

## Preparation and ferroelectric properties of freestanding $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin membranes

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2012 J. Phys. D: Appl. Phys. 45 185302

(<http://iopscience.iop.org/0022-3727/45/18/185302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 210.72.19.250

This content was downloaded on 01/11/2015 at 06:29

Please note that [terms and conditions apply](#).

# Preparation and ferroelectric properties of freestanding $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin membranes

Zhenghu Zuo<sup>1,2</sup>, Bin Chen<sup>1,2</sup>, Qing-feng Zhan<sup>1,2,4</sup>, Yiwei Liu<sup>1,2</sup>, Huali Yang<sup>1,2</sup>, Zhixiang Li<sup>3</sup>, Gaojie Xu<sup>3</sup> and Run-Wei Li<sup>1,2,4</sup>

<sup>1</sup> Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People's Republic of China

<sup>2</sup> Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People's Republic of China

<sup>3</sup> Division of Functional Materials and Nano-Devices, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People's Republic of China

E-mail: [zhanqf@nimte.ac.cn](mailto:zhanqf@nimte.ac.cn) and [runweili@nimte.ac.cn](mailto:runweili@nimte.ac.cn)

Received 11 November 2011, in final form 29 February 2012

Published 12 April 2012

Online at [stacks.iop.org/JPhysD/45/185302](http://stacks.iop.org/JPhysD/45/185302)

## Abstract

Freestanding  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) thin membranes were fabricated by pulsed laser deposition on 200 nm-thick Pt foils which were obtained by etching the platinized Si substrates with HF solutions. X-ray diffraction patterns and Raman spectra show that the crystal lattice distortion of the PZT membranes is relaxed after removing the rigid substrates. Compared with the substrate-clamped PZT films, the saturation polarization and the remanent polarization of the freestanding PZT membranes are increased by about 18% and 21%, respectively. In addition, the freestanding PZT thin membranes possess higher dielectric tunability and larger domain size. The novel facile fabrication method is important for developing flexible ferroelectric devices and also for studying the strain effects on the physical properties of flexible functional membranes.

(Some figures may appear in colour only in the online journal)

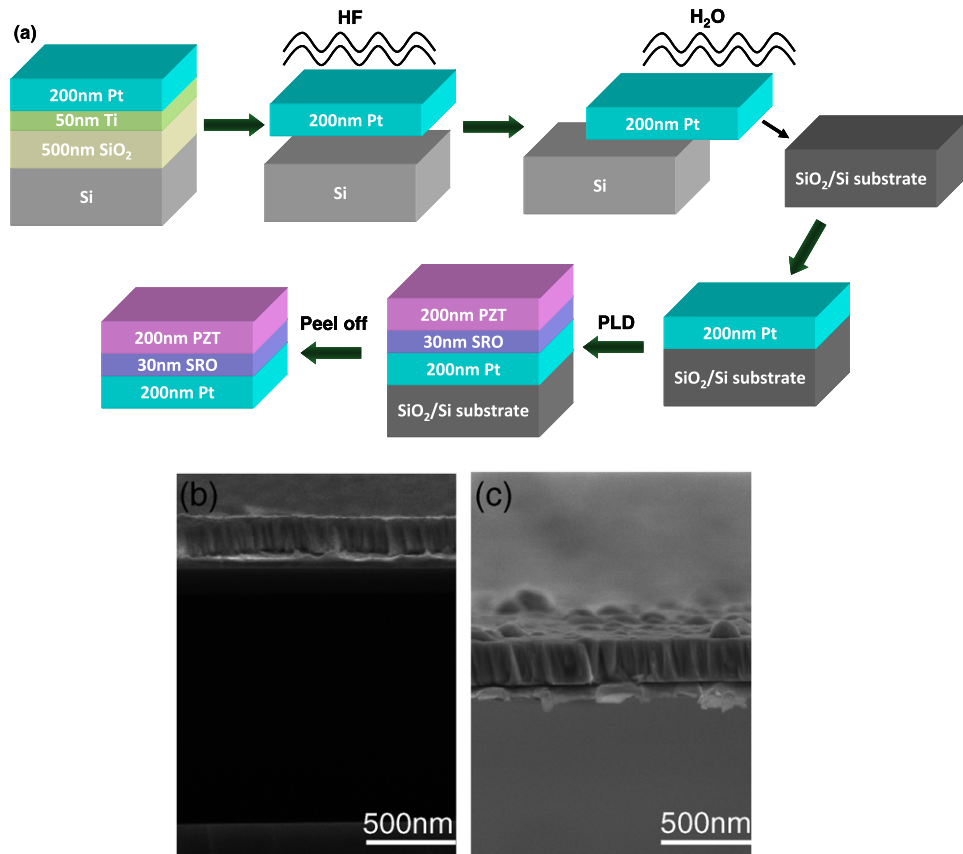
## 1. Introduction

Ferroelectric thin films have attracted considerable attention due to their potential applications in microelectromechanical systems (MEMS), strain actuators, nonvolatile random access memories and energy harvesting [1–4]. It is well known that there is a strong coupling effect between the physical properties and the applied stress/strain in ferroelectric materials [5–7]. Phase-field simulations indicated that the remanent polarization of epitaxial  $\text{BaTiO}_3$  thin films decreases as the in-plane strain changes from compressive to tensile [8]. On the other hand, the magnetoelectric (ME) composite materials comprising ferroelectric and ferromagnetic substances have drawn considerable attention recently due to their potential applications in novel

magnetoelectrical sensors and memories [9]. Strain-mediated ME coupling is an important route in ME composite systems [10]. However, for laminated ME composites, the substrate clamping effect may suppress the strain-mediated ME coupling due to the large in-plane constraint [11, 12]. If one could detach the rigid substrates and prepare freestanding laminated ME composites, the ME coefficient would be expected to be significantly improved [13]. Prior to studying the ME coupling effect in freestanding laminated ME composites, it is very important to develop effective fabrication techniques and to clarify the effects of strain on their properties in single-layered freestanding ferroelectric or ferromagnetic membranes.

Recently, Jang *et al* [14] fabricated freestanding (001)  $\text{BiFeO}_3$  (BFO) thin membranes using a dry etching process to remove Si substrates, and the freestanding BFO membranes showed a reduced coercive field. Ryu *et al* [15]

<sup>4</sup> Authors to whom any correspondence should be addressed.



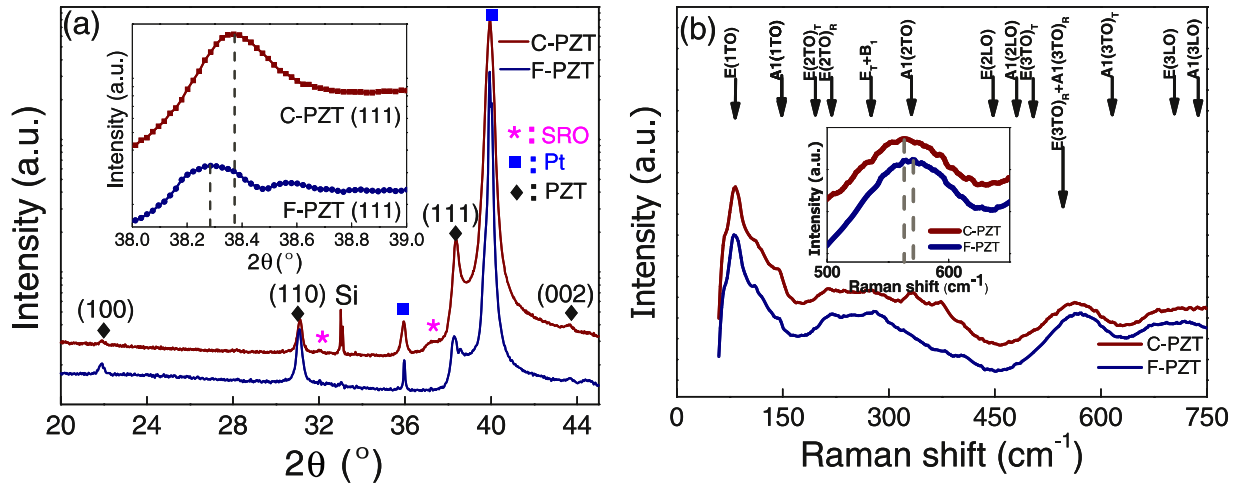
**Figure 1.** (a) Schematic diagrams for the fabrication process of freestanding PZT membranes. SEM images for the cross-sections of PZT films (b) before and (c) after being detached from the substrates.

prepared 10  $\mu\text{m}$ -thick freestanding  $0.9\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ – $0.1\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZNT) films by cooling the samples with a high cooling rate, and found that the remanent and saturation polarization are increased. Lee *et al* [16] synthesized micrometre-level  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  films using a carbon sacrifice layer, and found that the piezoelectric coefficient is independent of the film thickness. However, using the aforementioned preparation methods, it is still relatively difficult to obtain either large size or thin freestanding membranes. Herein, we propose a new facile method to obtain freestanding thin functional membranes using Pt foils, which are detached from the platinized Si substrates with HF solutions. By means of pulsed laser deposition (PLD), as an example, freestanding  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  (PZT) thin membranes with size of the order of centimetres were successfully fabricated on Pt thin foils. Moreover, we demonstrate that, by eliminating the substrate clamping effect, the polarization and relative permittivity of the PZT thin membranes could be enhanced without changing the fatigue obviously.

## 2. Experiment

The fabrication process of freestanding PZT (F-PZT) thin membranes is schematically shown in figure 1(a). The 200 nm-thick Pt foils were obtained by etching platinized Si substrates (Pt(200 nm)/Ti(50 nm)/SiO<sub>2</sub>(500 nm)/Si) in 10 wt%

HF solutions for 4 h. Ti layer and SiO<sub>2</sub> layer reacted with HF and produced soluble SiF<sub>4</sub> and TiF<sub>3</sub>, respectively. As a result, the thin Pt layers were released from the substrates. After rinsing and drying, the Pt foils were placed onto the Si wafer, which was thermally oxidized at 750 °C for an hour to increase the SiO<sub>2</sub> thickness. A 30 nm-thick SrRuO<sub>3</sub> (SRO) buffer layer was deposited on the Pt foils by PLD, employing a KrF excimer laser ( $\lambda = 248 \text{ nm}$ ) with a repetition rate of 2 Hz and an energy density of  $1.8 \text{ J cm}^{-2}$ . The temperature during SRO deposition was set at 550 °C and the oxygen pressure was maintained at 10 Pa. The subsequent 200 nm-thick PZT layer was grown at 520 °C and 10 Pa oxygen pressure, with a repetition rate of 5 Hz and an energy density of  $2.3 \text{ J cm}^{-2}$ . Finally, the freestanding PZT(200 nm)/SRO(30 nm)/Pt(200 nm) thin membranes with Pt foils serving as both flexible substrates and bottom electrodes were detached from the thermally oxidized Si wafers. Currently, F-PZT membranes with area larger than  $1 \times 1 \text{ cm}^2$  can be achieved using our fabrication processes. Figures 1(b) and (c) show the SEM images of the cross-sections of the F-PZT films before and after being detached from the substrates, respectively. A gap of about 2  $\mu\text{m}$  between the top layer and the bottom substrate can be observed, indicating that no chemical bonding is formed between Pt layers and the Si wafers during the high-temperature growth. In order to perform electrical measurements, arrays of circular Pt top electrodes (100 nm in thickness and 100  $\mu\text{m}$  in diameter) were deposited on the PZT(200 nm)/SRO(30 nm)/Pt(200 nm) membranes with a metal mask by e-beam evaporation.



**Figure 2.** (a) XRD patterns of both F-PZT membranes and C-PZT films. The peaks for PZT layers, SRO buffer layers and Pt electrodes are indexed with black rhombus, pink stars and blue squares, respectively. The inset shows a magnified view of the PZT (1 1 1) peak. (b) Raman spectra for both F-PZT membranes and C-PZT films. The inset shows the magnified peak around  $600\text{ cm}^{-1}$ .

For the purposes of comparison, substrate-clamped PZT (C-PZT) films grown on platinized Si substrates were also prepared.

### 3. Results and discussion

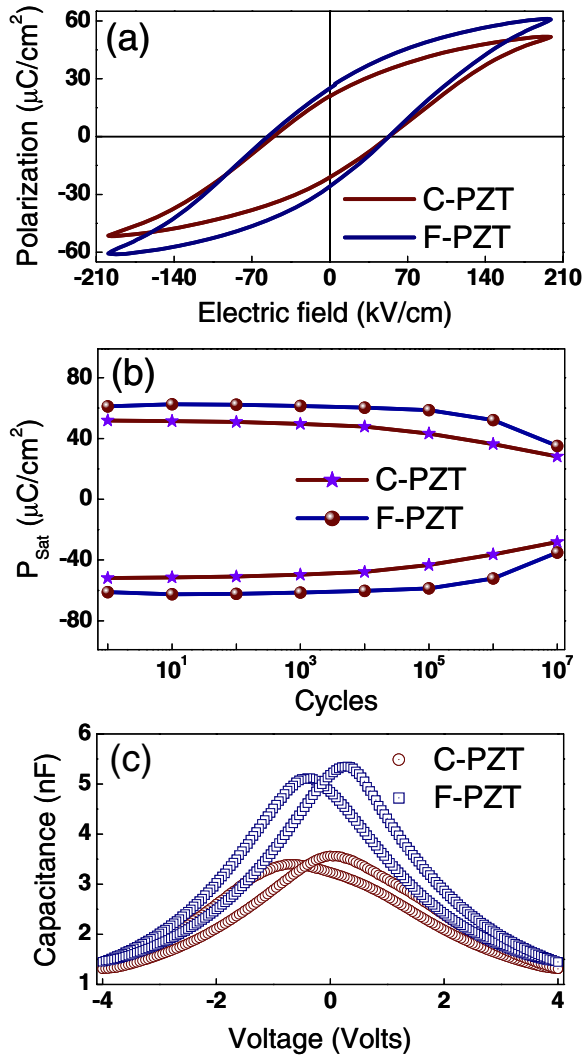
The crystalline structure was analysed by an x-ray diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu  $K\alpha$  radiation. A single phase with a perovskite structure was observed in both F-PZT membranes and C-PZT films, as shown in figure 2(a). The peaks of PZT layers, SRO buffer layers and Pt electrodes are indexed with black rhombus, pink stars and blue squares, respectively. As displayed in the inset of figure 2(a), the (1 1 1) diffraction peak of the F-PZT membranes shifts by about  $0.09^\circ$  towards the lower angle in comparison with that of the C-PZT films, which suggests that the C-PZT films suffer an out-of-plane compressive stress and an in-plane tensile stress, and the stresses could be relaxed in F-PZT membranes. The Raman spectra for the F-PZT membranes exhibit a red shift around the peak of  $600\text{ cm}^{-1}$  as compared with that for the C-PZT films, as shown in figure 2(b), which confirms the presence of the in-plane tensile stress in C-PZT films [17]. A similar result was reported by Ryu *et al* [15]. In their experiments, PZNT films deposited on platinized Si substrates were estimated to be under a tensile stress of 114 MPa. For C-PZT thin films, the crystalline orientation of PZT is substantially affected by the orientation of the bottom Pt layer [16]. Normally, PZT thin films possess a (1 1 1)-preferred growth orientation on platinized Si substrates due to the lattice matching between them or the presence of an intermetallic phase  $\text{Pt}_{5-7}\text{Pb}$  [18]. In our experiments, the intensity of the (1 1 1) diffraction peak is much higher than that of the (1 1 0) peak for the C-PZT films, but the reverse case is found for the F-PZT membranes. The difference in the preferred growth orientations of F-PZT and C-PZT is attributed to the different strain states of the Pt layers on platinized Si substrates and freestanding Pt foils.

The ferroelectric properties of the F-PZT membranes and C-PZT films were measured by a standardized ferroelectric

test system (Precision Premier II, Radiant Technologies). The leakage current for our samples is measured as small as  $10^{-9}\text{ A}$  at 1.5 V, so that it has little influence on the ferroelectricity measurements. The polarization hysteresis loops indicate that the saturation polarization  $P_s$  and the remanent polarization  $P_r$  are increased by about 18% (from  $51.5\text{ }\mu\text{C cm}^{-2}$  for C-PZT to  $60.8\text{ }\mu\text{C cm}^{-2}$  for F-PZT) and about 21% (from  $21\text{ }\mu\text{C cm}^{-2}$  for C-PZT to  $25.5\text{ }\mu\text{C cm}^{-2}$  for F-PZT), respectively, as shown in figure 3(a). Previous theoretical calculations have shown that the in-plane tensile stress applied on PZT thin films could reduce the remanent and saturation polarizations [19], which is in agreement with our experimental results. Moreover, the coercive field  $E_c$  increases slightly from  $51.5\text{ kV cm}^{-1}$  for the C-PZT films to  $54.9\text{ kV cm}^{-1}$  for the F-PZT membranes. The increasing ratio for the coercive field is only 6.7%, which is much smaller than that for polarization, but is consistent with the result reported by Lee *et al* [20]. In addition, we have prepared F-PZT membranes with various thicknesses down to 50 nm. They exhibit similar behaviour, and no significant effect of thickness is observed in the F-PZT films.

Fatigue characteristic, the decrease in the saturation polarization when switching the polarization orientation continuously due to the accumulation of oxygen vacancies at the interfaces [21], is one of the important factors to determine the reliability of ferroelectric materials. Without the substrate clamping effect, our F-PZT membranes exhibit a fatigue behaviour as good as C-PZT films, as displayed in figure 3(b). It seems that the relaxation of stress has a trivial influence on the fatigue feature. When the polarization switching is continuously repeated, the saturation polarizations for both F-PZT membranes and C-PZT films are reduced slowly. After  $10^7$  cycles, the saturation polarization of the F-PZT membranes remains at about 57% of the initial value while that for C-PZT is 54%.

Capacitance–Voltage (C–V) characteristics of the F-PZT membranes and C-PZT films were tested by an impedance analyser (HP 4284) at a frequency of 100 kHz. The C–V curves for both F-PZT membranes and C-PZT films exhibit the well-known butterfly shape, which is typical for



**Figure 3.** (a) Ferroelectric hysteresis loops, (b) fatigue endurance and (c)  $C$ - $V$  curves for both F-PZT membranes and C-PZT films.

ferroelectric materials, as displayed in figure 3(c). The relative permittivity  $\varepsilon$  of ferroelectrics can be extracted from the  $C$ - $V$  measurements using the relation  $\varepsilon = Ct/\varepsilon_0A$ , where  $C$  is the capacitance,  $t$  is the thickness of the dielectric films,  $\varepsilon_0$  is the vacuum permittivity and  $A$  is the area of the capacitor. Consequently, we obtain that the  $\varepsilon$  values for F-PZT membranes and C-PZT films are about 2650 and 1824, respectively. The increased relative permittivity of about 45% when the substrate clamping effect is removed can be ascribed to the reduction in in-plane tensile strain in ferroelectric thin films [22]. The dielectric tunability is defined as  $[\varepsilon_r(C) - \varepsilon_r(V)]/\varepsilon_r(C)$ , where  $\varepsilon_r(C)$  and  $\varepsilon_r(V)$  are the permittivities at the crossing point of the ascending and descending branches and at a bias voltage of  $V$ , respectively. The dielectric tunability for C-PZT films is obtained to be about 60% while for F-PZT membranes it can reach more than 70% at a bias voltage of 4 V. Servoin *et al* [23] reported that the dielectric tunability of ferroelectric films can be interpreted with the hardening of the soft modes. The influence of compressive strain along the applied electric field hardens the soft phonon mode and then reduces the dielectric tunability. In

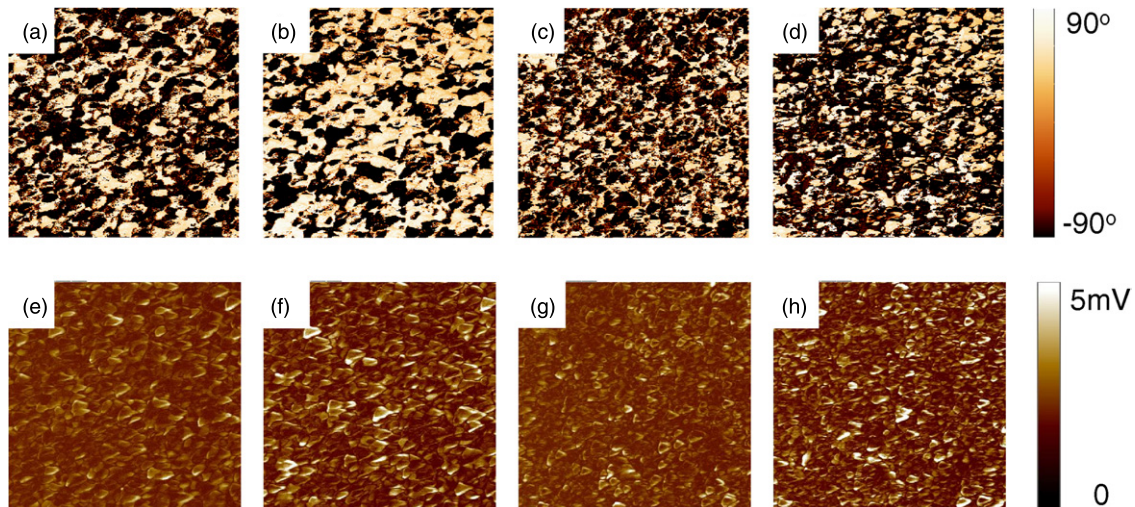
contrast, the tensile strain along the applied electric field could enhance the dielectric tunability [24]. Therefore, when the out-of-plane compressive stress in the C-PZT films is released, the unit cell of the F-PZT membranes along the electric field in the parallel plate capacitor structure is elongated, which is responsible for the enhancement of the dielectric tunable property.

The ferroelectric domain configurations of the F-PZT membranes and C-PZT films were observed by piezoresponse force microscopy (PFM, Dimension3100V), as displayed in figures 4(a)-(d). The phase images of both out-of-plane (OP) and in-plane (IP) display a dark and bright contrast. The dark contrast in the OP images represents domains with normal components of polarization oriented downwards (top-to-bottom) whereas the bright contrast denotes an upward (bottom-to-top) orientation. In the case of polycrystalline ferroelectric films with various crystalline orientations, it is very difficult to extract the information about the direction of spontaneous polarization. As displayed in the OP and IP images, the ferroelectric domains for the F-PZT membranes are integrated and large while that of the C-PZT films are fragmental and small. Since the fabrication processes of PZT films are identical for the two samples, we therefore conclude that the difference in the domain configurations between F-PZT membranes and C-PZT films is caused by the substrate clamping effect. Both the OP and IP amplitude images of F-PZT membranes and C-PZT films are shown in figures 4(e)-(h). According to the calculations of the integrated intensity of amplitudes, the ratio of OP amplitude to IP amplitude of the F-PZT membranes is around 57% while that of the C-PZT films is about 48%. Compared with the C-PZT films, the OP volume fraction of the F-PZT membranes is increased by 18% when the in-plane tensile stress is released, which is in good agreement with the changes in polarization, as shown in the hysteresis loops in figure 3(a). The remanent polarization is determined by the domain structures, especially by the volume fraction of the domains with out-of-plane polarization ( $c$ -domain). When applying external stresses on PZT films, the region under an in-plane tensile stress is ready to form the in-plane polarization domains ( $a$ -domains) while the in-plane compressive stress is in favour of forming  $c$ -domains. In our experiments, when the in-plane tensile stresses are released, parts of the  $a$ -domains turn to  $c$ -domains. Consequently, the OP volume fraction of the F-PZT membranes is more than that of the C-PZT films and the remanent polarization of the F-PZT membranes is increased, which was proved by the polarization hysteresis loops.

#### 4. Conclusions

In summary, a novel facile route to fabricate freestanding thin functional membranes without a substrate clamping effect was developed, which is important for developing flexible ferroelectric devices. Freestanding PZT membranes are prepared, as an example, and display better ferroelectric and dielectric performances as compared with the corresponding substrate-clamped PZT films. It is expected that the novel





**Figure 4.** PFM for F-PZT membranes and C-PZT films ( $3 \times 3 \mu\text{m}^2$ ). (a) OP and (b) IP phase images, and (e) OP and (f) IP amplitude images of F-PZT membranes; (c) OP and (d) IP phase images, and (g) OP and (h) IP amplitude images of C-PZT films.

fabrication method could significantly improve the ME coupling coefficient especially in ferromagnetic/piezoelectric heterostructures, the promising multiferroic materials.

### Acknowledgments

The authors acknowledge the financial support from the National Natural Foundation of China (10904156, 11174302), the State Key Project of Fundamental Research of China (2012CB933004), the Chinese Academy of Sciences (CAS), and the Ningbo Science and Technology Innovation Team (2011B82004, 2009B21005), the Projects of Nonprofit Technology & Research in Zhejiang Province (2010C31041), and the Zhejiang and Ningbo Natural Science Foundations.

### References

- [1] Bahr D F, Robach J S, Wright J S, Francis L F and Gerberich W W 1999 *Mater. Sci. Eng. A* **259** 126
- [2] Feng Z Y, He T H, Xu H Q, Luo H S and Yin Z W 2004 *Solid State Commun.* **130** 557
- [3] Auciello O, Scott J F and Ramesh R 1998 *Phys. Today* **51** 22
- [4] Priya S 2007 *J. Electroceram.* **19** 167
- [5] Spierings G, Dormans G J M, Moors W G J, Ulenaers M J E and Larsen P K 1995 *J. Appl. Phys.* **78** 1926
- [6] Desu S B 1993 *J. Electrochem. Soc.* **140** 2981
- [7] Tuttle B A, Voigt J A, Garino T J, Goodnow D C, Schwartz R W, Lamppa D L, Headley T J and Eatough M O 1992 *Proc. 8th Int. Symp. on Applied Ferroelectrics (Greenville, SC)* p 344
- [8] Choudhury S, Li Y L, Chen L Q and Jia Q X 2008 *Appl. Phys. Lett.* **92** 142907
- [9] Ma J, Hu J M, Li Z and Nan C W 2011 *Adv. Mater.* **23** 1062
- [10] Ryu S, Park J H and Jang H M 2007 *Appl. Phys. Lett.* **91** 142910
- [11] Nan C W, Bichurin M I, Dong S X, Viehland D and Srinivasan G 2008 *J. Appl. Phys.* **103** 031101
- [12] Levin I, Li J H, Slutsker J and Roytburd A L 2006 *Adv. Mater.* **18** 2044
- [13] Nan C W, Liu G, Lin Y H and Chen H D 2005 *Phys. Rev. Lett.* **94** 197203
- [14] Jang H W, Baek S H, Ortiz D, Folkman C M, Eom C B, Chu Y H, Shafer P, Ramesh R, Vaithyanathan V and Schlom D G 2008 *Appl. Phys. Lett.* **92** 062910
- [15] Ryu J, Priya S, Park C S, Kim K Y, Choi J J, Hahn B D, Yoon W H, Lee B K, Park D S and Park C 2009 *J. Appl. Phys.* **106** 024108
- [16] Lee J W, Park C S, Jo J H and Kim H E 2007 *Appl. Phys. Lett.* **91** 072903
- [17] Cerdeira F, Buchenauer C I, Poliak F H and Cardona M 1972 *Phys. Rev. B* **5** 580
- [18] Chen S Y and Chen I W 1998 *J. Am. Ceram. Soc.* **81** 97
- [19] Pertsev N A, Contreras J R, Kukhar V G, Hermanns B, Kohlstedt H and Waser R 2003 *Appl. Phys. Lett.* **83** 3356
- [20] Lee J W, Park G T, Park C S and Kim H E 2006 *Appl. Phys. Lett.* **88** 072908
- [21] Scott J F, Araujo C A, Melnick B M, McMillan L D and Zuleeg R 1991 *J. Appl. Phys.* **70** 382
- [22] Taylor T R, Hansen P J, Acikel B, Pervez N, York R A, Streiffer S K and Speck J S 2002 *Appl. Phys. Lett.* **80** 1978
- [23] Servoin J L, Luspain Y and Gervais F 1980 *Phys. Rev. B* **22** 5501
- [24] Ikuta K, Tsukada M and Nishimura H 1998 *Japan. J. Appl. Phys.* **37** 1960