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The ferroelectric and antiferroelectric behavior of $PbTiO_3/PbZrO_3$-multilayered thin films

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Abstract

$PbZrO_3/PbTiO_3$-multilayered thin films have been fabricated on $Pt/Ti/SiO_2/Si$ wafers using a sol–gel process. The multilayered thin film shows typical XRD patterns with a polycrystalline perovskite structure. The electric field-induced antiferroelectric-to-ferroelectric phase transformation behavior was examined by the polarization versus electrical field (*P–E*) and the capacitance versus voltage (*C–V*) measurements, both carried out at room temperature. Dielectric properties were measured as a function of temperature and frequency. The antiferroelectric layer was expected to reduce the degradation of polarization, and the ferroelectric layer was expected to maintain the remnant polarization in the multilayered thin film structure.

Keywords: A. Sol–gel process; C. Electric properties; Multilayered thin film; Ferroelectricity and antiferroelectricity

1. Introduction

The ferroelectric (FE) thin films have been wide applications since their ferroelectric and dielectric properties such as memory, sensor, infrared (IR) detectors, and microelectromechanical system. Antiferroelectric (AFE) thin films also receive attentions due to their applications in microactuators and high-energy storage capacitors. Antiferroelectric materials usually display a large field-induced strain resulted from the electric field-induced antiferroelectric to ferroelectric phase transition.

There are a few papers that are related to the ferroelectric multilayers have been reported [1–5]. Growth of the ferroelectric multilayers is of interest because of the exploration of new functional dielectric and ferroelectric materials. Furthermore, it is expected that the characterization of the dielectric multilayers provide some microscopic understanding of the origin of the excellent ferroelectricity.

In this study, we fabricated $PbZrO_3/PbTiO_3$ (PZ/PT) multilayered thin films using sol–gel processing by which the perovskite phase can be grown at relatively low temperatures and thermal interdiffusion of PZO and PTO layers can be avoided and reported their structural and ferroelectric properties.

2. Experimental processing

Details of the sol–gel process for PZO thin films can be found in the article by Zhai et al. [6]. The preparation of PTO thin films is same as processing of the PZO thin film. The difference is only the starting materials: the zirconium isopropoxide [$Zr(OC_3H_7)_4$] was substituted by titanium isopropoxide.

Lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$], titanium isopropoxide $Ti(OC_3H_7)_4$ and zirconium isopropoxide [$Zr(OC_3H_7)_4$] were used as starting materials. The 2-methoxyethanol $CH_3OC_2H_4OH$ was used as solvent. The concentration of the final solution was adjusted to about 0.3 M. After aging the hydrolyzed solution for 48 h, deposition was carried out on the $Pt/Ti/SiO_2/Si$ (1 0 0) substrates by spin coating at 3000 rpm for 30 s for each layer. The thickness of Pt, Ti, and SiO_2 layers are 150, 50, and 150 nm, respectively.

Each spin-on layer was heat-treated at 600 °C for 5 min. The deposition and heat treatment were repeated until the

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desired layers were reached. A capping layer of 0.1 M PbO precursor solutions was spin-coated on the top of the film before the final heat treatment at 650 °C for 30 min. The top PbO capping layer served the purpose to prevent excessive Pb loss during the final heat treatment, thus enabling the multilayered thin films to crystallize completely into the perovskite structure. The thickness of multilayered thin films is about 470 nm. The thickness of each layer is about 80 nm for $PbZrO_3$ and $PbTiO_3$, respectively. The structures of the multilayered films were represented as $[(PZO)_t/(PTO)_t]_n$, where t is the thickness of single layer and n is the number of $[(PZO)_t/(PTO)_t]$ layers. We prepared multilayered films of $[(PZO)_{40}/(PTO)_{40}]_6$ and $[(PZO)_{80}/(PTO)_{80}]_3$.

For electrical measurements, top gold electrodes of 400 μm × 400 μm were deposited by dc sputtering. The capacitance–voltage (C–V) and capacitance–frequency (C–f) characteristics were measured using an Agilent 4284A LCR meter. The sample's temperature was varied using a Delta chamber during the electrical property measurements. The ferroelectric properties were measured using a Radiant Technologies Precision Pro ferroelectric tester. The phase identification was examined using a BRUCKER D8 powder diffractometer equipped with Cu Kα radiation. The film thickness was determined by scanning electron microscopy (JOEL JSM-6335F).

3. Results and discussion

Fig. 1 shows the θ–2θ X-ray diffraction patterns of the multilayered thin films. The multilayered thin film shows typical XRD patterns with a polycrystalline perovskite structure, although no preferred orientation is observed. Diffraction peaks were observed in both $PbTiO_3$ and $PbZrO_3$ layers, but no Pb(Zr, Ti)O_3 solid solution was detected in the XRD analysis, suggesting that the $PbTiO_3$ and $PbZrO_3$ layers did not react at the interlayers upon heating to 650 °C.

The electric field-induced AFE-to-FE switching behavior was examined by P–E measurements performed at 1 kHz. The P–E double hysteresis loops obtained at room temperature are shown in Fig. 2 for the PZO/PTO multilayered thin films. The double hysteresis behavior in P–E curves clearly demonstrates the antiferroelectric nature of $[(PZO)_{80}/(PTO)_{80}]_3$ multilayered thin films at room temperature and exhibit larger remanent polarization. It is demonstrated that the coexistence of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ phase together. The antiferroelectric layer was expected to reduce the degradation of polarization, and the ferroelectric layer was expected to maintain the remnant polarization. In multilayered thin film $[(PZO)_{40}/(PTO)_{40}]_6$, the P–E loop looks like a normal response of ferroelectric thin film. The P–E response of multilayered thin film at room temperature could be attributed to the PZT phase coexisted with $PbZrO_3$ and $PbTiO_3$ phase, which caused the a strong ferroelectric and a weak antiferroelectric behaviors.

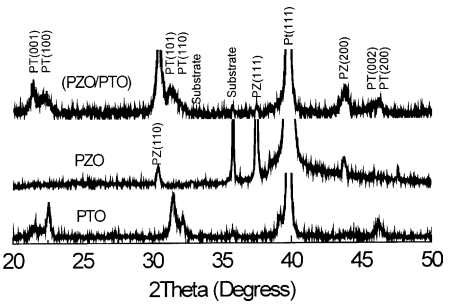

Fig. 1. XRD patterns of $[(PZO)_{40}/(PTO)_{40}]_3$-multilayered films annealed at 650 °C for 30 min.

The temperature dependencies of dielectric constant and dielectric loss of multilayered thin film measured at different frequencies are presented in Fig. 3. The films display a well-pronounced dielectric peak close to 150 °C, that is the Curie temperature of antiferroelectric phase $PbZrO_3$ [6,7]. It is evident from Fig. 3 that a strong frequency dispersion of dielectric constant exists at temperatures above the transition point. The origin of this frequency dependence is not absolutely clear. It could be due to the existing ferroelectric–antiferroelectric competition at temperatures above the transition.

The ε–E characteristics of multilayered thin films prepared on the Pt/Ti/SiO_2/Si substrate were measured at 1, 10, 100, and 1000 kHz, respectively. As shown in Fig. 4 the ε–E characteristics of multilayered thin film have the typical

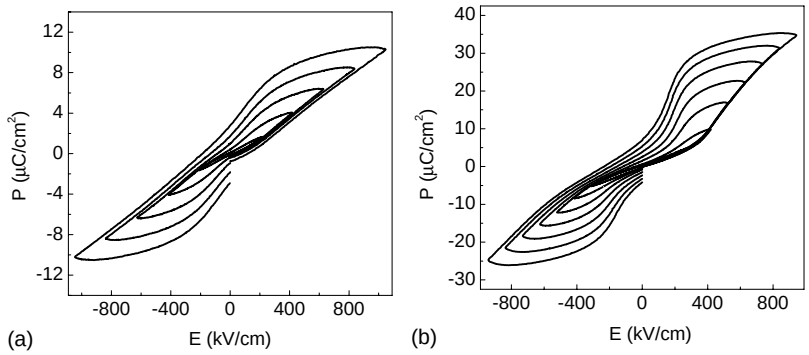

Fig. 2. Hysteresis loops (P–E) of PZ/PT-multilayered films (a) $[(PZO)_{40}/(PTO)_{40}]_6$ and (b) $[(PZO)_{80}/(PTO)_{80}]_3$ (measured at 1 kHz).

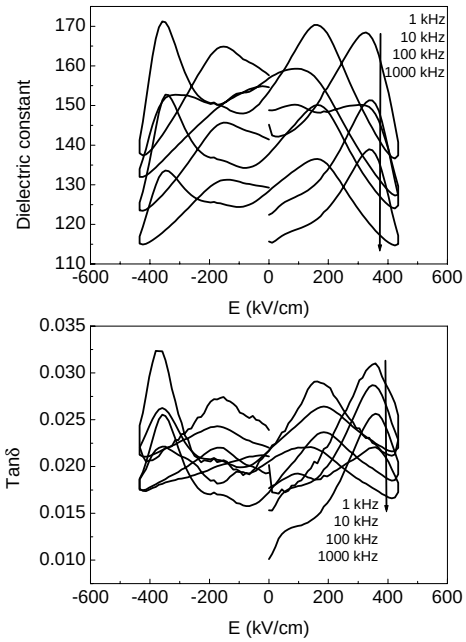

Fig. 3. Dielectric constant versus electric field (ε–E) curves of $[(PZO)_{80}/(PTO)_{80}]_3$-multilayered thin films annealed at 650 °C for 30 min.

patterns, which is similar to that of other antiferroelectric materials. The dielectric losses have also the similar patterns. As the dc bias field is increased, the incremental dielectric constant increases until the threshold field is reached. At this point the dielectric constant was decreased until a minimum at the ferroelectric saturation is observed. Upon reduction of the dc bias field, the dielectric constant

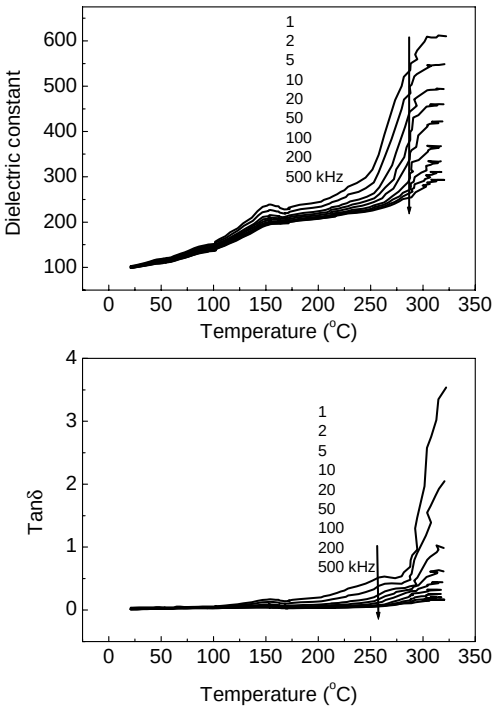

Fig. 4. Dielectric constants and tan δ loss as a function of temperature of $[(PZO)_{80}/(PTO)_{80}]_3$-multilayered films, measured at different frequency.

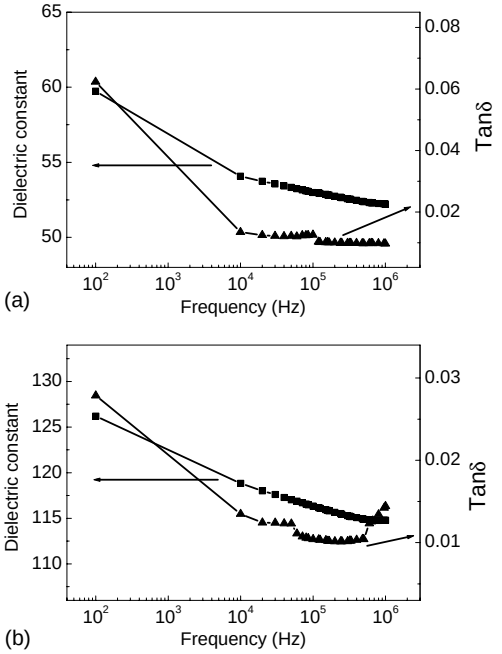

Fig. 5. Dielectric constant and loss of multilayered thin films (a) $[(PZO)_{40}/(PTO)_{40}]_6$ and (b) $[(PZO)_{80}/(PTO)_{80}]_3$, annealed at 650 °C, as function of frequencies.

was increased until reverse switching is initialized and then decreases to a zero field value that is greater than the dielectric constant of the virgin samples. This increase is due to poling of the sample [8]. It is evident from Fig. 4 that a strong frequency dispersion of dielectric constant exists at room temperatures under strong dc field.

Fig. 5 shows the frequency dependence of the dielectric constant and dielectric loss at room temperature. The dielectric constant shows dielectric dispersion typical of the thin films, and low losses are obtained at frequencies less than 1 MHz. The dielectric constant of the $[(PZO)_{80}/(PTO)_{80}]_3$ multilayered thin film was 116 with a dielectric loss of 0.01 and $[(PZO)_{40}/(PTO)_{40}]_6$ multilayered thin film was only 55 with a dielectric constant of 0.01 at 100 kHz. The dielectric constant of multilayered thin films decreased by increasing the stacking periodicity. This result is consistent with the $BaTiO_3/SrTiO_3$ superlattices [9]. The dielectric loss was about 1% irrespective of the stacking periodicity. The dielectric constant showed a slight tendency, to decrease with higher frequencies, the increasing tendency of dielectric loss was obviously at higher frequency ranges for $[(PZO)_{80}/(PTO)_{80}]_3$ multilayer films, over 8×10^5 Hz, several possible causes exist for such behavior, including the hypothesis of the influence of the contact resistance between the probe and the electrode, resonance due to high dielectric constant.

4. Conclusion

$PbZrO_3/PbTiO_3$-multilayered thin films were prepared on $Pt/Ti/SiO_2/Si$ wafers using a sol–gel process. The multiplayered thin film shows typical XRD patterns with a

polycrystalline perovskite structure. Diffraction peaks were observed in both $PbTiO_3$ and $PbZrO_3$ layers, but no Pb(Zr, Ti)O_3 solid solution was detected in the XRD analysis. The electric field-induced antiferroelectric-to-ferroelectric phase transformation behavior was affirmed by the polarization versus electrical field and the capacitance versus voltage measurements. The antiferroelectric layer was expected to reduce the degradation of polarization, and the ferroelectric layer was expected to maintain the remnant polarization in the $PbZrO_3$/$PbTiO_3$-multilayered thin film structure.

Acknowledgements

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