Shallow versus Deep Nature of Mg Acceptors in Nitride Semiconductors

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We investigate the properties of Mg acceptors in nitride semiconductors with hybrid functional calculations. We find that although the thermodynamic transition level is relatively close to the valence band in GaN (260 meV), $\mathrm{Mg_{Ga}}$ exhibits key features of a deep acceptor: the hole is localized on a N atom neighboring the Mg impurity, inducing a large local lattice distortion and giving rise to broad blue luminescence. We show that the ultraviolet photoluminescence peak attributed to Mg acceptors in GaN is likely related to Mg-H complexes, explaining the results of photoluminescence and electron paramagnetic resonance experiments. Predictions for Mg acceptors in AlN and InN are also presented.

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The low efficiency of p-type doping in GaN is an unresolved issue in nitride semiconductors [1,2]. Mg is the only known effective p-type dopant in GaN, making it an essential ingredient in all nitride-based solid-state lighting and electronic devices. While the reports on the electrical properties of Mg-doped GaN are fairly consistent, optical and magnetic resonance measurements indicate intriguing and complex behavior that depends on the growth, doping level, and thermal treatment of the samples [3–9]. Advancements in doping often rely on diagnostic techniques for assessing the presence and properties of dopants, and the lack of consensus on the interpretation of various observed signals currently impedes progress.

Mg-doped GaN exhibits two main luminescence peaks that are directly related to the presence of the Mg dopants: a peak at 3.27 eV, which we will refer to as the ultraviolet luminescence (UVL) [10], and a broader luminescence peak centered at 2.8 eV, which has been labeled the blue luminescence (BL). The UVL is usually observed in as-grown Mg-doped GaN and has commonly been attributed to a transition from a shallow donor to the supposedly shallow Mg acceptor [4–7]; other origins have been suggested, though [10]. Annealing or electron-beam irradiation aimed at activating the Mg acceptors by removing hydrogen impurities leads to a significant decrease in the intensity of the UVL [4,6,7]; simultaneously the deep, broad BL emerges [3,4,7]. The microscopic origins of this line have long been debated. Because the BL appears at much lower energy than the band gap of GaN (2.8 vs 3.5 eV), deep centers have traditionally been invoked to explain its origin [5,7,11]. In particular, it has often been ascribed to recombination from deep donors to shallow Mg acceptors, yet the donor centers have never been experimentally identified [8].

Based purely on the evolution of photoluminescence (PL) and conductivity upon annealing, Occam's razor would assign the UVL to Mg-H complexes, and the BL to the $\mathrm{Mg_{Ga}}$. Such an interpretation has been disregarded, however, because it seems to conflict with accepted notions. Indeed, Mg behaves as a shallow acceptor from an electrical point of view (ionization energy around 200 meV [4]), so how would it be able to emit BL? And Mg-H complexes are supposed to be electrically neutral, so should emit no light at all. In this Letter, we will show that these suppositions are incorrect, and that accurate calculations produce results that explain all of the features that have been reported but largely misinterpreted in the literature.

We find that although $\mathrm{Mg_{Ga}}$ gives rise to an acceptor level at 260 meV above the valence band, it leads to a broad luminescence peak at 2.70 eV, consistent with the observed BL. The luminescence peak is significantly shifted from the expected value for a shallow acceptor because of the large charge-state-dependent lattice relaxations around the Mg impurity [see Fig. 1(a)]. Furthermore, we propose that the UVL generally assumed to be associated with the isolated Mg acceptors is instead due to Mg-H complexes [Fig. 1(b)]. We will show that these assignments are consistent with the experimental data, and also offer

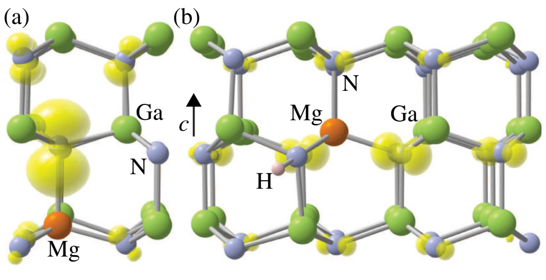

FIG. 1 (color online). (a) Local structure showing the distortion around a neutral Mg acceptor in GaN. The localization of the hole on the axial nitrogen neighbor is illustrated by the spin-density isosurface (yellow), set to 5% of the maximum. (b) Structure of the Mg-H complex in GaN in the positive charge state. The spin density shows the more delocalized nature of the complex. Large green spheres denote Ga atoms, medium light blue spheres N atoms, and the orange (darker) sphere denotes the $\mathrm{Mg_{Ga}}$.

predictions for the behavior of Mg acceptors in AlN and InN.

Our calculations are based on generalized Kohn-Sham theory [12] with the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [13] and the projector-augmented wave method [14,15], as implemented in the VASP code [16]. The parameter that determines the fraction of nonlocal Hartree-Fock exchange is set to 0.31 for GaN, resulting in a band gap of 3.50 eV, very close to the experimental value [17]. For AlN, we use a mixing parameter of 0.33, giving a calculated band gap of 6.15 eV; for InN, we use a mixing parameter of 0.25, giving a calculated band gap of 0.65 eV. Both values are again in close agreement with experiment [17]. The calculated lattice parameters ($a = 3.20$ Å, $c = 5.20$ Å, and $u = 0.38$) for wurtzite GaN are in good agreement with experiment [17]. We use 96-atom supercells, a plane-wave basis set with a 300 eV cutoff, and a $2 \times 2 \times 2$ Monkhorst-Pack k-point set for the defect calculations. Based on tests using larger supercells, errors of less than 0.1 eV in formation energies and transition levels are expected. We have previously found HSE to give accurate results for transition levels of defects in GaN [18]. All local relaxations associated with the Mg acceptors are performed using the HSE functional, and spin polarization is included in the defect calculations.

In order to examine the various charge states of the Mg acceptor in GaN, and the transitions between them, we calculated the formation energy [19]:

$$E^f(\mathrm{Mg}_{\mathrm{Ga}}^q) = E_t(\mathrm{Mg}_{\mathrm{Ga}}^q) - E_t(\mathrm{GaN}) + \mu_{\mathrm{Ga}} - \mu_{\mathrm{Mg}} + qE_F,$$

where $E_t(\mathrm{M}_{\mathrm{Ga}}^q)$ is the total energy of the crystal containing one $\mathrm{Mg}_{\mathrm{Ga}}$ in charge state q in the supercell, and $E_t(\mathrm{GaN})$ is the total energy of a perfect crystal in the same supercell. μ_{Ga} and μ_{Mg} are the Ga and Mg chemical potentials, i.e., the energies of the reservoirs with which atoms are exchanged. E_F is the energy of the electron reservoir, namely, the Fermi level, referenced to the bulk valence-band maximum (VBM). For charged defects, we include a correction based on the alignment of the averaged electrostatic potential in the bulk and in a region far from the impurity in the impurity-containing supercell [20].

The calculated formation energy of $\mathrm{Mg}_{\mathrm{Ga}}$ in GaN is shown in Fig. 2(a). The $(0/-)$ transition level (which determines the ionization energy) occurs at 260 meV above the VBM, within the range of reported experimental values [4,5,17]. However, $\mathrm{Mg}_{\mathrm{Ga}}$ does not exhibit conventional shallow acceptor behavior. Normally, for a shallow acceptor, the neutral charge state consists of a delocalized hole that is only loosely bound, by Coulomb attraction, to a negatively charged acceptor core. $\mathrm{Mg}_{\mathrm{Ga}}^0$, however, is characterized by a highly *localized* hole, as shown in Fig. 1(a), with most of the charge located on the axial nitrogen nearest neighbor. Concurrent with this localization we find a symmetry-breaking distortion whereby the axial Mg-N bond is lengthened by 15% of the bulk GaN bond length. Configurations in which the hole is localized on a planar nitrogen neighbor are higher in energy by 0.03 eV. Careful investigations reveal that there are no other metastable configurations, in contrast to previous theoretical work [2].

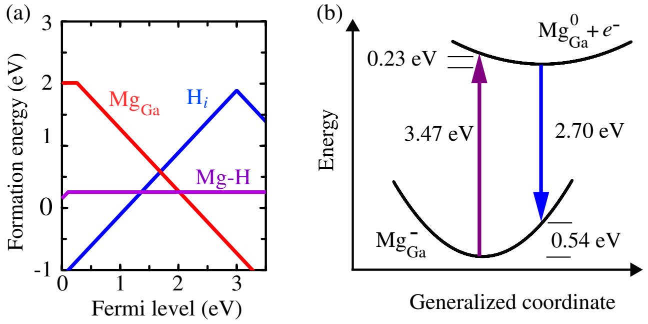

FIG. 2 (color online). (a) Formation energy versus Fermi level for the Mg acceptor ($\mathrm{Mg}_{\mathrm{Ga}}$), hydrogen interstitial (H_i), and their complex (Mg-H) in GaN. (b) Configuration-coordinate diagram illustrating optical processes related to Mg in GaN. Recombination of an electron at the CBM with $\mathrm{Mg}_{\mathrm{Ga}}^0$ leads to emission peaking at 2.70 eV, explaining BL in GaN.

The localization of the hole on $\mathrm{Mg}_{\mathrm{Ga}}^0$ indicates that Mg is only "accidentally" a shallow acceptor, with the $(0/-)$ transition level occurring close to the VBM—as opposed to a "conventional" shallow acceptor, for which the ionization energy describes the Coulomb attraction between a mostly delocalized hole and a negatively charged acceptor at the center, and can be derived from hydrogenic effective-mass theory (adjusted for the effective mass and dielectric constant of the host). For $\mathrm{Mg}_{\mathrm{Ga}}^-$ we find no asymmetric distortions, only breathing relaxations of the nearest neighbors.

The large difference in lattice relaxations of $\mathrm{Mg}_{\mathrm{Ga}}^0$ and $\mathrm{Mg}_{\mathrm{Ga}}^-$ indicates that the energies of optical transitions from the conduction-band minimum (CBM) (or a shallow donor level) to the neutral $\mathrm{Mg}_{\mathrm{Ga}}$ acceptor may greatly deviate from the band-gap energy. This is illustrated in the configuration-coordinate diagram of Fig. 2(b), in which the generalized coordinate represents the local lattice relaxations around the $\mathrm{Mg}_{\mathrm{Ga}}$ impurity. Recombination of an electron in the CBM with $\mathrm{Mg}_{\mathrm{Ga}}^0$ leads to light emission peaking at 2.70 eV. The energy difference between this peak and the zero-phonon line (at $3.50 - 0.26 = 3.24$ eV) is the relaxation energy of $\mathrm{Mg}_{\mathrm{Ga}}^-$; its large value (0.54 eV) indicates the PL line will be very broad. Both the peak position and the width agree with experimental observations of the BL in GaN [3,5,7,11,21].

The origin of the BL in Mg-doped GaN has been a longstanding problem. The BL most frequently appears in GaN grown by metal-organic chemical vapor deposition (MOCVD) [3,5], and its intensity has been observed to increase upon annealing in N_2 and decrease upon annealing in NH_3 [3]. BL has also been observed in Mg-doped GaN grown by molecular beam epitaxy (MBE) [21] and in semi-insulating Mg-containing GaN [22]. The BL has often been ascribed to deep donors (such as the nitrogen vacancy) created during Mg doping, yet optically detected magnetic resonance (ODMR) studies have not shown any evidence of a deep donor signal [8]. Our present results strongly suggest that the BL can in fact be attributed to the isolated $\mathrm{Mg_{Ga}}$ acceptor. ODMR on the BL has in fact revealed g tensors with modest anisotropies and characteristic of localized, deep centers [8,9], consistent with hole localization on $\mathrm{Mg_{Ga}}$. Our attribution is also consistent with the experimental correlation between the BL intensity and free hole concentrations [3,4,7] and its increase in intensity during annealing treatments [3,4].

Next, we consider how interstitial hydrogen (H_i) interacts with the Mg acceptor. As in previous work [23,24], we find that H_i^+ interacts with the $\mathrm{Mg_{Ga}^-}$ acceptor to form a stable complex, in which the H atom bonds to a planar N atom at the antibonding site [Fig. 1(b)] [23,24]. The calculated binding energy of the neutral Mg-H complex with respect to $\mathrm{Mg_{Ga}^-}$ and H_i^+ is 1.02 eV. In contrast to the usual assumption that the Mg-H complex is completely passive and exclusively neutral, we find that it can also be stable in the $+1$ charge state for Fermi levels close to the VBM. As shown in Fig. 2(a), the $(+/0)$ transition level occurs at 130 meV above the VBM.

The occurrence of this positive charge state has profound consequences for the optical properties. In contrast to the $\mathrm{Mg_{Ga}}$ acceptor, the relaxation energies of the Mg-H complex are much smaller (only 0.05 eV), and there is no distinct axial distortion. This is consistent with the more delocalized nature of the hole state related to the Mg-H complex, shown in Fig. 1(b). Thus, for optical transitions related to this complex we expect sharp, narrow lines in the ultraviolet region, as would be characteristic of shallow-donor–shallow-acceptor recombination [25]. Our calculated zero-phonon line for this emission is at 3.37 eV, with a PL maximum at 3.32 eV, consistent with experimental reports of the UVL at 3.27 eV [4–7].

The positive charge state of Mg-H also affects the electrical properties of Mg-doped GaN. If, after postgrowth annealing, some complexes are still present in p-type GaN, they act not only as a passivating agent (inactivating one Mg acceptor) but in addition as a compensating center (removing a hole from the valence band). Thus, these complexes are doubly detrimental in reducing free hole concentrations in Mg-doped GaN. Combined optical and electrical experiments to assess the presence and role of these complexes in Mg-doped GaN are called for.

Our attribution to the Mg-H complex can finally explain why this line is especially strong in as-grown, unannealed Mg-doped GaN samples (which contain the H-passivated Mg centers) [4,7] and systematically decreases in intensity upon annealing [3,4,7] or electron irradiation [6], which are known to lead to dissociation of the Mg-H complex. Confirmation of our proposed attribution could be obtained by monitoring the intensity of the UVL in material that is first activated and then intentionally hydrogenated: the formation of Mg-H complexes should lead to an increase in the intensity of the UVL.

Monemar *et al.* recently proposed the existence of two distinct Mg-related centers in GaN based on PL measurements of acceptor-bound excitons [1]. The "A2 acceptor" was found to be stable against UV (or electron) excitation and annealing, and dominant at high Mg doping; it was associated with the Mg acceptor that becomes activated upon annealing, consistent with the isolated $\mathrm{Mg_{Ga}}$. The exciton related to the "A1 acceptor," on the other hand, was associated with the UVL and was observed to be unstable against annealing above 500 °C. This is consistent with our assignment to Mg-H complexes, which are dissociated at high temperatures. Based on its observed features Monemar *et al.* [1] suggested that (in addition to Mg) hydrogen might be involved in the A1 line, a proposition that is now corroborated by our identification of Mg-H complexes as the source of the UVL.

We have also investigated the behavior of Mg acceptors in AlN and InN. We find $\mathrm{Mg_{Al}}$ to be a deep acceptor in AlN, with a $(0/-)$ transition level at 0.78 eV [Fig. 3(a)]. As in GaN, we find localization of the hole on the axial nitrogen neighbor in the neutral charge state, with the axial Mg-N bond length increasing by 18%. Different from GaN, we find that $\mathrm{Mg_{Al}}$ can stabilize a second hole, with $\mathrm{Mg_{Al}^+}$ stable for Fermi levels below 0.36 eV. As shown in Fig. 3(b), $\mathrm{Mg_{Al}^+}$ is a spin one defect center with holes localized on two nearest-neighbor nitrogen atoms. These results indicate that p-type doping of AlN and AlGaN with Mg is much more difficult than in GaN, as already known from previous experimental [26] and theoretical [27,28] works. Quantitative differences with the recent results of Szabó *et al.* [28] can be attributed to the fact that atomic relaxations in that work were performed using the

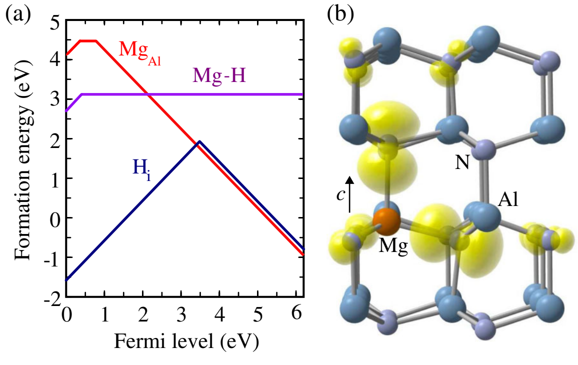

FIG. 3 (color online). (a) Formation energy versus Fermi level for the Mg acceptor, H interstitial, and their complex in AlN. (b) Structure and spin density associated with the localized hole states ($S = 1$) of $\mathrm{Mg_{Al}^+}$ (isosurface at 5% of the maximum in yellow). Large blue spheres denote Al atoms, medium light blue spheres N atoms, and the orange (darker) sphere $\mathrm{Mg_{Al}}$.

generalized gradient approximation, rather than the hybrid functional as in the present work.

Figure 3(b) shows the lattice configuration and spin density for the localized holes of Mg_{Al}^+. The relaxation energies associated with the optical transitions are similar to those of Mg in GaN. The total energy of Mg_{Al}^+ in the Mg_{Al}^0 configuration with respect to Mg_{Al}^- in its ground state is 0.65 eV; combined with the 0.78 eV ionization energy of Mg_{Al}, we predict an emission peak at 4.77 eV for the process analogous to that of Fig. 2(b). We also consider the emission process whereby an electron at the CBM recombines with a hole in Mg_{Al}^+ to create Mg_{Al}^0. The relaxation energy for this process is 0.41 eV, and the emission energy is 5.43 eV. Very similar signals have been observed in AlN:Mg [26]. The dominant PL line in Mg-doped AlGaN alloys shows a distinct blueshift with increasing Al content [26,29], from 2.8 eV in GaN to 4.7 eV in AlN, entirely consistent with a linear interpolation of our calculated luminescence emission peaks between GaN and AlN.

As in GaN, we find that H_i can interact with the Mg acceptor in AlN to form a stable complex. This complex is electrically neutral across most of the band gap, but below 0.43 eV the complex is stable in the positive charge state. The complex is thus optically active, with an emission energy of 5.13 eV.

Finally, we consider Mg in InN. Unlike in AlN and GaN, Mg_{In} does act as a genuine shallow acceptor in InN. No asymmetric distortion or hole localization occurs for Mg_{In}^0. Instead, the hole delocalizes over the InN supercell, indicative of effective-mass-like behavior. The $(0/-)$ transition level occurs at 190 meV above the VBM, the shallowest among the nitride semiconductors, consistent with the experimental literature [30,31].

We observe that the behavior of the Mg acceptor is intimately tied to the character of the valence bands of the nitrides, with deeper and flatter valence bands promoting localization. AlN, with the largest band gap (calculated to be 6.15 eV), the deepest valence band [32], and largest effective hole mass [17], has the highest acceptor ionization energy. GaN has a slightly higher VBM and a slightly smaller hole mass, and exhibits a smaller Mg ionization energy (260 meV) but still localization in the neutral charge state of Mg. InN, with the smallest band gap (0.65 eV in our calculations), highest valence band, and smallest hole mass, shows no hole localization and has the smallest Mg ionization energy.

In summary, we find that the Mg acceptor binds localized holes in GaN and AlN. In GaN, Mg_{Ga} has an acceptor ionization energy of 260 meV, but gives rise to a deep emission signal of 2.70 eV due to large local lattice relaxations. In InN, GaN and AlN, hydrogen can passivate the Mg acceptor, making it neutral for most Fermi levels. However, the Mg-H complexes remain optically active, and give rise to emission signals closer to the band gap than the deep emissions characteristic of the isolated acceptors. We also find that the Mg-H complexes are doubly detrimental to Mg doping: in addition to their widely recognized role in passivating Mg, they additionally act as electrically active compensating centers that remove holes. Our results resolve experimental results for GaN that have remained puzzling for almost two decades: Mg_{Ga} is responsible for the widely observed blue luminescence, and the Mg-H complex is responsible for 3.27 eV PL. Mg_{In} in InN is found to behave as a shallow, effective-mass acceptor, with the lowest ionization energy among the nitrides.

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