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Citation: Applied Physics Letters **91**, 082907 (2007); doi: 10.1063/1.2775044
View online: http://dx.doi.org/10.1063/1.2775044
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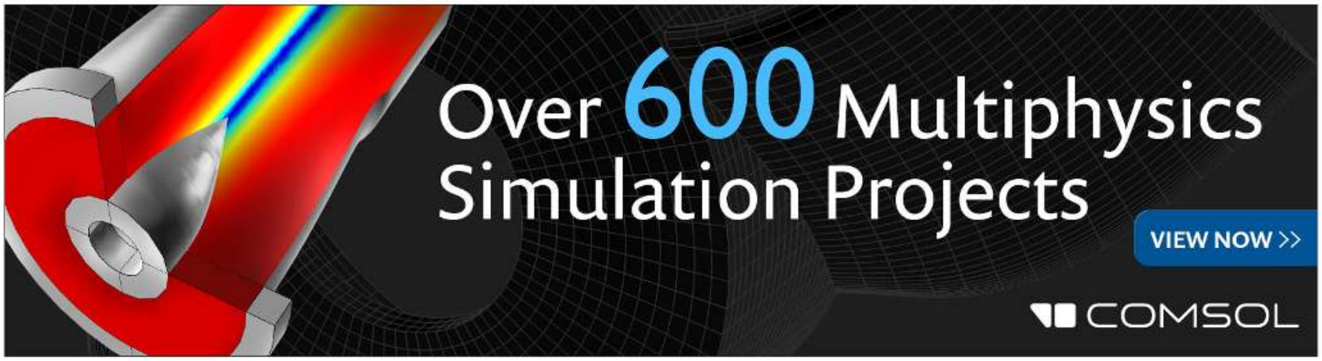

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APPLIED PHYSICS LETTERS **91**, 082907 (2007)

Antiferroelectriclike polarization behavior in compositionally varying $(1-x)$ $Pb(Mg_{1/3}Nb_{2/3})O_3-(x)$ $PbTiO_3$ multilayers

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(Received 7 June 2007; accepted 1 August 2007; published online 24 August 2007)

Compositionally varying multilayers of $(1-x)$ $Pb(Mg_{1/3}N_{2/3})O_3-(x)$ $PbTiO_3$ were fabricated using pulsed laser ablation technique. An antiferroelectriclike polarization hysteresis was observed in these relaxor based multilayer systems. The competition among the intrinsic ferroelectric coupling in the relaxor ferroelectrics and the antiferroelectric coupling among the dipoles at the interface gives rise to an antiferroelectriclike polarization behavior. An increment in the coercive field and the applied field corresponding to the polarization flipping at low temperatures, provide further insight on the competition among the long-range ferroelectric interaction and the interfacial interaction in the polarization behavior of these relaxor multilayers. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2775044]

Ferroelectric (FE) superlattices (SLs) and multilayers (MLs) have gained considerable interest in recent years due to their attractive properties and new opportunities they provide on engineering the ferroelectric materials for various applications.[1] Physical properties of ferroelectric multilayers and superlattices such as polarization, susceptibility, and dielectric constant vary from the homogeneous individual materials constituting the ML and SL.[2] Physical properties of ML and SL are highly dependent on the interface among the layers and the dimensions of the individual layers present.[3] The influence of various interactions such as short range, long range, and the interfacial interaction among the dipoles present in bilayers, multilayers, and superlattices has been an interest of study from both the technological importance and the fundamental understanding of ferroelectric interactions.[4] There has been various studies on interlayer interaction and its dimensional dependence in the case of ferroelectric heterostructures.[5–7] The importance of the interfacial interaction in the case of FE heterostructures has been studied by various theoretical models.[8–10]

The influence of the interfacial coupling in the polarization behavior has been studied theoretically using a continuum model based on the Landau free energy of the system as a function of polarization[9] and a discrete Ising model.[10] However, very few experimental evidences on the appearance of multiple loops in the case of ferroelectric heterostructures have been reported.[11,12] Most of the theoretical and experimental studies on heterostructures were devoted to normal ferroelectrics and not on the relaxor ferroelectrics (RFEs).

Relaxor ferroelectrics are a subclass of ferroelectric materials and have been a potential candidate of study for both fundamental and technological applications over few decades.[13,14] RFEs are well known for their intrinsic structural, chemical heterogeneity, and polarization fluctuations present inherent in the lattice.[14] Pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and PMN based solid solutions are one among the most widely studied RFEs for their interesting structural and physical properties.[14–16] Recently, few studies have been reported on the relaxor heterostructures based on PMN and the variation in physical properties by introducing strain and additional chemical heterogeneity to the parent compound.[11,17] RFEs do exhibit a polarization hysteresis with applied electric field with switchable remnant polarization which is commonly referred as a fingerprint of any FE material.[14] The presence of interactive nanopolar domains present in a RFE mimics the behavior of FE domains, whereas a diffused phase transition and the existence of remnant polarization beyond the transition are the characteristic features of a RFE.[14] The random field due to randomly oriented dipoles is known to play a crucial role in the polarization behavior of a RFE.[14] Polarization behavior of RFE heterostructures could throw light on the polarization mechanism and open up new applications of the existing classical RFE thin films.

In this work, relaxor multilayer thin films with four different individual layer compositions of $(1-x)$ $PbMg_{1/3}Nb_{2/3}O_3-(x)$ $PbTiO_3$ (PT) (x=0.0, 0.1, 0.2, and 0.3) were fabricated through pulsed laser ablation technique. A multiple loop polarization behavior was observed similar to the predictions made in theoretically simulated polarization curves of ferroelectric heterostructures.

Figure 1 shows the x-ray diffraction pattern of a laser ablated multilayer structure with an individual layer thick-

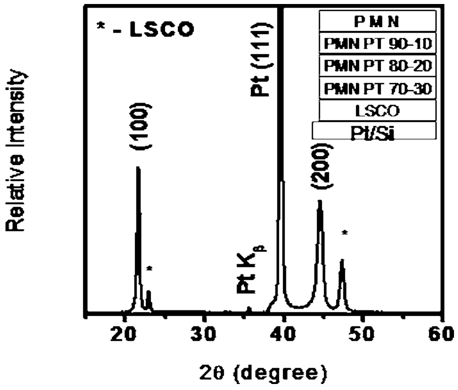

FIG. 1. X-ray diffraction pattern of a relaxor multilayer deposited on Pt/Si substrates with LSCO template. The inset shows a schematic of the multilayer thin film structure.

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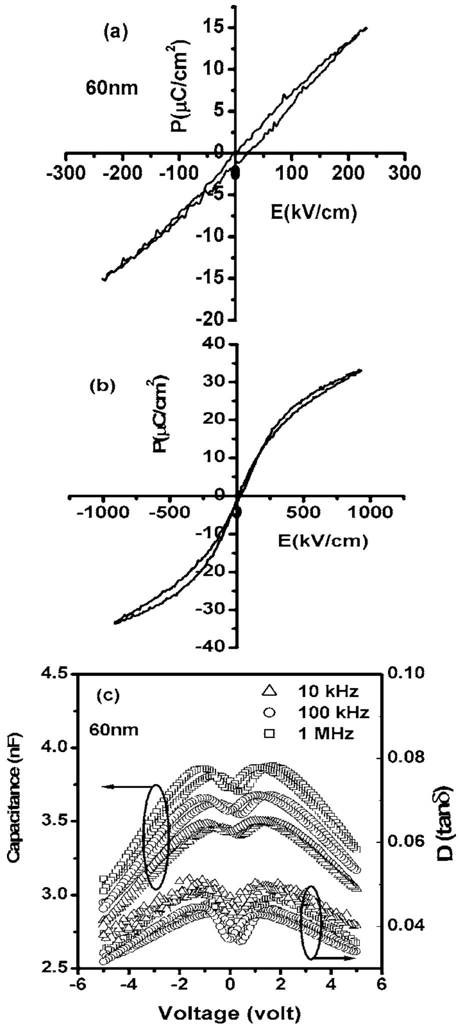

FIG. 2. [(a) and (b)] Room temperature polarization behavior of a relaxor multilayer at low and high applied fields. (c) Room temperature *C-V* curve of the same relaxor multilayer.

ness of 60 nm. The inset shows the schematic and the sequence of individual layers in the fabricated ML structure. PMN indicates $Pb(Mg_{1/3}Nb_{2/3})O_3$ and PMNPT refers to the solid solution of PMN with PT followed by the at. % of PMN and PT, respectively. The ML structure was fabricated over platinized silicon substrates with $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) (~50 nm) electronic conducting oxide acting as a template to assist phase formation. The details of the fabrication could be found elsewhere.[17] The thickness of the individual layers was maintained constant at 60 nm and was determined from secondary ion mass spectrometry based depth profile and cross-sectional scanning electron microscope. The FE characterization was carried out in a metal-insulator-metal configuration with circular gold dots of diameter 500 μm acting as top electrode and the underlying platinum layer acting as a bottom electrode, using a RT66A loop tester and an impedance analyzer (Agilent Technologies 4249A).

Figures 2(a) and 2(b) show the room temperature polarization behavior of the multilayer at low and high applied fields, respectively. A slim and narrow hysteresis loop was observed at low fields. The room temperature coercive field was found to be less (~7.28 kV/cm) than that observed in single layers [~24.18 kV/cm (PMNPT70-30)] of the different compositions present in the multilayer stacking. Reduction in the coercive field in a normal ferroelectric is attributed to defect assisted nucleation, growth, and switching of domain.[18] On the other hand, on increase of applied field, a field driven polarization crossover was observed in the multilayer thin films, similar to a double loop hysteresis in a normal antiferroelectric (AFE)-material-like $PbZrO_3$.[19,20] A zero coercive field at low applied field and formation of a hysteresis at high applied fields are well known characteristics of a conventional AFE system. The multiple loop behavior could be a combination of the intrinsic FE property and the AFE interfacial coupling at the interface. One among the basic models that explains the effect of the intrinsic coupling and the interfacial coupling, consists of a Hamiltonian, as given below.[10]

$$H = -\sum_{\langle i,j\rangle} J_{i,j} S_i^z S_j^z - \sum_i \Omega_i S_i^x - 2\mu E \sum_i S_i^z, \qquad (1)$$

where J_{ij} is the coupling constant among the dipoles present within a layer when the *i*th dipole and *j*th dipole belong to the same layer; it turns out to be the interfacial coupling when the *i*th dipole and the *j*th dipole belong to the adjacent layers. S_i^x and S_i^z are the components of the spin operator in the case of magnetism and they mimic the dipole moment present in the FE systems.[8,10] Ω_i is the transverse field across each layer and the third term couples the system with the applied electric field. The AFE interfacial coupling among the dipoles at the interface minimizes the energy of the system. In the case of the relaxor multilayers discussed in this paper, three active interfaces are present, (i) PMN/PMNPT90-10, (ii) PMNPT90-10/PMNPT80-20, and (iii) PMNPT80-20/PMNPT70-30.

In relaxor ferroelectrics, the randomly oriented dipoles and their alignment with applied field are attributed to the polarization mechanism. The antiferroelectric interaction at the interfaces among the dipoles of the relaxor multilayers dominates, which could be understood based on the energy arguments.[9,10] This AFE interaction among the dipoles at the interface align towards the applied field and could give rise to a polarization flip at higher applied fields. The intrinsic FE behavior of the system is responsible for the narrow central loop observed. The prevailing AFE coupling at the interfaces competes with the external applied field and on increase of applied field over a critical value, the AFE interfacial coupling flips along the field direction and gives rise to a second loop character in the polarization hysteresis. The same phenomenon is repeated when the field is reversed but in the other direction. Figure 2(c) shows the small signal capacitance-voltage (*C-V*) characteristics of the multilayer thin film, which acts as a cross-check for the observed *P-E* behavior. The variation of the capacitance with applied field with a valley as observed at zero fields is commonly observed in the case of AFE materials.[19] A similar reduction in coercive field and double loop behavior has been observed theoretically in homogeneous semiconductor ferroelectrics due to the space charge effect introduced by the spatial variation of polarization due to high defect concentration.[18] The leakage current density of the ML (~2×10^{-9} A/cm^2) was comparable to that of the homogeneous single layers [~3×10^{-9} A/cm^2 (PMNPT 70-30)]; hence, the possibility of the appearance of multiple loop due to polarization gradients arising due to the space charge effects arising from high defect or carrier concentration, as in the case of semiconductor ferroelectrics, could be ignored.[18] In contrast, one should

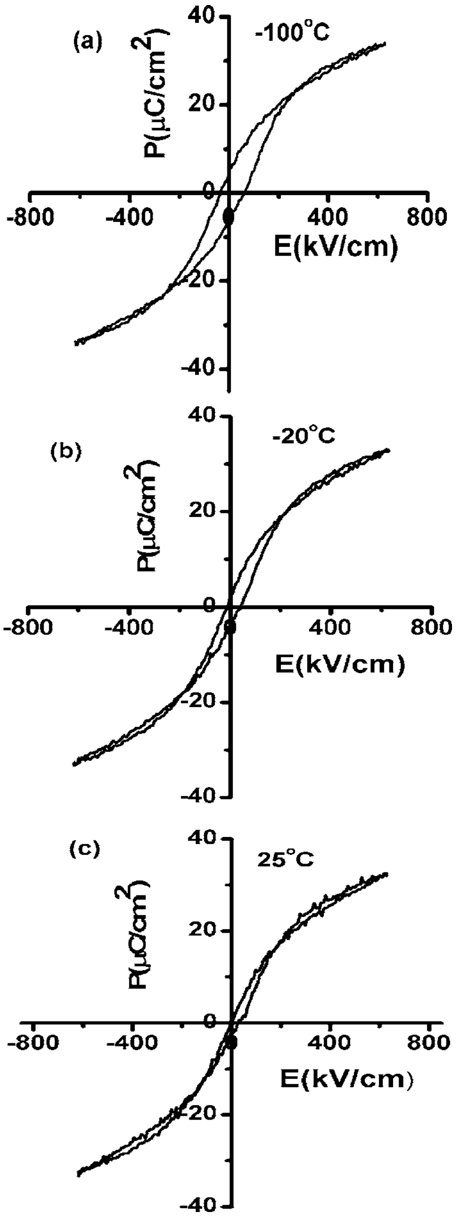

FIG. 3. (a), (b), and (c) shows the *P-E* hysteresis of the ML at −100, −20, and 25 °C, respectively.

not forget that the spatial fluctuation in polarization present inherent in a RFE is quite different from the polarization gradient due to space charge effect used in the theoretical models that explains the multiple loop behavior in semiconductor FE.[18] The theoretical models[5,8,10] assume an AFE coupling *a priori* based on energy arguments in the case of normal ferroelectrics, whereas the dimensional dependence of the interfacial coupling and the polarization fluctuation and the random fields in a relaxor needs more accurate calculations including the characteristic features of the relaxors to obtain a quantitative picture.

To obtain further insight among the competing interactions, temperature dependence of the *P-E* loops was studied and shown in Fig. 3. The pure PMN present in these heterostructures has a dielectric maximum below room temperature.[14] The PMN layer is expected to be in a superparaelectriclike phase, common for a relaxor ferroelectric above the dipolar glass freezing temperature. Hence, at room temperature, the PMN/PMNPT90-10 interface would be a superparaelectric-ferroelectric interface. On decrease of temperature, the interaction strength of both the intrinsic coupling and the interfacial coupling among the dipoles increases. This could effectively give rise to a larger central loop behavior and higher fields for the alignment of the interfacial dipoles to align in the direction of the applied field. The increment of the coercive field at low temperatures could be due to the onset of FE long-range interactions and hence a larger central loop is observed. Similarly, the enhancement of the strength of the interfacial interaction at low temperature could give rise to larger values of the applied field required for the polarization flips. Thus, the competition among the competing interactions, with the applied field and thermal energy, could be understood from the low temperature polarization hysteresis of the PMNPT ML. The details of the dimensional dependence of the individual layers present in a relaxor ML and the nature of the polarization are currently under study.

In summary, highly oriented compositionally varying relaxor MLs were fabricated by pulsed laser ablation deposition. An AFE-like behavior was observed in the *P-E* studies of the PMNPT ML. The observation was consistent with the loops simulated for FE heterostructures by various theoretical models. An antiferroelectric interaction among the dipoles at the interface could be attributed to the multiple loop behavior. The electric field required to flip the antiferroelectrically coupled dipoles to align in the applied field direction increased at low temperatures. The *P-E* studies at room temperature and below explain the competition present among the intrinsic dipolar interaction, the interfacial interaction among the dipoles, and the applied field.

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