_2}\right)\exp\frac{-(E_1 - E_2)}{kT_p} \quad (1)$$

where I_n, λ_n and E_n are the intensity, wavelength and photon energy ($E = hc/\lambda$) of corresponding OES peaks; g_n and A_n are the statistical weight and Einstein transition probability; k is the Boltzmann constant, T_p is the plasma temperature of the species under investigation. Using Eq. (1), the plasma temperature of Pb-species can be calculated from the formula[12]:

$$T_{plasma} = T_p = \frac{\alpha}{\beta} \quad (2)$$

where $\alpha = -hc/k((1/\lambda_1) - (1/\lambda_2))$ and $\beta = \ln((I_1/I_2) \times (\lambda_2/\lambda_1) \times (g_2/g_1) \times (A_2/A_1))$.

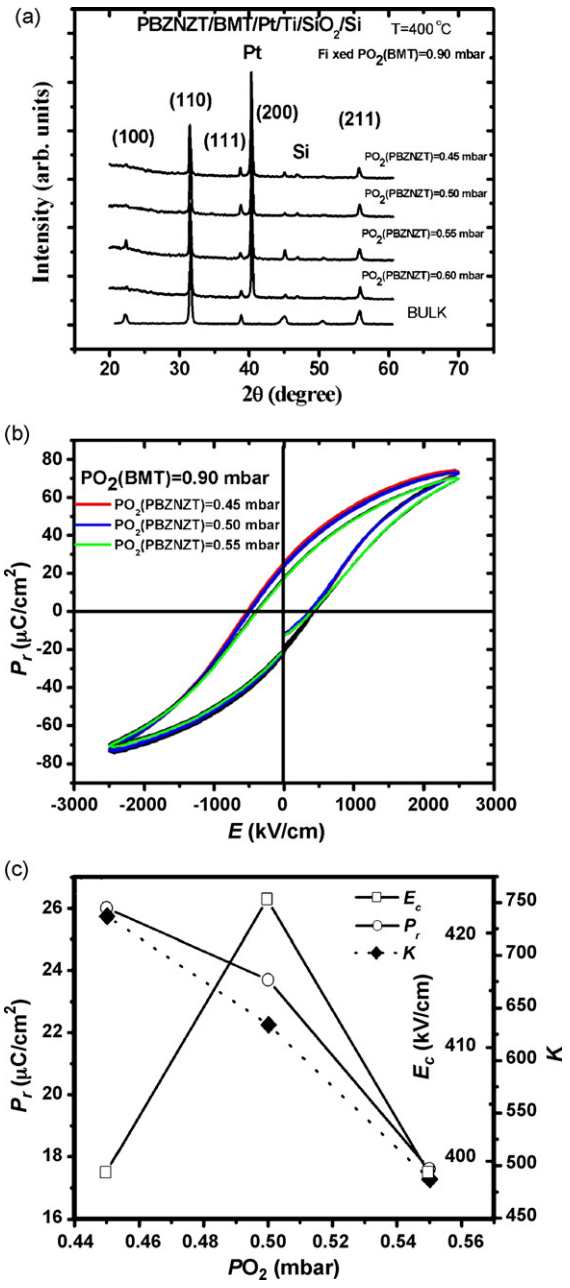

Fig. 2. (a) X-ray diffraction patterns and (b) electric polarization–electric field (P–E) hysteresis curves of PBZNZT/Pt(Si) thin films deposited with the PO_2 level controlled in 0.45–0.60 mbar; (c) variation of remanent polarization P_r, coercive field E_c and dielectric constant K of thin films with PO_2 level.

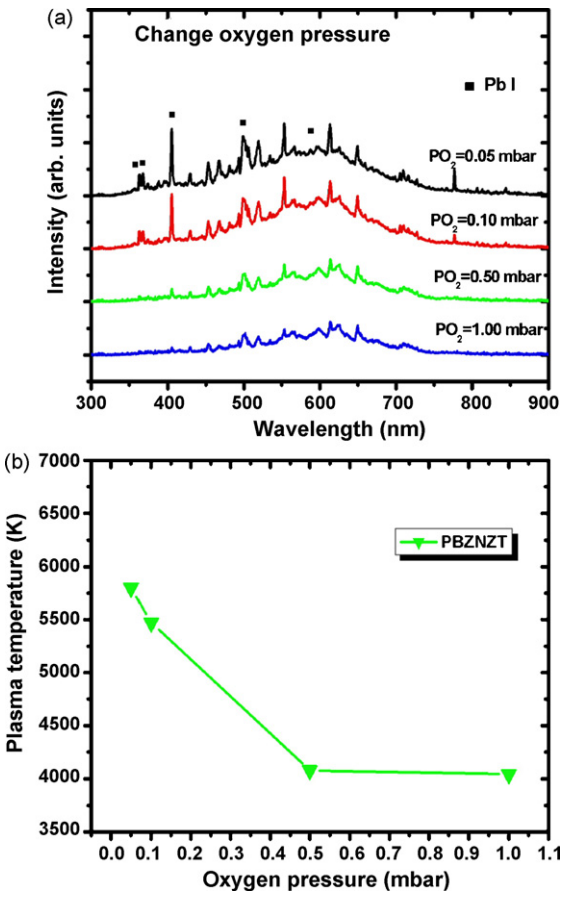

Fig. 3. (a) Optical emission spectra (OES) emitted from the laser-ejected species under different PO_2 levels (PO_2 = 0.05–1.00 mbar) and (b) the variation of plasma temperature (T_p) deduced from OES with the PO_2 level.

Table 1
The ferroelectric and dielectric properties of PBZNZT/Pt(Si) thin films deposited under 0.45–0.55 mbar oxygen pressure at 400 °C (BMT buffer layer was deposited in PO_2 = 0.85 mbar at 400 °C).[a]

Oxygen pressure (mbar)	P_r (μC/cm^2)	E_c (kV/cm)	K
0.45	26.0	399	737
0.50	23.7	423	634
0.55	17.6	399	487

[a] P_r is remanent polarization; E_c is coercive filed; K is dielectric constant.

The plasma temperature is calculated as T_p = 5800 K when PO_2 = 0.05 mbar, and decreases rapidly as PO_2 level increases, reaching T_p = 4000 K for PO_2 = 1.0 mbar case (Fig. 3(b)). The decrease in plasma temperature with oxygen partial pressure is apparently owing to the more frequent collisions of the laser-ejected species with the environmental gas molecules. Lower plasma temperature for the laser-ejected species indicates that the species are less active. Similarly, larger PO_2 level in the deposition chamber will also lower the activity of the other laser-ejected species (such as Zn, Nb, Zr, and Ti species), which is expected to hinder the crystallization process, and in the worst case, will result in incomplete crystallization for the PBZNZT materials. Therefore, the drastic decrease in remanent polarization (P_r) for the films deposited in PO_2 = 0.55 mbar (Fig. 2(b)) can be ascribed to the presence of non-crystalline phase. It should be noted that the existence of non-crystalline phase cannot be detected by X-ray diffractometer. However, the high-PO_2 deposited PBZNZT films contain some non-crystalline phase is also implied by the relatively smaller dielectric constant (K) of the films (K = 487–737, Table 1 and dotted curve in Fig. 2(c)), where the dielectric constant was measured at 40 MHz using the impedance analyzer.

To evaluate the dielectric properties in optical frequency regime of PBZNZT thin films, the films should be deposited on transparent substrates such as MgO and quartz, as the Pt(Si)

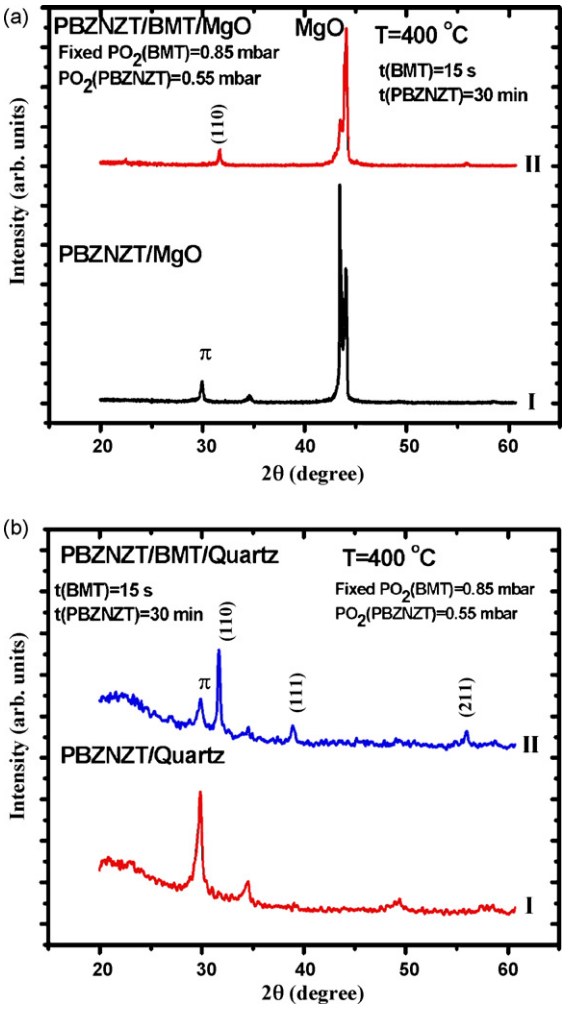

Fig. 4. X-ray diffraction patterns of PBZNZT thin films deposited on (a) MgO and (b) quartz substrates, without (I) or with (II) the utilization of BMT buffer layers.

substrate is not transparent to the visible light. The above-mentioned results indicate that utilization of BMT buffer layer can markedly enhance the kinetics for the PBZNZT films with complicated composition.[13,14] The same beneficial effect is also observed when the PBZNZT films were deposited on MgO or quartz substrates. Fig. 4(a) and (b) show the XRD patterns of the PBZNZT films deposited on MgO and quartz substrates, respectively. The MgO substrates, which readily form perovskite phase for PZT(PLZT)-series thin films, result in large proportion of pyrochlore phase, when the PBZNZT films were deposited without the utilization of BMT buffer layer (curve I, Fig. 4(a)). The presence of BMT buffer layer markedly enhances the crystallization kinetics of the perovskite phase such that pyrochlore phase free PBZNZT thin films can be obtained by growing the films at a substrate temperature as low as 400 °C (curve II, Fig. 4(a)). The beneficial effect of BMT buffer layer on suppressing the formation of undesired pyrochlore phase is even more pronounced for the case where the quartz was used as substrate material. Fig. 4(b) illustrates that only pyrochlore phase was obtained when the PBZNZT films were grown directly on quartz substrate (curve I, Fig. 4(b)). The use of BMT thin film as buffer

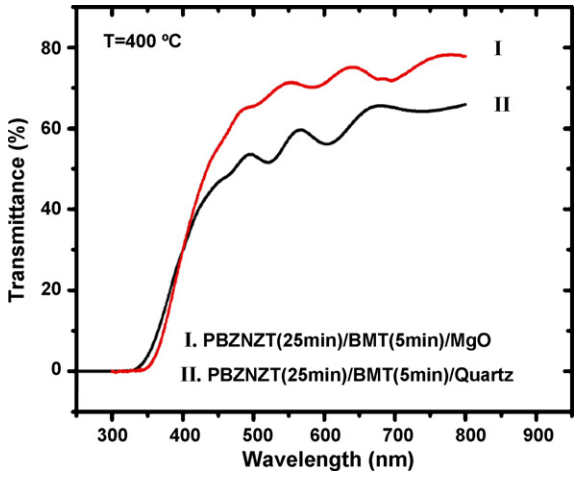

Fig. 5. (a) Optical transmittance spectra of thin films: (I) PBZNZT/BMT/MgO and (II) PBZNZT/BMT/Quartz.

layer results in large proportion of perovskite phase, although the pyrochlore phase cannot be completely eliminated (curve II, Fig. 4(b)).

The optical emission spectra (OES) of the PBZNZT thin films grown on MgO and quartz substrates with the BMT buffer layer are shown in Fig. 5. The PBZNZT/BMT/MgO thin films possess larger transmittance at optical frequency regime (about 75% transmittance at 800 nm) as compared with those for PBZNZT/BMT/quartz thin films (about 60% transmittance at 800 nm). It should be noted that, the analysis of the optical properties for the multilayer structure is quite complicated and not included in here. However, the data suggests that the refractive index and dielectric property of PBZNZT film grown on MgO are possibly higher as compared to that of the film grown on quartz substrate. The low transmittance properties (refractive index and dielectric property) of PBZNZT film deposited on quartz as composed with those for the film grown on MgO substrate can apparently be ascribed to the presence of larger proportion of pyrochlore phase.

4. Conclusion

PBZNZT thin films were deposited on Pt-coated silicon (Pt(Si)), MgO or quartz substrates, using pulsed laser deposition process. Utilization of BMT thin films as buffer layers markedly enhances the formation kinetics of perovskite structure of PBZNZT thin films, regardless of the substrate materials. The films grown on (Pt(Si)) substrates exhibit good ferroelectric properties $P_r = 26.0\,\mu C/cm^2$ and $E_c = 399\,kV/cm$ together with corresponding dielectric constant $K = 737$. The films grown on MgO substrates possess larger transmittance as compared to that of the films grown on quartz substrates. The presence of non-crystalline phase in PBZNZT/BMT/Pt(Si) thin films or pyrochlore phase in PBZNZT/quartz thin films is observed to degrade the ferroelectric or optical properties of the films. Most importantly, the utilization of BMT buffer layer markedly lower the substrate temperature necessary for synthesizing the PBZNZT

perovskite thin films, which is compatible to the silicon device process.

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