The study of electronic structures and optical properties of Al-doped GaN

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Abstract: The electronic structures and optical properties of undoped and Al-doped GaN (AlGaN, x=0.0625, 0.125, 0.25) have been studied based on generalized gradient approximation (GGA) method of density functional theory (DFT). The differences of the electronic structures and optical properties of undoped and Al-doped GaN have been discussed in detail. The result shows: according to total density of state of undoped and Al-doped GaN, the conduction band becomes width and moves to high energy level with gradual increase concentration of Al impurity. Impurity energy band isn’t found in energy band structures of AlGaN, the same as energy band structures of undoped GaN, but the band gaps gradually become wide with increase of Al impurity. Absorption spectra of undoped and Al-doped GaN of main absorption peak moves to high energy level with increase of Al impurity.

Keywords: GaN super cell, Al-doped, DFT, optical property

0. Introduction

Wide band gap of compound semiconductor materials, such as GaN, SiC, AlN, which are the third generation semiconductor materials after the first generation of the Ge and Si semiconductor materials and the second generation compound semiconductor materials of GaAs and InP, have been developed. It is one of currently the global semiconductor researched fronts and hot spots in research and application. GaN-based semiconductor materials have wide band-gap, large electron drift velocity, high thermal conductivity, resistance to high voltage, high temperature, corrosion and radiation, and so on. Especially, it can be used to produce high-frequency, high efficiency, high temperature, high pressure, high power microwave devices. III-nitride semiconductor materials represented by GaN are the direct band gap materials, including AlN, GaN, InN and the ternary alloy (AlGaN\textsuperscript{[1]}, InGaN), quaternary alloy\textsuperscript{[2]} (Al/InGaN) materials. They have a larger range of band gap from 1.9eV of the InN to 3.4eV of GaN, then to 6.2eV of AlN, equivalent to wavelength light-emitting area from 650nm to 200nm. This band covers the larger spectrum from visible light (red, yellow, green, blue) to the near UV range, so that the material system has a wide and continuous tunable direct band gap. Thus according to use III-nitride material system, blue, green LEDs, blue-violet, UV LDs, ultraviolet (UV) light detectors and high power electronic devices can be prepared. GaN-based AlGaN/GaN HEMT devices have output power density, high temperature, resistance to radiation, etc. They can meet the next generation of electronic equipment demands on the microwave power device of higher power, higher frequency, smaller size and work under more adverse conditions. So they can be widely used in
microwave millimeter sophisticated electronic equipment, civilian communications base stations. As the band structure of AlGaN band gap and the corresponding bending coefficient (bowing parameter)[3-6] are directly related to the emission wavelength, particularly in the design of bending coefficient emission wavelength of the light-emitting components play a vital role. Therefore there are many researchers at home and abroad to experiment or theoretical study. Now, Guo et al[7] studied the Al, Mg doped GaN ( sphalerite structure) electronic structures and optical properties. Xing et al[8] studied Mn doped GaN ( sphalerite structure) of the electronic structures and optical properties. Bo et al[9] studied the Al,Ga1-x,N, In,Ga1-x,N and Al3In1-x,N of the electronic structures and the bending coefficient. From then on, theoretical study of optical properties of Al doped wurtzite GaN crystals currently are not reported, and the use of plane wave pseudopotential method (PWP) of theoretical research has not been reported yet.

In order to study the optical properties of undoped and Al-doped the GaN crystals, this paper used plane wave pseudopotential method. The first, its different impurity concentration of the energy band structure, electronic densities of state were calculated and analysed. Then the optical properties of undoped and doped of the GaN crystals were studied under different impurity concentrations and the absorption spectra were obtained. Finally, the results of optical properties and electronic properties of undoped and Al-doped the GaN crystals were compared.

1. Theoretical model and calculation method

1.1 Theoretical Model
The most stable hexagonal wurtzite structure belongs to P63mc space group. It has C4v symmetry, lattice parameters α=β=90°, γ=120°, a=b=0.3189nm, c= 0.5185 nm, c/a is 1.626, which is smaller compared with the ideal hexagonal close packed structure of 1.633. The unit cell is made of the Ga and N of the hexagonal close-packing. In this paper, according to the ideal structural parameters of GaN, the super cell structure was obtained. Then based on super-cell model, 32, 16, 8 atoms of supercell systems were selected in term of different Al doping concentrations x. One Al atom was doped in one unit cell. In the super cell, one Al atom substituted for one Ga of lattice positions, thus we obtained 32, 16, 8 atoms of Al-doped super cell system of model structure.

1.2 Calculation Method
The calculation is completed using ab initio quantum mechanics program CASTEP based on DFT. Using periodic boundary conditions, the electronic wave functions are extended by plane wave basis vector. The ion core and valence electrons of the interaction is described by ultra-soft pseudo potentials [10] in order to reduce the number of plane wave basis vector. The selected Ga, N, Al of valence electron configuration are Ga: 3d104s24p1, N: 2s22p3, Al: 3s23p1, respectively. In the reciprocal k-space, plane wave cutoff energy Ecut is 440eV, the exchange related energy makes use of the generalized gradient approximation (GGA) of PBE approximation method. Systematic total energy and charge density make use of Monkhorst-Pack program for the Brillouin zone of integral calculations. 32, 16 and 8 atom super-cell systems select 4×4×2, 2×4×2, 2×2×2 of k grid point, respectively, in order to ensure the systematic energy of convergence in the quasi-plane wave basis of level, convergence accuracy is 2×10^-6eV/atom. Internal atomic force of convergence criteria is 0.003eV/Å, single atomic energy of convergence criteria is 1.0×10^-8eV/ atom. To make the results stability and accuracy, the cell structures are firstly optimized and then internal coordinates are optimized in terms of the cell parameters. Finally the electronic structure and optical properties [11] are calculated.

2. Results and discussion

2.1. Undoped and Al-doped GaN of Electronic Structure
2.1.1 Optimized Structure of Properties. In order to compare conveniently with Al-doped GaN of electronic structure and optical properties, Undoped and Al-doped GaN super cells were optimized respectively. The experimental values and the optimized structural parameters of GaN lattice constants were shown in Table 1.

From Table 1, we can see that the undoped GaN of lattice constant a and c are consistent with the experimental values. c/a is equal to 1.629, which are consistent with the experimental value 1.626, deviated of only 0.18%. So it shows this method is reliable. Table 1 show that different Al-doped GaN of lattice parameters is different.

| Lattice constants | GaN         | Al1/4Ga3/4N | Al1/3Ga7/8N | Al1/6Ga15/16N |
|-------------------|-------------|-------------|-------------|---------------|
| experiment        | 0.3189      | 0.3198      | 0.3211      | 0.3221        |
| theory            | 0.3225      | 0.5254      | 0.5226      | 0.5250        |
| c/a               | 1.626       | 1.626       | 1.628       | 1.629         |

Lattice constants slightly increase with decrease of Al-doped concentration. Because the Al$^{3+}$ ionic of radius is smaller than the Ga$^{3+}$ionic of radius. When one Al$^{3+}$ replace with one Ga$^{3+}$, the volume will become smaller, meanwhile the lattice parameter becomes smaller. This change can be seen from bond length (Ga-N bond is 0.196nm, Al-N bond is 0.187nm).

2.1.2 The Density of States. Figure 1 shows the total density of states of the undoped and Al-doped GaN super cell. From Figure 1, we can see that the undoped GaN (a) and Al-doped GaN (b), (c), (d) super cell have three electronic states, including band 1, band 2 and band 3. In the band 1 and band 2, the electronic density of states of (a), (b), (c), (d) super cell are complete consistency. Band 1 has three peaks, left and right peaks are not high. Because the electrons are few in this energy, the middle of peak is very high and sharp. This shows that the density of electronic state is lager in this energy. It shows a strong localization and is no significant interaction compared with the other valence band. In band 2, the peak is not high, but relative wide, about 7eV. This shows that a wide range of electronic state is presented. In the band 3, the electron density changes significantly with the increase of Al.
doping concentration. The distribution of the electron density of states becomes wide, and the conduction band moves to the high energy area, resulting in wider optical band gap. This is because the Al impurity is doped, its 3p state electron is contributed.

Figure 2 shows the partial density of states of the undoped and Al-doped GaN, super cell. From Figure 2, we can see that the left peak is the Ga 3d states and the N 2s state of the electron distribution and the right sharp peak is the Ga 3d states and a litter amount of the Ga 4s, N 2s states of the electron distribution in band 1. Band 2 of width is about 7.28eV, including mainly the N 2p state and Ga 4s states of the electron distribution. The N 2p electronic state determines the top of valence band of positions. Band 3 is absolutely different from band 1 and band 2. Its band width is about 7.68eV and becomes wide with the increase of Al-doped concentration. Meanwhile it moves to high energy zone. The main reason is contribution of Al 3p \(^{12}\) state of the electron distribution. Finally, band gap width is wider.

2.2 \(Al_\text{xGa}_{1-x}N\) Optical Properties

2.2.1 \(Al_\text{xGa}_{1-x}N\) Optical Band Gap. Figure 3 shows the energy band structures of GaN and \(Al_\text{xGa}_{1-x}N\) (x=0.0626, 0.125, 0.25). From Figure 3 (a), calculated band gap value is 1.72eV. Compared with the experimental value \(E_g=3.4eV\), it is quite lower. The reason is that used DFT calculation theory is the ground state theory, while the energy gap belongs to the properties of excited states. Therefore, the obtained result is very low and that is the prevailing theory of the phenomenon in the calculation. However, this phenomenon does not affect the theoretical analysis of electronic structure of GaN. From Fig. 3(b), (c), (d), we can see that Al-doped GaN super cells are still a direct band gap structure semiconductor, because the bottom of conduction band and the top of valence band lie at G-point of Brillouin zone (the point) Department. Different concentrations of Al doped GaN is not impurity energy level. Because Al atom is equivalence impurities, and different from other impurities. There are not the donor and the acceptor energy level between the top of valence band and bottom of conduction band. For different concentrations of Al-doped GaN, the energy gaps are different. \(Al_\text{xGa}_{1-x}N\)
N (x=0.25, 0.125, 0.0626) super cells of the energy gaps are 2.19eV, 1.95eV, 1.75eV, respectively. Their band gaps (Eg) are wider than the undoped GaN of band gap (Eg=1.72eV). The impurities concentration increase along with the wide of the energy gap. The reason is that the band gap of GaN is 3.4eV, while the band gap AlN is 6.2eV, Al-doped GaN of band gap should range from 3.4eV to 6.2eV.

2.2.2 The Absorption Spectrum of Al\textsubscript{x}Ga\textsubscript{1-x}N. The medium of light absorption properties can be described by the virtual part of relative dielectric functions. Generally speaking, the imaginary part of relative dielectric function caused the absorption of electromagnetic wave, light absorption coefficient and relative dielectric function\textsuperscript{[13]} are direct proportionality.

![Absorption Spectrum of Al\textsubscript{x}Ga\textsubscript{1-x}N](image)

Figure 4. Absorption spectrum of Al\textsubscript{x}Ga\textsubscript{1-x}N

Figure 4 shows the absorption spectrum of GaN and Al\textsubscript{x}Ga\textsubscript{1-x}N, that is the dispersion curve of imaginary part of dielectric function\textsuperscript{[14]}. The peaks come from the optical transitions of different critical point between valence band and conduction band. From Figure 4, we can see that when Al-doped concentration is equal to 0.0625 (b) and 0.125 (c), the absorption spectrum has three peaks and between the second peak and third peak there are the complete not-absorption state. When the Al doping concentration is equal to 0.25 (d), the absorption spectrum has three peaks which lie in completely the absorption state. This is because the absorption peaks come from the optical transition of different critical point between valence band and conduction band. The larger the doping concentration, the greater the valence band density of states, the more optical transitions different critical points between valence band and conduction band, so the not-absorb states disappear. Meanwhile, with Al doped concentration of increase, the main absorption peaks shift to higher energy\textsuperscript{[15]}. The reason is that the band gap GaN is 3.4eV, while the band gap AlN is 6.2eV, Al-doped GaN of band gap ranges from 3.4eV to 6.2eV. Different concentrations have a different band gap. Of course, the greater the concentration of Al doping, the wider the band gap, that is consistent with the band structure of conclusions. According to the relationship of the band gap and wavelength, we obtained that the wavelength becomes small along with increases of the band gap, then the frequency increases. Therefore the absorption peaks move to the higher energy zone.
3. Conclusion
In this paper, the geometric structures of undoped and Al-doped GaN (Al_xGa_{1-x}N, x=0.0625, 0.125, 0.25) have been optimized based on the plane wave pseudopotential method and generalized gradient approximation of density functional theory (DFT). The structure of the lattice parameters were obtained and compared with experimental parameters, therefore this calculation method has good reliability. The electronic structure and optical properties of pure and Al-doped GaN (Al_xGa_{1-x}N, x=0.0625, 0.125, 0.25) have been studied. The result shows the total densities of states of pure and Al-doped GaN have obvious change with the increase of Al-doped concentration. That means the conduction band energy levels become wide and move to high energy. Band structure of calculations show that the Al-doped GaN do not appear donor and acceptor impurity levels and are similar the energy band of the ideal structure of GaN, but the optical band gap is wider than the ideal structure. Optical band gap continuously becomes wider with the increase of Al-doped concentration. These results provide some theoretical basics for the further design and application at the molecular and atomic scale.

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4. References
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