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Structural and electrical properties of Pb(Zr,Ti)O₃ grown on (0001) GaN using a double PbTiO₃/PbO bridge layer

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Pb(Zr_{0.52}Ti_{0.48})O₃ films were deposited by rf magnetron sputtering on silicon-doped GaN(0001)/c-sapphire with a PbTiO₃/PbO oxide bridge layer grown by molecular beam epitaxy. X-ray diffraction data showed the highly (111)-oriented perovskite phase in lead zirconate titanate (PZT) films with PbTiO₃/PbO bridge layers, compared to the pyrochlore phase grown directly on GaN. The in-plane epitaxial relationships were found from x-ray pole figures to be PZT[11 $\bar{2}$] \parallel GaN[1 $\bar{1}$ 00] and PZT[1 $\bar{1}$ 0] \parallel GaN[11 $\bar{2}$ 0]. The polarization-electric field measurements revealed the ferroelectric behavior with remanent polarization of 30–40 $\mu\text{C}/\text{cm}^2$ and asymmetric hysteresis loops due to the depletion layer formed in GaN under reverse bias which resulted in a high negative coercive electric field (950 kV/cm). © 2007 American Institute of Physics. [DOI: 10.1063/1.2805220]

Lead zirconate titanate (PZT) has been extensively studied for many decades owing to its outstanding ferroelectric, piezoelectric, pyroelectric, and electro-optical properties offering great promise for various applications. In recent years, a renewed interest arose in the context of integration of PZT with semiconductor materials such as gallium nitride for device development. The emergence of this concept is in part due to the properties possessed by GaN such as high thermal and mechanical stabilities, breakdown voltage, and electron saturation velocity. Therefore, the combination of attractive properties of these two material systems could potentially form the basis for novel or new generation devices. Studies on the PZT/GaN system have been explored with respect to ferroelectric field effect transistors,^{1,2} ferroelectric gate on AlGaIn/GaN two-dimensional gas,^{3,4} rf devices,⁵ and electro-optic devices.^{6,7}

Despite the above reports, the integration of PZT with GaN is yet to receive much recognition due in part to the low quality of PZT films on GaN. Different crystalline structures forming the aforementioned composite (perovskite PZT versus wurtzite GaN) including a large lattice mismatch of PZT and GaN appear to hamper the pace of progress. Although postdeposition annealing is commonly used to facilitate the formation of perovskite PZT films, afforded by the high thermal and chemical stabilities of GaN, diffusions of Pb and Ti into GaN (Ref. 7) and cracking of PZT films because of the large lattice mismatch, act adversely and restrict the parameters of high-temperature annealing. Therefore, it is imperative to incorporate a bridge layer (as a nucleation or seed layer) between PZT and GaN, which can promote the crystallization of the perovskite-phase PZT films. Fuflyigin *et al.*⁸ reported the growth of highly (110)-oriented films by employing indium tin oxide for (Pb,La)(Ti,Zr)O₃ (PLZT) films on *n*-GaN/*c*-sapphire structures and Masuda *et al.*⁶ used MgO for Pb(Zr,Ti)O₃ on cubic GaN/GaAs structures to grow preferentially (100)-oriented PZT films. In this letter, we report on the growth of highly (111)-oriented PZT films

on GaN(0001)/*c*-sapphire by employing of a double PbTiO₃/PbO bridge layer.

2- μm -thick Si-doped GaN (0001) templates were prepared for PZT growth by metal-organic chemical-vapor deposition (MOCVD) on *c*-plane sapphire substrates. These conductive *n*-type GaN layers also served as the bottom electrode for the electrical characterization of PZT films. The carrier concentration and sheet resistance of the GaN templates were $2 \times 10^{18} \text{ cm}^{-3}$ and $300 \Omega/\square$, respectively.

As the first step, the PbTiO₃/PbO bilayer buffers were grown by peroxide molecular beam epitaxy (MBE) in a modified Riber 3200 system using a 50% aqueous solution of hydrogen peroxide (H₂O₂) as the source of reactive oxygen. More details of our MBE system as well as the growth technique of PbTiO₃ have been reported elsewhere.⁹ Lead oxide (PbO) was epitaxially grown on GaN as the first layer¹⁰ followed by the PbTiO₃ deposition. Both PbO and PbTiO₃ layers were grown under a H₂O₂/H₂O vapor pressure of 5×10^{-5} Torr and in a substrate temperature range of 580–600 °C. The thickness of PbO and PbTiO₃ thin films were approximately 2–3 and 10 nm, respectively. Reflection high-energy electron diffraction (RHEED) was used to monitor the growth of PbO and PbTiO₃ *in situ* which clearly indicated the RHEED pattern evolution from GaN to PbO and PbTiO₃. As illustrated in Figs. 1(c) and 1(d), the streaky patterns along the [1 $\bar{1}$ 00] and [11 $\bar{2}$ 0] azimuths of GaN signify the two-dimensional growth mode of the PbO film. For the following PbTiO₃ growth, the RHEED patterns partially transformed into three-dimensional one and showed twofold surface reconstructions along the both azimuths of GaN [see Figs. 1(e) and 1(f)]. The RHEED patterns of both PbO and PbTiO₃ repeated every 60° of substrate rotation. This behavior is inconsistent with the symmetries of bulk PbO and PbTiO₃ (cubic and tetragonal, respectively) and may suggest the formation of 60° domains or the pseudomorphous growth in the hexagonal structure.

The GaN templates with PbTiO₃/PbO bridge layers were then transferred into the sputtering growth chamber for PZT deposition. PZT films with composition at the morpho-

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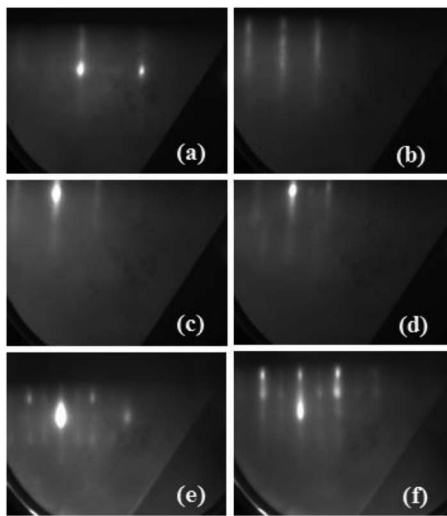


FIG. 1. RHEED patterns of PbO and PbTiO₃ grown on GaN: (a) GaN [1 $\bar{1}$ 00], (b) GaN [11 $\bar{2}$ 0], (c) PbO parallel to GaN [1 $\bar{1}$ 00], (d) PbO parallel to GaN [11 $\bar{2}$ 0], (e) PbTiO₃ parallel to GaN [1 $\bar{1}$ 00], and (f) PbTiO₃ parallel to GaN [11 $\bar{2}$ 0].

tropic phase boundary (MPB), Zr:Ti=52:48, were then deposited on the MBE grown PbTiO₃/PbO bridge layers by radio-frequency (rf) magnetron sputtering at about 600 °C using a 3-in.-diamater PZT target comprised of 10 mol % excess PbO to avoid Pb deficiency in the film. In addition, to avoid any possible PbTiO₃ decomposition,¹¹ the substrates with the MBE-grown bilayer buffer was kept at 6 mTorr pressure of oxygen gas during ramping up the temperature. For the growth of PZT films, the pressure of the 6:1 Ar/O₂ gas mixture was 2 mTorr. PZT films (300–400 nm) were deposited at 120 W rf power which yielded a growth rate of ~100 nm/h.

The crystalline structure and orientation of the as-deposited PbTiO₃/PbO and PZT films were determined by high resolution x-ray diffraction (XRD). A pure perovskite phase was observed in the PbTiO₃/PbO bridge layer, as shown in Fig. 2(a), corresponding to the PbTiO₃ (111) orientation. The 2θ angle of PbTiO₃ (111) reflection located at

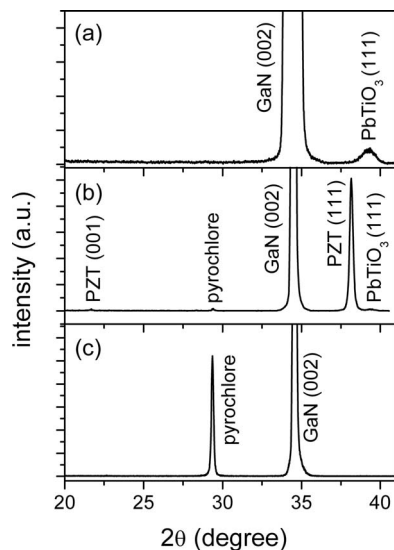


FIG. 2. X-ray diffraction patterns of (a) PbTiO₃/PbO/GaN, (b) PZT/PbTiO₃/PbO/GaN, and (c) PZT/GaN structures.

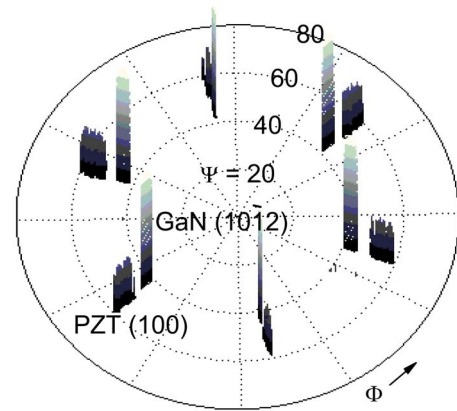


FIG. 3. XRD pole figure scan of Pb(Zr_{0.52}Ti_{0.48})O₃ on (0001) GaN with a double PbTiO₃/PbO bridge layer.

39.4°, which was close to the Bragg angle for the PbTiO₃ (39.17°) from the international center for diffraction data.¹² The XRD patterns of the as-grown PZT films deposited on the PbTiO₃/PbO layer are dominated by a peak at $2\theta=38.2^\circ$ which is consistent with the (111) reflection of a perovskite PZT with the MPB composition [see Fig 2(b)]. The peak position of this PZT (111) reflection is equal to the PZT data,¹³ which is corresponding to the d spacing of 2.35 Å. It is acceptable that the PZT with 300–400 nm thickness is strain relieved. Three additional weak peaks at 21.7°, 29.5°, and 39.4° can be indexed as being associated with PZT (001), pyrochlore, and PbTiO₃ (111), respectively. In contrast, PZT films directly grown on GaN without the PbTiO₃/PbO bridge layer did not show any perovskite phase reflection. Only a peak at 29.1° corresponding to the reflection of the pyrochlore phase was observed in the XRD patterns [see Fig. 2(c)]. Therefore, the XRD data strongly suggest that the PbTiO₃/PbO seed layer influences the orientation and crystal structure of PZT films and promotes heterogeneous PZT nucleation on GaN. Moreover, the (011) orientation of PZT reported for PZT/GaN structures^{8,14} has not been found in the PZT/PbTiO₃/PbO/GaN films. An XRD pole figure analysis was performed to investigate the in-plane epitaxial relationship between the PZT and GaN films. The reflection planes were GaN (10 $\bar{1}$ 2) and PZT (100) with the center Ψ angles of 43.2° and 54.5°, respectively. A sixfold symmetric reflection can be observed in Fig. 3 for PZT (100) with the same Φ angles as for GaN (10 $\bar{1}$ 2), which is in agreement with the RHEED data revealing the sixfold symmetry for the nucleation layers. These observations imply the existence of two sets of domains which are rotated by 60° with respect to each other. Therefore, the in-plane epitaxial relationships can be established as follows: PZT[11 $\bar{2}$] \parallel GaN[1 $\bar{1}$ 00] and PZT[1 $\bar{1}$ 0] \parallel GaN[11 $\bar{2}$ 0]. The same epitaxial relationships have been reported by Dey *et al.*¹⁵ for PZT films grown on GaN (0001) by MOCVD.

PZT/GaN capacitor structures were fabricated to characterize the electrical properties of the PZT films, the schematic diagram for which is illustrated as an inset in Fig. 4. Au/Cr circular top electrodes of 30/30 nm in thickness and 150 μm in diameter were defined on the PZT layer by successive use of photolithography, e-beam evaporation, and lift-off. Current-voltage measurements of the PZT films showed leakage current densities of 2×10^{-7} A/cm² at electric fields of 200 kV/cm and 1×10^{-5} A/cm² at 500 kV/cm.

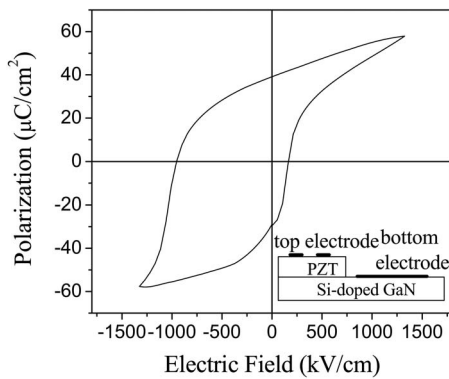


FIG. 4. P - E hysteresis loop of $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$ on Si-doped GaN.

The ferroelectric properties of the PZT films were examined by polarization–electric field (P - E) measurements at a frequency of 1 kHz with the top electrode connected to the driving voltage. Figure 4 shows a P - E curve for the PZT/PbTiO₃/PbO/GaN structure with large values of remanent polarizations, $+P_r = \sim 40 \mu\text{C}/\text{cm}^2$ and $-P_r = \sim 30 \mu\text{C}/\text{cm}^2$. The polarization switched abruptly near the coercive fields and the associated steep slopes further indicate the formation of highly oriented perovskite PZT films on GaN. In addition, it can be seen clearly that the hysteresis loop is asymmetric due to the dissimilar electrodes, especially for the polarization saturation area. The asymmetric hysteresis loop has an extraordinarily high coercive field of 950 kV/cm under reverse bias, whereas the positive coercive field is only 165 kV/cm. Asymmetry of P - E curves has also been reported previously for PLZT/GaN (Ref. 8) and PZT/SiO₂/Si (Ref. 16) structures. The observed asymmetry can be explained using an approach analogous to a metal-insulator-semiconductor structure. Ideally, neglecting any work function differences, the applied voltage will be shared by the insulator and the semiconductor. When the top electrode is connected to the positive terminal of the driving voltage, an accumulation of electrons occurs in the n -type GaN layer. As a result the total voltage appears mainly across the PZT layer. However, for the negative driving voltage, a depletion region is formed in series with the PZT layer near the GaN surface and the voltage drop occurs across both the PZT and the depletion layer. Consequently, the P - E curve becomes asymmetric which manifests itself as a relatively larger coercive field under reverse bias as compared to forward bias.

In summary, PZT thin films have been deposited on Si doped GaN (0001)/ c -sapphires substrates by rf magnetron sputtering. The use of a double PbTiO₃/PbO bridge layer grown by MBE prior to PZT deposition paved the way to achieve highly (111)-oriented PZT films on GaN (0001). A sixfold symmetry of PZT on GaN (0001) suggesting the presence of 60° rotation domains was observed by XRD pole figure analysis. The (100) reflection planes appeared at the same Φ angles as the (10 $\bar{1}2$) reflections for GaN, which indicates an in-plane epitaxial relationship with PZT $[11\bar{2}]\parallel\text{GaN} [1\bar{1}00]$ and PZT $[1\bar{1}0]\parallel\text{GaN} [11\bar{2}0]$. Ferroelectric characterization clearly exhibited the abrupt switching of polarization near the coercive fields with large values of remanent polarization with $+P_r = \sim 40 \mu\text{C}/\text{cm}^2$ and $-P_r = \sim 30 \mu\text{C}/\text{cm}^2$. The leakage current densities were $2 \times 10^{-7} \text{ A}/\text{cm}^2$ at electric fields of 200 kV/cm and $1 \times 10^{-5} \text{ A}/\text{cm}^2$ at 500 kV/cm.

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