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Stress-controlled $Pb(Zr_{0.52}Ti_{0.48})O_3$ thick films by thermal expansion mismatch between substrate and $Pb(Zr_{0.52}Ti_{0.48})O_3$ film

Guifang Han,[1] Jungho Ryu,[1,a)] Woon-Ha Yoon,[1] Jong-Jin Choi,[1] Byung-Dong Hahn,[1] Jong-Woo Kim,[1] Dong-Soo Park,[1] Cheol-Woo Ahn,[1] Shashank Priya,[2] and Dae-Yong Jeong[3,a)]
[1]*Functional Ceramics Group, Korea Institute of Materials Science (KIMS), Changwon, Gyeongnam 641-831, Korea*
[2]*Department of Materials Science and Engineering, Virginia Tech., Blacksburg, Virginia 24061, USA*
[3]*School of Materials Engineering, Inha University, Incheon 402-751, Korea*

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Polycrystalline $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thick films (thickness $\sim$10 μm) were successfully fabricated by using a novel aerosol deposition technique on Si wafer, sapphire, and single crystal yitria stabilized zirconia (YSZ) wafer substrates with Pt electrodes and their dielectric, ferroelectric, and piezoelectric properties, and in-plane stresses were investigated. The films with different stress conditions were simply controlled by the coefficient of thermal expansion (CTE) misfit of PZT films and substrates. The results showed that the films bearing in-plane compressive stress deposited on the YSZ and sapphire substrates have superior dielectric, ferroelectric ($\sim$90%), and piezoelectric (>200%) properties over that of the Si wafer. Among these three substrates, YSZ shows superior properties of the PZT films. However, films on Si wafer with tensile stress present lower properties. We believed that in-plane compressive stresses within the films are benefited, the formation of *c*-domain parallel to the thickness direction resulting in the higher piezoelectric properties. These results suggest that the properties of polycrystalline PZT thick films can be adjusted by simply choosing the substrates with different CTEs. © *2011 American Institute of Physics*. [doi:10.1063/1.3669384]

I. INTRODUCTION

Recently, it has been reported that the stress or strain can significantly affect the physical and electric properties of ferroelectric materials.[1–3] In epitaxial $BaTiO_3$ thin films, biaxial compressive strain resulted in a higher ferroelectric transition temperature (approximately 500 °C) and enhancement of remnant polarization (at least 250%) compared to bulk $BaTiO_3$ ceramics.[1] The stress magnitude and sign can be controlled by the interface between the film and substrate which have small lattice misfit strain. Regarding the electrical properties with residual stress level, Lee et al. reported that the ferroelectric properties of (111) oriented $Pb(Zr,Ti)O_3$ (PZT) thin films were enhanced by inducing compressive stress, which was introduced during annealing by bending the substrate.[2,3] Tuttle *et al.*[4] have also shown that the highly oriented PZT thin films (thickness is 300 nm) under compressive residual stress exhibited superior ferroelectric properties compared to the bulk polycrystalline ferroelectrics. However, prior studies are mostly based on the epitaxial thin films or require a special fixture to control the stress. The epitaxial film's thickness is difficult to fabricate with over 1 μm-thick because of the critical stress relaxing thickness. In practical piezoelectric applications of high power actuators, high sensitivity sensors, and energy harvesting devices, epitaxial grown or carefully orientation controlled piezoelectric films have limited use, because of high production cost and productivity. Thus, there is a critical need to understand the physical behavior of thick polycrystalline films and identify the process to modulate the piezoelectric response. In this study, we report $\sim$90% and 200% enhancements of ferroelectric and piezoelectric properties in PZT thick films, respectively, by controlling the magnitude of interfacial stress simply by choosing substrates with different coefficient of thermal expansions (CTEs) as shown in Fig. 1.

Aerosol deposition (AD) is a relatively new deposition process to fabricate thick films at room temperature. This technique offers the possibility of synthesizing films on a wide variety of substrates ranging from polymeric or metal to ceramics.[5–7] During the AD process, the micrometer-sized particles become accelerated at high speeds and collide with the substrate to form polycrystalline film. The deposited films exhibit small grain size, typically in the range of tens of nanometers. This size is smaller than the critical size for ferroelectricity, and thus, post-annealing treatment is conducted to achieve grain growth. During the cooling process after post-annealing, tensile or compressive stress is generated in thick film due to the mismatch in the CTE between films and substrates as shown in Fig. 1. The magnitude of the tensile and compressive stresses influences the crystal structure and domain alignment of thick films which is the subject of investigation in this study. We demonstrate that high quality thick films under high compressive stresses exhibit significantly improved piezoelectric property even in the polycrystalline PZT thick films.

II. EXPERIMENTAL DETAILS

The morphotropic phase boundary $Pb(Zr_{0.52}Ti_{0.48})O_3$ (MPB PZT) thick films were grown by the AD method, and

[a)]Authors to whom correspondence should be addressed. Electronic addresses: jhryu@kims.re.kr and dyjeong@inha.ac.kr.

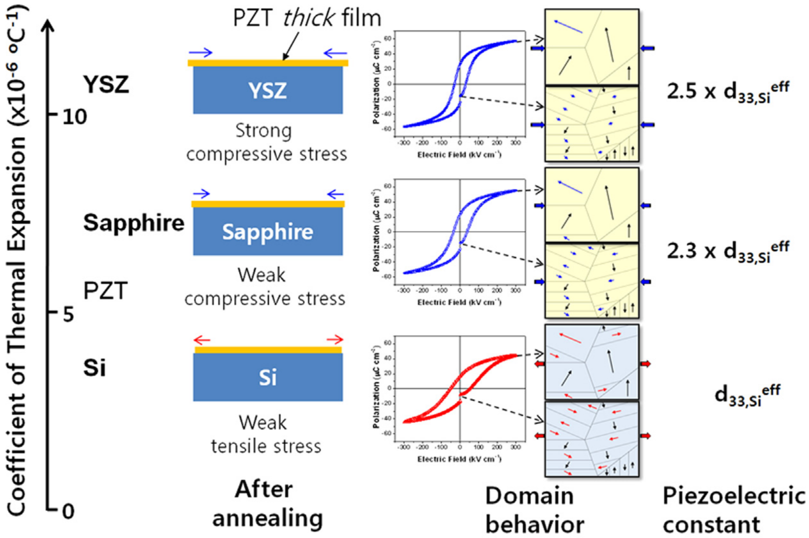

FIG. 1. (Color online) Schematic diagram of high piezoelectric performance in PZT thick films grown on various substrates; their stresses were controlled by the thermal expansion mismatch between substrates and PZT films.

single crystal silicon wafer (Si (100), Inostek Inc., Korea), *c*-cut sapphire (0001), and yitria stabilized zirconia (YSZ) with Ti/Pt bottom electrode were used as substrates. Regent grade raw materials of PbO, ZrO_2, and TiO_2 (Aldrich Co., Milwaukee, WI) were mixed in their appropriate proportion and ball milled for 24 h. After drying, the powder mixture was calcined at 800 °C/5 h to obtain the PZT powder for the AD process. All the ∼10 μm thick films were annealed at 700 °C for 1 h. The phases of the deposited films were identified by X-ray diffractometry. The residual stresses of the films were analyzed by a high-resolution X-ray diffraction system (HR-XRD, X'pert Pro MRD, Philips, Netherlands). The microstructures of the film surface and fracture section were identified by scanning electron microscopy (SEM: JSM-5800, JEOL CO., Tokyo, Japan). A Φ1 mm Pt top electrode was deposited to measure the electric properties by direct current sputtering method. The poling condition was 150 kV cm^{-1}, 40 min, and 100 °C. The dielectric measurement was carried out by using an impedance analyzer (4294A, Agilent, USA). The polarization-electric field (P-E) hysteresis loops were recorded by a standardized ferroelectric test system (P-LC100-K, Radiant Technologies). The piezoelectric coefficients (d_{33}^{eff}) of the poled films were measured by both a d_{33}-meter and laser beam interferometer.[8]

III. RESULTS AND DISCUSSION

In order to control the stress in PZT films, three single crystals with varying CTEs were employed as the substrates as shown in Fig. 1. Initially, the formation of thick PZT films was identified by SEM images as shown in Fig. 2. A highly dense microstructure of PZT films was formed in all the cases. In addition, the grain size was found to be in the range of 50–200 nm for the film with a thickness of ∼10 μm for all three cases as shown in the SEM cross-section in the insets of Fig. 2.

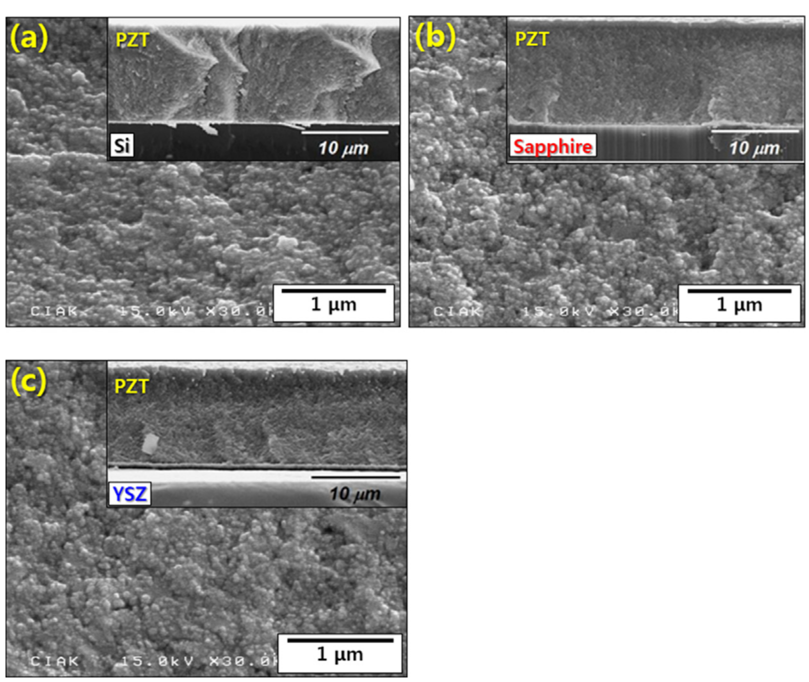

FIG. 2. (Color online) Cross-sectional SEM images of annealed PZT films grown on (a) Si, (b) Sapphire, and (c) YSZ substrates (insets: cross-sections of PZT films).

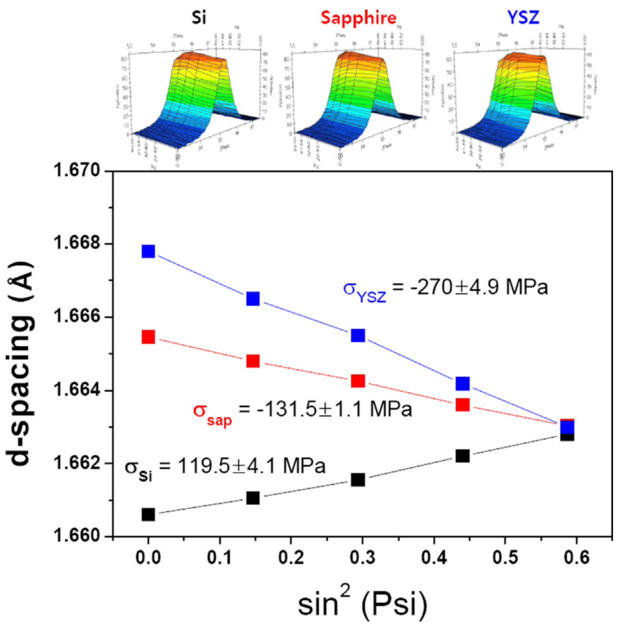

FIG. 3. (Color online) Variation of stress analysis based on d-spacing with different Psi orientations of the sample by HR-XRD (X'pert Pro MRD, Philips, Netherlands), $2\,\theta \sim 55°$ (112).

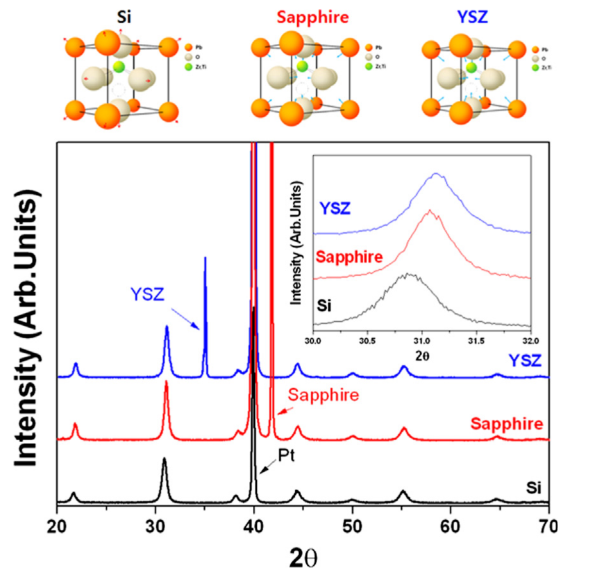

FIG. 4. (Color online) XRD patterns (top figures: variations of lattice parameters by tensile and compressive stresses) of PZT films deposited on various substrates.

Compared with CTE of PZT ($\alpha_f = 5.5$ ppm K^{-1}), silicon ($\alpha_{si} = 3.5$ ppm K^{-1}) has the smaller value, while both sapphire ($\alpha_{sap} = 7.5$ ppm K^{-1}) and YSZ ($\alpha_{YSZ} = 11$ ppm K^{-1}) have the larger values as shown in Fig. 1.[9–14] Hence, as exhibited in Figs. 3 and 1, during the cooling process, tensile stress was generated in PZT films grown on Si substrate while films on sapphire and YSZ substrates showed the opposite phenomenon.

X-ray diffraction patterns of the annealed PZT films are shown in Fig. 4. Except for the peaks of the Pt bottom electrode and substrate, all the annealed PZT films showed a typical perovskite structure. The peaks of PZT films on sapphire and YSZ substrates were shifted to a higher angle in comparison to PZT film grown on Si substrate as shown in the inset of Fig. 4. Thus, it could be suggested that the PZT films on sapphire and YSZ substrates had a smaller lattice constant compared to the films on Si substrates. The variation of lattice parameters is an indication of the residual stress generated by the CTE mismatch between the PZT films and substrates as listed in Fig. 1, Figs. 3 and 4, and Table I.

In order to investigate the domain reorientation with an electric field, the P-E hysteresis loop was measured under a high electric field at low frequency as presented in Fig. 5. All the PZT films showed typical ferroelectric characteristics, but the films on Si substrate exhibited the lowest remnant and saturated polarizations and highest coercive field. On the contrary, the films on YSZ substrate showed the highest remnant and saturated polarizations with the lowest coercive field. Because of the CTE mismatch between films and substrates, the films on sapphire and YSZ substrates have compressive stresses, with those on YSZ having the highest compressive stress. Thus, it could be expected that the domain alignment along the applied field direction is facilitated. Since the grain size in our thick films is above the critical grain size, the 90° domains will be readily formed as the film is cooled through the Curie temperature to minimize the effect of the stress. Especially, it could, therefore, be expected that the domain alignment at 3 directions might be easier for the PZT films on sapphire and YSZ substrates than Si substrate; this is due to the compressive stress in PZT films as indicated in Fig. 1. Furthermore, the compressive stress along the plane direction could squeeze the Ti^{4+}/Zr^{4+} ions along the thickness direction and give the large polarization and piezoelectric constant. However, the tensile stress, in the PZT film on Si substrate, gave the opposite effect resulting in the decrease of the amount of *c*-domain, polarization, and piezoelectric constant. The summaries of electrical properties of the PZT thick films are presented in Table I.

To precisely calculate the total stresses in PZT films, in-plane residual stress was determined from the $\sin^2\psi$ X-ray diffraction technique at (211) peak (2θ angle of $\sim 55.4°$) as shown in Fig. 3. Table I lists the magnitudes of residual stresses for PZT films grown on Si, sapphire, and YSZ substrates. The calculated magnitude of stress was found to be $\sigma_{tot}(25\,°C$, Si$) = +119.5 \pm 4.1$ (tensile), $\sigma_{tot}(25\,°C$, Sap$) = -131.5 \pm 1.1$ (compressive), and $\sigma_{tot}(25\,°C$, YSZ$) = -270.6 \pm 4.9$ MPa.

TABLE I. In-plane stress and electric/piezoelectric properties in PZT films deposited on various substrates.

Substrate	In-plane stress(MPa)	d_{33}^{eff}(pC N^{-1})	d_{33}^{eff}(pm V^{-1})	ε_r(1 kHz)	tan δ(1 kHz)	$\Delta P_r/2$(μC cm^{-2})	$\Delta E_c/2$(kV cm^{-1})
Silicon	119.5 ± 4.1(*Tensile*)	50	26.4	1026	0.025	17.0	52.6
Sapphire	−131.5 ± 1.1(*Compressive*)	80	59.8	1260	0.023	23.4	37.4
YSZ	−270.6 ± 4.9(*Compressive*)	95	66.1	1265	0.039	25.5	30.0

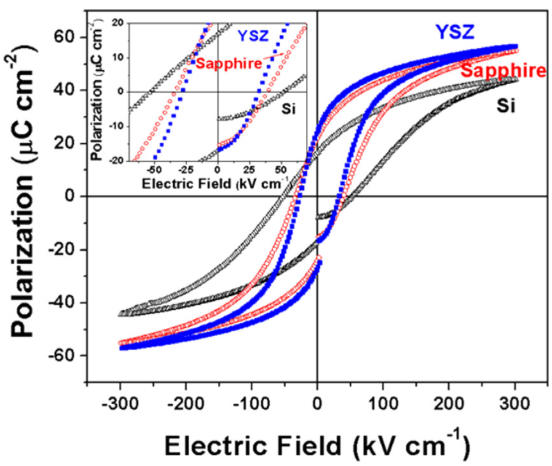

FIG. 5. (Color online) Ferroelectric properties in annealed PZT films deposited on various substrates.

These magnitudes of stress in AD thick films are significantly larger than those reported for thin films.[15]

Using the analysis presented by Desu, the total stress induced in thick film can be attributed to the contributions from thermal stress (σ_{th}), intrinsic stress (σ_i), and extrinsic stress (σ_e) given as[16]

$$\sigma_{tot} = \sigma_{th} + \sigma_i + \sigma_e, \tag{1}$$

where the thermal stress in the film can be expressed as

$$\sigma_{th} = \frac{E_f}{1-\nu_f}(\alpha_f - \alpha_S)(T_d - T), \tag{2}$$

where ν_f represents the Poisson's ratio of the film, E_f is the elastic modulus of the film, T_d is the film deposition/annealing temperature (700 °C), and T is the working temperature (25 °C in this study). The intrinsic stress arises from the combination of deposition process related parameters and film growth itself. The AD mechanism is based upon the impact adhesion of fine particles accelerated with high kinetic energy which results in internal stress that increases with thickness due to increased particle-particle interaction. This internal stress can impact the equilibrium atomic and ionic configurations leading to tensile or compressive stresses. The extrinsic stress arises from the dimensional changes as the material undergoes crystallization of the amorphous phase and phase transition. It can be expressed as

$$\sigma_e = \frac{E_f}{1-\nu_f}\left(\frac{\Delta V}{3V}\right), \tag{3}$$

where $\Delta V/3V$ ($=3.105 \times 10^{-4}$) is the fractional volume change in the PZT film near MPB. The lattice parameters for the tetragonal phase in the vicinity of MPB have been reported to be $a_T = 4.041$ Å and $c_T = 4.140$ Å ($V_T = 67.6$ Å^3). The lattice parameter for the paraelectric phase was reported to be 4.075 Å ($V_C = 67.668$ Å^3).[17]

Combining Eqs. (1)–(3), the total film stress for a given substrate can be expressed as

$$\sigma_{tot}(25\,^{\circ}\mathrm{C}, Si) = \frac{E_f}{1-\nu_f}(\alpha_f - \alpha_{Si})(T_d - 25) + \sigma_i^{Si} + \frac{E_f}{1-\nu_f}\left(\frac{\Delta V}{3V}\right), \tag{4}$$

$$\sigma_{tot}(25\,^{\circ}\mathrm{C}, Sap) = \frac{E_f}{1-\nu_f}(\alpha_f - \alpha_{sap})(T_d - 25) + \sigma_i^{Sap} + \frac{E_f}{1-\nu_f}\left(\frac{\Delta V}{3V}\right), \tag{5}$$

$$\sigma_{tot}(25\,^{\circ}\mathrm{C}, YSZ) = \frac{E_f}{1-\nu_f}(\alpha_f - \alpha_{YSZ})(T_d - 25) + \sigma_i^{YSZ} + \frac{E_f}{1-\nu_f}\left(\frac{\Delta V}{3V}\right). \tag{6}$$

Assuming $\sigma_i^{Si} = \sigma_i^{Sap} = \sigma_i^{YSZ}$, and inserting the magnitude of annealing temperature as 700 °C, the biaxial modulus $\frac{E_f}{1-\nu_f}$ of the film calculated using Eqs. (4) and (5) was found to be 92.96 GPa. Similar calculations, using Eqs. (4) and (6) and Eqs. (5) and (6), yielded the values of 76.93 and 58.62 GPa, respectively. There is significant variation in the magnitude of the biaxial modulus which could be related to the assumption that intrinsic stress is independent of the substrate. In order to determine the magnitude of intrinsic stress, as the AD film is quite thick, we utilized the bulk value of the biaxial modulus for the bulk PZT with MPB composition, $\frac{E_b}{1-\nu_b} = 111.94$ GPa.[18] Using this value, the magnitude of intrinsic stress [determined from Eqs. (5)–(7)] was found to be $\sigma_i^{Si} = -66.376$ MPa, $\sigma_i^{Sap} = -15.138$ MPa, and $\sigma_i^{YSZ} = 110.22$ MPa. Thus, the intrinsic stress increases as the substrate changes from Si to YSZ via sapphire, and it could be expected to provide enhancement in the piezoelectric coefficient.

The effective piezoelectric constants (d_{33}^{eff}), measured by laser beam interferometer, are shown in Fig. 6(a). The vibration amplitudes (displacement) were measured as a function of applied electric fields, and after fitting the line, the magnitude d_{33}^{eff} was determined from the slopes as shown in Fig. 6(a). The PZT films on Si substrate showed the lowest d_{33}^{eff} (~26.4 pm V^{-1}), whereas for the sapphire and YSZ substrates, the d_{33}^{eff} values are found to be considerably higher at 59.8 and 66.1 pm V^{-1}, respectively, than the PZT films on Si substrate. It is interesting that the PZT film on YSZ substrate showed a 2.5 times higher d_{33}^{eff} than the film on Si substrate. The direct piezoelectric constants, measured by the d_{33} meter, are also represented in Fig. 6(b), which reveals the same trend. The PZT films on YSZ showed the highest d_{33}^{eff} while the film on Si wafer had the lowest d_{33}^{eff} value. The variation of piezoelectric coefficient with residual stress can be expressed as a linear relation using the analogy with Rayleigh analysis, [19]

$$d^s = d^o + \alpha\sigma_{sub} \tag{7}$$

where σ_{sub} is positive for the tensile stress and negative for the compressive stress, d^o is the magnitude of piezoelectric coefficient at zero residual stress, and d^s is the magnitude of piezoelectric coefficient at the residual stress of magnitude σ_{sub}. Fitting the experimental data as shown in Fig. 6(b), the

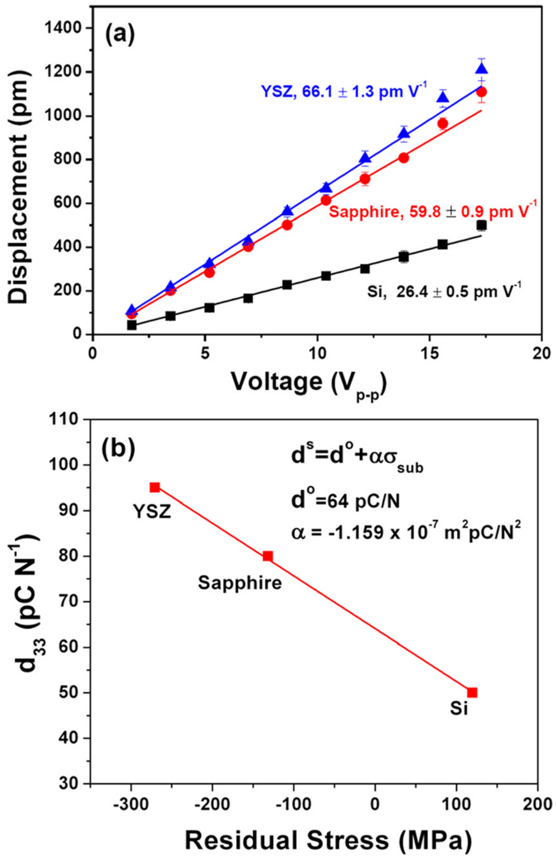

FIG. 6. (Color online) Variations of (a) displacements as a function of applied voltage and (b) direct piezoelectric constants (d_{33}^{eff}) in annealed PZT films deposited on various substrates.

magnitude of d^o was found to be 64 pC N^{-1} and α as -1.159×10^{-7} $m^2pC\ N^{-2}$.

IV. CONCLUSION

In summary, we have successfully fabricated the polycrystalline MPB composition PZT thick films on various substrates using aerosol deposition. The films with various magnitudes of residual stress were obtained by changing substrates with different CTEs. It was found that the PZT thick films on YSZ substrates under compressive stress exhibited large ferroelectric and piezoelectric responses ($\sim$2.5 times higher than that of the films on Si substrate). This result was found to be consistent with the theory that domain alignment was facilitated due to the compressive stress. Since polycrystalline thick films are very useful and have a low cost in real applications compared to epitaxial and textured thin film, this work suggested a new possibility to adjust polycrystalline thick film's properties by simply choosing substrates with different CTEs.

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[1]K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005 (2004).
[2]J.-W. Lee, G.-T. Park, C.-S. Park, and H.-E. Kim, Appl. Phys. Lett. **88**, 072908 (2006).
[3]J.-W. Lee, C.-S. Park, M. Kim, and H.-E. Kim, J. Am. Ceram. Soc. **90**, 1077 (2007).
[4]B. A. Tuttle, J. A. Voigt, T. J. Garino, D. C. Goodnow, R. W. Schwartz, D. L. Lamppa, T. J. Headley, and M. O. Eatough, in *Proceedings of the 8th IEEE International Symposium on Application of Ferroelectrics* (IEEE, New York, 1992), p. 344.
[5]J. Akedo, J. Therm. Spray Technol. **12**, 181 (2008).
[6]J. Ryu, S. Priya, C. S. Park, K. Y. Kim, J. J. Choi, B. D. Hahn, W. H. Yoon, B. K. Lee, D. S. Park, and C. Park, J. Appl. Phys. **106**, 024108 (2009).
[7]J. J. Choi, B. D. Hahn, J. Ryu, W. H. Yoon, B. K. Lee, and D. S. Park, Sens. Actuators, A **153**, 89 (2009).
[8]J. Ryu, J. J. Choi, B. D. Hahn, D. S. Park, and W. H. Yoon, Appl. Phys. Lett. **92**, 012905 (2008).
[9]T. R. Taylor, P. G. Hansen, B. Acikel, N. Pervez, R. A. York, S. K. Streiffer, and J. S. Speck, Appl. Phys. Lett. **80**, 1978 (2002).
[10]W. M. Yim and R. J. Paff, J. Appl. Phys. **45**, 1456 (1974).
[11]Y. Okada and Y. Tokumaru, J. Appl. Phys. **56**, 314 (1984).
[12]K. Sreenivas, M. Sayer, and P. Garrett, Thin Solid Films **172**, 251 (1989).
[13]E. Shaffir, I. Riess, and W. D. Kaplan, Acta Mater. **57**, 248 (2009).
[14]I. Garbayo, A. Tarancón, J. Santiso, F. Peiró, E. Alarcón-LLadó, A. Cavallaro, I. Gràcia, C. Cané, and N. Sabaté, Solid State Ionics **181**, 322 (2010).
[15]Y. C. Zhou, Z. Y. Yang, and X. J. Zheng, Surf. Coat. Technol. **162**, 202 (2003).
[16]S. B. Desu, J. Electrochem. Soc. **140**, 2981 (1993).
[17]B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, Phys. Rev. B **63**, 014103 (2000).
[18]A. Bouzid, E. M. Bourim, M. Gabbay, and G. Fantozzi, J. Eur. Ceram. Soc. **25**, 3213 (2005).
[19]D. Damjanovic, J. Appl. Phys. **82**, 1788 (1997).