

# *In situ* deposition of epitaxial $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$ thin films by pulsed laser deposition

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Epitaxial thin films of  $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$  (PZT) with  $0 \leq x \leq 0.6$  have been deposited *in situ* by pulsed laser deposition from stoichiometric targets onto  $\langle 100 \rangle$  oriented single crystals of  $\text{MgO}$  and  $\text{SrTiO}_3$ . Film composition was extremely sensitive to the substrate temperature and the oxygen deposition pressure. In a high (200–300 mTorr) oxygen ambient, phase-pure  $\langle 100 \rangle$  oriented PZT films ( $x = 0.54$ ) were formed at a substrate temperature of 550 °C on  $\text{SrTiO}_3$ . On  $\text{MgO}$ , competition between formation of the ferroelectric phase and a nonferroelectric (pyrochlore) phase was observed for compositions near the morphotropic phase boundary ( $x \sim 0.54$ ). Polycrystalline PZT films which were 70%–90% PZT were also deposited on Pt coated Si and GaAs under similar conditions.

Ferroelectric films offer the potential for important device applications (see review by Francombe and Kishanaswamy<sup>1</sup>) including transducers, infrared detectors, visual displays, and of considerable recent interest, in radiation-hard nonvolatile random access memories (NVRAM).<sup>2–4</sup> Ferroelectric materials with a high dielectric constant and large piezoelectric, pyroelectric, electrooptic coefficients and large remnant polarization are desirable for these applications, respectively. For  $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$  (PZT), a number of these properties are maximized near the phase boundary separating the rhombohedral (Zr-rich) and tetragonal (Ti-rich) crystallographic phases<sup>5</sup> (i.e., the morphotropic phase boundary) which occurs at a composition corresponding to  $x \approx 0.54$ .<sup>6,7</sup> Successful monolithic implementation of ferroelectric thin films in useful devices will require high quality thin films (i.e., phase pure and in some cases oriented) on technologically useful substrates such as metals or semiconductors. An *in situ* deposition technique for these complex materials is desirable since post-processing of amorphously deposited material requires high substrate temperatures and routinely leads to the production of large angle grain boundaries, impurity phases and randomly oriented material. Pulsed laser deposition (PLD) has emerged as an excellent technique for the deposition of thin films of perovskite materials (e.g., high temperature superconductors<sup>8</sup>) and recently to ferroelectric materials such as  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,<sup>9</sup>  $\text{BaTiO}_3$ .<sup>10–13</sup> In addition, papers have recently been published on the deposition of  $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$ .<sup>14–19</sup> In this letter, we report the *in situ* deposition of epitaxial thin films of  $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$  for various compositions ( $x = 0, 0.40, 0.50, 0.54, \text{ and } 0.6$ ) onto  $\langle 100 \rangle$   $\text{MgO}$  and  $\langle 100 \rangle$   $\text{SrTiO}_3$  substrates and the deposition of randomly oriented PZT onto Pt coated substrates of Si and GaAs by PLD.

The PLD apparatus used has been described previously.<sup>19</sup> Briefly, the output from a KrF excimer laser (300 mJ/pulse at 248 nm) operating at 5 Hz was focused onto a PZT target to an energy density of  $\sim 2 \text{ J/cm}^2$ . The vaporized material was deposited onto a substrate positioned  $\sim 4 \text{ cm}$  away. The substrate was thermally attached

with silver paint to a substrate stage which was heated by a quartz halogen projector lamp. The substrate temperature was monitored with a chromel-alumel thermocouple gauge embedded in the heated substrate block. The measured temperature, as reported in this paper, represents the block temperature which is higher than the actual substrate surface temperature by an estimated 25–50 °C at a block temperature of 600 °C. Films were deposited in an oxygen ambient at pressures up to 300 mTorr. Typically, 5000 laser pulses yielded films that were  $\sim 1.0 \mu\text{m}$  thick.

$\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$  targets were made from stoichiometric quantities of the metal oxides  $\text{PbO}$ ,  $\text{ZrO}_2$ , and  $\text{PbTiO}_3$  for  $x = 0.40, 0.50, 0.54, \text{ and } 0.60$ .  $\text{PbTiO}_3$  was used for  $x = 0$  and a commercial target purchased from Cerac was also used for  $x = 0.54$ . Pellets were pressed from the mixed oxide powders to  $\sim 34\,000 \text{ psi}$  and then annealed for one hour at 500 °C in flowing oxygen (50 sccm) and cooled slowly to room temperature at 1 °C/min. Several pellets were further sintered at 1300 °C to induce a solid state reaction. The target composition was analyzed by x-ray fluorescence (XRF) to determine the relative Pb/Zr/Ti ratio.

Films were deposited onto  $\langle 100 \rangle$   $\text{MgO}$  and  $\langle 100 \rangle$   $\text{SrTiO}_3$  substrates as a function of substrate temperature and oxygen deposition pressure. In comparison with other materials that have been deposited with this technique, e.g.,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , scanning electron microscope (SEM) images indicated that the PZT films had a smooth surface composed of grains on the order of 50 nm wide. Less than 1% of the surface was covered by 0.1–1.0- $\mu\text{m}$  particulates. No significant change in particle size or density was observed when the energy fluence was varied from 1 to 4  $\text{J/cm}^2$ . Particle density, normalized to film thickness, was estimated as  $\sim 1000/\text{cm}^2$  per Å of film.

Film composition was determined from elastic backscattering spectrometry (EBS) using 6.2-MeV  $\text{He}^{2+}$ . This energy allows complete separation of the metallic components in the films. As a function of substrate temperature and oxygen deposition pressure, the Zr and Ti metal fractions in the films were constant and identical to the target composition but the Pb metal fraction was extremely sen-

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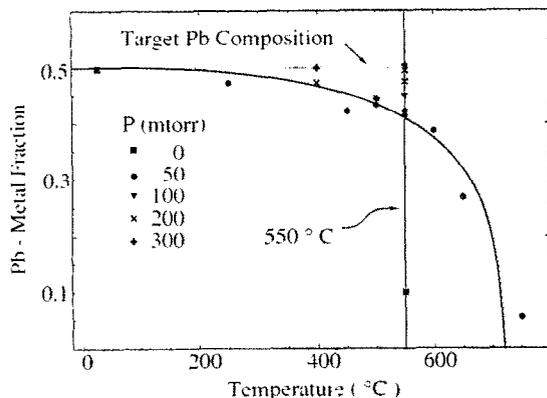


FIG. 1. The Pb metal fraction for thin films deposited from a commercial PZT target ( $x = 0.54$ ) as a function of substrate temperature at several oxygen deposition pressures. Following deposition, the films were cooled to room temperature in 1 atm of oxygen.

sitive to the deposition conditions. Films deposited at high substrate temperatures ( $> 400^\circ\text{C}$ ) and a low ( $< 100$  mTorr) oxygen ambient were lead deficient. In bulk processing of PZT, it has been shown that Pb loss occurs by volatilization of  $\text{PbO}$  at high temperatures and special precautions must be taken to maintain the correct Pb stoichiometry.<sup>20</sup>

Shown in Fig. 1 is the Pb metal fraction, determined by EBS, for PZT films deposited by PLD on  $\text{MgO}$  and  $\text{SrTiO}_3$  substrates versus the measured substrate temperature for several oxygen deposition pressures. Following deposition, the pressure inside the chamber was raised to 1 atm of oxygen in about 1 min (oxygen quench) at the same time the substrate heater was turned off. At room temperature, vacuum ( $10^{-6}$  Torr) deposition of PZT from the commercial target ( $x = 0.54$ ) yielded films of a stoichiometric metal composition. However, as the substrate temperature was increased, the lead metal fraction decreased. At  $550^\circ\text{C}$  in a vacuum, the lead metal fraction in the deposited film was  $\sim 20\%$  of the value obtained for a room-temperature substrate. Closer inspection of films grown at  $550^\circ\text{C}$  revealed that the lead content of the film increased systematically as the background pressure of oxygen was raised. For films deposited at a substrate temperature of  $550^\circ\text{C}$  the Pb metal fraction increased from 0.1 in  $10^{-6}$  Torr to 0.42 in 50 mTorr. The Pb metal fraction reached the ideal composition of 0.50 (within the accuracy of the measurement) at 200–300 mTorr of oxygen. The change in the metal fraction at  $550^\circ\text{C}$  as a function of the oxygen ambient from vacuum to 300 mTorr is also shown in Fig. 1 by the solid vertical line. The observed improvement in Pb content in films deposited at higher oxygen pressures is likely the result of a combination of effects related to both the vapor pressure of  $\text{PbO}$  and thermalization of the vaporized material as a result of vapor/ambient-gas-atom collisions. However, when an Ar ambient at 300 mTorr was used during deposition at a substrate temperature of  $550^\circ\text{C}$ , a Pb metal fraction of only 0.06 (Pb deficient) was measured in the deposited film.

X-ray diffraction (XRD) of the PZT films was per-

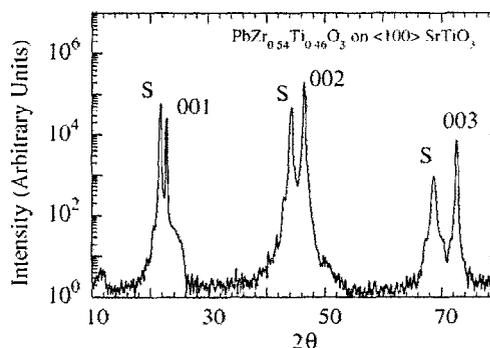


FIG. 2. X-ray diffraction pattern from a PZT film ( $\sim 4300 \text{ \AA}$ ,  $x = 0.54$ ) deposited on  $\langle 100 \rangle \text{SrTiO}_3$  at  $550^\circ\text{C}$  in 200 mTorr of oxygen. The 00/ lines are labeled and  $S$  corresponds to the substrate.

formed using a 12-kW-rotary-anode generator with a Cu target, a  $\theta/2\theta$  diffractometer, and a curved graphite monochromator. XRD showed that stoichiometric films ( $x = 0.54$ ) deposited at low substrate temperatures ( $25^\circ\text{C} < T < 250^\circ\text{C}$ ) were amorphous. Isochronal annealing of the amorphous films indicates that crystallization occurred at around  $550^\circ\text{C}$ . The phase produced was randomly oriented and consistent with a pyrochlore<sup>21</sup> structure which is paraelectric (nonferroelectric). Further annealing at  $600^\circ\text{C}$  resulted in crystallization of another phase with a pseudocubic perovskite structure. A lattice parameter  $a = 4.08 \text{ \AA}$  was determined, nominally in agreement with what is expected from PZT at this composition.<sup>22</sup> The perovskite phase in these post-annealed films was randomly oriented.

XRD of films deposited at elevated substrate temperatures between 350 and  $700^\circ\text{C}$  also showed the presence of the perovskite and nonferroelectric (pyrochlore) phases. These phases exhibited preferred  $\langle 100 \rangle$  and  $\langle 111 \rangle$  orientations. XRD of PZT films deposited on  $\langle 100 \rangle \text{MgO}$  and  $\langle 100 \rangle \text{SrTiO}_3$  by PLD at substrate temperatures between 250 and  $650^\circ\text{C}$  exhibited a correlation between ferroelectric phase content and Pb composition. The diffraction patterns indicated that lead deficient films contained predominantly the nonferroelectric, pyrochlore phase. As the oxygen deposition pressure was increased (concurrently raising the Pb metal fraction of the deposited film) the pyrochlore phase was reduced in favor of the perovskite phase although it could not be completely removed in stoichiometric films deposited onto  $\text{MgO}$ . However, this was not the case on  $\text{SrTiO}_3$ . The XRD spectrum of a PZT film ( $\sim 4300 \text{ \AA}$ ,  $x = 0.54$ ) deposited on  $\langle 100 \rangle \text{SrTiO}_3$  at  $550^\circ\text{C}$  in 200 mTorr of oxygen, shown in Fig. 2, indicates that the film is single phase  $\langle 100 \rangle$  oriented PZT. Stripping out the  $\text{Cu}_{K\alpha_2}$  component, the  $\{200\}$  peak was split into two components with  $d$  spacings of 4.100 and 4.081  $\text{ \AA}$ . These values are consistent with both the rhombohedral and tetragonal phases of PZT at this composition.<sup>22</sup> PZT films which were  $\langle 100 \rangle$  oriented were also grown on  $\langle 100 \rangle \text{MgO}$  at  $550^\circ\text{C}$  in 300 mTorr of oxygen containing nearly phase-pure perovskite-structure material for compositions off the morphotropic phase boundary ( $0 < x < 0.60$ ). At lower

substrate temperatures (350–500 °C) for these compositions, the pyrochlore phase dominated the film structure.

Electrical characterization and ultimately the use of PZT films in electronic applications requires PZT to be deposited onto conducting substrates. We deposited PZT onto Pt-coated substrates of GaAs and Si under similar conditions as were used for MgO and SrTiO<sub>3</sub>. The Pt coating on these substrates required intermediate layers including Ti to enhance adhesion. On Si the intermediate layers were Pt/Ti/TiW/SiO<sub>2</sub> with Pt and Ti layer thicknesses of 1000 and 1500 Å, respectively. On GaAs the intermediate layers were Pt/Ti/W/Si-O-N with Pt and Ti thicknesses of ~1300 and 175 Å, respectively. The Pt layer was fiber textured (rocking curve widths  $\Delta\omega \sim 10^\circ$ ) and resulted in PZT films that were polycrystalline. XRD analysis of PZT ( $x = 0.40, 0.54, 0.60$ ) films deposited on Pt-coated Si at  $T_{\text{substrate}} \leq 550^\circ\text{C}$  in 300 mTorr of oxygen indicated that the films were primarily pyrochlore. A similar result was obtained for Pt-coated GaAs. However, at a slightly higher temperature (600 °C) the perovskite phase was stabilized. From the diffraction data, it was estimated that the perovskite phase was from 70% to 90% of the crystalline material on Si and GaAs, respectively. At 650 °C, diffusion of the Ti into the Pt layer was observed by EBS and reacted compounds were observed by XRD. In addition, films deposited at this temperature contained less perovskite relative to pyrochlore.

In summary, epitaxial PZT films were deposited *in situ* onto  $\langle 100 \rangle$  MgO and SrTiO<sub>3</sub> by pulsed laser deposition from stoichiometric targets. The stability of the perovskite phase in the deposited film was found to be extremely sensitive to the Pb metal fraction in the film. Pb deficiencies could be minimized by depositing in a high pressure of oxygen (300 mTorr). At 550 °C in 300 mTorr of oxygen, phase pure oriented PZT films were deposited on SrTiO<sub>3</sub> (at  $x = 0.54$ ) and on MgO (for  $0 \leq x \leq 0.60$ ). However, at compositions near the morphotropic phase boundary and for MgO substrates subtle differences in deposition conditions occasionally led to formation of the nonferroelectric pyrochlore phase. At substrate temperatures between 350 and 500 °C, the pyrochlore phase dominates the film structure. Polycrystalline PZT ( $x = 0.54$ ) films were deposited at 600 °C on Pt-coated GaAs and Si which contained 70%–90% perovskite phase. Further experiments are in progress

to determine the effects of film phase purity and orientation on the electrical properties.

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- <sup>1</sup>M. H. Francombe and S. Krishnaswamy, *J. Vac. Sci. Technol. A* **8**, 1382 (1990).
- <sup>2</sup>J. E. Evans and R. Womak, *IEEE J. Solid-State Circuits* **SSC-23**, 1171 (1988).
- <sup>3</sup>G. C. Messenger and F. N. Copping, *IEEE Trans. Nucl. Sci.* **NS-35**, 1461 (1988).
- <sup>4</sup>C. A. Paz de Araujo, L. D. McMillan, B. M. Melnick, J. D. Cucharo and J. F. Scott, *Ferroelectrics* **104**, 241 (1990).
- <sup>5</sup>E. Sawaguchi, *J. Phys. Soc. Jpn.* **8**, 615 (1953).
- <sup>6</sup>D. A. Berlincourt, C. Cmolik, and H. Jaffe, *Proc. IRE* **48**, 220 (1960).
- <sup>7</sup>R. Takayma and Y. Tomita, *J. Appl. Phys.* **65**, 1666 (1989).
- <sup>8</sup>D. B. Chrisey, J. S. Horwitz, H. S. Newman, M. E. Reeves, B. D. Weaver, K. S. Grabowski, and G. P. Summers, *J. Superconductivity* **4**, 57 (1991).
- <sup>9</sup>R. Ramesh, K. Luther, B. Wilkins, D. L. Haart, E. Wang, J. M. Tarascon, A. Inam, X. D. Wu, and T. Venkatesan, *Appl. Phys. Lett.* **57**, 1505 (1990).
- <sup>10</sup>S. B. Ogale, S. M. Kanetkar, S. M. Chaudhari, V. P. Godbole, V. N. Koinkar, S. Joshi, R. Nawathey, R. D. Vispute, S. K. Date, and A. R. Moghe, *Ferroelectrics* **102**, 85 (1990).
- <sup>11</sup>H. Buhay, S. Sinharoy, W. H. Kasner, M. H. Francombe, D. Lampe, and E. Stepke, *Appl. Phys. Lett.* **58**, 1 (1991).
- <sup>12</sup>G. M. Davis and M. C. Gower, *Appl. Phys. Lett.* **55**, 112 (1989).
- <sup>13</sup>M. G. Norton and C. B. Carter, *J. Mater. Res.* **5**, 2762 (1990).
- <sup>14</sup>K. L. Saenger, R. A. Roy, K. F. Etzold, and J. J. Cuomo, *Mat. Res. Soc. Symp. Proc.* **200**, 115 (1990).
- <sup>15</sup>K. Ramkumar, J. Lee, A. Safari, and S. C. Danforth, *Mat. Res. Soc. Symp. Proc.* **200**, 121 (1990).
- <sup>16</sup>C. K. Chiang, L. P. Cook, P. K. Schenck, P. S. Brody, and J. M. Benedetto, *Mat. Res. Soc. Symp. Proc.* **200**, 133 (1990).
- <sup>17</sup>D. B. Chrisey, J. S. Horwitz, and K. S. Grabowski, *Mat. Res. Soc. Symp. Proc.* **191**, 25 (1990).
- <sup>18</sup>S. Otsubo, T. Maeda, T. Minamikawa, Y. Yonezawa, A. Morimoto, and T. Shimizu, *Jpn. J. Appl. Phys.* **29**, 1133 (1990).
- <sup>19</sup>K. S. Grabowski, J. S. Horwitz, and D. B. Chrisey, *Ferroelectrics* **116**, 19 (1991).
- <sup>20</sup>S. -S. Chiang, M. Nishioka, R. M. Fulrath, and J. A. Pask, *Am. Ceram. Soc. Bull.* **60**, 484 (1981).
- <sup>21</sup>F. Martin, *Phys. Chem. Glasses* **6**, 143 (1965).
- <sup>22</sup>B. Jaffe, R. S. Roth, and S. Marzullo, *J. Res. Nat. Bur. Stand.* **55**, 239 (1965).