

Epitaxial $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ thin films synthesized by metal-organic chemical vapor deposition

G. R. Bai, S. K. Streiffer,^{a)} P. K. Baumann, O. Auciello, and K. Ghosh
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439-4838

S. Stemmer

Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005-1892

A. Munkholm

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Carol Thompson

Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439-4838

R. A. Rao and C. B. Eom

Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708-0300

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Metal-organic chemical vapor deposition was used to prepare $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) thin films on (001) SrTiO_3 and $\text{SrRuO}_3/\text{SrTiO}_3$ substrates, using solid Mg β -diketonate as the Mg precursor. Parameters including the precursor ratio in the vapor phase, growth temperature, growth rate, and reaction pressure in the reactor chamber were varied in order to determine suitable growth conditions for producing phase-pure, epitaxial PMN films. A cube-on-cube orientation relationship between the thin film and the SrTiO_3 substrate was found, with a (001) rocking curve width of 0.1° , and in-plane rocking-curve width of 0.8° . The root-mean-square surface roughness of a 200-nm-thick film on SrTiO_3 was 2 to 3 nm as measured by scanning probe microscopy. The zero-bias dielectric constant and loss measured at room temperature and 10 kHz for a 200-nm-thick film on $\text{SrRuO}_3/\text{SrTiO}_3$ were approximately 1100 and 2%, respectively. The remnant polarization for this film was $16 \mu\text{C}/\text{cm}^2$. © 2000 American Institute of Physics. [S0003-6951(00)04321-7]

The relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and its solid solution with PbTiO_3 (PT) have attracted much attention recently because of excellent dielectric and electro-mechanical properties.¹ For many applications benefiting from integrated devices, deposition of thin film PMN-PT would be required. It has, however, proven difficult to synthesize phase pure perovskite PMN films because of the relatively poor stability of the perovskite phase relative to, for example, the pyrochlore phase. Despite this, a variety of thin film synthesis techniques have been used to fabricate PMN-PT films, including chemical solution deposition,²⁻⁴ sputtering,⁵ pulsed laser ablation,⁶⁻⁸ and metal-organic chemical vapor deposition (MOCVD).⁹ Among these methods MOCVD offers advantages for composition selection and control, film uniformity, high deposition rate, conformality, and scalability to large deposition areas. However, only limited effort has been directed at obtaining PMN-PT using MOCVD:⁹ thin films were grown with perovskite as the main phase only for compositions with $\text{Ti}/(\text{Mg}+\text{Nb}+\text{Ti}) > 25$ mol %, and little information on microstructure and properties was reported. Additionally, for many applications, it is desirable to obtain highly oriented or single-crystal PMN-PT thin films in order to fully utilize the aniso-

tropic piezoelectric properties. Thus, epitaxial PMN films are essential as model systems so as to better understand properties.

As MOCVD processes for PbTiO_3 are relatively well developed, it is expected that many issues in the deposition of PMN-PT may be more simply addressed by investigation of the growth of pure PMN. Here we report the MOCVD synthesis of epitaxial perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ thin films on (001) SrTiO_3 and $\text{SrRuO}_3/\text{SrTiO}_3$ substrates. Results from initial structural and electrical characterization are described.

PMN thin films were grown in a cold-wall, horizontal, low-pressure MOCVD reactor with a resistive substrate heater. Tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, niobium pentaethoxide, $\text{Nb}(\text{OC}_2\text{H}_5)_5$, and solid magnesium β -diketonate, $\text{Mg}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ were chosen as the metal ion precursors. A mixture of the metal-organic precursor vapor was introduced into the reactor via high purity nitrogen carrier gas. The temperatures, pressures, and carrier gas flow rates for each of the precursor chambers were controlled to adjust the film composition. Pure oxygen was used as the oxidant and introduced into the reactor via a separate delivery line. The precursor delivery lines, as well as the inlet flange, were heated to a temperature higher than the highest source temperature in order to avoid condensation of the precursors. Single-side polished, single crystal (001) SrTiO_3 was chosen as the substrate for samples used for growth optimization and struc-

^{a)}Electronic mail: streiffer@anl.gov

TABLE I. Growth conditions for PMN thin films.

Substrate temperature:	700–780 °C
Reactor pressure:	6 Torr
Precursor temperature:	Pb: 28–30 °C Mg: 120–135 °C Nb: 78–84 °C
Pressure in evaporation chamber:	Pb: 500 Torr Mg: 18 Torr Nb: 18 Torr
Flow rate of carrier gas (N ₂):	Pb: 20–25 sccm Mg: 36–42 sccm Nb: 55–62 sccm
Flow rate of O ₂ :	O ₂ : 400 sccm
Flow rate of background gas (N ₂):	N ₂ : 200 sccm
Growth rate:	4–5 nm/min.

tural characterization. For electrical characterization, PMN films were grown on 140-nm-thick epitaxial films of the metallic oxide SrRuO₃, which had previously been deposited by off-axis sputtering at 600 °C on 2° miscut (001) SrTiO₃.¹⁰ Substrates were cleaned with acetone and methanol; no further surface treatments were performed. The typical growth conditions are given in Table I.

The temperatures of the Mg and Nb precursors in our case are reduced compared to those used by others.⁹ Because of this, process reproducibility and controllability were improved significantly. Dielectric characterization was performed at 10 kHz and 0.1 V root-mean-square (rms) oscillation level using an HP4192A impedance analyzer, on capacitors formed by electron beam evaporation of Pt top electrodes through a shadow mask at a temperature of 350 °C. Electric displacement—electric field hysteresis loops were measured using a Radiant RT6000 test system.

Film phase content and crystallinity were characterized by x-ray diffraction both on a laboratory source using Cu *K*α radiation, and on BESSRC-CAT beamline 12-ID-D of the Advanced Photon Source using 14.5 keV photons. Depending on the growth conditions, x-ray diffraction demonstrated that the resultant films were either pure PMN or PMN plus significant quantities of impurity phase; identification of specific impurity phases will be discussed elsewhere.¹¹ Once the relationships between the growth conditions and the resulting phases were established, phase-pure perovskite PMN could be easily obtained by optimization of precursor temperatures and carrier gas flow rates, until such time as significant sintering of the solid Mg precursor occurred. This was typically of the order of 10–20 h at temperature, after which the growth conditions required reoptimization.

The Cu *K*α radial scan along the specular direction of a typical 200 nm film deposited on (001) SrTiO₃ at 700 °C is shown in Fig. 1. In addition to the strong (001) and (002) peaks of the SrTiO₃ substrate (labeled *S*), peaks occur at approximately 21.9° and 44.6° (labeled *P*) corresponding to the (001) and (002) reflections of the pseudocubic PMN phase, respectively.¹² Four circle x-ray diffraction using synchrotron radiation indicated a purely cube-on-cube orientation relationship between the PMN film and SrTiO₃ substrate, with a PMN (001) rocking curve width of 0.1° and an in-plane width of 0.8°. A tetragonal structure was found for the PMN film, with out-of-plane and in-plane lattice parameters of 0.406 and 0.404 nm, respectively. This tetragonal

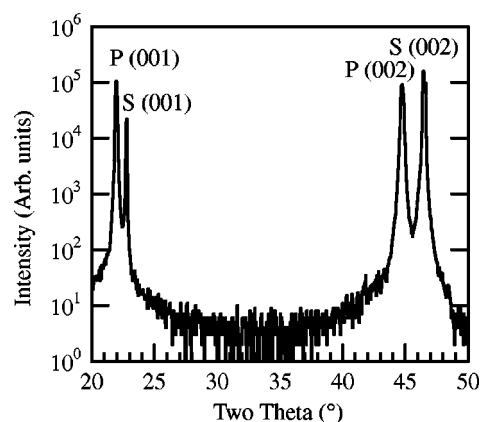


FIG. 1. X-ray diffraction spectrum of a 200 nm PMN/SrTiO₃ sample. This radial scan along the specular direction demonstrates that the film has pure (001) orientation. PMN peaks are indicated by “P,” substrate peaks by “S.”

distortion is most likely the result of temperature-dependent misfit strain (i.e., lattice mismatch and difference in thermal expansion coefficient) induced by the substrate, and which has only been partially relieved. Extremely weak, broad superlattice reflections were found at the (1/2,1/2,1/2) reciprocal lattice positions of the PMN, indicating a very small degree of *B*-site ordering.^{13–15} The degree of ordering is less than has been observed in, for instance, PMN films prepared by chemical solution deposition,⁴ and which were processed at higher temperatures (800–850 °C).

PMN films grown at temperatures from 700 to 780 °C appeared almost identical based on x-ray diffraction spectra. However, if the growth temperature was increased to 800 °C it became exceedingly difficult to deposit phase-pure films, presumably because of difficulty in maintaining proper stoichiometry due to poor lead incorporation. This is corroborated by a strong drop in deposition rate at the higher temperatures.

A scanning probe microscope image of the surface of this sample is shown in Fig. 2. The rms roughness of a 2 μm × 2 μm region was 2 nm, with a maximum peak to valley height of approximately 12 nm. Despite the fact that there is a strong three-dimensional orientation relationship between the PMN and the SrTiO₃, the surface microstructure appears granular with a length scale slightly less than 100 nm. This suggests a growth mode with a relatively high nucleation density followed by columnar growth. This is not unexpected

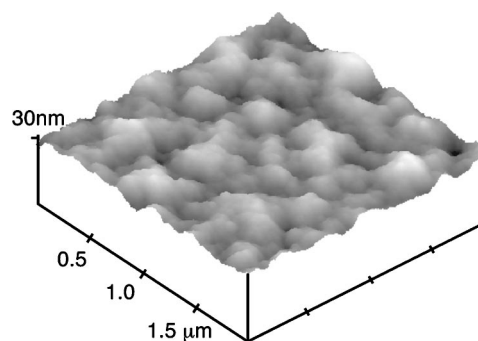


FIG. 2. Scanning probe microscope image of the surface of a 200 nm PMN film on SrTiO₃. The rms roughness is approximately 2 nm over the 2 μm × 2 μm region.

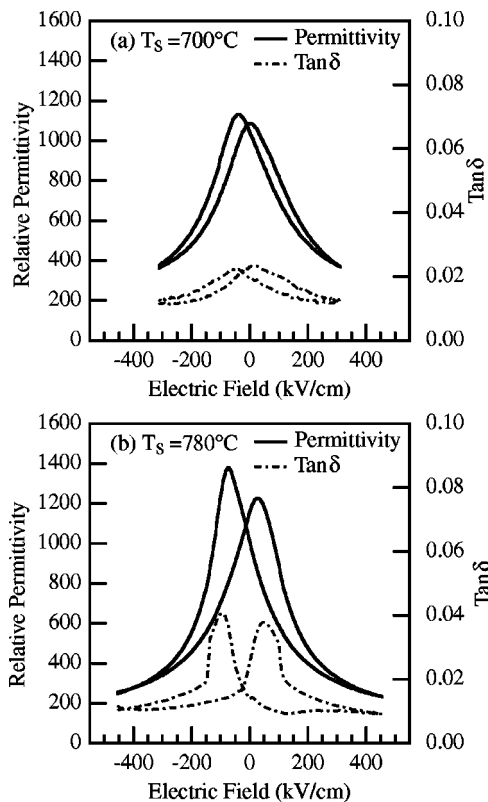


FIG. 3. Forward and reverse permittivity-electric field curves taken at 10 kHz for (a) a 300 nm PMN film grown at 700 °C and (b) a 200 nm PMN film grown at 780 °C.

given the relatively large lattice mismatch between SrTiO₃ and PMN (3.5% at room temperature), and the relatively low growth temperature.

The room temperature relative permittivity and dielectric loss as a function of electric field for 200 nm films grown at 700 and 780 °C are shown in Figs. 3(a) and 3(b), respectively. Significant improvement in the shape of the permittivity-field curves is observed for films deposited at the higher temperature. Zero-bias relative permittivities of approximately 1100 were found, still substantially lower than has been obtained in bulk materials or by other thin film deposition techniques. Interestingly, substantial hysteresis is observed even at room temperature in the forward and reverse sweeps. This is also reflected in electric displacement-electric field measurements, Fig. 4. A remnant polarization of approximately 16 $\mu\text{C}/\text{cm}^2$ was measured for this sample, despite the fact that, as a relaxor ferroelectric, PMN measured at room temperature is typically expected to demonstrate only a very slim-loop response. Although a time-dependent transition from the relaxor state to an electric-field-induced ferroelectric state has been demonstrated in bulk materials,¹⁶ the measurements described here are outside the bounds of reported phase diagrams. Therefore, the observed ferroelectric-like behavior may be a result of the imposed tetragonality as seen by x-ray diffraction, or of the very high electric fields that these films can support.

In summary, an MOCVD process has been developed for growth of nearly phase-pure perovskite, epitaxial PMN films. The films show very high structural quality, although relative permittivities are somewhat lower than is obtained in

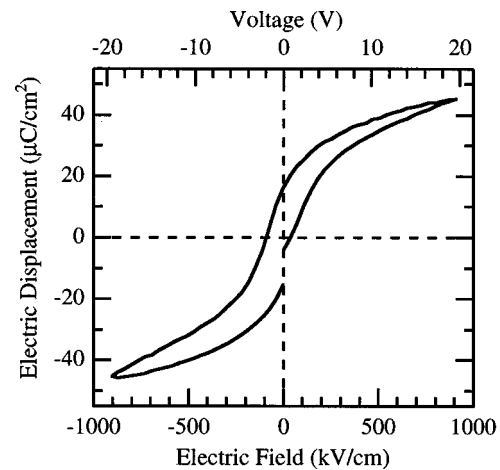


FIG. 4. Electric displacement-electric field hysteresis loop for a 200 nm PMN film grown on SrRuO₃/SrTiO₃ at 780 °C, showing significant remnant polarization.

bulk materials and using other thin-film synthesis techniques. The films display substantial remnant polarization when driven to high fields, by mechanisms which remain to be explored.

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- ¹Seung-Eek Park and Thomas R. ShROUT, *J. Appl. Phys.* **82**, 1804 (1997).
- ²K. R. Udayakumar, J. Chen, P. J. Schuele, L. E. Cross, V. Kumar, and S. B. Krupanishi, *Appl. Phys. Lett.* **60**, 1187 (1992).
- ³L. E. Francis and D. A. Payne, *Mater. Res. Soc. Symp. Proc.* **200**, 173 (1990).
- ⁴Z. Kighelman, D. Damjanovic, A. Seifert, L. Sagalowicz, and N. Setter, *Appl. Phys. Lett.* **73**, 2281 (1998).
- ⁵M. C. Jiang, T. J. Hong, and T. B. Wu, *Jpn. J. Appl. Phys., Part 1* **33**, 6301 (1994).
- ⁶K. L. Saenger, R. A. Roy, D. B. Beach, and K. F. Etzold, *Mater. Res. Soc. Symp. Proc.* **285**, 421 (1993).
- ⁷D. Lavric, R. A. Rao, Q. Gan, J. J. Krajewski, and C.-B. Eom, *Integr. Ferroelectr.* **21**, 499 (1998).
- ⁸J.-P. Maria, W. Hackenberger, and S. Trolier-McKinstry, *J. Appl. Phys.* **84**, 5147 (1998).
- ⁹Y. Takeshima, K. Shiratsuyu, H. Takagi, and K. Tomono, *Jpn. J. Appl. Phys., Part 1* **34**, 5083 (1995).
- ¹⁰C. B. Eom, R. J. Cava, R. M. Fleming, J. M. Phillips, R. B. van Dover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski, and W. F. Peck, Jr., *Science* **258**, 1799 (1992).
- ¹¹S. Stemmer, G. R. Bai, N. D. Browning, and S. K. Streiffer, *J. Appl. Phys.* **87**, 3526 (2000).
- ¹²X-Ray Powder Diffraction Data Card, JCPDS 81-861, calculated from A. Verbaere, Y. Piffard, Z. G. Ye, and E. Husson, *Mater. Res. Bull.* **27**, 1227 (1992).
- ¹³J. Chen, H. M. Chan, and M. Harmer, *J. Am. Ceram. Soc.* **72**, 593 (1989).
- ¹⁴M. A. Akbas and P. K. Davies, *J. Am. Ceram. Soc.* **80**, 2933 (1997).
- ¹⁵Y. Yan, S. J. Pennycook, Z. Xu, and D. Viehland, *Appl. Phys. Lett.* **72**, 3145 (1998).
- ¹⁶see E. V. Colla, E. Yu. Koroleva, N. M. Okuneva, and S. B. Vakhrushev, *Phys. Rev. Lett.* **74**, 1681 (1995), and references therein.