Effect of mechanical constraint on the dielectric and piezoelectric behavior of epitaxial Pb(Mg_{1/3}Nb_{2/3})O_3(90\%)–PbTiO_3(10\%) relaxor thin films

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The effect of heteroepitaxy-induced constraint on the structure and piezoelectric properties of the relaxor ferroelectric lead magnesium niobate–lead titanate (PMN–PT) was investigated. Relaxor PMN–PT epitaxial thin films with oxide electrodes were grown by pulsed-laser deposition on (100) LaAlO_3 substrates. We observe a systematic decrease in the phase transition temperature (temperature at which a maximum in dielectric response occurs), from around 250 to around 60 °C as the relaxation thickness is increased from 100 to 400 nm. This is accompanied by an increase in the relative dielectric constant (\(\epsilon_r\)), measured at room temperature and 10 kHz, from 300 to 2000. The piezoelectric coefficient \(d_{33}\) measured using a scanned probe microscope, increase by almost an order of magnitude with increasing film thickness. © 1999 American Institute of Physics.

Recently, relaxor ferroelectrics have attracted much attention due to their very large piezoelectric responses and unique dielectric behavior. The large dielectric permittivity and electromechanical constants make these materials very attractive for actuators, multilayer capacitor structures, displacement transducers, and microelectromechanical systems-based applications. In bulk ceramics, Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) -based systems and their solid solutions with PbTiO_3 (PT) have been the most widely studied in terms of structural properties and electrostrictive coefficients with unipolar strains as large as 1.7% along the [001] direction and a longitudinal piezoelectric coefficient \(d_{33}\) of 2500 pm/V being observed in single crystals.

The potential impact of thin-film relaxor ferroelectrics in integrated actuators and sensing applications has stimulated research on the growth and characterization of thin films. Thin films have been made by pulsed-laser deposition (PLD), sol–gel, and metalorganic chemical-vapor deposition. Typically, the \(d_{33}\) values of PMN and PMN–PT thin films range from 50 to 100 pm/V and values of the relative dielectric constants \(\epsilon_r\) in the range of 800–2000 have been reported. Both these properties are considerably lower than those in the bulk and in single crystals. The exact origins of this dramatic difference is still not clear, although several possible origins have been identified. In this letter, we demonstrate the distinct role of epitaxial film thickness on the dielectric and piezoelectric responses of these relaxors.

Thin-film capacitors of composition Pb(Mg_{1/3}Nb_{2/3})O_3(90\%)–PbTiO_3(10\%) (PMN–PT) were grown by PLD on (001)-oriented LaAlO_3 (LAO) substrates. 30-nm-thick La_{0.5}Sr_{0.5}CoO_3 (LSCO) layers were deposited as top and bottom electrodes at 650 °C under 10 mTorr of oxygen partial pressure and subsequently cooled under 760 Torr of oxygen pressure. The temperature for the deposition of PMN–PT was between 570 and 590 °C and oxygen pressure was varied from 250 to 300 mTorr. The thickness of the ferroelectric film was varied from 100 to 400 nm. All films were then patterned with 25×10^{-4} mm² platinum capacitors. The films were then analyzed for epitaxial quality and other crystallographic features with a Siemens D5000 diffractometer and the electrical measurements were carried out using a Hewlett–Packard (HP 4194A) impedance gain analyzer. The piezoelectric measurements were carried out using an atomic force microscope (AFM) in conjunction with a superimposed ac signal to elicit a piezoelectric response from the capacitor, details of which are presented in earlier papers.

Figure 1 illustrates a typical Bragg scan (θ–2θ) showing the film is phase pure while the inset shows the ϕ scan of the PMN–PT layer where we confirm fourfold cube-on-cube growth. A lattice parameter of 0.405 nm was calculated from the (200) peak of PMN–PT, which is slightly higher than the c-axis lattice parameter of the bulk tetragonal phase (0.404 nm). Figure 2 shows the full width at half maximum (FWHM) of the ω scan around the (200) PMN–PT peak as a function of film thickness, which gradually decreases from 0.69° to 0.49°, indicating a progressive decrease of the local strain and/or an improvement of crystallinity within the film. X-ray diffraction results also indicate that the bottom LSCO electrode layer is pseudomorphic with the substrate.

Figure 3 plots the temperature of dielectric maximum

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and the relative dielectric constant \( \varepsilon_r \) (or permittivity) as a function of film thickness. In relaxor ferroelectrics it is well known that the ferroelectric phase shows considerable dielectric dispersion below \( T_m \) while above \( T_m \) there is no dielectric dispersion. Figure 3 shows \( T_m \) measured by the characteristic dielectric behavior increases as we decrease the film thickness. In fact, for the thinnest film \( T_m \) is higher than the reported bulk value \(^2\) by at least 150 °C.

Thus, a decrease in the permittivity would result in a decrease in the value of \( d_{33} \) with decreasing relaxor film thickness. This is clearly seen in Fig. 4 where we plot the \( d_{33} \) constant measured by electric force microscopy (EFM) as a function of sweep voltage for different thicknesses. The value of \( d_{33} \) drops from around 85 pm/V for the 400 nm film to just 10 pm/V for the 100 nm film. The drop in \( d_{33} \) values shows that compared to the thicker films, the thin films are electromechanically less compliant. It is interesting to note that even the highest values for \( d_{33} \) and \( \varepsilon_r \) in thin films are still about 20 times smaller than the reported bulk values.

These results can be interpreted as follows. During growth and cooling down, the heteroepitaxial stress and the thermal stresses due to different thermal expansion coefficients of the film and the substrate relax through the formation of misfit dislocations at the film–bottom-electrode interface. The degree of relaxation depends on the thickness of the film. It decreases with decreasing film thickness. Therefore, before the transition temperature, the thinner films have relatively larger internal compressive stresses than the thicker films. This different value of the compressive stress results in a different shift in \( T_m \) with respect to its position in the bulk (see Fig. 3).

After the transition to the relaxor state, the average misfit stress is relieved due to the arising of a nonuniform (chemically disordered) state. Then, the average stress in the film is transformed into a nonuniform stress distribution of alternating sign which is observed as broadening of the \( \omega \) scans around the \( (200) \) peak of PMN–PT (Fig. 2). This mechanism of stress relaxation acts at each point of the film. Therefore, it does not depend on the film thickness. It means that the final level of residual stress is the same for all the films. It corresponds to a small compression [bulk lattice parameter 0.404 nm compared to 0.405 nm of the films calculated from the \( (200) \) peak of PMN–PT]. However,
the amplitude of the nonuniform stress is determined by the stress state before the transformation. Therefore, it is larger in thinner films as evidenced from the relatively broader ω scans for the thinner films. The larger amplitude of the stress field corresponds to larger film stiffness. Taking into account that $e_{r}^{-1}$ for a clamped film is proportional to the elastic stiffness, it is possible to explain that $e_{r}$ grows with film thickness. $d_{33}$ follows the same trend since it is proportional to $e_{r}$. We cannot exclude that the degree of clamping of thicker films with a higher degree of relaxation due to the high density of misfit dislocations at the film–bottom-electrode interface is less than the coherent thinner films. However, even the thickest film (~400 nm) is clamped considerably. This can explain at least partially that $d_{33}$ and $e_{r}$ cannot attain their respective bulk values. A detailed quantitative analysis will be given elsewhere.

Although we have identified one key source that impacts the dielectric and piezoelectric response, in the relaxor system, the degree of chemical ordering and the coupling of chemical effects with electromechanical effects are also important parameters that determine the magnitude of these responses. In thin films, these may be further heightened due to deposition-induced disorder. We are presently carrying out experiments to further understand the origin of these differences.

To summarize, we have studied the effect of film thickness on the dielectric and electromechanical behavior of PMN–PT thin films. A strong dependence of both properties on the thickness of the PMN–PT layer is shown. We have related these effects to the clamping and relaxation of stresses in these relaxor films.

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1 S. Nomura and K. Uchino, Ferroelectrics 41, 117 (1982).