Selected Growth of Cubic and Hexagonal GaN Epitaxial Films on Polar MgO(111)

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Selected molecular beam epitaxy of zinc blende (111) or wurtzite (0001) GaN films on polar MgO(111) is achieved depending on whether N or Ga is deposited first. The cubic stacking is enabled by nitrogen-induced polar surface stabilization, which yields a metallic MgO(111)-(1 × 1)-ON surface. High-resolution transmission electron microscopy and density functional theory studies indicate that the atomically abrupt semiconducting GaN(111)/MgO(111) interface has a Mg-O-N-Ga stacking, where the N atom is bonded to O at a top site. This specific atomic arrangement at the interface allows the cubic stacking to more effectively screen the substrate and film electric dipole moment than the hexagonal stacking, thus stabilizing the zinc blende phase even though the wurtzite phase is the ground state in the bulk.

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Polar heterointerfaces have been studied extensively in the context of *III-V* compound semiconductors, with electrostatic considerations suggesting that huge dipole moments, and subsequent charge accumulations, should occur at atomically abrupt interfaces [1,2], implying that such sharp interfaces do not exist. The fact that ionicity is even more pronounced in oxides than in compound semiconductors suggests that polarity could have a significant effect on the growth and structure of polar oxide films on polar oxide substrates; experimentally, a polar MgO(111) surface affects the epitaxial growth of a polar $Fe_3O_4(111)$ film by inducing phase separation within and at the interface of the magnetite film [3]. In this Letter, we explore effects of the oxide surface polarity and the initial interface on the growth of GaN, a wide band gap semiconductor that has attracted considerable attention for applications in blue-green lasers, high temperature electronics, and spintronics [4–6]. At room temperature and atmospheric pressure, GaN can exist in two forms: 2H wurtzite (WZ) and 3C zinc blende (ZB) structure, with the WZ polytype being energetically favorable. We demonstrate that by controlling the structure of the oxide-nitride interface, selective growth of both polytypes is possible. High-resolution transmission electron microscopy (HRTEM) and density functional theory (DFT) are used to investigate the structural properties of the GaN(111)/MgO(111) interface and to elucidate the stabilization mechanism for the cubic GaN polytype.

GaN films were grown by electron-cyclotron resonance plasma-assisted molecular-beam epitaxy (MBE) on single crystal MgO(111) substrates. The substrates were degreased in acetone and methanol and then annealed at 800 °C in UHV for 1 h. This procedure produces a (1 × 1) surface terminated by OH, as shown by recent x-ray photoelectron diffraction, core level spectroscopy, and first-principles calculations [7]. Prior to growth, some substrates were exposed to a nitrogen plasma of 30 W at 800 °C for 30 min. GaN films were grown at 600 °C on both as-annealed and nitridized substrates under identical deposition conditions: Ga effusion cell temperature of 950 °C, nitrogen flow rate of 3 sccm, and plasma power of 30 W. Reflection high-energy electron diffraction was used to monitor the growth process. Details of the MBE system can be found elsewhere [8].

Cross-sectional bright field transmission electron microscopy (TEM), high-resolution TEM, and selected area diffraction (SAD) using a 300 kV Hitachi H9000-NAR microscope were employed to study the morphology and crystal structure of the films. The atomic structures were determined by comparing calculated images of model interface structures to experimental HRTEM images recorded for a series of microscope defocus values. The JEMS

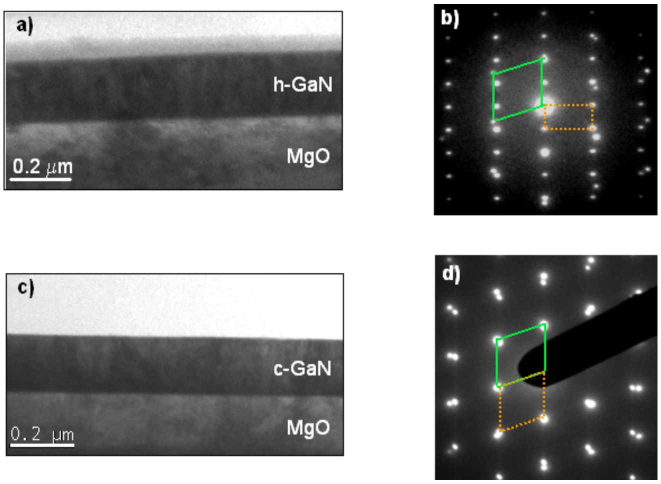

FIG. 1 (color online). Bright field TEM images and SAD patterns of (a),(b) *h*-GaN(0001) film grown on as-annealed MgO(111) surface and (c),(d) *c*-GaN(111) film grown on nitridized MgO(111) surface. MgO and *c*-GaN patterns are in the $[1\bar{1}0]$ zone, while *h*-GaN is in the $[11\bar{2}0]$ zone.

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software package was used for the multislice calculations [9] of the HRTEM images. First-principles local density approximation total energy and electronic structure calculations for the same model interfaces were done using the full-potential linearized augmented plane wave (FLAPW) method [10,11], as implemented in *flair*.

TEM images (Fig. 1) of the two types of growth illustrate that the GaN films have flat surfaces and form abrupt nonfaceted interfaces with the polar MgO substrate. (See also the HRTEM interface image in Fig. 2.) SAD patterns from GaN films grown on the nitridized MgO(111) surface show that the films are cubic [Fig. 1(d)] and that GaN films grown on the as-annealed surface are hexagonal [Fig. 1(b)]. For the nitridized substrates, the orientation relationship is simple cube-on-cube, GaN(111) ∥ MgO(111) and GaN[$1\bar{1}0$] ∥ MgO[$1\bar{1}0$], while for the as-annealed substrates, the orientation is GaN(0001) ∥ MgO(111) and GaN[$11\bar{2}0$] ∥ MgO[$1\bar{1}0$]. The crystallinity and phase purity of both types of films are very high, with a surprising absence of *h*-GaN within the *c*-GaN films, as judged from SAD and HRTEM data.

The experimental fact that both *c*-GaN and *h*-GaN can be grown on the (111) surface of the same cubic substrate under conditions that differ only in prior exposure to N indicates that the order of deposition of the very first N layer is critical in determining the film phase. Although MgO is a cubic substrate, its close-packed (111) planes have sixfold symmetry, thus growth of the more stable *h*-GaN phase is not excluded by in-plane symmetry constraints. The layered nature of a polar direction usually implies that, once the cation or anion surface termination is established, the polar film must initiate with a layer of opposite sign, giving a predetermined film structure and polarity. That MgO(111) can apparently take N to initiate cubic growth, or Ga to initiate hexagonal growth, is surprising. We first present the best-fit model of the interface, and then address the role the first surface monolayer plays in the stabilization of the cubic phase and its persistence at the heterointerface.

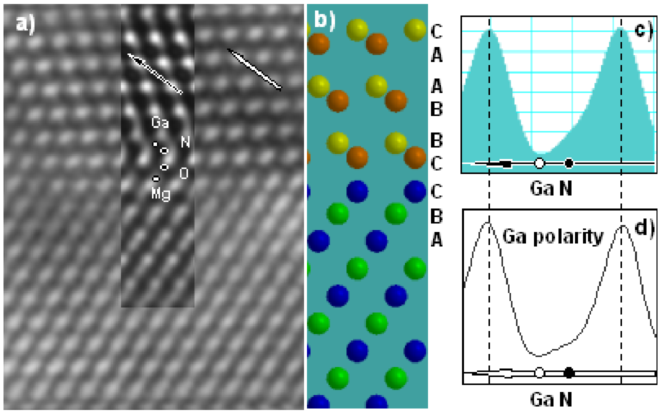

FIG. 2 (color online). (a) Experimental HRTEM image of the *c*-GaN(111)/MgO(111) interface; inset, the best-fit simulated N-top model. (b) Atomic model of the Mg-O-N-Ga interface. (c) Calculated intensity profile from bulk *c*-GaN along a dumbbell direction. (d) Averaged experimental intensity profile along 25 dumbbells in the direction indicated with arrow in image (a).

MgO forms in the rocksalt structure, with lattice constant $a = 4.217$ Å, while cubic GaN has the ZB structure with $a = 4.52$ Å. Along the common polar [111] direction, MgO has equidistant alternating Mg and O planes in the characteristic fcc ABC stacking. Similarly, GaN stacking along [111] can be represented as an AABBCC stacking with alternating interplanar distances corresponding to "short" (e.g., AB) and "long" (e.g., BB) bond projections along the imaged [$1\bar{1}0$] direction. There are 12 geometrically distinct cubic stackings of zinc blende (111) on O-terminated MgO(111), as given in Table I; allowing for either Ga or N as the first layer doubles the number of models to 24. HRTEM through-focus through-thickness maps were calculated for all 24 interface atomic models, using optimized interplanar distances obtained from our DFT calculations for the same models. Figure 2(a) shows the experimental HRTEM image, taken at a defocus of +25 nm and a thickness 5 ± 1 nm, together with a simulated image from the best-fit N-top model shown as an inset. This "N-top" model [Fig. 2(b)] starts with N on top of O, followed by a short bond to Ga in an hcp-like site, i.e., close-packed (111) planes ...O/Mg/O/N/Ga/N/Ga/N/G... in a cubic ...ABC-CBBAAC... stacking. Comparisons of HRTEM intensity profiles [12] along the dimer Ga-N direction from the experimental [Fig. 2(d)] and simulated images [Fig. 2(c)] show that *c*-GaN films have Ga polarity, the same as the N-top model, and can be used to rule out an interface layer Ga.

To investigate the relative stability of the interface, total energies of the 24 model interfaces were calculated, including structural relaxations. The various interfaces (and other calculations discussed here) were modeled using 9 to 13-layer MgO(111) substrates, and up to 9 GaN bilayers on each surface. The hexagonal stacking is energetically favorable for all interface models that start with an O-Ga

TABLE I. Possible stacking arrangements for *c*-GaN(111) on the MgO(111) substrate in terms of the A, B, and C sites. The stackings in *italics* have a stacking fault (i.e., hcp-like site) in the GaN.

First layer: top site	
Next layer: top	Next layer: hollow
ABC-CCBBAA	*ABC-CBBAAC*
ABC-CCAABB	ABC-CAABBC
First layer: hollow site	
Next layer: top	Next layer: hollow
ABC-AACCBB	*ABC-ACCBBA*
ABC-BBAACC	*ABC-BAACCB*
ABC-AABBCC	ABC-ABBCCA
ABC-BBCCAA	ABC-BCCAAB

bond. Cubic stacking is calculated to be favorable only when the interface has an on-top O-N bond (N-top model); the same model with hexagonal stacking is 11 meV/dimer higher in energy than the cubic one. (For comparison, the bulk energy difference between *h*- and *c*-GaN is 16 meV/dimer.) The calculated results are consistent with the experimental observations of *h*-GaN(0001) growth on as-annealed MgO(111) substrates and *c*-GaN(111) growth on the same substrates when nitridized. In addition, the lowest energy cubic model agrees with the preferred N-top interface model obtained from the HRTEM image analysis.

The essential aspect needed to understand the structure of the initial interface, and the subsequent continued growth of the cubic GaN film, is that the structure that forms is the one with the lowest energy at that particular stage of the growth and not the one that globally has the lowest energy; i.e., the resulting structure and growth process are both metastable. This conclusion can be understood by comparing the calculated total energies corresponding to different stages in the growth. If N is placed on the O-terminated MgO(111) surface first, the top site is favored by 2.95 eV compared to the hollow (top) site; for Ga, however, the hollow site is favored by 1.8 eV. If both Ga and N are present, the preferred bonding (by ~0.37 eV) is Mg-O-Ga-N, but this initial arrangement leads to *h*-GaN films. Assuming a N-rich environment initially, the N will bond on top of the surface O, and the first Ga can take either the fcc- or hcp-like hollow site, or the on-top site. For both hexagonal and cubic stacking of three bilayers of GaN, the fcc-like (ABC-CA…) interface is favored over the hcp (ABC-CB…) one by ~10 meV/bilayer, in contradiction to the experimental result. However, when the fcc- and hcp-like stackings of the first Ga layer on the MgO-N surface are compared, the hcp-like interface is very strongly favored, by 74 meV (the top site for the Ga is even much higher in energy by ~1.3 eV). This large energy, resulting from charge transfer or bonding between the Ga and the substrate Mg, causes the first Ga layer to go down in the hcp-like site, as observed. As more layers are deposited, the interface Ga will remain in the original hcp site since rearrangement to the thermodynamically lowest global state is kinetically hindered. This resulting metastability is a common feature of MBE (and related) growths. Once the initial interface is determined, the cubic stacking is lower in total energy compared to the hexagonal for several additional bilayers. However, because *h*-GaN is favored compared to *c*-GaN for the bulk, after about 6 bilayers the full *h*-GaN film is lower in total energy. Naively, one might expect the film to revert to *h*-GaN at this point, but the surface stacking fault energy for the *c*-GaN film—the energy for the next Ga to take the hcp instead of the fcc site—is 9 meV, a small but still significant value on the scale of energy differences between structures. Because this energy cost will remain regardless of how thick the film becomes, thick metastable *c*-GaN will be possible; experimentally, we see cubic films in the range of 300 nm. This preference for the continued cubic stacking can be attributed in part to subtle changes in the surface Ga density of states (DOS) near the Fermi level: near the surface, where there are states in the gap, the DOS at the Fermi level is lower for Ga in the fcc site compared to the hcp one.

The total energy calculations clearly show that the first interface monolayer is critical for the subsequent film crystalline structure. Our recent studies demonstrated the existence of the MgO(111)-(1 × 1)-OH structure [7], consistent with the predicted covalent bonding of H on top of oxygen and insulating surface properties [13]. Our calculations indicate that N can favorably (~ 0.3 eV) displace H from the interface, giving Mg-O-N-H. Indeed, HRTEM studies of the interface lattice spacing rule out the presence of H as a distinct plane between cubic MgO and GaN. (For Ga, the MgO-H-Ga is preferred by ~0.7 eV compared to the MgO-Ga-H ordering.) At this time it is not known if H desorbs upon growth of the first monolayer, remains as a surfactant top monolayer, or diffuses to bulk interstitial sites.

Figure 3 gives the local density of states for the interface O and N layers for (a) the MgO(111) O-terminated surface after nitridation and (b) after growth of a (6 bilayer) cubic film. Strong covalent bonding characteristic of the molecular O-N bond is seen in both cases, with the larger separation between the 2*s*-derived bonding and antibonding orbitals at the surface indicating a stronger N-O interac-

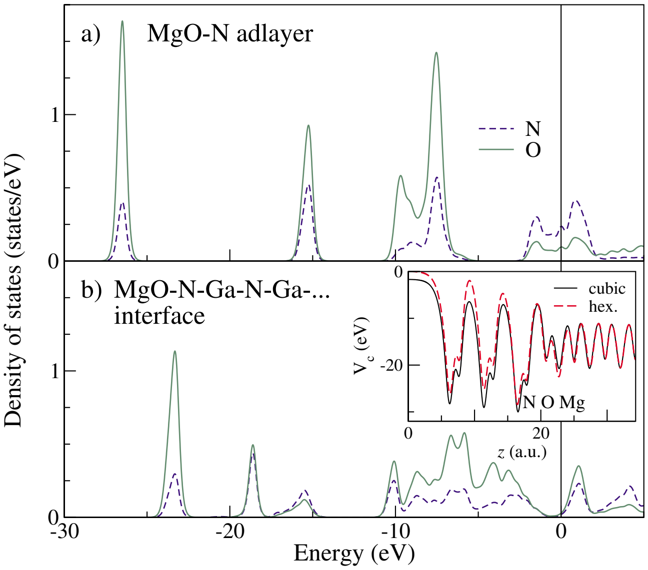

FIG. 3 (color online). Local density of states for interface O and N atoms for (a) a single N-top monolayer on the O-terminated MgO(111) surface and (b) the N-top *c*-GaN/MgO interface model. The inset gives the planar-averaged Coulomb potential for 3 bilayers of GaN on MgO for both cubic (solid black line) and hexagonal (dashed red line) stackings.

tion. The N monolayer also induces a significant number of states around the Fermi level that give rise to the metallic nature of the MgO(111)-(1 × 1)-ON surface, in contrast to the (1 × 1)-OH surface that is predicted to be insulating [7,13]. The N adsorption stabilizes the unreconstructed MgO(111) surface through a surface metallization mechanism for covalently bonded adsorbates that differs from the 2D metallization predicted in prior DFT studies of the clean O- or Mg-terminated polar MgO surface [7,13] and for metal monolayers on these surfaces [14].

When the *c*-GaN film growth starts on the nitridized surfaces, there are significant changes in the local DOS (Fig. 3); in particular, the interface becomes semiconducting again. Comparing the planar-averaged Coulomb potentials (inset of Fig. 3) shows that for cubic GaN, in contrast to *h*-GaN, the potential on either side of the interface reaches bulklike values within one bilayer of the surface; i.e., the cubic stacking more effectively screens the substrate and film dipole moments than the *h*-GaN film, all without the need for atomic mixing at the interface.

The connection among the GaN film stacking, the MgO substrate polarity, and possible O-N bonding is further supported by three related calculations: (1) When the MgO(111) substrate is removed from the interface supercells, the hexagonal stacking is always energetically favorable compared to the cubic stacking, as expected from the bulk. (2) For InN on MgO(111), the same trend is found as for GaN, although the energies between the *c*-InN and *h*-InN films on MgO(111) are smaller (~1 meV/bilayer). Because of the larger mismatch in lattice constants between MgO and InN, strain may make it difficult to grow defect-free epitaxial films of either polytype. (3) When the MgO(111) substrate is replaced by a metal with similar lattice constant, such as Ti(0001), a monolayer of N is found to strongly prefer the hollow site, and the hexagonal GaN film structure is preferred even when the interface N is forced in a top site. The presence of an oxygen monolayer to form a Ti-O-N-Ga interface (with N in an on-top site) stabilizes the cubic GaN phase compared to the hexagonal phase. Taken together, these results imply that the polarity of the substrate and the initial interface are important factors determining which phase will be grown.

In summary, we report the first selected growth of cubic zinc blende and hexagonal wurtzite GaN films on the polar MgO(111) substrate by controlling the first interface atomic layer. The cubic stacking is enabled by a nitrogen-induced polar surface stabilization, predicted to yield a MgO(111)-(1 × 1)-ON metallic surface structure via covalent O-N bonding. We determine that the atomically abrupt cubic GaN(111)/MgO(111) interface structure has a Mg-O-N-Ga stacking, with each N atom bonded on top of O, and has semiconducting properties at the interface. This specific atomic arrangement at the interface allows cubic stacking to more effectively screen the substrate and film electric dipole moment than the hexagonal stacking, stabilizing the zinc blende phase. Finally, metastable growth of different polytypes is possible because the growth is determined by the local, not global, minimum at each stage of the growth; this local minimum can be strongly affected by the interface structure even for film thickness so large that there are no direct interactions with the interface.

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