Magnetism induced by Ga vacancy in rare earth
R(R=Gd,Eu,Tm)doped GaN

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Abstract. In recent years, GaN doped with rare earth has attracted much attention due to its potential application in spintronic devices and optoelectronic devices. Based on the density functional theory, we investigate the magnetic moment, formation energy, and electronic structure in R (R= Gd, Eu, Tm) doped GaN semiconductors. We focus on the contribution of Ga vacancy to the magnetism, and calculate the formation energy of different Ga vacancies in the presence of Gd, Eu, or Tm dopants, and that of Gd, Eu, Tm dopants in native defects of Ga vacancy. The possible stable defect structures in GaN are given according to their formation energy. It is found that the Ga vacancies prefer to form cluster, and the formation energy of concentrated Ga vacancies is low compared to separated Ga vacancies. The 5d electrons of rare earth as well as 4f electrons have a larger contribution to the magnetism of GaN:R with Ga vacancy than without Ga vacancy. In addition, intermediate bands were observed in GaN:R with intrinsic defects, which possibly opens the potential application of R-doped semiconductors in the third generation high efficiency photovoltaic devices.

1. Introduction
Over the past decades, rare-earth doped semiconductors have received wide attention because of their possible applications in spintronic and optoelectronic devices. In 1989, Favennec et al.\cite{1} demonstrated that the thermal queching of the luminescence in the erbium doped semiconductors decreases with the increase of band gap of the host materials. As one of typical wide band gap semiconductors, GaN is an ideal host candidate for rare-earth ions because of its high field transport characteristics and incorporating with the rare-earth ions very well. Recently, Gd-doped GaN (GaN:Gd) has attracted considerable interest due to the characters of its high temperature ferromagnetism and colossal magnetic moment\cite{2, 3, 4, 5}. However, the microscopic mechanism of ferromagnetism in GaN:Gd still remains controversial since the ferromagnetism was discovered first in 2000\cite{6}. Dhar et al.\cite{7, 8, 9} pointed out that the ferromagnetic coupling in the GaN:Gd system cannot be explained simply in terms of direct, double, or superexchange between Gd atoms since the average Gd-Gd distance is too large. Gohda et al.\cite{10} proposed that the ferromagnetism of GaN:Gd should be derived from the occurrence of cation vacancy, and Thiess et al. found that Ga vacancy cluster in GaN:Gd has the stable structure and may induce the enlargement of magnetic moment\cite{11}.
In this paper, we investigate the magnetic moment, formation energy, and electronic structures of R (R=Gd, Eu, Tm) dopants and their complexes with cation Ga vacancies in wurtzite GaN by the density functional theory. We first calculate the crystal parameters of isolated Gd dopant and defect complexes with one Ga or N vacancy. Then five Ga vacancies are systematically considered in GaN:R to explore the origin of magnetism, and the formation energies of different defect complex configurations are discussed. Finally, we analyze the electronic structures of the most stable defect configurations of Gd, Eu, Tm-doped GaN.

2. Computational details
In this work, all calculations are performed with the Vienna ab-initio simulation package (VASP) by using the pseudopotential plane-wave scheme[12]. The interactions between ions and electrons are described by the projector augmented wave (PAW) method developed by Blöchl [13, 14]. The cutoff energy of the plane wave basis set is 500 eV, and the Brillouin-zone integration is performed by 5×5×3 Mokhorst-Pack special k-points. All atoms are fully relaxed with the total energy change less than 10⁻⁵ eV and the force on each ion less than 0.03 eV/Å. The Ga 4s²4p¹, N 2s²2p³, Gd 5s²5p⁶4f⁷5d¹6s², Eu 5s²5p⁶4f⁶5d¹6s², and Tm 5s²5p⁶4f¹²5d¹6s² are considered as valence electrons. The strong correlation effect of the R-4f electrons is treated by the local spin density approximation with Hubbard-U corrections (LSDA+U) with \( U = 9.2, 8.506, 10.082 \) eV and \( J = 1.2, 1.109, 1.317 \) eV for Gd, Eu, Tm taken from Ref.[15].

To explore the defect properties, a 3×3×2 GaN supercell containing 72 atoms (Ga_{36}N_{36}) is used. We substitute one R for one Ga atom, corresponding to a 2.78% R doping concentration. Here, one Ga-site is considered for R substitution because the R_{Ga} has been both experimentally and theoretically confirmed to be the most stable configuration in all states[16, 17, 18]. In this paper we focus on six different defect complexes constituted by replacing one Ga atom with one R atom and simultaneously removing five Ga atoms on different neighboring positions, i.e., GaN:R+5V_{Ga}, as illustrated in Fig. 1.
Table 1. Relaxed crystal parameters and calculated magnetic moments of three defect systems, i.e., GaN, GaN:Gd, and GaN:Gd+V_Ga.

|        | a(Å) | c(Å) | c/a | m_Gd(μ_B) | m_tot(μ_B) |
|--------|------|------|-----|-----------|-----------|
| GaN   | 3.211| 5.238| 1.631| -         | -         |
| GaN:Gd| 3.282| 5.737| 1.748| 7.173     | 7.045     |
| GaN:Gd+V_Ga | 3.292| 5.383| 1.635| 7.171     | 9.110     |

3. Results and discussions

In table 1 we show the relaxed crystal parameters and the calculated magnetic moments for two simple defect systems, i.e., the isolated dopant Gd (GaN:Gd) and the defect complexes (GaN:Gd+V_Ga) constituted by one Gd and one Ga vacancy, and also pure GaN for comparison. For GaN:Gd, the lattice constants a and c expand about 2.2% and 9.5% compared with the pure GaN due to the ionic radius of Gd (0.94 Å) larger than that of Ga (0.62 Å). For the defect complexes, the lattice constant c shrinks compared to isolated Gd dopant due to the presence of Ga vacancy, which agrees with the previous study[19]. The magnetic moment of Gd atom is about 7.1 μ_B, and Ga vacancy can induce 2μ_B. Therefore, the Ga vacancies are possibly responsible for the enlarged magnetic moment of GaN:Gd. In the following, the various defect complexes containing dopants R and five Ga vacancies are theoretically investigated for exploring the effect of vacancy on the magnetism.

Table 2. Magnetic moment(m_R) of R atom and the total magnetic moment(m_tot) in GaN:Gd+5V_Ga, GaN:Eu+5V_Ga, and GaN:Tm+5V_Ga. The unit of magnetic moment is μ_B.

|        | m_Gd | m_tot | m_Eu | m_tot | m_Tm | m_tot |
|--------|------|-------|------|-------|------|-------|
| a      | 8.096| 17.178| 6.444| 16.756| 2.226| 11.311|
| b      | 8.258| 17.428| 6.392| 16.829| 2.205| 12.735|
| c      | 11.153| 21.110| 1.652| 10.872| 0.218| 9.127 |
| d      | 7.815| 18.744| 6.465| 17.089| 2.211| 12.986|
| e      | 8.111| 18.742| -0.174| 10.655| 1.924| 12.690|
| f      | 8.209| 18.899| 4.330| 14.885| 0.222| 10.859|

Table 2 lists the magnetic moments of six defect complex configurations for GaN: R+5V_Ga (see Fig. 1). It can be seen that the largest magnetic moment is obtained for Gd in configuration-c, Eu in configuration-d, and Tm in configuration-a. For the total magnetic moment, the largest value of GaN:Gd+5V_Ga occurs in configuration-c, where all vacancies lie in the same cation plane as Gd, while GaN:Eu+5V_Ga and GaN:Tm+5V_Ga have the largest total magnetic moments in configuration-d. In addition, compared with Gd atom, the magnetic moments of Eu (Tm) atoms rather strongly depend on the Ga vacancy configurations. This should be attributed to the different crystal field effect on the delocalized f states of Eu (Tm) atoms for different Ga vacancy configurations. We further calculate the formation energies of six defect complex configurations to explore their energetic stability. ∆E_R(V) represents the formation energy of
Ga vacancies in the presence of dopants and $\Delta E_V(R)$ is that of dopant atom in the native Ga vacancies. They are respectively expressed as[20]

$$\Delta E_V(R) = E_{R+V} - E_V + \mu_{Ga} - \mu_R,$$

and

$$\Delta E_R(V) = E_{R+V} - E_R + n_{Ga}\mu_{Ga},$$

where $E_{R+V}$ is the total energy of the supercell containing R dopants and Ga vacancies. $E_R$ is the total energy of GaN:R without Ga vacancies, and $E_V$ is the total energy of GaN with Ga vacancies and without R dopants. $\mu_i$ is the corresponding chemical potential of atom $i$ ($i=Ga, R$) referenced to elemental solid with energy $E(i)$, and $n_{Ga}$ ($n_{Ga} > 0$) indicates the number of Ga atoms removed from the supercell.

Table 3. Formation energies of Gd, Eu, Tm dopants in the native Ga vacancy (Eq. 1) and that of Ga vacancies in the presence of R dopants (Eq. 2). The unit of formation energy is $eV$

| GaN:Gd+5V$_{Ga}$ | GaN:Eu+5V$_{Ga}$ | GaN:Tm+5V$_{Ga}$ |
|------------------|------------------|------------------|
| $\Delta E_V(Gd)$ | $\Delta E_{Gd}(V)$ | $\Delta E_V(Eu)$ | $\Delta E_{Eu}(V)$ | $\Delta E_V(Tm)$ | $\Delta E_{Tm}(V)$ |
| a | -0.081 | 38.874 | -1.528 | 35.439 | -1.584 | 36.460 |
| b | 0.287 | 39.312 | -1.571 | 36.695 | 2.579 | 40.851 |
| c | -16.545 | 22.448 | 4.673 | 41.869 | -0.497 | 37.718 |
| d | 1.163 | 40.448 | 0.154 | 37.979 | -0.368 | 38.451 |
| e | -0.310 | 39.019 | 4.382 | 41.878 | -0.157 | 38.397 |
| f | -0.043 | 39.493 | 1.403 | 39.171 | -1.208 | 37.591 |

In table 3 we list the above two types of formation energies. It is found that the Ga vacancies in GaN doped with R are very difficult to form, and the R doping in GaN with the native Ga vacancies is relatively easy. According to the formation energy $\Delta E_V(R)$, GaN:Gd+5V$_{Ga}$-c has the lowest formation energy, and GaN:Eu+5V$_{Ga}$-b and GaN:Tm+5V$_{Ga}$-a have the lowest formation energy. For the three configurations, Ga vacancies have a dense distribution, which is in qualitative agreement with the other work[11]. Thus our calculated results show that GaN:Gd+5V$_{Ga}$-c, GaN:Eu+5V$_{Ga}$-b, GaN:Tm+5V$_{Ga}$-a are the stabllest defect structures among all defect structures studied.

Fig. 2 shows the total and partial density of states (PDOS) of GaN:Gd+5V$_{Ga}$-c, GaN:Eu+5V$_{Ga}$-b, GaN:Tm+5V$_{Ga}$-a, and also GaN:Gd for comparison. We see that the conduction band of GaN doped with R is primarily attributed to N-2p, Ga-4s, Ga-4p, and R-4f states. The magnetic moment of R atoms is mainly contributed by their d and f states. The N atoms around Ga vacancies can induce the localized levels close to the Fermi level in the down spin channel, which leads to the magnetic moment, as shown in Figs. 2(b)-2(d). In contrast to that of GaN:Gd+5V$_{Ga}$, the f states of GaN:Eu+5V$_{Ga}$ and GaN:Tm+5V$_{Ga}$ are relatively delocalized and are closer to Fermi level, so that the crystal field effect of f states is more significant for GaN:Eu+5V$_{Ga}$ and GaN:Tm+5V$_{Ga}$ than GaN:Gd+5V$_{Ga}$. 
Figure 2. The density of states (DOS) of (a) isolated substitutional GaN:Gd, and of defect complexes (b) GaN:Gd+5V\textsubscript{Ga}, (c) GaN:Eu+5V\textsubscript{Ga}, and (d) GaN:Tm+5V\textsubscript{Ga} with the stable defect structures.

4. Conclusions
In summary, we have performed an investigation of the magnetic moment, formation energy, and electronic structure of GaN:R (R=Gd, Eu, Tm) with Ga vacancy defects by using DFT calculation. Our calculated results show that the introduction of R dopants in GaN with the native Ga vacancies is relatively easy, but the formation of Ga vacancies in the presence of R dopants is very difficult. The magnetic moment of rare earth R in GaN:R is strongly dependent on the defect complex configurations. The f states in GaN:Eu+5V\textsubscript{Ga} and GaN:Tm+5V\textsubscript{Ga} are more delocalized and closer to the Fermi level than that in GaN:Gd+5V\textsubscript{Ga}.

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