Gallium vacancies and the yellow luminescence in GaN

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We have investigated native defects and native defect-impurity complexes as candidate sources for the yellow luminescence in GaN. Using state-of-the-art first-principles calculations, we find strong evidence that the Ga vacancy (V_{Ga}) is responsible. The dependence of the V_{Ga} formation energy on Fermi level explains why the yellow luminescence is observed only in *n*-type GaN. The V_{Ga} defect level is a deep acceptor state, consistent with recent pressure experiments. Finally we show that the formation of V_{Ga} is enhanced by the creation of complexes between V_{Ga} and donor impurities. © *1996 American Institute of Physics.* [S0003-6951(96)01130-8]

GaN exhibits some unique properties, such as a large direct band gap, strong interatomic bonds, and a high thermal conductivity, which make it an ideal material for optoelectronic and high-temperature/high-power devices. Very efficient GaN-based blue and green light-emitting diodes have been fabricated[1] and recently a blue laser has been reported.[2] Despite the impressive progress in devices, the role of various defects in the material and their effect on device performance is not yet understood. In this letter we focus on the so-called ''yellow luminescence,'' a defect-induced transition which affects the efficiency of optoelectronic devices.

The yellow luminescence (YL) in GaN is a broad luminescence band centered around 2.2–2.3 eV. The YL appears to be a universal feature: it has been observed in bulk GaN crystallites as well as in epitaxial layers grown by techniques as different as molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), and hydride vapor phase epitaxy (HVPE). The intensity can vary over a wide range, with good samples exhibiting almost no YL. The origin of the YL is still being debated, however, and no clear correlation between growth conditions and YL intensity has been identified.

Even the position of the electronic levels participating in the YL is controversial. Ogino and Aoki[3] proposed a model in which the YL is a transition between a shallow donor and a deep acceptor level. Glaser *et al.*[4] proposed an alternative model, based on ODMR (optically detected magnetic resonance) experiments: a transition between a deep double donor (about 1 eV below the conduction band) and an effective-mass acceptor. The microscopic nature of the deep level is equally uncertain: Ogino and Aoki[3] proposed a complex between a Ga vacancy and a C on a N site (C_N); Suski *et al.*[5] suggested a N_{Ga} antisite. Our calculations will actually show that both of these models are thermodynamically unstable.

The current uncertainty about the nature of the defect responsible for the YL impedes efforts to control and improve the materials quality. In this letter we investigate various potential sources of the YL, using state-of-the-art first-principles calculations. Detailed analysis of the calculational results and their correlation with experiment enables us to conclude that the Ga vacancy (V_{Ga}) is the key defect responsible for the YL.

Our approach is based on density-functional theory, *ab initio* pseudopotentials, and a supercell approach. Details of the method and convergence checks have been discussed elsewhere.[6–8] An important quantity we will focus on is the *formation energy* of a defect or impurity: a *low* formation energy implies a high equilibrium concentration of the defect; defects with *high* formation energies are unlikely to form.

Let us first review some of the experimentally observed features of the YL. Suski *et al.*[5] carried out high-pressure experiments; they found that the YL exhibits a pressure dependence very similar to that of the band gap. They concluded that the YL results from a recombination between a shallow donor and a deep level located in the lower half of the band gap. Growth studies have provided another important piece of information: the YL can be suppressed by incorporating acceptors (Mg) in GaN,[9,10] i.e., by making the material *p*-type. This observation indicates that the YL is due to a defect which has a low formation energy under *n*-type conditions, but a high formation energy under semiinsulating and *p*-type conditions. Such a behavior is characteristic for *acceptors*: due to the energy gained by partly compensating the donors, it is easier to form acceptors in *n*-type GaN than in *p*-type GaN. Deep *donors* would be easier to form in *p*-type GaN, inconsistent with experiment. We conclude that the defect involved in the YL is a *deep acceptor*.

The next question concerns the microscopic nature of this deep acceptor. The level could be due to native defects or impurities, or alternatively to extended defects such as dislocations or grain boundaries. The fact that the YL is present also in bulk GaN, which has a much lower extended-defect density than thin films,[11] indicates that the extended defects themselves are not the source of the YL. We note that an investigation of the spatial dependence of the YL by cathodoluminescence microscopy[12] indicated that the YL originates from extended defects inside of grains and at low-angle grain boundaries. However, it is well known that extended defects can act as traps for native defects or impurities; the surrounding strain field may enhance the formation of point defects, or getter impurities from the bulk regions. We will therefore focus on point defects. The behavior of native defects or impurities trapped at extended defects is

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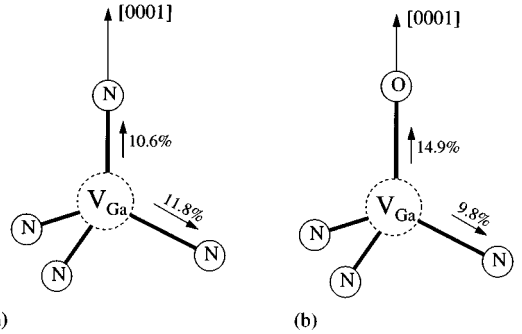

FIG. 1. Atomic geometry of the Ga vacancy (a) and the V_{Ga}-O_N complex (b) in the $3-$ and $2-$ charge state (where all defect levels are fully occupied) respectively. The numbers give the increase of the bond length in %. The bulk bond length is $d_0 = 1.94$ Å .

likely to be similar to that of the isolated point defects, except for a shifting and broadening of the defect levels.

We first address the model proposed by Ogino and Aoki[3] according to which the deep acceptor level is related to a V_{Ga}-C_N complex. We find that this configuration is unstable; the complex has a *negative* binding energy and is therefore unstable against dissociation into a Ga vacancy and a C_N acceptor. Complex formation is typically driven by electrostatic forces: a negatively charged acceptor and a positively charged donor attract each other and gain energy by forming a complex. Since V_{Ga} and C_N are both acceptors, they occur in a negative charge state (in *n*-type GaN) and repel each other.

Carbon had been put forward by Ogino and Aoki[3] as being intimately involved in the YL: we therefore investigated several other configurations involving carbon, including C on a Ga site (C_{Ga}, a donor), various interstitial positions, etc.; however, all these configurations have prohibitively high formation energies. Under *n*-type conditions (in which the YL is most prevalent), the energetically by far most stable site is C_N, which is a shallow acceptor. We conclude that carbon does not give rise to any deep acceptor level in GaN, and hence carbon is not directly involved in the YL. The prevailing form of carbon in GaN will be as a *shallow* acceptor, which can readily be unintentionally incorporated in *n*-type GaN; the presence of carbon in material which exhibits YL is therefore *coincidental*, rather than the *cause* of the YL. We note that even the authors of Ref. 3 acknowledged that the YL can also be produced in the absence of carbon, e.g., by ion implantation.[13]

We now turn our attention to native defects. The fact that the YL is only observed in *n*-type GaN points toward an acceptor-type defect. In a previous study we have investigated all native defects in detail,[6] finding that the N vacancy and the Ga interstitial are donors, the antisites and the N interstitial are amphoteric, and the Ga vacancy is an acceptor.[14] Furthermore, under *n*-type conditions the Ga vacancy is the dominant native defect; all other native defects are much higher in energy, implying negligible concentrations, and can therefore be ruled out as a source for the YL.

Therefore, if native defects are responsible for the YL the Ga vacancy is the most likely candidate from an energetic point of view. Figure 1(a) shows the atomic geometry of the Ga vacancy; it is characterized by a strong outward relaxation of the surrounding N atoms. Our calculations also yield information about the position of the electronic transition levels and the pressure dependence. In *n*-type GaN the Ga vacancy is in a $3-$ charge state. The transition level to the $2-$ charge state is at $E^{2-/3-} \approx 1.1$ eV (referenced to the top of the valence band);[15] the Ga vacancy thus gives rise to a deep acceptor level. The calculated pressure dependence of this level is very similar to that of the valence-band maximum. This behavior can be attributed to the similarity of this defect state with the top of the valence band: it is characterized by *p*-like states localized at the four N neighbors.

So far we have focused on the Ga vacancy as an isolated point defect. However, it is also conceivable that impurities, incorporated during growth, enhance the formation of Ga vacancies by forming energetically stable vacancy-impurity complexes. We have therefore studied whether complex formation is favorable and how it changes the properties (defect levels, formation energy) of the isolated defect. In light of our comments about the driving force for complex formation, the impurities most likely to form stable complexes with V_{Ga} are *donors*, since a negatively charged V_{Ga} acceptor and a positively charged donor attract each other and gain energy by forming a complex. Silicon, and to a lesser extent oxygen, are well established donor impurities in GaN, leading us to study V_{Ga}-Si_{Ga} and V_{Ga}-O_N complexes. The atomic structure of the V_{Ga}-O_N complex is shown in Fig. 1(b); it is characterized by a strong outward relaxation of the surrounding atoms, particularly of the O atom.

The electronic structure of the V_{Ga}-Si_{Ga} and V_{Ga}-O_N complexes is very similar: both act as double acceptors (as expected by bringing a triple acceptor and a single donor together). Consequently, in *n*-type GaN the relevant transition level is $E^{1-/2-}$ which is at 0.9 eV for V_{Ga}-Si_{Ga} and 1.1 eV for V_{Ga}-O_N. Both are very close to the $E^{2-/3-}$ transition level of V_{Ga}. We conclude that the electronic structure of the Ga vacancy dominates the electronic structure of the complex; the position of the transition level remains almost unaffected.

For the V_{Ga}-Si_{Ga} complex we find a binding energy of 0.23 eV (a positive binding energy indicating that complex formation is an exothermic process). For the V_{Ga}-O_N complex our calculations show a much larger binding energy (≈ 1.8 eV), indicating that the V_{Ga}-O_N complex is much more stable. The difference in stability can again be understood in terms of electrostatic attraction: in the V_{Ga}-O_N complex the V_{Ga} and O_N are nearest neighbors whereas in the V_{Ga}-Si_{Ga} complex V_{Ga} and Si_{Ga} are only second nearest neighbors.

We now use our calculated total energies to obtain the concentration of defects, impurities and complexes. The concentration of defects at a temperature T is given by

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

where N_{sites} is the number of sites where the defect may be formed, E^f is the formation energy, and k_B the Boltzmann constant. Thermodynamic equilibrium is assumed at each temperature, which may correspond to the growth temperature or to the temperature at which the concentrations of the relevant defects become fixed. The formation energy de-

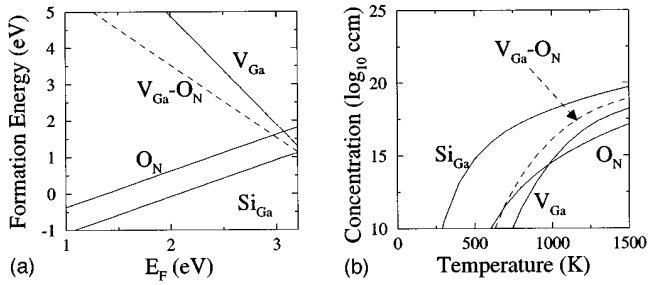

FIG. 2. Formation energy vs Fermi energy for native defects (Ga vacancy), O and Si donors and the V_{Ga}-O_N complex (a). The corresponding equilibrium concentrations are given in (b).

pends on the specific growth conditions (determined by chemical potentials[6,16]) and the position of the Fermi level. Typical results can be obtained by assuming Ga-rich conditions (common in many growth techniques) and assuming that O and Si are in equilibrium with Ga_2O_3 and Si_3N_4, respectively, corresponding to an upper limit for the O and Si concentrations.[16] These conditions fix the chemical potentials and the formation energy becomes solely a function of the Fermi energy. The results are shown in Fig. 2(a) for the case where both Si and O are present, along with native defects and the V_{Ga}-O_N complex (the V_{Ga}-Si_{Ga} concentration is very low).

Given the calculated formation energies, charge neutrality determines the position of the Fermi level, and hence the equilibrium defect concentrations [Eq. (1)] at each temperature.[16] [Note that the Fermi level position may change when the system is cooled down, while the defect concentrations remain unchanged.] The results displayed in Fig. 2(b) show that the Si donor has the highest concentration over the entire temperature range, and the system will therefore be *n*-type conductive. (Note that, in accord with our previous work,[6] the nitrogen vacancy is a high-energy defect in *n*-type GaN, and plays no role in doping the material. We also note that in the *absence* of Si, the concentration of O donors can be significantly higher.) The concentration of the V_{Ga}-O_N complex is at least an order of magnitude smaller than that of Si, and therefore too small to cause any signifant compensation. However, its concentration and that of V_{Ga} are sufficiently high to explain the YL.

The rapid increase of the formation energy of V_{Ga} and V_{Ga}-O_N with decreasing Fermi energy [see Fig. 2(a)] implies that the equilibrium concentration of the V_{Ga}-related defects decreases rapidly as the Fermi level moves away from the conduction band, explaining why the YL is observed only in *n*-type GaN. Our results also explain why the YL is suppressed under Ga-rich conditions:[9] Ga vacancies are less likely to form under Ga-rich conditions.[6] Thus, the Ga vacancy and its complex with O are consistent with the experimental observations, both concerning the electronic properties and the energetic features.

Our discussion has focused on incorporation of Ga vacancies during growth. However, it can be envisioned that Ga vacancies can also be created by ion implantation. Indeed, Pankove and Hutchby[13] found that ion implantation with a variety of elements produced a broad luminescence band around 2.15 eV.[13] Again, formation of Ga vacancies provides a consistent explanation for the yellow luminescence.

Finally, we point out that metal vacancies and their complexes with donor impurities are well known in II-VI compounds such as ZnS and ZnSe. The so-called *SA* centers (complexes between V_{Zn} and donors) exhibit behavior which is strikingly similar to the YL in GaN,[3] including a broad luminescence band of Gaussian shape, and a large shift between emission and adsorption bands.[17]

In summary, based on our first-principles calculations we find strong evidence that the deep acceptor level introduced by the Ga vacancy (or related complexes) is responsible for the infamous YL in GaN, and that the formation of Ga vacancies may be enhanced by complex formation with donor impurities.

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