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Fatigue characteristic and pyroelectric properties of highly (1 1 1)-oriented Nb doped $Pb(Zr_{0.2},Ti_{0.8})O_3$ thin films with $Pb_{0.8}La_{0.1}Ca_{0.1}Ti_{0.975}O_3$ seed layer prepared by a sol–gel route

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ABSTRACT

A series of highly (1 1 1)-oriented tetragonal Nb-doped $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PNZT) films with and without $Pb_{0.8}La_{0.1}Ca_{0.1}Ti_{0.975}O_3$ (PLCT) seed layer were deposited on the Pt(1 1 1)/Ti/SiO_2/Si substrates by sol–gel processing; it was found the pyroelectric properties and fatigue resistance characteristics of PNZT films could be improved by introducing PLCT seed layer. Because the rough surface structures of 5 nm-thick PLCT seed layer can offer nucleation sites to reduce activation energy for the crystallization and lead to the polarization response easily, a large pyroelectric coefficient (460 $\mu C/(m^2 K)$) and a high figure-of-merit (F_d = 161 $\mu C/(m^2 K)$) was obtained for PLCT/PNZT/PLCT structure film. It was also found that PLCT seed layer could act as a capacitive interface layer possibly compensating for the vacancy-type defects from PNZT film effectively, which results in enhanced fatigue resistance characteristics of PLCT/PNZT/PLCT structure film.

1. Introduction

During the past decades, the pyroelectric detection of infrared radiation (IR) had became well known due to the important advantages offered by the pyroelectric detectors: room temperature operation, flat spectral response from near ultraviolet up to far infrared, good sensitivity, low cast, and simple device structure etc. [1,2]. Pyroelectric applications of these thin films that have been commercialized or demonstrated to date include thermal imaging and gas detection [3]. To evaluate the quality of a pyroelectric material, different figures of merit exist, depending upon the device requirement. For good voltage response [4], it is necessary to maximize pyrocoefficient p, and lower dielectric constant and loss δ, to increase the figure of merit F_V (p/ε_r) and the figure of merit of F_d $(p/(\varepsilon_r \tan\delta)^{1/2})$. Because tetragonal $Pb(Zr,Ti)O_3$ (PZT) films with better pyroelectric coefficient, Ti-rich tetragonal PZT films have received much attention for infrared detectors applications [5,6].

As is well known, due to the substrate constraint effects and limited thickness, the PZT films usually shows inferior electric properties compared to bulk ceramic materials. However, it is possible to enhance the electric properties of PZT films by growing highly oriented films on Pt/Ti/SiO_2/Si substrates, and many researchers have done a great quantity of work [7–9]. Nevertheless, the issue has not been fully resolved yet, as to pyroelectric films, the effect of film–electrode interface has shown that this effect may be of key importance to the polarization response of pyroelectric thin films, and properties are very much degraded by a defective material at the film–electrode interface [10,11]. So it is necessary to improve electric properties by optimizing the film–electrode interface, and the use of seed layer has been regarded as a simple and effective method [12]. In addition, the fatigue phenomenon and its mechanisms in PZT have been the topic of an extensive number of studies, and several mechanisms have been proposed to explain fatigue, such as oxygen vacancy migration [13] or carrier injection from the electrodes [14]. So it is very important to reduce the oxygen vacancies or other point defects from to overcome the fatigue problem, modifying the film–electrode interface such as using seed layers is regarded as an active and effective solution.

Moreover, it is accepted that Nb doping is effective in improving the pyroelectric coefficient of PZT films [15], but it is a pity that the dielectric constant and loss become very large with the pyroelectric coefficient increasing [6], which is not conducive to obtain large the figure of merit. Therefore, an advantageous property for PNZT thin films applied to pyroelectric device should include two aspects: one is large pyroelectric coefficient, the other is the films must exhibit low dielectric constant and loss.

In this study, the effect of 5 nm thick $Pb_{0.8}Ca_{0.1}La_{0.1}Ti_{0.975}O_3$ (PLCT) seed layer on microstructures of PNZT thin films was stud-

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ied, furthermore, the pyroelectric properties and fatigue resistance characteristics of PNZT film with and without PLCT seed layer were also investigated.

2. Experimental

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-$CH_3OCH_2CH_2OH$] as the solvent, the 10 mol% excess Pb solution was used to overcompensate for any Pb loss during high temperature annealing, and 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 0.4 M. The PLCT solution was also prepared for seed layers using the similar procedure and the raw materials were lead acetate trihydrate, titanium isopropoxide, and 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 was 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 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, and the PLCT upper layer was deposited on top of the PNZT thin films and was also pyrolyzed at 450 °C for 2 min. Finally, the films were annealed at 625 °C for 3 min by a rapid thermal annealing (RTA) in oxygen ambience. X-ray diffraction (XRD) characterization of the PNZT thin film was performed by using CuKα radiation. The surface morphology was studied by atomic force microscopy (AFM). Surface and cross-sectional morphologies were observed by scanning electron microscopy (SEM). In order to measure the electrical properties of the films, dot-type platinum electrodes with an area of 3.14×10^{-4} cm^2 were deposited by direct current sputtering, forming the stacked capacitors. Fatigue characteristics of the PNZT films were evaluated using Radiant Precision workstation ferroelectric measurement system (USA). The pyroelectric current was measured using an electrometer, and the temperature was controlled using a temperature test chamber. The formula for calculating pyrocoefficient and detailed measurement were indicated by Sun et al. [16].

3. Results and discussion

In our previous study, the thickness of PLCT seed layer was characterized by X-ray reflectivity techniques [17], and the thickness of PLCT seed layer is chosen to 5 nm in the present study. The inserted illustrations in Fig. 1 shows the AFM images of the surface of 5 nm PLCT seed layer [Fig. 1(b)] and the Pt(1 1 1)/Ti/SiO_2/Si substrate [Fig. 1 (c)], and it can be found that the surface structure have

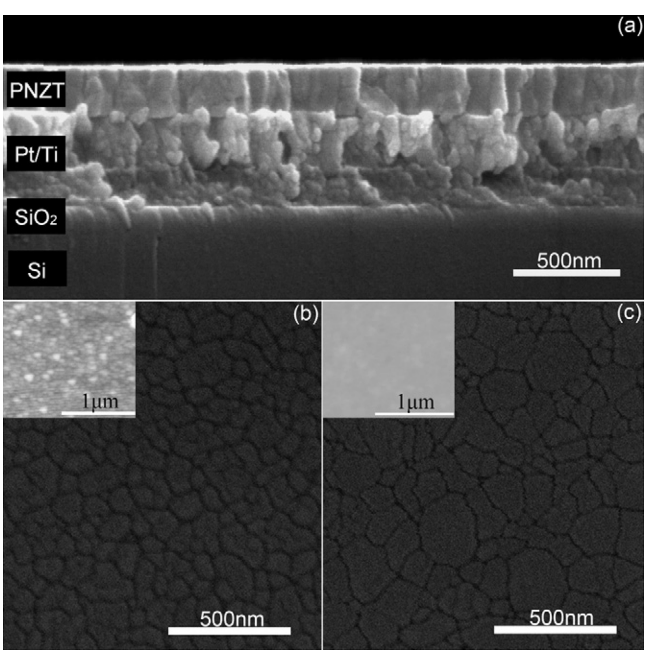

Fig. 1. (a) Cross-sectional view of PNZT/5 nm PLCT thin film; surface morphologies of (b) PNZT/5 nm PLCT thin film and (c) PNZT thin film. The inserted illustrations in (b) and (c) show AFM patterns of 5 nm PLCT/Pt seed layer and Pt(1 1 1)/Ti/SiO_2/Si substrate.

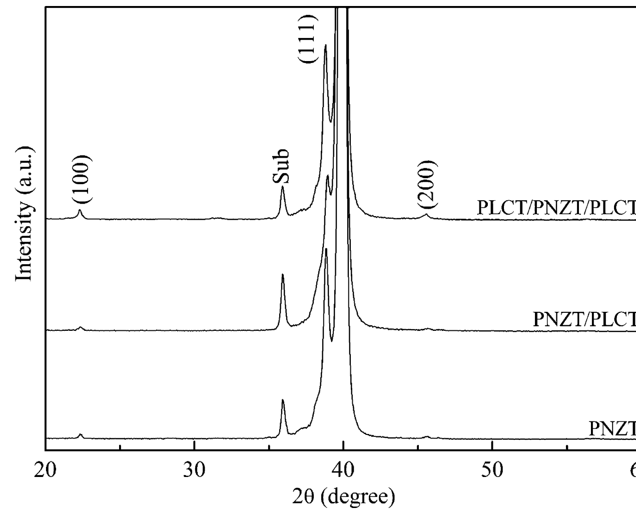

Fig. 2. XRD patterns of PNZT films with and without PLCT seed layer.

obvious difference from the inserted figure. For Pt(1 1 1)/Ti/SiO_2/Si substrate, the surface is very smooth, the surface roughness (RMS) is 1.2 nm. When 5 nm PLCT seed layer is deposited on the Pt (1 1 1)/Ti/SiO_2/Si substrate, the rough surface structures can be observed on the surface, and the RMS increases to 2.1 nm. For comparison, Fig. 1 also shows the morphologies of PNZT thin films with and without PLCT seed layer. As shown in Fig. 1(a), the PNZT film with 5 nm PLCT seed layer exhibits a smooth and crack-free surface, which is composed of densely packed uniform grains, and the clear columnar grain growth demonstrates that this film is well crystallized and high oriented. From Fig. 1(a), it is clear that the film thickness is about 300 nm. Fig. 1(b) and (c) shows the surface morphologies of PNZT thin films with and without PLCT seed layer, respectively, as shown in Fig. 1(b); it was found that the PNZT thin films with 5 nm PLCT seed layer show denser and finer grains, and the grains were uniform, while the PNZT thin film without seed layer shows uneven grain size (large grains among smaller ones). Based on the above results, it is found that the 5 nm thick PLCT as a seed layer could be conducive to obtain good grain growth and smooth surface morphology of the PNZT film, and it is associated with rough surface structures of 5 nm PLCT seed layer, which can offer nucleation sites and reduce the activation energy for the crystallization of PNZT films, forming small uniform grains and low surface roughness.

In the present study, we also fabricate a double-side layer structure (5 nm PLCT/PNZT/5 nm PLCT) to investigate the pyroelectric property and fatigue resistance characteristics. Fig. 2 shows the XRD patterns of the prepared PNZT films, PNZT/5 nm PLCT film and 5 nm PLCT/PNZT/5 nm PLCT film respectively; it can be found that the PNZT films are well crystallized with pure tetragonal perovskite structure after 625 °C for 3 min by a RTA in oxygen ambience, and all of the PNZT thin films exhibit highly (1 1 1)-oriented. Fig. 3 shows the frequency dependence of dielectric constant and loss of the three kinds of PNZT thin films. As shown in Fig. 3, it was found that the dielectric constant of the PNZT thin films changes over the measured frequency range. For the PNZT film, PNZT/5 nm PLCT film and 5 nm PLCT/PNZT/5 nm PLCT, the values of dielectric constant measured at a frequency of 1 kHZ are 653, 480 and 431, and the values of loss tangent are 0.035, 0.022 and 0.019, respectively. It was clear that the dielectric constant and loss of the PNZT films was reduced obviously by using PLCT seed layer.

Pyroelectric coefficient was obtained using a charge integration technique [16]; an electrometer was used to measure the charges at different temperatures with a heating rate of 1 °C/min. Fig. 4 shows the temperature dependence of pyroelectric coefficient, and it was

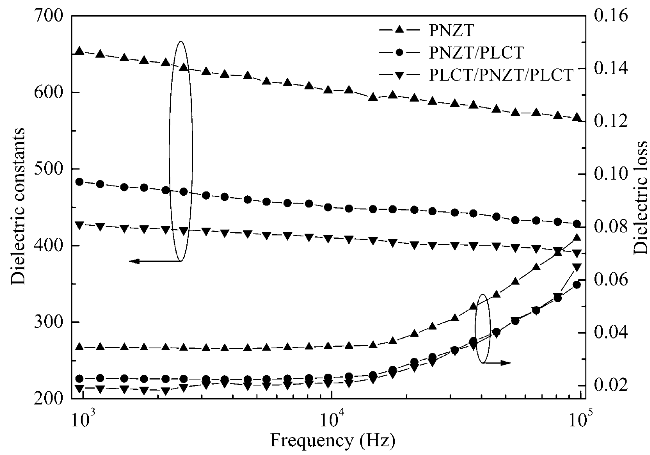

Fig. 3. The dielectric constant and loss of the PNZT thin films with and without PLCT seed layer.

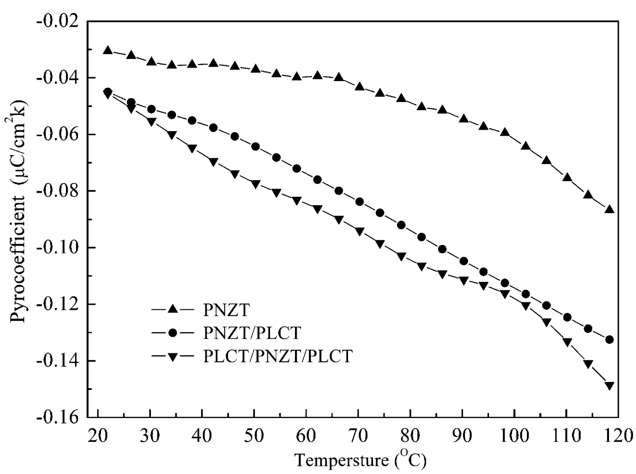

Fig. 4. Temperature dependence of pyroelectric coefficient of the PNZT thin films with and without PLCT seed layer.

found that the pyroelectric coefficient of PNZT thin films could be improved obviously by using PLCT seed layer, the pyroelectric coefficient of PLCT/PNZT/PLCT film obtained from the derivative of the p–T curve is 460 $\mu C/(m^2 K)$ at room temperature (22 °C), and this value is larger than those of films without seed layer and with single-sided bottom PLCT seed layer. This value is also high compared to reported values for the leading pyroelectric thin films, such as 250 $\mu C/(m^2 K)$ for PZT at room temperature [18], 410 $\mu C/(m^2 K)$ at 16 °C for $Ba_{0.8}Sr_{0.2}TiO_3$ [19]. According to the definition of figure of merit: $F_d = p/(\varepsilon_o \varepsilon_r \tan\delta)^{1/2}$, where ε_o is the permittivity of free space; and p, c, ε_r, and $\tan\delta$ are the pyroelectric coefficient, dielectric constant, and dielectric loss of the pyroelectric materials, respectively. Table 1 shows that the pyroelectric parameters of the PNZT films without and with PLCT seed layer at room temperature (22 °C). It was found that the figure of merit F_d for PLCT/PNZT/PLCT film is calculated to be 161 $\mu C/(m^2 K)$, the value is comparable to those of leading pyroelectric thick films [6] or pyroelectric porous

Table 1
Electrical parameters of sandwich structure PNZT films measured at room temperature (22 °C).

	ε_r	$\tan\delta$	p ($\mu C/(m^2 K)$)	F_V ($\mu C/(m^2 K)$)	F_d ($\mu C/(m^2 K)$)
PNZT	653	0.035	296	0.46	62
PNZT/PLCT	480	0.022	445	0.93	137
PLCT/PNZT/PLCT	431	0.019	460	1.07	161

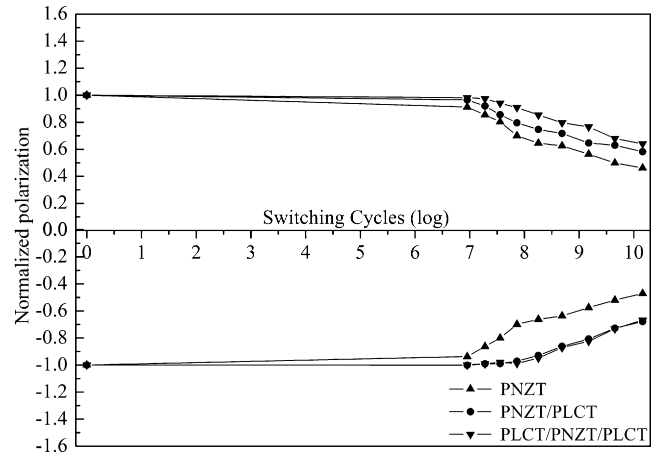

Fig. 5. Fatigue characteristics of PNZT thin films with and without PLCT seed layer.

film [20]. The high figure-of-merit results from PLCT seed layer used on double-side, which effectively reduces the dielectric properties and enhance the pyrocoefficient of PNZT thin film.

Finally, the loss of switchable polarization with repeated polarization reversals that characterized ferroelectric fatigue in the PNZT film is shown in Fig. 5, when cycles with 1 MHz square wave pulse are performed, the PNZT structures without seed layer displays normal and symmetric fatigue behavior, and degradation starts after 10^5 cycles and the film loses more than 53% of its initial polarization value at the end of 10^{10} cycles. The PNZT films with PLCT seed layer, on the other hand, display an asymmetric fatigue behavior. The fatigue resistance was improved obviously on the seed layer side, and it was found that the PNZT/5 nm PLCT film showed a fatigue-free behavior up to 10^8 cycles and 30% degradation at the end of 10^{10} cycles. It must be noted that, for the PNZT/5 nm PLCT film and 5 nm PLCT/PNZT/5 nm PLCT film, the fatigue resistance was very similar in negative region (seed layer side), but PLCT/PNZT/PLCT structure has significant improvement gains over PNZT/PLCT structure in the positive (top electrode) side.

In other works, as to Pb-based ferroelectric thin films, the common seed layer using for interface optimization is $PbTiO_3$ [5] or PbO_x [5,7]. For $PbTiO_3$ seed layers, due to the rather large lattice distortion (c/a = 1.06), this might introduce very large residual stress, thus decreasing the quality and mechanical properties of films, and resulting in film surface cracking, which is not conducive to the application, while for PLCT seed layer, La and Ca doping reduce the lattice distortion (c/a) effectively, which improves the mechanical properties and the film quality greatly. Furthermore, compared to PbO_x seed layers, Shannigrahi and Jang [21] has reported that the effect of La^{3+} from the PLCT seed layer may cause the enhanced fatigue resistance characteristics of PNZT film deposited PLCT seed layer. In addition, in our previous study [22], the PLCT thin films not only shows higher pyroelectric coefficient, more importantly, compared to other PT based ferroelectric thin films, it express relatively low dielectric constant and loss. While for the PNZT thin films, although the pyroelectric coefficient was improved considerably by Nb doping, however, the high dielectric constant is not conducive to obtain large pyroelectric figure of merit [6]. Based on the above reason, the PLCT/PNZT/PLCT structure was prepared and it could be considered as the PNZT and PLCT capacitors connected in series [16], and this structure reduced the dielectric constant and loss of PNZT film greatly.

In the growth process of ferroelectric thin films, nucleation is the first most important step, which determines the quality of the final film. 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, and ferroelectrics materials typically switch by the generation of many new reverse domains at particular nucleation sites [23], so it is very necessary to form nucleation sites at the electrode–ferroelectric interface to improve the electric properties.

In our present study, the concentration of PLCT solutions was very low (0.05 M), and PLCT Sol can overspread the surface of Pt(1 1 1)/Ti/SiO_2/Si substrate completely in the process of spin coating. However, after pyrolyzing at 450 °C on a plate hot, the surface energy of PLCT seed layer is very large, and the residual stress may be also very large, and the process similar to "Ostwald ripening" may occur [24], that is to say, the growth rate of the larger grains is much higher, this is the reason that the RMS of 5 nm thickness PLCT seed layer is comparatively large. When the PLCT seed layer is not applied, no rough surface structures are observed on the surface of Pt(1 1 1)/Ti/SiO_2/Si substrate, and there is also no increased nucleus size at the border of the seed layer. While the activation energy for the continuation of growth is much smaller, such a growth is prone to start from arbitrary defects, which might lead to abnormally large grains among smaller ones, or at least to a large grain size variation, which degrades the electrical properties of the thin film. When 5 nm PLCT is used as seed layer, the introduction of the PLCT seed layer between the PNZT film and Pt electrode interlayer can form many rough surface structures, and these structures can offer nucleation sites and reduce the activation energy for the crystallization of PNZT films. In this case, the PNZT film switch by the generation of many new reverse domains at particular nucleation sites, which makes the film polarization response easily, thus improves the pyroelectric coefficient [(dP_r/dT), P_r is remnant polarization and T is temperature] of PNZT film. Similarly, for PLCT/PNZT/PLCT film, besides the nucleation sites at the electrode–ferroelectric interface, the PLCT seed layer in the top electrode can also offer nucleation sites, and the amount of reverse domains of the PLCT/PNZT/PLCT film is more than those of the PNZT/PLCT film, which results in that the pyroelectric coefficient is much larger. In addition, as mentioned above, for the PNZT thin film with 5 nm thickness PLCT seed layer, the rough surface structures on the surface of Pt(1 1 1)/Ti/SiO_2/Si substrate can offer nucleation sites to reduce the activation energy and make the PNZT films crystallize at low temperature [17], which might reduce or compensate for the Pb-site vacancies as well as the oxygen vacancies effectively. Furthermore, in the case of this PLCT/PNZT/PLCT structure, at their interfaces between the electrode and PNZT films, the effect of La^{3+} from the PLCT seed layer can be considered as a donor [21], and these donor doping processes can also help to reduce or compensate for the vacancy-type defects which can be created with Pb volatilization. These reasons may cause the enhanced fatigue resistance characteristics of PNZT film deposited PLCT seed layer.

4. Conclusion

In the present study, the PNZT thin films with and without PLCT seed layer have been prepared on Pt/Ti/SiO_2/Si substrates by using a sol–gel process. It is found that the rough surface structures caused by 5 nm thick PLCT seed layer can offer nucleation sites and reduce the activation energy for the crystallization of PNZT films, and also lead to the polarization response easily. By introducing 5 nm thick PLCT seed layer between the PNZT film and Pt electrode, PLCT/PNZT/PLCT structure thin film displayed enhanced large pyroelectric coefficient (460 $\mu C/(m^2 K)$) and high figure-of-merit ($F_d = 161\ \mu C/(m^2 K)$) at room temperature. In addition, the PLCT seed layer helps to attain better PNZT/PLCT/Pt interfaces, which leads to decrease of oxygen vacancies or other point defects from the PNZT film, and achieving the enhanced fatigue resistance characteristics of thin film. These results indicate that it is a good method for obtaining excellent pyroelectric properties of PNZT film using PLCT seed layer, which indicate that the film prepared is a good candidate for infrared detectors applications.

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