Phys. Status Solidi A **214**, No. 4, 1600445 (2017) / **DOI** 10.1002/pssa.201600445

physica status solidi a
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applications and materials science

Demonstration of the donor characteristics of Si and O defects in GaN using hybrid QM/MM

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Received 20 June 2016, revised 8 November 2016, accepted 15 November 2016

Keywords cluster calculations, doping, GaN, *n*-type semiconductors, oxygen, silicon

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Using hybrid quantum mechanical/molecular mechanical (QM/MM) embedded cluster calculations, we investigate the stabilization of silicon and oxygen dopants in GaN. Formation energies of Si on a Ga site and O on an N site are calculated at two levels of theory using conventional thermochemical and kinetic exchange and correlation density functionals (B97-2 and BB1k). We confirm the shallow donor nature of these substitutional defects. We find that the 0/1+ transition levels for both Si and O species lie well above the bottom of the conduction band, in agreement with previous supercell-based simulations. The origin of this artifact is discussed in the context of relevant experimental results and we show how correct in-gap shallow levels can be ascertained in good agreement with experiment.

1 Introduction

GaN has many industrial applications such as solid state lighting and high power microelectronics [1]. For many devices, both n-type and p-type layers are required, and oxygen and silicon are most commonly used as n-type dopants [2]. Indeed, oxygen is often assumed to incorporate in as-grown GaN unintentionally and be the source of n-type conductivity [3, 4]. Although many spectroscopical data are available on intentionally O- and Si-doped GaN [5–10], indicating the presence of carrier traps and particular luminescence bands [5–8], as well as electron spin resonance signatures [9, 10], to date there have been only a small number of theoretical studies on the subject [11–18], mostly performed using density functional theory within a supercell approach, which do not support the presence of such traps [13–18].

Here, we report the first hybrid quantum mechanical/molecular mechanical (QM/MM) embedded cluster calculations on the electronic properties of O and Si defects in GaN. The advantage of our approach is in the accurate account of polarization effects and unambiguous definition of the vacuum reference energy.

2 Methodology

In our method, the inner cluster of 116 atoms centered on the defect is treated with density functional theory using (i) the second generation thermochemical exchange and correlation hybrid functional B97-2 [19], which is similar to those commonly used in recent plane-wave supercell calculations (21% exact exchange compared with 25% for PBE0 [20] or HSE06 [21]); (ii) the SBKJC small-core pseudopotentials on Ga [22] within the cluster and large-core refitted pseudopotentials [23, 24] on the outside that provide a suitable embedding potential on the defect; and (iii) the atomic basis set of def2-TZVP quality on N, O, and Si [25] and matching SBKJC basis on Ga [22]. For comparison, we use a second hybrid exchange and correlation functional employing 42% exact exchange (BB1k) [26], fitted to reproduce kinetic barriers and thermochemical data, which gives a more accurate description of electron localization than B97-2 [24, 27]. This QM region is embedded in an outer cluster which is treated with an MM level of theory using polarizable-shell interatomic potentials [24, 28]. The method has been implemented in ChemShell [29–31] that employs Gamess-UK [32] for the QM and GULP [33] for MM single point energy and gradient calculations. Technical details are discussed elsewhere [31, 34]. This method was applied successfully to treat defects in ZnO [35] and GaN [24] and the band alignment of polymorphs of TiO_2 [36, 37].

Using the approach above, we investigate the stability and electronic properties of the industrially relevant substitutional O_N and Si_{Ga} defects in GaN by calculating their formation energy as a function of electron chemical potential (or Fermi level). Our study corresponds to low doping levels, so we do not consider interstitial defects, which, under high doping conditions, may form [2]. In previous studies, we have established the thermodynamical stability of electrons in GaN, which demonstrates that n-type doping will be favorable [34, 38, 39].

The formation energies of defects are determined by the following reactions:

$$N_N^X + \frac{1}{2}O_2 \rightarrow O_N^X + \frac{1}{2}N_2, \tag{1}$$

$$N_N^X + \frac{1}{3}Ga_2O_3(s) + \frac{1}{3}Ga(s) \rightarrow O_N^X + GaN(s), \tag{2}$$

$$Ga_{Ga}^X + \frac{1}{3}Si_3N_4(s) \rightarrow Si_{Ga}^X + GaN(s) + \frac{1}{6}N_2, \tag{3}$$

$$Ga_{Ga}^X + Si(s) \rightarrow Si_{Ga}^X + Ga(s), \tag{4}$$

where Eqs. (1) and (3) correspond to O_N^X and Si_{Ga}^X formation, respectively, in anion-rich conditions and Eqs. (2) and (4) correspond to their formation in anion-poor conditions (we follow here the standard Kröger–Vink [40] notations with a cross reserved for neutral defects). The chemical potentials of N_2, O_2 molecules, and single atoms of Ga, Si are calculated using Gamess-UK with the same basis set and pseudopotentials as in the cluster calculations described above, while the formation energies of GaN, Ga_2O_3, and Si_3N_4 are derived from the standard thermochemical enthalpies of formation [41].

The latter approach has been adopted as calculating formation energies of solids using hybrid QM/MM embedded clusters is highly challenging and beyond the scope of this study, although technically feasible (cf. Ref. [42]). Accurate thermochemical functionals, such as those we have used in this study, are known to reproduce well binding energies for representative sets of molecules, from which bulk formation energies could be computed that match experiment closely, within ~0.1 eV [24, 26, 27]. Next, experimental ionization potentials for atoms have been used to minimize basis set superposition errors. To describe cations in GaN accurately and efficiently, we have removed outer diffuse functions from the respective basis sets. As a consequence, the description of neutral atoms using these basis sets is poor, whereas, cations in their formal oxidation states are described well. As the ionization potentials formed the training set of thermochemical properties, along with the binding energies, for the hybrid functionals we use, the experimental and calculated values should be in agreement. We estimate the overall basis set superposition error for the Si impurity as 0.6 eV, while for O, whose valence states in the neutral molecule are described well, the error is negligible.

3 Results We show the formation energy of O_N (assuming N-rich conditions) determined using Eq. (1), as a function of Fermi level relative to the valance band maximum (VBM) in Fig. 1. One disadvantage of our approach is a significant overestimation of the band gap in this class of material due to the artificial localization of diffuse charge carriers, as discussed in Ref. [31]. To rectify this error, we realign idealized conduction states at the bottom of the conduction band, which are, therefore, not modeled directly, using the experimental value of ~3.5 eV [1].) We find that O_N is a single carrier donor as the positive charge state is most stable for all Fermi levels within the band gap. This formation energy is significantly lower than that obtained using periodic supercell models [15–18], which we attribute to the different treatment of polarization and our use of experimental enthalpies of formation in Eqs. (1)-(4) rather than computed values [43]. The formation energy of O_N in the neutral charge state is −0.398 eV in N-rich (and O-rich) conditions with B97-2 functional (cf. −0.244 eV with BB1k), where the negative value means that O_N is

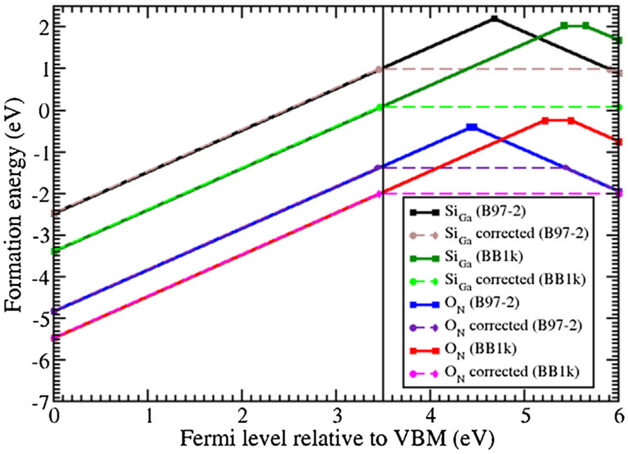

Figure 1 Formation energy of O_N and Si_{Ga} as a function of Fermi level relative to the VBM. Two hybrid exchange and correlation functionals are employed. Anion-rich conditions are assumed. Only the most stable defect charge state is shown. Corrected transition levels are also shown (see main text for details).

favorable to form in GaN (in N-poor conditions, the formation energy has a rigid energy shift of +2.617 eV compared with N rich conditions, which results in reasonable agreement with the periodic LDA determined value reported by Mattila and Nieminen [16]). We argue that this low formation energy is a consequence of the much lower chemical potential of nitrogen than oxygen, cf. the 9.93 and 5.12 eV dissociation energies of N_2 and O_2 molecules [41]. The +1/0 transition level is in the conduction band at 0.920 eV above the conduction band minimum (CBM), which implies that the defect will be autoionized in the material up to high doping levels.

Next, we discuss the formation energy of $\mathrm{Si_{Ga}}$ (assuming N rich conditions), shown in Fig. 1. We find that $\mathrm{Si_{Ga}}$ is also a shallow donor, with the +1 charge state most favorable for all Fermi levels within the band gap. The formation energy of neutral state of $\mathrm{Si_{Ga}}$ is 2.499 eV with B97-2 functional (cf. 2.048 eV with BB1k, the discrepancy being due to the difference in accuracy of the relevant calculated 3rd and 4th ionization energies of Ga and Si, respectively). The +1/0 transition level lies 1.094 eV above the CBM, which implies that, similar to the case of $\mathrm{O_N}$, the defect will be autoionized in the material. Under N poor conditions, there is an energy shift of −1.423 eV compared with N rich conditions. The discrepancy between our results and those obtained using supercell techniques is significantly lower for the ionized species (within 0.1 eV of each other [17]), but the neutral impurity energy differs strikingly by ca. 2 eV. Our result for the ionized species in Ga rich conditions is also ca. 2 eV lower than that of Mattila and Nieminen [16]. The periodic calculations differ in a shift of the (0/+) transition level to the bottom of the conduction band, adopted by Gordon et al. [17]. Whatever the choice of the reference, however, the source of disagreement between our results and theirs is in the value of the ionization energy, which is well defined in the hybrid QM/MM embedding approach [31], but a topic of debate regarding supercell approaches [17].

Thus, both transition levels calculated at the current level of theory are in the conduction band meaning no activation is required for the donor ionization and that neither can serve as a carrier trap, but only as a scattering center (cf. [44, 45]). This naïve conclusion should, however, be reconsidered in light of shallow donor theory that describes diffuse electronic states, introduced by defects (cf. [10]). Below we use the atomic units of Hartree in theory, thus simplifying the expressions, but conventional units of eV and Å when discussing the results. In the effective mass approximation, the ground (1s) state energy of a hydrogenic impurity is $E_\mathrm{H} = -m^*/2\varepsilon$, where m^* is the effective mass and ε is the dielectric constant of the material. Using the well-established experimental value of $m^* = 0.22\ m_\mathrm{e}$ [46] and calculated angular averaged value of $\varepsilon = 10.09$ [47], we obtain a generic donor energy of −0.029 eV, which should be compared to −0.022 ± 0.004 eV for $\mathrm{Si_{Ga}}$ [48] and −0.029 eV for $\mathrm{O_N}$ [49], with reference to the bottom of the conduction band. The Bohr radius of the impurity electron, $a_\mathrm{H} = \varepsilon/m^*$, is 45.9 Å. It is, therefore, necessary to correct our (0/+) transition levels as the donor bound electron will be much more delocalized than permitted by the size of our QM region (the radius R_QM of which is ca. 6.8 Å), in common with conventional supercell methods.

Table 1 Donor activation energies, E_D(eV), determined with two exchange and correlation density functionals in the hybrid QM/MM approach, compared to experiment [48, 49].

	B97-2	BB1k	experiment
$\mathrm{Si_{Ga}}$	−0.046	−0.037	−0.022 ± 0.004
$\mathrm{O_N}$	−0.056	−0.041	−0.029

We introduce species-corrected donor electron energies (E_D), by adopting a two-region approach:

$$E_\mathrm{D} = n_\mathrm{QM} E_\mathrm{QM}^{0/+} + n_\mathrm{MM} E_\mathrm{H}, \tag{5}$$

where the energy contribution from the QM region is calculated as above, whereas the contribution from outside is taken as E_H, but both scaled by the fraction of an electron localized in the two respective regions, as determined by integrating the hydrogenic solution (we calculate, $n_\mathrm{QM} = 0.02$ and $n_\mathrm{MM} = 0.98$). We note, however, that, based on the hybrid QM/MM approximation, E_QM is underbound due to quantum confinement (see Ref. [50]), which, for a spherical Coulomb potential well is given by $\pi^2/2m^* R_\mathrm{QM}^2 - 1/2\varepsilon$. Our results, taking into account these corrections, are shown in Table 1 and Fig. 1.

Compared to the generic hydrogenic center, both impurities are found to have slightly deeper values. On comparison with experiment, the kinetic functional BB1k performs somewhat better, but still overbinds both donors.

To improve further our approach, we should include nonlocal screening effects in the QM region and allow for a redistribution of the electron density between the QM and outer simulation regions, which will target the analysis of activation energies, for example, reported from deep level transient spectroscopy [51–54] studies on intentionally doped GaN, photoluminescence measurements, and other optical spectroscopic techniques. Finally, following the argument of Gordon et al. [17], we find no evidence of DX centers associated with O or Si substitutional defects in GaN, as the (+/−) transitions occur above the conduction band minimum (see Fig. 1). Further investigation of potential DX centers in GaN will be made possible by the current methodological developments.

4 Conclusions In summary, we have studied the O and Si defect formation in GaN, using a hybrid QM/MM embedded cluster approach. Our results show $\mathrm{O_N}$ and $\mathrm{Si_{Ga}}$ are both shallow donors in GaN whose formation is energetically favorable.

Acknowledgements Zijuan Xie thanks the China Scholarship Council (CSC) for support. We are grateful to Alex Ganose and Stephen Shevlin for technical help and Audrius Alkauskas for useful discussion. The EPSRC is acknowledged for funding (EP/K038419, EP/I03014X, EP/K016288). Computational resources were provided though the Materials Chemistry Consortium supported by EPSRC grant EP/L000202.

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