Novel Defect Complexes and Their Role in the p-Type Doping of GaN

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Hydrogen is known to play a key role in p-type doping of GaN. It is believed that H passivates Mg dopants and then is removed by annealing. We present first principles calculations in terms of which we show that the doping process is significantly more complex. Several substitutional-interstitial complexes form and can bind H, with vibrational frequencies that correlate well with hitherto unidentified observed lines. We predict that these defects, which limit doping efficiency, can be eliminated by annealing in an atmosphere of H and N prior to the final anneal that removes H. [S0031-9007(99)08520-8]

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GaN has emerged as the wide-gap material of choice for blue-green optoelectronics, but additional improvements are needed to enhance performance and reliability for commercial applications. A major issue is to increase p-type conductivity. It has been established that H enhances the incorporation of dopants such as Mg, but it must be removed by postgrowth annealing in order to achieve dopant activation [1,2]. In general, only a relatively small fraction of the total Mg is activated [3,4].

Theory has offered a simple account of the process [5,6]: In the absence of H, Mg shallow acceptors are compensated by N vacancies (V_N^+) and Ga interstitials (Ga_i^{+++}) [7], both of which are donors and have low formation energies in p-type material [7]. When H is present, it passivates substitutional Mg (Mg_{Ga}^-) by forming an Mg_{Ga}-N-H complex [5]. The Fermi level then rises to the midgap region and the formation of V_N^+ and Ga_i^{+++} is suppressed. Subsequent annealing removes H and activates Mg_{Ga}^-. Theory in fact predicted the vibrational frequency of the Mg_{Ga}-N-H complex at 3360 cm^{-1} [5] and, more recently, experiments [4] observed a line at 3125 cm^{-1} whose intensity decreases during annealing. Nevertheless, there are unambiguous indications that the doping process is actually more complex. The process of annealing H occurs with an activation energy that is higher than the energy needed to break the Mg_{Ga}-N-H bond [5]. Photoluminescence, infrared, and Raman data show clear evidence that other Mg-related defects are present [1,3,4]. In particular, in material grown by molecular beam epitaxy (MBE), where typically only 10% of Mg is electrically active, infrared and Raman lines in the 2000-cm^{-1} range have been attributed to direct Mg-H bonds [3]. Theory so far has not offered any potential candidates for these complexes.

In this Letter, we present new first-principles calculations of key defect reactions and show that p-type doping is in fact a significantly more complex process. In particular we found that, in addition to Mg_{Ga}-N-H, interstitial Mg (Mg_i) and its complexes play a significant role in controlling the process. In Ga-rich growth conditions, compensation of Mg_{Ga}^- occurs mainly though the formation of Mg substitutional-interstitial pairs with a configuration $(Mg_{Ga}\text{-N-Mg})^+$ analogous to Mg_{Ga}-N-H (Fig. 1a). Other defects that play a role are V_N^+, Mg_i^{++}, Ga_i^{+++}, $(Mg_{Ga}\text{-N-}Ga_i)^{++}$, and Mg_{Ga}-V_N. This plethora of substitutional-interstitial (SI) Mg-related complexes accounts for the high degree of Mg incorporation in electrically inactive forms. When H is present, all of these complexes are passivated, forming *direct* Ga-H and Mg-H bonds. The calculated vibrational frequencies of these bonds are in the 2000-cm^{-1} range and suggest a possible connection with the infrared and Raman lines that have been observed in MBE-grown material and have hitherto remained unexplained [3]. Finally, our analysis yields a testable prediction: For samples that show the vibrational signatures of hydrogenated SI complexes, a preanneal in an atmosphere of N and H followed by annealing in an N atmosphere would significantly enhance Mg activation.

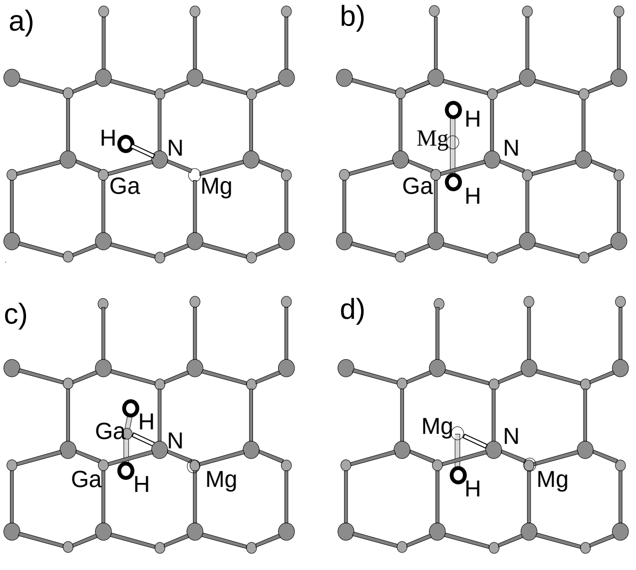

FIG. 1. Schematic representation of some complexes studied in this work. (a) Mg_{Ga}-N-H complex, (b) Mg_iH_2, (c) Mg_{Ga}-N-Ga_i-H_2, and (d) Mg_{Ga}-N-Mg_i-H.

The calculations were performed in the framework of density functional theory and the local density approximation for exchange and correlation, using ultrasoft pseudopotentials and a plane-wave basis set [8]. The Ga $3d$ electrons and the Mg $2p$ electrons were treated as valence electrons. Additional details for the pseudopotentials can be found in Ref. [9]. The energy cutoff for the basis set was chosen at 25 Ry after studies showed convergent results. Supercells of 32 atoms were used in general but some key results were tested in a 64-atom cubic cell to ensure convergence with supercell size. Such supercells were also found to be well converged in similar cases by earlier investigators [9,10]. We used three special $\mathbf{k}$ points corresponding to the hexagonal symmetry [11] in the wurtzite phase and the $\{.5, .5, .5\}$ special $\mathbf{k}$ point in the cubic structure. Results for cubic and wurtzite GaN are generally the same (within 0.1 eV), except in some cases where topology matters. Those cases will be discussed explicitly. All atoms in the supercell were relaxed until the force on each atom was less than 0.15 eV/Å. The calculation of the H-related normal modes involved a partial dynamical matrix that included the H atoms and their neighbors. The normal modes were calculated in the harmonic approximation. In a second step, the anharmonic corrections for the transition from the ground to the first excited state of the stretching modes were calculated in a standard way [12] using the coefficients of the polynomial that fits the energy as a function of the amplitude along the normal mode trajectory.

Much of the theoretical literature on defects and impurities in GaN has so far focused on formation energies. However, in a compound semiconductor the formation energies of point defects are functions of the chemical potential of one of the host atoms and the Fermi energy. In the presence of impurities, formation energies of defect complexes are also functions of the impurity chemical potentials. A comprehensive table of formation energies under all conditions and charge states would be a daunting task, in view of the number of defect complexes we have discovered. Instead, we have carried out our analysis by examining key *sequences of defect reactions*. This approach has the advantage that several total-energy calculations are with the same supercell containing identical atomic species and excess charges. The resulting reaction energies (differences of formation energies using the same supercell) are more accurate, especially when charged point defects are involved, because calculations of accurate absolute formation energies for the latter entail larger uncertainties [5,7]. Absolute formation energies of isolated charged native defects are available in the literature [5–7,9,10]. We have availed ourselves of these results, in particular the more accurate calculations that treat the Ga d electrons as valence electrons.

We start with the doping process in the absence of H. For p-type material and Ga-rich conditions, V_N^+ and Ga_i^{+++} have low formation energies and comparable concentrations [7]. These native defects are deep donors and their electrons recombine with holes so that p-type doping is thwarted. We have taken the next step and investigated the possible reactions of V_N^+ and Ga_i^{+++} with Mg_{Ga}^-. We found the following: (a) Mg_{Ga}-V_N pairs form with a *small gain in energy* (0.4 eV) with respect to the isolated point defects. (b) $(Mg_{Ga}\text{-N-}Ga_i)^{++}$ complexes form with a large gain in energy (1.6 eV). These complexes have a structure similar to that of the Mg_{Ga}-N-H (Fig. 1a) complexes that have been studied extensively by Van de Walle and Neugebauer [5]. In particular, the Ga_i occupies the antibonding site on the N side of a Mg_{Ga}-N bond. Once the complex $(Mg_{Ga}\text{-N-}Ga_i)^{++}$ forms, additional energy is gained by exchanging Mg_{Ga}^- and Ga_i^{+++} to yield interstitial Mg (Mg_i^{++}). The additional energy gain is 1.7 eV, for a net gain of 3.3 eV. Once Mg_i^{++} are available, they pair with isolated Mg_{Ga}^- to form $(Mg_{Ga}\text{-N-}Mg_i)^+$ complexes. This pairing yields an extra energy gain of 0.7 eV, for a *large net energy gain of 4.0 eV* (Table I).

We emphasize that the results of Table I are obtained with identical supercells (same atoms, same charge states) so that the relative energies listed are very accurate. For comparison of the energies of interstitial- and vacancy-related complexes one needs the absolute formation energies of Ga_i^{+++} and V_N^+, which represent a major challenge. Boguslawski *et al.* have reported the most accurate calculations that current capabilities allow and found the two energies to be comparable [7]. Note, however, that, even if the formation energy of Ga_i^{+++} were to be larger than that of V_N^+ by as much as 2.5 eV [5], the SI complexes just described would have to be taken into account to properly describe the physics of p-type doping.

The clear conclusion then is that the entire family of SI defects plays a role in controlling doping. Under equilibrium Ga-rich conditions in the absence of other impurities, $(Mg_{Ga}\text{-N-}Mg_i)^+$ is the dominant defect responsible for thwarting p-type doping, followed by Mg_i^{++}, and $(Mg_{Ga}\text{-N-Ga})^{++}$. In p-type material under equilibrium N-rich conditions, Ga_i are suppressed in favor of other native defects [5,7] which do not exchange with Mg_{Ga}. On the other hand, if thermodynamic equilibration does not occur during growth at low temperatures, the formation of defects is governed by kinetics so that any or all stable defects may form irrespective of their formation energies.

We turn now to the case when H is present. We confirmed the known result that Mg_{Ga}^- binds an H

TABLE I. Relative formation energies of different defects in p-type GaN in Ga-rich conditions. A doped crystal with a concentration of sustitutional Mg_{Ga}^- and a Ga_i^{+++} or V_N^+ is the zero energy references, as indicated.

Complex	Energy (eV)
$[Mg_{Ga}^-]; Ga_i^{+++}$	0 (reference)
$(Mg_{Ga}\text{-N-}Ga_i)^{++}$	−1.6
Mg_i^{++}	−3.3
$(Mg_{Ga}\text{-N-}Mg_i)^+$	−4.0
$[Mg_{Ga}^-]; V_N^+$	0 (reference)
Mg_{Ga}-V_N	−0.3

atom in a Mg_{Ga}-N-H configuration. In addition, the SI complexes bind one or two H atoms, depending on their formal charge, and Ga_i^{+++} binds up to three H atoms. In particular, we carried out detailed calculations on the following complexes $(Mg_{Ga}\text{-N-}Ga_i\text{-H})^+$, Mg_{Ga}-N-Ga_i-H_2, $(Mg_iH)^+$, Mg_iH_2, and Mg_{Ga}-N-Mg_i-H. In this context we note that the distinction between cubic and hexagonal GaN is important: The geometries of some of the hydrogenated SI complexes are quite different in the two isomorphs (we will discuss the geometries later in the paper). From here on, we will confine our discussion to hexagonal GaN, which is the material that is most commonly used for experiments and device fabrication.

There is a substantive difference between Mg_{Ga}-N-H and the hydrogenated SI (SI-H) complexes: In Mg_{Ga}-N-H, H acts as a donor constituent, whereas in the SI-H complexes, H acts as an acceptor constituent. The latter have occupied energy levels in the gap which are consistent with higher formation energies (Table II below). Nevertheless, as we shall see below, the SI-H complexes play a key role in the nonequilibrium processing that is needed to achieve p-type doping.

Local vibrational modes (LVMs) are often powerful tools that allow identification of defects. In early GaN work, several lines in the vicinity of 2150 cm^{-1} were detected by infrared and/or Raman [3] and were attributed to Mg_{Ga}-H stretch modes because they were absent in control samples without Mg [3]. Subsequent theory, however, found that H does not bind directly to Mg_{Ga}, but rather forms the Mg_{Ga}-N-H complex whose calculated vibrational frequency is 3360 cm^{-1} [5]. It was also found that, in a hydrogenated N vacancy, the Mg-H LVM is only 700 cm^{-1} [6]. In recent experiments, however, Götz *et al.* [4] detected the 3125-cm^{-1} infrared line that corresponds to Mg_{Ga}-N-H and observed it decrease as a function of annealing that activates Mg acceptors. They did not report measurements in the 2000-cm^{-1} range. Measurements below 2000 cm^{-1} are not available at all, largely because the common substrates are opaque for much of this range. Thus, the experimental picture is incomplete and has not established the conditions under which different lines can be detected.

We calculated the LVMs of several SI-H complexes and found Mg-H and Ga-H modes in the vicinity of 2000 cm^{-1}. The uncertainty in the calculations is about 200 cm^{-1} so that defect identification cannot be made by simply comparing theoretical and experimental vibrational frequencies. Symmetry and other considerations, however, allow us to suggest possible connections with the reported observations.

Mg_iH_2 is a stable complex with the Mg_i near the hexagonal (O) interstitial site [7] (see Fig. 1b). The two H's are oriented along the c direction at both sides of the Mg_i. The defect has a C_{3v} point group symmetry. There is no reflection symmetry along the c direction. Accordingly, the two H's are located in inequivalent positions and, as a consequence, the two Mg-H bond lengths are different, namely, 1.55 and 1.78 Å. The two "spring constants" are also different and, as a result, the two H's oscillate almost independently of each other. The short Mg-H bond yields a stretch mode at 2001 cm^{-1} (including anharmonic corrections). The long Mg-H bond yields a stretch mode at 1570 cm^{-1}. In order to complete the description of the system, we give the wag-mode frequencies of the defect at 1370 and 1200 cm^{-1} for the short and long bonds, respectively. The entire "molecule" oscillates with frequencies lower than 500 cm^{-1}.

In both Mg-H stretch LVMs, the atoms vibrate in the c direction, making it difficult to detect by infrared absorption if the wave vector of the incident light is also in the c direction. This result and the calculated frequencies of the short-bond stretch LVM of Mg_iH_2 correlate well with the lines at 2151 and 2185 cm^{-1} observed in Raman but not in infrared experiments [3]. The long-bond stretch LVM frequency is too small compared with the second peak of the pair in the experimental data. The latter may be due to an anharmonic coupling between the stretch mode and the vibration of the whole molecule. The frequencies of these "molecular" modes are low enough for their first excited states to be populated at room temperature. If this is the case, the relative amplitude of these peaks should be a function of the temperature.

We now consider the complex Mg_{Ga}-N-Ga_i-H_2. In this structure, the H's (see Fig. 1c) are located on either side of Ga_i as in Mg_iH_2 (see Fig. 1b). Again, we found a short Ga-H bond (150 Å) and a long Ga-H bond (182 Å). The symmetry is no longer C_{3v} because of the presence of Mg_{Ga}. Consequently, the Ga_i-H bonds are not oriented exactly in the c direction so that the stretch modes are accessible to infrared spectroscopy when the wave vector of the light is in the c direction. We obtained a frequency of 2270 cm^{-1} for the short-bond stretch LVM and 1500 cm^{-1} for the long-bond stretch LVM. The high-frequency LVM correlates well with the second pair of peaks reported by Brandt *et al.* at 2168 and 2219 cm^{-1} [3]. Here again the pair of excitations may be due to the influence of anharmonic couplings.

Finally, in Fig. 1d we show schematically the structure of Mg_{Ga}-N-Mg_i-H. The stretch mode frequency of this complex is calculated to be 1320 cm^{-1}. Measurements in the range 1000–2000 cm^{-1}, presently hampered by opaque substrates, would be highly desirable to test the theoretical predictions.

We now discuss the implications of the above results on understanding the doping process during growth by MBE or chemical vapor deposition (CVD). During growth by MBE, the temperature is relatively low (~800 °C) and H is present unintentionally [3]. Experiments have shown that p-type doping is achieved with about 10% of the Mg in the sample being active. In material with very high Mg content (10^{20} cm^{-3}), moderate H content ($>10^{19}$ cm^{-3}), and low doping efficiency, distinct infrared and Raman lines have been observed in the vicinity of 2200 cm^{-1} [3]. Our analysis correlates these lines with SI-H

TABLE II. Relative formation energies of H-compensated defects (in eV). The H chemical potential is chosen to be the formation energy of H_2 in an interstitial site.

Complex	Ga-rich, H-rich	N-rich, H-rich
Mg_{Ga}-N-H	0 (reference)	-3.6
Mg_iH_2	3.9	3.9
Mg_{Ga}-N-Ga-H_2	4.2	4.2
Mg_{Ga}-N-Mg_i-H	4.1	0.5

complexes, which limit doping efficiency. It also suggests a process to eliminate the undesirable SI-H complexes and increase doping efficiency: Annealing in a *H-rich atmosphere* or, better yet, in an atmosphere rich in both H and N will lead to the conversion of the SI-H complexes to Mg_{Ga}-N-H complexes. This result follows naturally from the fact the SI-H complexes have larger formation energies (Table II). The N atmosphere helps by suppressing formation of Ga_i and V_N, both of which are detrimental to p-type doping [5,7], and favors formation of V_{Ga} *whose presence helps convert* Mg_i to Mg_{Ga}. A subsequent anneal in a N-rich atmosphere would activate Mg as in the case of the CVD-grown films [1] (see also below).

During CVD growth of GaN, H is introduced in ample quantities at relatively high temperatures (>1000 °C). If the material was fully equilibrated, the dominant hydrogenated defect would indeed be Mg_{Ga}-N-H, as suggested by earlier theory [5] and confirmed by Table II. There are strong indications, however, that the material is generally not fully equilibrated. In their pioneering and extensive studies of CVD GaN, Nakamura *et al.* [1] found photoluminescence peaks which they attributed to Mg-H complexes. These experiments provide information about the energy levels of the underlying defects but no structural information. Theoretical results on energy levels are not reliable for identification purposes. It would be highly desirable to correlate the luminescence data with infrared and/or Raman data to facilitate identification.

It is possible that, by empirical means, suppression of SI-H defects is currently achieved in the growth of high-quality GaN. Nevertheless, systematic infrared and Raman data in both the 2000- and 3000-cm^{-1} range would help unravel further the complexity of p-type doping. For example, SI-H defects are a natural candidate to account for the fact that annealing CVD material to remove H requires higher temperatures than theory can account for in terms of breaking the H bonds in the Mg_{Ga}-N-H complexes [5]. The rate-limiting step for Mg activation may very well be determined by the conversion of SI-H complexes to Mg_{Ga}-N-H. We, therefore, propose the following: CVD samples should be checked for the presence of SI-H complexes via their infrared signatures in the 2000-cm^{-1} range. If present, a preanneal in a H and N atmosphere, followed by annealing in an N atmosphere, would again produce optimum activation.

In summary, we have shown that complexes involving self-interstitials and interstitial impurities play a major role in the p-type doping process. The theoretical prediction of these defects correlates very well with the infrared and Raman lines observed in MBE-grown material. The combined experimental and theoretical information suggests that the control of these defects is the ultimate key in achieving higher p-type conductivity. Systematic experimental studies, especially using infrared and Raman spectroscopies, guided by the present theoretical results, would offer the promise of achieving higher p-type conductivity. The most important conclusion of the present work is that an annealing stage in H-rich atmosphere, followed by annealing in a N-rich atmosphere would generally improve p-type doping efficiency. We anticipate that similar defect complexes may also form in the case of other dopants such as Be and possibly in the case of n-type dopants as well as in other wide-gap semiconductors.

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Note added.—Kaschner *et al.* (MRS Fall meeting, abstract G3.57) report several new Raman lines and attribute them to Mg-H bonds.

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