

First-principle calculation for luminescent-effects of Si and Zn impurities in GaN

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Abstract

Phosphor-free GaN-based white-light LED which is usually generated as a combination of the blue bandedge emission and a yellow-green broad-band emission has been approved to be more reliable than phosphor-based white-light LED. First-principle method was employed to investigate the luminescent-effects of Si and Zn impurities in phosphor-free GaN-based LED. By explicitly calculating the formation energies and defect levels, the origin of yellow-green broad-band emission in Si and Zn co-doped InGaN/GaN multi-quantum wells(MQWs) were discussed and determined. We propose that the electron transition between Zn_i/Zn_N -Si_N D-A pairs are responsible for the observed yellow-green broad-band emission.

Introduction

White light-emitting diode (LED) is one of the most important applications of III-nitride material. The common method of making white LED involves coating an LED with monochromatic color (mostly blue LED made of InGaN) with phosphor to produce a desired white-light spectrum. However, the degradation of phosphor during the long period of optical pumping would deteriorate the output efficiency. In recent years, several research groups have attempted to develop phosphor-free GaN-based white LED [1-5] in order to improve the reliability. Sheu and Su *et al* [1,2] reported that by incorporating Si and Zn atoms into the well layers of InGaN-GaN MQW LEDs, white light could be generated as a combination of the blue InGaN bandedge emission and a 500~560nm broad-band emission. However, the intensity of the latter emission saturates with increasing injection current. Although this 500~560nm emission was attributed to Zn-Si donor-acceptor (D-A) pair in GaN[6,7], the detailed microscopic mechanism such as corresponding transition energy levels, charge states of Zn-Si of this broad-band emission and the reason for its saturation effect remain unclear. In this paper, the luminescent-effects of Si and Zn related point defects in GaN were explicitly studied using first-principles method. Based on the results, the effects of Si and Zn impurities in GaN on the origin of emission spectrum were discussed and determined.

Calculation Details

The calculations were executed in a 96-atom ($3a \times 2\sqrt{3}a \times 2c$) supercell structure which has been used in a number of previous studies in bulk GaN[8-10]. First-Principles calculations were performed using the GGA (PW91) exchange potential and ultra-soft pseudopotential. The plane wave cutoff energy was set to 430eV. The Brillouin-zone was sampled using a Γ centered $2 \times 2 \times 2$ grid, producing eight k points in the irreducible Brillouin zone (IBZ).

The formation energy [8] of a defect or impurity X in charge state q is described as Eq. 1:

$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[GaN, bulk] - \sum_i n_i \mu_i + q[E_F + E_v + \Delta V]$$

(1)

where $E_{tot}[X^q]$ is the total energy derived from a supercell calculation with one impurity or defect X in charge state q, $E_{tot}[GaN, bulk]$ is the total energy of the reference 96-atom GaN supercell. n_i indicates the number of atoms of type that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect or impurity is created, and the μ_i are the corresponding chemical potentials of these species. E_F is the Fermi level for the supercell with the vacancy, E_v is the energy of the bulk valence-band maximum, and ΔV is a correction term to align the reference potential in the defect with that in the bulk.

In order to find out the corresponding defects, we considered all six kinds of Si and Zn related point defects in GaN: Ga substituted by Silicon (Si_{Ga}), N substituted by Si (Si_N), Si interstitial defects (Si_i), Ga substituted by Zinc (Zn_{Ga}), N substituted by Zn (Zn_N), and Zn interstitial defects (Zn_i).

Results and Discussions

The formation energies of the six point defects are displayed in Fig.1, where Si_{Ga} and Zn_{Ga} curves meet well with the results in Ref. 11. It could be observed that: 1) Si_i and Zn_i are both +2 donors and easier to form in p-type; 2) Si_{Ga} has very low formation energy and favors to be a donor at +1 state; 3) Zn_{Ga} works as acceptor all the time; 3) Si_N and Zn_N are amphoteric defects, however, it's less probable for them to form in GaN than other defects.

The energy levels of each defects at their stable states were calculated and the DOS distribution were plotted in Fig.2 and Fig.3 for Si and Zn doped situation respectively. It's worth noting that: 1) For the amphoteric defects such as Si_N and Zn_N , all their stable states were calculated in order to find out explicitly what energy levels they may introduce into the gap; 2) Although the previous calculations predict that Si_N and Zn_N are energetically unfavorable, there are a few experimental observations supporting the existence of Si_N acceptors in GaN[11], thus they were still considered in the energy level calculation.

From the charged DOS results, we may obtain the energy level(s) of each defect, as shown in Table 1, and estimate the wavelength of the transition-emit light between these levels.

Table 1 Energy level(s) of Defect X in GaN

Defect X	Energy level(s)(ev)	
	$E_A(E_X - E_v)$	$E_D(E_c - E_X)$
Zn_N	1.900, 2.410	0.333, 0.847
Zn_{Ga}	0.037	--
Zn_i	--	0.122, 0.296, 0.411
Si_N	0.695, 1.280	2.411
Si_{Ga}	--	0.105
Si_i	--	1.418, 1.790

The results indicate that the transition between Zn_i/Zn_N - Si_N D-A pairs are responsible for the 500~560nm broad-band emission, as illustrated in Fig.4. And the reasons for its saturation may be given as follow:1) Since Zn_i , Zn_N and Si_N all have relatively high formation energies, the density of Zn_i/Zn_N - Si_N DAPs should be limited; 2) The yellow-green band corresponding DAPs are composed of deep level defects, however, the probability of the DAP transition decreases for deeper energy levels due to a smaller overlap of the electron and hole wave functions. Therefore, the intensity of the 500~560nm band saturates as the injection current increases due to the relatively low DAP density and small transition probability.

Conclusions

The effects of Si and Zn impurities in GaN were theoretically studied by First Principle calculation. From the calculation results we conclude that:1) Zn_i/Zn_N - Si_N D-A pairs should account for the observed 500~560nm broad-band emission in Si and Zn co-doped InGaN/GaN multiquantum wells(MQWs); 2) The result may explain the device performance under high excitation density, and built up a good base for the further theoretical study the luminescent-effect of impurities in III-nitride material.

References

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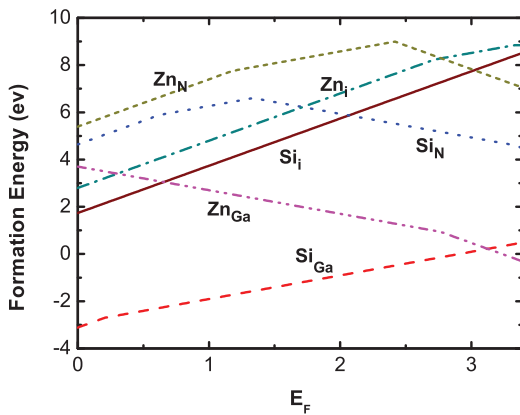


Fig.1. Formation energies as a function of Fermi level for Si and Zn impurities in GaN. Ga-rich conditions are assumed. The zero of Fermi level corresponds to the top of the valence band. Only segments corresponding to the lowest-energy charge states are shown. The slope of these segments

indicates the charge state. Kinks in the curves indicate transition between different charge states.

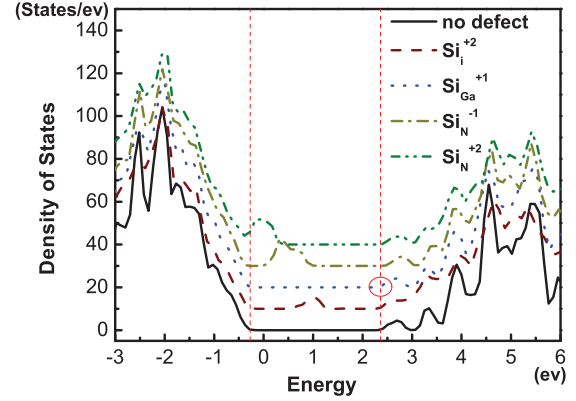


Fig.2. DOS comparison between perfect crystal and crystal with Si_i^{+2} , Si_{Ga}^{+1} and Si_N^{-1} defects

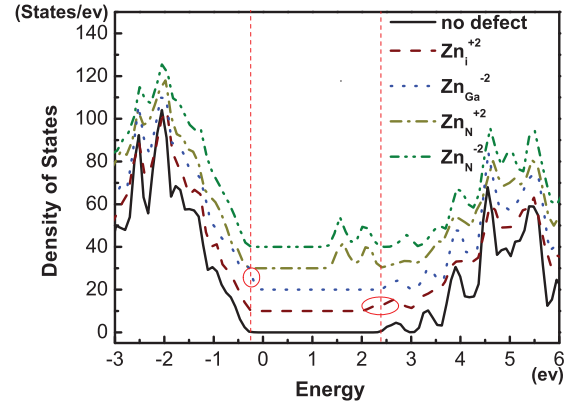


Fig.3. DOS comparison between perfect crystal and crystal with Zn_i^{+2} , Zn_{Ga}^{-2} and Zn_N^{+2} defects.

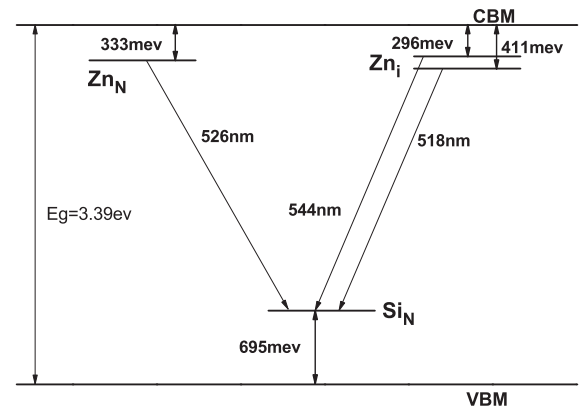


Fig.4. Schematic illustration of the transition between Zn_i - Si_N and Zn_N - Si_N D-A pairs in GaN that lead to the 500~560nm broad-band emission.