



Posadas, A. and Yau, J.-B. and Ahn, C. H. and Han, J. and Gariglio, S. and Johnston, Karen and Rabe, K. M. and Neaton, J. B. (2005) Epitaxial growth of multiferroic YMnO₃ on GaN. Applied Physics Letters, 87. ISSN 0003-6951 , <http://dx.doi.org/10.1063/1.2120903>

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Citation: *Applied Physics Letters* **87**, 171915 (2005); doi: 10.1063/1.2120903

View online: <http://dx.doi.org/10.1063/1.2120903>

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Epitaxial growth of multiferroic YMnO₃ on GaN

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(Received 12 May 2005; accepted 6 September 2005; published online 21 October 2005)

In this work, we report on the epitaxial growth of multiferroic YMnO₃ on GaN. Both materials are hexagonal with a nominal lattice mismatch of 4%, yet x-ray diffraction reveals an unexpected 30° rotation between the unit cells of YMnO₃ and GaN that results in a much larger lattice mismatch (10%) compared to the unrotated case. Estimates based on first principles calculations show that the bonding energy gained from the rotated atomic arrangement compensates for the increase in strain energy due to the larger lattice mismatch. Understanding the energy competition between chemical bonding energy and strain energy provides insight into the heteroepitaxial growth mechanisms of complex oxide-semiconductor systems. © 2005 American Institute of Physics.

[DOI: [10.1063/1.2120903](https://doi.org/10.1063/1.2120903)]

The ubiquity of Si-based semiconductor devices today results in part from the ability to grow a high quality SiO₂ insulator to serve as the gate dielectric in field effect transistor applications. As various physical scaling limitations are approached, however, new high κ dielectric oxide materials are being explored to replace SiO₂. The concurrent development of similar, suitable dielectrics for III–V and wide band gap semiconductors is also being examined to enhance the functionality of these classes of semiconductors, as discussed by Doolittle and co-workers.¹

Here, we demonstrate the epitaxial growth of the complex oxide YMnO₃ on the wide band gap semiconductor GaN. Both YMnO₃ and GaN have hexagonal symmetry and have a nominal lattice mismatch of about 4% (to half the lattice constant of YMnO₃). We observe an unexpected 30° rotation between the two unit cells, resulting in a much larger lattice mismatch of ~10%. A similar 30° rotation between unit cells is also observed for GaN grown on *c*-plane sapphire.² In the case of GaN on sapphire, chemical bonding considerations drive the in-plane rotation. In the case of YMnO₃ on GaN, though, such a rotation results in a large increase in strain, leaving the possibility that YMnO₃ on GaN could grow unrotated. To understand the observed epitaxial relationship between YMnO₃ and GaN, we have carried out first principles calculations of the elastic energy of highly strained YMnO₃. Because the relative stability of the first 1–2 layers determines the orientation of subsequent layers, we focus our calculations on the first unit cell at the interface. These calculations show that a large energy stabilization from bonding at the interface must overcome the

elastic energy cost to result in the 30° rotation.

One potential advantage of using YMnO₃ for applications is its multiferroicity (i.e., simultaneous ferroelectricity and magnetism).³ Recently, thin films of YMnO₃ have been grown epitaxially on Si (111).^{4,5} These structures have been proposed for use in nonvolatile memory devices, taking advantage of the ferroelectric properties of YMnO₃ as well as its chemical stability at high temperatures. The mechanism of YMnO₃ epitaxy on GaN serves as a model for the development of epitaxial routes for other complex oxides grown on wide band gap semiconductors, providing a test case for the development of multifunctional devices that incorporate diverse kinds of correlated behavior with semiconductors.

For these experiments, 2- μ m-thick, Ga terminated [(0001) face] epitaxial layers of GaN grown by metalorganic chemical vapor deposition on *c*-plane sapphire wafers were used as substrates. X-ray diffraction experiments reveal relaxed *c*-axis oriented growth of GaN, with a full width at half maximum (FWHM) of the rocking curve around the GaN 0002 peak of <0.2°.

YMnO₃ epitaxial films were grown by off-axis rf magnetron sputtering performed in a pure Ar atmosphere with a total pressure of 7.5×10^{-2} Torr and a rf power density of ~5 W/cm². The substrates were maintained at temperatures of 650–675 °C during growth, as measured by an optical pyrometer, and were cooled to room temperature in vacuum after growth. Samples thicknesses ranged from 40 to 400 nm.

The as-grown films were characterized by atomic force microscopy (AFM), x-ray diffraction, and electrical and magnetic measurements. AFM scans of optimized films show a regular, continuous, smooth surface with a rms roughness of 1–1.5 nm over an area of 10 μ m \times 10 μ m.

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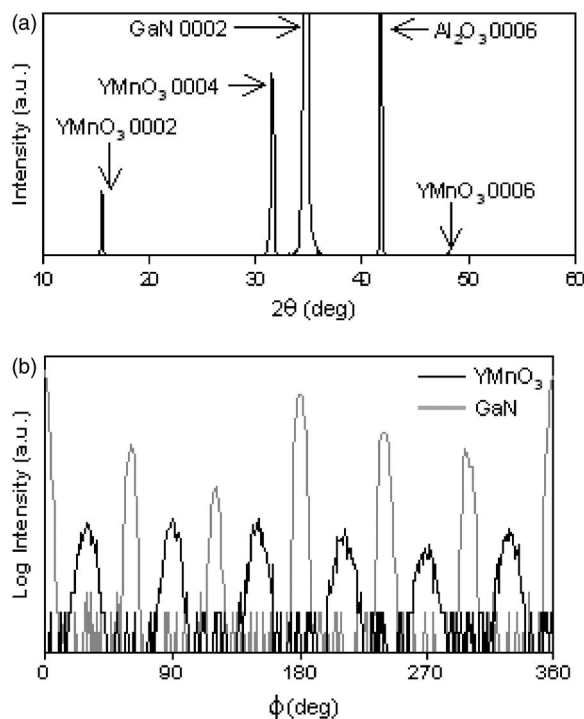


FIG. 1. (a) X-ray diffraction θ - 2θ scan of a YMnO₃ film showing c -axis oriented growth. The rocking curve around the 0004 peak has a full width at half maximum of 0.25°; (b) Off-axis ϕ scans of YMnO₃ (10 $\bar{1}$ 6) and GaN (10 $\bar{1}$ 4) reflections. The scans reveal a 30° in-plane rotational offset between the two unit cells.

θ - 2θ scans show peaks from the 000 l reflections, indicating c -axis oriented growth [Fig. 1(a)]. No impurity phases are detected. Rocking curves performed around the 0004 reflection yield a FWHM of 0.25°, similar to that of the GaN substrate, indicating high crystalline quality. To determine the in-plane orientation of the YMnO₃ film relative to GaN, off-axis ϕ scans were performed using the 10 $\bar{1}$ 6 reflection of YMnO₃ and the 10 $\bar{1}$ 4 reflection of GaN [Fig. 1(b)].⁶ The ϕ scans reveal the sixfold symmetry of both the substrate and film, and an in-plane epitaxial relationship of $[11\bar{2}0]_{\text{YMnO}_3}/[10\bar{1}0]_{\text{GaN}}$ is found. From the diffraction scans, the YMnO₃ films are determined to be relaxed with lattice constants $a=6.13$ Å and $c=11.38$ Å. The striking feature about Fig. 1(b) is the 30° rotation of the YMnO₃ lattice relative to the GaN lattice. This in-plane orientation produces a large lattice mismatch between YMnO₃ and GaN of ~10%, whereas for the unrotated case, the lattice mismatch is only ~4%. In order to understand the origin of the 30° rotation, we estimate the energies of formation of the rotated and aligned configurations, which is described in more detail below.

Ferroelectric characteristics of the YMnO₃ films were measured using standard electrical measurements. Gold contacts were deposited on samples that had been grown on Si-doped GaN/sapphire substrates (10^{18} cm⁻³ dopant concentration). The resulting ferroelectric hysteresis yields a coercive field of ~50 kV/cm and a remnant polarization of ~2 $\mu\text{C}/\text{cm}^2$ (Fig. 2). These values agree with recently reported values for YMnO₃ thin films on Si.⁴

The magnetic properties were measured using a superconducting quantum interference device magnetometer. Under an applied field of 0.1 T, the in-plane magnetization of

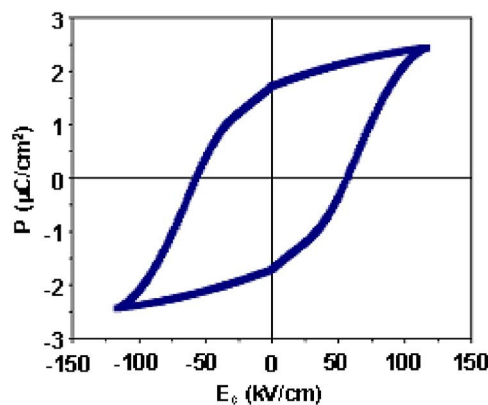


FIG. 2. Ferroelectric hysteresis loop of YMnO₃ with a coercive field of 50 kV/cm and a remnant polarization of 2 $\mu\text{C}/\text{cm}^2$.

the sample was measured as a function of temperature in both field-cooled and zero field-cooled configurations. The magnetization shows Curie-Weiss behavior at high temperatures with a steep increase in the field-cooled measurement at ~45 K, indicating the Néel temperature of the YMnO₃ thin films.

We now turn to the discussion of the in-plane epitaxial relationship between YMnO₃ and GaN. To understand the observed orientation, we estimate the relative energies of formation of the unrotated interface and the 30° rotated interface.⁷

First, we consider the elastic strain energy. First-principles computations⁸ were performed for strained bulk YMnO₃, with the measured strains imposed in the plane, relative to theoretical unstrained bulk YMnO₃. Other structural parameters were allowed to relax within the $P6_3mc$ space group. For unstrained bulk YMnO₃ the calculated lattice parameters are $a_{\text{theory}}=6.116$ Å and $c_{\text{theory}}=11.40$ Å. For the unrotated case, the film strain,⁹ defined as $(|(a_{\text{film}}/2) - a_{\text{substrate}}|)/(a_{\text{film}}/2)$, is a 4.1% expansion. The resulting c lattice parameter is 1% larger than c_{theory} , and the elastic strain energy was calculated to be 0.158 eV per YMnO₃ formula unit. For the 30° rotation, the strain, defined as $(|(a_{\text{film}}/\sqrt{3}) - a_{\text{substrate}}|)/(a_{\text{film}}/\sqrt{3})$, is much larger: a 9.9% compression. The resulting c lattice parameter is 7% larger than c_{theory} , and the elastic strain energy is 1.241 eV per YMnO₃ formula unit. It is necessary to calculate the strain energies explicitly as these large strains are outside the harmonic region. To illustrate this we also evaluated the strain energy using bulk elastic constants within the harmonic approximation. The computed elastic constants are $c_{11}=317$ GPa, $c_{12}=204$ GPa, $c_{13}=87$ GPa, and $c_{33}=282$ GPa (the bulk modulus is $K=165$ GPa, which is comparable to the measured bulk moduli of other common rare earth manganites).¹⁰ Using the expression $W=\frac{1}{2}\epsilon_i c_{ij} \epsilon_j$, the strain energies are 0.34 and 1.96 eV for +4.1% and -9.9% mismatches, respectively, both significantly larger than the energies determined from the explicit calculations discussed earlier.

As a guide to the relative bonding energies at the interface between the GaN (0001) surface and the first unit cell layer of YMnO₃, we turn to reported first-principles calculations on the adsorption energies of oxygen atoms on GaN surfaces.¹¹⁻¹³ The energy gained from the bonding between the oxygen atoms and the Ga surface atoms depends on the degree of coverage of O atoms on the GaN surface and on

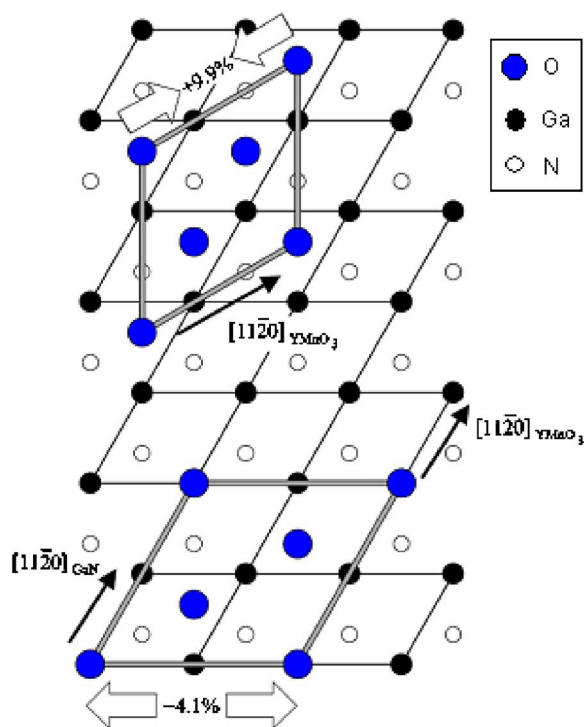


FIG. 3. (Color online) Schematic of the in-plane orientational relationship between the GaN substrate and the YMnO_3 film for aligned unit cells with 4.1% tensile strain (bottom) and unit cells with a 30° offset with 9.9% compressive strain (top). The filled black circles are Ga surface atoms; the unfilled circles are N subsurface atoms of the substrate; and the filled blue circles are the atoms of the apical oxygen layer of YMnO_3 . The black lines represent GaN unit cells, and the gray lines represent YMnO_3 unit cells.

the specific bonding sites at which the O atoms sit. There are four types of bonding sites on the GaN (0001) surface: the hcp site (on top of subsurface N), the fcc site (on top of the threefold cavity), the on-top site (on top of surface Ga), and the bridge site (in between two Ga surface atoms). The calculations show that at low coverages, the fcc site is the most energetically favorable oxygen bonding site. At high coverages, the adsorption energy is reduced by oxygen-oxygen repulsion,¹² but this repulsion is expected to be strongly offset by the electrostatic interaction with the cations in the overlying YMnO_3 layers. For our estimates, we use the values of the adsorption energies per oxygen atom for each of the four bonding sites as tabulated in Ref. 13: 4.24 eV for hcp; 4.86 eV for on-top; 5.06 eV for bridge; and 6.38 eV for fcc.

The expected bonding between YMnO_3 and GaN is shown in Fig. 3. Each YMnO_3 unit surface unit cell contains three apical oxygens, which must bond to the GaN surface. In the unrotated case (Fig. 3, bottom), these three oxygens will bond to GaN such that one oxygen sits on an fcc site, one on an on-top site, and one on an hcp site. This results in an average energy gain of 5.16 eV per YMnO_3 formula unit. For the 30° rotated case (Fig. 3, top), the three oxygens of the YMnO_3 unit cell all sit on the minimum energy fcc sites. This bonding arrangement results in an energy gain of 6.38 eV per YMnO_3 formula unit. Comparing the net energy gained from each interface configuration (chemical bonding energy minus strain energy), the 30° rotated case results in an energy gain of 0.15 eV per YMnO_3 formula unit (or 0.45 eV per YMnO_3 unit cell) over the aligned case, making the

30° rotated case more energetically favorable, in agreement with the experimental observations. If the high oxygen coverage causes the energy ordering in the GaN bonding sites to change, e.g., on-top becomes most stable instead of fcc as in Ref. 12, the 30° rotation would still hold, but with the two lattices shifted laterally compared to our model. These estimates indicate that energetic gains from the chemical bond formation can more than compensate for the cost of large epitaxial strain and stabilize the rotated configuration during the initial stages of growth.

In conclusion, we have grown epitaxial thin films of multiferroic YMnO_3 on GaN/sapphire. We observe an epitaxial relationship of $[11\bar{2}0]_{\text{YMnO}_3} // [10\bar{1}0]_{\text{GaN}}$, which is determined to be the most stable configuration from calculations of the energy of formation of the interface. These calculations highlight the role of chemical bonding at the interface in determining the epitaxial relationship. The ability to grow epitaxial crystalline complex oxides such as YMnO_3 on GaN allows one to consider the development of multifunctional devices that couple correlated oxides with wide band gap semiconductors. The availability of thin films of multiferroic YMnO_3 also enables study on the origin of multiferroicity and the interaction between ferroelectricity and magnetism in this material.

The authors would like to thank Craig Fennie for valuable assistance. This work is supported by the Office of Naval Research Grant No. N00014-02-1-0959, Department of Energy Grant No. DE-FG02-01ER45937, and the Sloan and Packard Foundations.

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⁶The ϕ scan was performed on a diffractometer without sample tilt perpendicular to the beam (χ angle), resulting in unequal intensities for symmetry related peaks.

⁷In our model, the GaN is Ga terminated, and the subsequent layers are an apical oxygen layer of YMnO_3 followed by either a MnO layer or a Y layer. Bonding is assumed to occur between the Ga surface atoms and the apical oxygen layer of YMnO_3 . The formation of the YMnO_3 -GaN interface then results from a competition between elastic strain and Ga-O bond formation in the first deposited layer.

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⁹The strain was defined with respect to the experimentally observed in-plane spacing of YMnO_3 .

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