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## High quality epitaxial growth of PbTiO<sub>3</sub> by molecular beam epitaxy using H<sub>2</sub>O<sub>2</sub> as the oxygen source

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## High quality epitaxial growth of PbTiO<sub>3</sub> by molecular beam epitaxy using H<sub>2</sub>O<sub>2</sub> as the oxygen source

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Single crystalline PbTiO<sub>3</sub> films have been epitaxially grown on SrTiO<sub>3</sub> (001) substrates by molecular beam epitaxy using H<sub>2</sub>O<sub>2</sub> as the source of active oxygen. The optimum growth conditions have been determined by analyzing a range of growth parameters affecting growth and used to attain single phase and stoichiometric PbTiO<sub>3</sub> thin films. *In situ* reflection high-energy electron diffraction pattern indicated the PbTiO<sub>3</sub> films to be grown under a two-dimensional growth mode. The full width at half maximum of the rocking curve of a relatively thin 65 nm (001) PbTiO<sub>3</sub> film is 6.2 arc min which is indicative of high crystal quality. The band gap of PbTiO<sub>3</sub>, as determined by ellipsometric measurement, is 3.778 eV. © 2006 American Institute of Physics.

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Ferroelectric thin films have recently attracted a great attention because of their potential applications in nonvolatile memory, various aspects of microelectronics, and multifaceted sensor technologies.<sup>1</sup> Among the ferroelectric films, lead titanate based thin films such as PbTiO<sub>3</sub> (PTO) and Pb(Zr,Ti)O<sub>3</sub> offer attractive advantages for a wide variety of applications such as integrated piezoelectric devices,<sup>2</sup> pyroelectric infrared sensors,<sup>3</sup> nonvolatile memory,<sup>4</sup> gate material for ion-sensitive field-effect transistors,<sup>5,6</sup> ferroelectric field-effect transistor,<sup>7</sup> optical waveguide devices,<sup>8</sup> and electro-optic modulators.<sup>9</sup> This is mainly due to PTO's unique combination of properties such as large pyroelectric coefficient ( $\gamma=9.5 \times 10^{-8}$  C/cm K), large dielectric constant ( $\epsilon_r=200$ ), and high Curie temperature (493 °C).<sup>10</sup> However, it is well known that devices fabricated using polycrystalline PTO typically show degraded electrical properties such as reduced remanent polarization and relatively high coercive fields due to inferior quality of the material, while epitaxial PTO prepared by hydrothermal method exhibited record values of 96.5  $\mu\text{C}/\text{cm}^2$  and 97 pc/N for remanent polarization<sup>11</sup> and effective piezoelectric constant,<sup>12</sup> respectively (both listed values exceed the theoretically predicted ones<sup>13</sup>).

Obviously, attainment of high quality, single crystalline lead titanate based materials is imperative in order to fully exploit the intrinsic properties of this class of materials for device applications. In this vein, PTO thin films have been prepared by various methods such as chemical-vapor deposition (CVD),<sup>14</sup> rf magnetron sputtering,<sup>15</sup> pulsed laser deposition,<sup>16</sup> hydrothermal method,<sup>11,12,17</sup> electrostatic spray deposition,<sup>18</sup> and sol-gel technique.<sup>19</sup> Note that molecular beam epitaxy (MBE), which is a powerful technique featured by its precise control of composition of grown films, has not been widely applied to the growth of lead-containing ferroelectric materials except for a few reports.<sup>20,21</sup> The low level activity may in part be due to the perceived view that in MBE the sources would be oxidized as well as a perceived

lack of precise control of Pb and PbO due to their volatility in high vacuum. Because of large bonding energy of O<sub>2</sub>, plasma sources are commonly used in oxide MBE to produce oxygen species. However, this approach has such disadvantages as possible surface damage by high-energy particle, degradation of the plasma sources due to the high reactivity of oxygen radicals, and limitation of oxygen pressure to maintain the ignition of the plasma source. An alternative approach reported by Theis and Schlom *et al.*<sup>20</sup> employed an ozone source for growing oxide materials. One more alternative source of reactive oxygen is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which was successfully used for ZnO growth by Izyumskaya *et al.*<sup>22</sup> In this letter, we report on the growth of high quality single crystalline PTO layers by peroxide MBE. The surface morphology and structural properties of the deposited films were studied by reflection high-energy electron diffraction (RHEED), x-ray diffraction (XRD), and growth mechanisms to achieve single phase PTO are discussed. Refractive index and band gap energy of grown PTO were determined by variable angle spectroscopic ellipsometry (VASE).

Lead titanate thin films with thickness between 250 to 650 Å have been grown on SrTiO<sub>3</sub> (STO) (001) substrates in a modified Riber 3200 MBE system using 50% aqueous solution of H<sub>2</sub>O<sub>2</sub> as the source of reactive oxygen. Ti flux was provided by a high-temperature Knudsen effusion cell and Pb was deposited from a double-zone Knudsen cell. For all the growth runs, a Pb/Ti ratio of  $\geq 1$  was used, and the H<sub>2</sub>O<sub>2</sub> pressure was set to the maximum that can be safely handled by the MBE system (around  $5 \times 10^{-5}$  Torr). The details of the system related issues for growth of oxides will be discussed elsewhere. A range of substrate temperatures ( $T_s$ ) and growth rates were explored and used to study the nature of the applicable growth mechanisms. Figure 1 displays a series of XRD  $\theta$ - $2\theta$  scans of PTO/STO films grown under different growth conditions. While the particular PTO epitaxial layer grown at 580 °C contains the unwanted PbO (100) phase [see Fig. 1(a)], the layer grown at 600 °C is composed of single PTO (001) phase only [Fig. 1(c)], indicating the self-tuning of the stoichiometry of the

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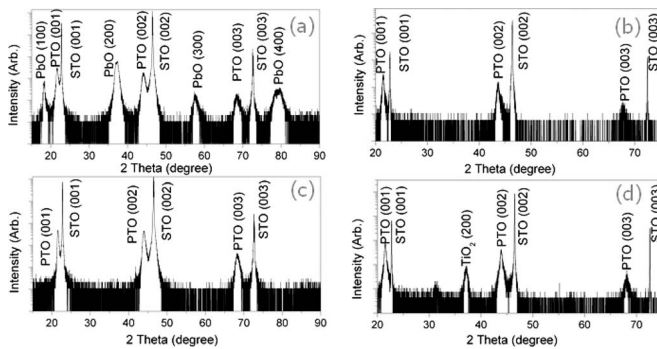


FIG. 1. XRD  $\theta$ - $2\theta$  scans of PTO/STO (a) as grown at 580 °C (b), as grown at 580 °C then annealed at 800 °C, (c) as grown at 600 °C with a growth rate of  $\sim 12$  nm/h, and (d) as grown at 600 °C with a growth rate of  $\sim 25$  nm/h.

thin film at this temperature. Although the undesirable PbO phase could be removed by *ex situ* annealing [Fig. 1(b)], a noticeable surface roughening makes this post-treatment process not so desirable compared to growing the sample above the critical temperature which automatically leads to stoichiometric PTO as seen in Fig. 1(c).

Figure 1(d) shows the PTO layer grown at 600 °C but with increased growth rate by means of increasing the Ti flux. The Pb flux had to be also increased to maintain the same Pb/Ti ratio as we used for lower Ti flux. Unfortunately, the presence of unwanted TiO<sub>2</sub> phase was found besides the PTO phase by XRD. This observation is consistent with earlier reports which made mention of the TiO<sub>2</sub> impurity phase occurring with relatively higher temperature and/or lower ozone pressure.<sup>21</sup> A common account for these observations is the limitation of the available reactive oxygen. Basically, increasing the Pb flux alone is not able to form sufficient PbO in the matrix to maintain the stoichiometry of the thin film.

Another critical issue of PTO growth is that the material consists of three elements having very different vapor pressures. Relevant to growth, lead oxidation could be insufficient unless reactive oxygen species are supplied in abundance to facilitate reaction between Pb and oxygen and compensated for the loss of highly volatile PbO from the surface. Serendipitously, the volatile nature of Pb and PbO can be exploited for stoichiometry control. Doing so under appropriate growth temperatures would pave the way for the film to automatically incorporate just the precise amount of reactive species to maintain stoichiometric PTO, while the excess lead oxide is dispensed by evaporation. To achieve this growth regime, the “critical substrate temperature” must be determined and maintained during the entire growth as has been done in our experiments. However, the real situation is more complicated than just an adsorption control growth of PTO dominated by the vapor pressure of PbO, as proposed by Theis *et al.*<sup>21</sup> To study this systematically, a series of PTO and PbO samples were grown under the same conditions (Pb flux, H<sub>2</sub>O<sub>2</sub> pressure, and  $T_s=600$  °C). We found that the growth rate of PbO was higher than that of PTO by factor of  $\sim 5$ , while PTO contained no traces of PbO phase according to XRD data [shown in Fig. 1(d)]. This finding indicates that other mechanisms beyond the vapor pressure of PbO also play important roles. To provide more accurate description of the mechanism responsible for the self-adjusting growth, surface chemistry of PTO, that is,

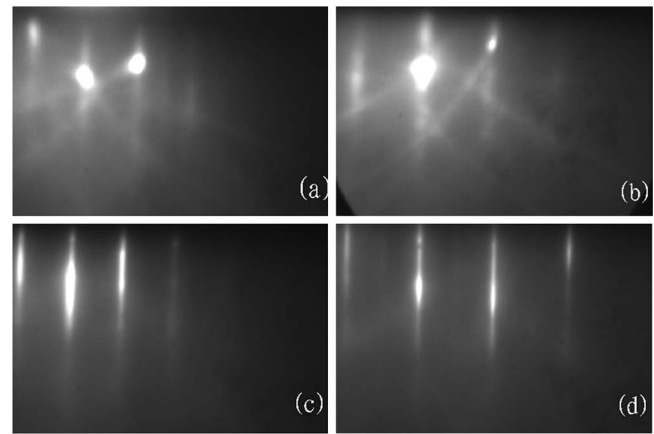


FIG. 2. RHEED patterns of (a) STO substrate along the [100] direction, (b) STO substrate along the [110] direction, (c) PTO epitaxial layer along the [100] direction, and (d) PTO epitaxial layer along the [110] direction.

absorption energies of Pb and PbO species on the PTO surface and dangling bond configuration, should be taken into consideration.

During the growth, RHEED was used for *in situ* monitoring of the growth progression. Figure 2 represents a set of RHEED patterns of a STO substrate and a 500-Å-thick PTO epitaxial layer grown at 600 °C taken along the [100] and [110] azimuths. The streaky pattern of the PTO [Figs. 2(c) and 2(d)] indicates growth of PTO film in the two-dimensional mode. Notice that a twofold surface reconstruction of the PTO film along the [110] direction was observed as well. The smoothness of the surface morphology is characterized by a root-mean-square value of 1.3–2 nm measured by AFM.

$\Phi$  scan of asymmetrical (101) reflection was performed for the STO substrate and PTO layer and fourfold rotation symmetry was observed [Fig. 3(a)], suggesting a PTO [100]/STO[100] and PTO(001)//STO(001) in-plane and out-of-plane epitaxial relationships, respectively. The crystalline quality of the PTO thin film was evaluated by XRD rocking curves, and the results are shown in Fig. 3(b). The full width at half maximum (FWHM) of PTO (001) is 15.9 arc min for a 25-nm-thick sample and reduces to 8.2 and 6.2 arc min for a 50-nm- and 65-nm-thick films, respectively. The value of 6.2 arc min is comparable to the best figures reported for PTO films grown by metal-organic chemical-vapor deposition<sup>23</sup> (MOCVD) and hydrothermal methods<sup>17</sup> with thickness of over 100 nm.

The out-of-plane  $c$  and  $a$  in-plane lattice constants of the PTO were deduced from the peak position for symmetrical (001) and asymmetrical (101) reflections, respectively, in  $\theta$ - $2\theta$  XRD patterns. For 40-nm-thick PTO film, we obtain  $c=4.11$  Å and  $a=3.92$  Å which represent the strained values. The out-of-plane and in-plane misfit strains were determined to be  $-1.11\%$  and  $0.41\%$ , respectively, using  $\varepsilon_{\perp}=(c-c_0)/c$  and  $\varepsilon_{\parallel}=(a-a_0)/a$ , where  $c_0=4.156$  Å and  $a_0=3.904$  Å are bulk values. This indicates that our PTO thin films are under in-plane tensile strain. Considering the small lattice mismatch of 0.1% between STO and PTO, we believe that the strain is contributed to a larger extent from thermal expansion rather than the lattice mismatch. Moreover, with increasing thickness, the  $c$  lattice constant of PTO tends to increase as well. For 65 nm layer we found that  $c$  is still smaller than the bulk value that indicates that the layer is not

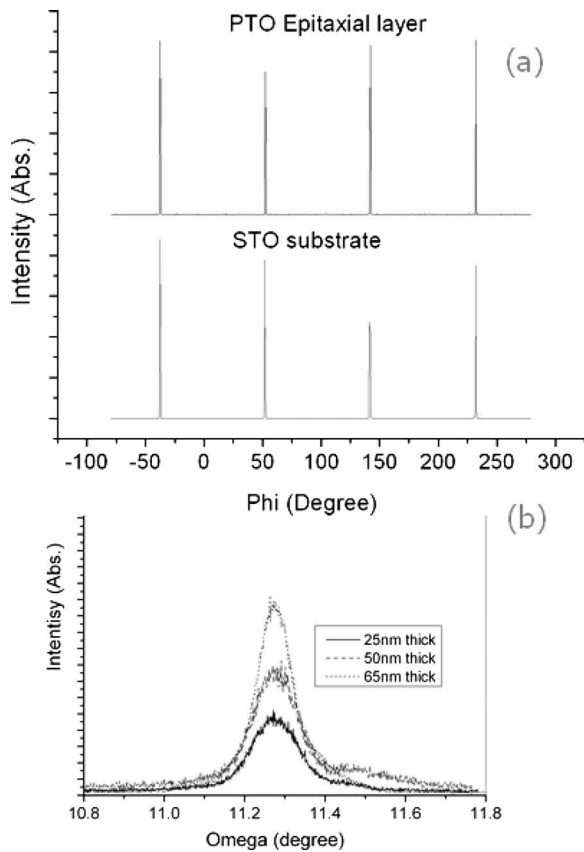


FIG. 3. (a)  $\Phi$  scan of asymmetrical (101) reflection for the STO substrate and PTO layer. (b) XRD rocking curve of PTO (001) with a thickness of 25 nm (solid line), 50 nm (dotted line), and 65 nm (dashed line).

yet fully relaxed. As demonstrated by Ohno *et al.*,<sup>24</sup> the volume change during transformation from the cubic phase to tetragonal phase affects the residual stress more than the difference in the thermal expansion coefficients between PTO and the substrates.

Optical properties of the PTO thin film have been characterized by VASE, which helped determine the dielectric function and the electronic band structure of PTO unambiguously. The refractive index is determined as 2.605 at 633 nm and is consistent with a previous report.<sup>25</sup> The energy band gap of PTO was determined as  $3.778 \pm 0.005$  eV by fitting the spectra of the second derivative of the PTO dielectric function using standard critical point (SCP) line shape analysis. Moret *et al.*<sup>25</sup> measured the dielectric function of MOCVD prepared PTO/STO by ellipsometry and reflectivity and estimated the band edge energy as  $3.6 \pm 0.1$  eV, which is

near the absorption edge. Our 3.778 eV value as determined by SCP model is therefore slightly larger and deemed to more accurately represent the band gap.

In summary, by employing  $\text{H}_2\text{O}_2$  as the reactive oxygen source, we attained high quality epitaxial growth of PTO (001) films on STO (001) substrates. The FWHM of the rocking curve of a 65 nm (001)  $\text{PbTiO}_3$  film is 6.2 arc min, indicating the high crystalline quality. The band gap of the PTO film is 3.778 eV, as determined by analyzing the spectroscopic ellipsometry data.

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