Preparation, Structure, and Properties of $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.7PbTiO_3$ Thin Films on $LaNiO_3$/YSZ/Si Substrates

Shuhui Yu,[†,‡] Kui Yao,*[,†] and Francis Eng Hock Tay[†,‡]

Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, and
Department of Mechanical Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260

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Perovskite $0.3Pb(Zn_{1/3}Nb_{2/3})O_{3-}0.7PbTiO_3$ (PZN−0.7PT) thin films with (100)-orientation were prepared by a sol−gel method on Si(100) substrates. An yttrium-stabilized ZrO_2 (YSZ) film was used as a buffer layer between a $LaNiO_3$ (LNO) film and the Si substrate, where the LNO layer served as both the bottom electrode and seeding layer for the PZN−0.7PT films. The YSZ suppressed the diffusion of the LNO into the Si substrate. Our prepared LNO film on the YSZ buffer layer showed a strong (100)-orientation. Its resistivity was as low as 7.6×10^{-4} Ω·cm. The thickness of the PZN−0.7PT film fabricated on the LNO/YSZ/Si substrate was about 1.0 μm, and the average grain size was approximately 0.1−0.2 μm. We have demonstrated that the LNO seeding layer plays a key role in obtaining the perovskite structure with (100)-preferred orientation in the PZN−0.7PT film. The dielectric and ferroelectric properties of our PZN−0.7PT films on the LNO/YSZ/Si substrate were also characterized.

Introduction

Lead−zinc−niobate $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a ferroelectric compound with perovskite structure showing a diffuse phase transition from rhombohedral phase at room temperature to cubic phase at about 140 °C.[1,2] PZN−xPT single crystals exhibit very high dielectric permittivities ($\epsilon_r > 3000$), high coupling coefficients ($k_{33} > 90\%$), and high piezoelectric coefficients ($d_{33} > 1500$ pC/N) along the [001] direction.[3−8] These properties are significantly superior to those of the most widely used Pb(Zr,Ti)O_3 (PZT) ($\epsilon_r < 2000$, $k_{33} < 70\%$, and $d_{33} < 800$ pC/N).[4] Therefore, perovskite PZN-based thin films have the potential to replace PZT for applications in microelectronic devices such as capacitors, ferroelectric random access memories, and transducers. However, the preparation of high-quality perovskite PZN−PT thin films is challenging, due to difficulties in removing the detrimental pyrochlore phase and tailoring the orientation.[9−12] The instability of the perovskite phase may be caused by the high polarizability of Pb^{2+} and its interaction with Zn^{2+} cations, resulting in both steric and electrostatic interactions.[13] One approach to overcome this difficulty is to introduce perovskite phases, such as $PbTiO_3$ (PT), $BaTiO_3$ (BT), and $SrTiO_3$ (ST), in order to stabilize the perovskite phase in PZN-based materials.[9−15]

Although much effort has been directed toward preparing perovskite PZN thin films, obtaining high-quality, oriented films has proven to be difficult. For example, Hu reported that to stabilize the perovskite phase, large amounts of PT (≥70%), BT (≥7%), or both are required, and the film thickness has to be increased to be more than 3 μm.[10] In addition, none of the previously reported films exhibit a preferred (100) orientation, and the properties of the randomly oriented PZN−PT films are typically not better than those of PZT.[11−13]

In this work, a seeding $LaNiO_3$ (LNO) thin film was used to promote the perovskite structure as well as the (100) orientation in PZN−0.7PT films. The LNO has a pseudocubic perovskite structure with a lattice parameter of 3.84 Å. It has been employed as the bottom electrode for PZT thin films due to its high electrical conductivity.[16] As far as we know, there have been no

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* To whom correspondence should be addressed. Telephone: 65 68745160. Fax: 65 68720785. E-mail: k-yao@imre.a-star.edu.sg.

[†] Institute of Materials Research and Engineering.

[‡] National University of Singapore.

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reports in the literature on the promotion of perovskite structure in PZN-based films with a seeding layer. Our LNO film was produced by a sol−gel process and has a strong (100) orientation. It functions as both the bottom electrode and seeding layer in order to effectively promote the formation of the (100)-oriented perovskite structure in the PZN−PT films. An yttrium-stabilized ZrO_2 (YSZ) buffer layer was deposited between the LNO film and the Si substrate to suppress interfacial chemical diffusion.

Experimental Section

Sol−gel methods were used to prepare all the YSZ, LNO, and PZN−0.7PT films. To prepare the YSZ buffer layer, Zr propoxide was dissolved in acetic acid to obtain a 0.2 M solution. The zirconia was doped with yttrium oxide by adding 8 mol % yttrium nitrate hexahydrate in order to stabilize its tetragonal phase. The precursor solution was deposited on the Si(100) substrate by spin-coating, followed by annealing at 700 °C for 30 min. It had a thickness of ~50 nm.

To prepare the LNO seeding layer, lanthanum nitrate and nickel acetate were used as starting chemicals; both were dissolved in acetic acid with a molar ratio of La:Ni = 1:1. The 0.3 M LNO solution was deposited on the YSZ-coated Si substrates by repeating the spin-coating cycles to achieve a thickness of 0.2 μm. The annealing was carried out at 650−800 °C.

To prepare PZN−0.7PT thin films, lead acetate, zinc acetate, niobium isopropoxide, titanium isopropoxide, and 2-methoxyethanol solvent were used as starting chemicals. The PZN and PT solutions were prepared separately and mixed according to the targeted compositions. To compensate for Pb loss during thermal treatment, a Pb excess of 15% with respect to the stoichiometric amount was added. The concentration of the solution was 0.4 M. The sol was spin-coated on top of the LNO layer. The wet films were dried at 100 °C for 2 min, followed by pyrolysis at 430 °C.[17] The thickness was about 0.1 μm for each coating. A thickness of 1.0 μm was obtained by repeating the above procedure. The films were finally annealed at higher temperatures. For comparison, the PZN−0.7PT film was also deposited on $Pt/Ti/SiO_2/Si$ followed by the same heat-treatment procedure. A gold top electrode was deposited by sputtering.

X-ray diffraction analysis (Bruker GADDS, D8-ADVANCED) was carried out to determine the structures of all the films annealed at different temperatures. The morphology of the samples was examined using field emission scanning electron microscopy (JSM-6700F). Secondary ion mass spectrometry (ION-ToF GmbH, ToF−SIMS−IV) was used to investigate the diffusion between the LNO and the Si substrate. The resistivity of the LNO electrode was measured with a four-point probe system (MCP-T360). The dielectric constant and loss of the PZN−xPT film were measured using an impedance analyzer (HP4194A). Polarization−electric field (P−E) hysteresis loops were obtained with a RT66A testing unit connected with a high-voltage interface. At least three points were measured to ensure repeatability.

Results and Discussion

A. YSZ Buffer Layer. SIMS analysis confirmed that the YSZ layer suppressed diffusion of LNO, especially lanthanum, toward the Si substrate. Figures 1 and 2 show SIMS depth profiles of LNO films grown on Si and YSZ-buffered Si substrates, respectively. As revealed in Figure 1, for the LNO grown directly on the Si substrate, both the La and Ni concentrations at the LNO−Si interface are relatively high, indicating a strong interaction between the LNO and Si. It is also apparent that La diffuses into the Si substrate. In contrast, for the LNO grown on the YSZ-coated Si substrate, the concentration of La and Ni at the LNO−YSZ/Si interface is substantially reduced and the diffusion of La into Si is suppressed, as shown in Figure 2.

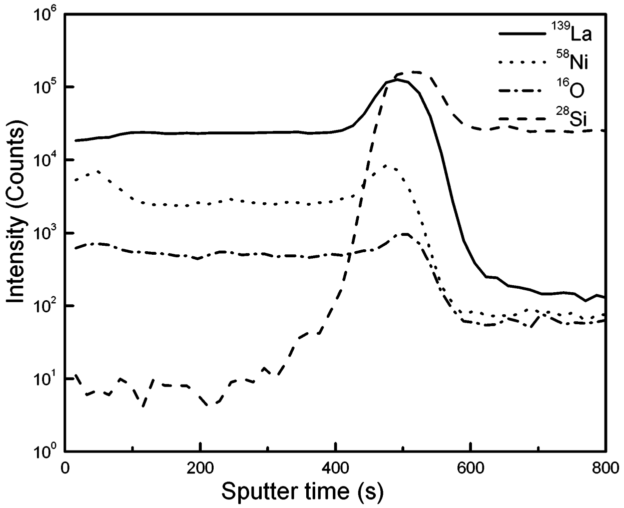

Figure 1. Composition−depth profiles of the LNO film deposited on a Si substrate obtained by secondary ion mass spectrometry (700 °C for 1 h).

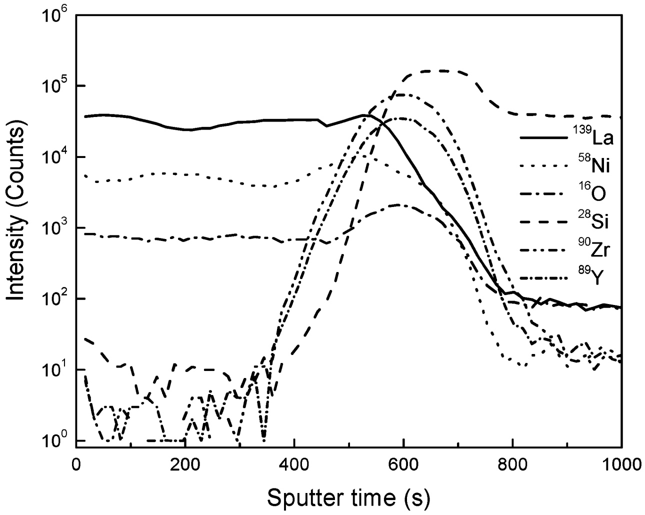

Figure 2. Composition−depth profiles of the LNO film deposited on a YSZ/Si substrate obtained by secondary ion mass spectrometry (700 °C for 1 h).

B. LNO Electrode on YSZ. LNO films grown on YSZ-coated Si substrates show the perovskite structure, and (100) orientation, as evident from the XRD data in Figure 3. It has been reported that the (100)-plane of LNO, which has the smallest surface energy, can develop parallel to the substrate surface when adhesive bonding between the film and substrate is strong.[18−20]

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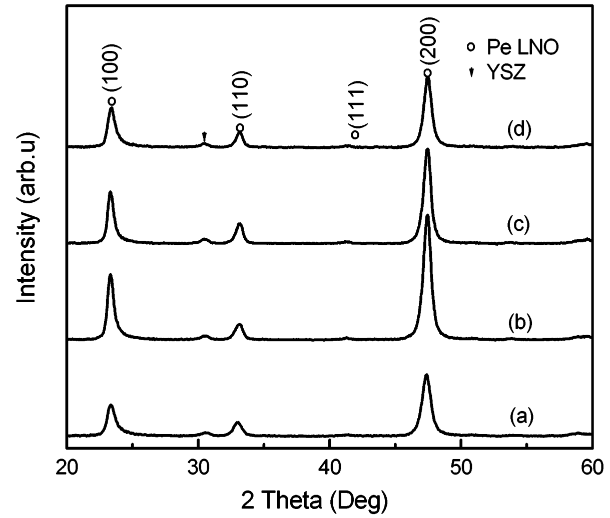

Figure 3. XRD patterns of LNO films annealed at different temperatures: (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C for 1 h.

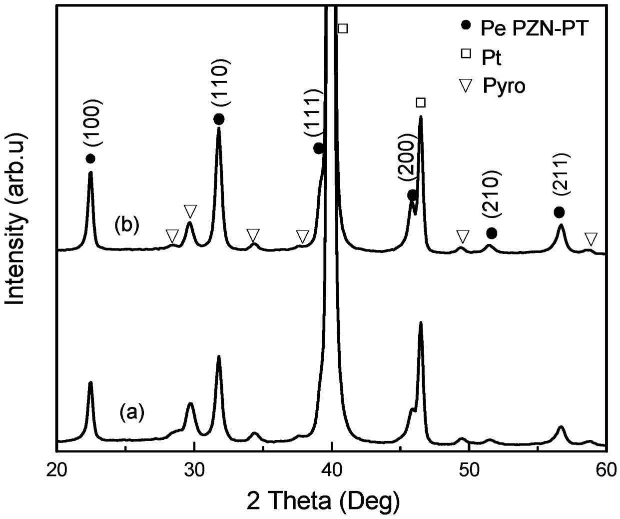

Figure 4. XRD patterns of PZN−0.7PT thin films deposited on Pt/Ti/SiO_2/Si: (a) 570 °C and (b) 800 °C for 10 min.

Therefore, the (100)-oriented nuclei might tend to grow more rapidly than the others.

The resistivity at room temperature of our LNO film annealed at 700 °C for 1 h was 7.6×10^{-4} Ω·cm, which is comparable to the values of LNO films obtained by physical techniques, such as laser ablation sputtering and radio frequency magnetron sputtering.[20, 21]

C. Structure of PZN−0.7PT with (100) Orientation. Figures 4 and 5 show the XRD patterns of PZN−0.7PT films grown on Pt and LNO, respectively. For the film grown on Pt, as shown in Figure 4, a large amount of pyrochlore phase exists in the film after preannealing at 570 °C, and it is not removed completely after annealing at 800 °C. The film has no preferred orientation. In contrast, the film grown on LNO has a relatively high (100) orientation with a small amount of pyrochlore phase after preannealing at 570 °C. The pyrochlore phase has been transformed completely into the perovskite phase after annealing at 800 °C, as shown in Figure 5.

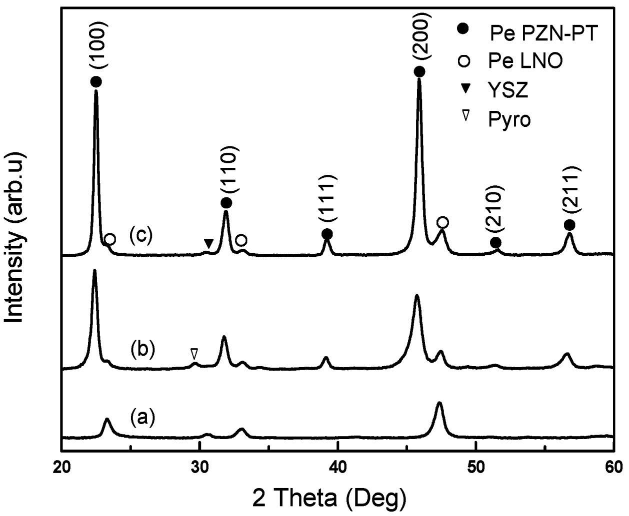

Figure 5. XRD patterns of PZN−0.7PT thin films deposited on LNO/YSZ/Si: (a) LNO, 700 °C for 1 h, (b) PZN−0.7PT, 570 °C for 10 min, and (c) PZN−0.7PT at 800 °C for 10 min.

The calculated lattice parameters are 3.82 and 3.95 Å for LNO and PZN−0.7PT, respectively. The results indicate that the crystallization and growth of the PZN−0.7PT film are significantly influenced by the (100)-textured LNO film. Due to the lattice matching, the PZN−0.7PT grains can heterogeneously nucleate at the surface of the LNO layer and grow preferably along the [100] direction.

Results previously reported by Yi Hu[10] and Yi Yang[9] et al. showed that the stability of the perovskite phase over the pyrochlore phase decreased as the film thickness decreased. They had to increase the thickness of the PZN−PT films up to 3.0 μm to stabilize the perovskite phase in their films, which were prepared on Si or Pt/Ti/SiO_2/Si substrates. The Pt or Si substrates had little effect on the formation and orientation of the perovskite phase in the PZN−PT films. In contrast, by using the LNO seeding layer in this study, we obtained perovskite PZN−PT films less than 1.0 μm thick and a preferred (100) orientation.

D. Morphology. Figure 6 shows SEM images of the surface and the cross section of PZN−0.7PT films grown on LNO and Pt electrodes. The thickness of both the films is around 1 μm. The films on the LNO are polycrystalline with a narrow grain size distribution. The average grain size of PZN−0.7PT grown on LNO is approximately 0.1−0.2 μm. The perovskite grains of the PZN−0.7PT grown on Pt are much smaller, mixed with larger grains of the pyrochlore phase. This observation agrees with the results of XRD analysis, and similar results have been reported by other researchers.[12] It is likely that the LNO layer provides nucleation sites for the formation of the PZN−PT grains, thus decreasing the nucleation energy for the perovskite phase. Once the perovskite phase is formed at a lower temperature, the grains can grow rapidly as the temperature increases. Therefore, the average grain size in the PZN−0.7PT film on LNO is much larger than that of the film on Pt. However, an amount of porosity was observed in both films, which was caused by the pyrolysis of the organic compositions.

E. Electric Properties. The dielectric properties of the PZN−0.7PT film grown on LNO were investigated

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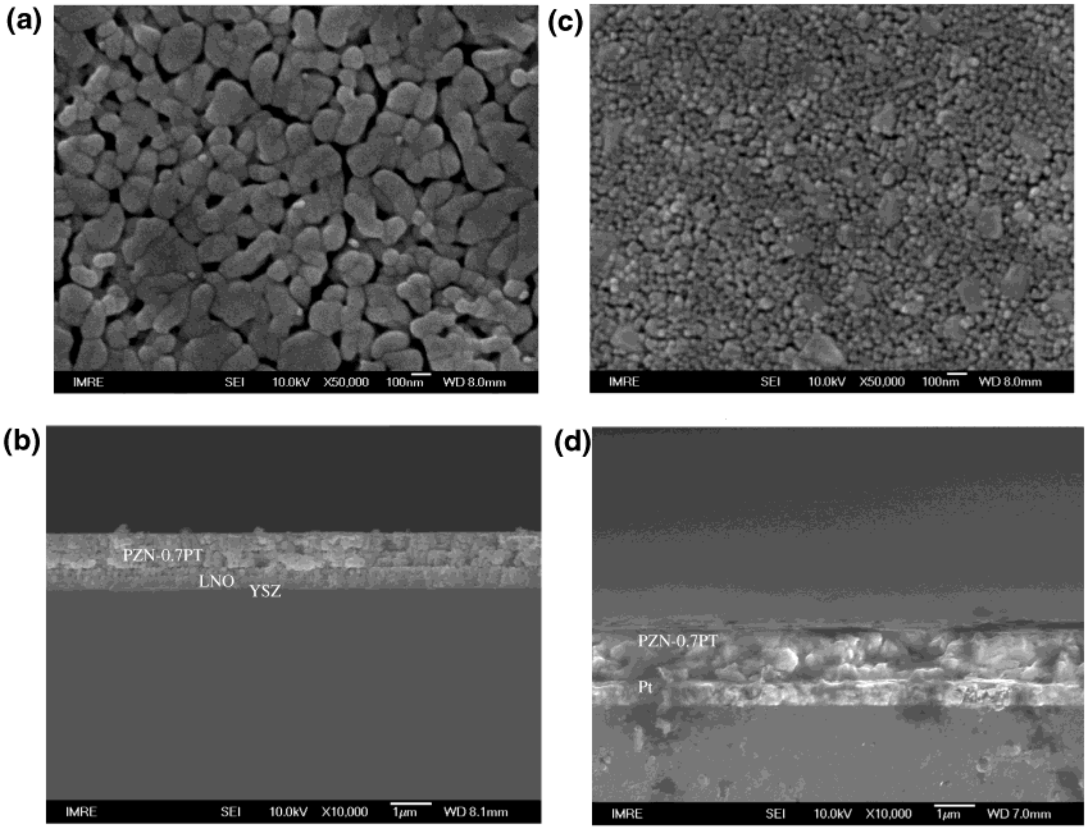

Figure 6. SEM images of the PZN−0.7PT films: (a) surface and (b) cross section of the film on LNO and (c) surface and (d) cross section of the film on Pt.

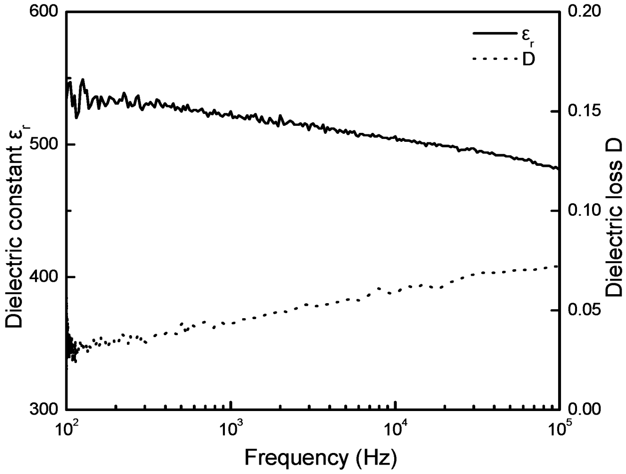

Figure 7. Frequency dependence of the dielectric constant and dielectric loss of PZN−0.7PT deposited on a LNO/YSZ/Si substrate (800 °C for 10 min).

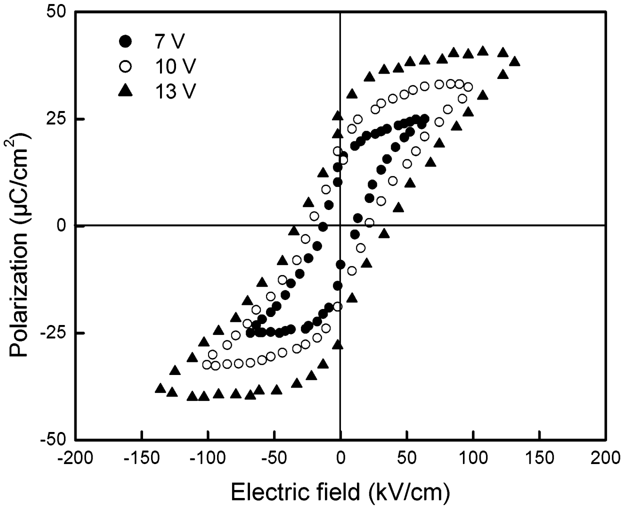

Figure 8. P−E hysteresis loops for a PZN−0.7PT film deposited on a LNO/YSZ/Si substrate, measured at different electric fields.

in the frequency range of 100 Hz−10 kHz. Figure 7 shows the frequency dependence of the dielectric constant (ϵ_r) and the dielectric loss (D) at room temperature. The dielectric constant and dielectric loss at 1 kHz are 525 and 0.03, respectively. The value of the dielectric constant slightly decreases, while the dielectric loss slightly increases with increasing frequency. The smaller dielectric constant may be due to the considerable amount of porosity in the film, as observed in Figure 6a. The processing conditions need to be further optimized to improve the film density and properties.

P−E hysteresis loops of the 800 °C-annealed thin films grown on LNO are presented in Figure 8. The loops are symmetric and saturated. The apparent remnant polarizations are 10.2, 15.3, and 21.3 μC/cm^2, and the corresponding coercive fields are 13.2, 21.0, and 35.2 kV/cm, in response to applied electric fields of 7, 10, and 13 V, respectively. The leakage current became substantial when the applied voltage was increased in the P−E hysteresis measurement, which may result in an inflation of the remnant polarization. The electrical leakage was possibly caused by the porosity in the films. Penetration of gold particles during the top-electrode sputtering could be possible, which may result in extrinsic leakage current and dielectric loss.

Conclusions

We have produced (100)-oriented perovskite PZN−0.7PT thin films using a sol−gel deposition method on LNO/YSZ/Si substrates. Conductive LNO thin films with strong (100) orientation were first deposited as a bottom electrode for the PZN−0.7PT films on Si(100) substrates with a precoated YSZ buffer layer. SIMS results showed that the YSZ was a suitable buffer layer to suppress diffusion of LNO into the Si substrate. The (100) orientation in the perovskite LNO layers promoted formation of the (100)-oriented perovskite phase in the PZN−0.7PT films; our PZN−0.7PT films on LNO showed a perovskite structure with a strong (100) orientation, while those grown on Pt/Ti/SiO_2/Si substrates were randomly oriented with a large amount of pyrochlore phase. SEM showed that the average grain size of the PZN−0.7PT films on the LNO was 0.1−0.2 μm, which was much larger and more uniform than that of films grown on Pt electrodes. Our (100)-oriented PZN−0.7PT films on LNO had a dielectric constant of 525 and a dielectric loss of 0.03 at 1 kHz. A ferroelectric hysteresis loop with a remnant polarization (P_r) of 21.3 μC/cm^2 and a coercive field (E_c) of 35.2 kV/cm was observed at an applied electric field of 135 kV/cm. These results demonstrate the potential of obtaining perovskite PZN−xPT thin films with x below 70% using a conductive ceramic film as both the electrode and seeding layer. In addition, a strong (100) orientation can be obtained in PZN−xPT films with this method.

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