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D. M. Kim, C. B. Eom, V. Nagarajan, J. Ouyang, R. Ramesh, V. Vaithyanathan, and D. G. Schlom

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Thickness dependence of structural and piezoelectric properties of epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ films on Si and $SrTiO_3$ substrates

D. M. Kim and C. B. Eom[a]
Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706

V. Nagarajan and J. Ouyang
Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742

R. Ramesh
Department of Materials Science and Engineering, University of California, Berkeley, California 94720

V. Vaithyanathan and D. G. Schlom
Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

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We report the structural and longitudinal piezoelectric responses (d_{33}) of epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) films on (001) $SrTiO_3$ and Si substrates in the thickness range of 40 nm–4 μm. With increasing film thickness the tetragonality of PZT was reduced. The increase in d_{33} value with increasing film thicknesses was attributed to the reduction of substrate constraints and softening of PZT due to reduced tetragonality. The d_{33} values of PZT films on Si substrates (~330 pm/V) are higher than those on $SrTiO_3$ substrates (~200 pm/V). The epitaxial PZT films on silicon will lead to the fabrication of high performance piezoelectric microelectromechanical devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2185614]

High strain piezoelectric materials have drawn much attention for the fabrication of microelectromechanical systems (MEMS), such as microactuators, micromotors, pressure transducers, strain gauges, and high-frequency ultrasound transducers.[1–3] $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics with composition ($x=0.45-0.5$) close to the morphotropic phase boundary (MPB) are the most commonly used piezoelectric material for various sensors and actuators.[4] With the increasing demand of micromechanical and nanomechanical devices, and their integration into Si technology, it is desirable to fabricate thick PZT films with high piezoelectric properties. Depending on various device dimensions and the frequency range it requires growing piezoelectric films with different thicknesses (1–100 μm). The key advantages of the thick films over bulk ceramics are the lower driving voltage with multilayer stacks and parallel wiring and high frequency applications.[5] On the other hand, epitaxial thick films are expected to have enhanced piezoelectric characteristics over bulk ceramics due to their high crystalline quality, which will significantly improve the performance of high-frequency electromechanical devices.

There has been substantial progress on the fabrication and understanding of the piezoelectric characteristics of PZT thin films. In most of the cases, the observed piezoelectric coefficients of the thin films were much lower (~130 pm/V) than the respective bulk PZT ceramics (~220 pm/V) and were explained by the substrate-induced constraints.[6–10] Theoretically, Haun *et al.*[11] and Du *et al.*[12] have predicted the d_{33} value of rhombohedral PZT single crystals to be about 600 pm/V. Recently, Nagarajan *et al.*[9] observed a reduction of the substrate clamping effect on PZT thin films by patterning discrete islands, which facilitates the removal of the substrate-induced constraint. The same is desirable of high-quality epitaxial PZT thick films, which are expected to have a higher piezoelectric response for high performance electromechanical systems. In this letter, we report the fabrication of high-quality epitaxial PZT thick films up to 4 μm on both (001) $SrTiO_3$ and (001) Si substrates with higher piezoresponse. We have also studied the thickness-dependent structural and piezoelectric properties with close correlation to the substrate constraints and degree of tetragonality of the PZT lattice.

Epitaxial (001) PZT films with various thicknesses (0.4–4 μm) were grown on (001) $SrTiO_3$ and (001) Si substrates using off-axis radio-frequency (rf) magnetron sputtering. The nominal composition of the sputtering target was PZT (Zr/Ti=52/48). Molecular-beam epitaxy (MBE) was used to fabricate 100 Å of epitaxial (001) $SrTiO_3$ on the Si substrate as a template layer.[13] Prior to the PZT film deposition, the epitaxial $SrRuO_3$ bottom electrode was deposited by a 90° off-axis rf magnetron sputtering.[14] During the PZT film deposition the substrate temperature was maintained at 600 °C with an oxygen pressure of 400 mTorr.

Epitaxial arrangement and three-dimensional strain states of the PZT films as a function of thickness were determined using a four-circle x-ray diffractometer (XRD). Figure 1 shows the typical θ-2θ scans of 0.8 and 3.8 μm thick films on (001) Si. Thinner films are purely (00ℓ) oriented texture. However, the 101 peaks from randomly oriented PZT grains were observed for thick films above 2 μm, and pronounced for higher thicknesses. The 3.8-μm-thick PZT films on Si show a relatively higher intensity of the 101 PZT peak than the PZT films on $SrTiO_3$. The crystalline

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[a] Author to whom correspondence should be addressed; electronic mail: eom@engr.wisc.edu

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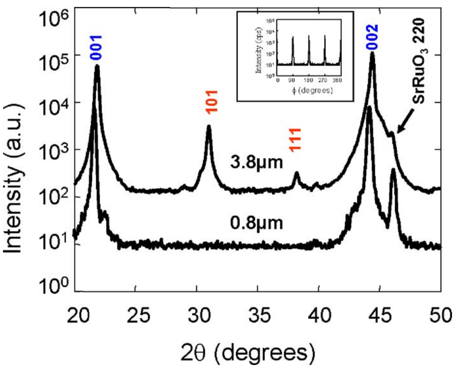

FIG. 1. X-ray diffraction θ-2θ scan of 0.8 and 3.8 μm thick PZT films on (001) Si substrates. The inset shows the azimuthal ϕ scan of PZT 101 reflection, which shows the PZT films on Si growth with cube-on-cube epitaxy.

quality of the PZT films was determined from their rocking curve widths of the PZT 002 reflections. With increasing the film thickness for both substrates the full width at half maximum (FWHM) of the rocking curve increases. The measured FWHM of the rocking curve, for the 3.8-μm-thick PZT films on SrTiO$_3$ and Si was $\sim$0.57° and $\sim$0.67°, respectively. The inset in Fig. 1 shows the azimuthal ϕ scan of PZT 101 reflection. It is clear that in-plane texture is cube-on-cube epitaxy without misoriented grains.

Figure 2 shows the variation of in-plane and out-of-plane lattice parameters of PZT films on Si and SrTiO$_3$ substrates as a function of film thicknesses. The out-of-plane lattice parameters were determined by normal θ-2θ scans. The in-plane lattice parameters were determined by off-axis reflections. It was found that the out-of-plane lattice parameter decreased, and in-plane lattice parameter increased, with film thicknesses irrespective of the substrate. As shown in Fig. 2, the out-of-plane lattice parameter of PZT thin films on SrTiO$_3$ substrates has a higher value in comparison to the respective bulk. Since the thermal expansion coefficients of PZT and SrTiO$_3$ are nearly the same ($\sim 11 \times 10^{-6}/{}^\circ\mathrm{C}$), it could be possible that the thinner PZT films (<0.5 μm) carry a large amount of compressive strain due to the lattice mismatch between the films and substrate ($\sim$3.35%). At higher thickness the influence of epitaxial strain could be minimal and the lattice structure has a tendency from tetragonal to pseudo-rhombohedral-like behavior with reduced tetragonality factor, which is clear from the converging nature of the in-plane and out-of-plane lattice parameters. The nature of variation of in-plane and out-of-plane lattice parameters of PZT films on Si was similar to that of films on SrTiO$_3$, however the effect was more pronounced. It could be possible that the films on Si carry a large amount of tensile strain in the plane due to the mismatch of thermal expansion coefficients. The exact mechanism of the converging nature of the in-plane and out-of-plane lattice parameters of PZT at higher thicknesses was not clearly understood. According to Pertsev *et al.*,[15] the substrate constraint can affect the stability of phases and the thermodynamic potential can change with film thicknesses. Therefore, it could be possible with increasing thicknesses of the PZT films that the crystal structure follows the pseudorhombohedral behavior.

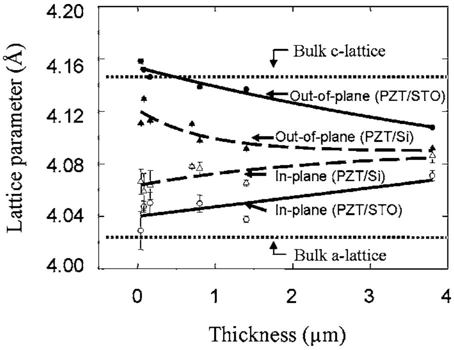

FIG. 2. In-plane and out-of-plane lattice parameters vs film thickness of PZT films on (001) SrTiO$_3$ and (001) Si substrates.

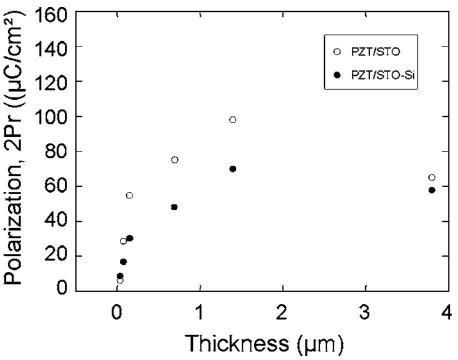

FIG. 3. Thickness-dependent polarization of PZT films on (001) SrTiO$_3$ and (001) Si substrates.

The above results were supported by the reduction of the tetragonality (c/a) of PZT films with increase in thicknesses. The PZT films on Si showed tetragonality smaller in comparison to films on SrTiO$_3$ substrates. This result suggests that the PZT films on Si have a higher tendency towards a rhombohedral structure, which is expected to show enhanced piezoreponse. The puzzle of rhombohedral-like behavior in the tetragonal phase was investigated using the wavelength dispersive spectrometer (WDS). It was found that the Zr/Ti ratio of the target and the films were 52/48 and 45/55, respectively. Although the compositions are in the tetragonal phase region of the phase diagram, it is possible that the lattice distortion increased with typical deposition parameters, cooling process, and growth-induced strain. As a result, the lattice structure followed pseudorhombohedral characteristics rather than large tetragonality at higher thicknesses.

The ferroelectric behavior of the films was examined using ferroelectric tester (RT66A, Radiant Technologies) at virtual ground mode. It was found that the PZT films on Si have a relatively low value of remanent polarization (P_r) and a higher value of coercive field (E_c) than the films on SrTiO$_3$ substrates. We believe that the PZT films on Si might carry relatively large amounts of epitaxial and thermal strain and as a result exhibited larger values of E_c. Figure 3 shows the thickness-dependent remanent polarization of PZT films on Si and SrTiO$_3$ substrates. It is clear that the remanent polarization was increased with the film thicknesses up to 2 μm and reduced for higher thicknesses (>2 μm). As we increase the thickness of films the switching of domains (both 180° and non-180°) might be increased with the reduction of substrate constraints, which leads to increased remanent polarization; even the tetragonality of (00ℓ) domains reduced with the thicknesses. At higher thicknesses (>2 μm) the PZT films get softened, which reduces

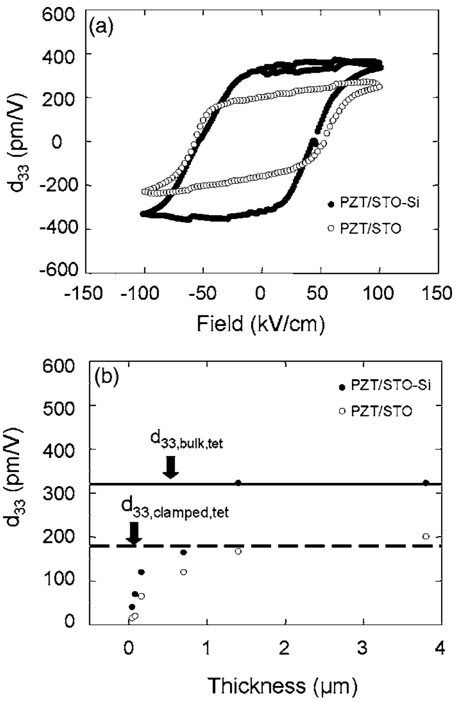

FIG. 4. (a) Typical longitudinal piezoelectric coefficient of 3.8 μm thick PZT films on (001) $SrTiO_3$ and (001) Si substrates. (b) Thickness dependence of longitudinal piezoelectric coefficient (d_{33}) of PZT films on (001) $SrTiO_3$ and (001) Si substrates.

the P_r and E_c value irrespective of the substrate. Thick PZT films on $SrTiO_3$ substrates exhibited relatively higher values of remanent polarization in comparison to films on Si. These results are consistent with the lower tetragonality of PZT films on Si substrates, and also indicative of significant extrinsic contributions to the polarization components.

The piezoelectric measurements were carried out using a piezoresponse force microscope (PFM).[16] In general, the longitudinal piezoelectric coefficient (d_{33}) of thin or thick films is often influenced by the composition, orientation, and presence of non-180° domains. By fabricating ideal epitaxial films on suitable substrates, it could be possible to modify the domain orientations of PZT, and also their piezoresponse. Figure 4(a) shows the typical field-dependent d_{33} characteristics of 4 μm PZT on $SrTiO_3$ and Si substrates. It is clear that the films on Si have a much higher value of d_{33} ($\sim$330 pm/V) than that of films on $SrTiO_3$ ($-$200 pm/V). This result can be correlated to the pseudorhombohedral characteristics of PZT, as observed from structural data. Figure 4(b) shows the piezoelectric coefficients of the PZT films on $SrTiO_3$ and Si substrates as a function of film thicknesses. The nature of the increment of d_{33} value with film thicknesses was similar for the PZT films on both the substrates, however the films on Si have a significant enhancement of d_{33}. The increased piezoelectric coefficient with film thickness could be due to the reduction of substrate constraints and softening of the material by structural modification from higher to lower tetragonal symmetry. This behavior could be directly correlated to the microstructure of the films on both the substrates. From the surface morphology by scanning electron microscopy (SEM), microcracks were observed at the thickness above 2 μm of PZT films on Si substrates. There were no cracks found on PZT films on $SrTiO_3$ substrates. The cracks on thick ($>$2 μm) PZT films on Si substrates could be analogous to the PZT cut capacitors or islands of various sizes. However, the aspect ratio of those small capacitors is much higher than the observed cracks on PZT films on Si. We have observed cracks on PZT films at a separation of 60 μm. We believe that our continuous films still have substrate-induced constraints and by patterning into small capacitors (1 $\mu m \times 1$ μm) could further improve the d_{33} value. This result suggests that the thick epitaxial PZT films on Si with such a high value of piezoelectric coefficients will open a direction for the fabrication of high performance electromechancal systems for high-frequency applications.

In summary, we have fabricated epitaxial PZT films up to 4 μm thickness on $SrTiO_3$ and Si substrates. Irrespective of the substrates, it was observed that increasing the thickness of the PZT films led to the reduction of the tetragonality factor of (00ℓ) domains. The piezoelectric coefficients were found to be higher for PZT films with higher thicknesses. The enhanced piezoelectric coefficient of PZT films on Si than that of $SrTiO_3$ was explained in terms of changes in the microstructure.

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