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Enhanced ferroelectric properties of $0.95Pb(Sc_{0.5}Ta_{0.5})O_3–0.05PbTiO_3$ thin films with $Pb(Zr_{0.52},Ti_{0.48})O_3$ seed layer

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Abstract

$0.95Pb(Sc_{0.5}Ta_{0.5})O_3–0.05\%PbTiO_3$ (PSTT5) thin films with and without a $Pb(Zr_{0.52},Ti_{0.48})O_3$ (PZT52/48) seed layer were deposited on Pt/Ti/SiO_2/Si(1 0 0) substrates by RF magnetron sputtering. X-ray diffraction patterns indicate that the PSTT5 film with a PZT52/48 seed layer exhibited nearly pure perovskite crystalline phase with highly (4 0 0)-preferred orientation. Piezoresponse force microscopy observations reveal that a large out-of-plane spontaneous polarization exists in the highly (4 0 0)-oriented PSTT5 thin film. The PSTT5/PZT(52/48) possesses good ferroelectric properties with large remnant polarization P_r (12 μC/cm^2) and low coercive field E_c (110 kV/cm). Moreover, The perfect butterfly-shaped capacitance–voltage characteristic curve and the relative dielectric constant as high as 733 is obtained in this PSTT5 thin film at 100 kHz.

Keywords: C. Dielectric properties; C. Ferroelectric properties; PSTT film; PZT seed layer

1. Introduction

Ferroelectric films have considerable potential applications in many microdevices such as surveillance, night vision, thermal management, and missile tracking and guidance, because of their excellent dielectric, piezoelectric and optical properties [1–4]. During the last several years, interest in ferroelectric relaxors with enhanced ferroelectric properties, in particular, solid solution of complex lead perovskite compounds and $PbTiO_3$, such as $Pb(Sc,Ta)O_3–PbTiO_3$ and $Pb(Mg,Nb)O_3–PbTiO_3$, has continuously increased. However, there are relatively few reports about $0.95Pb(Sc_{0.5}Ta_{0.5})O_3–0.05\%PbTiO_3$ (PSTT5) thin films in literature [5–12].

It is well known that many factors may affect properties of ferroelectric films, such as the orientation, composition, seed layers, and so on. Among these, the seed layer is an important factor for improving electrical properties and phase purity of the films [13–15]. During the preparation of lead-based thin films, the lead element is easy to volatilize, which results in undesirable pyrochlore phase. Moreover, the pyrochlore phase with a very low dielectric constant has been confirmed to be harmful for the performance of PSTT thin films. Therefore, it is necessary to improve the phase purity of the lead-based ferroelectric films.

In order to enhance the formation of perovskite structure, a $Pb(Zr_{0.52},Ti_{0.48})O_3$ (PZT52/48) seed layer was chosen in this work for the preparation of PSTT5 thin films, which were deposited on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by RF magnetron sputtering method. The effects of $Pb(Zr_{0.52},Ti_{0.48})O_3$ seed layer on the orientation, phase purity, domain structure and ferroelectric properties of PSTT5 thin films were investigated.

2. Experimental procedures

In this work, using powder target, $0.95Pb(Sc_{0.5}Ta_{0.5})O_3–0.05\%PbTiO_3$ thin films with a PZT(52/48) seed layer were prepared on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by RF magnetron sputtering. The PZT(52/48) and PSTT5 thin films were deposited sequentially on the Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates. During deposition, the substrates were not heated and their temperature was only dependent on ion bombardment. The thicknesses of PZT(52/48) seed layer and PSTT5 thin film, estimated by the deposition time according to deposition rate, are about 150 nm and 500 nm, respectively. All of the

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Table 1
Deposition conditions for the PZT(52/48) seed layer and PSTT5 thin film prepared by RF magnetron sputtering.

Sample	PZT(52/48)	PSTT5
Substrate	Pt(1 1 1)/Ti/SiO_2/Si(1 0 0)	PZT(52/48)/Pt(1 1 1)/Ti/SiO_2/Si(1 0 0)
Substrate temperature	Room temperature	Room temperature
Substrate-target distance	5 cm	5 cm
Working pressure	2 Pa	2 Pa
Sputtering atmosphere	O_2:Ar = 10 sccm:40 sccm	O_2:Ar = 10 sccm:40 sccm
Sputtering power	75 W	75 W
RF power density	2.5 W/cm^2	2.5 W/cm^2
Depositing rate	4–8 nm/min	4–8 nm/min
Thickness	150 nm	500 nm

preparation parameters are listed in Table 1. The PSTT5 thin films with and without a PZT(52/48) seed layer were annealed at 700 °C in a rapid thermal annealing (RTA) furnace in the oxygen atmosphere for 10 min to compensate oxygen vacancies.

Crystallographic properties of special seed layer PZT and PSTT thin films were examined by X-ray diffraction using Cu Kα radiation (λ = 1.54178 Å) in the mode of θ–2θ scan (DX-1000, Dandong, China). The domain patterns of the films were obtained by means of scanning force microscope (SFM, Seiko SPA 300HV, Japan) in piezoresponse mode, namely, PFM. All scans were performed at room temperature using a conductive Au coated Si_3N_4 cantilever (Seiko) with an elastic constant of 1.4 N/m and an integrated tip of about 20 nm in diameter. The polarization hysteresis loops (*P–E* loops) were evaluated by Radiant precision ferroelectric measurement system (RT2000 Tester, USA). The dependence of capacitance of the PSTT5 thin film with PZT(52/48) seed layer on the dc voltage (*C–V* curve) was studied by using an HP 4194A LCR meter.

3. Results and discussion

The preparation of PSTT films without a PZT seed layer on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) is not easily straight to form perovskite phase, and the pyrochlore phase always forms

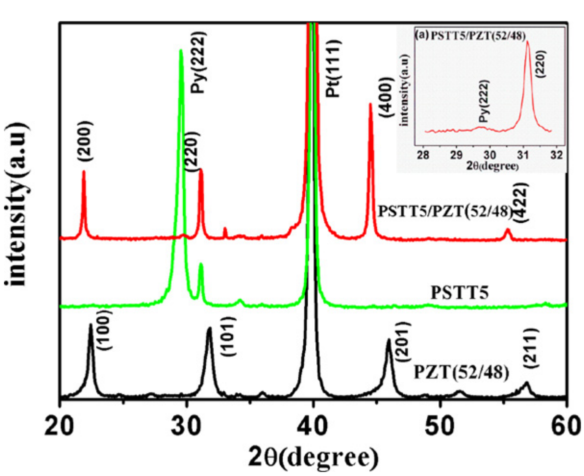

Fig. 1. XRD patterns of the PZT(52/48) seed layer, PSTT5 thin film and PSTT5 thin film with a PZT(52/48) seed layer. The inset (a) is the simulated curve of the XRD pattern for the PSTT5 thin film with a PZT(52/48) seed layer in the 2θ range of 28–32°.

during the preparation process. In order to improve the phase purity of PSTT5 films, PZT(52/48) thin film was used as the seed layer for preparation of PSTT5 films [16]. Because the material of PZT(52/48) which has a tetragonal (lattice constants of 4.10 and 4.15 Å) and rhombohedral coexist perovskite structure is structurally close to PSTT5 with a rhombohedral structure of perovskite type with lattice constant $a = 4.063$ Å [8]. Fig. 1 shows the XRD patterns of the PZT(52/48) seed layer and the PSTT thin films without and with a PZT(52/48) seed layer.

As shown in Fig. 1, the PSTT5 thin film with a 150 nm PZT(52/48) seed layer possesses almost pure perovskite phase. The ratio of the intensities of pyrochlore (2 2 2) peak and perovskite (4 0 0) peak was used to determine the volume fraction of perovskite phase [17]. The perovskite phase ratio, calculated by Eq. (1) is about 95% in the PSTT5 thin film with a PZT seed layer.

$$\text{Perovskite phase (\%)} = \frac{I_{\text{perovskite}(4\,0\,0)}}{I_{\text{perovskite}(4\,0\,0)} + I_{\text{pyrochlore}(2\,2\,2)}} \times 100 \qquad (1)$$

Also, the PSTT5 thin film with a PZT seed layer possesses (4 0 0)-preferred orientation. The preferential (4 0 0) orientation, $a_{h\,k\,l}$, can be calculated by the following formula:

$$a_{h\,k\,l} = \frac{I_{h\,k\,l}}{\Sigma I_{h\,k\,l}} \qquad (2)$$

where the $a_{h\,k\,l}$ (%) = $I_{\text{perovskite}(4\ 0\ 0)}/(I_{\text{perovskite}(4\ 0\ 0)} + I_{\text{perovskite}(2\ 2\ 0)}) \times 100$. Accordingly, the calculated preferential (4 0 0) orientation of the PSTT film with about a 150 nm PZT seed layer is about 60%.

Fig. 2(a) shows the effect of the PZT(52/48) seed layer on the improvement of out-of-plane-polarization (OPP) PFM images (3 μm × 3 μm) of the PSTT5 thin film. In this image, the output of the lock-in amplifier for each lateral position is displayed as different gray levels in such a way that bright areas have high vibration amplitude with negative phase; dark areas have a high piezoactivity with positive phase, and the gray regions were not vibrating induced by the applied ac field [15]. When a pulse voltage is applied to the PSTT5/PZT(52/48) thin film, different intensities between dark and bright lamellae representing different domains are observed as it shows in Fig. 2(b), in which dark and bright areas are crossed and correspond to the hills and valleys along line scan piezoresponse signal A–B. The

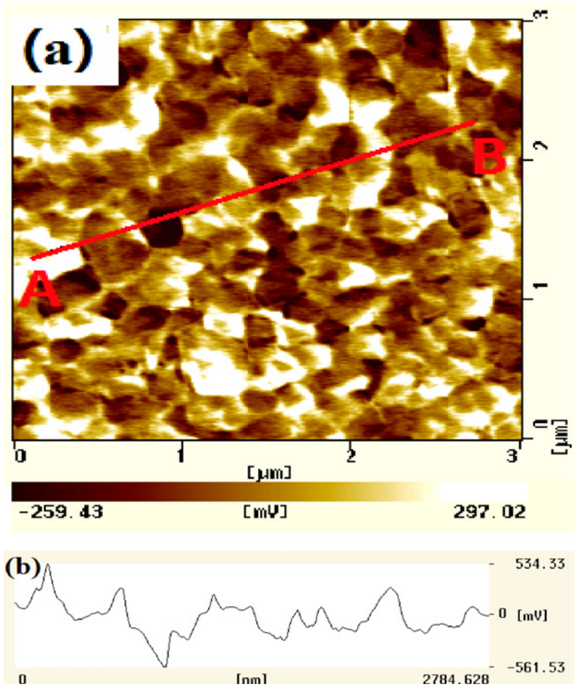

Fig. 2. (a) The corresponding image (3 µm × 3 µm) of out-of-plane polarization (OPP) of the PSTT5 thin film with a PZT(52/48) seed layer. Line scan piezoresponse signal related to (a) along line A–B is shown in (b).

formation of alternating banded domains with adjacent lamellae induced by the mechanical strain at the surface and at the interface between the film and the substrate can minimize the mechanical energy of the film and be more stabled [18]. Moreover, The OPP PFM patterns of the (4 0 0)-oriented PSTT5/PZT(52/48) thin film exhibit strong dark and bright contrasts due to a large out-of-plane spontaneous polarization.

Fig. 3 shows the room temperature polarization behavior of the PSTT5/PZT(52/48) thin film with different applied fields. With sufficient increase in the applied field, the *P*–*E* loops tend to become saturated. It can be concluded that compared to the PSTT5 film without PZT(52/48) seed layer, the (4 0 0)-oriented PSTT5/PZT(52/48) thin film possesses higher phase purity and stronger out-of-plane polarization, as shown in Fig. 2, and thus exhibits larger remnant polarization ($P_r = 12\ \mu C/cm^2$) and lower coercive field ($E_c = 110$ kV/cm).

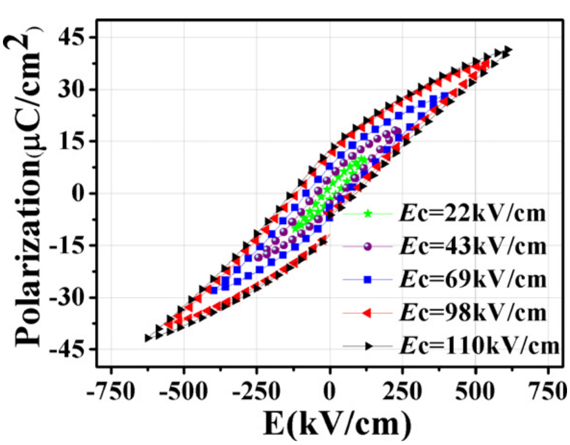

Fig. 3. *P*–*E* curves of the PSTT5/PZT(52/48) thin film with different applied fields, measured at room temperature.

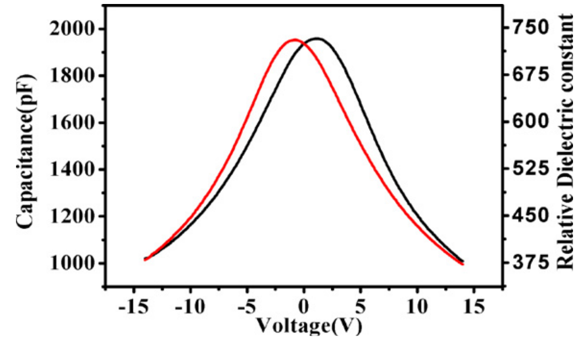

Fig. 4. Capacitance–voltage curves of the PSTT5 thin film with a PZT(52/48) seed layer, measured at 100 kHz and 300 K. The dielectric constant, calculated by using the classic formula for parallel-plate capacitors, is also shown in this figure.

Fig. 4 gives the dependence of the capacitance of the PSTT5 thin film with a PZT(52/48) seed layer on the applied voltage (*C*–*V* curve). The *C*–*V* curve was obtained at a frequency of 100 kHz with an oscillation amplitude of 200 mV. The DC voltage was swept from a negative bias (−14 V) to a positive bias (+14 V) and vice versa. Strong dependence of the capacitance on the dc bias field is observed. From Fig. 4, it is obvious that the *C*–*V* loop has good symmetry and butterfly-type shape. The *C*–*V* loop, which usually appears in ferroelectric materials due to polarization reversal, indicates that the deposited film is in a polar state. The PSTT5 thin film with a PZT(52/48) seed layer in the present work possesses perfect butterfly-shaped *C*–*V* characteristic curve with good symmetry, which gives further evidence for the enhancement of the film's ferroelectricity [19]. The relative dielectric constant (ε_r) at zero bias reaches 733 at 100 kHz, which is quite high compared to single PSTT thin films without seed layer and most dielectric thin films [5].

However, the electrical properties of the PSTT5 thin film without a PZT(52/48) seed layer could not be measured because the film between the bottom and the top electrodes is easily broken by applying the voltage for measurement. The reason may be because the PSTT5 thin film without a PZT(52/48) seed layer mainly forms a pyrochlore phase structure.

4. Conclusions

(4 0 0)-oriented $0.95Pb(Sc_{0.5}Ta_{0.5})O_3$–$0.05\%PbTiO_3$ thin films were successfully prepared on the $Pb(Zr_{0.52},Ti_{0.48})O_3$/Pt(1 1 1)/Ti/$SiO_2$/Si(1 0 0) substrate by RF magnetron sputtering, with high phase purity, strong intensity of out of plane spontaneous polarization and good ferroelectric properties. The measured ferroelectric hysteresis loop has shown that the remnant polarization P_r of the Au/PSTT5/PZT/Pt capacitor is about 12 $\mu C/cm^2$ and coercive field E_c about 110 kV/cm. In addition, the relative dielectric constant ($\varepsilon_r = 733$) is obtained in the PSTT5/PZT(52/48) thin film at 100 kHz. The perfect butterfly-shaped *C*–*V* characteristic curve gives further evidence for the improved ferroelectric property in the films.

Acknowledgement

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