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Perovskite structure development and electrical properties of PZN based thin films

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Abstract

$Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a well known relaxor ferroelectric with excellent dielectric properties for capacitor applications and electromechanical properties for sensor and actuator applications. The perovskite structure stabilization of PZN based ceramics and their respective thin films has limited their applications in these devices. The crystallization behavior and the development of the perovskite structure in PZN with the addition of $Pb(Zr_{0.47}Ti_{0.53})O_3$ (PZT) thin films were investigated using a metal–organic decomposition technique. When the annealing temperature was higher than 600 °C, the perovskite phase crystallized together with a pyrochlore phase. The fractions of the perovskite structure were kept at approximately 80% if the annealing temperature was higher than 700 °C. Otherwise, a new phase appeared when the annealing temperature was approximately 900 °C. Using a lead oxide upper-layer coating technique, a highly ⟨111⟩ oriented PZN based thin film with ~96% perovskite was prepared. The electrical properties of this thin film were characterized with the remnant polarization, $P_r = 25\ \mu C/cm^2$, and the dielectric constant, $\varepsilon' = 712$, respectively.

Keywords: Electrical properties; Films; Perovskites; PZN; PZT; Sol-gel processes

1. Introduction

The relaxor ferroelectric, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), has attracted much attention recently due to its excellent dielectric and electromechanical properties.[1–4] For many applications benefiting from integrated devices, the deposition of PZN thin film would be required. However, synthesizing pure perovskite PZN films has proven difficult because of the relatively poor stability of the perovskite phase relative to, for example, the pyrochlore phase.[5–7] Despite this, using some additive barium titanate (BT), and/or lead titanate (PT) as stabilizer, a variety of thin film synthesis techniques have been used to fabricate PZN and other relaxor based thin films. These include metal–organic decomposition (MOD), sputtering, pulsed laser ablation, and metal–organic chemical vapor deposition (MOCVD).[8–12] Among these, MOD provides a fast and easy way to produce complex oxide thin films and allows the rapid investigation of the inter-relationship among processing, microstructure, composition, and film properties.

For a typical MOD process, an amorphous phase is observed at temperatures around 300 °C. As the annealing temperature is increased, the film transforms from the amorphous phase to a pyrochlore phase and finally to a perovskite phase. However, a polycrystalline PZN with pure perovskite structure is very difficult to prepare by the conventional route due to the high polarizability of Pb^{2+} and its interaction with Zn^{2+} cations, resulting in both a steric and an electrostatic interaction. This destabilizes the perovskite phase, which rapidly transforms to secondary pyrochlore-type phases due to lead loss in thin film fabrication processing. On the other hand, the stability of modified PZN ceramics depends on both the amount of perovskite compound added and the amount of A- or B-site cation replacement. The phase development of PZN with Ti-rich tetragonal $Pb(Zr_{0.47}Ti_{0.53})O_3$ (PZT) addition in bulk materials, prepared by sintering the mixed oxide powder, has been investigated intensively in our previous work.[13] Pure perovskite structure can be obtained when 50% PZT is added. In addition, it is the morphotropic phase

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boundary composition that shows the highest electrical properties in this system.

In the present work, PZN–PZT thin films were grown by a sol-gel process and spin coating on a $Pt/Ti/SiO_2/Si$ substrate. The crystallization behavior and orientation of the thin film is discussed in terms of the annealing and the pyrolysis temperature. Using a lead oxide upper-layer coating, an almost pure perovskite PZN–PZT thin film was obtained and characterized by electrical measurements.

2. Experimental procedure

Sol-gel processing and the spin-coating technique have been frequently used for lead-based thin film preparation.[14] The procedure used in the present study is shown schematically in Fig. 1. The precursors were prepared by reacting niobium ethoxide [$Nb(OC_2H_5)_5$, 99.95%, Aldrich, USA], zinc acetate dihydrate [$(CH_3COO)_2Zn{\cdot}2H_2O$, 99.0%, Kanto, Japan], zirconium propoxide [$Zr(OC_3H_7)_4$, 70%, Fluka Chemie, Switzerland], and titanium isopropoxide {$Ti[(CH_3)_2CHO]_4$, 97.0%, Aldrich, USA} with lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$, 99.0%, Kanto, Japan] in 2-methoxyethanol [$CH_3OCH_2CH_2OH$, 99.0%, Kanto, Japan] as formula of $Pb[(Zn_{1/3}Nb_{2/3})_{0.5}\ (Zr_{0.47}Ti_{0.53})_{0.5}]O_3$ (abbreviated as PZNZT). All the starting precursors dissolved in 2-methoxyethanol separately, and then the B-site precursors were mixed together and refluxed for 1 h. A lead acetate solution was added last and stirred for 1 h. Ethylacetoacetate (0.5%mol) ($CH_3COCH_2COOC_2H_5$, 99.0%, Kanto, Japan) was added dropwise to the solution as a chelating agent. After aging the partially hydrolyzed stock solution for 24 h, the 0.8 M PZNZT precursors were coated onto $Pt/Ti/SiO_2/Si$ substrates with a self-textured Pt (111) orientation. The depositions were made with a 3000 rpm for 40 s three times using a spin coater. The films were baked at 80 °C in air and pyrolyzed on a hot plate at 350 °C between each deposition to first evaporate the solvent and then to decompose the compounds to yield an amorphous inorganic film (move/remove the substrate onto/from hotplate at suitable temperature). After 3 layer depositions of the PZNZT precursor solution, an additional PbO precursor solution for the chosen specimen was deposited to suppress pyrochlore phase formation on the surface due to lead loss by evaporation during annealing. After spin coating the PbO solution the substrate was dried at 150 °C. Finally, a quick, final, annealing process at different temperatures for 10 min was done to study the crystallization behavior and phase development in a rapid thermal annealing furnace, capable of heating the substrates with very rapid (up to 400 °C/min) controlled heating cycles. In order to measure the electrical properties, Pt top electrodes were deposited on the PZNZT films.

The thickness and the morphology of thin films were measured using a field-emission scanning electron microscope (FE–SEM) (JSM-6330F, JEOL, Japan). The crystallinity of the PZNZT thin film was analyzed by X-ray diffraction (XRD) (MXP18A-HF, MAC Science, Japan) using CuK_α radiation and a graphite monochromator with a 2θ range of 20 to 60°. A step scan with a step size of 0.02 was used with a counting time of 1 s/step. The capacitance dependence of the electric field (C–V) curves of the PZNZT thin films were measured using a computer-controlled impedance analyzer

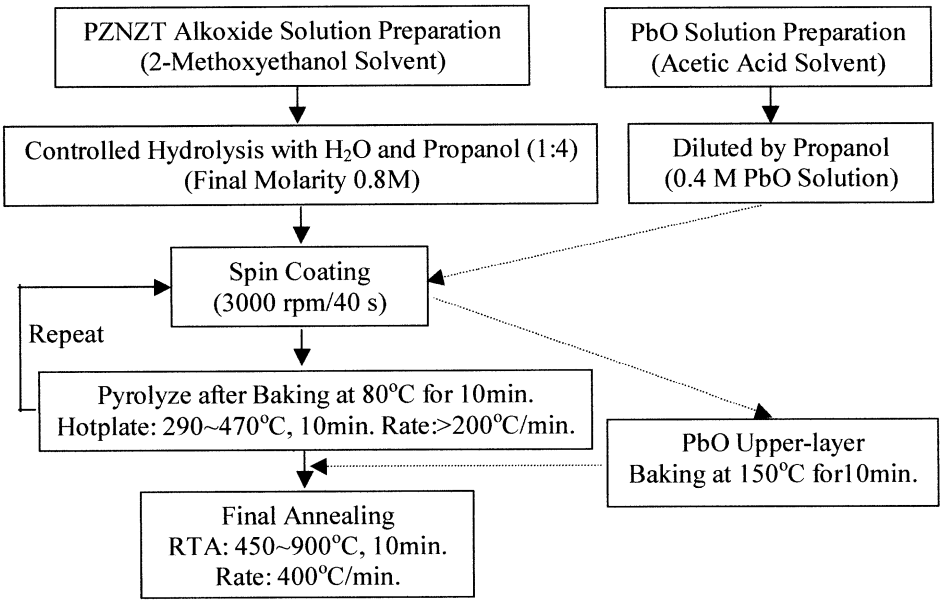

Fig. 1. Procedure for preparing sol-gol derived PZNZT thin film on a $Pt/Ti/SiO_2/Si$ substrate.

(HP4194A, Hewlett-Packard, USA). The polarization–electric field (P–E) hysteresis loops were performed with a standardized ferroelectric test system (TF Analyzer 2000, AixACT Technologies, Germany).

3. Results and discussion

The phase development in the annealed coatings was analyzed by XRD and the results are shown in Fig. 2. A broad peak was evident between 28–30° after thermal treatment at 450 °C, and was assigned to the (111) peak of the fluorite structure and reflects the nanocrystalline nature of the phase. This peak developed into the pyrochlore phase together with the appearance of (111) peaks of a perovskite phase above 600 °C. The crystallization behavior of the perovskite phase increased with increasing annealing temperature, which indicates the coexistence of the two phases in the specimens. Even after high-temperature heat treatment, the specimen also contained the perovskite as well as the pyrochlore phase. On the other hand, some new second phase appeared when the temperature approached 900 °C. Using the formula, $100\times I_{(111)\text{perov.}}/[I_{(222)\text{pyro.}}+I_{(111)\text{perov.}}]$, it was determined there was an approximately 80% perovskite concentration when the annealing temperature was above 700 °C.

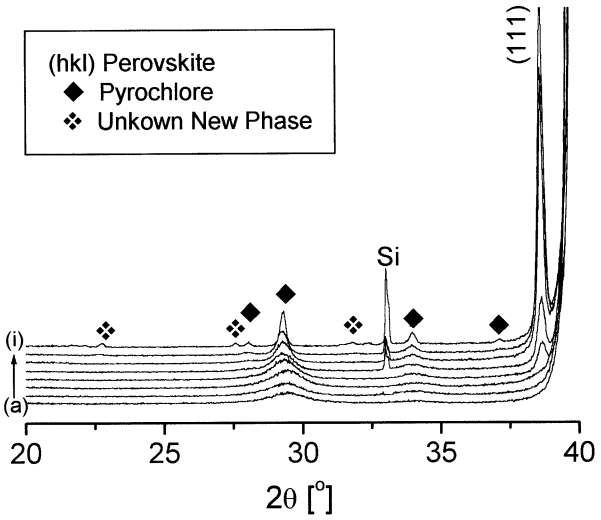

Fig. 2. XRD patterns of the PZNZT thin films annealed at different temperatures. Annealing temperature is 450, 500, 550, 600, 650, 700, 800 and 900 °C from (a) to (i), respectively.

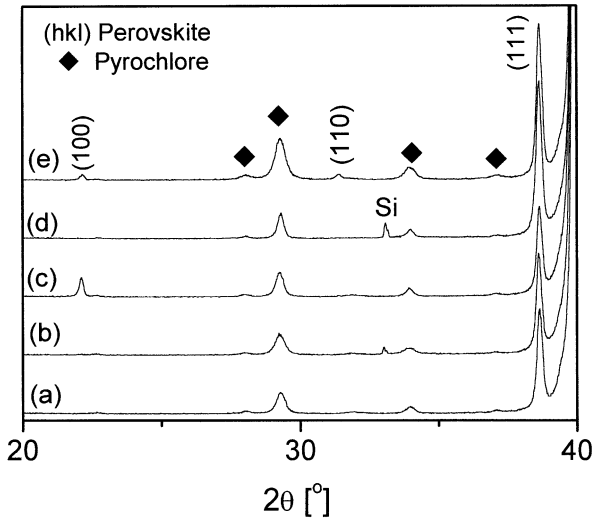

Fig. 3. Orientation of the XRD patterns of PZNZT thin films prepared at different pyrolysis temperatures. At (a) 290 °C, (b) 350 °C, (c) 410 °C and (d) 470 °C from a fresh solution, and (e) 350 °C from an aged solution.

XRD data also indicated a highly preferred (111) orientation for this PZNZT thin film on $Pt/Ti/SiO_2/Si$ substrates. Tani et al.[15] suggested that upon heat treatment, Ti diffuses into the Pt layer and is believed to alter the surface energy and lattice spacing so as to promote crystallization of (111) perovskite by epitaxial nucleation and growth. Fig. 3 shows the XRD pattern of PZNZT

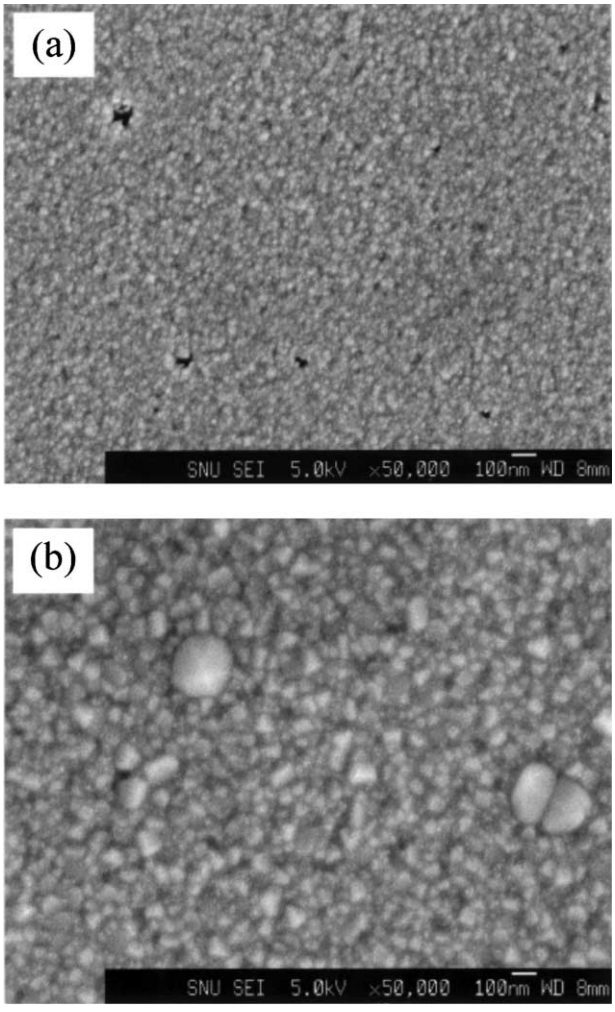

Fig. 4. SEM image of PZNZT thin films annealed at (a) 800 °C and (b) 900 °C for 10 min.

thin films prepared at different pyrolysis temperature (a–d) from a fresh solution and also using a solution aged for 1 week (e). It can be observed that the orientation of the PZNZT thin film was related to the pyrolysis temperature and the ageing time of the precursor solutions. The crystallinity of a (111) oriented and a (100) oriented perovskite grain is different and is influenced by pre-annealing and solution ageing.

FE–SEM studies were undertaken to provide a more detailed description of the phase composition and morphology. Fig. 4(a) and (b) are photographs of the PZNZT thin film surface after annealing at 800 and 900 °C for 10 min. The grains are nano-sized, and there are some larger second phase grains in the film annealed at 900 °C, which coincides with the former XRD analysis.

It is commonly known that during sol-gel processing of lead-based perovskite thin layers, the formation of a thin surface layer of a lead-deficient intermediary phase can occur, which causes a dilution in the perovskite and electric properties. A lead excess is a simple way to eliminate the influence of instability of the perovskite of lead based thin films. Therefore, different amounts of lead excess in the PZNZT precursor solution to control the perovskite structure were used. Fig. 5 shows the XRD patterns of the films that were prepared from precursor solutions with a 5, 10, 15 and 20% excess lead concentration. The perovskite structure is the major phase and almost the same fraction except with 5% excess lead content. This analysis shows that using a lead excess in the starting solution is a good method of eliminating lead evaporation from the surface of a thin film but it cannot eliminate it totally.

Recently, Tani et al.[15] and Tani and Payne[16] proposed a simple method by which the material can crystallize into the surface layer. The method involves the deposition of a single layer of an unhydrolyzed PbO precursor solution after all the required solution depositions have been completed. Subsequent annealing yields a phase-pure perovskite coating. In this study, thin film layers were prepared with and without a PbO cover coat. Fig. 5(e) shows the XRD pattern for the film prepared from the precursor with 5% lead excess and an upper-layer PbO coating. The fraction of perovskite improved to as high as 96%. Furthermore, this film was highly oriented along (111), but the (100) and (110) peaks were also present. It should be noted that the fluorite intermediate phase transforms into (100) and (110)

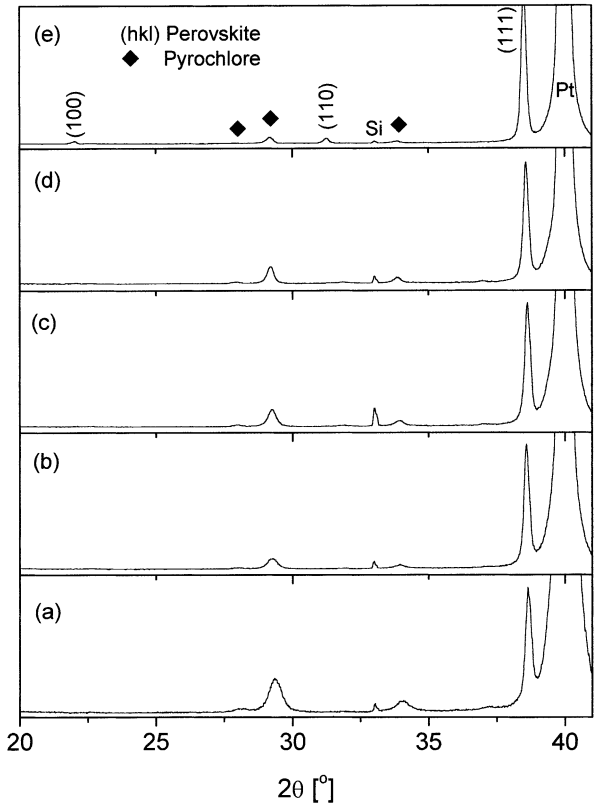

Fig. 5. XRD patterns of PZNZT thin films prepared from precursors with (a) 5%, (b) 10%, (c) 15% and (d) 20% excess lead content, and (e) 5% excess lead content and PbO layer over coat.

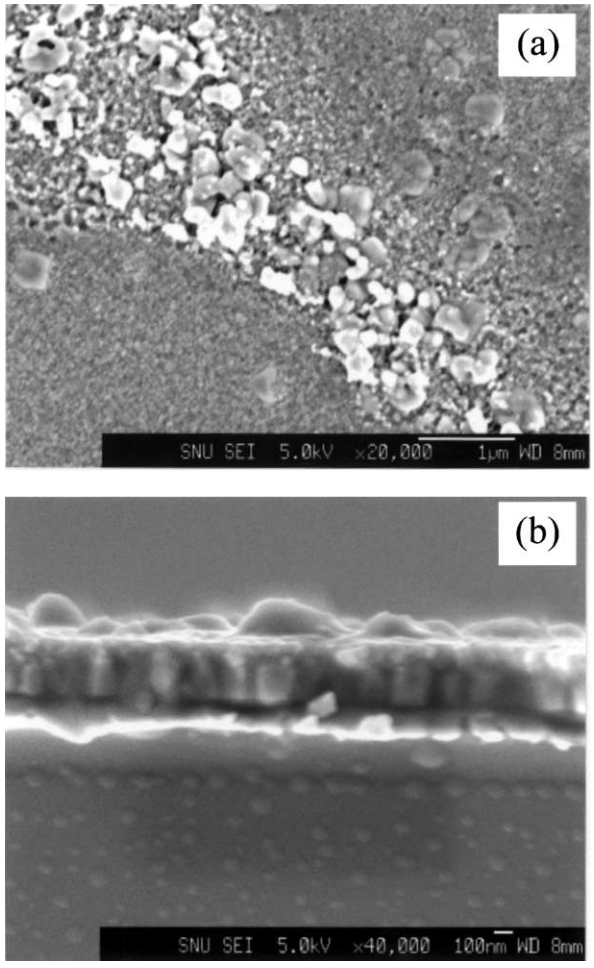

Fig. 6. SEM micrograph of the PZNZT thin film with a PbO over coat. (a) plan view, (b) cross-section.

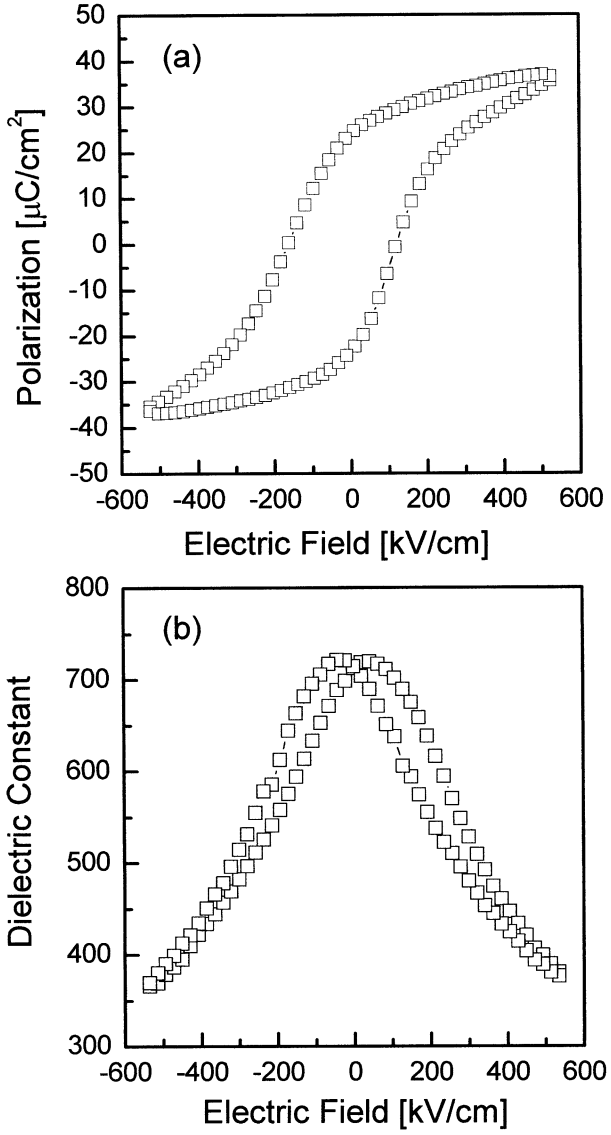

Fig. 7. Ferroelectric hysteresis loop (a) P–E and dielectric constant vs electric field curve (b) $\varepsilon' - E$ of PZNZT thin films with a high perovskite structure.

perovskite through a liquid lead phase during annealing. Fig. 6 shows the SEM images of both plan view and cross section of a typical PZNZT thin film with a PbO cover coat. When compared with Fig. 4(a), the thin surface layer vanished and some relatively large grains (some rossette- and square-type grains) appeared. These grains were assumed to be due to the formation of a new perovskite phase from fluorite. There also exist some excess PbO particles on the surface of the thin layers, which should be removed by dissolution in acetic acid prior to electroding for electrical measurements.

The ferroelectric and dielectric properties of PZNZT thin films with a high perovskite structure are given in Fig. 7(a) and (b). Fig. 7(a) shows the P–E curve, which exhibits a typical ferroelectric P–E hysteresis loop. The remnant polarization (P_r) and the coercive field (E_c) are 25 μC/N, 140 kV/cm, respectively. Fig. 7(b) represents the dielectric constant (ε′) vs the electric field (E) characteristics for the PZNZT thin film with 280 nm film thickness. This curve was measured at a frequency of 10 kHz with a small amplitude of 0.02 V, while the dc bias voltage was swept from a negative bias (−15 V) to a positive bias (+15V) at sweep rate of 0.1 V/s and back again. The dielectric constant $\varepsilon' = 712$ and loss angle tangent $\mathrm{tg}\delta = 3.8\%$ were obtained without a d.c. bias at 10 kHz. The $\varepsilon' - E$ curve showed the hysteresis, which resulted from the switching of the ferroelectric domains. The hysteresis is slim, which is a characteristic of relaxor ferroelectrics. Both maximum capacitances due to polarization reversal were observed clearly in the vicinity of the coercive field of the films. The ε'-E and P–E curves are all slightly asymmetric about the zero bias axis, which indicates that the film contains some mobile ions or charge accumulation at the interface between the film and the electrode.

4. Conclusions

PZN based thin films were grown on $Pt/Ti/SiO_2/Si$ substrates by spin coating using a metal–alkoxide precursor solution. The films began to crystallize at 600 °C and became concentrated with 80% perovskite phase from 700 to 900 °C. The orientation of PZNZT thin film was influenced not only by the substrate orientation but also by the pyrolysis temperature and the precursor solution ageing time. Using a PbO layer over coat, thin films with a 96% perovskite phase were obtained and were characterized by electric measurements. The PZNZT thin film showed a good P–E hysteresis loop and $\varepsilon' - E$ characteristics due to switching of the ferroelectric domains.

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