June 2004

Investigation of $Pb(Zr,Ti)O_3$ /GaN heterostructures by scanning probe microscopy

Alexei Gruverman
University of Nebraska-Lincoln, agruverman2@unl.edu

W. Cao
Arizona State University, Tempe, Arizona

S. Bhaskar
Arizona State University, Tempe, Arizona

S. K. Dey
Arizona State University, Tempe, Arizona

Investigation of $Pb(Zr,Ti)O_3/GaN$ heterostructures by scanning probe microscopy

A. Gruverman[a)]
Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7920

W. Cao, S. Bhaskar, and S. K. Dey
Department of Chemical and Materials Engineering, & Electrical Engineering, Arizona State University, Tempe, Arizona 85287-6006

(Received 8 December 2003; accepted 1 May 2004; published online 4 June 2004)

Piezoresponse force microscopy (PFM) technique has been utilized to study the evolution of domain structure with varying $Pb(Zr,Ti)O_3$(PZT) thickness on GaN substrate. Sol-gel PZT films were deposited on the GaN/sapphire substrate with PZT thickness of 100, 200, and 300 nm. The films exhibit ferroelectric properties that vary as a function of the film thickness. This is explained by the mechanical stress at the PZT/GaN interface. The thicker film (300 nm) is characterized by the presence of a number of oppositely polarized domains and a relatively high value of the effective piezoelectric constant. The laminar domain structure, consisting of 90° and 180° domains, has been revealed in the thinner (200 nm) PZT film. Both films show clear ferroelectric switching behavior, which is in contrast to the thinnest film (100 nm), where no switching has been observed due to mostly in-plane polarization orientation. The observed results indicate the utility of the PFM technique for characterization of the electronic properties of the PZT/GaN heterostructures. *© 2004 American Institute of Physics*. [DOI: 10.1063/1.1765740]

Over the last decade, considerable research efforts have focused on integrating insulating ferroelectric materials on Si semiconductors. A major driving force behind these efforts is the development of a new generation of nonvolatile memory devices, which employ integrated ferroelectric thin films.[1–3] Moreover, ferroelectric-semiconductor heterostructures have the potential for use in integrated optoelectronic, piezoelectric, and microwave devices.[4,5] The complexity of integration, however, generally stems from the difference in deposition methods, etching conditions, and postdeposition annealing treatments required for ferroelectric films and other elements of the devices. The relatively high processing temperature, necessary for most technologically relevant ferroelectric films, leads to chemical reactions and structural changes at the ferroelectric–Si interfaces. Therefore, molecular beam epitaxy, chemical vapor deposition, and sol-gel processing coupled with the use of buffer layers or direct wafer bonding have been used to overcome these problems and to produce high quality ferroelectric films on Si.[6–9] Recently, perovskite ferroelectric films have been successfully grown on semiconductor GaN surfaces.[10] The high chemical and mechanical stability, high thermal conductivity and breakdown voltage of GaN makes it suitable for field effect transistors in high power and high frequency devices.

The integration of ferroelectric materials with Group III-nitrides can lead to electronic devices that will exploit the advantageous properties of both groups of materials.[11,12] Therefore, future progress in the practical use of ferroelectric-semiconductor heterostructures is contingent on our ability to perform high-resolution characterization of the electrical and dielectric response of these heterostructures. This letter reports on the characterization of $Pb(Zr,Ti)O_3$ (PZT) films on GaN surface by means of scanning probe microscopy.

The epitaxial Ga-terminated (0001) GaN films (~1 μm) were grown, as low-temperature buffer layer at 530 °C and high-temperature layer at 1120 °C, on *c*-plane sapphire substrates using an Aixtron HT2000 reactor. The III–V nitride semiconductors grown in the (0001) direction have the hexagonal wurtzite crystal structure, which allows the existence of piezoelectricity and spontaneous polarization. Additionally, the GaN was Si-doped ($\sim 10^{17}$ cm^3) and exhibited a resistivity of 0.0169 Ω/cm. The $Pb(Zr_{0.3}Ti_{0.7})O_3$ thin films were deposited on the GaN/sapphire substrate by the sol-gel technique as described in detail elsewhere.[13] The precursors used were lead acetate, $Pb(OAc)_2 3H_2O$, titanium isopropoxide, $Ti(O-Pr-^{i})_4$, and zirconium *n*-propoxide, $Zr(O-Pr-^{n})_4$. The spun-on PZT films were crystallized using rapid thermal annealing at 700 °C for 5 min in oxygen. The composition of the films that was studied by Rutherford backscattering spectrometry showed the intended stoichiometry.[12,13] The crystal structure and orientation of PZT and GaN films were examined by x-ray diffraction (XRD) using a Rigaku D/Max-IIB diffractometer. The XRD results (Fig. 1) indicate a phase-pure partially textured PZT on (0001) GaN. Note the tetragonal splitting and absence of the pyrochlore peak (at ~29°). Specifically, the PZT films were partially textured along (111) and (100) directions in comparison to the 100% (110) PZT peak from JCPDS powder data. The calculated lattice parameters (a=3.974 Å and c=4.121 Å) from the diffraction pattern of the tetragonal PZT(30/70) film match well with previously published data.[14] For the current study, three PZT samples with thickness of 100, 200, and 300 nm were prepared.

The PZT/GaN heterostructures have been characterized by piezoresponse force microscopy (PFM)—one of the scan-

[a)]Electronic mail: alexei_gruverman@ncsu.edu

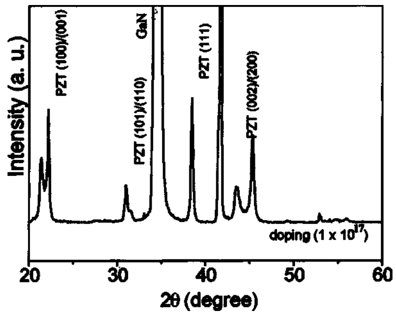

FIG. 1. x-ray diffraction patterns of PZT films (300 nm) on GaN/sapphire annealed at 700 °C.

ning probe microscopy-based methods developed for high-resolution visualization of domain structures in ferroelectric thin films.[14–21] In PFM, a modulation voltage is applied to a sample via a conductive probing tip, which, being in mechanical contact with the sample, accurately follows the displacement of the sample surface resulting from the converse piezoelectric effect. The amplitude of the tip vibration provides information on the piezoelectric strain, from which the effective piezoelectric coefficient can be determined. The polarity distribution in the ferroelectric film can be determined based on the dependence of the sign of the piezoelectric coefficient on the polarization direction, i.e., the oscillation of the film is either in-phase or out-of-phase with the modulation voltage. In a conventional, i.e., vertical mode of PFM, which detects only vertical surface displacement, antiparallel *c*-domains with out-of-plane polarization exhibit black–white contrast. In the case of the domain structure that includes both *c*-domains and domains with in-plane polarization (*a*-domains) contrast may vary as black/gray or white/gray.

The PZT/GaN heterostructures have been analyzed using a commercial force microscope Autoprobe M5 (Park Scientific Instruments). A conductive Pt-coated Si cantilever with a spring constant of 2.1 N/m and a resonant frequency of 34 kHz was used both for domain imaging and for local strain hysteresis loop measurements. The sample surfaces have been scanned with an oscillating tip bias of 1.5 V_{rms} at 10 kHz. The hysteresis loop measurements were performed by positioning the probing tip at a selected point and by measuring the local PFM signal as a function of a dc voltage superimposed on the imaging tip bias.[16]

An inspection of the PZT surface morphology with the force microscope reveals the film microstructure, comprised of large plate-like grains. As illustrated in Fig. 2, the grain size decreases with increase in the PZT layer thickness. In the 100-nm-thick PZT, the grain sizes vary from 2 to 6 μm, whereas the average grain size in the 300-nm-thick PZT is less than 2 μm.

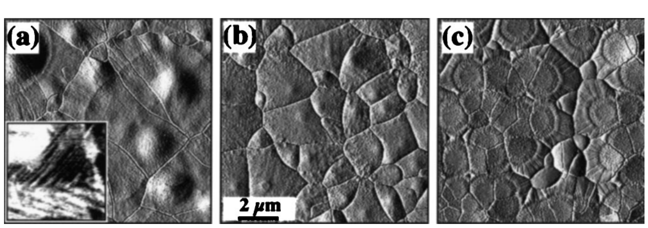

FIG. 2. Topographic images of the PZT films on GaN/sapphire. PZT layer thickness: (a) 100 nm; (b) 200 nm; (c) 300 nm. Inset in (a) shows a lateral PFM image of the 100 nm PZT film. The inset size is 2×2 μm^2.

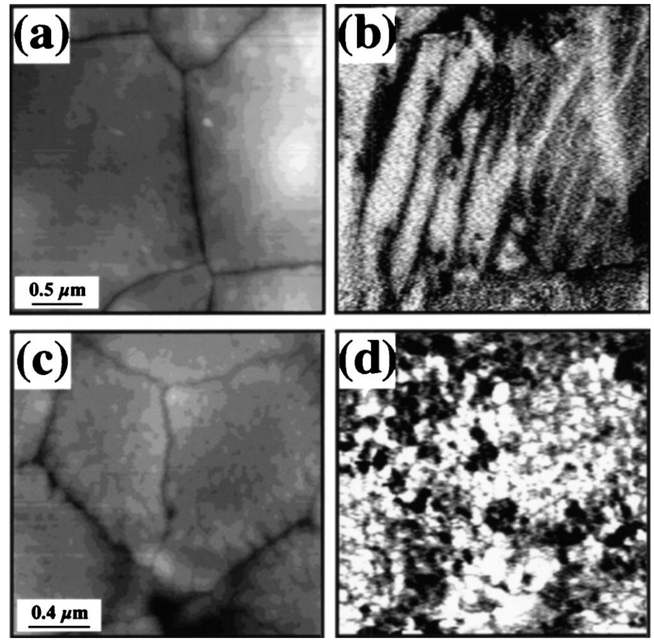

FIG. 3. Topographic (left) and vertical PFM (right) images of the 200-nm-thick (a), (b) and 300-nm-thick (c), (d) PZT films.

It has been found that the 100-nm-thick PZT film does not exhibit any vertical PFM domain contrast. PFM imaging of the 200-nm-thick PZT film reveals a characteristic laminar structure, typical for a domain arrangement consisting of 90° and 180° domains [Figs. 3(a) and 3(b)]. The periodicity of domains varies in the range from 40 to 300 nm suggesting the inhomogeneous stress distribution from grain to grain. In the 300-nm-thick PZT film, the domain arrangement is dramatically different [Figs. 3(c) and 3(d)]: it consists of a number of opposite 180° domains, which are about 120–150 nm in size. The thicker PZT films are also characterized by the higher values of the effective piezoelectric coefficients. For 300- and 200-nm-thick films, the coefficients are estimated to be 8 and 5 pm/V, respectively. In contrast, for the 100-nm-thick PZT film, it was just about 2 pm/V, which is close to the piezoelectric coefficient of GaN.

The observed results can be explained by bi-axial tensile stress due to the lattice mismatch between PZT and GaN layers. It can be assumed that in the thinnest PZT film (100 nm) tensile stress leads to the mostly in-plane orientation of polarization that is not detectable in conventional (vertical) PFM. To clarify this problem we examined this film by using lateral PFM[16,21] sensitive to the in-plane polarization. Indeed, this examination revealed a clear domain contrast typical for *a–a* domain pattern [inset to Fig. 2(a)]. Furthermore, no switching behavior has been observed thus supporting the assumption of the in-plane oriented polarization in the 100 nm PZT film. In the thicker 200 nm film, the interfacial stress is relieved via the formation of the domain structure consisting of *a*- and *c*-domains. As the stress effect decreases with the film thickness, the thickest film (300 nm) is less constrained and the PZT/GaN system appears to find the energy minimum in a ferroelectric pattern, consisting of small antiparallel 180° domains. A higher density of grain boundaries that serve as stress release centers might also help the formation of such domain pattern.

The local strain hysteresis loop measurements show that thicker PZT films exhibit a distinct ferroelectric switching

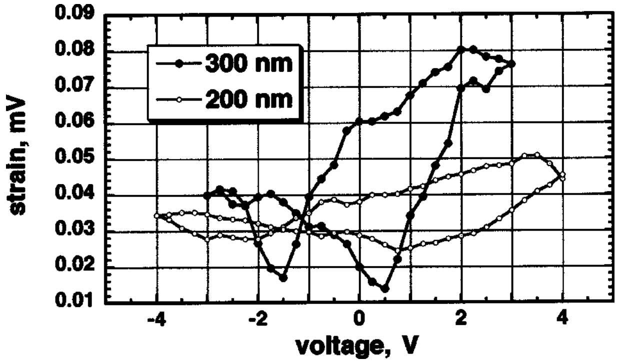

FIG. 4. Local piezoelectric hysteresis loops measured in PZT/GaN heterostructures (for PZT thickness of 200 and 300 nm).

behavior (Fig. 4). Note the asymmetric character of the measured hysteresis loops, which is due to the asymmetry of the boundary conditions at the top and bottom interfaces. This is consistent with the previously measured low polarization values in Pt/PZT/GaN (metal-ferroelectric-semiconductor) structure, which are correlated to the various charge densities and the resulting spatial distribution of the electric field.[11,12] In addition, the piezoelectric effect in GaN itself might affect the electron sheet concentration in the interface PZT/GaN regions thus contributing to the asymmetry of the switching behavior of the PZT/GaN heterostructures.

In summary, the sol-gel PZT films deposited on the GaN/sapphire substrate have been characterized by PFM. The films exhibit ferroelectric properties that vary as a function of the film thickness. This effect is explained by the mechanical stress at the PZT/GaN interface. The thicker film (300 nm) is characterized by the presence of a number of oppositely polarized domains and a relatively high value of the effective piezoelectric constant. The laminar domain structure, typical for a ferroelectric containing *a*- and *c*-domains, has been revealed in the thinner (200 nm) PZT film. Both films show clear ferroelectric switching behavior, which is in contrast to the thinnest film (100 nm), where no switching has been observed due to the mostly in-plane orientation of polarization. The observed results indicate the utility of the PFM technique for characterization of the electronic properties of the PZT/GaN heterostructures.

The work at NCSU has been supported by the National Science Foundation (Grant No. DMR-0235632). Technical assistance of Dr. B. J. Rodriguez is greatly appreciated. S.K.D. gratefully acknowledges the support of a DARPA-sponsored consortium on RF nanoMEMS devices (Contract No. 1236318-004), and the provision of GaN/sapphire wafers by M. A. Khan, G. Simin, and J. Yang of the University of South Carolina.

[1]J. F. Scott and C. A. Araujo, Science **246**, 1400 (1989).
[2]O. Auciello, J. F. Scott, and R. Ramesh, Phys. Today **51**, 22 (1998).
[3]S. L. Miller and P. J. McWhorter, J. Appl. Phys. **72**, 5999 (1992).
[4]T. Ueda, A. Noma, and D. Ueda, Integr. Ferroelectr. **7**, 45 (1995).
[5]Y. Xu, C. J. Chen, R. Xu, and J. D. Mackenzie, Phys. Rev. B **44**, 35 (1991).
[6]K. Aizawa, H. Ishiwara, and M. Kumagai, Appl. Phys. Lett. **63**, 1765 (1993).
[7]Y. Xu, C. J. Chen, R. Xu, and J. D. Mackenzie, J. Appl. Phys. **67**, 2985 (1990).
[8]Y. Fujisaki, T. Kijima, and H. Ishiwara, Appl. Phys. Lett. **78**, 1285 (2001).
[9]M. Alexe, G. Kastner, D. Hesse, and U. Gosele, Appl. Phys. Lett. **70**, 3416 (1997).
[10]F. Wang, V. Fuflyigin, and A. Osinsky, J. Appl. Phys. **88**, 1701 (2000).
[11]S. K. Dey, S. Bhaskar, M.-H. Tsai, and W. Cao, presented at the Tenth European Meeting on Ferroelectricity, EMF 2003, Cambridge, UK.
[12]S. K. Dey, S. Bhaskar, M.-H. Tsai, and W. Cao, Appl. Phys. Lett. (submitted).
[13]S. K. Dey, in *Ferroelectric Thin Films: Synthesis and Basic Properties*, edited by C. P. Araujo, J. F. Scott, and G. W. Taylor (Gordon and Breach, Amsterdam, 1996).
[14]A. Gruverman, O. Auciello, and H. Tokumoto, Annu. Rev. Mater. Sci. **28**, 101 (1998).
[15]T. Hidaka, T. Maruyama, I. Sakai, M. Saitoh, L. A. Wills, R. Hiskes, S. A. Dicarolis, and J. Amano, Integr. Ferroelectr. **17**, 319 (1997).
[16]B. J. Rodriguez, A. Gruverman, A. I. Kingon, R. J. Nemanich, and J. S. Cross, J. Appl. Phys. **95**, 1958 (2004).
[17]S. Hong, E. L. Colla, E. Kim, D. V. Taylor, A. K. Tagantsev, P. Muralt, K. No, and N. Setter, J. Appl. Phys. **86**, 607 (1999).
[18]K. Franke, J. Besold, W. Haessle, and C. Seegebarth, Surf. Sci. Lett. **302**, L283 (1994).
[19]C. S. Ganpule, A. L. Roytburd, V. Nagarajan, B. K. Hill, S. B. Ogale, E. D. Williams, R. Ramesh, and J. F. Scott, Phys. Rev. B **65**, 014101 (2002).
[20]S. V. Kalinin and D. A. Bonnell, Phys. Rev. B **65**, 125408 (2002).
[21]C. Harnagea, A. Pignolet, M. Alexe, and D. Hesse, Integr. Ferroelectr. **38**, 23 (2001).