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Improvement of the dielectric and ferroelectric properties in superlattice structure of $Pb(Zr,Ti)O_3$ thin films grown by a chemical solution route

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Making heterolayered perovskite materials constitutes an approach for the creation of better dielectric and ferroelectric properties. In the experiment reported here, heterolayered PZT40/PZT60 films were grown on $Pt/Ti/SiO_2/Si$ (100) by a chemical solution deposition. The dielectric constant of the heterolayered thin film was significantly enhanced compared with that of pure PZT40 and PZT60 thin films. A dielectric constant of 701 at 100 kHz was observed for a stacking periodicity of six layers having a total thickness of 150 nm. The heterolayered film exhibited greater remanent polarization than PZT60 and PZT40 films. The values of remanent polarization were 7.9, 18.5, and 31 $\mu C/cm^2$, respectively, for pure PZT60, PZT40, and heterolayered thin films, suggesting that the superior dielectric and ferroelectric properties of the heterolayered thin film resulted from a cooperative interaction between the ferroelectric phases made from alternating tetragonal and rhombohedral phases of PZT, simulating the morphotropic phase boundary of this system. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1751623]

For many years a great deal of interest has focused on the practical applications of perovskite-type compounds, including $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $Pb_{1-x}Zr_xTiO_3$, $Pb_{1-x}La_xTiO_3$, due to their potential to be used as memory cell capacitors (DRAMs) and nonvolatile memories (FRAM).[1,2] Traditionally, most of these studies have dealt with single-phase thin films, but an important technology that has emerged recently involves heterolayered or superlatticed thin films consisting of alternate layers of materials, phases, structures, and composition at gradient structures.[3] First and foremost, this type of structure has been identified as possessing physical properties different from those of bulk materials, causing it to become a subject of intensive scientific research. It offers opportunities for potential application in high-density, nonvolatile memories and in other technologies. In recent years, this superlattice technology has taken a revolutionary step forward in response to the challenging requirements of high-density memories. Heterolayered thin films with composition gradients normal to the substrate surface offer a preferable alternative approach, since they display properties superior to those of conventional ferroelectric thin films.[4,5] Various deposition techniques have been used to prepare heterolayered thin films with such superior properties.[6–8] The most recent approach can make films with high dielectric constant and large remanent polarization, as well as long reliability of the ferroelectric layers with fatigue and imprint resistance.[9] Recent research has concentrated on a number of heterolayered thin films whose layers include $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, $Pb_{1-x}Ca_xTiO_3$, $Ba_{1-x}Sr_xTiO_3$, and $PbZr_xTi_{1-x}O_3$.[10–13] The phase diagram of the $PbZr_xTi_{1-x}O_3$ solid solution system is particularly complex, containing a large number of structural transformations. At room temperature, the PZT properties are strongly influenced by the Zr:Ti ratio, exhibiting useful dielectric, ferroelectric, and piezoelectric properties.[14,15] The current interest in PZT is ascribed to its interesting physical properties[16,17] particularly for those with composition close to the morphotropic phase boundary (MPB) around $x \sim 0.45-0.5$, where all the properties are enhanced.[18] The morphotropic phase boundary (MPB) that separates rhombohedral Zr-rich PZT from tetragonal Ti-rich PZT is not well defined, since it appears to be associated with a region of phase coexistence whose width depends on the compositional homogeneity and on the processing conditions employed in its preparation. To overcome processing difficulties and chemical homogeneity problems, artificially engineered thin film heterostructures or superlattices with tetragonal and rhombohedral phase PZT offer a good alternative for tailoring the morphotropic-like phase boundary (MPB). This approach to multilayered heterostructures with MPB is expected to modulate and maximize the performance of the electrical properties of PZT thin films, potentially leading to a wealth of applications in electronic devices. Wang *et al.*[11] have reported the enhancement of the dielectric constant in multilayered $Pb(Zr_{0.2}Ti_{0.8})O_3/Pb(Zr_{0.8}Ti_{0.2})O_3$ thin films prepared by rf magnetron sputtering. Xu *et al.*[6] reported on polycrystalline multilayered $BaTiO_3/SrTiO_3$ thin films. A dielectric constant of 527 at 100 kHz was reported recently in multilayered $SrTiO_3/BaTiO_3$ thin films, and was explained as the sum of each individual thin film using a series connection model.[19]

This letter reports the fabrication of a crack-free, dense, heterolayered PZT thin film with dielectric and ferroelectric properties characteristic of the MPB. However, its superior performance was artificially controlled and prepared by a chemical solution route. Figure 1 shows the schematic rep resentation of the ferroelectric structure considered here.

The multilayered PZT thin films were grown on $Pt/Ti/SiO_2/Si$ substrate by chemical solution routes. Two so-

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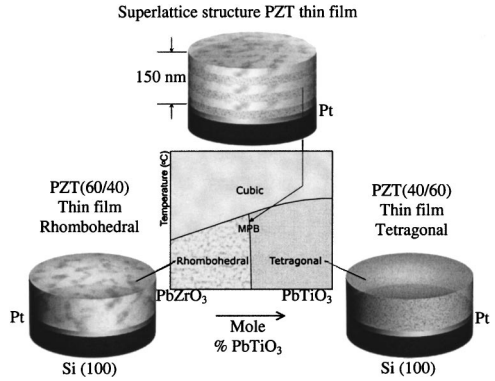

FIG. 1. Schematic representation of the ferroelectric structure considered here.

lutions were prepared with nominal compositions of $PbZr_{0.4}Ti_{0.6}O_3$ (PZT40) and $PbZr_{0.6}Ti_{0.4}O_3$ (PZT60) for deposition by spin coating. The method employed in the preparation of chemical solutions for PZT thin films has been reported elsewhere.[20] The first deposition layer was made with the PZT40 solution on the substrates, using spin coating at a 4600 rpm rotation speed and 30 s deposition time. After the first deposition, the films were dried on a hot plate at 150 °C for 20 min to remove residual solvents. The films were then heat treated in two stages. The first stage consisted of heating to 400 °C for 2 h to decompose the organic materials. In the second stage, the films were heated to 700 °C for crystallization. The process was repeated for the second layer using the PZT60 solution. Alternating materials were deposited until the film consisted of six layers, with the first and last being PZT40 and PZT60 layers, respectively.

The structure of the heterolayered thin films was analyzed by x-ray diffraction (XRD) in the θ–2θ scan mode, recorded on a Rigaku diffractometer (D/max-2400) using Cu K_α radiation. The microstructure and thickness of the heterolayered thin film were examined using, respectively, an atomic force microscope (AFM) (Digital Instruments, Nanoscope IIIa) and a high-resolution transmission electron microscope (HRTEM) (JEOL 3010 operated at 300 kV). The electrical properties of the Au/PZT40/PZT60/Pt capacitor structure were investigated. To prepare the capacitor cells, dots of Au were deposited on the multilayered thin films by evaporation through a shallow mask, on an area of 4.9×10^{-2} mm^2. The capacitor's dielectric properties were measured by an HP4192A impedance/gain phase analyzer, while the ferroelectric properties were verified using a Radiant Technology RT6000HVS apparatus in virtual ground mode.

The XRD patterns shown in Fig. 2 indicate that the heterolayered thin films were polycrystalline in nature and had a perovskite structure. The XRD patterns consists of two sets, one for PZT40 and the other for PZT60, so the (101)/(110), (002)/(200), and (112)/(211) peaks are displayed separately in the heterolayered thin film. This result indicates that the tetragonal and rhombohedral phases coexist in the heterolayered thin film. The inset in the Fig. 2 clear shown the symmetry signature of the PZT40 as begin of tetragonal nature and PZT60 as begins of rhombohedral nature. In addition, analysis by micro-Raman revealed clearly the tetragonal and rhombohedral nature of the PZT40 and PZT60, respectively. Wang *et al.* found a similar behavior in PZT20 and PZT80

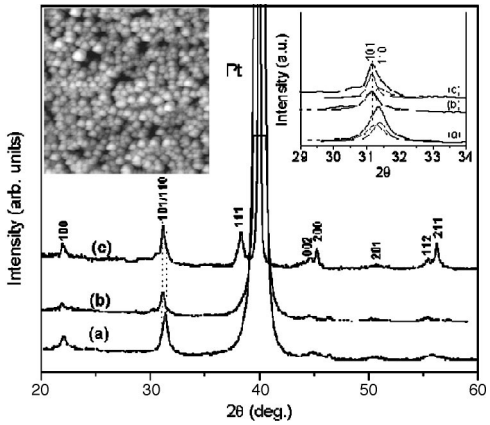

FIG. 2. X-ray diffractograms of (a) PZT40 thin film, (b) PZT60 thin film, and (c) heterolayered PZT thin film. The inset shown a limited region x-ray data fitted to (101) and (110) reflections, as well as AFM micrograph (1×1 μm).

thin films with heterolayered structures. Xu *et al.*[6] and Pontes *et al.*[19] reported that $BaTiO_3/SrTiO_3$ heterolayered thin films did not diffuse together and did not form a solid solution. It should be noted that the XRD patterns are composed of a $BaTiO_3$ phase and a $SrTiO_3$ phase.

Figure 3 shows the cross section of the PZT heterolayered thin film analyzed by HRTEM. The thickness of the thin films after one drying/annealing cycle was approximately 25 nm. As can be seen in the cross-sectional micrograph, the interface between the PZT40 layer and the substrate is distinct, presenting a good quality [see inset in Fig. 3(b)]. A total of six layers were deposited, varying the stacking sequences to achieve a total thickness of about 150 nm. The surface morphology of the PZT60 layer, which was the top layer, was found to be very smooth, pinhole-free, and continuous, devoid of cracks or rosette-like structures. The average surface roughness of the heterolayered thin film was 3 nm and the average grain size varied from 50 to 60 nm; see inset in Fig. 2.

Figure 4 shows the dielectric constant and dielectric loss as a function of frequency at room temperature. As can be seen, the dielectric constant of the heterolayered thin film was greater than that of single-phase thin films. Many studies have shown dielectric constant enhancement in heterolayered thin films associated with capacitors in series. To confirm the validity of capacitor series models, we have assumed the effective dielectric constant of the heterolayered structure to be a series connection model of poly-PZT40 and polyPZT60 dielectric layers, whose effective dielectric constant,

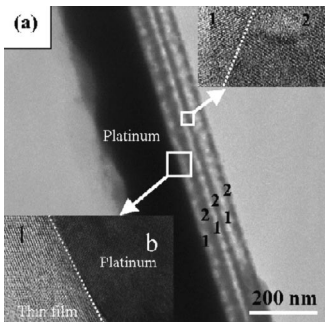

FIG. 3. (a) Cross-sectional HRTEM micrograph of the heterolayered PZT thin film; The inset shows the film/film/substrate interface 1=PZT40; 2=PZT60.

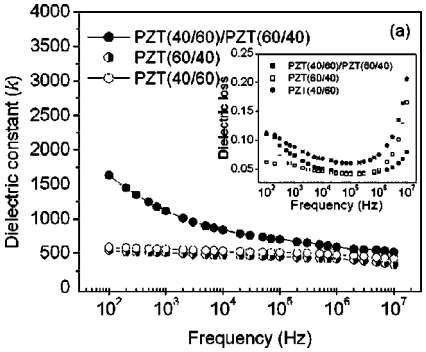

FIG. 4. (a) Dielectric constant and (b) loss of the PZT40, PZT60, and heterolayered PZT thin films as a function of frequency.

ε_{eff}, can be expressed theoretically as

$$\frac{1}{\varepsilon_{\text{eff}}}=\left(\frac{t_1}{\varepsilon_{\text{PZT40}}}+\frac{t_2}{\varepsilon_{\text{PZT60}}}+\frac{t_3}{\varepsilon_{\text{PZT40}}}+\frac{t_4}{\varepsilon_{\text{PZT60}}}+\frac{t_5}{\varepsilon_{\text{PZT40}}}+\frac{t_6}{\varepsilon_{\text{PZT60}}}\right) /(t_1+t_2+t_3+t_4+t_5+t_6), \quad (1)$$

where t_1, t_3, and t_5 are the thicknesses of poly-PZT40 and t_2, t_4, and t_6 are the thicknesses of poly-PZT60. Thus, based on the heterolayered capacitors, ε_{eff} was calculated theoretically to be about 481, assuming that the relative dielectric constants of PZT40 and PZT60 are 512 and 452, respectively, at a frequency of 100 kHz. These values were obtained from layers of PZT40 and PZT60 films prepared individually. As shown in Fig. 4, the dielectric constant value was much higher than the latter ($\varepsilon_r \sim 701$ at a frequency of 100 kHz), and was calculated by assuming the series connection model of two components. The calculated dielectric constant value showed a difference of more than 45% compared to the experimental dielectric constant value of the heterolayered thin film. This suggests that heterolayered thin film cannot be explained as the sum of each individual thin film (PZT40 and PZT60) using a series connection capacitor model. The behavior observed here is consistent with that reported by Wang *et al.*[11] for heterolayer-structured PZT20/PZT80 thin films obtained by rf magnetron sputtering.

The hysteresis loops of single-layer PZT40, PZT60, and PZT heterolayered thin films are shown in Fig. 5. The hysteresis loop of the single-layer PZT60 (rhombohedral phase) and PZT40 (tetragonal phase) thin films showed small remanent polarization values of $P_r \sim 7.9$ and 18.5 μC/cm^2, respectively. On the other hand, the heterolayered PZT thin film exhibited a higher remanent polarization value than the other single-phase thin films with $P_r \sim 31$ μC/cm^2. In addition, the remanent polarization value obtained here was found to be greater than the remanent polarization of 15 μC/cm^2 reported by Wang *et al.*[11] These findings demonstrate that inserting PZT60 (rhombohedral phase) layers between PZT40 (tetragonal phase) layers improves the dielectric and ferroelectric properties of heterolayered thin film. These results can be interpreted as a cooperative interaction between two ferroelectric phases (tetragonal and rhombohedral) of similar energy. This cooperative effect, simulating MPB, allows for optimization of the reorientation of domains during the poling process.[7,18] Due to the polycrystalline nature of the processed thin film, the stress effects caused by film/substrate mismatching can be disregarded. Thus, the influence of this effect on the dielectric and ferroelectric properties should be minimal. Consequently, we believe that the properties of heterolayered thin films made from alternating tetragonal and rhombohedral phases of PZT mimic those of PZT ceramic at the morphotropic phase boundary.

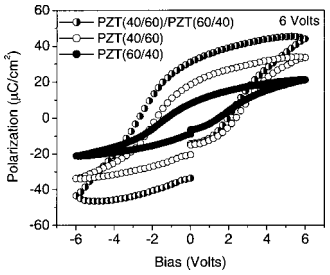

FIG. 5. Hysteresis loops of the PZT40, PZT60, and heterolayered PZT thin films.

In summary, the use of heterolayered thin films for achieving better performance than homogenous single layered thin films is well established. We have shown here that heterolayered PZT thin films prepared by a chemical solution route provide remarkable improvement to the dielectric and ferroelectric properties. The enhancement might be interpreted as the MPB effect, similar to the MPB effect in bulk PZT ceramics. Our results also demonstrate that the chemical solution route is an effective method for tailoring heterolayered structures to obtain specific properties or materials.

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