

ROLE OF HYDROGEN AND HYDROGEN COMPLEXES IN DOPING OF GaN

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ABSTRACT

We have calculated electronic structure, energetics and migration for hydrogen and hydrogen complexes in GaN employing state-of-the-art first-principles calculations. Using these results in combination with previous detailed investigations about native defects we have calculated the concentration of hydrogen and dopants for different growth conditions. Our results reveal a fundamental difference in the behavior of hydrogen in *p*-type and *n*-type material. In particular, we explain why hydrogen has little effect on donor impurities and why H concentrations are low in *n*-type GaN. We discuss why hydrogen is beneficial for acceptor incorporation in GaN, and identify the limitations of this process.

INTRODUCTION

Hydrogen is a well known impurity which plays an important role in semiconductors by compensating or passivating native defects and impurities, saturating dangling bonds or forming complexes. In high-temperature growth techniques [such as metalorganic vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE)] which are commonly employed for GaN growth hydrogen is highly abundant. Several experimental investigations indicate that hydrogen plays an important role in the doping of GaN: Nakamura *et al.* demonstrated that Mg-doped and initially semiinsulating GaN can be made *p*-type by thermal annealing in vacuum and nitrogen ambient but not in NH₃ or H ambient.[1] Furthermore, Nakamura *et al.* showed that the activation of the Mg acceptors can be reversed by annealing in a hydrogen ambient,[1] revealing the crucial role played by hydrogen. Based on these observations Van Vechten *et al.* suggested that hydrogen enables *p*-type doping by suppressing compensation by native defects.[2] These authors went on to propose the incorporation (and subsequent removal) of hydrogen as a general method for improving *p*-type as well as *n*-type doping of wide-band-gap semiconductors. The Van Vechten model highlights the important role of hydrogen, but leaves various issues unexplained, such as the lack of hydrogen incorporation in *n*-type GaN, and the success of *p*-type doping (without post-growth treatments) in MBE (molecular-beam epitaxy).

In the present paper we summarize the properties H exhibits in GaN and discuss how H affects doping in GaN. In particular, we explain why H is beneficial for *p*-type doping but has little effect on donor impurities. Based on these results we identify the specific conditions under which H is beneficial and discuss the limitations of this process.

METHOD

Employing first-principles density-functional theory we have calculated the total energy surface, electronic structure and atomic geometry for hydrogen in all relevant charge states (H^+ , H^0 , H^-). [3] 32-atom supercells were used and atomic relaxation is fully taken into account. The calculations were performed for cubic GaN which has a higher symmetry than the wurtzite structure. As shown in Ref. [4] the wurtzite and the cubic phase show nearly equivalent formation energies and electronic structure for defects. We expect therefore that the results are valid both for H in zincblende and wurtzite GaN. The electron-ion interaction is described by soft Troullier-Martins pseudopotentials. [5] Details of the computational approach can be found elsewhere. [6, 7, 8]

The key to describing doping issues is the calculation of the equilibrium concentrations of dopants, impurities and native defects:

$$c = N_{\text{sites}} \exp^{-E^f/k_B T} \quad (1)$$

where N_{sites} is the number of sites the defect or impurity can be built in, k_B the Boltzmann constant, T the temperature, and E^f the formation energy. The formation energy is not a constant but depends on the various growth parameters. To be more specific, the formation energy of a Mg acceptor is determined by the relative abundance of Mg, Ga, and N atoms. If the Mg acceptor is charged, the formation energy depends further on the Fermi level (E_F), which acts as a reservoir for electrons. Forming a substitutional Mg acceptor requires the removal of one Ga atom and the addition of one Mg atom; the formation energy is therefore:

$$E^f(\text{GaN:Mg}_{\text{Ga}}^q) = E_{\text{tot}}(\text{GaN:Mg}_{\text{Ga}}^q) - \mu_{\text{Mg}} + \mu_{\text{Ga}} + qE_F \quad (2)$$

where $E_{\text{tot}}(\text{GaN:Mg}_{\text{Ga}}^q)$ is the total energy derived from a calculation for substitutional Mg, and q is the charge state of the Mg acceptor. Similar expressions apply to the hydrogen impurity, and to the various native defects.

For the following discussion we will fix the chemical potentials. For the Ga chemical potential we assume Ga-rich conditions (which appear to be common in experimental growth conditions). For Mg we are interested in the highest possible concentration. We therefore set the Mg-chemical potential to its upper limit which is given by the formation of Mg_3N_2 ($\mu_{\text{Mg}} = \mu_{\text{Mg}_3\text{N}_2}$); increasing the Mg-chemical potential further makes the system thermodynamically unstable against the formation of Mg_3N_2 droplets or precipitates. Using the same arguments we set the H chemical potential to that of H_2 molecules and the Si chemical potential to that of Si_3N_4 . Using these values for the chemical potentials the formation energy is solely a function of the Fermi energy.

ROLE OF H IN DOPING

Before discussing the role of H in p -type doping let us briefly focus on the H-free case, i.e., only the acceptor (Mg) and native defects are present. Figure 1(a) shows the corresponding formation energies as a function of the Fermi energy. The dominant native defect under p -type conditions is the N vacancy; all other defects are higher in energy. The slope of the formation energies characterizes the charge state; a positive slope (as found for the N vacancy) indicates a positive charge state, corresponding to a donor. For Mg the kink in the formation energy describes a change in the charge state from neutral to negative as characteristic for an acceptor. The position of the kink at $E_F \approx 0.2 \text{ eV}$ gives

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Page 2 of 6

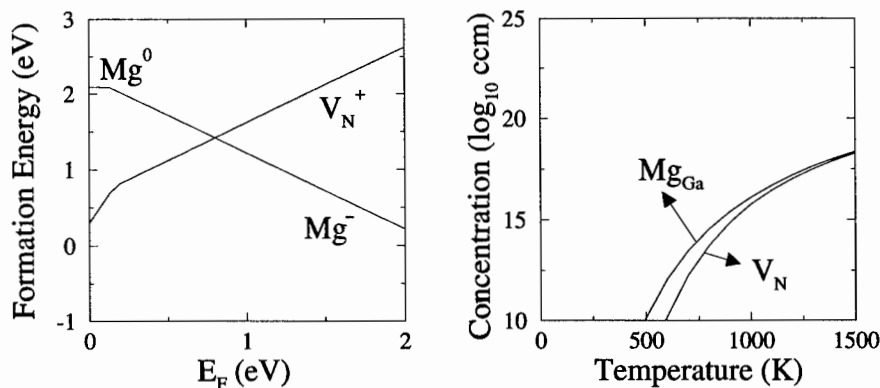


Figure 1: Formation energy vs. Fermi level for the Mg_{Ga} acceptor and the native defects. The corresponding equilibrium concentrations are given in (b). Ga-rich conditions are assumed.

the position of the calculated acceptor level, which is close to the experimental value of 0.16 eV.[9]

Using the calculated formation energies, and taking into account that the Fermi energy is fixed by the condition of charge neutrality, the equilibrium concentration [Eq. (1)] for each defect can be calculated as a function of temperature. The results are shown in Fig. 1(b). As expected, the Mg concentration increases with increasing temperature. However, with increasing temperature the N vacancy concentration also increases; at temperatures exceeding 1000 K the Mg acceptors become increasingly compensated by N vacancies. Native defect compensation is therefore potentially an important concern for high-temperature growth techniques. Low temperature growth techniques such as MBE should suffer less from this problem. This conclusion would be consistent with the fact that only in MBE-grown GaN can *p*-type conductivity be achieved without any post-growth processing.[10, 11]

We will now consider H-rich conditions which are characteristic for many of the high-temperature growth techniques such as MOCVD and HVPE. Figure 2(a) shows that under these conditions H becomes the dominant donor; the formation energy of H is in the considered interval of Fermi energies always lower than the dominant native defect, the N vacancy. The calculated equilibrium concentrations are displayed in Fig. 2(b). The Mg and H concentration are for all temperatures virtually identical indicating that H completely compensates the Mg acceptors. Further, compared to the H-free case the concentration of Mg acceptors is *increased* and the defect concentration is *decreased*. Both effects are crucial to increase doping levels.

What is the mechanism by which H changes the acceptor and defect concentration? In a plot such as Fig. 1(a) and 2(a), the Fermi level position can be roughly estimated to be near the crossing point between the acceptor and the dominant donor species. At this point their formation energies (and hence their concentrations) are equal, ensuring charge neutrality.[12] By going from H-free conditions (only Mg and N-vacancies are present) to H-rich conditions the crossing point shifts to higher Fermi energies (from ≈ 0.8 eV to ≈ 1.2 eV). An increase in the Fermi energy *generally* decreases the formation energy

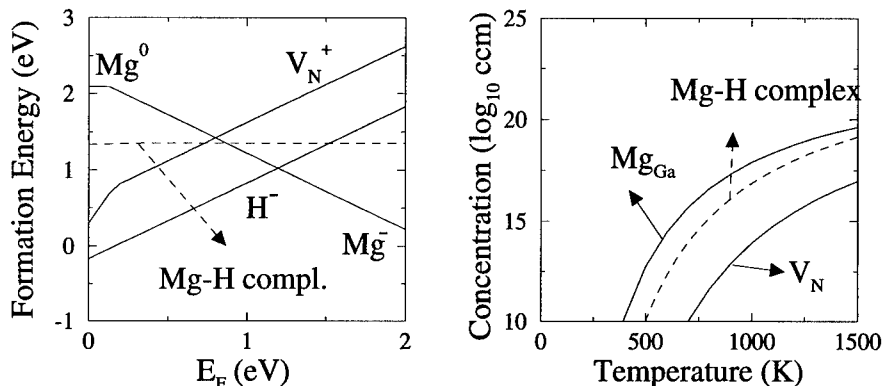


Figure 2: Formation energy vs. Fermi level for the Mg_{Ga} acceptor and the neutral $Mg-H$ complex. Also included are the native defects and interstitial H. The corresponding equilibrium concentrations are given in (b) as a function of the growth temperature. H rich conditions are assumed.

of acceptors and increases the formation energy of donors (defects), thus resulting in a lowered defect concentration and an increased acceptor concentration. We note that this mechanism works only if H is able to significantly shift the Fermi energy which is the case if (i) H is the dominant donor (i.e., its formation energy must be lower than that of all native defects) and (ii) its formation energy must be comparable to that of the dopant impurity (a crossing point must exist in the band gap). It is interesting to note that condition (ii) is not valid for n -type doping with, e.g., Si.[13] The reason is that H under n -type conditions has a higher formation energy than under n -type conditions;[3] the Si donor has for all Fermi energies a lower formation energy.

ACTIVATION MECHANISM OF THE DOPANTS

Despite the fact that growing under H-rich conditions improves acceptor and defect concentrations, Fig. 2(a) shows that the Mg acceptors are almost completely compensated by the H impurities. In order to activate the Mg acceptors, post-growth treatments are necessary to eliminate the compensation by H.

The H donors and Mg acceptors can actually form electrically neutral complexes with a binding energy of ≈ 0.7 eV [see Fig. 2(a)].[3] For the specific choice of chemical potentials made here, this binding energy is low enough for the complexes to be dissociated at the growth temperature; however, the Mg and H will form pairs when the sample is cooled to room temperature, consistent with experimental observations.[14]

The first step in the activation process is the dissociation of the $Mg-H$ complex (see Fig. 3). Our estimated dissociation barrier for the complex is 1.5 eV, calculated by considering a jump to a nearest-neighbor site; the total barrier may be slightly higher.[3] This barrier should be low enough to be overcome at modest annealing temperatures (around 300°C). Experimental results show, however, that activation has to be carried out at much higher temperatures ($> 600^\circ\text{C}$) [1]. The reason is that dissociation alone is insufficient; in

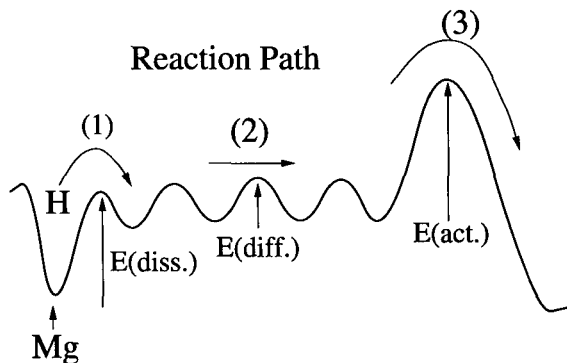


Figure 3: Schematic picture of the reaction path and characteristic energy barriers for the activation of the Mg acceptors. At low temperatures the H forms a neutral complex with the Mg atom. With increasing temperature the Mg-H complex dissociates (1), the positively charged H can then easily migrate through the GaN crystal (2). Increasing further the temperature allows the H to overcome the activation barrier (3) and become electrically inactive.

order to prevent the H from compensating the Mg acceptor it has to be either removed (to the surface or into the substrate) or neutralized (e.g., at an extended defect).

The calculated diffusion barrier for H^+ in GaN is low ($\approx 0.7\text{ eV}$ [3]) indicating that H^+ is highly mobile and can easily migrate to the surface or extended defects. The high temperature necessary to activate the Mg acceptors therefore reflects an activation barrier for eliminating H as compensating center by incorporating it at extended defects (which typically occur in high concentrations in GaN[15]) or by removal of H through desorption at surfaces.

GENERAL CRITERIA FOR HYDROGEN TO ENHANCE DOPING

The mechanism by which hydrogen enhances doping works only under specific conditions. First of all, hydrogen must be the dominant compensating defect (i.e., its formation energy must be lower than that of all native defects, and comparable to the formation energy of the dopant impurity). Second, it must be possible to remove hydrogen from the doped layer after growth; an anneal at high temperature will work only in a specific temperature window. On the one hand, the temperature must be *high* enough to enable all three processes necessary to eliminate H as compensating center: complex dissociation, migration, and overcoming of the activation barrier (see Fig. 3). We call the lowest temperature where this mechanism occurs T_1 . On the other hand the temperature must be *low* enough ($< T_2$) to keep the dopant impurity immobile, and to prevent the formation of other compensating defects; in the case of Mg doping of GaN, an anneal at too high a temperature would lead to Mg compensation by N vacancies, as shown in Fig. 1. Thus, a necessary condition for this mechanism to work is $T_1 < T_2$.

This condition is met in *p*-type GaN, judging by the success of thermal annealing

procedures.[1] We note that the above analysis is *general* and applies to dopants in any semiconductor. Whether the condition is realized, however, depends on the specific parameters of a system (migration barriers of impurities and defects, activation energies, etc.) and must therefore be addressed independently for each system. It is interesting to note that even for GaN (where the method works well for acceptor doping) it does not work for donor impurities. First of all, the formation energy of H is too high in *n*-type GaN for it to be incorporated in significant concentrations. And even if H *were* incorporated, the high diffusion barrier of H in *n*-type GaN (≈ 3.4 eV [3]) would render it immobile even at very high annealing temperatures, preventing the H from reaching the zones where it can be neutralized or removed.

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