

Phase development and electrical property analysis of pulsed laser deposited $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (70/30) epitaxial thin films

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(001)-oriented heterostructures consisting of LaAlO_3 substrates, SrRuO_3 bottom electrodes, and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) (70/30) films were deposited by pulsed laser deposition from Pb-enriched ceramic targets. The epitaxial growth of all layers was confirmed by four-circle x-ray diffraction. Film growth was carried out over a wide range of processing space where substrate temperature, ambient pressure, and laser parameters were varied in order to determine suitable conditions for producing high quality crystals with good electrical properties. In general, strong similarities were observed between thin film and ceramic processing of the same compositions. The associated pyrochlore phase was very difficult to avoid and, in the absence of excess Pb-containing second phases, could only be done at very high temperatures and high oxygen/ozone pressures for films on LaAlO_3 substrates. When deposited at temperatures below approximately 640 °C, PMN-PT films grown from lead-enriched targets exhibited depressed ferroelectric transition temperatures. For depositions at or above 660 °C, the electrical properties approached those of bulk single crystals. In particular, films showed room temperature dielectric constants greater than 1500, well developed Curie-Weiss behavior, and remanent polarization values between 13 and 20 $\mu\text{C}/\text{cm}^2$. © 1998 American Institute of Physics. [S0021-8979(98)08520-X]

I. INTRODUCTION

Recently, ultralarge piezoelectric responses have been observed in single crystal solid solutions of relaxor-ferroelectric perovskites and PbTiO_3 : the specific systems being $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT). Optimized electromechanical properties are observed for compositions just on the rhombohedral side of the morphotropic phase boundary. Piezoelectric d_{33} coefficients of 2500 $p\text{C}/\text{N}$ and unipolar strains as large as 1.7% have been observed when PZN-0.09 PT crystals were measured along $\langle 100 \rangle$ type directions, even though the polar axis of these compositions lies along $[111]$.^{1,2} Given this measurement orientation and the low strain-field hysteresis, it is believed that domain wall motion does not contribute extensively to the large field-induced strains. This is in contrast to soft piezoelectric PZT ceramics in which more than 50% of the room temperature piezoelectric response is of extrinsic origin.³

For the case of ferroelectric microelectromechanical systems (MEMS), it is desirable to generate large strains, or sense very small ones, in thin constrained piezoelectric layers. For $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) thin films, the most widely studied piezoelectric composition, when thicknesses are less than 1 μm , it has been demonstrated that the piezoelectric response due to non-180° domain wall motion is limited.⁴ Given the ferroelastic nature of domains in PZTs, it is likely that, at least in part, this limitation results from local residual stresses that act to clamp the overall response.⁴ Other possibilities include very fine grain size (typically $\leq 0.2 \mu\text{m}$) and

high defect concentrations. As a result of these factors, the piezoelectric coefficients (d_{ij}) measured for PZT thin films are limited to those values typical of hard PZT ceramics.⁵⁻⁷ Since it appears that alternate mechanisms not involving non-180° domain wall motion are responsible for the piezoelectric activity in (001)-oriented relaxor-PT single crystals, it is possible that substrate clamping will have a much less pronounced effect on the thin film electromechanical properties. For a well-poled (001)-oriented rhombohedral crystal measured normal to the face, no driving force exists for non-180° domain wall motion as a result of the crystal symmetry.

With these considerations in mind, a study of relaxor-PT epitaxial films for MEMS applications has been performed. The composition $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (70/30) was chosen over the Zn-containing phase since the latter contains two volatile atomic species. In single crystal studies, the PZN composition is favored because its morphotropic composition contains only ~9% PbTiO_3 ; lower PbTiO_3 concentrations facilitate more homogeneous crystal growth. The (70/30) ratio was chosen because it lies about 5 mole % to the rhombohedral side of the morphotropic phase boundary where the composition dependence of the electrical properties is the least dramatic.¹

There are several previous reports concerning the deposition and measurement of PMN and PMN-PT thin films. Deposition methods include sol-gel, rf sputtering, pulsed laser deposition, and chemical vapor deposition.⁸⁻¹² For polycrystalline PMN-PT compositions near the morphotropic phase boundary, maximum dielectric constant values near 2000 with low loss tangents were observed.^{8,9,12} Remanent polarizations as large as 8 $\mu\text{C}/\text{cm}^2$ have been measured for morphotropic sol-gel derived (001)-oriented material.⁸ To

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TABLE I. Processing conditions for SrRuO₃ and PMN-PT epitaxial thin films.

Parameters	SrRuO ₃	PMN-PT
Temperature (°C)	680	620–700
Atmosphere	10% O ₃ , 90% O ₂	10% O ₃ 90% O ₂
Pressure (mTorr)	200	100–700
Laser power (mJ)	250	250
Laser energy density (J/cm ²)	1.5	1.8–2.2
Target	Stoichiometric	15%–40% excess PbO
Target to substrate distance	7.5 cm	5.5 cm

the best of the authors' knowledge, the deposition of epitaxial relaxor-PT solid solutions has not been previously reported. In addition, there have been few conclusive demonstrations of true relaxor behavior (i.e., dispersive dielectric permittivity below T_m) for any thin film PMN-PT composition.

II. EXPERIMENTAL PROCEDURE

PMN-PT (70/30) epitaxial thin films with SrRuO₃ bottom electrodes were prepared on (001) LaAlO₃ substrates (Lucent Technologies) by pulsed laser deposition. The specific processing conditions for both materials are given in Table I. Substrates were heated by fixing them to a stainless steel block-style hot stage using silver paint (Demetron). The temperatures given refer to readings taken from a *K*-type thermocouple embedded in the heater block. The 10% O₃ atmosphere refers to the undistilled output of a commercially available ozone generator (PCI). The laser used was a Lambda Physik Compex 102, operating at 248 nm. The PMN-PT samples were cooled in an atmosphere of 250 Torr oxygen/ozone mix immediately after deposition.

PMN-PT laser targets were fabricated by first processing stoichiometric PMN-PT powder of the desired 70/30 ratio; the columbite method was followed.¹³ The desired mass percent of PbO was added to the PMN-PT powder and ball milled in ethanol for 4 h to insure homogeneous distribution. Pellets 1 in. in diameter were uniaxially pressed without binder. The samples were placed on Pt foil in an alumina crucible and covered with a Pb source (a 5:1 mixture of PbO and PbZrO₃ powders), and an alumina lid was placed on top (no cement was used). The samples were sintered at 950 °C for 1 h. Using this method, less than 1% mass loss occurred in the pellet during the temperature cycle. The SrRuO₃ target was purchased from Target Materials Inc. After each deposition, the targets were resurfaced using SiC abrasive paper.

Samples were then characterized to determine the phase assemblage, the crystalline quality, and the low- and high-field electrical properties. Structural analysis was performed on a Picker four-circle diffractometer equipped with a Cu target and a graphite monochromator. Electrical measurements were made through the film thickness using Pt top electrodes 300 μm in diameter prepared by pulsed laser deposition (PLD) through a shadow mask in vacuum. Hysteresis measurements were made using a Radiant Technologies RT66A standard ferroelectrics tester. For low temperature analysis of the polarization hysteresis, the samples were

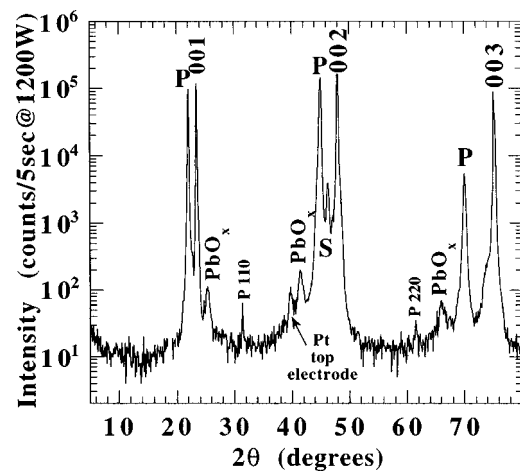


FIG. 1. θ - 2θ diffraction pattern of a PMN-PT thin film containing excess PbO_x. Peaks indexed with P indicate perovskite PMN-PT, while those indexed with S denote SrRuO₃. 001 indices correspond to substrate reflections.

immersed in liquid nitrogen. Dielectric constant and loss values were measured with an HP47240 LCR meter as a function of temperature (−170 °C–200 °C) and frequency (100 Hz–100 kHz) at an excitation field of 0.05 kV/cm. High and low temperature measurements were made using a laboratory oven with both refrigerating and heating capabilities. Contacts to the samples for room temperature measurements were made using point probes, while contacts for temperature dependent analysis were made by aluminum ultrasonic wire bonding.

III. RESULTS AND DISCUSSION

A. Structural analysis

Initially, deposition parameters for PMN-PT were chosen which afforded growth with reasonable rates, smooth morphologies, and uniform thicknesses over 0.5 cm² wafers. In general, temperatures between 620 °C and 640 °C, pressures of 200 mTorr, and a target to substrate distance of ~6 cm were found to be appropriate. Using these conditions, the temperature and laser frequency were adjusted so that a film rich in lead was grown, i.e., a mixture of epitaxial perovskite and polycrystalline PbO_x. Once these conditions were achieved, the processing parameters were adjusted to provide increased lead volatility during growth. Figure 1 gives a θ - 2θ pattern for a Pb-rich PMN-PT epitaxial film. In this pattern, peaks corresponding to both perovskite and PbO_x are present. In addition to the epitaxial perovskite, a small peak corresponding to the (110) orientation is present at 31.5°. When large quantities of excess PbO_x are present in the films, small volumes of nonepitaxial perovskite (typically <1 vol %) were unavoidable. Although not shown in all of the figures, azimuthal scans and rocking curves were taken for all the samples discussed. All samples were oriented in plane with peak widths between 0.6° and 0.8° in ϕ and between 0.4° and 0.7° in ω . Representative ϕ and ω scans are given in Fig. 2.

The next step in structural optimization was to remove the excess lead-containing phases and arrive at a globally

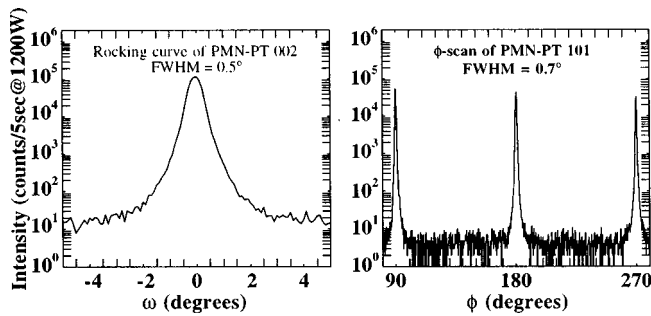


FIG. 2. Rocking curve and ϕ scan for typical PMN-PT epitaxial films.

stoichiometric epitaxial film. To systematically increase the sublimation rate of a volatile element during deposition, the best laser parameters to change are laser pulse frequency and substrate temperature. Reducing the laser frequency increases the amount of time between pulses during which sublimation can occur, while increasing the temperature exponentially increases the sublimation rate of the solid.¹⁴ Adjustments in the thin film Pb stoichiometry may also be accomplished by changing other parameters, i.e., laser fluence, pressure, and target to substrate distance. These parameters, however, are coupled to other aspects of the deposition such as instantaneous growth rate, energetic bombardment, and phase stability. To avoid these cross-coupled effects, when possible, these parameters were fixed. Figure 3 is a θ - 2θ pattern for a PMN-PT film deposited at a reduced laser frequency (by $\sim 20\%$) in reference to the film in Fig. 1. It is clear in this pattern that the quantity of excess PbO_x is reduced; however, before it is completely removed, a significant amount of pyrochlore has evolved. The observed pyrochlore phase has an x-ray pattern similar to that of $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$, however, many phases with nearly identical x-ray signatures and plausible stoichiometries exist, thus an unambiguous phase assignment is not possible. This coexistence of stoichiometric, Pb-rich, and Pb-deficient phases occurs in bulk processing of ceramics as well, and is

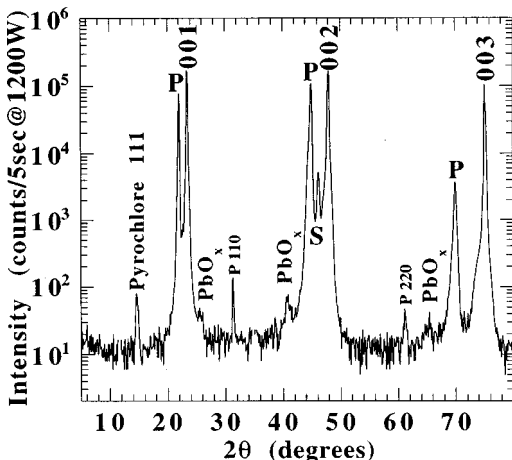


FIG. 3. θ - 2θ diffraction pattern of a PMN-PT thin film deposited under conditions favoring increased PbO_x volatility compared to that shown in Fig. 1. The coexistence of perovskite, PbO_x , and pyrochlore is demonstrated.

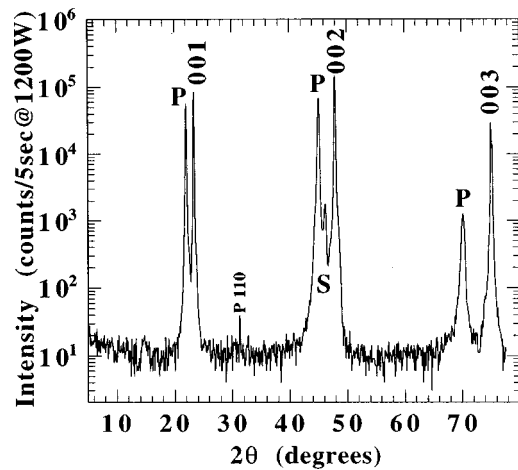


FIG. 4. θ - 2θ diffraction pattern of a PMN-PT thin film deposited at 700°C and $700\text{ mTorr O}_3/\text{O}_2$. To the detection limits of x-ray diffraction, the material is single phase and epitaxial.

a result of the relatively similar thermodynamic stabilities of the perovskite and pyrochlore phases of PMN-PT at the temperatures of interest.¹³

From the ceramic processing and single crystal growth literature it is known that increased temperature and oxygen partial pressures will favor the perovskite phase.^{13,15} Thus, the deposition pressures and temperatures were raised to 710°C and 700 mTorr , and the Pb content was again optimized. Figure 4 shows a θ - 2θ pattern for a structurally optimized film deposited under these conditions. In addition to the increased pressure and temperature, the target to substrate distance was reduced to 3.5 cm . This was necessary to increase the instantaneous deposition rate in order to supply enough Pb to the growing film. To the detection limits of our diffractometer, no pyrochlore or Pb-rich phases are present. Intermediate oxygen pressures and temperatures ($\sim 400\text{ mTorr}$ and $\sim 680^\circ\text{C}$) were also attempted with improved results over the initial case.

A mild dependence of the lattice constants on Pb stoichiometry was observed (this assumes that the ratio of the other elements remained constant with changing laser frequency). In samples containing excess quantities of lead, the lattice parameter reflected bulk values (4.03 \AA), while for samples showing no excess lead, that is, either phase pure or pyrochlore containing, the lattice constant was consistently reduced by approximately 0.02 \AA . A limited number of films were deposited using SrTiO_3 substrates. When used, these epitaxial templates widened the processing window for phase-pure PMN-PT films. Most likely, the superior lattice match improved the stability of the PMN-PT phase.

B. Electrical property analysis

Initially, phase-pure samples were electrically characterized, and were found to have insufficient resistivity for any meaningful dielectric analysis to be performed. Since these samples showed lattice constants which were slightly smaller than what is observed in the bulk, it was assumed that lead deficiency was responsible for the high leakage. Thus the deposition conditions were modified to reduce the lead defi-

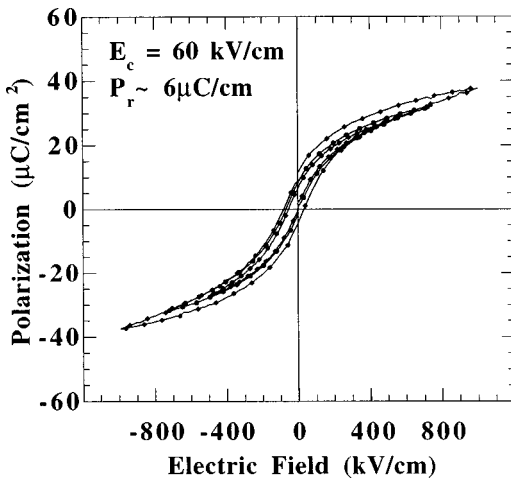


FIG. 5. Polarization hysteresis of a PMN-PT thin film deposited at 620 °C containing excess PbO_x . The film thickness is approximately 2000 Å.

ciency. Using LaAlO_3 substrates, samples with appreciable resistivities ($\geq 10^8 \Omega \text{ cm}$) were unable to be grown in the absence of excess PbO_x (as observed in the x-ray patterns). As a result of this observation, the processing temperatures were reduced to $\sim 620^\circ\text{C}$ where samples containing measurable amounts of PbO_x could be easily grown. It is advantageous to work at these lower temperatures given the reduced lead volatility and improved process stability.¹⁴

Figure 5 shows the polarization hysteresis loop for such a sample. The pertinent processing conditions are a pressure of 200 mTorr, a laser frequency of 11 Hz, and a deposition temperature of 620 °C. Although the tails of the hysteresis loop indicate high resistivity, the value of remanent polarization (P_r) is much smaller than expected. In general, this sample resembles a relaxor in the vicinity of T_m (the temperature at which the maxima in the dielectric constant occurs), where P_r falls rapidly with temperature and the hysteresis loop tilts towards the positive field axis.¹⁶ To verify this, the sample was immersed in liquid nitrogen and again the hysteresis was measured, Figure 6 shows these data. At this temperature, a well developed hysteresis evolves with a

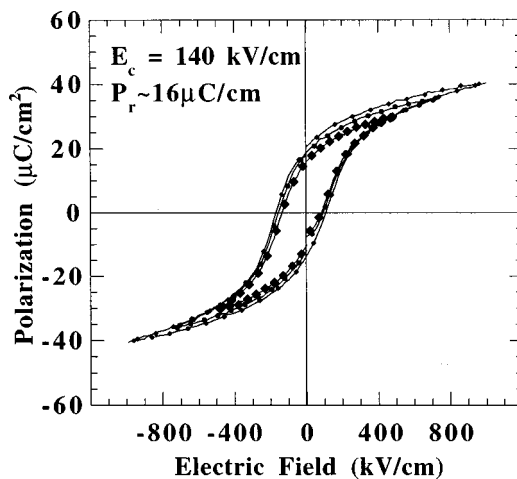


FIG. 6. Polarization hysteresis of the same PMN-PT thin film shown in Fig. 5 measured at 77 K.

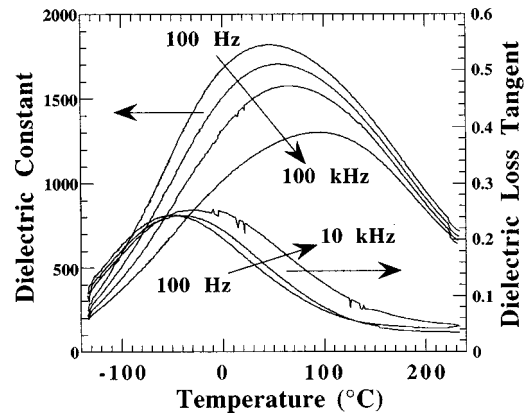


FIG. 7. Temperature dependence of the dielectric constant and dielectric loss of a PMN-PT thin film deposited at 620 °C and containing excess PbO_x .

remanent polarization of $16 \mu\text{C}/\text{cm}^2$. Evidence of a reduced transition temperature value was also observed in the temperature dependence of the dielectric constant. As can be seen in Fig. 7, a T_m of approximately 50 °C at 1 kHz was found. In contrast, a transition temperature of $\sim 150^\circ\text{C}$ is expected. Samples processed in conditions favoring slightly more and less Pb volatility were synthesized, but no changes in T_m were observed. Thus, temperature depression of the development of a stable polarization cannot be solely attributed to the Pb content of the films.

In order to determine the cause of the temperature-shifted transition four factors were investigated: film thickness, deposition rate, substrate thermal expansion mismatch induced strain, and deposition temperature.

Previous investigators have reported on the influence of film thickness on ferroelectric thin film properties.^{17,18} Factors which have been identified as influential include depletion layers, film microstructure, and residual stresses, all of which will depend upon film thickness. To see if these factors were important in determining the electrical properties of PMN-PT epitaxial layers, several 15 000 Å thick samples were deposited and characterized (previous samples were routinely grown to a thickness of ~ 2000 Å). Figures 8 and 9 show the hysteresis data for the thicker film at room and liquid nitrogen temperatures. With the exception of a more square hysteresis loop with a lower coercive field, the electrical properties are quite similar to the thinner film. These modest changes in the low temperature hysteresis parameters are consistent with those observed by others concerning the effects of film thickness in polycrystalline PZT.^{17,18} For this sample, (at 77 K) 80% of the room temperature remanent polarization observed in high quality single crystals of the same composition is realized. This result indicates that film thickness or factors which depend solely upon it are not responsible for the depressed T_m .

A second factor which was considered was the effect of film growth rate, which may alter the properties of thin films due to its influence on film structure. An increase in the concentration of structural defects is expected for films grown at rates where material accumulates faster than rearrangement on the growth surface can occur. This may be

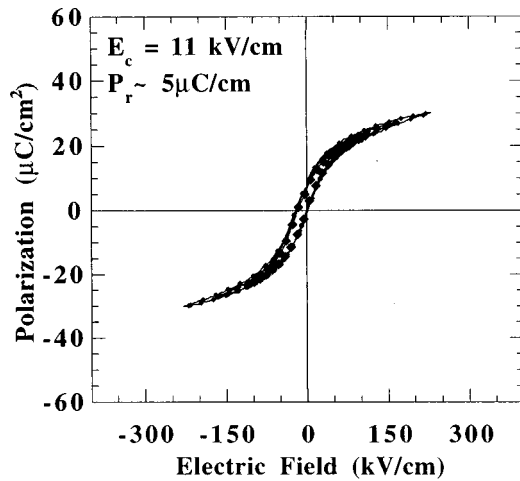


FIG. 8. Polarization hysteresis of a PMN-PT thin film deposited at 620 °C containing excess PbO_x . The film thickness is approximately 15 000 Å.

especially true in PLD where the growth is discontinuous, and the instantaneous rate may be as large as 10^4 Å/s, i.e., 1 Å per laser pulse, where the plasma lifetime is on the order of 10^{-6} – 10^{-4} s.¹⁹ This rate can be controlled by a combination of laser fluence, target to substrate distance, and pressure. To determine whether the growth rates during deposition are too fast for sufficient structural arrangement on the surface, two additional rates were tested where the Å deposited per pulse was reduced, but the average rates expressed in Å deposited per unit time were held constant. The original growth rate was 0.5 Å/pulse, and the two additional rates were 0.3 and 0.15 Å/pulse, respectively. These rates were determined by measuring the film thicknesses and dividing by the total number of laser pulses used. Highly resistive films were deposited using each of the growth rates and were electrically characterized. Upon comparison, no appreciable differences were observed in the polarization hysteresis.

It is well known that the transition temperature of ferroelectric materials is strongly dependent upon externally applied stress.^{20,21} To determine the importance of residual stress on the electrical properties, additional PMN-PT

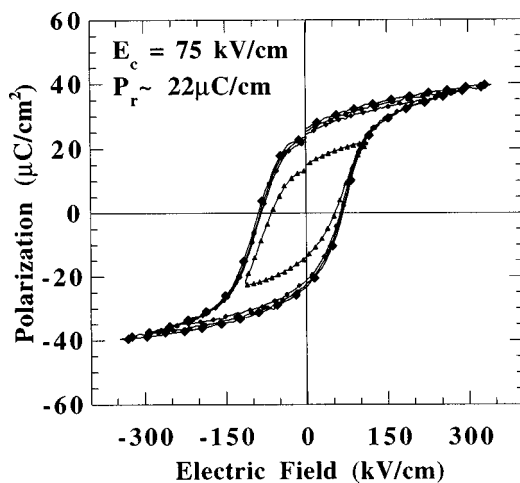


FIG. 9. Polarization hysteresis of the same PMN-PT thin film shown in Fig. 7 measured at 77 K.

TABLE II. Reference properties for flux-grown (001)-oriented PMN-PT (70/30) single crystals.

Parameters ^a	PMN-PT (70/30)
Dielectric constant (25 °C)	3000
Transition temperature	150 °C
Remanent polarization	25 $\mu\text{C}/\text{cm}^2$
Saturation polarization	27 $\mu\text{C}/\text{cm}^2$
Lattice constant	4.03 Å
Symmetry	Rhombohedral

^aSee Ref. 25.

samples were deposited on KTaO_3 substrates. KTaO_3 was chosen because of its small thermal expansion coefficient—approximately 6 ppm/°C over the temperature range of interest.²² In contrast, the average thermal expansion coefficient of LaAlO_3 has been reported to be 11 ppm/°C between room temperature and 700 °C.²³ The average thermal expansion coefficient of PMN-PT (70/30) is approximately 8 ppm/°C; this value is a combination of the lower temperature coefficient, which is less than 1 ppm/°C, and the high temperature coefficient which is approximately 10 ppm/°C.²⁴ The coefficient falls sharply from the higher temperature value at Burn's temperature (T_b) which corresponds to the onset of a stable root-mean-square (rms) polarization. It is assumed here that the thin films are stress free at the deposition temperature due to the presence of accommodating dislocations. The net stress at room temperature was thus attributed to the thermal expansion coefficient mismatch between the films and the substrate. Given the differences in the thermal expansion coefficients of the two substrates, a significant difference in the thin film residual stress state will exist. The films grown on LaAlO_3 would be in compression, while those deposited on KTaO_3 would be in tension. The polarization hysteresis was measured for both heterostructure types (identically prepared) and compared; no apparent difference was observed. It was thus concluded that the thermal expansion mismatch induced strain did not dominate the behavior of the electrical properties or the transition temperature shift.

Finally, the influence of crystalline quality on the electrical properties was investigated. Deposition temperatures were increased to values greater than 660 °C. In this range, PMN-PT thin films with optimal electrical properties were deposited using a target to substrate spacing of 5.5 cm and an atmosphere of a 400 mTorr oxygen/ozone mixture. The laser repetition rate required to achieve the desired Pb stoichiometry was 17 Hz. This corresponded to a relatively rapid average deposition rate of 3 $\mu\text{m}/\text{h}$. As a result of this rapid deposition, the film surface became irregular with a rms roughness of approximately 0.05 μm . Under these deposition conditions, significantly improved electrical properties were observed. Table II lists the electrical properties for a well-prepared single crystal of PMN-PT (70/30).²⁵ These values serve as the reference of comparison for the thin film samples. It should be noted that ceramic data cannot be used for comparison because of the strong property anisotropy between the $\langle 111 \rangle$ and $\langle 001 \rangle$ orientations.

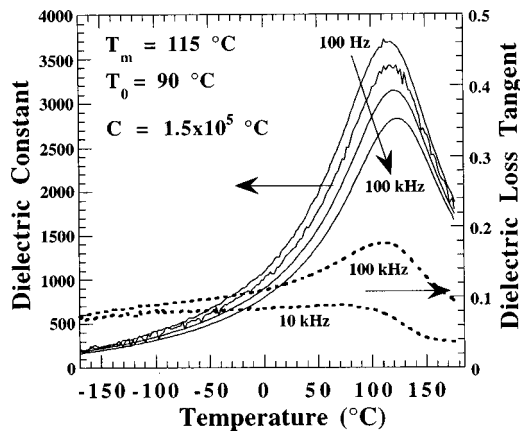


FIG. 10. Temperature dependence of the dielectric constant and dielectric loss of a PMN-PT thin film deposited at 660 °C containing excess PbO_x . T_m refers to the temperature of the maxima in the dielectric constant at 100 Hz, T_0 refers to the extrapolated Curie-Weiss temperature, and C refers to the Curie-Weiss constant.

Because of the difficulty in reproducing high quality samples at elevated temperatures (a result of increased lead and lead oxide volatility), a target containing 2% Ba doping was introduced. Ba was chosen because of its ability to stabilize the perovskite phase with respect to the associated lead-deficient pyrochlore. The addition of Ba into the PMN-PT increases the tolerance factor (a calculated quantity indicative of the thermodynamic stability of the perovskite structure) of the crystal.²⁶ For Ba-substituted PMN and PT, a decrease in T_m of approximately 20 °C/mol % has been reported.^{27,28} Although it has never not been demonstrated for the specific PMN-PT composition investigated here, it is likely that the Ba addition will have a similar effect. Indeed, reports on the substitution of La and Sr into the morphotropic composition show very similar transition shifts, i.e., approximately 20 °C/mol %.^{27–29} Since T_m for undoped (70/30) single crystals is 150 °C,²⁵ with 2% Ba doping, the T_m value would be expected to fall to approximately 110 °C. Figures 10 and 11 give the temperature dependence of the dielectric constant and the polarization hysteresis for a PMN-PT film deposited under the optimized deposition con-

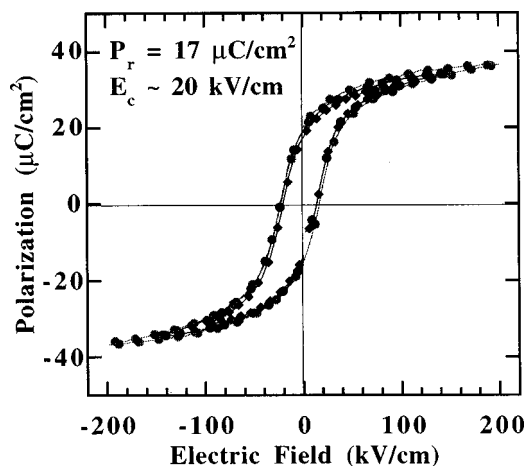


FIG. 11. Room temperature polarization hysteresis of a PMN-PT thin film deposited at 660 °C containing excess lead.

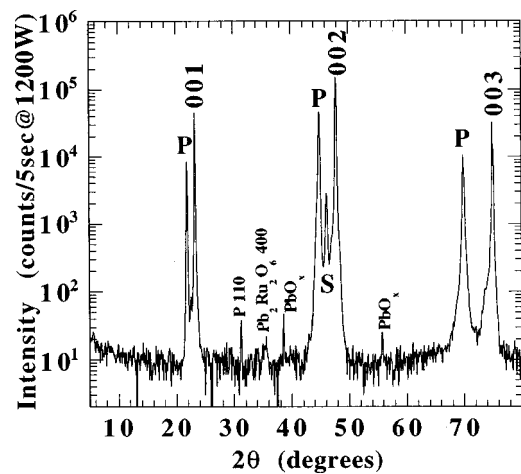


FIG. 12. θ - 2θ diffraction pattern of a PMN-PT thin film deposited at 660 °C. The peak corresponding to lead ruthenate is a result of reaction with the underlying SrRuO_3 electrode.

ditions. As is shown in Figs. 10 and 11, the T_m value is 115 °C and the remanent polarization is 17 $\mu\text{C}/\text{cm}^2$. This remanent polarization value is about 75% of that measured in undoped single crystals of the same composition.²⁵ Extrapolation of the saturation polarization gives the single crystal value. The temperature dependence of the capacitance in the paraelectric region was fitted to Curie-Weiss behavior using

$$\epsilon = \frac{C}{(T - T_0)}.$$

A Curie-Weiss constant, C , of 1.5×10^5 °C was calculated. This value is on the same order as other relaxor-PT solid solutions in the vicinity of the morphotropic composition and was found to be frequency independent.²⁵ Figure 12 gives a θ - 2θ pattern for the higher temperature deposited material. Again, this sample contains a small amount of PbO_x .

Upon comparison of the x-ray patterns for the low and higher temperature deposited PMN-PT films, only subtle differences in the structure are observed. In general, for the lower temperature deposited samples, the x-ray linewidths are approximately 10% greater and peak intensities are nearly 30% larger. The differences in the electrical property temperature dependencies of the PMN-PT samples grown at 620 °C and those deposited at or above 660 °C are attributed to the sample crystallinity.

In a very straightforward manner, the x-ray analysis indicates that the high temperature grown samples have a larger coherent x-ray scattering dimension. Using a Williamson-Hall analysis, a dimension of ~ 500 Å is calculated.³⁰ In comparison, with the same treatment, the scattering size for the lower temperature deposited samples was found to be ~ 100 Å. This analysis gives a semiquantitative picture of the sub-grain structure. Combining this data with the permittivity temperature dependence one finds that the smaller scattering regions are accompanied by the temperature shifted transition, the broadened and more dispersive dielectric maxima, and the deviation from Curie-

Weiss behavior. Interestingly, the 100 Å dimension is consistent with the 100 Å diameter ordered regions observed in ceramic relaxors of several compositions.¹⁶

The broadened x-ray reflections in the lower temperature deposited sample are produced by two factors: (i) larger variations in interplanar spacings in the crystal and (ii) a mosaic subgrain structure. The more pronounced mosaic structure of the lower temperature deposited sample would result in greater concentrations of dislocations which occur at the interfaces of the slightly misoriented subgrains.³¹ The higher defect concentrations are believed to interrupt the long-range order of the lattice, and to produce electrical behavior more consistent with that of relaxor ferroelectrics. It is likely that if deposition temperatures could be further increased, or if a better lattice matched substrate/electrode/film system were used, electrical properties more similar to those of single crystals could be realized.

The optimized samples deposited at temperatures greater than 660 °C still contained lead-rich second phases, which, if removed, would be expected to further improve the film properties. In particular, the presence of a low K second phase may be responsible for the comparatively low dielectric constant values observed (approximately a factor of 2 smaller than expected). Samples with excess lead oxide in the x-ray patterns were etched for 5 min in concentrated acetic acid in an attempt to remove PbO_x from the film surface. Postetching x-ray analysis revealed no changes in the structure or phase assemblage. It was thus concluded that the excess lead oxide does not reside principally on the film surface. This information, coupled with the high film resistivities, suggests that the excess lead oxide must exist as a noncontiguous second phase.

Ex situ annealing was also performed in an attempt to improve the film properties. Three specific experiments were performed: (i) annealing of a lead-rich film in air, (ii) annealing of a Pb-rich film in the presence of a Pb-compensated atmosphere, and (iii) annealing a phase-pure film in a Pb-compensated atmosphere. The Pb-compensated atmosphere was provided by a loosely covered crucible partially filled with a PbO-PbZrO_3 powder, into which the sample was placed. The samples were introduced and removed from a preheated tube furnace to minimize the amount of time spent at high temperatures.

A film similar in structure to that shown in Fig. 1 (i.e., containing excess Pb) was introduced to the 750 °C furnace in a closed, empty crucible for 30 min. X-ray analysis of the crystal after annealing indicated that PbO_x was still present in the film, in addition to a newly formed pyrochlore. This situation is analogous to the phase development observed during growth at 200 mTorr oxygen/ozone pressure; under these conditions as well, three phases can exist simultaneously, perovskite, pyrochlore, and PbO_x . Following this result, no other samples were annealed in a non-Pb atmosphere. In the postanneal x-ray pattern, a peak corresponding to $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ appeared and was attributed to reaction with the bottom electrode. For this reason, the annealing temperatures were dropped to 650 °C.

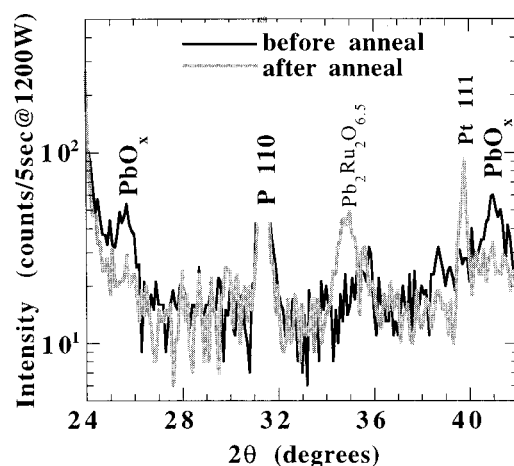


FIG. 13. θ - 2θ pattern of a PMN-PT thin film containing excess lead before and after a 30 min anneal in a lead-compensated atmosphere.

The next experiment involved annealing films in a Pb-rich environment. In the previously described crucible system, three volatile components existed, perovskite, the Pb source, and PbO_x (listed in order of expected decreasing stability at high temperatures). During the anneal, ideally, the most volatile component, the PbO_x , would evaporate initially, leaving the remaining Pb source and phase-pure perovskite behind. A film synthesized with a large amount of excess lead was heat treated in this fashion; the result is shown in Fig. 13, an x-ray diffraction pattern of the film before and after heat treatment. This sample contains some (110)-oriented material as a result of the large initial amount of excess PbO_x . After annealing, it is apparent that much of the PbO_x has sublimed without the formation of pyrochlore. At $2\theta = 35.1^\circ$, however, a $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ 400 reflection is again observed. Several samples containing slightly different amounts of excess Pb were annealed in this manner and characterized. Structurally, the PMN-PT x-ray patterns were unchanged with annealing; however, the amount of reacted $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ was directly related to the amount of excess lead oxide prior to heat treatment. Annealed films with the smallest amounts of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ showed resistivities increased by as much as a factor of 100, and slight increases of the permittivity. Polarization hysteresis measurements, however, gave misshapen hysteresis loops which may be associated with the newly formed ruthenate.

The annealing experiments indicate that, in the presence of a lead source with a stability between that of perovskite and PbO_x , excess Pb can be extracted without the formation of a pyrochlore type phase. In the present case, the inability to do so completely was a result of reaction between the SrRuO_3 bottom electrode and Pb. Quite possibly, with a more stable electrode, phase-pure perovskite films with good electrical properties can be achieved. Pt and LaNiO_3 are possible choices.

Finally, those films deposited at temperature and pressure combinations high enough to promote phase-pure perovskite growth were annealed in a lead-rich atmosphere. X-ray analysis of the annealed films indicated no appreciable differences in film structure, and electrical property measure-

ments revealed that the resistivities remained unacceptably low. It appears that, under the annealing conditions examined, sufficient amounts of lead could not be driven into the films for improved electrical properties to be observed.

IV. CONCLUSIONS

To the authors' knowledge, this is the first report of epitaxial films of the relaxor-PbTiO₃ solid solution Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (70/30) deposited by PLD. Avoiding the occurrence of the pyrochlore phase was found to be very difficult, and was only possible in a narrow processing window. In general, the trends observed in ceramic processing of PMN-PT were analogous to those observed in this study. In one PMN-PT film, it was possible to simultaneously observe perovskite, pyrochlore, and, PbO_x. As in bulk processing work, higher temperatures and oxygen pressures favored the perovskite phase. The epitaxial effect of the LaAlO₃ substrate during growth was insufficient to avoid pyrochlore. Phase-pure material could be deposited at temperatures in excess of 700 °C and oxygen pressures approaching 1 Torr, however, electrically, these samples were typified by unacceptably low resistivities. In general, films with excess PbO_x showed good electrical properties (large resistivities and low loss tangent values). Electrically, samples deposited at temperatures near 620 °C resembled relaxors in the vicinity of T_m ; the T_m value of these samples was found to be decreased by ~100 °C. This behavior was attributed to high defect densities. When the deposition temperatures were increased to 660 °C or higher, electrical properties more similar to those of bulk single crystals were observed. X-ray analysis of these films confirmed improved crystallinity. In samples deposited in the lower temperature regime, true relaxor behavior was observed, i.e., a frequency dependent permittivity and loss tangent in the ferroelectric region, and converging values in the paraelectric state. Post-deposition annealing in a Pb-rich atmosphere was attempted in order to produce phase-pure films. This annealing strategy was found to be effective in removing excess Pb without nucleation of pyrochlore; however complete removal was limited by an unavoidable reaction of Pb with the SrRuO₃ bottom electrode.

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- ¹S. Park and T. R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **44**, 1140 (1997).
- ²S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
- ³X. L. Zhang, Z. X. Chen, L. E. Cross, and W. A. Schulze, J. Mater. Sci. **18**, 968 (1983).
- ⁴S. Trolier-McKinstry, J. F. Shepard, Jr., T. Su, J. L. Lacey, G. Zavala, and J. Fendler, Ferroelectrics **206–207**, 381 (1997).
- ⁵P. Murali, A. Kholkin, M. Kohli, T. Maeder, and N. Setter, Microelectron. Eng. **29**, 67 (1995).
- ⁶I. Kanno, S. Fujii, T. Kamada, and R. Takayama, Appl. Phys. Lett. **70**, 1378 (1997).
- ⁷S. Watanabe, T. Fujiu, and T. Fujii, Appl. Phys. Lett. **66**, 1481 (1995).
- ⁸M. Shyu, T. Hong, and T. Wu, Mater. Lett. **23**, 221 (1995).
- ⁹T. Nakamura, A. Masuda, A. Morimoto, and T. Shimizu, Jpn. J. Appl. Phys., Part 1 **35**, 4750 (1996).
- ¹⁰M. C. Jiang, T. Hong, and T. B. Wu, Jpn. J. Appl. Phys., Part 1 **33**, 6301 (1994).
- ¹¹Y. Takeshima, K. Shiratsuyu, H. Takagi, and K. Tomono, Jpn. J. Appl. Phys., Part 1 **34**, 5083 (1995).
- ¹²M. C. Jiang and T. B. Wu, J. Mater. Res. **9**, 1879 (1994).
- ¹³S. L. Swartz and T. R. Shrout, MRS Bull. **17**, 1245 (1982).
- ¹⁴D. L. Smith, *Thin Film Deposition* (McGraw-Hill, New York, 1995).
- ¹⁵N. Wakia, A. Sakai, N. Ishizawa, K. Shinosaki, and N. Mizutani, MRS Bull. **28**, 137 (1993).
- ¹⁶L. E. Cross, Ferroelectrics **151**, 305 (1993).
- ¹⁷J. F. M. Cillessen, M. W. J. Prins, and M. R. Wolf, J. Appl. Phys. **81**, 2777 (1997).
- ¹⁸A. K. Tagantsev, M. Landivar, E. Colla, K. G. Brooks, and N. Setter, Integr. Ferroelectr. **6**, 309 (1995).
- ¹⁹J. P. Zheng, Z. Q. Huang, D. T. Shaw, and H. S. Kwok, Appl. Phys. Lett. **54**, 280 (1989).
- ²⁰P. W. Forsbergh, Jr., Phys. Rev. **93**, 686 (1954).
- ²¹G. A. Samara, Phys. Rev. **151**, 378 (1966).
- ²²Y. S. Touloukian, *Thermophysical Properties of Matter*, TPRC Data Series Vol. 13 (IFI/Plenum, New York, 1979).
- ²³H. M. O'Bryan, P. K. Gallagher, G. W. Berkstresser, and C. D. Brandle, J. Mater. Res. **5**, 183 (1990).
- ²⁴S.-J. Jang, Ph.D. thesis, The Pennsylvania State University, 1979.
- ²⁵S. Park and T. R. Shrout (unpublished data).
- ²⁶T. R. Shrout and A. Halliyal, Am. Ceram. Soc. Bull. **66**, 704 (1987).
- ²⁷S. J. Butcher and N. W. Thomas, J. Phys. Chem. Soc. **52**, 595 (1991).
- ²⁸B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, Marrietta, OH, 1971).
- ²⁹N. Kim, M.S. thesis, The Pennsylvania State University, 1990.
- ³⁰G. K. Williamson and W. H. Hall, Acta. Metall. **1**, 22 (1953).
- ³¹B. D. Cullity, *Elements of X-ray Diffraction*, 2nd ed. (Addison-Wesley, Reading, MA, 1978).