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Magnetoelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$–$La_{0.65}Sr_{0.35}MnO_3$ composite thin films derived by the pulse laser deposition method

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ABSTRACT

The magnetoelectric (ME) $Pb(Zr_{0.52}Ti_{0.48})O_3$–$La_{0.65}Sr_{0.35}MnO_3$ (PZT–LSMO) composite thin films were grown on single crystalline $SrTiO_3$ substrates by the pulse laser deposition (PLD) method with different growth sequences of PZT and LSMO yielding the following layered structures: PZT/LSMO/substrate (PL) and LSMO/PZT/substrate (LP). The experimental results show that these composite films exhibit both good ferroelectric and magnetic properties, as well as magnetoelectric effects at room temperature. The layer sequences have an obvious influence on the magnetoelectric coupling behavior of these double-layered thin films. The maximum values of ME voltage coefficient for the PL thin film is larger than the LP structure, which may be caused by the substrate clamping and interface bonding of PZT and LSMO.

1. Introduction

Multiferroic materials simultaneously exhibiting multiple ferroic orders, have attracted significant attention due to the fundamental science and the tantalizing technological perspective [1,2]. Importantly, the coupling between the magnetic and ferroelectric order parameters can lead to magnetoelectric (ME) effects, in which the magnetization can be tuned by an applied electric field and vice versa, thus yielding entirely new device concepts, such as electric field-controlled magnetic data storage [3,4]. However, the ME effect of the single-phase multiferroic materials is often very weak [5]. Some researches indicate that developing composite multiferroics by artificially making ferroelectrics and ferromagnets into nanoscale heterostructures may be an effective technique for obtaining the large ME effect. Due to the high remnant polarization, low coercive field, and high Curie temperature, perovskite $PbZr_xTi_{1-x}O_3$ is a good ferroelectric candidate [6]. Perovskite $La_xSr_{1-x}MnO_3$ is an interesting candidate for ferromagnetic layer element. It has high Curie temperature and a close lattice constant and similar crystalline structure matching with perovskite ferroelectric $PbZr_xTi_{1-x}O_3$. Moreover, $La_xSr_{1-x}MnO_3$ is a half-metallic material and exhibits colossal magnetoresistance [7]. Based on the above reasons, PZT and LSMO were selected as the ferroelectric and ferromagnetic component respectively to fabricate multiferroic double-layered films. In constructing the layered ME composite film structures, there are many parameters to be optimized, in which the growth sequence of these two phases on the substrate should result in an influence on the properties of the resultant composite films [8]. In the present work, we have succeeded in synthesizing nano-particulate $Pb(Zr_{0.52}Ti_{0.48})O_3$–$La_{0.65}Sr_{0.35}MnO_3$ (PZT–LSMO) composite films with both ferroelectric and ferromagnetic properties, as well as ME effect at room temperature.

2. Experimental

The PZT–LSMO composite thin films were grown on single crystalline $SrTiO_3$ (STO) substrates by the pulse laser deposition (PLD) method with different growth sequences of PL and LP. Firstly, ferromagnetic LSMO (about 100 nm in thickness) was deposited on a STO substrate at a substrate temperature of 800 °C and an oxygen partial pressure of 0.5 mbar. Subsequently, ferroelectric PZT (about 150 nm in thickness) film was deposited on LSMO film at a substrate temperature of 720 °C and vice versa. Bottom electrode ($SrRuO_3$) was deposited on the STO substrate for electrical measurements. And Pt top electrodes were e-beam evaporated on the composite films. The crystal structure was characterized by x-ray diffraction (XRD). The microstructures of the films were examined by scanning electron microscopy (SEM). The ferroelectric and leakage current measurements were performed using a Radiant Technologies Precision Workstation ferroelectric test system. Magnetic properties and ME effects of the films were measured using a vibrating sample magnetometer and a ME measuring system at room temperature, respectively.

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3. Results and discussion

Fig. 1(a) shows the typical XRD patterns of PL and LP composite films. All the peaks are indexed according to the standard powder diffraction data of PZT and LSMO. The results show that only the (00l) peaks are observed for both PZT and LSMO layers which are single crystalline. Fig. 1(b) displays the SEM surface morphologies of the PL and LP composite thin films. One can see that the surface of the PL film with the PZT as the top layer is more compact and smoother, compared with that of LP film, which implies that PZT layer is more compact than LSMO layer. So the electrical properties will be sensitively influenced by the different layered structures, which will be discussed later.

The typical leakage current characteristics of PL and LP structured composite thin films are shown in Fig. 2(a). The PL film has a smaller leakage current density as compared to the LP film, since the surface of the PL film is more compact than that of the LP film, which indicates that the insulating property of PL is better than that of LP. The polarization versus electric field (*P*–*E*) hysteresis loops of PL and LP structured composite thin films are given in Fig. 2(b). As shown in Fig. 2(b), the well-defined ferroelectric loops are observed in the PL and LP films, while the imprint behavior is perhaps caused by oxygen loss via dislocations generated by the misfit strain relaxation at the growth temperature [9]. The remnant polarization (P_r) values of the deposited PL and LP composite thin films are 25.6 μC/cm^2 and 21.2 μC/cm^2, corresponding to the coercive fields of 121 and 110 kV/cm, respectively. Obviously, compared with the LP film, the PL composite film exhibits a higher P_r, which is maybe owing to the better insulating property of PL film.

The magnetic hysteresis loops of PL and LP composite thin films are presented in Fig. 3. As shown in Fig. 3, slim hysteresis loops with saturation magnetization $M_s \sim 420$ emu/cm^3 of the PL film and ~ 400 emu/cm^3 of the LP film are observed, which hints the presence of an ordered magnetic structure. The PL film shows larger saturation magnetization M_s than the LP film on account of the strong (00l) orientation of LSMO in PL film.

The coexistence of the ferroelectric PZT and ferromagnetic LSMO phases in the present composite thin films generates a distinct ME effect, which is characterized by the ME voltage coefficient $\alpha_E = dE/dH$. Fig. 4 gives the measured values of the ME voltage coefficient α_E as a function of the bias field H_{bias} at the fixed AC magnetic frequency $f = 1$ kHz for PL and LP composite films, measured at room temperature by applying an AC magnetic field *H* (12 Oe) [10]. The ME sensitivity of the composite films illustrates the strong dependence on the H_{bias}. As H_{bias} increases, α_E increases in magnitude and peaks at 110 Oe. With further increase in H_{bias}, α_E shows a rapid decline and then a gradual decrease to near zero. In multiferroic composites, since the ME coupling arose from the AC field initiated dynamic Joule magnetostriction, caused by domain wall motion (at low fields close to coercivity) and rotation (at large fields far from coercivity), the magnetostrictive layer of high permeability, simultaneously showing large magnetostriction constant, would expect to produce a large ME effect [11]. This

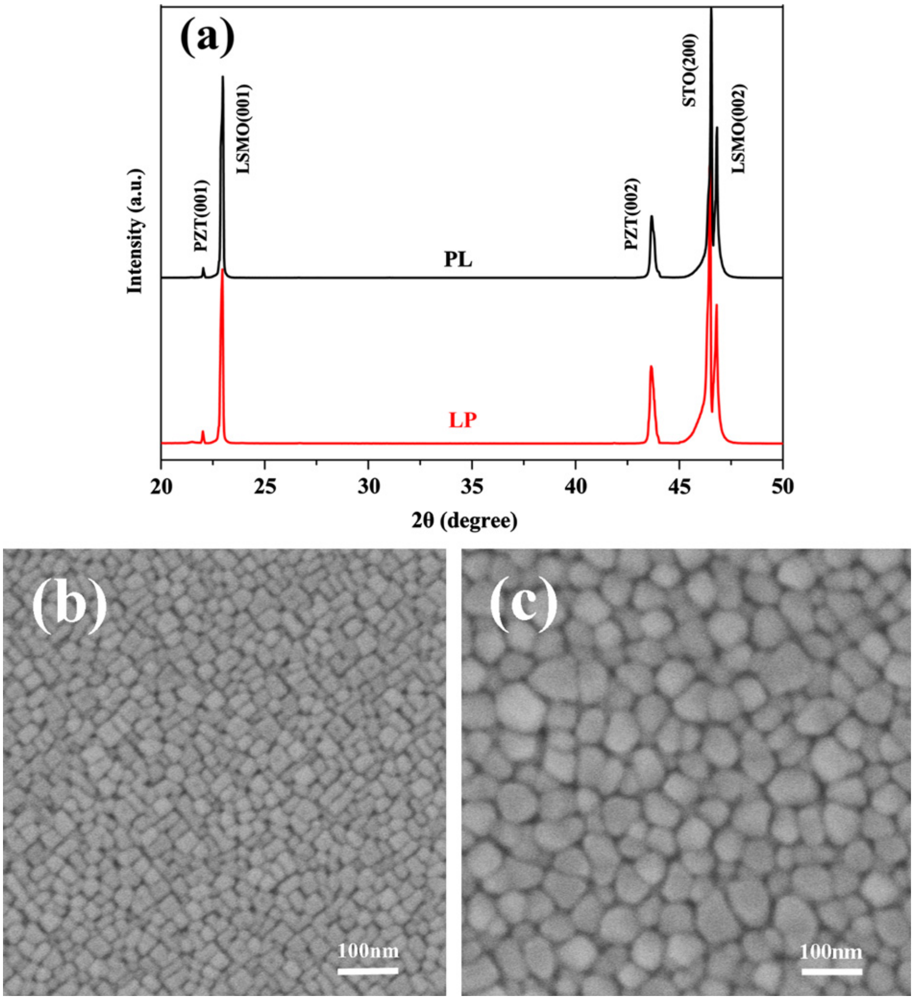

Fig. 1. XRD patterns (a) and plan-view SEM images of the composite thin films: (b) PL structure and (c) LP structure.

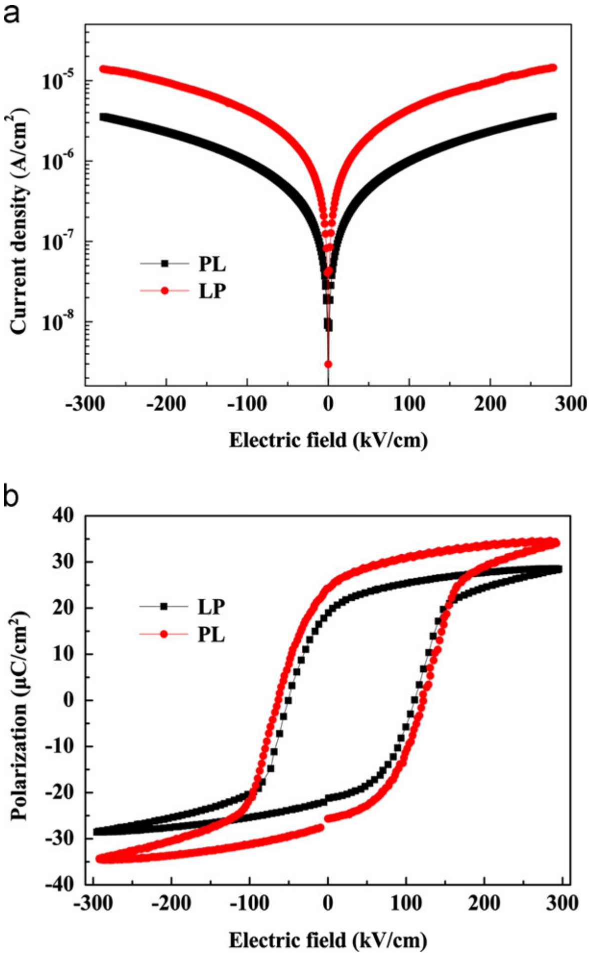

Fig. 2. *C–E* curves (a) and *P–E* hysteresis loops (b) of the PL and LP composite thin films.

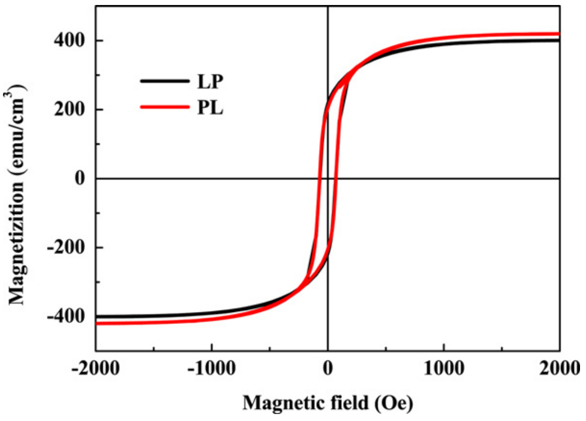

Fig. 3. Magnetic hysteresis loops of the PL and LP composite thin films.

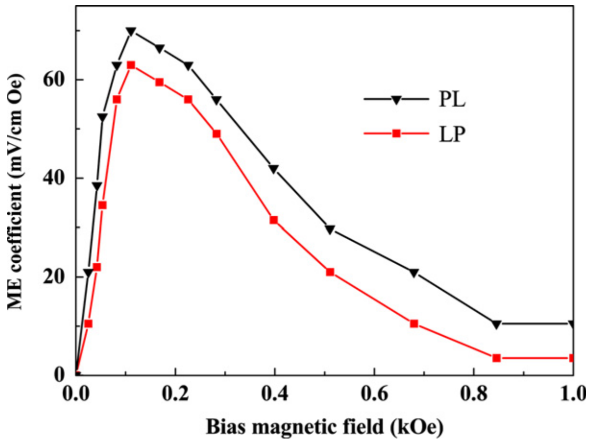

Fig. 4. Variation of α_E with H_{bias} at magnetic frequency $f=1$ kHz for PL and LP composite thin films.

might explain the sharp increase of α_E in the low field. On the other hand, α_E reached its largest value at bias magnetic fields, one order larger than the coercivities. It suggested that the domain rotation might have more contributions to the ME coupling than the wall motion. At higher bias fields, the magnetostriction of the LSMO layer gets saturated producing a nearly constant electric field in the PZT ferroelectric phase and led to a slow reduction of α_E. In addition, it is obvious that the value of α_E of PL film is somewhat larger than that of LP film at any fixed H_{bias} in the range of 0–1 kOe while they exhibit a similar rise-and-fall. The maximum values of the α_E for the PL and LP structures are 70 and 63 mV/cm Oe, respectively. The larger α_E value for PL composite thin film might be due to the enhancing of the interfacial coupling, as the magnetic–mechanical–electric interaction between the magnetic and ferroelectric phases through the stress/strain in the interface [12]. As top PZT layer in the PL film has less defects and better crystallization than LSMO, while the $SrTiO_3$ substrate layer has a smaller lattice mismatch with LSMO than PZT, it also could be ascribed to the strong substrate clamping for the thin film structures.

4. Conclusions

In summary, the bi-layer PZT–LSMO ME composite thin films with two different structures, i.e., PL structure and LP structure, have been obtained by pulse laser deposition. These two kinds of double-layered thin films exhibit coexistence of ferroelectric and ferromagnetic orderings at room temperature, but different ferroelectric and magnetic properties depending on their structures. The PL structured films have better ferroelectric properties and higher saturation magnetization than the LP structured films. The composite thin films exhibit distinct ME coupling behaviors, while the ME voltage coefficient α_E of the PL composite film is larger than that of the LP composite film due to a possible enhancing of interface coupling and substrate clamping.

Acknowledgments

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