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Inversion of wurtzite GaN(0001) by exposure to magnesium

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Abstract

Magnesium incorporation during the molecular beam epitaxy growth of wurtzite GaN is found to invert the Ga-polar (0001) face to the N-polar face. The polarity is identified based on the two different sets of reconstructions seen on the film prior to and after about 1 monolayer Mg exposure. The inversion boundary is seen to lie on the (0001) plane from transmission electron microscopy images, and a structural model is presented for the inversion. On the Ga-polar face, Mg is also seen to stabilize growth in the N-rich regime.

The development of blue light emitting devices requires better understanding of growth and dopant incorporation in GaN. Though Mg is the most commonly used p-type dopant in GaN based diodes, its incorporation in GaN is poorly understood. Early studies on p-type doping of GaN in metallorganic chemical vapor deposition (MOCVD) revealed that Mg dopant atoms were strongly passivated in these films and the carrier concentration was therefore very low [1,2]; dopant activation can be achieved by various methods [2,3,4]. In molecular beam epitaxy (MBE) growth of p-doped GaN, the high vapor pressure of Mg at GaN growth temperatures is an issue and dopant incorporation may be rather inefficient [5,6]. Studies have shown that the Mg concentration decreases from the surface to the interior of the film [7] suggesting dopant incorporation from a surface Mg layer. Some workers have noted Mg-induced changes in the growth rate of GaN on different crystallographic planes [8], pointing to a surfactant effect of Mg on GaN. The presence of Mg atoms during the growth of GaN has also been associated with the appearance of stacking faults [9].

It is clear that understanding the effects of Mg on GaN crystal stacking and polarity is very important. Most devices are built on the polar basal plane of wurtzite GaN, and the characteristics of these devices depend on whether the GaN film is Ga-polar or N-polar [10]. The identification of polarity has been done by several groups using different methods. Seelmann-Eggebert [11] *et al.* found that etching of the crystal by an alkali solution was sensitive to polarity. Smith *et al.* [12] used surface reconstruction to identify polarity of wurtzite GaN, and we use the same technique in this work. We monitor the surface reconstruction of our films using reflection high energy electron

diffraction (RHEED) and scanning tunneling microscopy (STM). On the Ga-polar face, when the sample cools down after growth, the reconstructions seen are the 2×2, 5×5, 6×4, and "1×1" in order of increasing Ga content, while on the N-polar surface, the reconstructions seen are 1×1, 3×3, 6×6, and c(6×12) [12]. We find that the reconstruction of the films changes from the former group to the latter upon exposure to Mg during growth.

The films are grown in a MBE chamber with base pressure less than 1×10^{-10} Torr, on Si-polar 6H-SiC(0001) substrates. The substrates are prepared *ex-situ* by hydrogen etching [13]. The surface oxide is removed by Si pre-deposition and desorption until a $\sqrt{3}\times\sqrt{3}$R-30˚ reconstructed surface is obtained [14]. Immediately after this, the substrate is brought to a temperature of 600–700˚C and growth is initiated. Ga and Mg fluxes are produced by effusion cells, while a RF-plasma is used to excite N_2 molecules, facilitating reaction. Typical values for the Mg flux and GaN growth rate are 0.017 ML/s and 0.4 ML/s respectively (1 ML = 1.14×10^{15} atoms/cm^2).

Let us first consider growth in the absence of any Mg; growth conditions are usually Ga rich, in which regime we see a streaky, dim 1×1 RHEED pattern. After interrupting the growth and cooling the sample to about 300˚C a "1×1" RHEED pattern (pseudo-1×1 pattern, with satellite streaks near the first order streaks) is observed, as shown in Fig. 1(a). Annealing this sample at temperatures above 700˚C till the RHEED pattern becomes bright leads to a 2×1 RHEED pattern. Successive depositions of Ga on this surface and flashes to 700˚C produce the 5×5 and 6×4 RHEED patterns. As mentioned above, all these reconstructions are indicative of a Ga-polar film and their appearance in STM images is similar to those reported by Smith *et al.* [12].

During growth, films are briefly exposed to a Mg flux. A surfactant effect of Mg is seen on the Ga-polar films in the Ga-poor regime, where reducing the Ga-flux in the absence of Mg causes the RHEED pattern to change from streaky to spotty indicative of a growth mode transition from 2-dimensional to 3-dimensional [15]. Exposing this surface to about 0.2 ML of Mg under Ga-poor conditions leads to a reversal of the RHEED pattern to streaky. Also, when the growth is made severely N-rich, by reducing the Ga flux to about one half of that at the transition point, exposure to Mg often produces a streaky 2×2 pattern, as shown in Fig. 1(b).

When the film is exposed to 1.2±0.4 ML or more of Mg during growth, we find that the polarity switches to N-polar. After terminating the growth and cooling the sample to below about 300˚C, a 1×1 RHEED pattern is obtained. Exposing this surface to Ga produces 3×3, 6×6, and c(6×12) surfaces with increasing Ga coverage. The 3×3 and 6×6 RHEED patterns are shown in Fig. 1(c) and (d). Without exposure to Mg, such an inversion is never seen and so we conclude that the Mg exposure causes the inversion. In the Ga-poor regime the inversion can be observed *during* growth. The 2×2 RHEED pattern seen in the Ga-poor regime in the presence of Mg changes, upon prolonged Mg exposure, to a spotty 1×1 pattern arising from Ga-poor growth on the N-polar face [15].

In Fig. 2(a) and (b), we show cross-sectional TEM images of a GaN film which was grown at about 680˚C. The inversion domain boundary (IDB) is clearly visible, as indicated by the two solid arrowheads on the sides of the picture. This particular sample was exposed to about 8 ML of Mg, although inversion occurred during the initial part of this exposure. The IDB is seen to lie in the (0001) plane and it divides the sample into two parts with distinct contrast patterns. High-res-

olution images reveal good crystalline order at and around the IDB, as shown in Fig. 2(b) (the interface at which the inversion occurs is not perfectly flat, so that the IDB appears to be distributed over several atomic layers in high-resolution TEM images). From Fig. 2(a) it is clear that the growth is of poorer quality after the inversion. There are a large number of vertical lines that are seen above the IDB which are either prismatic stacking faults, of the variety mentioned in Ref. [16], or screw dislocations. The defect density above the inversion boundary is about 10× larger than that before inversion. Several other planar features lying in the (0001) plane are also seen in this micrograph, some of which are labeled with hollow arrowheads. These correspond to growth interrupts; in some cases, brief exposures to Mg were made during these interrupts.

To understand the origin of the polarity inversion we performed calculations of the total energy of various possible inverted structures. These calculations were performed within the local density approximation using first principles pseudopotentials as described elsewhere [17]. The Ga 3d electrons were treated as part of the valence band and the plane wave cutoff was 60 Ry. An IDB may form if, for a Mg concentration above a certain threshold, it is energetically favorable to form a Mg-terminated $(000\bar{1})$ surface atop an IDB instead of a Mg-terminated (0001) surface. One such structure is shown in Fig. 3(a). In this case the IDB consists of a plane of Ga-Ga bonds and the surface is terminated by a monolayer of Mg in H_3 sites. The N atoms in the outermost layer are six-fold coordinated with a local structure that is more like that of bulk Mg_3N_2 than bulk GaN. We find that this inverted structure is more stable (by 0.05 eV/1×1) than the non-inverted, stoichiometrically identical, structure shown in Fig. 3(b). We think the inverted structure forms the template for subsequent growth of GaN, with the IDB frozen in place as a thicker N-face film grows on top. It may also be possible that a few layers of bulk Mg_3N_2 form above the IDB. In this picture the c-plane IDB that results consists of a layer of Ga-Ga bonds of length 2.45 Å. We note that the N-plane bonded to the upper Ga-plane of the IDB can have two possible stacking arrangements [zinc-blende-like or wurtzite-like, with the latter shown in Fig. 3(a)]; variation between these would result in prismatic stacking faults of the type mentioned above.

Inversion domains (IDs) have also been observed in MOCVD-grown Mg-doped GaN layers, as shown in Fig. 2(c). This sample consists of a 1 μm thick Mg-doped GaN layer overgrown on a thinner Mg-doped GaN layer. The IDs initiate in the layer above the regrowth interface and are approximately 30 nm in diameter. Similar regrowth is used for fabricating distributed feedback lasers [18] but the overgrown layer in that case is AlGaN. No IDs are found in those AlGaN layers, suggesting possible differences in the probability of IDB formation between AlGaN and GaN.

In summary, we have grown GaN films on hydrogen-etched 6H-SiC(0001) by MBE at growth temperatures of 600–700˚C with brief exposures to Mg. The Mg exposures are seen to have a surfactant effect, but more significantly, to invert the Ga-polar GaN film to a N-polar film. The inversion boundary lies in the c-plane and a model of such a boundary has been presented. Finally we note that the ability to induce an inversion may be *useful* in devices where control over polarity is desired, although in this regard we point out that the opposite inversion (N-polar to Ga-polar) has not been achieved to date.

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[1] S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, Jpn. J. Appl. Phys. **31**, L139 (1992).

[2] S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, Jpn. J. Appl. Phys. **31**, 1258 (1992).

[3] H. Amano, M. Kito, K. Hiramatsu and I Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (1989).

[4] S. J. Pearton, J. W. Lee and C. Yuan, Appl. Phys. Lett. **68**, 2690 (1996).

[5] S. Guha, N. A. Bojarczuk and F. Cardone, Appl. Phys. Lett. **71**, 1685 (1997).

[6] C. Bungaro, K. Rapcewicz, and J. Bernholc, Phys. Rev. B **59**, 9771 (1999).

[7] T. S. Cheng, C. T. Foxon, N. J. Jeffs, D. J. Dewsnip, L. Flannery, J. W. Orton, S. V. Novikov, B. Ya Ber and Yu A. Kudriavtsev, MRS Internet J. Nitride Semicon. Res. **2**, 13 (1997).

[8] B. Beaumont, S. Haffouz and P. Gibart, Appl. Phys. Lett. **72**, 921 (1998).

[9] Z. Lilienthal-Weber, S. Ruvimov, M. Benamara, J. Washburn, I Grzegory and S. Porowski, submitted to Phys. Rev. Lett.

[10] R. Gaska, J. W. Wang, A. D. Bykhovski, M. S. Shur, V. V. Kaminski and S. M. Soloviov, Appl. Phys. Lett. **72**, 64 (1998).

[11] M. Seelmann-Eggebert, J. L. Weyher, H. Obloh, H. Zimmermann, A. Rar and S. Porowski, Appl. Phys. Lett. **71**, 2635 (1997).

[12] A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer and J. Northrup, Appl. Phys. Lett. **71**, 3934 (1997); J. Vac. Sci. Technol. **B 16**, 2242 (1998); Surf. Sci. **423**, 70 (1999).

[13] V. Ramachandran, M. F. Brady, A. R. Smith, R. M. Feenstra and D. W. Greve, J. Electron. Mater. **27**, 308 (1998).

[14] V. Ramachandran, A. R. Smith, R. M. Feenstra and D. W. Greve, to appear in J. Vac. Sci. Technol. A. Jul/Aug (1999), and references therein.

[15] A. R. Smith, V. Ramachandran, R. M. Feenstra, D. W. Greve, A. Ptak, T. H. Myers, W. L. Sarney, L. Salamanca-Riba, M. -S. Shin and M. Skowronski, MRS Internet J. Nitride Semicond. Res. **3**, 12(1998).

[16] J. E. Northrup, Appl. Phys. Lett. **72**, 2316 (1998).

[17] J. Neugebauer, T. Zywietz, M. Scheffler, J. E. Northrup and C. G. Van de Walle, Phys. Rev. Lett. **80**, 3097 (1998); J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, 10477 (1996).

[18] L. T. Romano, D. Hofstetter, M. D. McCluskey, D. P. Bour, and M. Kneissl, Appl. Phys. Lett. **73**, 2706 (1998).

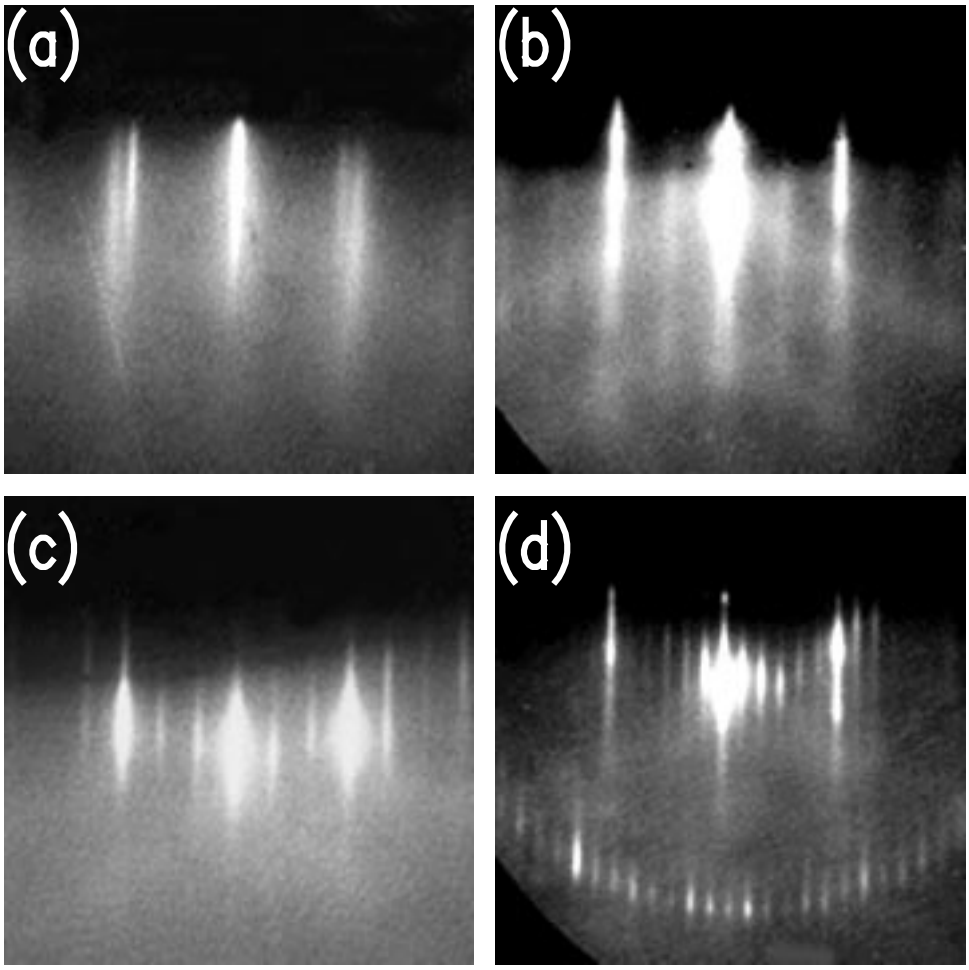

Figure 1 RHEED patterns seen after cooling of GaN films. Non-inverted surface: (a)“1×1” and (b) 2×2. After Mg exposure, inverted surface: (c) 3×3 and (d)6×6.

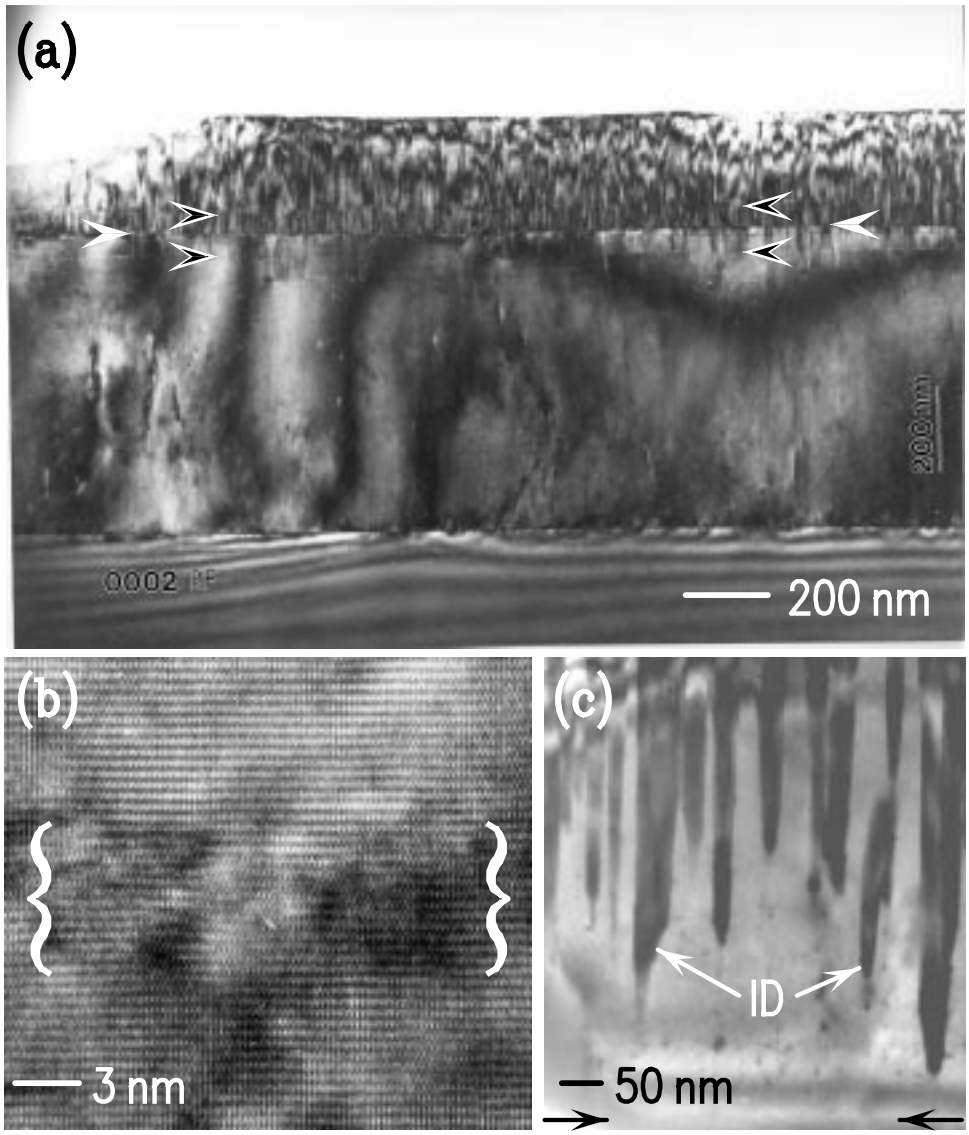

Figure 2 (a) Bright field TEM image in (0002) two-beam condition of MBE-grown GaN film grown on SiC showing inversion boundary labeled with solid arrowheads and growth interrupts labeled with hollow arrowheads. (b) High-resolution image of same sample as in (a). Brackets indicate the region of the inversion boundary. (c) Bright field (0002) two-beam TEM image of a MOCVD-grown GaN film showing inversion domains (ID). Regrowth interface is indicated by arrows.

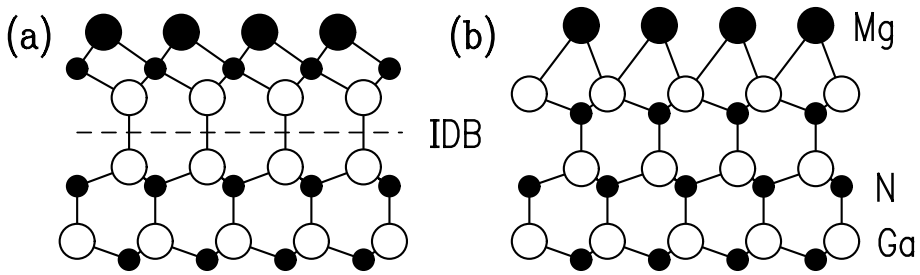

Figure 3 (a) Structural model of a c-plane inversion domain boundary (IDB) induced by Mg atoms. (b) Noninverted structure. Both models are shown in a $(11\bar{2}0)$ projection. Height of the Mg layer above the underlying atomic plane is 1.29 Å and 2.43 Å for inverted and noninverted structures respectively.