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Thickness scaling and electric properties of highly (111) oriented Nb-doped $Pb(Zr,Ti)O_3$ thin film prepared at low temperature by a sol–gel route

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Abstract A series of highly (111) oriented $Pb(Nb_{0.01}Zr_{0.2}Ti_{0.8})O_3$ (PNZT) thin films of variant thickness were successfully achieved on $Pt/Ti/SiO_2/Si$ substrate by a sol–gel route. By introducing $Pb_{0.8}Ca_{0.1}La_{0.1}Ti_{0.975}O_3$ (PLCT) layer between the PNZT film and Pt electrode, the PNZT film could be crystallized at as low as 500 °C. When a maximum applied voltage is 3 V, it was found that the PNZT film with PLCT seed layer possessed higher remnant polarization (22 $\mu C/cm^2$) as film thickness was scaled down to 50 nm. It was also found that enhanced pyroelectric properties could be observed in 50-nm thickness PNZT thin film due to its relatively low dielectric constant. The results demonstrated that the film thickness could be scaled down for low voltage operations using lattice matched interface between PNZT film and PLCT seed layer on $Pt/Ti/SiO_2/Si$ substrate, and this interface optimization is the key technology for synthesizing thin PNZT films at low temperature with good insulating and electric properties.

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Introduction

Thin $Pb(Zr,Ti)O_3$ (PZT) family films are one of the most important ferroelectric varieties because of their large remnant polarization that can be applied to high-density ferroelectric random access memories (FeRAM), pyroelectric infrared detectors, and electro-optic devices for data storage and displays [1, 2], and the applications are expected to be widened due to the realization of low voltage operation and low power consumption [3]. Low voltage operations have been achieved by decreasing the film thickness of the ferroelectric materials, such as in the widely investigated PZT family films, while good ferroelectricity and insulating characteristics were maintained. However, to achieve low voltage operations, films with high crystal qualities and sufficient electrode interfaces are needed. Although most research has concentrated on decreasing the operating voltage by growing epitaxial films on single crystal substrates [4, 5], the issue has not been fully resolved yet. Because the devices on platinized silicon substrate can be integrated with a complementary metal-oxide semiconductor process, it is very important to prepare PZT film with low voltage operation on platinized silicon substrate. Furthermore, for polycrystalline PZT family films deposited on platinized silicon substrate, the preferential orientation of the crystallized film is also expected for improving film properties, because the electric properties of ferroelectric films are strongly dependent on their crystalline orientation [6, 7]. So it is very necessary for PZT family films to maintain high orientation when decreasing the film thickness.

For ferroelectric thin films, in many cases of application, such as integrating PZT thin film directly with a silicon-based readout integrated circuit (ROIC), the processing temperature should not exceed 500 °C [8], due to the

silicon semiconductor being seriously damaged at high temperatures, however, generally speaking, at 500 °C, poor crystallinity of the ferroelectric phase occurs and non-ferroelectric second phases such as pyrochlore or fluorite are stable [9].Therefore, an advantage preparation method for PZT family ferroelectric thin film should include two aspects: one is the films must obtain a usable ferroelectric response at low processing temperature; the other is scaling down the film thickness in order to decrease the operating voltage.

As to ferroelectric films, the decrease in electric properties with decreasing film thickness has been related to many factors. It is well accepted that the stress decreases with increasing thickness, and the electric properties increases with decreasing the stress, for example, Lian and Sottos [10] and Ong et al. [11] have demonstrated that as the film thickness decreased, the dielectric constant decreased and the dissipation factor increased. Zhu [12] has also reported that the P_r value for the PNZT film increases with film thickness. In addition, it is shown that the effect of ferroelectric–electrode interface may be of key importance to the polarization response of ferroelectric thin films, and the electrical properties dependence with the thickness can be also explained by the existence of an interfacial layer (a "dead" layer) [13, 14]. So it is necessary to improve electric properties by optimizing the electrode–ferroelectric interface, and the use of a seed layer has been regarded as a simple and effective method [15]. In this study, because $Pb_{0.8}Ca_{0.1}La_{0.1}Ti_{0.975}O_3$ (PLCT) seed layer can be crystallized at low temperature in our previous study [16], and it also matches PZT with regard to the crystal structure and lattice parameter. The PLCT seed layers are chosen to optimize the ferroelectric–electrode interface.

In this study, highly (111) oriented $Pb(Nb_{0.01}Zr_{0.2}Ti_{0.8})O_3$ (PNZT) thin films of variant thickness were successfully achieved on $Pt/Ti/SiO_2/Si$ substrate using a sol–gel route. By introducing PLCT seed layer between the PNZT film and Pt electrode, the PNZT films can be obtained at low annealing temperature. The polarization–electric field (P–E) characteristics of PNZT films of variant thickness were measured at low voltage operation (3 V). Furthermore, the dielectric and pyroelectric properties are also investigated.

Experimental

The PNZT was deposited by a sol–gel spin-on technique. Lead acetate trihydrate, zirconium *n* propoxide, titanium isopropoxide, and niobium ethoxide were used as the raw materials and 2-methoxyethanol [$2\text{-}CH_3OCH_2CH_2OH$] as the solvent. The 10 mol% excess Pb solution was used to overcompensate for any Pb loss, the solution composition was controlled in the ratio of Pb:Nb:Zr:Ti = 1.1:0.01:0.2:0.8, and the concentration of final solution of PNZT could be diluted to 0.2 M. The PLCT solution was also prepared for seed layers using the similar procedure, and the raw materials were lead acetate trihydrate, titanium isopropoxide, lanthanum acetate hydrate, and calcium acetate. The solution composition was controlled in the ratio of Pb:La:Ca:Ti = 0.88:0.1:0.1:0.975, and the concentration of PLCT solutions were adjusted to 0.05 M. The first processing step was to deposit a thin PLCT layer onto the $Pt/Ti/SiO_2/Si$ substrate and pyrolyze it at 450 °C for 2 min, the thickness of PLCT seed layer was about 5 nm. The next processing step was to repeatedly deposit PNZT layers on top of the PLCT coating and also pyrolyze them at 450 °C for 2 min, until the desired film thickness was reached. Finally, the films were annealed at 500 °C for 10 min by a rapid thermal annealing (RTA) in oxygen ambience. X-ray diffraction (XRD) characterization of the PNZT thin film was performed using Cu$K\alpha$ radiation. The ferroelectric hysteresis loops were evaluated using a Radiant Precision Workstation Ferroelectric Measurement System. The pyroelectric current was measured using an electrometer, and the temperature was controlled using a temperature test chamber. The formula for calculating pyroelectric coefficient and detailed measurement were indicated by Sun et al. [17].

Results and discussion

The thicknesses of PNZT thin films with 5 nm PLCT seed layer annealed at 500 °C were characterized by X-ray reflectivity (XRR) techniques. As shown in Fig. 1, a Kissige fluctuation that characterized the thickness of the film can

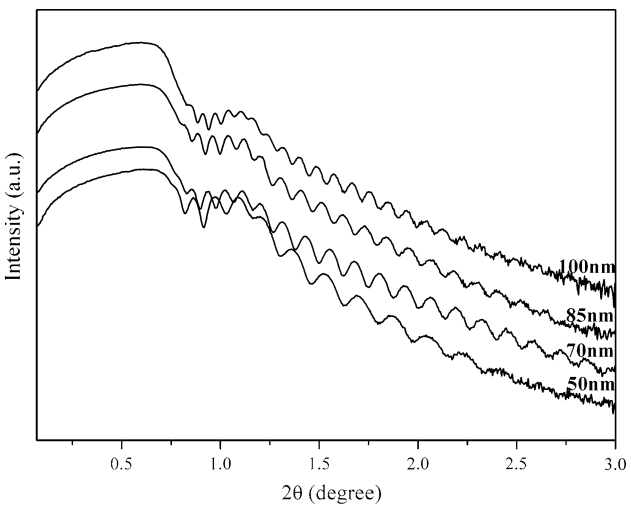

Fig. 1 XRR curves of PNZT thin films with different thicknesses

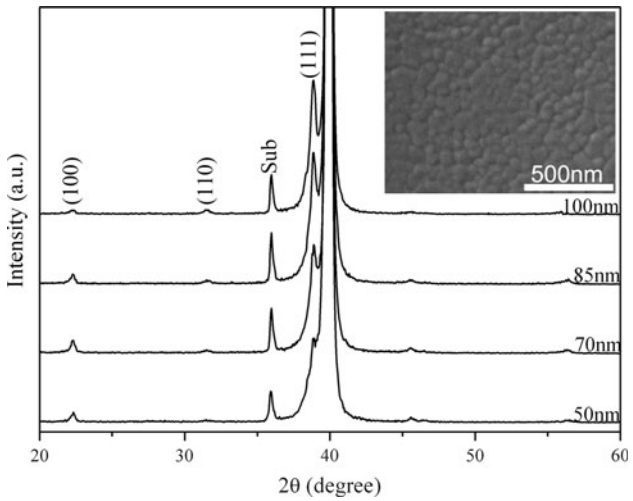

Fig. 2 XRD patterns of PNZT thin films with different thicknesses. The *inserted illustration* is the surface morphology of 50-nm thickness PNZT thin film

be found at low angle. According to the XRR result, the thicknesses of PNZT thin films were about 50, 70, 85, and 100 nm, respectively. Figure 2 shows the XRD patterns of PNZT thin films of variant thickness annealed at 500 °C, it can be found that by introducing PLCT seed layer between the film and Pt electrode, the PNZT thin films are well crystallized with pure tetragonal perovskite structure only after 500 °C annealing treatment, and all of films exhibit high (111) orientation. Figure 2 also shows that the surface morphology of 50-nm thick PNZT thin film by the scanning electron microscope, and it is clearly showed that the film exhibits a smooth and crack-free surface, which is composed of densely packed uniform grains.

The typical ferroelectric hysteresis loops measured at 3 V are shown in Fig. 3. From Fig. 3, the *P–E* hysteresis of 50-nm thick PNZT thin film annealed at 500 °C shows

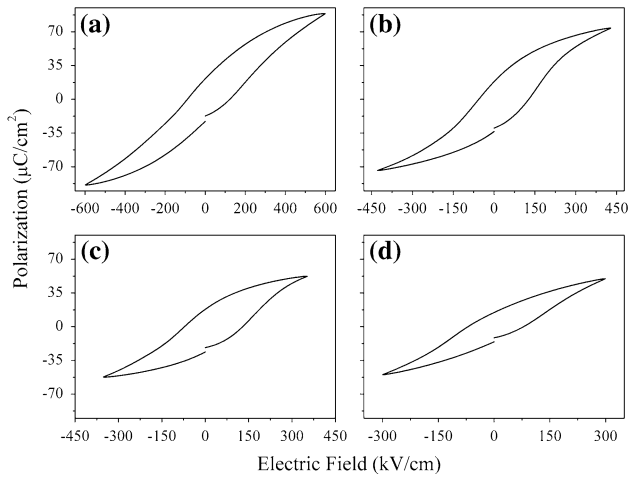

Fig. 3 *P–E* hysteresis loops of PNZT thin films measured at 3 V with different thicknesses: **a** 50 nm, **b** 70 nm, **c** 85 nm, and **d** 100 nm

higher remnant polarization ($P_r = 22$ μC/cm^2), which is close to the reported values of $P_r = 15$–30 μC/cm^2 for relatively thick lead ferroelectric films annealed at high temperature, such as PZT films with 480-nm thickness annealed at 650 °C prepared by magnetron sputtering [18], PZT films with 600-nm thickness annealed at 550 °C prepared by pulsed laser deposition [19], and PZT films with 240-nm thickness annealed at 650 °C prepared by a Sol–Gel method [20]. It indicates that this thin film possesses potential application prospect in ferroelectric random access memory. However, with increasing the thickness of the PNZT thin film, the P_r becomes smaller and smaller at a maximum applied voltage of 3 V, which results from the decrease of external electric field with increasing the film thickness at the same applied voltage. Figure 4 shows the frequency dependence of dielectric constant and tangent loss of the PNZT thin films of different thicknesses, as shown in Fig. 4, it is found that the dielectric constants of the PNZT thin films changed over the measured frequency range. For the PNZT thin films of different thicknesses (i.e., 50, 70, 85, and 100 nm), the

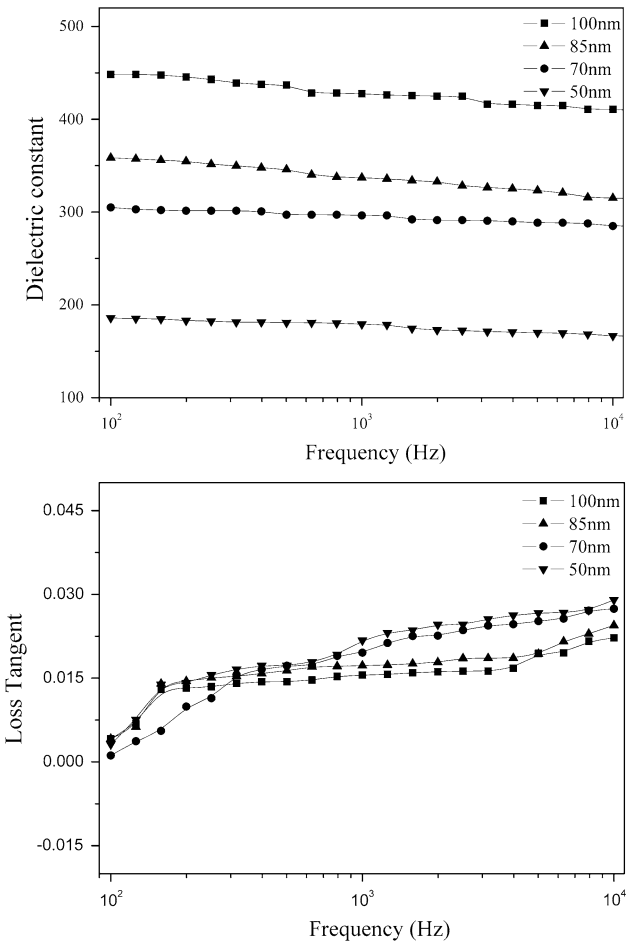

Fig. 4 Dielectric constant and tangent loss of the PNZT thin films with different thicknesses

Table 1 Pyroelectric parameters of PNZT films with different thicknesses

	p (μC/m^{2}K)	F_V (μC/m^{2}K)	F_d (μC/m^{2}K)
PNZT[a]	197	1.1	102
PNZT[b]	216	0.73	91
PNZT[c]	235	0.70	98
PNZT[d]	257	0.60	100

[a] 50 nm, [b] 70 nm, [c] 85 nm, [d] 100 nm

values of dielectric constant measured at a frequency of 1 kHz are 179, 297, 336, and 427, and the values of loss tangent are 0.021, 0.019, 0.017, and 0.015, respectively. As film thickness decreases, it is found that the dielectric constant decreased and the dielectric loss increases.

To evaluate the quality of a pyroelectric material, different figures of merit exist, depending upon the device requirement. For good voltage response [21], it is necessary to maximize pyroelectric coefficient p and lower the permittivity ε_r, to increase the figure of merit $F_V = p/\varepsilon_r$. For high detectivity (signal to noise ratio), the dielectric loss becomes important and the figure of merit is $F_d = p/(\varepsilon_r \tan\delta)^{1/2}$. The pyroelectric coefficient p at room temperature and the calculated figures of merit F_V and F_d of the PNZT samples of different thicknesses (i.e., 50, 70, 85, and 100 nm) are given in Table 1. It is found that a drop for p can be observed with decreasing the film thickness, the measured p of PNZT thin film with 50-nm thickness is 197 μC/m^{2}K, and the figure of merit F_V and F_d for the PNZT film with 50-nm thickness were calculated to be 1.1 and 102 μC/m^{2}K, separately. These values are comparable to those for relatively thick PZT pyroelectric thin films annealed at high temperature [22]. This result indicates that highly (111) oriented PNZT film with 50-nm thickness annealed at low temperature (500 °C) is a good candidate for uncooled IR detector.

When a field is applied, the ferroelectric materials switch by the nucleation of domains and the movement of domain walls, and not by the spontaneous reorientation of all of the polarization in a domain at once. In contrast to ferromagnetic materials in which switching usually occurs by the sideways movement of existing domain walls, ferroelectrics materials typically switch by the generation of many new reverse domains at particular nucleation sites, which are not random; i.e., nucleation is inhomogeneous. The initial stage is nucleation of reverse domains at the electrode, followed by fast forward propagation of domains across the film, and then slower widening of the domains [23]. So for domain switch of ferroelectric thin film, it is very necessary to form nucleation sites at the electrode–ferroelectric interface. When 5 nm PLCT is used as seed layer, the introduction of a 5-nm thick PLCT layer can offer nucleation sites and reduces the activation energy for the crystallization of PNZT films, which helps the PNZT films to crystallize at low temperature (500 °C). When an electric field is applied, the PNZT films typically switch by the generation of many new reverse domains at particular nucleation sites, which makes film polarization response easily, thus obtains enhanced ferroelectric properties.

In this study, the presented values are measured over a PLCT/PNZT stack. The measured relative permittivity of the film is given by:

$$1/\varepsilon = 1/\varepsilon_1 + (d_i/d)(1/\varepsilon_i)(d \gg d_i) \quad (1)$$

where ε_1 and ε_i are the relative permittivity of the PNZT film and the PLCT interface layer on the Pt electrode, separately; d and d_i are the thickness of the film and the interface layer, separately. According to the formula (1) [24], with increasing PNZT film thickness, the value of (d_i/d) becomes smaller and smaller, so the measured relative permittivity becomes larger and larger. In addition, the residual stress can change with film thickness, and it may have a significant effect on the dielectric properties, for example, Lian and Sottos [10] have demonstrated that dielectric properties of PZT thin films depend strongly on film thickness, it was found that as the film thickness decreased, the dielectric constant decreased and the dissipation factor increased. Due to relatively low dielectric constant, enhanced figures of merit (F_V, F_d) can be observed in 50-nm thick PNZT thin film.

Conclusion

Low temperature of highly (111) oriented PNZT thin films of variant thickness, as low as 500 °C, were successfully achieved by a sol–gel route using PLCT seed layer. The film thickness can be scaled down for low voltage operations using lattice matched interface between a PNZT film and PLCT seed layer on Pt/Ti/SiO_2/Si substrate, and this interface optimization is the key technology for synthesizing thin PNZT films with good insulating and electric properties. When a maximum applied voltage was 3 V, as film thickness increased, it was found that ferroelectric properties decreased, and the 50-nm thick PNZT film possessed better ferroelectric properties with higher remnant polarization P_r (22 μC/cm^2) at a maximum applied voltage of 3 V. It is also found that better pyroelectric properties can be observed in 50-nm thick PNZT thin film due to a relatively low dielectric constant. The results indicate that the PNZT thin film with PLCT seed layer annealed at low temperature is a good candidate for FeRAM and uncooled IR detector or IR imaging applications.

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