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Structural and electrical properties of Pb(Zr,Ti)O₃ films grown by molecular beam epitaxy

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Single-crystal, single-phase $Pb(Zr_xTi_{1-x})O_3$ films (x=0-0.4) were grown on (001) SrTiO₃ and SrTiO3:Nb substrates by molecular beam epitaxy. Layer-by-layer growth of the Pb(Zr, Ti)O₃ films was achieved by using PbTiO₃ buffer layers between the SrTiO₃ substrates and the Pb(Zr,Ti)O₃ films. The layers with low Zr content showed high crystallinity with full width at half maximum of ω -rocking curves as low as 4 arc min, whereas increase in Zr concentration led to pronounced angular broadening. The $PbZr_{0.07}Ti_{0.93}O_3$ films exhibited remanent polarization as high as 83 μ C/cm², but local areas suffered from nonuniform leakage current. © 2007 American Institute of Physics. [DOI: 10.1063/1.2804571]

Due to their attractive properties¹ such as large piezoelectric coefficient, electrical polarization, and electromechanical coupling factor, ferroelectric $Pb(Zr_rTi_{1-r})O_3$ (PZT) thin films are of considerable current interest for a wide range of applications, among which are the gate material for field effect transistor based ultrasonic and motion sensors, infrared detectors, surface acoustic wave devices, microactuators, ferroelectric field effect transistors, and nonvolatile ferroelectric random access memory devices, as well as a plethora of applications in nonlinear optics. To exploit the unique properties of PZT for device applications, highquality single-crystal films are required. Epitaxial PZT thin films have been prepared by various methods such as $sol-gel^{2,3}$ and hydrothermal^{4,5} techniques, metal-organic chemical vapor deposition,^{6,7} rf magnetron sputtering,^{8,9} and pulsed laser deposition.¹⁰ However, the growth of singlecrystal PZT films by molecular beam epitaxy (MBE), a modern technique providing high crystal perfection and precise control over material composition, has not been yet reported. In this letter, we report on the growth of high-quality singlecrystal PZT layers by peroxide MBE (the method developed previously for ZnO growth¹¹) and their structural and ferroelectric characteristics.

The PZT layers were grown on (001) SrTiO₃ substrates in a modified Riber 3200 MBE system. A 50% aqueous solution of hydrogen peroxide (H₂O₂) was employed as a source of reactive oxygen, while 99.999% pure Pb and 99.995% pure Ti were supplied from double-zone and hightemperature effusion cells, respectively. Due to the very low equilibrium pressure of metallic Zr, a metal-organic source of Zr was used. Zirconium tetra butoxide was chosen as the precursor, and 6N-purity Ar was used as the carrier gas. Before loading into the chamber, the SrTiO₃ substrates were etched in a buffered NH₄F-HF solution, rinsed in de-ionized water, and dried with nitrogen. The substrates were loaded into the air lock, followed by the growth chamber, and then heated to and kept at 600 °C for 20 min under a H₂O₂/H₂O vapor pressure of 1×10^{-5} Torr. PZT layers were grown at a H_2O_2/H_2O pressure of about 5×10^{-5} Torr, a substrate temperature of 600-625 °C, and a Pb-to-Ti flux ratio of >1. The thicknesses of the layers measured with an Alpha-step 250 profilometer were in the range of 40-80 nm. The PZT film composition was determined by Rutherford backscattering spectroscopy (RBS).

The growth process was monitored in situ by reflection high-energy electron diffraction (RHEED). Spotty RHEED patterns were observed for PZT films at the beginning of the growth on SrTiO₃ due to a three-dimensional (3D) growth mode, leading to rough surface morphology. The spotty RHEED patterns of the PZT films became progressively worse with further deposition, with the spots transforming into short arcs as an indicative of textured polycrystalline films. To overcome this problem, a PbTiO₃ buffer layer was introduced between the SrTiO₃ substrate and the PZT film. As a result, PZT layers grown on PbTiO₃/SrTiO₃ templates showed streaky RHEED patterns, characteristic of twodimensional (2D) growth and smooth film surfaces. The PbTiO₃ buffer worked well for PZT layers with low Zr concentration (up to $\sim 10\%$), but PZT films with higher Zr content (up to $\sim 40\%$ Zr) showed more complex behavior. Initially, 2D RHEED patterns were observed, which switched to 3D patterns as growth progressed, then returning to 2D patterns, as illustrated in Fig. 1. The higher the Zr content was, the earlier the 2D-3D transition started and the more pronounced the 3D pattern was. The MBE growth and characterization of the ternary compounds PbTiO₃ and PbZrO₃ are described in more detail elsewhere.^{12,13}

Phase composition and structural properties of the films were determined by x-ray diffraction (XRD) and RBS. XRD studies revealed that the PZT films were single-phase and c-axis oriented. Figure 2 presents a ω -2 θ scan of a PZT/PbTiO₃/SrTiO₃ structure. Only the (00*l*) reflections of the substrate and the layers are visible. However, (h00) reflections of tetragonal PZT with low Zr content should vir-

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FIG. 1. RHEED pattern evolution during MBE growth of $Pb(Zr_{0.3}T_{0.7})O_3$ film on $SrTiO_3$ substrate with $PbTiO_3$ buffer layer.

tually coincide with (00l) reflections from the SrTiO₃ substrate. Therefore, to detect *a*-axis-oriented regions (*a* domains) possibly present in the films, rocking curves (ω scan) were measured at the 2θ angle corresponding to $PbTiO_3(100)$ reflection overlapping with the $SrTiO_3(001)$ reflection.^{14,15} Only the diffraction peak corresponding to the substrate was observed, and no evidence of a domains was found. XRD and RHEED data indicated that the PZT layers exhibited the epitaxial relationship $PZT(100) \parallel SrTiO_3(100)$ and PZT[001]||SrTiO₃[001]. The measured full width at half maximum of (001) ω -rocking curve for an 80-nm-thick PbZr_{0.07}Ti_{0.93}O₃ film was as low as 4 arc min, as compared to 2.3 arc min for the substrate, indicative of the high crystal quality of the epitaxial layer. However, increase in Zr content resulted in broadening of the XRD rocking curves up to 24 arc min for a PbZr_{0.4}Ti_{0.6}O₃ film. The out-of-plane and in-plane lattice parameters calculated from the 2θ positions of symmetrical (001) and asymmetrical (101) XRD reflections were a=3.93 Å and c=4.19 Å for PbZr_{0.4}Ti_{0.6}O₃ and a=3.88 Å and c=4.17 Å for PZT layers containing 7% Zr. The c/a ratio decreases slightly from 1.075 to 1.066 as the Zr content increases from 7% to 40%. The values of the c/aratio for our films are higher than those for PZT bulk ceram-



FIG. 3. Cross-sectional electron micrograph of $Pb(Zr_{0.07}T_{0.93})O_3$ film grown on PbTiO₃ buffer layer on SrTiO₃ substrate.

ics of the same compositions (1.057 and 1.035 for 7% and 40% Zr, respectively¹⁶), which is indicative of biaxial compressive strain in the films. It is interesting to note that the *a* parameter for the PbZr_{0.07}Ti_{0.93}O₃ layers is very close to the bulk *a* parameter for PbTiO₃, suggesting that the PbZr_{0.07}Ti_{0.93}O₃ films are pseudomorphic to the PbTiO₃ buffer layers.

The film microstructure was further examined by transmission electron microscopy (TEM). Figure 3 shows a cross-sectional electron micrograph of a $PbZr_{0.07}Ti_{0.93}O_3/PbTiO_3/SrTiO_3$ structure. Misfit dislocations are visible at the $PbTiO_3/SrTiO_3$ interface, but there is no distinct boundary between the $PbTiO_3$ buffer and the PZT layer, confirming that the $PbZr_{0.07}Ti_{0.93}O_3/PbTiO_3$ bilayer structure had partially relaxed as a whole by introduction of the misfit dislocations at the $PbTiO_3/SrTiO_3$ interface. It should also be mentioned that no *a* domains were visible in the electron micrographs, in agreement with the XRD data.

The PZT films were also grown on conductive, Nbdoped SrTiO₃ substrates in order to examine their ferroelectric properties. Au/Pt top electrodes of 30 nm/30 nm in thickness and 300 μ m in diameter were deposited by e-beam evaporation. Polarization versus applied electric field (P-E)characteristics were measured at room temperature with a Radiant Technologies Precision LC ferroelectric test system. Figure 4 shows the *P*-*E* hysteresis loop for a 70-nm-thick PbZr_{0.07}Ti_{0.93}O₃ film grown on a thin (6 nm) PbTiO₃ buffer layer. The remanent polarization is 83 μ C/cm², and the coercive field is 77 kV/cm. It should be mentioned, however, that current-voltage characteristics of the PZT films suffered from high leakage current (from 10^{-4} to 10^{-2} A/cm² for an applied bias of 2 V), which resulted in distortion of the hysteresis loop at high fields. High leakage currents have been reported previously for PZT layers with low Zr content (be-





This a FIG. 2. XRD ω -2 θ scan for 60-nm-thick Pb(Zr_{0.07}T_{0.93})O₃ film grown on sub FIG. 4. *P*-*E* hysteresis curve measured for 70-nm-thick Pb(Zr_{0.07}T_{0.93})O₃ to IP PbTiO₃ buffer layer on SrTiO₃ substrate. 128 172.48 59 On: Wed. film.



FIG. 5. $3 \times 3 \ \mu m^2$ C-AFM image for Pb(Zr_{0.07}T_{0.93})O₃ film recorded at a bias voltage of -2 V; Δz =4 pA and a mean of -1 pA.

low 30%) by Foster *et al.*,¹⁷ although the source of the high leakage was unclear.

To shed some light on the origin of the electrical leakage in our layers, conductive atomic force microscopy (C-AFM) studies were performed. Figure 5 shows typical C-AFM scan for PbZr_{0.07}Ti_{0.93}O₃. The darker tone of the image corresponds to higher current. A nonuniform distribution of electrical current over the sample surface is apparent. Most of the sample surface exhibits current values below the detection limit of our apparatus (~ 1 pA), but some local areas are highly leaky. Such a distribution of current allows us to assume that structural defects might be responsible for high leakage in the PZT film. These defects could originate from the SrTiO₃:Nb substrates, which are known to have inferior crystal quality compared to undoped SrTiO₃ substrates. However, second-phase inclusions, such as lead oxide, cannot be ruled out. Further TEM investigation of PZT films grown on conductive substrates is necessary to clarify this issue.

In conclusion, single-crystal, single-phase PZT films were grown on (001) SrTiO₃ substrates by peroxide MBE. The use of PbTiO₃ buffer layer resulted in layer-by-layer growth of epitaxial PZT films. A nearly square-shaped P-E

hysteresis loop was observed for a 70-nm-thick PbZr_{0.07}Ti_{0.93}O₃ film with a remanent polarization of 83 μ C/cm². Nonuniform distribution of leakage current across the films was found by conductive AFM. Defects penetrating from the SrTiO₃:Nb substrate and/or second-phase inclusions are presumably responsible for the electrical leakage.

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