Effect of fabrication conditions on phase formation and properties of epitaxial (PbMg1/3Nb2/3O3)0.67-(PbTiO3)0.33 thin films on (001) SrTiO3
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Effect of fabrication conditions on phase formation and properties of epitaxial (PbMg1/3Nb2/3O3)0.67-(PbTiO3)0.33 thin films on (001) SrTiO3

Muhammad Boota,1,2 Evert P. Houwman,1,a Minh D. Nguyen,1 Giulia Lanzara,2 and Guus Rijnders1
1MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands
2Engineering Department, University of Rome “ROMA TRE”, Via della Vasca Navale 79, 00146 Rome, Italy

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The pulsed laser deposition process of 300nm thick films of Pb(Mg1/3Nb2/3)O30.67-(PbTiO3)0.33 on (001)-oriented SrTiO3 was studied by varying deposition pressure, substrate deposition temperature, laser fluence on the target and target-substrate distance. Perovskite phase pure, (001)-oriented, epitaxial smooth films were obtained in a narrow range of deposition parameters. The ferroelectric and dielectric properties of films fabricated within this parameter range still vary significantly. This shows the sensitivity of the system for growth conditions. The best film has a polarization value close to that expected for a (001) poled, stress free single crystal film. All films show deposition conditions dependent variations in the self-bias field. The self-bias is very stable during long cycling for films made at optimum deposition conditions. The piezoelectric coefficients of the films are strongly reduced with respect to bulk single crystal values due to the film clamping. The properties variations are ascribed to changes in the grain boundary properties in which film defects are expected to accumulate. Notably slight off-stoichiometry may cause localized screening charges, affecting specifically the polarization and dielectric constant. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Micro-electromechanical systems (MEMS) based on ferroelectric oxides are among the highest performing devices for the purpose of sensing and actuation. Lead zirconium titanate (PbZr1−xTiO3 or PZT) is one of the frequently employed piezoelectric materials for the fabrication of such devices.1,2 An alternate to PZT are relaxor ferroelectrics like Pb(Mg1/3Nb2/3)O3(x−(PbTiO3)1−x (notably PMN-PT(x=0.67) also denoted as PMN-PT(67/33)), Pb(Zn1/3Nb2/3)O3−(PbTiO3)3 (PZN-PT(91/09)). Recent developments demonstrating superior piezo response in the relaxor ferroelectrics compared to the well-known piezoelectric material PZT have propelled them to the forefront of sensor and actuator research and development.3,4

S. E. Park and T. R. Shrouq reported an ultrahigh strain in PMN-PT and PZN-PT single crystals oriented and poled in the (001) direction. Specifically PMN-PT(67/33) was shown to show a record high longitudinal piezo-electric coefficient d33 ≈ 2500 pm/V and transverse piezo-electric coefficient e31 = −27 ± 3 C/m2 in a cantilever configuration.3,4 The giant piezo strain up to 1.7% observed for (001) oriented PMN-PT(67/33) single crystal is an order of magnitude higher than of bulk PZT ceramics. Similarly the giant piezo response (e31) observed in epitaxial PMN-PT(67/33) thin films is significantly higher than of epitaxial PZT thin films.4 The high coupling coefficient

aE-mail: e.p.houwman@utwente.nl

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PMN-PT is a crystalline solid solution of a typical relaxor (PMN) and a classic ferroelectric material (PT). In many ferroelectric solid solutions, the ferroelectric, dielectric and piezoelectric properties are maximized at the morphotropic phase boundary. This morphotropic phase boundary occurs at approximately 33 percent of PT in the bulk PMN-PT solid solution system.

For many applications one requires PMN-PT in thin film form instead of bulk single crystals. This necessity initiated efforts to synthesize this hyperactive material in thin film form. Thin film boundary conditions like clamping to the substrate can modify the morphotropic phase boundary. To gain better understanding of the properties of the PMN-PT thin film system it is necessary to develop a reproducible growth procedure to obtain high quality (epitaxial) PMN-PT thin films. Epitaxial films are highly desirable compared to polycrystalline films due to a lower leakage current and therefore higher piezo response. The growth of high quality epitaxial PMN-PT films is known to be difficult because of the relatively poor stability of the perovskite phase and its compositional complexity. Often prominent, stable pyrochlore phases like the cubic Pb$_2$Nb$_2$O$_{13}$, the rhombohedral Pb$_2$Nb$_2$O$_5$ and the tetragonal Pb$_2$Nb$_2$O$_8$ appear during growth. These non-piezoelectric phases cause degradation of the functional properties of the deposited films. Further the properties of PMN-PT films are sensitive to exact the stoichiometry of all five elements. Off-stoichiometry not only degrades the film properties but also causes the formation of impurity phases (pyrochlore phases). Epitaxial films are usually deposited at high substrate temperature, which may result into lead loss due to the high volatility of this element. Lead loss not only promotes higher leakage current but also can cause the formation of the lead deficient pyrochlore phases. Besides lead stoichiometry, the Mg/Nb ratio is also found essential to fabricate perovskite phase pure PMN-PT films. It is noticed that PMN-PT is commonly preferred over PZN-PT, since the later contains two volatile elements (Zn and Pb) although both exhibit superior properties compared to the presently widely used (PZT) ferroelectric material.

A number of methods and approaches had been adopted to fabricate high quality PMN-PT material. For instance, the columbite process was developed by S. L. Swartz and T. R. Shrout in 1982 for the synthesis of bulk PMN-PT ceramics. This process can bypass the pyrochlore phase formation by facilitating the reaction between MgO and NbO prior to the addition of and reaction with PbO. Nonetheless, this method is not useful for thin film growth. High quality epitaxial PMN-PT films have been deposited with different techniques, such as metal-organic chemical vapor deposition, sputtering and pulsed laser deposition (PLD). J.P. Maria et al. were the first who successfully deposited epitaxial PMN-PT(70/30) thin films, using pulsed laser deposition (PLD) on LaAlO$_3$ substrates by carefully controlling the fabrication conditions. S. D. Bu et al. adopted the approach of miscut SrTiO$_3$ (STO) substrates to achieve perovskite phase pure, epitaxial PMN-PT(67/33) films. The high density of steps on the miscut substrate surface was thought to promote the growth of the perovskite phase by facilitating the incorporation of volatile PbO into the film. Afterward S. H. Baek et al. demonstrated the fabrication of high quality epitaxial PMN-PT(67/33) films with giant piezo response on STO buffered, miscut silicon substrates.

From the literature, it is known that the (PLD) deposition of high quality PMN-PT film is difficult (pyrochlore phase impurity) and only a relatively narrow process window exists to obtain perovskite phase pure films. Within this window the properties of the films vary strongly with the exact process conditions. It is therefore important to establish the process window (which is clearly somewhat specific for the deposition equipment used) and a (qualitative) relation between the process conditions and the film properties. This is the goal of this report. To our knowledge this is the first paper to describe in detail the effect of processing conditions, such as laser fluence, substrate temperature, target-substrate distance and ambient gas pressure, on phase formation (structural properties) and ferroelectric and piezoelectric properties of epitaxial PMN-PT(67/33) thin films within the narrow process window for (001)-oriented perovskite phase growth. Additionally, we have observed that the built in bias in our phase and orientation pure epitaxial PMN-PT
films depends on the fabrication conditions. This indicates that the fabrication conditions can be used to tune the self-bias in epitaxial PMN-PT films.

II. EXPERIMENTAL PROCEDURE

For this study (001) oriented STO substrates with B-site termination were used for their well-defined crystalline surface and close lattice match to the thin films. The STO substrates were pre-treated to achieve B-site termination using the method developed by Koster et al.\textsuperscript{15} 100nm thick SrRuO\textsubscript{3} (SRO) thin films were deposited as top and bottom electrodes, because SRO grows uniformly on a TiO\textsubscript{2} terminated STO substrate with a high crystalline quality.\textsuperscript{16} Further the use of oxide electrodes is very beneficial for the long-term stability of ferroelectric oxides, as compared to metal electrodes.\textsuperscript{17} For the ferroelectric the PMN-PT(67/33) composition was selected because of its giant piezoelectricity in thin film form on STO-buffered silicon as was shown by S. H. Baek et al.\textsuperscript{4} All films were deposited on a heated substrate with PLD using a KrF Excimer laser operating at 248nm, using commercial targets. The deposition conditions are given in table I.

The complete SRO/PMN-PT/SRO heterostructure was deposited without breaking the vacuum. After deposition the samples were cooled down to room temperature in a pure, 1 bar oxygen atmosphere during one hour (cooling rate $= 10^\circ\text{C}/\text{minute}$). The growth conditions for both SRO electrodes (table I) were fixed, whereas the conditions for the PMN-PT growth were varied around an initial set of values usually used for Pb(Zr\textsubscript{x},Ti\textsubscript{1-x})O\textsubscript{3} in our lab.\textsuperscript{2}

Structural properties and epitaxial relationships were investigated by High Resolution-X-Ray Diffraction (XRD, Bruker D8 Discover). The lattice parameters were obtained from reciprocal space maps (RSM). The surface morphology and surface roughness’s were determined using images recorded with atomic force microscopy (AFM, Bruker Icon). Ferroelectric capacitor structures (200 $\times$ 200 $\mu$m$^2$) were patterned with a standard photolithography process and structured by argon ion beam etching. Polarisation-electric field ($P$-$E$) hysteresis loops were measured using a modified Sawyer Tower circuit (AixACCT TF Analyser 3000) at a scan frequency of 1 kHz using a bipolar triangular pulse with an amplitude of 170 kV/cm. Fatigue measurements were performed using a rectangular, bipolar pulse train at a frequency of 10 kHz and an amplitude of 200 kV/cm. The longitudinal piezoelectric coefficient as function of electrical field ($d_{33}$-$E$) were obtained with the Polytec MSA-400 Micro Scanning Laser Doppler Vibrometer. Capacitance versus electric field vs. capacitance ($C$-$E$) loops were measured at 10 kHz frequency with a Suss MicroTech PM300 probe station equiped with a Keithley 4200 semiconductor characterisation.

III. RESULTS AND DISCUSSION

A. Phase optimization and structural properties

In the first optimization step the laser fluence was optimized to achieve uniform ablation of the target material (PMN-PT) to avoid droplet formation in the plasma plume. Droplets can be incorporated in the growing film and are a major cause for electrical shorts in the film causing

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SrRuO\textsubscript{3}</th>
<th>PMN-PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient gas</td>
<td>Oxygen</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Pressure $p$ (mbar)</td>
<td>0.130</td>
<td>0.158 – 0.318 (0.278)</td>
</tr>
<tr>
<td>Laser fluence $F$ (J/cm$^2$)</td>
<td>2.50</td>
<td>2.0 – 2.5 (2.5)</td>
</tr>
<tr>
<td>Laser repetition rate (Hz)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Substrate temperature $T$ ($^\circ\text{C}$)</td>
<td>600</td>
<td>550 – 625 (575)</td>
</tr>
<tr>
<td>Target-substrate distance $D$ (cm)</td>
<td>4.90</td>
<td>5.5 – 6.5 (5.5)</td>
</tr>
<tr>
<td>Film thickness $t$ (nm)</td>
<td>100</td>
<td>300</td>
</tr>
</tbody>
</table>
FIG. 1. (a) θ-2θ diffraction pattern of epitaxial PMN-PT films deposited with different laser fluences. (b) φ scans of the PMN-PT (101) reflection and the STO substrate (101) reflection of sample P1, showing the in-plane (relaxed) epitaxial relation with the substrate.

degradation of the film properties. Uniform ablation of the PMN-PT target (no droplet formation) was found in the range 1.5 – 2.5 J/cm², consistent with frequently employed laser energy density values found in literature.8,11,18 Figure 1(a) shows the θ-2θ scan of the samples deposited at the fluences $F = 2.0, 2.25$ (sample P1) and 2.5 J/cm², keeping the other deposition conditions equal to the initial values given in table I.

The PMN-PT reflections indicate a (001)-oriented film without other growth orientations. The extra diffraction peaks at approximately 34° in the samples deposited with a fluence of 2.0 and 2.5 J/cm² are due to the pyrochlore phase ($\text{Pb}_3\text{Nb}_4\text{O}_{13}$), which is caused by lead deficiency in the film. For the high fluence case this was ascribed to re-evaporation of PbO from the substrate, due to the energetic bombardment by atoms and ions from the plasma. In the low fluence case it is assumed that the PbO particles do not have enough kinetic energy to reach the substrate in sufficient amount. In both cases the optimum film stoichiometry is lost resulting in the formation of the pyrochlore phase.

The azimuthal φ-scan of the PMN-PT (101) reflection of the perovskite phase and (001) orientation-pure film P1 shows in-plane epitaxy with an epitaxial relation with the STO substrate that is largely strain relaxed. The full width at half maximum (FWHM) of the ω-scan of the PMN-PT (002) reflection of this film is 0.53°, and a broad shoulder of this reflection is observed at lower angles in the θ-2θ scan. This indicates that part of the film is in-plane compressively strained, as may be expected from the lattice mismatch of the film (the pseudo-cubic lattice constant of PMN-PT is $a_{\text{PMN-PT}} = 4.022$ Å with the substrate ($a_{\text{STO}} = 3.905$ Å). It is important to indicate here that the SRO bottom electrode is in-plane strained to the STO substrate as indicated by reciprocal space mapping (not shown here). The main diffraction peak corresponds to a PMN-PT out-of-plane lattice parameter of $c = 4.034$ Å, whereas the maximum of the shoulder due to the strained layer corresponds to $c_{\text{str}} = 4.091$ Å (see detail in figure 2(d)). From the reciprocal space map the out-of-plane and in-plane lattice parameters $c$ and $a$ were determined, from which a $c/a$ ratio equal to 1.0057 and a pseudocubic lattice parameter (defined as $a_{\text{pc}} = (ca^2)^{1/3}$, of 4.024 Å were calculated. Thus the bulk of the film is largely relaxed and has a pseudo-cubic lattice parameter practically equal to that of the rhombohedral phase of PMN-PT(67/33) single crystals.

In order to investigate the influence of substrate temperature on phase formation and properties of the epitaxial PMN-PT films, PMN-PT films were deposited at different temperatures, while maintaining the other deposition parameters the same as for sample P1. The substrate temperature was changed to 550, 600 (sample P2) and 625 °C. Figure 2(a) shows the θ-2θ scan of these samples. For $T = 550$ and 625 °C the pyrochlore phase appears again and a large increase of the shoulder of the (002) reflection is observed. For $T > 600$ °C also a small peak corresponding to a PbO phase shows up. The shoulder on the (002) reflection and the FWHM of the (002) ω-scan slightly decreases when the substrate temperature is increased from 575 °C (sample P1) to 600 °C (P2). The lattice parameters of sample P2 are within the error margins equal to that of P1 (see table II).
FIG. 2. θ-2θ diffraction pattern of PMN-PT films deposited with different substrate temperatures while maintaining the other deposition parameters same as for sample P1(a). Idem for different target to substrate distances, with the other parameters equal to those of P2(b). Idem for different deposition pressures, with the other parameters equal to those of P3 (c). Detail of the diffraction pattern of the PMN-PT (002) reflections of the samples P1-P5 showing the variation in shoulders (d).

shows a small reflection peak on the right shoulder of the reflections around 22-23 degrees, which probably corresponds to PbO.

The target-substrate distance was varied in the range 5.5-6.5 cm to investigate the influence on phase formation and properties of the deposited epitaxial PMN-PT films. Figure 2(b) shows the θ-2θ scans of the samples fabricated with the conditions of sample P2, but with a target-substrate distance of 6.0 and 6.5 cm. For $D = 6.0$ cm (sample P3) no PbO reflection is observed and the scan does not show any sign of any other phase than pure (001)-oriented PMN-PT, whereas for $D = 6.5$ cm strong pyrochlore phase reflections are present. For P3 there is hardly any effect on the shoulder of the (002) reflection compared to sample P2 and the lattice parameters are nearly equal to that of P1 and P2. The increase in the target-substrate distance (from 5.5 to 6.0 cm) helped to adjust the Pb stoichiometry in the PMN-PT films. This is believed to be due to a reduction of arriving Pb and PbO on the growing film due to scattering by the background gas. However, no influence

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F$ ($J/cm^2$)</th>
<th>$D$ (cm)</th>
<th>$T$ (°C)</th>
<th>$P$ (mbar)</th>
<th>$a_{pc}$ (Å)</th>
<th>$c/a$</th>
<th>FWHM (002)</th>
<th>Roughness Ra (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>2.25</td>
<td>5.5</td>
<td>575</td>
<td>0.278</td>
<td>4.024</td>
<td>1.0057</td>
<td>0.53</td>
<td>1.80</td>
</tr>
<tr>
<td>P2</td>
<td>2.25</td>
<td>5.5</td>
<td>600</td>
<td>0.278</td>
<td>4.026</td>
<td>1.0035</td>
<td>0.50</td>
<td>0.78</td>
</tr>
<tr>
<td>P3</td>
<td>2.25</td>
<td>6.0</td>
<td>600</td>
<td>0.278</td>
<td>4.025</td>
<td>1.0045</td>
<td>0.48</td>
<td>0.78</td>
</tr>
<tr>
<td>P4</td>
<td>2.25</td>
<td>6.0</td>
<td>600</td>
<td>0.238</td>
<td>4.027</td>
<td>1.0052</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>P5</td>
<td>2.25</td>
<td>6.0</td>
<td>600</td>
<td>0.198</td>
<td>4.031</td>
<td>1.0060</td>
<td>0.60</td>
<td>0.90</td>
</tr>
</tbody>
</table>
of the target-substrate distance on the surface roughness of PMN-PT film was observed under the conditions for (001) oriented and pure perovskite phase.

The deposition pressure has also an important effect on the crystal structure when growing films at high substrate temperatures. For example Catalan et al. reported the influence of the oxygen partial pressure on the electromechanical properties for PLD deposited relaxor (PMN) films.\textsuperscript{19,20} Using the deposition conditions of sample P3, the deposition pressure was varied in the range \( p = 0.158 - 0.318 \) mbar. For low pressure \( p = 0.158 \) mbar both the pyrochlore and the PbO phase are present in the XRD scans (fig. 2(c)), whereas for the highest pressure the pyrochlore phase is observed. In the narrow intermediate pressure range \( p = 0.198 - 0.278 \) mbar no spurious phases are observed and smooth films are obtained. The lowest FWHM(002) = 0.44° was obtained for \( p = 0.238 \) mbar (sample P4).

The deposition conditions and structural properties of the perovskite phase and (001) orientation pure epitaxial PMN-PT films fabricated during the optimisation process (P1-P5) are summarized in table II.

\textbf{B. Ferroelectric, dielectric and piezoelectric properties}

For all samples that showed no spurious crystal phases the polarization loops (\( P-E \) loops) of capacitor devices were measured. Figure 3(a) shows the polarization hysteresis loops of the devices P1 to P5. All loops show the characteristic slanting of relaxor type films. A second common feature is a shift of all loops due to a positive internal field bias \( E_{sb} \). In general compressive in-plane stress causes an anti-closewise rotation of the polarization hysteresis loops of perovskite ferroelectric materials, whereas in-plane tensile strain rotates the \( P-E \) loops in clockwise direction.\textsuperscript{21} The self-bias in our deposited films is due to in-plane compressive strain as observed from XRD diffraction data. In addition to the in-plane epitaxial compressive strain (resulting from lattice parameter difference), the difference in thermal expansion coefficients also causes in-plane compressive strain in PMN-PT films deposited on STO substrates. The contribution of thermal strain might be small because of the small film thickness in our case. The magnitude of the internal field bias \( E_{sb} \) varies from 4.0 kV/cm to 9.4 kV/cm. In general built-in bias is beneficial for applications of PMN-PT films in many ways. The positive self-bias enhances the negative remnant polarization (\( P_r \), in this case), as can be observed in fig. 3(a). An enhancement of the remanent polarization may enhance...
the piezoelectric response at zero applied field. A built-in bias stabilizes the polarization in a certain direction (upward in this case) and reduces substantially the aging of the piezoelectric response. Devices based on films with self-bias are more robust against depolarization due to temperature or voltage excursions. Additionally, the built in bias also decreases dielectric permittivity at zero applied field, as shown in fig. 3(c), which in turn increases the figure of merit (Figure of Merit \( = e_{33}^2/\varepsilon_0 \varepsilon_r \)) for sensors operating in a voltage sensing mode as well as for piezoelectric energy harvesting devices.

As a characteristic polarization parameter, we use the average out-of-plane component of the spontaneous polarizations \( |P_{s3}| \), estimated from the extrapolated value \( P_{s3}(E_{sb}) \) of the tangents at the loop at the applied field strength \( E_{tang} = (\pm 120 + E_{sb}) \) kV/cm of the decreasing (increasing) section of the loop. At \( E_{tang} \) the domain switching is expected to be complete and above (below) this value the loops become approximately linearly dependent on the field. \( |P_{s3}| \) is a measure for the out-of-plane component of the spontaneous polarization, which may be affected by screening or strain induced rotation of the polarization vector away from the easy axis (111) directions of an unstrained single crystal.

Figure 4 shows \( |P_{s3}| \) as function of deposition pressure \( p \). There is a shallow maximum for \( p = 0.238 \) mbar (sample P4). The changes due to the effect of variation in substrate temperature and target-substrate distance at \( p = 0.278 \) mbar result in a lower polarization value. The maximum value of 0.24 C/cm\(^2\) of P4, is close to the value expected for the out-of-plane component of the spontaneous polarization directed along the body diagonal of the rhombohedral distorted pseudocubic lattice of single crystal PMN-PT, \( |P_{s3}| = P_r/\sqrt{3} = 0.26 \) C/m\(^2\). The scatter in values for samples fabricated with slight different process conditions is ascribed to variations in screening by charged defects, for example in grain boundaries, or by rotation of the polarization vector away from or towards the film plane due to strain variations. The latter is less likely, considering the observation that for all films the lattice appears slightly tetragonally strained, with the long axis in the out-of-plane direction, which would give an increased \( P_{s3} \) instead of a decreased value. Therefore we believe that the differences are mainly due to differences in screening and thus to the defect concentration. The polarization vector in a relaxor material can easily rotate under external influences, hence the presence of for example charged grain boundaries is expected to have a significant reducing effect on the measured polarization value. The dependence of small variations of target-substrate distance and substrate deposition temperature in the deposition pressure range \( p \approx 0.198-0.278 \) mbar indicates the high sensitivity of \( |P_{s3}| \) on these deposition parameters, requiring good parameter control.

The dielectric constant hysteresis (CV) loops of sample P1-5 show hardly any hysteresis (Fig. 3(d)), much less than that of the PE-loops. A significant spread in the maximum values \( \varepsilon_{33,\text{max}} \)
is observed, again reflecting the large sensitivity for the process conditions. The \( \varepsilon_{33max} \) values are plotted in fig. 4(b) as function of process conditions. The maximum values are approximately equal to the zero field values \( \varepsilon_{33}(0) \), which are in between the values for constant strain \( (\varepsilon_{33}^S(bulk)) \) and constant stress, \( (\varepsilon_{33}^T(bulk)) \) conditions reported for bulk polydomain single crystals poled in the (001) direction.\(^{24} \) In the case of the clamped films discussed we expect that the polarization rotation is hampered by the clamping and the screening by charged grain boundaries, causing a lower dielectric constant. On the other hand there may be a contribution of the domain motion to the dielectric constant.

The maximum values of the effective longitudinal piezoelectric values of the \( d_{33} \) hysteresis loops of the samples P1-5 (fig. 3(e)) are given in table III. The average value is 51 pm/V and it varies only ±10\% over the samples. This value is orders of magnitude less than the value reported for the (001)-poled polydomain single crystal samples \( (d_{33} = 2500 \text{ pm/V}).^3 \) Thus the clamping of the PMN-PT thin films causes a large reduction of \( d_{33} \) as compared to that of a single crystal, while there is little effect of the process conditions on this parameter.

The polarization (and the dielectric constant) are sensitive to the process conditions and can therefore be used as a monitor for optimizing film properties. To estimate the relative effect of the different deposition parameters on the polarization value \( |P_{33}| \) in the regime in which smooth, phase pure films are obtained, the variation of \( |P_{33}| \) with the relative variation of the different deposition parameters \( x \), may be expressed as \( \Delta P_{33} = \sum_x S_x \left( \frac{\Delta x}{x_{0}} \right) \). The normalized parameter sensitivities \( S_x \) are estimated as,

\[
S_p = \left( \rho_{0x} \frac{\Delta P_{33}}{\Delta p} \right)_{F,T,D}, \quad S_T = \left( T_{0x} \frac{\Delta P_{33}}{\Delta T} \right)_{p,F,D}, \quad S_D = \left( D_{0x} \frac{\Delta P_{33}}{\Delta D} \right)_{p,F,T}, \quad S_F = \left( F_{0x} \frac{\Delta P_{33}}{\Delta F} \right)_{p,T,D} \tag{1}
\]

Table III. Summary of the ferroelectric, dielectric and piezoelectric properties of perovskite phase and (001) orientation pure sample (P1-P5) deposited during phase optimization steps.

| Sample | \(|P_{33}| (\text{C/m}^2)\) | \(E_{sb}(\text{kV/cm})\) | \(E_{c}(\text{kV/cm})\) | \(\varepsilon_{33max}\) | \(d_{33,eff.} (\text{max})\) |
|--------|------------------|-----------------|----------------|--------------|----------------|
| P1     | 0.11             | 9.3             | 13.6           | 1084         | 51             |
| P2     | 0.19             | 8.3             | 18.0           | 1419         | 57             |
| P3     | 0.27             | 9.4             | 15.3           | 1949         | 55             |
| P4     | 0.29             | 4.7             | 17.4           | 1538         | 47             |
| P5     | 0.23             | 4.0             | 16.1           | 1658         | 46             |

Here the average and the gradient are taken over the maximum differences of the measured \( |P_{33}| \) values of the dataset P1-5, for which the other deposition conditions are (nearly) constant. We find \( S_p = 0.34 \), \( S_T = 1.76 \), \( S_D = 1.16 \), and \( S_F = 0.50 \) ((C/m\(^2\))/relative change) hence a change in the substrate temperature has the largest relative effect on \( |P_{33}| \), followed by variation of the target-substrate distance. The PMN-PT thin film system appears least sensitive to pressure variations, as long as one is in the (narrow) range of deposition conditions that allows phase-pure growth of smooth films. The number of samples is limited and the above numbers therefore are only qualitative indications of the sensitivities relative to each other. However, we think that the observed trends are systematic and are related to small changes in the crystal structure, and especially in the quality of the grain boundaries, where one would expect that most of the off-stoichiometry and crystal defects accumulate.

In figure 3(b) and 3(c) the average coercive field \( E_c = (E_c^+ - E_c^-)/2 \) and the self-bias field \( E_{sb} = (E_s^+ + E_s^-)/2 \) are shown as function of the number of fatigue cycles. The coercive fields are in the range of 13-18 kV/cm and the self-bias field is in the range 4-10 kV/cm. Apart from sample P1, which shows a steady increase of \( E_c \) with cycling, indicative for an increase of domain wall pinning, thus probably of a (charged) defect density, all other films are very stable up to the maximum number of cycles. In reference 25 the self-bias in PMN-PT capacitor devices grown on 25nm thick PZT seed layers of different compositions was discussed. There it was shown that the observed very large self-bias (up to 101 kV/cm) could be related to a strain gradient layer in the PZT seed layer. In the case of the 200nm thick PMN-PT film without PZT seed layer (S0) discussed in that reference,
it was argued that the effect of the strain gradient in the PMN-PT layer was largely cancelled by the incorporation of free charge. The data suggested that this free charge was introduced in the film immediately after deposition in the case of S0, whereas for the devices with PZT seed layer it was slowly incorporated during cycling, resulting in a decreasing self-bias. Here we see that $E_{b}$ and $E_{c}$ of the sample P1-55 are somewhat changing with cycling, which is interpreted as being due to a change of the mobile charge distribution in the (grain boundaries of the) film. It is noted that the polarization values hardly change upon cycling, apart from the consequences of loop shift and changing self-bias field, and changing/opening of the hysteresis loops, due to a changing coercive field. Sample P4 is the most stable upon cycling. This is also the sample with the highest polarization value $|P_{33}|$, close to that expected for a single crystal film with no screening. These findings suggest that the deposition conditions for P4 are close to the best that can be achieved with the PLD system used.

A further indication for the importance of screening charges in this material is the fairly large variation in $|P_{33}|$ between the different samples, suggesting that PMN-PT can relatively easily incorporate charges during the deposition process. The build-up of the thin film crystal structure is clearly very sensitive to the exact deposition conditions and defects are easily build into the film.

This extreme sensitivity is also reflected in the large variation of the zero-field relative dielectric constant with a factor 2. On the other hand the maximum effective piezoelectric constant $d_{33,eff}$ hardly depends on the deposition conditions and varies between 46 and 57 pm/V, but the loops are field-shifted with a magnitude approximately equal to that of the PE-loops. Similarly the difference in longitudinal piezoelectric coefficient (max and average) is also due to self-bias which enhances the response in preferential direction. The ferroelectric, dielectric and piezoelectric properties of the perovskite phase and (001) orientation pure PMN-PT films (P1-P5) are summarised in table 3.

**CONCLUSIONS**

The growth of 300nm thick PMN-PT(67/33) thin films by pulsed laser deposition on a SrTiO$_3$ (001) substrate with SrRuO$_3$ electrodes was optimized with respect to phase purity and smoothness of the film, by varying the deposition conditions, the substrate temperature, laser fluence, oxygen background gas pressure and substrate-target distance. A narrow parameter regime was found in which phase pure and smooth films were obtained. The properties of the polarization hysteresis loop of devices made with growth conditions in this regime were investigated. In the optimized parameter regime the polarization value is most sensitive to variations in the substrate temperature, then to substrate-target distance and much less to fluence and gas pressure. The highest polarization value at the self-bias field, extrapolated from the loop at high fields, corresponds well to the value expected for rhombohedrally distorted pseudocubic lattice of PMN-PT, with a $\langle 111 \rangle$ easy axis.

Due to the clamping of the films to the substrate the dielectric and piezoelectric properties of the films are much less than the literature values for single crystals.

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