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High energy-storage performance of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ relaxor ferroelectric thin films prepared by RF magnetron sputtering

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ABSTRACT

$0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ (PMN-PT 90/10) relaxor ferroelectric thin films with different thicknesses were deposited on the $LaNiO_3$/Si (100) by the radio-frequency (RF) magnetron sputtering technique. The effects of thickness and deposition temperature on the microstructure, dielectric properties and the energy-storage performance of the thin films were investigated in detail. X-ray diffraction spectra indicated that the thin films had crystallized into a pure perovskite phase with a (100)-preferred orientation after annealed at 700 °C. Moreover, all the PMN-PT 90/10 thin films showed the uniform and crack-free surface microstructure. As a result, a larger recoverable energy density of 31.3 J/cm^3 was achieved in the 750-nm-thick film under 2640 kV/cm at room temperature. Thus, PMN-PT 90/10 relaxor thin films are the promising candidate for energy-storage capacitor application.

1. Introduction

Capacitors are widely used in the electronic and electrical systems and occupy much of the volume and weight of the powder systems. With the development of the devices toward miniaturization, light weight, and integration, capacitors with high energy-storage performance are eagerly desired [1–6]. Generally, the recoverable energy-storage density W of a capacitor could be estimated from the polarization–electric field hysteresis (P–E) loops via the formula expressed:

$$W = \int_{P_r}^{P_{max}} \mathrm{Edp}, \tag{1}$$

where E is the applied electric field, P is the polarization, P_r is the remnant polarization and P_{max} is the maximum polarization [7–9]. According to the formula, the area between the polarization axis and the discharge curve of the P–E loop represents the stored and recoverable energy, and the area enclosed by the P–E loop stands for the exhausted energy owing to the hysteresis loss [6]. Based on this formula, the W values could be improved by increasing the critical breakdown fields (BDS) and/or enlarging the different between P_{max} and P_r. Thus, it could be predicated that relaxor ferroelectric materials may be a promising candidate for energy-storage application, because of their slim P–E loops with large (P_{max}–P_r) values. Recently, remarkable successes have been obtained in polyvinylidene fluoride (PVDF)-based and lead-based relaxor ferroelectric films. The large recoverable W values of 25 J/cm^3 and 28.7 J/cm^3 were reported in P(VDF-CTEE) copolymer and $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) films, respectively [10,11].

(1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PMN-PT) system is a typical kind of relaxor ferroelectrics, and its relaxor behavior and dielectric properties have been widely investigated. However, the studies on the energy-storage characterization of the PMN-PT materials are rarely reported up to now. Only recently, a moderate W value of 15 J/cm^3 was reported in $0.462Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.308Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.23PbTiO_3$ (PZN-PMN-PT) relaxor ferroelectric thin films by Yao et al. [12]. In addition, it was reported that PMN-PT relaxor ferroelectric materials with a typical composition of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ (PMN-PT 90/10) usually possessed slim P–E hysteresis loop with a relatively small P_r and a relatively high P_{max} [13,14]. These results highlighted the possibility that high energy-storage density could be obtained in PMN-PT relaxor ferroelectrics. Moreover, capacitors based on films are likely to exhibit better energy-storage performance than bulk ceramic, due to the higher BDS of thin films [15,16]. Hence, in present work, PMN-PT 90/10 relaxor ferroelectric thin films were prepared on $LaNiO_3$/Si (100) bottom electrode by the radio-frequency (RF) magnetron sputtering technique. The effects of deposition temperature and the film thickness on their dielectric and energy-storage performance were explored.

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2. Experimental procedure

In this work, $LaNiO_3$ (LNO) film was used as the bottom electrodes due to its good metallic conductivity, and also was served as an effective surface for the preferred growth of the ferroelectric thin films [17–20]. 250-nm-thick LNO layers with (100)-preferred orientation were first deposited at 550 °C on silicon substrate by RF magnetron sputtering. Then the PMN-PT 90/10 thin films were deposited by RF magnetron sputtering from a sintered PMN-PT 90/10 ceramic target. For the synthesis of the target, PMN-PT 90/10 powders was prepared firstly by calcining the mixture of Nb_2O_5, MgO, Pb_3O_4, and TiO_2 starting materials. In order to compensate for the loss of Pb during high-temperature heat treatment and to enhance perovskite phase formation, an extra amount of 10 mol% lead was added. The calcined powders were ball milled for 24 h, pressed into pellets with polyvinyl alcohol and then sintered at 1270 °C for 5 h. A series of PMN-PT 90/10 thin films were deposited on the LNO layers at different substrate temperatures. The crystallized films with a thickness of 375, 500, 750 and 1000 nm were obtained after the as deposited amorphous films were annealed at 700 °C for 10 min. The target information and RF magnetron sputtering deposition conditions are given in Table 1.

The phase structure and microstructure of PMN-PT 90/10 relaxor ferroelectric thin films was investigated by using X-ray diffractometer (XRD Bruker D8 Advance diffractometer, German) and field-emission scanning electron microscopy (FE-SEM, ZEISS Supra 55, German), respectively. For the measurements of electrical properties, gold pads of 0.2 mm in diameter were coated on the surface as top electrodes by using a dc sputtering method. The frequency, dc applied electric field and temperature-dependent dielectric properties were measured by a computer controlled Agilent E4980A LCR analyzer. The electric field-induced polarization (*P*–*E*) hysteresis loops were obtained at different frequencies and temperatures by a Ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM). The energy-storage performance was calculated according to the *P*–*E* results.

3. Results and discussion

Fig. 1(a) presents the X-ray diffraction patterns of the 500-nm-thick PMN-PT 90/10 thin films deposited at different substrate temperatures of 200, 250, 300, 350 and 400 °C, respectively. All the annealed films exhibited a pure perovskite phase with pseudo-cubic structure, and no pyrochlore phase was found in the films. The diffraction peaks were indexed according to the previous study [21]. Clearly, the deposited PMN-PT 90/10 thin films also showed the same (100)-preferred orientation as with the LNO bottom electrodes. The full width at half maximum of PMN-PT 90/10 was greatly smaller than that of LNO, which indicated that the grain size of PMN-PT 90/10 was larger than that of LNO [22]. It can be

Table 1
Summary of deposition and annealing parameters.

Parameters	
Target composition	PMN-PT 90/10
Target diameter	60 mm
Gas	Ar
Pressure	2 Pa
RF power	30 W
Substrate	LNO/Si
Substrate temperature	200, 250, 300, 350 and 400 °C
The final thickness	375, 500, 750 and 1000 nm
Annealing temperature	700 °C
Annealing atmosphere	Air
Time at annealing temperature	10 min

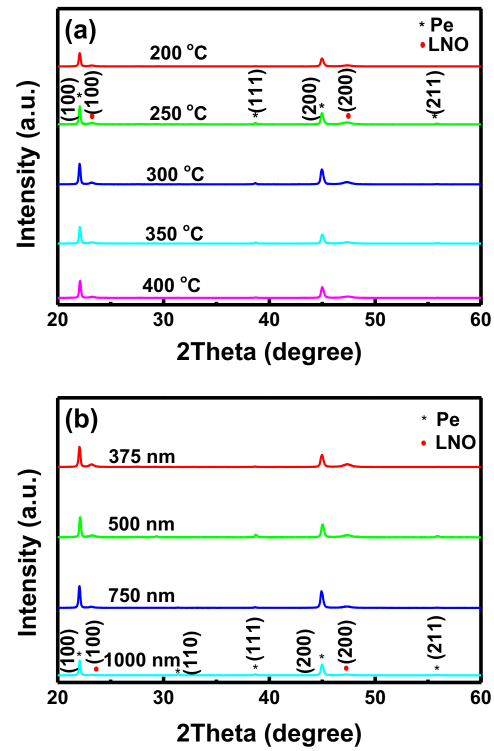

Fig. 1. (a) XRD patterns of 500-nm-thick PMN-PT 90/10 thin films deposited at different substrate temperatures. (b) XRD patterns of PMN-PT 90/10 thin films with different thicknesses deposited at 300 °C (Pe: perovskite phase).

confirmed from the surface FE-SEM images in the following part. Moreover, no evident difference was observed from the curves for the films deposited at different substrate temperatures. Fig. 1(b) gives the X-ray diffraction curves of PMN-PT 90/10 thin films with a thickness of 375, 500, 750, and 1000 nm, respectively, which were deposited at 300 °C. It was also found that the thickness had no evident effect on the crystallized behavior of the films.

Fig. 2(a–e) shows the surface FE-SEM images of PMN-PT 90/10 thin films deposited at different substrate temperatures. No crack or phase segregation was appeared in these images. The films deposited at different substrate temperatures shared a similar grain sizes with an average value of 200–300 nm. Some small pores appeared on the surface at grain boundaries, which could be related to the deposition condition such as the RF power, pressure, and annealing temperature [23–25]. The inset of the Fig. 2(a) shows the surface FE-SEM image of LNO bottom electrode. The LNO film microstructure consists of fine crystallites (20–50 nm in size) of rounded morphology. As a typical example, Fig. 2(f) gives the cross-section image of PMN-PT 90/10 films deposited at 300 °C. No obvious inter-diffusion between PMN-PT 90/10 and LNO bottom electrode was detected. In addition, the image also demonstrated that a dense and void-free microstructure was obtained within the films.

The dielectric constant and loss of the 500-nm-thick PMN-PT 90/10 thin films deposited at different substrate temperatures are shown as a function of frequency at room temperature in Fig. 3(a). It could be observed that, as the frequency increasing, the dielectric constant for all the samples was gradually decreased. The declined tendency was due to the long-time polarization process of some frameworks, such as space charges, which had no contribution to the overall polarization at higher frequency [26]. With the increase of the substrate temperature, the dielectric constant of PMN-PT 90/10 relaxor ferroelectric thin films were firstly increased, and then decreased. The maximum dielectric constant values of 1143 at