First principle study of the influence of vacancy defects on optical properties of GaN

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Received November 4, 2011; accepted December 12, 2011; posted online February 17, 2012

We employ plane-wave with ultrasoft pseudopotential method to calculate and compare the total density of states and partial density of states of bulk-phase GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$ systems based on the first-principle density-functional theory (DFT). For Ga and N vacancies, the electronic structures of their neighbor and next-neighbor atoms change partially. The $Ga_{0.9375}N$ system has n-type semiconductor conductive properties, whereas the $GaN_{0.9375}$ system has p-type semiconductor conductive properties. By studying the optical properties, the influence of Ga and N vacancy defects on the optical properties of GaN has been shown as mainly in the low-energy area and very weak in high-energy area. The dielectric peak influenced by vacancy defects expands to the visible light area, which greatly increases the electronic transition in visible light area.

OCIS codes: 160.4760, 250.1500, 300.6170.

doi: 10.3788/COL201210.051601.

GaN is commonly used as a new semiconductor material for a wide range of applications in optoelectronic and microelectronic devices. GaN has some fascinating properties, such as wide band gap, high thermal conductivity, high breakdown voltage, high melting point, and chemical stability, among others. GaN and its alloy materials have a wide range of wavelengths that cover nearly the entire visible light and ultraviolet range, and have promising applications in the field of electronic devices[1,2], such as in high-temperature devices, high-power devices, and optoelectronic devices field such as blue light-emitting diodes (LEDs)[3,4], blue lasers (LDs)[5,6], ultraviolet detectors[7,8]. In recent years, most research has focused on its physical properties, which has become a hot issue of semiconductor materials and photoelectric devices[9,10].

Defects produced in the GaN material growth process may interact with carriers. The existence of defects will affect the electronic structures and optical properties of GaN materials, and subsequently affect the performances of photoelectric devices. Simulation is a good method to study semiconductor defects[11,12]. Theoretical studies of the eigen defects of GaN have been reported[13−15]; however, the influence of such defects on GaN optical properties has not been determined. In this letter, we employ plane-wave with ultrasoft pseudo method to study the influence of Ga and N vacancy defects on the optical properties of GaN, such as dielectric function, refractive spectra, absorption spectra, reflection spectra, and energy loss spectra, among others, based on the first-principle density-functional theory (DFT). Our findings will provide theoretical reference for further experimental research.

All calculations were performed with the quantum me-

chanics program *Cambridge Serial Total Energy Package* (CASTEP)[16] based on DFT. The Broyden-Flecher-Goldfarb-Shanno (BFGS) algorithm was used to relax the structure of the crystal model. The valence electronic wave function was expanded in a plane-wave basis vector. The final set of energy was computed with an energy cutoff of 400 eV. The convergence precision was set to energy change of below 2×10^{-6} eV/atom, force of less than 0.005 eV/nm, convergence tolerance of a single atomic energy of below 1×10^{-5} eV/atom, stress of less than 0.05 GPa, and change in displacement of less than 0.0001 nm in iterative process. All calculations were performed with a plane-wave pseudopotential method based on DFT combined with the *generalized gradient approximation* (GGA)[17,18]. The integral in the Brillouin zone was sampled with the Monkhorst-Pack scheme[19] and special k points of high symmetry. The number of k points was 7×7×7. All calculations were carried out in reciprocal space with $Ga:3d^{10}4s^24p^1$ and $N:2s^22p^3$ as valence electrons.

In the linear response range, the macro-optical response function of solids is often described by the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ or by the complex refractive index $N(\omega) = n(\omega) + ik(\omega)$, where

$$\varepsilon_1 = n^2 - k^2, \tag{1}$$

$$\varepsilon_2 = 2nk. \tag{2}$$

According to the definition of direct transition probability and Kramers-Kronig dispersion relation, the imaginary and real parts of the dielectric function, absorption coefficient, and reflection coefficient, among others, can be deduced. The derivation process does not require much elaboration. Consider the theoretical for-

mulae below[20−22]:

$$\varepsilon_2(\omega) = \frac{\pi}{\varepsilon_0}\left(\frac{e}{m\omega}\right)^2 \cdot \sum_{V,C}\left\{\int_{BZ}\frac{2dK}{(2\pi)^2}|a\cdot M_{V,C}|^2\delta\right.$$

$$\left.\cdot[E_C(K) - E_V(K) - \hbar\omega]\right\}, \qquad (3)$$

$$\varepsilon_1(\omega) = 1 + \frac{2e}{\varepsilon_0 m^2}$$

$$\cdot\sum_{V,C}\int_{BZ}\frac{2dK}{(2\pi)^2}\frac{|a\cdot M_{V,C}(K)|^2}{[E_C(K)-E_V(K)]/\hbar}$$

$$\cdot\frac{1}{[E_C(K)-E_V(K)]^2/\hbar^2-\omega^2}, \qquad (4)$$

$$\alpha \equiv \frac{2\omega k}{c} = \frac{4\pi k}{\lambda_0}, \qquad (5)$$

$$R(\omega) = \frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \qquad (6)$$

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = -i\frac{\omega}{4\pi}[\varepsilon(\omega)-1], \qquad (7)$$

where n is the refractive index; k is the extinction coefficient; ε_0 is the vacuum dielectric constant; λ_0 is the wavelength of light in vacuum; C and V are the conduction band and valence band respectively; BZ is the first Brillouin zone; K is the electron wave vector; a is the unit direction vector of the vector potential A; $M_{V,C}$ is the transition matrix element; ω is the angular frequency; and $E_C(K)$ and $E_V(K)$ are the intrinsic energy levels of the conduction band and valence band, respectively. The above formulae expound the mechanism of spectrum produced by electron transitions between crystal energy levels and provide a theoretical basis for analyzing the band structures and optical properties of crystal.

These calculations were carried out with wurtzite GaN, which belongs to the P63$_{mc}$ space group. With a symmetry of C$_{6v-4}$, the lattice constants using the experimental value can be described by $a=b=0.3189$ nm, $c=0.5185$ nm[23], $\alpha=\beta=90°$, and $\gamma=120°$, where c/a is 1.626. In calculating $2\times2\times2$ supercells of wurtzite GaN composed of 16 Ga atoms and 16 N atoms were used. One Ga atom or one N atom was removed in research vacancy defects respectively (shown in Figs. 1 and 2). The wurtzite GaN supercells, Ga$_{0.9375}$N and GaN$_{0.9375}$ were optimized. The lattice constants of GaN supercells were $a=b=0.32247$, $c=0.52537$ after optimization, which are in good agreement with the experimental value, thereby validating shows the correctness of the calculation method.

The total density of states (TDOS) and partial density of states (PDOS) of Ga$_{0.9375}$N system are shown in Fig. 4. By the comparing the total density of states of Ga$_{0.9375}$N system (Fig. 4(a)) with the one of bulk phase GaN (Fig. 3(a)), the Fermi level of Ga$_{0.9375}$N system moves to the low-energy area and comes into the valence band top for the Ga vacancy. A small number of hole levels are present above the Fermi level. The Ga$_{0.9375}$N system shows p-type semiconductor conductive properties; its band gap grows wider with the same changing trend, similar to the results of Refs. [14] and [15]. In order to further study the influence of Ga vacancy on the electronic structures of Ga$_{0.9375}$N system,
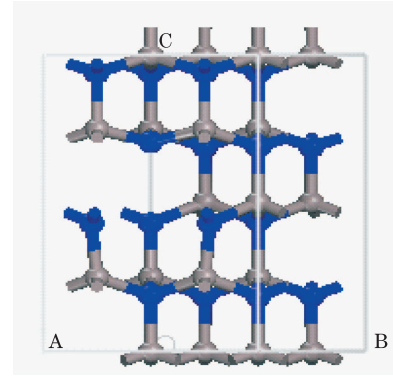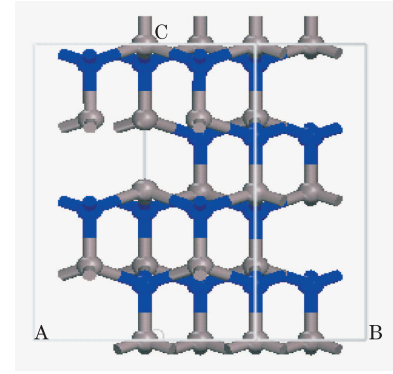

Fig. 1. Ga vacancy defect.
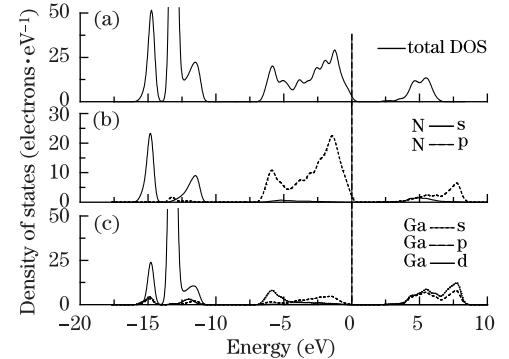

Fig. 2. N vacancy defect.
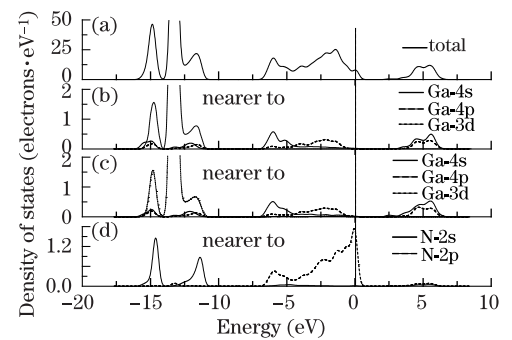

Fig. 3. Total and partial DOS of GaN.

Fig. 4. Total and partial DOS of Ga$_{0.9375}$N.

PDOS of the atoms near Ga vacancy were also studied, as shown in Figs. 4(b), (c), and (d). The influences of Ga vacancy on the PDOS of Ga vacancy neighbor and next-neighbor atoms are weak; however, these influences

are greater on the PDOS of Ga vacancy neighboring N atoms. The N2p-state electrons move to the high-energy area whether in valence band or in conduction band comparing with the PDOS of N atoms in bulk phase GaN. Therefore, the main reason the electronic density of states of $Ga_{0.9375}N$ system change is that the vacancy causes partial changes of the electronic structures of the vacancy neighbor and next-neighbor atoms.

TDOS and PDOS of $GaN_{0.9375}$ system are shown in Fig. 5. By the comparing TDOS of $GaN_{0.9375}$ system (Fig. 5(a)) with that of bulk-phase GaN (Fig. 3(a)), clearly, the Fermi level of $GaN_{0.9375}$ system moves to the high-energy area and comes into the conduction band for the existence of N vacancy. The $GaN_{0.9375}$ system shows n-type semiconductor conductive properties; its band gap grows wider, showing the same changing trend as in the results of Refs. [14] and [15]. In order to make further study of the influence of N vacancy on the electronic structures of $GaN_{0.9375}$ system, PDOS of the atoms near the Ga vacancy was studied, as shown in Figs. 5(b), (c), and (d). We can see that the N2s- and N2p-state electrons of N vacancy neighbor N atoms move to low-energy area, and that the Ga3d-, Ga4s-, and Ga4p-state electrons of N vacancy neighbor Ga atoms do as well. Therefore, the main reason the electronic density of states of $GaN_{0.9375}$ system change is that the vacancy causes partial changes of the electronic structures of the vacancy neighbor and next-neighbor atoms.

The photoelectric properties of optoelectronic materials are characterized mainly by the dielectric function, absorption coefficient, refractive index and reflection coefficient, and others. Optical constants linking with the microscopic model of physical process and the microelectronic structure of solid, which can better characterize the physical properties of material, are mainly decided by the electronic structures and carrier concentration near the Fermi level. The changes of GaN electronic structures caused by Ga and N vacancy defects would influence its optical properties. Theoretical and experimental researches on GaN optical properties have been conducted[10,24]; however, the optical properties of Ga and N vacancy defects system have thus far not been reported. In the following, forecast and analysis are carried out by comparing the optical properties of Ga and N vacancy defects systems with GaN system. In order to improve the calculation precision of optical properties, scissor-operator correction was used referring to the experimental value. The band gap of GaN was calculated as 1.66 eV, which is in agreement with Ref. [25], but smaller than the actual experimental value 3.39 eV. This problem is universal for the local density approximation (LDA) and generalized gradient approximation (GGA) having low band gap value; however, this problem does not affect the results of the theoretical analysis. The scissor-operator correction in the above three systems were adopted as 1.73 eV for convenient comparisons.

Dielectric function as a bridge connecting the microscopic physical of transition between bands with the electronic structures of solid reflects the band structures of the solid and information of its spectra[17]. The spectra of the GaN semiconductor material were produced by electronic transitions between bands. Each dielectric peak can be explained by band structures and density of

states of GaN. The imaginary parts of dielectric functions of bulk phase GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$ systems were calculated, as shown in Fig. 6. The three obvious main peaks of bulk phase GaN, correspond to the photon energies of 4.59, 9.25, and 12.65 eV, respectively, which are in good agreement with the experiment of Kawashima[26]. The peak at 4.59 eV is produced by the transition of N2p state (upper valence band) to Ga4s state, the peak at 9.25 eV is produced by the transition of N2p state (lower valence band) to Ga4s state, and the peak in 12.65 eV is produced by the transition of Ga4p state to N2p state. By comparing the imaginary parts of dielectric function of bulk phase GaN with that of $Ga_{0.9375}N$ and $GaN_{0.9375}$ systems, differences in their dielectric function imaginary parts are clearly bigger in the low-energy area ($\leqslant 8.7$ eV), and scarcely any are evident in high-energy area. For $Ga_{0.9375}N$ system, the maximum peak of the imaginary part of dielectric function moves slightly to the high-energy area due to the existence of the Ga vacancy defect; the peak at 9.25 eV disappears, and a strong new peak emerges at 1.9 eV. The reason this new dielectric peak emerges is the
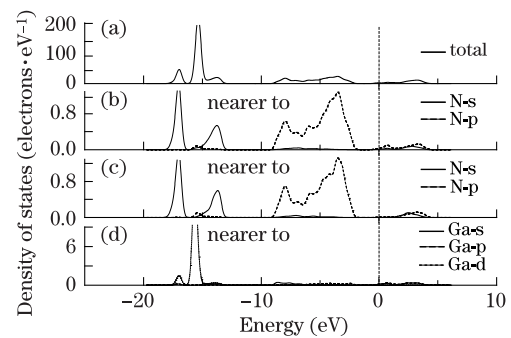
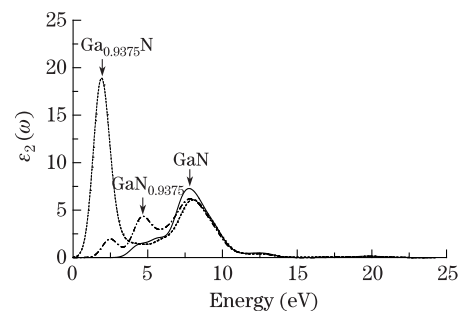Fig. 5. Total and partial DOS of $GaN_{0.9375}$.

Fig. 6. Imaginary parts of dielectric function of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.
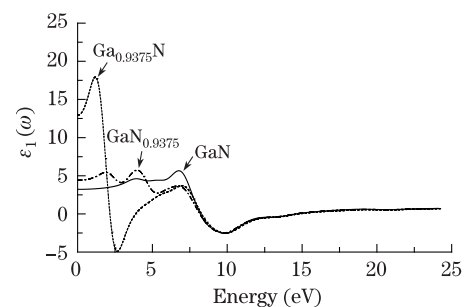
Fig. 7. Real parts of dielectric function of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.

transitions of electrons in conduction band to vacancy energy level generated in the top of valence band for the influence of Ga vacancy defect on the electronic distributions of its neighbor N atoms. For the $GaN_{0.9375}$ system, a new dielectric peak emerges at 2.4 eV is due to the move of the bottom of conduction band to the low-energy area due to the influence of N vacancy defect on the electronic distributions of its neighbor Ga and N atoms (see Figs. 5(b), (c), and (d)). Compared with bulk phase GaN, the dielectric peaks of the $Ga_{0.9375}N$ and $GaN_{0.9375}$ systems expand to visible light area influenced by Ga, N vacancy defects; this greatly increases the electronic transitions in visible light area. Figure 7 shows the real parts of dielectric functions of bulk phase GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$ systems. The change trends are basically same as in the imaginary parts of dielectric functions. The differences between them are mainly concentrated in low-energy area and scarcely any in high-energy area.

The absorption spectra, reflective spectra, refraction spectra, and the energy loss spectra of bulk phase GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$ systems are shown in Figs. 8–11, respectively. The optical absorption boundary of bulk phase GaN at 3.4 eV corresponds to the experimental band gap values, and is caused mainly by the transitions of N2p-state electrons to the bottom of conduction band. The optical absorption boundaries of $Ga_{0.9375}N$ and $GaN_{0.9375}$ systems clearly changed compared with the one of bulk phase GaN. Red shifts occur and new absorption peaks appear in the low-energy areas in both. The main reason for this phenomenon is that the Ga and N vacancy defects cause the changes of electronic structures of its neighbor atoms. The changes of absorption spectrum, reflective spectrum, and refractive index
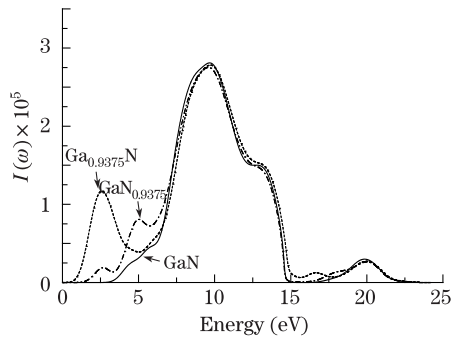

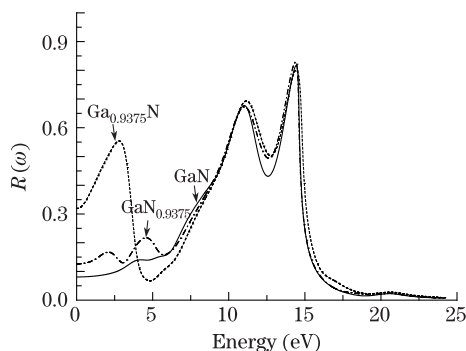Fig. 8. Absorption spectra of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.
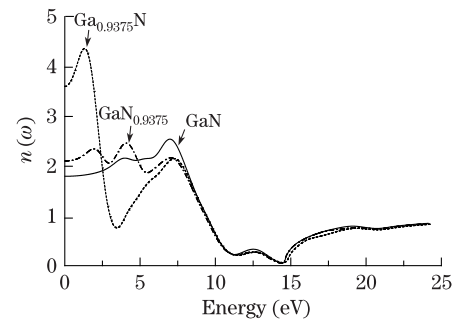

Fig. 9. Reflection spectra of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.

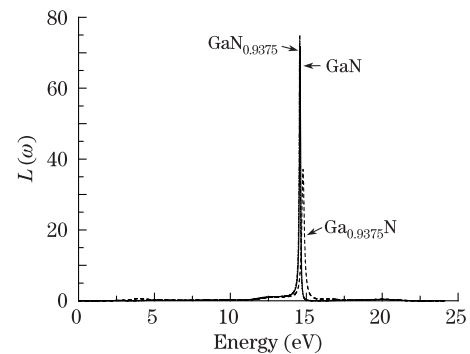Fig. 10.   Refraction spectra of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.

Fig. 11.   Energy loss spectra of GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$.

caused by the Ga and N vacancy defects are mainly in the low-energy area, similar to the change of the imaginary part of dielectric function. The refractive index of bulk phase GaN is same basically as the result in Ref. [24]. The static refractive indices of $Ga_{0.9375}N$ and $GaN_{0.9375}$ systems increase comparing with the one of bulk phase GaN. The peak position of energy loss spectrum indicates the transition point of material from metallic properties to dielectric properties. Compared with that of the bulk-phase GaN, the energy loss peak of $Ga_{0.9375}N$ system increases, whereas that of the $GaN_{0.9375}$ system decreases and moves slightly to the high-energy area.

In conclusion, plane wave with ultrasoft pseudopotential method was used to calculate and compare the electronic structures and optical properties of bulk-phase GaN, $Ga_{0.9375}N$, and $GaN_{0.9375}$ systems based on the first-principle DFT. Results show that Ga and N vacancy defects may cause relaxations of its surrounding electrons and band gap changing wider, but the systems still are direct band gap semiconductor. The influence of Ga and N vacancy defects on the optical properties of GaN is mainly concentrated in the low-energy area ($\leqslant$8.7 eV) and weak in the high-energy area. The expanding of dielectric peak to visible light area under the influence of Ga and N vacancy defects greatly increases the electronic transitions in visible light area. The main reason for the optical properties change is that the Ga and N vacancies cause electronic transitions of their neighbor atoms.

J10LG74).

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