THEORY OF POINT DEFECTS AND INTERFACES

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ABSTRACT

First-principles theoretical results can predict and explain a variety of materials properties of the nitride semiconductors. For *n*-type GaN, we summarize the current understanding about incorporation of unintentional donor impurities, as opposed to nitrogen vacancies. For *p*-type GaN, we discuss the cause of the limited doping levels, and the role of hydrogen. We describe the role of gallium vacancies in the yellow luminescence, and the interaction between these vacancies and donor impurities. Finally, we discuss our first-principles investigations of the atomic and electronic structure of heterojunction interfaces between the III-nitrides, and provide values for natural band lineups.

INTRODUCTION

Tremendous progress has recently been made in the growth and fabrication of GaN-based electronic and optoelectronic devices. A number of problems still exist, however, which may hamper further progress. One such problem is doping. In 1994 we countered the conventional wisdom by suggesting that nitrogen vacancies were *not* responsible for the commonly observed *n*-type conductivity in GaN [1]. Instead we proposed that donor impurities are unintentionally incorporated, with oxygen and silicon the main candidates for donors in GaN [2]. Our proposals have recently been confirmed in a number of experimental investigations, showing that oxygen and silicon concentrations in well characterized samples are high enough to explain the observed electron concentrations. Our current understanding will be discussed in the section on "*N*-TYPE DOPING."

With regard to *p*-type doping, the doping levels are still lower than desirable for low-resistance cladding layers and ohmic contacts. Achieving higher hole concentrations with Mg as the dopant has proved difficult; various explanations have been proposed for this limitation. Our investigations of compensation mechanisms [3] have revealed that the determining factor is the solubility of Mg in GaN, which is limited by competition between incorporation of Mg acceptors and formation of Mg_3N_2. Incorporation of Mg on interstitial or substitutional nitrogen sites was found to be unfavorable. Some compensation by native defects may occur, in particular by nitrogen vacancies; however, such compensation is significantly suppressed in the presence of hydrogen. We addressed the role of hydrogen during *p*-type doping and subsequent anneals in Refs. [4] and [5]. One may wonder whether the limitations encountered with Mg could be overcome by using other acceptor impurities; we will report on these issues in the section on "*P*-TYPE DOPING.'

A major concern for optoelectronic devices is the presence of alternate recombination channels, such as the "yellow luminescence" (YL) in GaN. Our investigations of native defects have revealed that gallium vacancies are the most likely source of this YL [6], and an increasing number of experiments support this assignment. An assessment of the current understanding follows in the section on "YELLOW LUMINESCENCE".

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Finally, we address another issue of importance for device design, namely the atomic and electronic structure of heterojunction interfaces. The III-nitride semiconductors exhibit large differences in lattice constant, and the resulting lattice mismatch complicates an assessment of the heterojunction band discontinuities. We will report on our results in the section on "INTERFACES".

METHODS

Our calculations are based on first-principles density-functional theory [7], using a supercell geometry and soft Troullier-Martins pseudopotentials [8]. The effect of d electrons in GaN and InN was taken into account either through the so-called non-linear core correction or by explicit inclusion of the d electrons as valence electrons; the latter proved to be necessary for obtaining accurate results in certain cases [9]. Our results should apply to both the wurtzite and zincblende phases of the nitride semiconductors; indeed, in Ref. [9] we reported that the wurtzite and the cubic phase show nearly equivalent formation energies and electronic structure for defects. Further details of the computational approach can be found elsewhere [1, 10, 11].

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

$$c = N_{\rm sites} \exp^{-E^f/k_B T} \tag{1}$$

where $N_{\rm sites}$ is the number of sites the defect or impurity can be incorporated on, k_B the Boltzmann constant, T the temperature, and E^f the formation energy. Equation (1) shows that defects with a *high* formation energy will occur in *low* concentrations.

The formation energy is not a constant but depends on the various growth parameters. For example, the formation energy of an oxygen donor is determined by the relative abundance of O, Ga, and N atoms, as expressed by the chemical potentials $\mu_{\rm O}$, $\mu_{\rm Ga}$ and $\mu_{\rm N}$. If the O donor is charged (as is expected when it has donated its electron), the formation energy depends further on the Fermi level (E_F), which acts as a reservoir for electrons. Forming a substitutional O donor requires the removal of one nitrogen atom and the addition of one O atom; the formation energy is therefore:

$$E^f({\rm GaN{:}O_N^q}) = E_{\rm tot}({\rm GaN{:}O_N^q}) - \mu_{\rm O} + \mu_{\rm N} + qE_F \tag{2}$$

where $E_{\rm tot}({\rm GaN{:}O_N^q})$ is the total energy derived from a calculation for substitutional O, and q is the charge state of the O donor. E_F is the Fermi level, Similar expressions apply to other impurities and to the various native defects. We refer to Refs. [1] and [12] for a more complete discussion of formation energies and their dependence on chemical potentials.

The Fermi level E_F is not an independent parameter, but is determined by the condition of charge neutrality. However, it is informative to plot formation energies as a function of E_F in order to examine the behavior of defects and impurities when the doping level changes. As for the chemical potentials, these are variables which depend on the details of the growth conditions. For ease of presentation, we set these chemical potentials to fixed values in the figures shown below; however, a general case can always be addressed by referring back to Eq. (2). The fixed values we have chosen correspond to Ga-rich conditions ($\mu_{\rm Ga} = \mu_{\rm Ga(bulk)}$), and to maximum incorporation of the various impurities, with solubilities determined by equilibrium with Ga_2O_3, Si_3N_4, and Mg_2N_3.

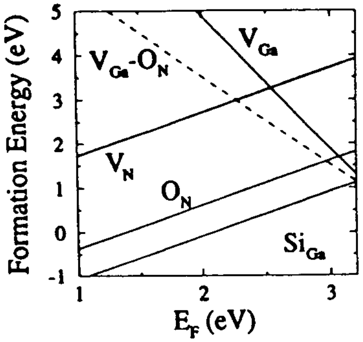

Figure 1: Formation energy *vs.* Fermi energy for native defects (nitrogen and gallium vacancies), donors (oxygen and silicon) and the $V_{\rm Ga}$-$O_{\rm N}$ complex. The zero of Fermi energy is located at the top of the valence band.

N-TYPE DOPING

Figure 1 summarizes our first-principles results for native defects and impurities relevant for n-type doping. We observe that nitrogen vacancies ($V_{\rm N}$) are high-energy defects in GaN, and are thus unlikely to occur in significant concentrations. We have also found that self-interstitial and antisite defects are high-energy defects [1]. Similar results for native defects were obtained by Boguslawski *et al.* [13]. These findings allow us to conclude that nitrogen vacancies are not responsible for n-type conductivity in GaN. In contrast, Fig. 1 shows that oxygen and silicon have relatively low formation energies in n-type GaN, and can thus be readily incorporated. Both oxygen and silicon form shallow donors in GaN. The slope of the lines in Fig. 1 indicates the charge state of the defect or impurity: $Si_{\rm Ga}$, $O_{\rm N}$, and $V_{\rm N}$ all appear with slope +1, indicating single donors.

The possibility that oxygen could be responsible for n-type conductivity in GaN was recognized by Seifert *et al.* [14] and by Chung and Gershenzon [15]. Still, the prevailing conventional wisdom, attributing the n-type behavior to nitrogen vacancies, proved hard to overcome. Recent experiments have confirmed that unintentionally doped n-type GaN samples contain silicon or oxygen concentrations high enough to explain the electron concentrations. Götz *et al.* [16] reported electrical characterization of intentionally Si-doped as well as unintentionally doped samples, and concluded that the n-type conductivity in the latter was due to silicon. They also found evidence of another shallow donor with a slightly higher activation energy, which was attributed to oxygen. Götz *et al.* have also recently carried out SIMS (secondary-ion mass spectroscopy) and electrical measurements on hydride vapor phase epitaxy (HVPE) material, finding levels of oxygen or silicon in agreement with the electron concentration [17].

High levels of n-type conductivity have traditionally been found in GaN bulk crystals grown at high temperature and high pressure [18]. It has recently been established that the characteristics of these samples (obtained from high-pressure studies) are very similar to epitaxial films which are intentionally doped with oxygen [19]. The n-type conductivity of bulk GaN can therefore be attributed to unintentional oxygen incorporation.

Finally, we note in Fig. 1 that gallium vacancies ($V_{\rm Ga}^{3-}$) have relatively low formation energies in highly doped n-type material (E_F high in the gap); they could therefore act as compensating centers. Yi and Wessels [20] have found evidence of compensation by a triply charged defect in Se-doped GaN.

P-TYPE DOPING

Figure 2 summarizes some of our results for acceptor doping in GaN. The Mg acceptor has a low enough formation energy to be incorporated in large concentrations in GaN. For the purposes of the plot, we have assumed Ga-rich conditions (which are actually the least favorable for incorporating Mg on Ga sites), and equilibrium with Mg_2N_3, which determines the solubility limit for Mg. We note that the formation energies for Mg_{Ga}^0 and Mg_{Ga}^- intersect for a Fermi level position around 250 meV; this transition level would correspond to the ionization energy of the Mg acceptor. However, since our calculated formation energies are subject to numerical error bars of ±0.1 eV, this value should not be taken as an accurate assessment of the ionization energy.

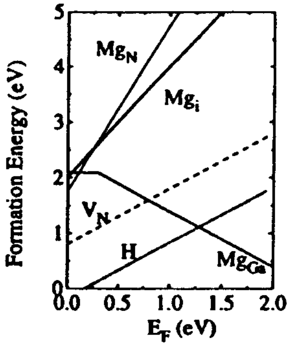

Figure 2: Formation energy as a function of Fermi level for Mg in different configurations (Ga-substitutional, N-substitutional, and interstitial configuration). Also included are the native defects and interstitial H.

We have investigated other positions of Mg in the lattice, such as on substitutional N sites (Mg_N) and on interstitial sites (Mg_i), always finding much larger formation energies. We therefore conclude that Mg overwhelmingly prefers the Ga site in GaN, the main competition being with formation of Mg_2N_3, which is the solubility-limiting phase. It would be interesting to investigate experimentally whether traces of Mg_2N_3 can be found in highly Mg-doped GaN.

Other potential sources of compensation are also illustrated in Fig. 2. The nitrogen vacancy, which had a high formation energy in *n*-type GaN (see Fig. 1) has a significantly lower formation energy in *p*-type material, and could potentially act as a compensating center. However, we also note that hydrogen, when present, has a formation energy much lower than that of the nitrogen vacancy. In growth situations where hydrogen is present [such as metal-organic chemical vapor deposition (MOCVD) or HVPE] Mg-doped material will preferentially be compensated by hydrogen, and compensation by nitrogen vacancies will be suppressed. The presence of hydrogen is therefore beneficial – at the expense, of course, of obtaining material which is heavily compensated by hydrogen! Fortunately, the hydrogen can be removed from the active region by post-growth treatments, such as low-energy electron-beam irradiation [21] or thermal annealing [22]. A more complete discussion of the role of hydrogen in GaN is given in Refs. [4] and [5].

For Mg, we thus conclude that achievable doping levels are mainly limited by the solubility of Mg in GaN. We have investigated other candidate acceptor impurities, and evaluated them in terms of solubility, shallow *vs.* deep character, and potential compensation due to incorporation on other sites. Some of these results are summarized in Ref. [23]. None of the candidate impurities exhibited characteristics superior to Mg.

Finally, we note the importance of avoiding any type of contamination during growth of *p*-type GaN. For instance, the oxygen formation energy shown in Fig. 1 clearly extrapolates to very low values in *p*-type GaN. Any oxygen present in the growth system will therefore be readily incorporated during *p*-type growth. In addition, complex formation between oxygen and magnesium can make oxygen incorporation even more favorable [24].

YELLOW LUMINESCENCE

The yellow luminescence (YL) in GaN is a broad luminescence band centered around 2.2 eV. Its origins have been extensively debated; we have recently proposed that gallium vacancies are the source of the YL [6]. Here we summarize the arguments in favor of this assignment, and discuss recent experimental results.

n-type *vs.* *p*-type

The gallium vacancy is an acceptor-type defect, and hence its formation energy decreases with increasing Fermi level (see Fig. 1). Gallium vacancies are therefore more likely to occur in *n*-type than in *p*-type GaN. The correlation of the YL with Ga vacancies is therefore consistent with experimental observations indicating suppression of the YL in *p*-type material [25, 26, 27]. Conversely, an increase in *n*-type doping increases the intensity of the YL [28]. Additional systematic studies of the YL as a function of doping level are desirable; however, care should be taken in the analysis of such experiments, since the ratio of the magnitude of the YL to the band-gap luminescence depends on the excitation intensity [29, 30].

Ga-rich *vs.* N-rich

It is obvious that the concentration of gallium vacancies will be lower in Ga-rich material. The YL was indeed found to be suppressed in MOCVD samples grown with higher TMGa flow rates [25, 31]. Singh *et al.* [29] observed that the YL was stronger in samples grown at higher microwave power in ECR (electron-cyclotron resonance) assisted MBE (molecular beam epitaxy); this could be consistent with higher V_{Ga} concentrations when the growth is more N-rich, provided no plasma-induced damage is involved. It has also been observed that the YL is weak in material grown by HVPE [32], which could be consistent with growth conditions in HVPE being more Ga-rich than in MOCVD.

Role of carbon

A number of authors have related the YL to the presence of carbon in the material [33, 34]. However, our extensive investigations of carbon on different sites and as a component of various complexes did not produce any defect with properties consistent with the known facts about the YL [6]. We have concluded that the presence of carbon in material that exhibits YL is merely coincidental; indeed, an increase in *n*-type doping facilitates the incorporation of C (an acceptor) at the same time as enhancing the YL.

Recombination mechanism

Our calculations indicate that the Ga vacancy has a deep level (the 2-/3- transition level) about 1.1 eV above the valence band. Transitions between the conduction band (or shallow donors) and this deep level therefore exhibit the correct energy to explain the YL. Various experiments have indeed linked the YL with a deep level, located about 1 eV above the valence band [35, 36]. In addition, our calculated pressure dependence of this level is also consistent with experiment [35].

Complexing with donor impurities

Gallium vacancies can form complexes with donor impurities in GaN. The V_{Ga}-Si_{Ga} complex has a rather small binding energy, due to its components being only second-nearest neighbors. The V_{Ga}-O_N complex, on the other hand, has a large binding energy (1.8 eV), and can therefore play a role in enhancing the concentration of Ga vacancies (see Fig. 1). The electronic structure of this complex is very similar to that of the isolated gallium vacancy, giving rise to a deep level again about 1.1 eV above the valence band.

Ion implantation

The YL has been observed after ion implantation: Pankove and Hutchby [37] found that implantation with a variety of elements produced a broad luminescence band around 2.15 eV [37]. Implantation damage is likely to result in preferential creation of Ga-site defects; indeed, the displacement energy threshold in III-V compounds tends to be lower for the cation site [38]. Formation of Ga vacancies is thus likely during implantation, once again consistently explaining the increase in the YL.

Similarity with SA centers in II-VI compounds

Finally, we point out the similarity between the YL in GaN and the so-called self-activated (SA) luminescence in II-VI compounds. Metal vacancies and their complexes with donor impurities are well known in II-VI compounds (e.g., ZnS, ZnSe). The metal vacancy complexes (the so called *SA* centers) exhibit features which are strikingly similar to the YL: recombination between a shallow donor-like state and a deep acceptor state, and a broad luminescence band of Gaussian shape [39, 40].

INTERFACES

Most nitride-based devices incorporate heterojunctions between GaN, AlN, or InN, or their alloys. The most important parameters characterizing such heterojunctions are the band discontinuities in the conduction and valence bands. It is well known that these band offsets sensitively depend on the strain condition of the materials joined at the interface; however, these strains have not always been properly taken into account in the analysis of experimental data or computational results.

Lattice constants and band gaps for the nitrides (in the zincblende phase) are listed in Table 1. The lattice mismatch between AlN and GaN is about 3%; between GaN and InN, the mismatch is over 11%. The band offsets are only well defined in the case of a pseudomorphic interface, in which the materials on either side of the junction are strained in order to match a common in-plane lattice constant. For instance, when InN is grown on a thick layer of GaN, the InN should be compressed in the plane of the interface to match the GaN lattice constant, and expanded in the perpendicular direction (by Poisson's ratio). The critical layer thickness (beyond which dislocation formation sets in and the interface is no longer pseudomorphic) for growth of pure InN on GaN is probably vanishingly small, but the same logic applies for growth of InGaN alloys on GaN. Results for alloys can usually be obtained by linear interpolation.

Table 1: Experimental lattice constants (a, in Å) and room-temperature band gaps (E_g, in eV) for zincblende AlN, GaN, and InN.

	AlN	GaN	InN
a	4.37	4.50	4.98
E_g	6.20	3.39	1.89

We have focused on computations for (110) interfaces between the nitrides in the zincblende phase. We expect very little difference for the wurtzite phase, which differs from zincblende only in the atomic arrangements beyond third nearest neighbors. We also expect only minor changes for other interface orientations.

Our calculations are performed in a superlattice geometry, for various values of the in-plane lattice constant. The materials are strained according to their elastic constants, and relaxation of the atoms around the interface is explicitly allowed. The superlattice calculation yields the lineup of average electrostatic potentials across the interface; the position of the valence-band maximum with respect to the average electrostatic potential is obtained from bulk calculations [41].

Instead or re-calculating the bulk electronic structure for every strain situation, we have derived ***deformation potentials*** describing the changes in band edges due to various strain components. We have also calculated the ***absolute*** deformation potentials for the valence-band maximum. Using the band lineups at strained interfaces together with the deformation potentials allows us to derive a so-called ***natural*** band lineup between unstrained materials. This natural band lineup can be used as a starting point to calculate offsets at an arbitrary interface, by using information about the strains and the deformation potentials. Complete information about deformation potentials will be published elsewhere [42].

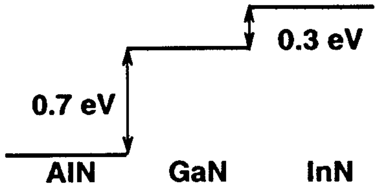

Figure 3: Natural valence-band lineups between AlN, GaN, and InN, obtained from first-principles calculations for zincblende (110) interfaces.

The natural band lineups for the nitrides are illustrated in Fig. 3. the valence-band offset between AlN and GaN (for which the lattice mismatch is relatively modest) is about

0.7 eV, consistent with other recent determinations [43, 44, 45]. For GaN/InN we find a surprisingly small offset, 0.3 eV. Atomic relaxations play an important role at this interface, driving the valence-band offset toward lower values.

CONCLUSIONS

We have presented a variety of results obtained from theoretical and computational investigations of the III-nitride semiconductors. Strong evidence now exists attributing the residual n-type conductivity of GaN to unintentional donor impurities. Additional computational work is in progress to address the behavior of these donors in GaN under pressure, and in alloys. For p-type material, we attribute the limitation in doping levels to solubility constraints, rather than compensation. More work is needed to clarify the behavior of acceptors other than Mg. It is very clear, however, that oxygen contamination is detrimental to p-type conductivity. Regarding the yellow luminescence, we have presented our arguments for linking this luminescence with gallium vacancies. Finally, we have reported results for natural band lineups at interfaces between the III-nitrides.

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