Faceted inversion domain boundary in GaN films doped with Mg

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Homoepitaxial GaN films doped with Mg were grown by rf-plasma molecular beam epitaxy on Ga-polarity (0001) MOCVD templates. Convergent beam electron diffraction analysis establishes that the film polarity changes from [0001] to [000$\underline{1}$] when the Mg flux during growth is approximately one monolayer per second. Secondary ion mass spectrometry indicates a doping concentration of ~10^{20}cm^{-3} in the film where the inversion occurs and shows a reduced Mg incorporation efficiency after further growth. Transmission electron microscopy shows that the inversion domain boundary is faceted predominantly along the {0001} and {*h,h,-2h,l*} planes, with *l/h* approximately equal to 3. Using first-principles total energy calculations we show that the {*h,h,-2h,l*} segments of the boundary are stabilized by the incorporation of Mg in threefold coordinated lattice sites.

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Because magnesium is the most common dopant used to achieve p-type conductivity in the Ga(Al)N alloys employed in optoelectronic devices [1], its incorporation during growth has been the subject of a number of recent studies. [1-6] These studies have shown that the incorporation of high levels of Mg is often accompanied by the formation of extended defects. In single crystals of bulk-grown GaN:Mg, the presence of enclosed pyramidal defects and an ordered array of Mg-rich basal plane faults has been reported. [3]. Pyramidal defects have also been observed following the annealing of GaN:Mg layers at 1400 ^{o}C [4]. These enclosed pyramidal defects have been identified as inversion domains with boundaries lying in (000$\underline{1}$) and {11$\underline{2}$3} planes [2]. Studies of GaN films grown by molecular beam epitaxy [5] have shown that exposure of the (0001) surface to ~ 1 ML of Mg can cause an inversion of polarity from Ga-face to N-face, and transmission electron microscopy images [5] have revealed the presence of inverted regions in Mg-doped layers of films grown by metal organic chemical vapor deposition (MOCVD).

In this paper transmission electron microscopy (TEM) is used to study the microstructure of Mg-doped GaN films grown by rf-plasma molecular beam epitaxy (MBE). The substrates used for this study were undoped GaN films grown by MOCVD on c-plane sapphire. Films were also grown directly on c-plane sapphire for comparison. Convergent beam electron diffraction (CBED) was used to determine the polarity of the films. The MOCVD substrates were found to have [0001] polarity (Ga-face) whereas the films grown directly on sapphire had [000$\underline{1}$] polarity (N-face). The Mg flux was controlled during growth by varying the effusion cell temperature (T_{Mg}) in a stepwise fashion over a temperature range from 250^{o}C to 400^{o}C. GaN spacer layers that were ~ 0.1 microns thick and nominally undoped were grown between the doped layers. Secondary ion mass spectrometry (SIMS) was used to determine the Mg concentration [Mg]. Cross sectional TEM analysis (XTEM) was performed on samples that were polished along the {1$\underline{1}$00} and {11$\underline{2}$0} directions and then argon ion thinned to electron transparency using a liquid nitrogen cold stage and low voltage to minimize damage.

Figure 1 shows a SIMS profile for a Mg step-doped film grown at 710^{o}C on a MOCVD substrate. This and other SIMS measurements [7] suggest that a Mg-accumulation layer may be forming during the growth since the doping profile is not as

abrupt as the growth profile, and the undoped spacer layers are not clearly observed. For T_{Mg} = 250 ^{o}C, the Mg concentration [Mg] in the film was below detectable levels. The average [Mg] was ~ 2 x 10^{17} cm^{-3} at T_{Mg} = 300 ^{o}C and increased to ~ 8 x $10^{19}$$cm^{-3}$ at T_{Mg} = 350^{o}C. Then, after T_{Mg} was increased to 400^{o}C, there was a sharp decrease in the [Mg] to values below 10^{19} cm^{-3}. At this point in the growth, T_{Mg} was cycled through the same temperature range of 250-400 ^{o}C. Even though hydrogen was present during this second cycle, which tends to *increase* the Mg incorporation rate [7], the SIMS data shows that the concentration of Mg incorporated was significantly reduced for the same corresponding values of T_{Mg} used in the first cycle. The lower [Mg] obtained in the second cycle is, however, consistent with doping profiles measured for N-face polarity MBE films grown directly on sapphire [7], thus suggesting the possibility that the polarity of the film is inverted by the Mg exposure.

A bright field TEM image of this film is shown in Fig. 2 along with convergent beam diffraction patterns. A low magnification image (Fig. 2b) indicates the existence of a structural interface where the Mg concentration was observed to drop in the SIMS profile. We note that structural interfaces were *not* observed between the MOCVD and MBE-grown layers or at any of the other doping changes (not shown). Threading dislocations from the MOCVD substrate are found to extend through this interface with some bending in the vicinity of the interface. To check for an inversion of the film polarity, convergent beam electron diffraction (CBED) was performed along the <11$\underline{0}$0> axis in regions of the film above and below the interface. The <11$\underline{0}$0> direction is conveniently chosen since it has inversion symmetry and the diffraction disks are well separated [8]. The sample thickness was kept constant during the measurement since the contrast within the diffractions disks is thickness dependent [9]. The results are shown in Figs. 2a and 2c. The contrast within the zero order disk is the same in both patterns which corresponds to a sample thickness, t ~ 125nm, by comparing to computer simulations [9]. The (0002) and (000$\underline{2}$) disks are seen to have opposite contrast in the CBED patterns taken above and below the interface, indicating that the polarity has inverted across the interface. By comparing the diffraction contrast to computer simulations [9], it was determined that the polarity switched from [0001] polarity below the interface to [000$\underline{1}$] above the interface. Thus, the MBE growth of the [0001] polarity film is a continuation

of the polarity of the MOCVD substrate, but for sufficiently high Mg exposures (T_e = 400 ^oC) an inversion domain boundary is formed and the polarity of the film is inverted. The incident Mg flux for T_{Mg} = 400^oC is ~ 1 ML/sec and the incorporated Mg concentration (measured by SIMS) is approximately 8×10^{19} cm^{-3} in the film where the inversion takes place. These results are consistent with the recent observations by Ramachandran *et al* for GaN films grown by MBE on SiC(0001) substrates in which a Ga-face to N-face polarity reversal was observed by induced by exposing the film to several monolayers of Mg during growth [5].

High magnification TEM images of the interface indicate that the IDB is faceted as shown in Fig. 3. The dark field image in Fig. 3a is taken along the [11$\underline{2}$0] axis with a diffraction vector g = (000$\underline{2}$). In this image, facets can be observed and complimentary contrast is revealed in the film above and below the interface to confirm the inversion symmetry [8]. The high resolution lattice image in Fig. 3b taken along the [1$\underline{1}$00] axis shows that the facets contain segments lying in the (0001) plane as well as segments that are inclined with respect to the basal plane. The inclined facets were found to be sharp when imaged in the <1$\underline{1}$00> projection and diffuse in the <11$\underline{2}$0> projection. This observation is consistent with the existence of inversion domain boundaries lying in {*h,h,-2h,l*} planes. In the <1$\underline{1}$00> projection, the facet angle (θ) ranges from ~ 45-50 degrees with respect to the basal plane. The existence of Mg-induced (0001) inversion domain boundaries was reported by Ramachandran *et al*. [5], but {*h,h,-2h,l*} facets were not observed in that work.

A possible atomic model for inversion boundaries lying on the (0001) plane has been discussed elsewhere [5]. We will focus here on the {*h,h,-2h,l*}facets. As a first step we considered the (11$\underline{2}$2) plane. An energetically plausible model for an inversion domain boundary lying on this plane may be constructed as shown in Fig 4. In this model all of the N atoms and most of the Ga atoms remain fourfold coordinated as in bulk GaN, but the Ga atoms that are closest to the boundary are each bonded to only three N atoms. In this configuration electrons will occupy the dangling bond ($4p_z$) orbitals of the Ga atoms. However, by replacing 3 out of 4 Ga atoms by Mg we obtain a configuration in which there is *no* occupation of the Ga dangling bonds, *i.e.* such a structure satisfies the electron counting rule. We have performed first principles total energy calculations [10]

for structural models of (11$\underline{2}$2) boundaries in which either 0 or ¾ of the threefold Ga atoms are replaced by Mg atoms. The unit cells employed in these calculations contain 4 threefold-coordinated Mg or Ga atoms. The relative energy of these structures depends on the chemical potentials of the atomic constituents; μ_{Mg}, μ_{Ga}, and μ_N. For conditions in which there is equilibrium with bulk GaN ($\mu_{Ga} + \mu_N = \mu_{GaN(bulk)}$) and for which the Mg chemical potential is equal to its maximum possible equilibrium value ($3\mu_{Mg} + 2\mu_N = \mu_{Mg3N2(bulk)}$), we find that the energy of the (11$\underline{2}$2) boundary having ¾ Mg occupation is energetically favorable compared to the boundary containing no Mg. The calculated energy difference is ~3.5 eV per unit cell for Ga-rich conditions. This result indicates that the formation energy of such a (11$\underline{2}$2) inversion domain boundary is reduced significantly under Mg-rich conditions.

We have also performed calculations for a boundary lying on the (11$\underline{2}$3) plane. This plane is inclined by ~ 47 degrees with respect to the basal plane. The structure we considered is indicated in Figure 4. Such a boundary may be described as a mixture of two (11$\underline{2}$2) segments (P) and a (0001) segment (B), as defined in Figure 4. As for the (11$\underline{2}$2) boundary, our total energy calculations indicate that the energy of the (11$\underline{2}$3) boundary is reduced significantly by replacing some of the Ga atoms by Mg atoms. We performed calculations for (11$\underline{2}$3) boundaries having 6 threefold-coordinated Mg or Ga atoms in each unit cell. We calculate the energy of a structure in which 4 out of 6 Ga atoms are replaced by Mg and compare this with the energy of a structure in which all 6 threefold-coordinated atoms are Ga atoms. [10] For the same conditions on the chemical potentials discussed above, we find that the energy of the Mg-containing structure is lower by 2.75 eV/cell under Ga-rich conditions. On the basis of the calculations for these (11$\underline{2}$2) and (11$\underline{2}$3) inversion domain boundaries we propose that the inclined segments of the boundaries observed in the films are Mg-rich, with Mg atoms occupying threefold-coordinated sites.

One may construct inversion domain boundaries inclined at various angles with respect to the basal plane by mixing (11$\underline{2}$2) and (0001) segments. The (33$\underline{6}$8) plane, inclined by ~51 degrees, is such a mixture. It contains a mixture of three P-segments and one B-segment as defined in Figure 4. It is possible that the range of inclination angles observed in the TEM images can be accounted for in terms of boundary structures

consisting of nanometer scale mixtures of (11$\underline{2}$2) and (0001) segments. The local atomic structure of these boundaries is expected to be similar to those indicated in Figure 4.

In summary we have observed that for sufficiently high Mg doping levels the (0001) growth surface of GaN exhibits an instability with respect to polarity inversion, with the formation of a multifaceted IDB. First principles total energy calculations indicate that Mg incorporates in threefold-coordinated binding sites along the facetted segments of the IDB. Since Mg incorporation on the (000$\underline{1}$) surface is much less efficient than on the (0001) surface, this Mg-induced polarity inversion may limit the p-type doping levels achievable in MBE grown GaN.

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Figure Captions

Fig.1. SIMS data showing growth profile and Mg incorporation as a function of depth for a set Mg cell temperatures repeated over two growth cycles at a substrate $T_s = 710^oC$. The second cycle was grown also with hydrogen (H).

Fig.2. Convergent beam electron diffraction patterns taken (a) above and (c) below the interface that is indicated by the arrow in (c). (c) is a bright field image taken with a diffraction vector g = 0002 near the [11$\underline{2}$0] axis of a GaN:Mg film.

Fig. 3 (a) High magnification image of the inversion domain boundary (IDB) taken along the [11$\underline{2}$0] axis with diffraction vector g = 0002. (b) Lattice image of the IDB taken along the [1$\underline{1}$00] axis showing facets that form along the (0001) plane and at an angle $\theta \sim$ 50 degrees with the basal plane.

Fig. 4 Schematic representations of various possible inversion domain boundaries in GaN. A (11$\underline{2}$2) boundary is shown on the left. The shaded atoms are threefold coordinated Mg or Ga atoms. Shown on the right is a (11$\underline{2}$3) boundary comprised of a nanometer scale mixture of (11$\underline{2}$2) segments (denoted P) and (0001) segments (denoted B). The (11$\underline{2}$2) and (11$\underline{2}$3) boundaries are stabilized by replacement of ¾ of the Ga atoms by Mg atoms. The IDB shown here is formed by switching the chemical identity of Ga and N atoms on one side of the boundary, and then performing a translation along the [0001] direction by (5/8) **c**.

References

1. S. Nakamura, *The blue laser diode: GaN based light emitters and lasers*, (Springer, Berlin, 1997).

2. P. Vennegues, M. Benaissa, E. Feltin, P. De Mierry, S. Dalmasso, M. Leroux, and P. Gibart, unpublished

3. Z. Liliental-Weber, M. Benamara, W. Swider, J. Washburn, I. Gregory, S. Porowski, D. J. H. Lambert, C. J. Eiting, and R. D. Dupuis, Appl. Phys. Lett, **75**, 4159 (1999)

4. M.D. McCluskey, L.T. Romano, B.S. Krusor, N. M. Johnson, T. Suski, and J. Jun, Appl. Phys. Lett, **73**, 1281 (1998)

5. V. Ramachandran, R. M. Feenstra, W. L. Sarney, L. Salamanca-Riba, J. E. Northrup, L. T. Romano, and D. W. Greve, Appl. Phys. Lett, **75**, 808 (1999)

6. I.P. Smorchkova, E. Haus, B. Heying, P. Kozodoy, J. P. Ibbetson, S. Keller, S. P. DenBaars, J.S. Speck, and U.K. Mishra, Appl. Phys. Lett, 76, 718, 2000

7. T.H. Myers, A. Ptak, L.T. Romano, J.E. Northrup, C.G. Van de Walle, unpublished

8. L.T. Romano, J. E. Northrup, M. A. O'Keefe, Appl. Phys. Lett. **69**, 2394 (1996)

9. J.M. Zuo, CBED Simulation Program, Arizona State University

10. R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994). The plane wave cutoff energy used in these calculations is 40 Ry.

11. The construction of a (11$\underline{2}$3) boundary structure that satisfies the electron counting rule requires replacement of ¾ of the Ga atoms by Mg. Calculations for such structure would require the use of a unit cell containing 12 threefold atoms.

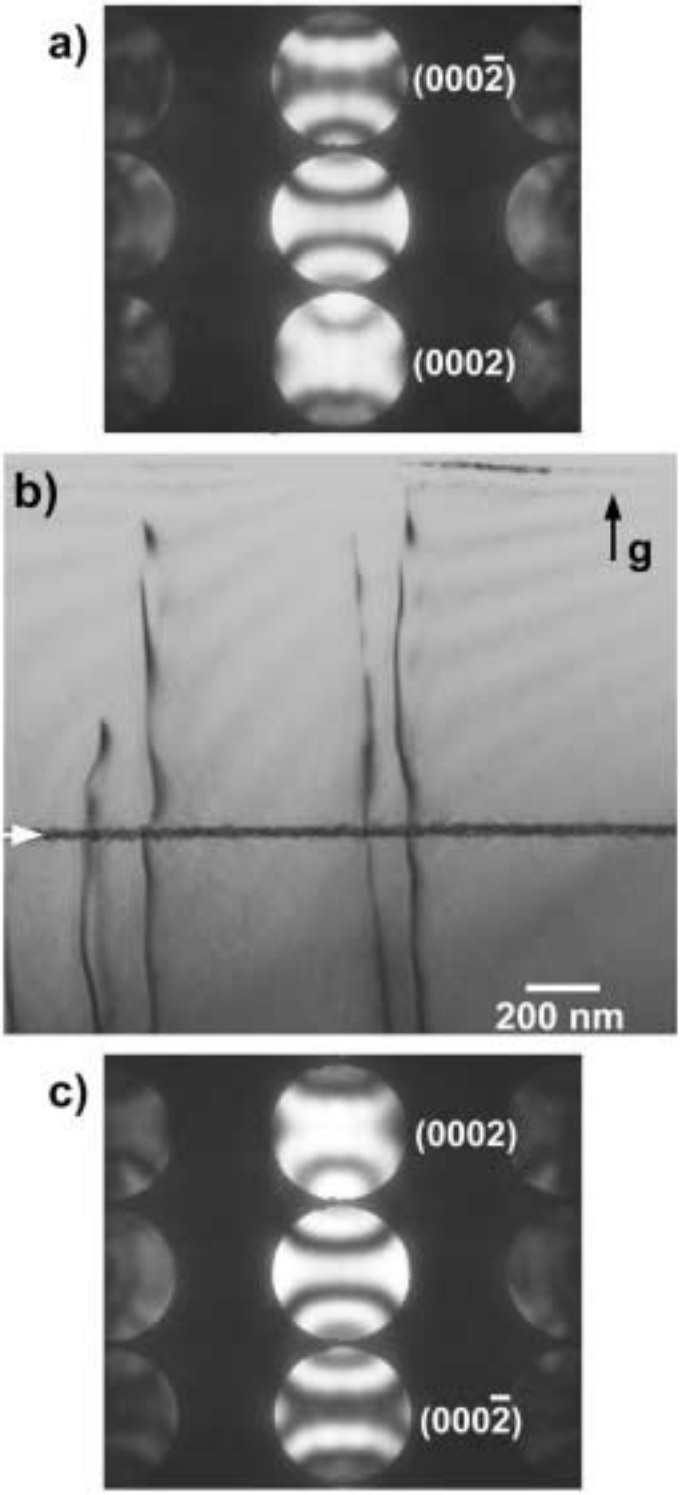


Fig. 2

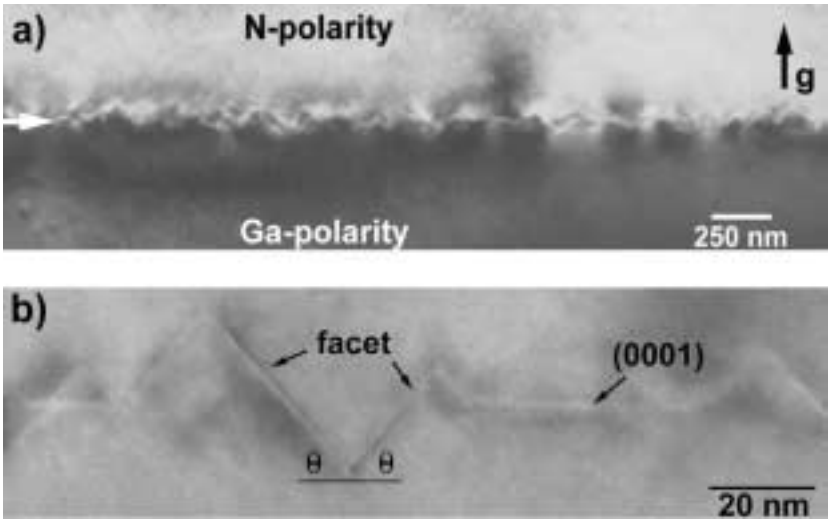
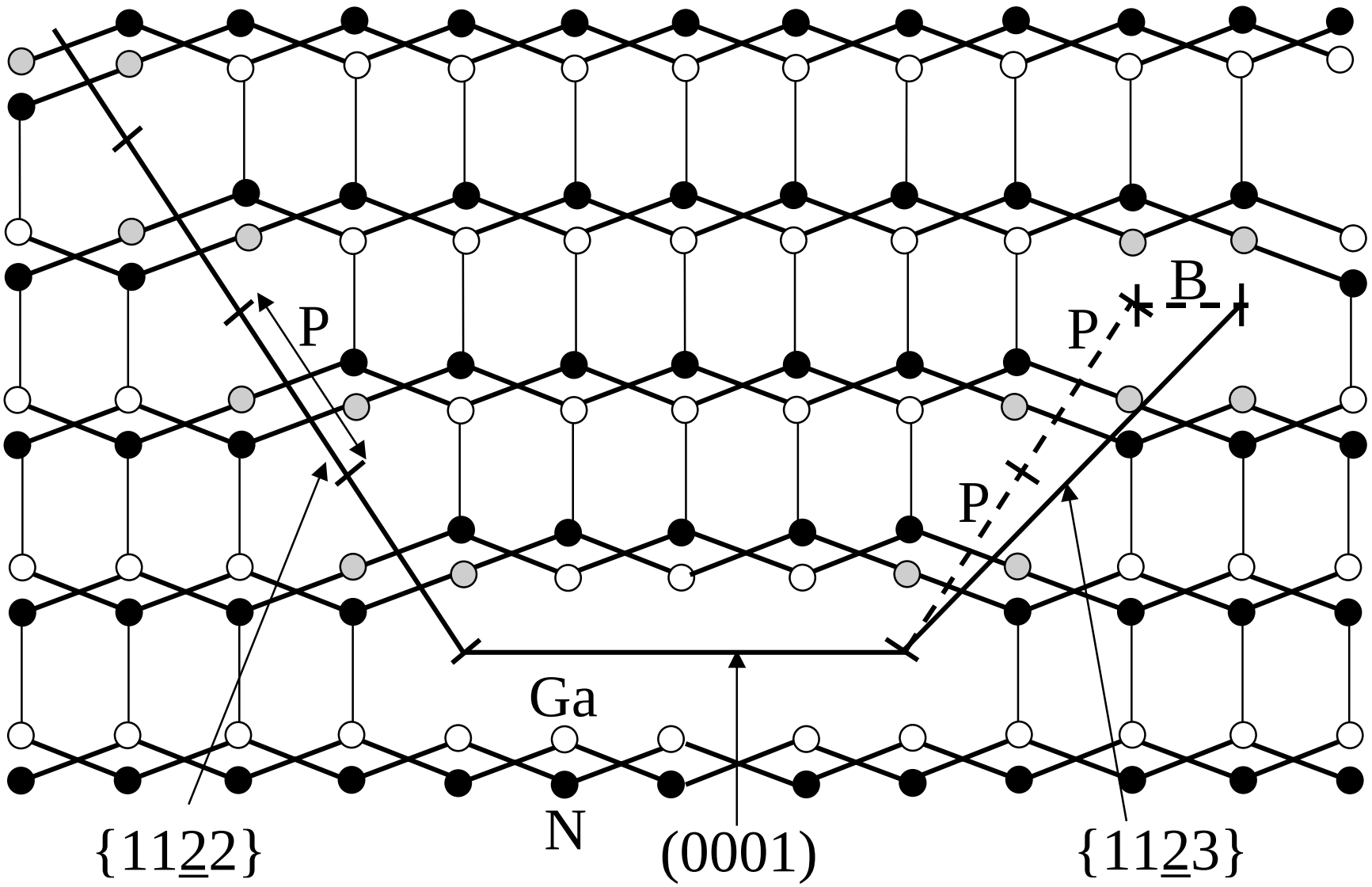
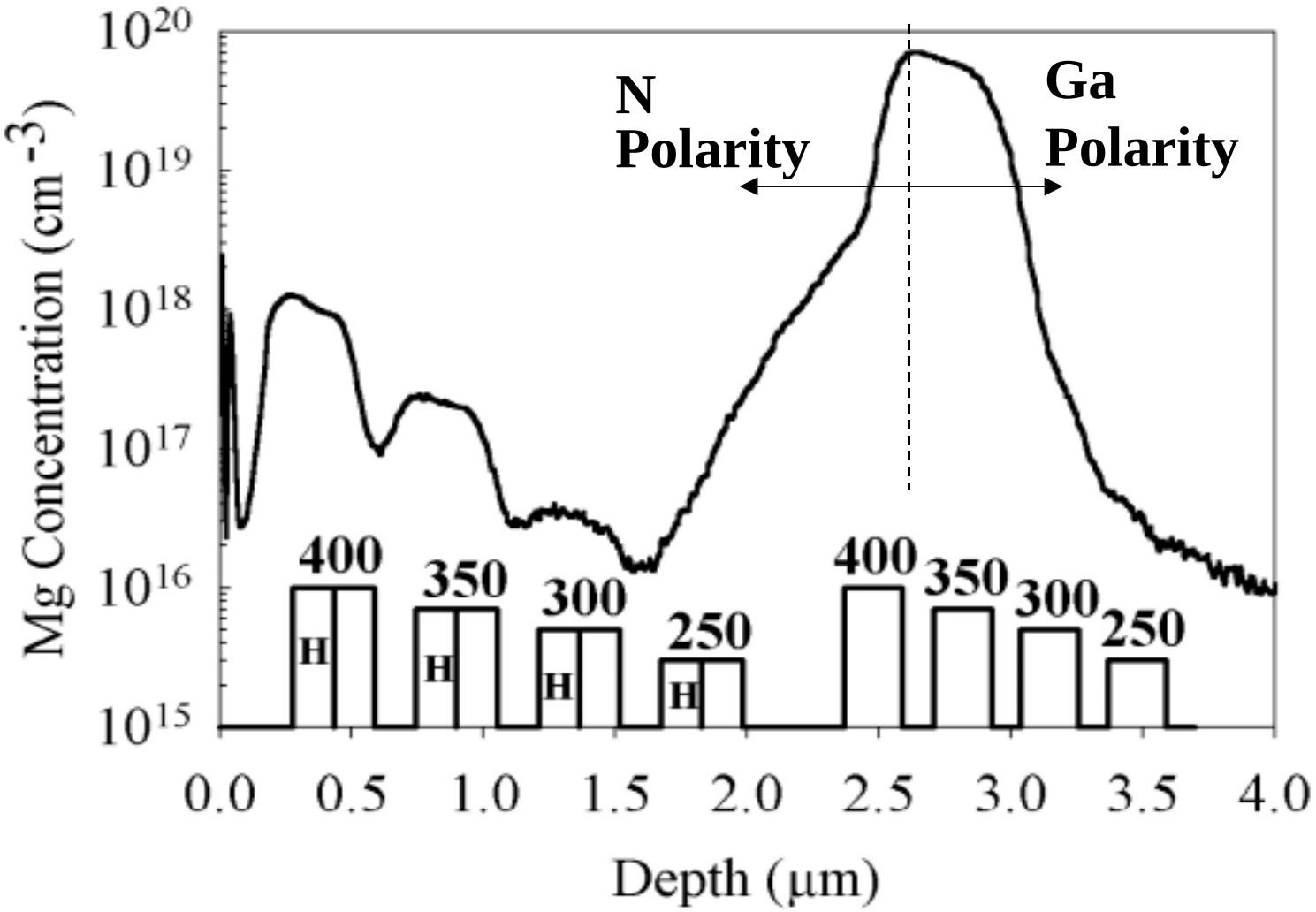


Fig. 3


P
P
B
P
Ga
N
{11$\bar{2}$2}
(0001)
{11$\bar{2}$3}


N
Polarity
Ga
Polarity
400
350
300
250
400
350
300
250
H
H
H
H
Mg Concentration (cm -3)
10^20
10^19
10^18
10^17
10^16
10^15
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Depth (μm)