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2003 J. Phys.: Condens. Matter 15 963

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Direct current field adjustable ferroelectric behaviour in (Pb, Nb)(Zr, Sn, Ti)O₃ antiferroelectric thin films

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Received 13 November 2002, in final form 24 December 2002

Published 3 February 2003

Online at stacks.iop.org/JPhysCM/15/963

Abstract

(Pb, Nb)(Zr, Sn, Ti)O₃ antiferroelectric (AFE) thin films have been fabricated on LaNiO₃/Pt/Ti/SiO₂/Si wafers using a sol-gel process. The electric field-induced antiferroelectric-to-ferroelectric (AFE-FE) phase transformation behaviour and its dependence on the temperature were examined by investigating the dielectric constant and dielectric loss versus temperature and electrical field. The AFE-FE phase transformation temperature can be adjusted as a function of the DC bias field and the thickness of the thin film. With increasing DC bias field, the FE phase region was enlarged, the AFE-FE transformation temperature shifted to lower temperature, and the ferroelectric-to-paraelectric transformation temperature shifted to higher temperature. With increasing film thickness, the modulation effect of the DC bias field on the AFE-FE phase transformation temperature is increased.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The antiferroelectric (AFE) materials exhibiting the electric field-induced antiferroelectric-to-ferroelectric (AFE-FE) phase switching have received increasing attention due to their potential usage in micro-actuators, digital memories, and high-energy storage capacitors. Some of the recently studied AFE systems include PbZrO₃ [1], (Pb, La)(Zr, Sn, Ti)O₃, and (Pb, Nb)(Zr, Sn, Ti)O₃ [2–8]. The composition-dependent electric properties of the AFE-FE phase switching [3–5] as well as the strain and the temperature dependence of the dielectric response have been examined [4–6].

In true AFE materials the switching of the polarization has a different mechanism; no spontaneous polarization exists in AFE materials, and the orientations of the dipoles are alternately aligned in opposite directions. The field-induced ferroelectric (FE) phase is stable only under high field, and at low fields the FE phase returns to the AFE state. The

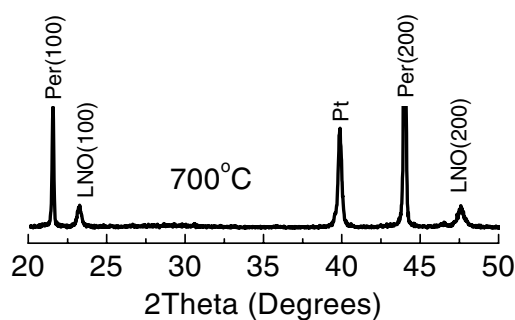


Figure 1. An XRD pattern of a sol-gel-derived $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ thin film annealed at 700°C .

phase change between the AFE state and the FE state can be forced by an electric field, or a hydrostatic pressure, or temperature change. AFE materials may also display a large field-induced strain resulting from the electric field-induced switching from the AFE to the FE state. $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ is the most extensively studied AFE material. However, AFE-FE switching properties have not been investigated in detail for the highly oriented $(\text{Pb, La})(\text{Zr, Sn, Ti})\text{O}_3$ and $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ thin films or at high DC bias field.

In this paper, the $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ thin films *with strongly preferred (100) orientation* were prepared by sol-gel processing. The DC bias field-and temperature-induced AFE-FE phase transformation, the ferroelectric-to-paraelectric (FE-PE) phase transformation, and the phase transformation as a function of film thickness and temperature are discussed.

2. Experimental procedures

The AFE composition $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.82}\text{Sn}_{0.12}\text{Ti}_{0.04})_{0.98}\text{O}_3$, which is close to FE phase boundary in the PNZST ternary system, was chosen for this work. The details of the sol-gel process for PNZST thin films were described in [9]. After aging the hydrolysed solution for about 48 h, deposition was carried out on the $\text{LaNiO}_3/\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}(100)$ substrates by spin coating at 3000 rpm for 30 s for each layer. The thicknesses of the LaNiO_3 (LNO), Pt, Ti, and SiO_2 were 150, 150, 50, and 150 nm, respectively. The LNO layer was deposited on platinumized Si substrates using the magnetron sputtering technique [10]. The deposition and heat treatment were repeated several times to obtain films of different thicknesses. A capping layer of 0.8 M PbO precursor solution was added at the end before the films were annealed at 700°C for 30 min to form the perovskite phase. For the electrical measurements, gold electrode pads— $400\ \mu\text{m}$ squares—were made on top of the PNZST films by DC sputtering. The electrical properties were measured using an Agilent 4284A LCR meter and a Radiant Technologies Precision Pro FE tester. The phase and preferred orientation of the PNZST were studied using a SIEMENS D-500 powder x-ray diffractometer. The thicknesses of the thin films were determined by SEM.

3. Results and discussion

Figure 1 shows XRD patterns taken at room temperature from $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ films annealed at 700°C . The perovskite phase for the $(\text{Pb, Nb})(\text{Zr, Sn, Ti})\text{O}_3$ thin films deposited on LNO/Pt/Ti/SiO₂/Si substrates was obtained and had a preferred (100) orientation.

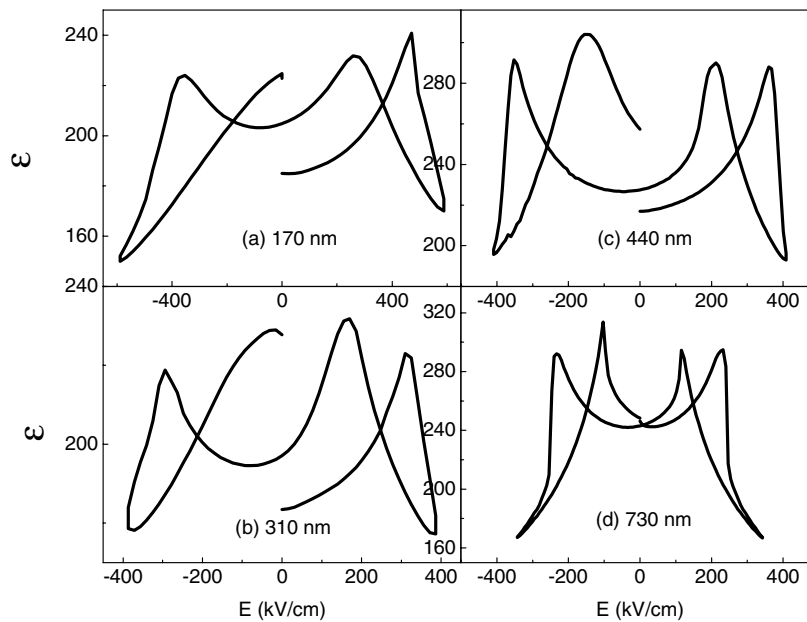


Figure 2. Variation of the dielectric constant of (Pb, Nb)(Zr, Sn, Ti)O₃ thin film as a function of the DC bias at 20 °C. (a) 170 nm, (b) 310 nm, (c) 440 nm, and (d) 730 nm.

Figure 2 shows the ϵ - E (DC bias) characteristics of the PNZST films deposited on the LaNiO₃/Pt/Ti/SiO₂/Si substrates with thicknesses of the thin films of (a) 170 nm, (b) 310 nm, (c) 440 nm, and (d) 730 nm. The mode of measurement is as follows: 0 to E_{max} , then E_{max} to $-E_{max}$, and $-E_{max}$ to 0. The presence of the double-butterfly variation corresponds to the forward and reverse switching fields of the phase transformation (from the AFE-FE phase transformation to the FE-to-AFE phase transformation). The shapes of the ϵ - E curves change and depend on the thickness. The switching field of the AFE-FE phase transformation decreased rapidly with increasing of film thickness. For the thickness of 170 nm when the cycle was finished, polarization was induced in the thin films due to the dipoles which cannot return to the initial state of antiparallel configuration after only one switching cycle (figure 2). We will discuss this phenomenon in another paper.

The P - E curves of thin films of different thicknesses, (a) 170 nm, (b) 310 nm, (c) 440 nm, and (d) 730 nm, measured at 20 °C, are shown in figure 3. It is evident that the magnitude of the AFE-to-FE switching field decreased with increasing thin-film thickness. The phase AFE-to-FE transformation was investigated over a broad temperature range. It is clear from figure 4 that the magnitude of the AFE-to-FE switching field (determined from P - E curves) decreased nearly linearly with increasing temperature for the thin films of thickness 440 nm. On the other hand, as can be seen from figure 5, the magnitude of the AFE-to-FE switching field (determined from P - E curves) decreases rapidly with film thickness. For these thin films, the values of the switching fields for the AFE-FE phase transformation determined from the P - E curves (from the intersections of the tangents drawn to the steepest portions of the P - E curves) are in good agreement with the values determined from the C - V curves (DC bias field). It turns out that, with decreasing film thickness, there is evidence of diminishing AFE behaviour in favour of FE ordering. This is probably due to a combination of the effects of several factors, such as the grain size, the interface layer, and internal stress. The roles of all three effects in modulating the switching field are dependent on the film thickness.

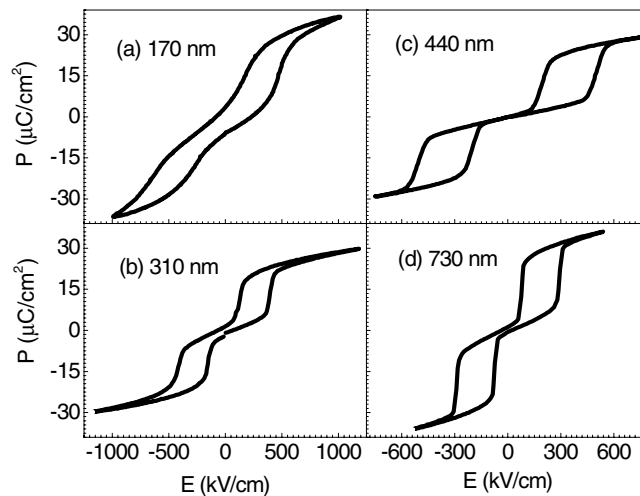


Figure 3. The P - E curves for thin films of different thicknesses, (a) 170 nm, (b) 310 nm, (c) 440 nm, and (d) 730 nm, measured at 20 °C.

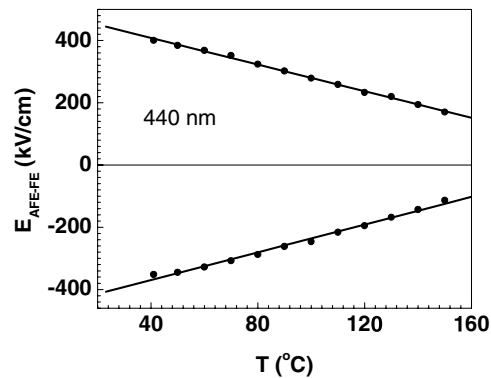


Figure 4. The dependences of the AFE-FE switching field on temperature for the thin films of thickness 440 nm.

Figure 6 shows the dielectric constant of $(\text{Pb}, \text{Nb})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ thin film as a function of temperature for DC bias levels of 0, 120, 150, 180, 222, 250, and 280 kV cm^{-1} . It can be seen in figure 6 that the transition between the paraelectric and AFE phases occurs at about 170 °C for the 440 nm film under no DC bias. When the DC bias was applied to the sample, a transition point appeared in each of the curves. With temperature decreasing to the transition point the dielectric constant increased, while the dielectric constant decreased as the temperature increased to the transition point.

With the application of 180 kV cm^{-1} , the transition of the AFE-FE phase was induced at about 90 °C and was shifted to lower temperature with increasing DC bias field. The FE-PE transition was shifted up in temperature and the FE phase region was enlarged with increasing DC bias. With the application of the DC bias field 280 kV cm^{-1} , the AFE-to-FE phase transformation was at about 42 °C.

The results indicate that the DC bias field strength can adjust the AFE-FE transformation temperature, increase the dielectric constant in the AFE phase region, and decrease the

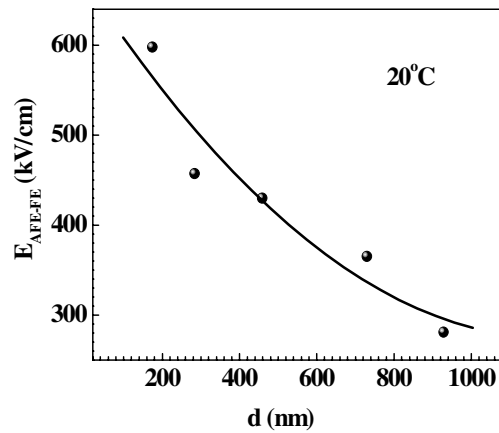


Figure 5. The dependences of the AFE–FE switching field for different thicknesses of the thin films.

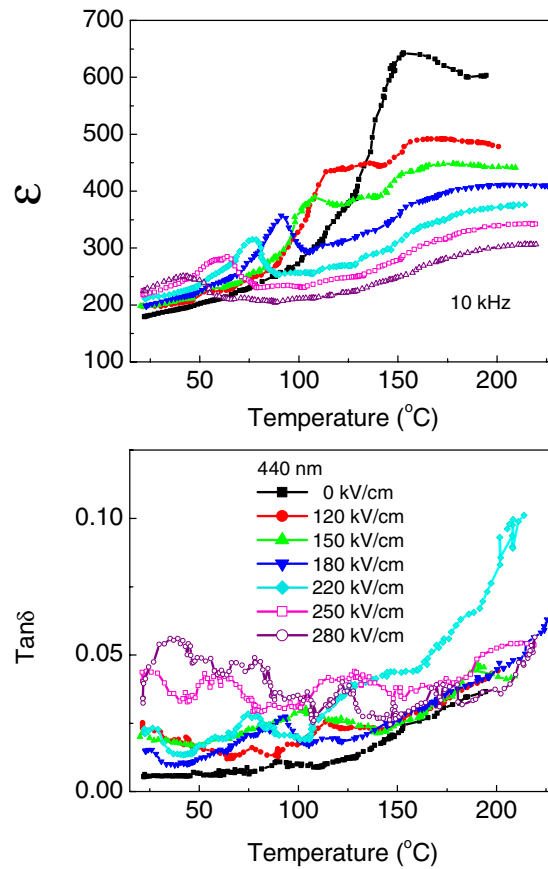


Figure 6. Dielectric constant and dielectric loss as a function of temperature under various DC bias fields for the 440 nm thin film (measured at 10 kHz).

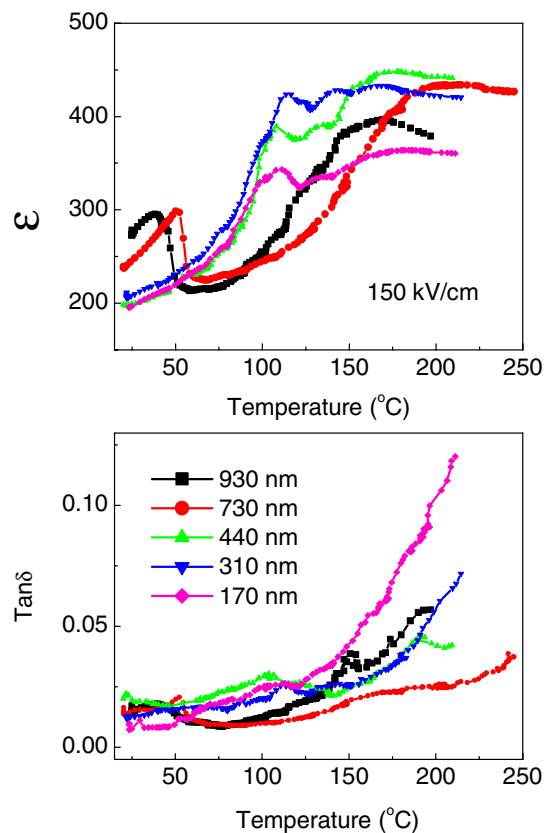


Figure 7. The dielectric constant and dielectric loss of $(\text{Pb,Nb})(\text{Zr,Sn,Ti})\text{O}_3$ thin film as a function of temperature under the DC bias 150 kV cm^{-1} for thin films of different thicknesses (measured at 10 kHz).

dielectric constant in the FE phase region. These results show that the enhancement of long-range force by a DC bias tends to stabilize the low-temperature FE phase, and extend its thermal stability region to higher temperatures. The FE-to-PE peak was shifted to higher temperature and broadened with increasing DC bias field. This behaviour could be due to the presence of a diffuse phase transition in the films, and the characteristics of a diffuse phase transition become more obvious with increasing DC bias field.

Figure 7 shows the dielectric constant as a function of temperature under a DC bias field 150 kV cm^{-1} for different thicknesses of the thin films. It is clearly seen that with increasing thickness of the thin film, the temperature range of the FE phase was enlarged. Under the same 150 kV cm^{-1} DC bias, the AFE-to-FE transition temperatures were 36, 50, 108, 112, and 110°C for thicknesses of the thin film of 930, 730, 440, 310, and 170 nm, respectively. The AFE-to-FE peak was broadened with decreasing thickness of the thin film. When the film thickness is smaller than 440 nm, the modulation effect of the DC bias field on the AFE–FE phase transformation temperature is obviously decreased. A possible explanation for this behaviour is the fine structure of the individual grains, substrate, and thin films (the size effect) [11].

In true AFE materials, the field-induced FE phase is stable only under high field, and at low fields the FE phase returns to the AFE state. The phase change between the AFE state and

the FE state can be forced by means of an electric field or the temperature. Therefore, the FE phase was stabilized either

- (1) by heating the (Pb, Nb)(Zr, Sn, Ti)O₃ thin films under a particular DC bias field or
- (2) by applying high biases at room temperature.

If the electric field and increase in temperature were applied to the sample at the same time, the magnitude of the AFE-to-FE switching field and transition point could be adjusted to a *certain* extent, and the adjustability depends on the thickness of the thin films. The observed electric field-induced shifting of the transformation temperature makes the AFE materials attractive for uncooled infrared sensing applications, where modulation of the operational temperature range is required.

4. Conclusions

The AFE-to-FE phase switching temperature can be adjusted as a function of the DC bias field and the thin-film thickness. With increasing DC bias field, the FE phase region was enlarged and the FE-PE transformation temperature shifted to higher temperature. With decreasing thin-film thickness, the adjustability of the AFE-to-FE temperature is reduced. When the film thickness is larger than 700 nm, the modulation effect of the DC bias field on the AFE-FE phase temperature is clearly increased.

Acknowledgments

This research was supported by grants from the City University of Hong Kong under the project numbers 7001237 and 9380015. The technical assistance of Eric Fu and Daniel Yau is acknowledged.

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