Surface sensitivity of impurity incorporation: Mg at GaN (0001) surfaces

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The interplay of surface termination, reconstruction patterns, and availability of species involved determines the incorporation of impurities during growth. We study *ab initio* this interplay for Mg at the GaN (0001) surfaces and find that optimal incorporation conditions *strongly depend* upon surface orientation and *cannot be predicted* using bulk stoichiometric arguments. With reasonable assumptions on the kinetics, high densities of Mg can be achieved in the absence of hydrogen and the Ga surface displays superior incorporation characteristics to that of the N surface. [S0163-1829(99)02615-6]

Controlled incorporation of impurities is critical to semiconductor science and technology. Specific dopant concentrations are necessary to achieve desired conductivities, recombination rates in light emitting devices, or other electrical characteristics. In general, doping of bulk materials can be performed in three different ways: (i) by in-diffusion following growth, (ii) by ion implantation, and (iii) during growth. The in-diffusion of impurities is limited by the maximum solubility, which is a thermodynamic quantity that can be determined from either experiments or calculations. Ion implantation has no such limit, but in many materials the implantation damage is severe and cannot be annealed out, limiting the usefulness of this technique. During growth, the incorporation of an impurity occurs at the surface and depends sensitively upon the surface and its environment. For example, Tersoff[1] has emphasized that impurity energetics and consequently its solubility in the near-surface region can be significantly different from that in the bulk. This is because under typical growth conditions, diffusion at the surface is much faster than in the bulk and the impurity density of the near-surface region can be frozen in as the film grows, leading to a concentration in the grown film different from that expected on the basis of its bulk solubility. Indeed, under these conditions it is the surface properties, instead of the bulk properties, that most strongly influence the impurity concentration. This is particularly true in a compound semiconductor, where many variables affect impurity incorporation during growth. Surface reconstruction patterns are often complex; in a given growth direction there are at least two possible surface terminations, and the surface structure varies as a function of the chemical potentials of the atomic constituents. The interplay of these effects leads to a complicated doping behavior, which, however, can be used to achieve a desired impurity concentration.

In the following, we examine the incorporation of Mg in wurtzite GaN, which is an important paradigmatic case. There is a growing awareness that the two polarities of the (0001) GaN surface, nominally corresponding to the Ga and N faces, exhibit very different behavior. Indeed, striking differences have been observed in the morphology of the (0001) and $(000\bar{1})$ surfaces,[2–9] and the strongly ionic nature of the GaN bond together with the low symmetry of the surface results in unusual reconstruction patterns that differ significantly from those observed in other III-V semiconductors. Since as-grown GaN exhibits unintentional *n*-type conductivity and controlled doping of GaN is necessary for optoelectronic devices, the achievement of good *p*-type conductivity has been a priority. However, Mg, which is the preferred *p*-type dopant, has a relatively large ionization energy. Consequently, high Mg concentrations are required to achieve the desired hole densities. In practice, the refined control of doping required to obtain reproducibly the particularly high Mg concentrations needed has been difficult to accomplish. In a number of experiments, post growth processing by either electron irradiation[10] or thermal annealing[11] was necessary to obtain *p*-type conductivity, and it has been proposed that H plays a major role in increasing the incorporation of electrically active Mg. In contrast, other experiments have shown that a relatively high incorporation of Mg can be achieved independently of H,[12–15] demonstrating that incorporation of impurities is a process highly sensitive to the particular growth conditions. The aim of the following article is to investigate the influence of surface orientation on the growth conditions for optimal impurity incorporation while including the chemical effects. For the case of Mg, the growth conditions for optimal dopant incorporation are *reversed* when the Mg is incorporated through a surface of different orientation (in this case, the film has different polarity). We will further show that the interplay of surface orientation, reconstruction patterns, and the availability of the species involved (as measured by their chemical potentials) determines the incorporation characteristics, and that intuition derived from bulk solubility considerations may be misleading. For example, superior incorporation of Mg at the Ga-substitutional site (Mg_{Ga}), which is the preferred site in the bulk,[16] is expected under N-rich conditions, because of the decreased competition between Mg and Ga for the Ga site. However, this reasoning is a poor guide for determining the conditions for efficient incorporation. Growth procedures may therefore need to be tailored in a nontrivial fashion to the properties of the particular growth surface(s) in order to achieve effective doping with specific impurities.

All calculations were carried out within the framework of density-functional theory using a multigrid-based total-energy method that employs a real-space grid as the basis.[17] The Perdew-Zunger parametrization[18] of the exchange-correlation energy was used. Nonlocal, norm-conserving pseudopotentials[19–21] were applied with the Kleinman-

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Bylander approach.[22] We employed a recently developed pseudopotential that includes a nonlinear core correction[23] and permits an efficient description of the gallium species without the need for an explicit treatment of the d-valence electrons.[7,24] For calculations involving the Ga-polar surface, pseudohydrogens of charge 0.75 e passivated the N-terminated, N-polar face, while for those involving the N-polar face, pseudohydrogens of charge 1.25 e passivated the Ga-terminated, Ga-polar surface.[26] A supercell with a grid spacing of 0.27 a.u. was employed after a careful convergence study, thereby ensuring that the real-space description of the pseudopotentials is accurate. Further details of the calculations are given elsewhere.[7,24] Convergence in k points and vacuum size was also investigated. The results obtained using two k-point sampling and four bilayers, of which three were relaxed, provide a level of accuracy of about 0.05 eV.[25]

As the surface stoichiometry is not the same for all the configurations considered here, the relative formation energies depend upon the chemical potentials of the excess atomic species. The relative formation energy is

$$E_f = E - E^{\mathrm{reference}} - \Delta n_{\mathrm{Mg}}\mu_{\mathrm{Mg}} - \Delta n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} - \Delta n_{\mathrm{N}}\mu_{\mathrm{N}},$$

where E is the total energy of the configuration under consideration, $E^{\mathrm{reference}}$ is the total energy of the reference configuration, μ_i is the chemical potential of the ith species, and Δn_{Mg} is the excess or deficit of Mg atoms with respect to the reference; similar definitions hold for Δn_{Ga} and Δn_{N}. At equilibrium, the chemical potential of a given species is equal in all phases that are in contact. This can be exploited to impose constraints on the possible equilibrium values. In particular, we assume that the surface is in equilibrium with the GaN bulk so that $\mu_{\mathrm{Ga}} + \mu_{\mathrm{N}} = \mu_{\mathrm{GaN}}$. Therefore, the phase diagram is simply a function of the III/V ratio and the Mg chemical potential. Further, the chemical potential for Ga cannot be above the chemical potential of its elemental bulk phase, since the bulk phase would then be unstable with respect to precipitation of bulk Ga, while μ_{N} cannot be above $\frac{1}{2}\mu_{\mathrm{N}_2}$. This provides limits for the values that the Ga and N chemical potentials can take. Since we are interested in the highest possible Mg concentration, Mg-rich conditions are chosen. This corresponds to a situation in which the Mg chemical potential is equal to its value in Mg_3N_2.

Since recent experiments have revealed 2×2 RHEED patterns of the Mg-doped GaN surface similar to those occurring during the growth of undoped GaN,[14] we carried out an extensive study of configurations of 2×2 symmetry involving Mg on the most stable 2×2 reconstructions[7,8] and relaxed 1×1 Ga- and N-polar surfaces. We also investigated the behavior of Mg in and below the first bilayer.

At the Ga-polar surface, we studied Mg on four on-surface sites (see Fig. 1) and in the Ga- and N-substitutional sites on the relaxed 1×1 surface and also in combination with the 2×2 adatom reconstructions with $\mathrm{Ga}_{\mathrm{T}_3}$ and $\mathrm{N}_{\mathrm{H}_3}$ adatoms. The calculated relative formation energies for the more energetically favorable configurations are shown in Fig. 2. For most of the range of the chemical potential, Mg in the Ga-substitutional site is the most stable, strongly favored with respect to on-surface adsorption and the N-substitutional site. The adatom reconstructions of the clean Ga surface are deconstructed and the most stable configuration is a 2×2 $\mathrm{Mg}_{\mathrm{Ga}}$ structure. As the environment becomes progressively more gallium-rich, the relative stability of the $\mathrm{Mg}_{\mathrm{Ga}}$ with respect to adsorbed configurations decreases. In extreme gallium-rich conditions, the 2×2 Ga adatom in the T_3 site becomes the most stable. This suggests that Mg adsorption is unfavorable in gallium-rich conditions. Calculations performed at full and 1/16 monolayer coverage show that the 1/4 monolayer of Mg has the lowest energy, consistent with the observed 2×2 RHEED pattern.[14] Thus a saturated surface phase consisting of a 1/4 monolayer of $\mathrm{Mg}_{\mathrm{Ga}}$ is formed as the Mg overpressure is increased. Thus we expect that Mg incorporation should increase with increasing Mg overpressure until the surface phase becomes stable. Subsequent to the formation of this surface phase, the incorporation of Mg should be independent of Mg overpressure. This conclusion is consistent with the dependence of Mg incorporation upon Mg overpressure previously observed.[14]

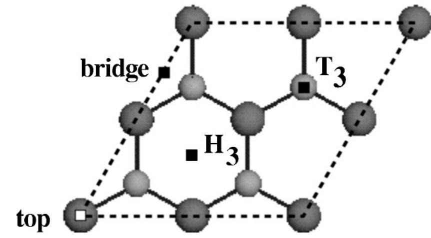

FIG. 1. Schematic top view of the (0001) GaN surface. On the Ga-polar (0001) surface, the dark atoms are gallium atoms, while the light atoms are nitrogen atoms; the situation is reversed on the N-polar $(000\bar{1})$ surface. An atom in the T_3 site (represented by a black square inside of a light circle) sits above a subsurface atom (a light circle), while an atom in the H_3 site (represented by a black square) sits in the hollow site as shown. An atom in the top site (represented by a white square on the inside of a dark circle) sits above a surface atom and an atom in the bridge site is represented by a black square equidistant between two surface atoms. The dashed line shows the 2×2 cell.

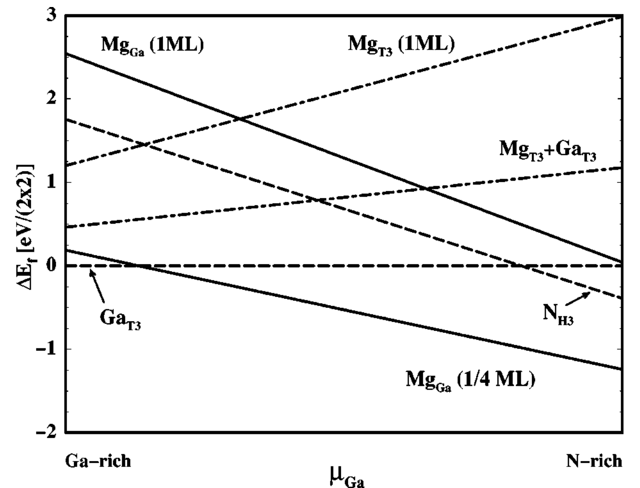

FIG. 2. Relative formation energies for a Mg atom adsorbed at the Ga-polar (0001) surface of GaN as a function of the gallium chemical potential. The energies are reported in eV with respect to the 2×2 $\mathrm{Ga}_{\mathrm{T}_3}$ adatom reconstruction. The dashed lines denote the most stable reconstructions of the undoped system. Only the most stable configurations are shown.

In order to investigate incorporation into a growing film, we studied the behavior of Mg in sites buried in and below the first GaN bilayer. A Mg atom buried in the interstitial or nitrogen-substitutional sites is unstable. It displaces a surface Ga atom and becomes Mg_{Ga}. The ejected Ga atom migrates to a site on the surface. This process occurs spontaneously during the relaxation, indicating a very small or no activation barrier. We conclude that in the near-surface region of the Ga-polar face, Mg is mainly found in the Ga-substitutional site. Further, this suggests that Mg is incorporated through a kick-out mechanism in the near-surface region. For Mg_{Ga} in the third layer the formation energy is 0.48 eV higher than in the surface layer. Over most of the range of chemical potential, Mg_{Ga} in the third layer is more stable than adsorbed sites on the surface. Further, it is energetically more favorable for an Mg to enter the third layer than to desorb and create vacancy.

With reasonable assumptions for the kinetics[1,27] at the GaN surface, we can understand the implications of these results for incorporation. We assume that diffusion in the first two bilayers (the near-surface region) is rapid so that these layers are in equilibrium but that diffusion into, out of, and in the deeper layers (bulk) is negligible. This is consistent with the experimental indications of rapid diffusion[28] and with the available estimates of the diffusion rates in the bulk and at the surface: for N, the activation barrier for diffusion in the bulk is about 4.1 eV,[29] while it is about 1.4 eV and 0.9 eV at the (0001) and $(000\bar{1})$ surfaces, respectively.[30] As the bilayer steps of GaN flow across the surface, the third and fourth layers are converted into bulk and the Mg concentration frozen in. Thus the density of impurities in the bottom bilayer of the near-surface region determines the impurity concentration of the grown GaN film. Using our calculated formation energies, we can estimate the incorporated density. At 1000 K in moderate Ga-rich and N-rich conditions, the density of Mg_{Ga} is on the order of 10^{19} cm^{-3}. This value is near the high end of the range of experimentally observed Mg densities. Thus when growth conditions are judiciously chosen, the presence of H is not necessary to obtain good incorporation densities, as has also been observed in some growth studies.[12–15]

We now turn to the N-polar surface. Already in the absence of Mg, the situation on the N face is very different from the Ga surface. In moderate Ga-rich and N-rich conditions, a 2×2 Ga_{H_3} adatom reconstruction is the most stable, while in a Ga-rich environment a 1×1 Ga adlayer is the most stable and the surface is Ga terminated.[8] At the N-polar surface, we studied Mg on four on-surface sites, namely the T_3, H_3, bridge, and top site, and in the Ga- and N-substitutional sites. We considered adsorption on the relaxed 1×1 N-terminated and Ga-terminated surfaces and also in combination with the 2×2 Ga_{H_3} adatom reconstruction. The calculated relative formation energies for the more energetically favorable configurations are shown in Fig. 3. We first discuss the case of moderate Ga-rich and N-rich conditions and then that of gallium-rich conditions.

Over most of the range of chemical potential, corresponding to moderate Ga-rich and N-rich conditions, a complex consisting of a Ga_{H_3} together with an Mg_{H_3} is the most stable (see Fig. 3). In effect, the presence of Mg extends the stability of the Ga_{H_3} reconstruction further into the gallium-rich regime, thereby decreasing the range of stability of the gallium adlayer. The energy difference between the most stable configuration containing Mg_{Ga}, namely a Mg_{Ga}-Ga_{H_3} complex, and the Mg_{H_3}-Ga_{H_3} adatom complex is at least 1.7 eV. The very large energy required for Mg to go from an on-surface Mg_{H_3} to a Mg_{Ga} in the second layer indicates that there is a strong tendency for Mg to segregate under these conditions.

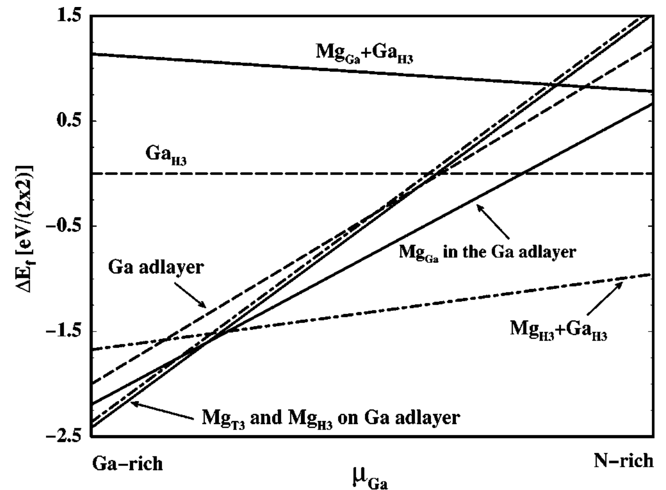

FIG. 3. Relative formation energies for a Mg atom adsorbed at the N-polar $(000\bar{1})$ surface of GaN as a function of the gallium chemical potential. The energies are reported in eV with respect to the 2×2 Ga_{T_3} adatom reconstruction. The dashed lines denote the most stable reconstructions of the undoped system. Only the most stable configurations are shown.

In an environment rich in Ga, Mg prefers to adsorb on the Ga-adlayer in the T_3 and the H_3 positions. The T_3 site is slightly more stable than the H_3 site; however, the energy difference is at the limit of our computational precision. Further, under these conditions Mg_{Ga} is only slightly disfavored with respect to on-surface adsorption. It becomes degenerate over a small range of chemical potential as moderate gallium-rich conditions are approached. The formation energy of Mg_{Ga} buried below one bilayer is 0.8 eV higher than the corresponding site in the surface layer. Making the same assumptions on the kinetics as were made for the Ga face, we estimate the density of incorporated Mg_{Ga} to be on the order of 10^{18} cm^{-3} at 1000 K in somewhat Ga-rich conditions. Thus the presence of the gallium adlayer favors the incorporation of Mg and superior incorporation should occur in somewhat Ga-rich conditions. Thus, beginning in Ga-rich conditions and increasing the N overpressure, one initially expects to see an increased Mg incorporation. However, as the N overpressure continues to increase, the Ga adlayer becomes unstable and a precipitous drop in the concentration of incorporated Mg is expected. This is contrary to conclusions obtained exclusively on the basis of bulk considerations, namely that superior incorporation is expected in N-rich conditions because of a decreased competition between Mg and Ga for Ga sites. Comparing the incorporated densities obtained for the N face with those of the Ga face, we find that the Ga face displays better incorporation characteristics.

In conclusion, the surface orientation, termination, and

availability of species involved play a critical role in impurity incorporation at the low symmetry faces of compound semiconductors. In these semiconductors, the complexity of surface reconstruction patterns, the presence of two polarities for a given growth direction, and the values of the chemical potentials of the atomic constituents (which determine the surface structure) all contribute to a complicated doping behavior. Consequently, bulk solubilities are a poor guide for estimating the conditions for efficient incorporation. Furthermore in materials with significant ionic character, polarity plays a major role in determining the behavior of impurities in the near surface region. In particular, the growth conditions for optimal incorporation may be *reversed* when the same impurity is incorporated into a film of different polarity. For the paradigmatic case of Mg at wurtzite GaN surfaces, superior incorporation occurs when the surface is gallium terminated. Indeed, for the (0001) Ga surface, we find that the best incorporation occurs at N-rich and moderate Ga-rich conditions. On the contrary, for the $(000\bar{1})$ N surface, in N-rich conditions Mg displays a strong tendency to segregate and superior incorporation occurs in a Ga-rich environment. High impurity concentrations can be achieved without hydrogen. Knowledge of the orientation of the growth surface and its behavior is important if the refined control of doping needed to reliably obtain desired incorporation densities is to be achieved.

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