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Temperature-dependent ferroelectric properties of $(Pb_{0.75}La_{0.25})TiO_3$ thin films

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$(Pb_{0.75}La_{0.25})TiO_3$ (PLT25) thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by pulsed laser deposition. X-ray diffraction revealed that the well-crystallized films have a perovskite structure and are randomly oriented. Uniform surface with rodlike grains and dense cross-section microstructures with sharp interfaces were recorded by scanning electron microscopy. The remanent polarization and coercive field of the films increased with the temperature decreased from 296 K to 97 K, while the saturated polarization remained almost constant. This temperature-dependent electrical property of PLT25 films was discussed in detail by the trapped defect induced domain pinning model.

Key words: $(Pb_{0.75}La_{0.25})TiO_3$, room temperature, low temperature, ferroelectric property

1. INTRODUCTION

Ferroelectric thin films are potentially important for various functional devices. Therefore, probing the way to improve ferroelectric properties is of great interest. Generally, optimizing the known ferroelectrics by substitution and searching for new ferroelectrics are the basic two ways to get ferroelectrics with improved properties. Recently, it is reported that by using the selective substitution concept, one can design the electrical property of ferroelectrics.[1] For example, in the La-substituted $PbTiO_3$, $(Pb_{1-x}La_x)TiO_3$ (PLTx), material system, an appropriate control of La composition allows for a wide range of dielectric, piezoelectric, pyroelectric, nonlinear electro-optic, and ferroelectric properties.] Thus PLTx are the promising candidates for use in various technological applications such as dynamic random access memory (DRAM), micro-electro-mechanical system (MEMS), and pyroelectric infrared (IR) sensors, and non-volatile ferroelectric random access memory (NVFRAM), etc. [2-5]

In recent years, temperature-dependent structural and dielectric properties of PLTx thin films with different La composition were studied. [6,7] However, in the case of ferroelectric properties, in spite of the intensive investigation of PLTx thin films with various La compositions at room temperature, [8,9] the low temperature ferroelectric properties of PLTx thin films have seldom been investigated. Nevertheless, the temperature dependence of ferroelectric properties is one of the most important characteristics in view of not only engineering but also physical properties. Also, It is well known that PLTx films suffer from serious polarization degradation, i.e. ferroelectric fatigue. The temperature dependence can be used to study the activation process fatigue. Therefore, it is necessary to investigate the low temperature ferroelectric properties of PLTx films. In this letter, $Pb_{0.75}La_{0.25}TiO_3$ (PLT25) thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by pulsed laser deposition (PLD) and their room temperature structural characteristics and temperature-dependent ferroelectric properties were studied

2. EXPERIMENTS

PLT25 ceramics used as PLD targets were prepared by conventional solid state reaction method. The starting materials are PbO (excess by 20%), TiO_2, and La_2O_3. The sintering process is similar with other report.[2] The PLD processes were performed by using a KrF excimer laser (LPX205i, Lambda Physik) with wavelength of 248 nm and pulse-width of 30 ns. The PLT25 thin films were fabricated on Pt/Ti/SiO2/Si substrates at 700°C for 25 min. During each deposition, the pressure of flowing oxygen was 30 Pa and the laser frequency was 5 Hz. After deposition, the films were *in-situ* annealed at 700°C for 10 min with 0.5 atm oxygen pressure. For electrical measurements, Pt top dot electrodes of 200 μm in diameter were sputter deposited with shadow mask at room temperature. Finally, these $Pt/PLT25/Pt/Ti/SiO_2/Si$ (Pt/PLT25/Pt) capacitors were post-annealed at 700°C for 10 min with flowing oxygen.

The crystallinity of the PLT25 films was analyzed by x-ray diffraction (XRD) using a

Rigaku-D/Max-rA diffractometer with Cu $K\alpha$ radiation. The surface and cross-section microstructures were recorded by a XL30 Philips scanning electron microscopy (SEM). A RT66A ferroelectric tester of Radiant Technologies was used for ferroelectric properties measurements. Low temperature ferroelectric behaviors were measured in a temperature-controllable vacuum chamber (20Pa) where the samples were packaged. A pair of shielded cables was used to connect the Pt electrodes and the RT66A ferroelectric tester.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD scan pattern of the Pt/PLT25/Pt capacitors. The peaks in the XRD pattern are indexed to be the film and substrate diffraction planes. Two emphasizes should be noted about the result. Firstly, it indicates the PLT25 thin films are randomly oriented. Secondly, the sharp peaks suggest that the PLT25 films are well-crystallized.

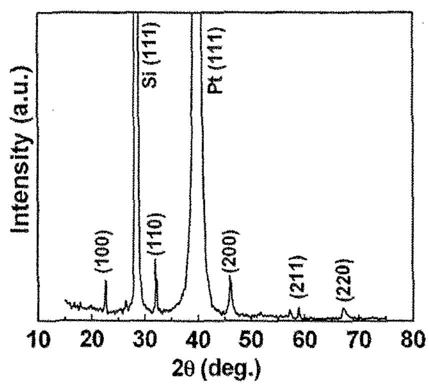
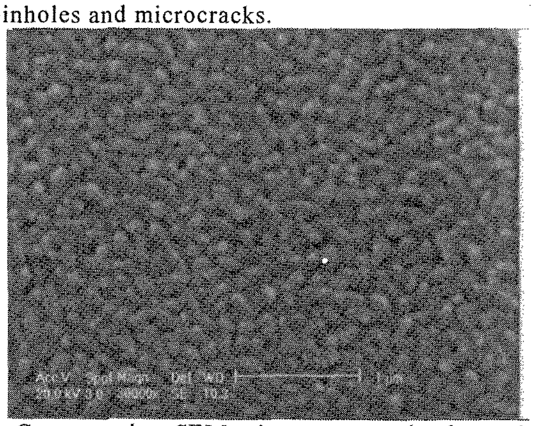
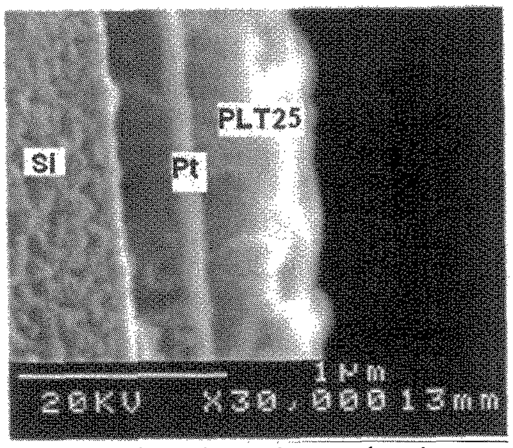


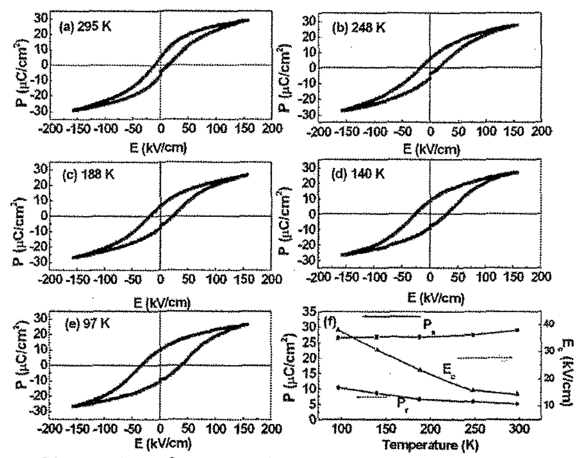
Fig. 2 shows the SEM surface morphologies of the PLT25 films. It can be seen that the PLT25 films consist of rodlike grains. In the scanned area, the dense and uniform surface shows no pinholes and microcracks.



Cross-section SEM microstructure is shown in Fig. 3. Clearly, the dense and homologous PLT25 films are column-like grown. The interface between PLT25 films and Pt bottom electrodes is very sharp, indicating that there is no interdiffusion between the capacitors. The average thickness of PLT25 films was determined to be 510 nm.



Temperature-dependent hysteresis loops of PLT25 films with the applied field of about 157 kV/cm are plotted in Fig.4(a)-(e). Note that all the loops are well-saturated. With the temperature decreased from 295 K (room temperature) to 97 K, the saturated polarization (P_s) shows almost neglectable decrease. However, the remanent polarization (P_r) and coercive field (E_c) increased greatly from 5.2 $\mu C/cm^2$ and 14.8 kV/cm to 10.1 $\mu C/cm^2$ and 38.1 kV/cm, respectively. The variations of P_s, P_r, and E_c against temperature were plotted in Fig. 4(f).



Charged defects such as oxygen vacancy are mobile and will diffuse during electrical switching of ferroelectric domain. This diffusion results in trapping of the defects at domain boundaries because these energetically favorable positions act as energy well and such trapping can minimize free energy. Trapped defects suppresses the switchable polarization by pinning the neighboring domains, which leads to the decrease of switchable polarization.[10] With the temperature decreasing, the wall potential will show a boxlike shape, which induces a defect to strongly pin it.[11] Also, the potential well is deepened with the decreasing temperature.[12] Therefore, to detrap these trapped defects at low temperature, high E_c is necessary. i.e., lower the temperature, higher the E_c value, as plotted in Fig. 4(f). Nevertheless, at low temperature, if the trapped defects are detrapped by an external electrical field, the ferroelectric domains can be switched and thus contribute to switchable polarization as almost normally as that at room temperature, suggesting the almost constant P_s for saturated hysteresis loop against the temperature. However, when the external electrical field is decreased from maximum to zero, the defects can trap at the domain boundaries again and low temperature will make it difficult for the switched domain to depolarize, i.e., the switched domain is frozen. This results in less relaxed polarization at lower temperature, which is responsible for the observed increasing P_r with decreasing temperature.

4. CONCLUSION

In conclusion, polycrystalline PLT25 thin films were fabricated on Pt/Ti/SiO2/Si substrates by PLD. The crystallinity and microstructures were analyzed by XRD and SEM. Temperature-dependent ferroelectric properties of the films were studied. It is experimentally established that at the same applied external electrical field, the Ps kept almost constant while Pr and Ec increased with decreasing temperature. The results might be useful for understanding low temperature ferroelectric behavior of ferroelectric thin films.

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