Ab initio study of metastability of Eu^{3+} defect complexes in GaN

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Abstract

Density functional theory (DFT) within the generalized gradient approximation (GGA) has been used to study the structural and electronic properties of Eu^{3+} defect complexes in GaN under Ga-rich conditions. Two distinct configurations of the $Eu_{Ga}V_N$ defect complex, the *axial* and *basal* configuration, have been investigated. We report two forms of metastable defects namely; the Negative U defect in the lower half of the GaN band-gap and a metastable defect with two distinct configurations each with levels at E_C −0.46 eV and −0.56 eV in the upper half of the GaN band-gap.

Keywords:
Metastability
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1. Introduction

Rare-earth (RE) species in semiconductors are currently intensively being studied both experimentally and theoretically as possible optical dopants in GaN since the early works of Ennen et al. [1]. Studies have shown that the photoemission from RE ions in semiconductors covers the entire visible spectrum, and are characterized by very sharp optical emissions ranging from the ultraviolet (UV) to the infrared (IR) [2–4]. This makes them extremely suitable for application in optoelectronic devices and in the manufacture of the next generation phosphors [1,2,5–7].

GaN is an ideal host candidate for optical dopants because of its thermal stability and its large and direct band gap [2–4,6]. Compared to standard semiconductors like Si or Ge, GaN is a good host for RE dopants (Eu, Er, and Tm) which have been associated with red, green, and blue luminescence respectively [1–8]. The intra-*f* electronic transitions in rare-earth (RE) ions, are believed to be related to their emission spectrum [1,2,5,6]. Europium (Eu) has the electronic configuration [Xe] $4f^7 6s^2$. In common with other members of the series, it exhibits a number of intense and relatively narrow luminescence bands in the visible and near infrared region of the photoemission spectrum. As an ion, Eu can exist in two oxidation states: Eu^{2+} and Eu^{3+}, with the former being rarely encountered in semiconductors.

Several studies have been done on Eu in GaN both theoretically [2–4,9,10] and experimentally [11–18]. However, to the best of our knowledge, it is only Auret et al. [16] who recently experimentally observed a metastable defect with charge-state controlled metastability in 300 keV Eu doped GaN, annealed at 1000 °C. The two configurations had DLTS activation energies for electron emission of 0.18 eV and 0.27 eV respectively. None of the above mentioned theoretical studies have reported any form of metastability of Eu in GaN.

In this work, we focus specifically on Eu_{Ga}, which has been shown by various authors [2–4] to be the minimum energy configuration of Eu in wurtzite GaN. In an attempt to explain the experimentally observed metastability, we considered $Eu_{Ga}V_N$ complex. Sanna et al. [2,9] have shown that this complex is stable and may occur in two possible configurations (axial and basal). Since this complex does not involve further impurity atoms, and can occur in two configurations, we believe that this complex is the most reasonable candidate to consider as a possible explanation for the experimentally observed charge-state metastability.

2. Computational details

The exchange-correlation (XC) functional is a fundamental issue in density functional theory (DFT). It is normally approximated in the form of local density approximation (LDA) [19,20] or generalized gradient approximation (GGA) [21] with Perdew–Burke–Ernzerhof (PBE) version of GGA being the most commonly used. The chronic over-binding of the local density approximation (LDA) [22] which has been shown to lead to underestimation of equilibrium properties by about 1%, can be overcome by using the PBE functional even though it usually overestimates equilibrium properties by about the same amount [23]. In this work we have used PBE XC-functionals to study the metastability of Eu^{3+} defect complexes in GaN. We have used [Xe] $4f^6$ psedopotentials for Eu^{3+}.

The electronic structure calculations were done based on the generalized Kohn–Sham approach [24] and the Projector-augmented wave (PAW) method [25,26] as implemented in the VASP code [27]. PAW potentials for Ga, N and Er^{3+} were used in this study. After optimizing the unit cell we obtained 3.19 Å and

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1.62 for a and c/a respectively and a quasi-particle band gap E_g of 2.71 eV compared to 3.186 Å, 1.627 and 3.4 eV reported experimentally for a, c/a and E_g. For defect calculations, a 96 atom supercell was used with a kinetic energy cutoff of 500 eV, Methfessel–Paxton (MP) smearing of 0.02 eV and the Brillouin zone was sampled with a Γ centered $2\times2\times2$ Monkhorst–Pack grid of k-points.

The formation energy of the defects were calculated according to the Zhang and Northrup formalism [28]. Using this formalism, the formation energy of a defect (say Eu on Ga site) at charge state q is

$$E^f(Eu^q_{Ga}) = E_{tot}(Eu^q_{Ga}) - E_{tot}(GaN) + \mu_{Ga} - \mu_{Eu} + q[E_F + E_V] \quad (1)$$

Where, $E_{tot}(Eu^q_{Ga})$ is the total energy of the supercell containing Eu_{Ga} at charge state q, $E_{tot}(GaN)$is the total energy of the pristine GaN supercell, μ_{Ga} and μ_{Eu} are the chemical potentials for Ga and Eu respectively, *i.e.*, energies of reservoirs with which atoms are exchanged. E_F is the Fermi level, referenced to the valence-band maximum in the bulk and E_V is the energy of the valence-band maximum (VBM) of the defect. If the formation energy is calculated in the infinite crystal, then VBM of the defect is equal to the VBM of the bulk (pristine) system [29]. The thermal transition energies $\varepsilon(q/q')$ is defined as the Fermi energy where the lowest-energy charge state changes from q to q' as E_F rises in the gap. Thus, for Eu on a Ga site,

$$\varepsilon(q/q') = \frac{E^f(Eu^{q'}_{Ga}) - (Eu^q_{Ga})}{q - q'} \quad (2)$$

As mentioned earlier, we investigated the properties of the $Eu_{Ga}V_N$ complex. This complex has two configurations namely the *axial* and *basal* configurations, which might give rise to the observed metastable properties. The axial configuration has $\mathbf{C_{3v}}$ symmetry while the basal configuration has $\mathbf{C_{1h}}$ symmetry [see Fig. 1]. The C_{1h} symmetry arises because the Eu–N bond is longer along the c-axis than the other three.

3. Results and discussion

Using Eqs. (1) and (2) mentioned above, we obtained both the formation energies and the thermodynamic transition energies for all the defect configurations considered under Ga-rich conditions. As seen in Table 1, the formation energies at various charge states are reported.

From the table, it is evident that the *basal* configuration of the $Eu_{Ga}V_N$ defect complex has lower formation energies for the neutral and positive charge states compared to the *axial* configuration. However for the negative charge states, the *axial* configuration is more stable compared to the *basal* configuration. This indicates that, even though the two configurations of the defect complex have the same number and type of atoms, the stability of one configuration over the other is charge-state dependent. This observation is consistent with the experimental observation of Auret et al. [16].

Fig. 2 shows the formation energy of the defect in both configurations as a function of Fermi-level. Only the most stable charge state is shown. From this it is possible to deduce the thermodynamic transition levels.

The metastability predicted from the results in Table 1 is also observed in Fig. 2.

In the upper half of the GaN band-gap, it is evident that from the −1 charge state and lower, the formation energy of the two configurations are almost equal with the thermodynamic transition levels for the two different configurations of the defect complex occur at almost equal energies. In some instances, the charge states overlap or even cross each other. This implies that, experimentally, if a Eu doped GaN sample containing the defect complex is annealed at relatively high temperatures with the defect in the negative charge state (*e.g.* under forward bias in an n-type sample, as in the case of Auret et al. [16]), the defect will be found in both configurations (*axial* and *basal*). Upon cooling down, these two configurations will be frozen in, and two DLTS peaks (or a broadened peak, if they are close together) should be observed.

Table 1
Formation energies in eV of the different configurations of the defect complexes.

q	$Eu_{Ga}V_N$-*axial*	$Eu_{Ga}V_N$-*basal*
−3	**8.35**	8.37
−2	**5.64**	5.66
−1	**3.35**	3.38
0	1.19	**1.13**
1	−0.72	−**0.88**
2	−1.01	−**1.19**
3	−1.50	−**1.76**

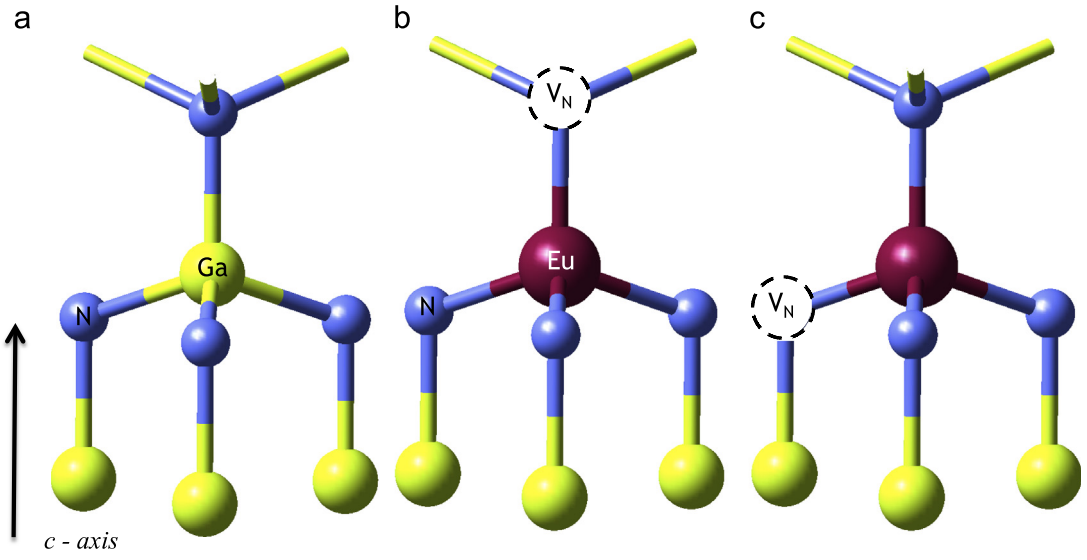

Fig. 1. (a) GaN unit cell, (b) $Eu_{Ga}V_N$-*axial* and (c) $Eu_{Ga}V_N$-*basal*.

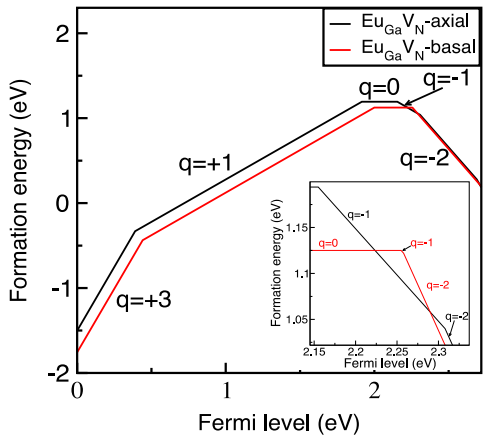

Fig. 2. Thermodynamic transition levels for $Eu_{Ga}V_N$ defects complex.

If the sample is annealed under forward bias, only the lower energy basal configuration should be observed.

In their paper, Auret et al. [16] found two defects, the shallower E1 at $E_C - 0.18$ eV and the deeper E2 at $E_C - 0.27$ eV. The E1 was found to be stable under reverse bias, while the E2 was found to be stable under zero bias conditions. The sum of the heights of the two defects remained constant, indicating that they are due to two configurations of the same defect.

The results obtained by Auret et al. [16] may be explained by observing the area enlarged in the inset in Fig. 2. In the neutral charge state (horizontal lines) the basal configuration is stable. Also, it can be seen in Fig. 2 that the $0/-1$ transition of the basal configuration occurs at a level shallower from the conduction band, compared to the axial configuration. We therefore associate the $0/-1$ transition of the basal configuration with the shallower E1 DLTS peak that is stable under reverse bias.

When the defect is in the -1 state, the axial configuration is more stable. The axial configuration has a $0/-1$ transition level further from the conduction band, which we associate with the E2 DLTS peak.

In our study we report the defect levels at $E_C - 0.46$ eV and $E_C - 0.56$ eV compared to $E_C - 0.18$ eV and $E_C - 0.27$ eV reported by Auret et al. [16]. Our calculated levels are much deeper in the band gap compared to the experimentally reported levels. This can be attributed to the approximation of the XC functional associated with the DFT technique. However despite the shortcomings of DFT, DFT has been successfully used as a tool for predicting defect levels in GaN [2–4,9]. Despite the large absolute difference in energies, the relative difference in energy between the two transition levels is of the correct order of magnitude: the predicted differences in formation energy of the defects are 0.06 eV and 0.03 eV in the 0 and -1 states respectively. These differences are in the order of a few kT at 135 K, where the experiments were performed, explaining the complete conversion of the defect from one configuration to the other.

Another form of metastability observed in Fig. 2: in the lower half of the GaN band-gap, there is evidence of a negative U defect. The system changes its charge state from $+3$ to $+1$ without changing into the $+2$ charge state. A negative U defect occurs when an ionized defect captures two (2) electrons with the second electron being more tightly bound that the first. This probably results from lattice relaxations and gives rise to metastability. This defect was not observed by Auret et al., probably because it is too deep in the band gap to be ionized at a measureable rate in n-type material.

4. Conclusion

We have used *ab initio* DFT to investigate the charge-state controlled metastability of Eu in GaN, which to the best of our knowledge, has not previously been done. We have shown the existence of metastable defects in Eu implanted GaN in both the upper and lower halves of the GaN band-gap. We have also compared the theoretically predicted metastable defect behavior to experiment, and found possible agreements.

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