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First-principles studies of electronic structure and optical properties of GaN surface doped with Si☆

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ABSTRACT

The electronic structure of wurtzite GaN doped with Si was calculated using the first-principles plane-wave pseudopotential method, based on the density function theory. The results show that GaN doped with Si is n-type semiconductor with direct band-gap, band gap increases, compared with that of undoped GaN. The doped system was sectioned in (0 0 0 1) and (0 0 0 $\bar{1}$) direction. (0 0 0 $\bar{1}$) surface has larger change in morphology than (0 0 0 1) surface, and is against the escape of electrons. The electronic non-locality of (0 0 0 1) surface is enhanced. The electronic structure and optical properties of GaN(0 0 0 1) surface with Si doping were analyzed and compared with those of undoped surface. The studies show that the absorption to visible light enhances, absorption to ultraviolet light abates. Doped surface is fit for ultraviolet detection.

1. Introduction

GaN as III-nitrides has important applications in optoelectronic devices and micro-electronics devices because of its direct and wide band-gap, high thermal conductivity, high breakdown voltage, high melting point, and chemical stability, among others [1–3]. At present, the research has made a great progress in GaN materials and devices, especially in GaN high brightness blue and green LED and long life blue laser and UV detector [4–9]. The dopants have been largely used to modify the growth modes and consequently the surface properties of GaN. For example, incorporation of Be or Mg is available for p type semiconductor [10,11], Si is available for n type semiconductor [12–14] providing injected electrons for light-emitting. In order to obtain diluted magnetic semiconductor, the p, n type dopants and Mn co-doped GaN has been investigated [15]. The electronic properties, mechanism of strain relaxation and defect formation of GaN doped with Si are under discussion experimentally [16–18]. With the wide application of n type GaN photoelectric devices, the studies to surface properties of Ga(Si)N such as surface electronic structure, surface polarity, surface stability, surface relaxation and optical properties have very important meaning in improving the performance and understanding the photoelectric emission mechanism of n type GaN photoelectric device.

In this work, we report first-principles calculations of surface relaxation, electronic structure and optical properties of Si doped GaN(0 0 0 1) surface. We identify (0 0 0 1) surface is superior to (0 0 0 $\bar{1}$) surface of Si doped GaN and we suggest a mechanism based on surface level pinning to explain its optical properties.

2. Theoretical model and calculation methodology

Before starting the surface calculations, we first optimized bulk GaN having a $(2 \times 2 \times 1)$ periodicity with one Si atom replacing one Ga atom in the supercell center, the doping concentration is 12.5% [shown in Fig. 1(a)]. The lattice parameters of GaN doped with Si can be described by $a = b = 0.3189$ nm, $c = 0.5185$ nm before optimization [19]. The side view of (2×2) GaN(0 0 0 1) surface with Si in the outermost layer is shown in Fig. 1(b) and (2×2) GaN(0 0 0 $\bar{1}$) surface with N in the outermost layer is shown in Fig. 1(c) by cleaving the Ga(Si)N bulk supercell. The surface slab is modeled with six Ga(Si)-N bilayers. Among these bilayers, the bottom three bilayers are fixed at the ideal positions in order to simulate a bulk environment and others relaxed, and at least a 1.3 nm vacuum thickness has been used to avoid the interaction between repeated slabs. The bottom side of the slab is saturated by pseudo-hydrogens atoms to avoid the transfer of surface charges. In calculation, the valence electronic wave function is expanded in a plane wave basis

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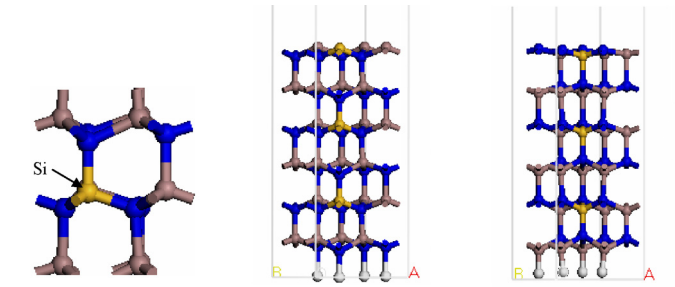

(a) Ga(Si)N supercell (b) Ga(Si)N(0001) surface (c) Ga(Si)N(000 $\bar{1}$) surface

Fig. 1. Ga(Si)N supercell and its surface.

vector. The final set of energies was computed with an energy cutoff of 400 eV. The convergence was set to energy change below 2×10^{-6} eV/atom, force less than 0.005 eV/nm, the convergence tolerance of a single atomic energy below 1×10^{-5} eV/atom, stress less than 0.05 GPa, and change in displacement less than 0.0001 nm. All calculations were performed with a plane-wave pseudopotential method based on DFT combined with the generalized gradient approximation (GGA). The integral in the Brillouin zone was sampled with the Monkhorst–Pack scheme [20] and special *k* points of high symmetry. The number of *k* points is $11 \times 11 \times 11$ for supercell and $4 \times 4 \times 1$ for surfaces. All calculations were carried in reciprocal space with Ga: $3d^{10}4s^24p^1$, N: $2s^22p^3$ and Si: $3s^23p^2$ as valence electrons.

3. Results and discussion of Ga(Si)N bulk phase

The lattice parameters of Si doping GaN are shown in Table 1 after optimization. It can be seen the lattice parameters and volume decrease slightly in agreement with experiment [21]. Due to the decrease of lattice parameters, bonding between atoms is more tightly than before doped, intensity of periodic potential field is enhanced, the filling part of band will move down, the energy gap will increase.

The band structure, total density of states and partial density of states of Ga(Si)N bulk are shown in Fig. 2. The bottom of the conduction band and the top of valence band are located in the brillouin zone G point, Si doped GaN is still direct band-gap semiconductor. The band structure moves to low-energy area integrally after doping. The Si atom becomes donor after taking the place of +3 valence Ga atom for its outer electron configuration is 1s2 2s2p6 3s3p2, it devotes a certain amount of excess carrier-electronics near the bottom of the conduction band, and makes the conduction band bottom of GaN drop from 1.663 eV to −2.034 eV, the Fermi level into the conduction band [18]. The doped GaN shows n-type conduction, the band gap change from 1.663 eV to 1.702 eV after doping. The top of valence band is determined by the N2p states, the bottom of the conduction band is determined by Si3s states. Repulsive interaction between Si electrons in the bottom of the conduction and N2p electrons in the top of valence band makes the valence band to low-energy area and band gap increase. The lower valence bands are mainly attributed to Ga3d, N2s states and small of Si 3s states, its peak decrease after Ga replaced by Si.

Table 1
Lattice parameters of GaN before and after Si doping.

	a (nm)	*b* (nm)	*c* (nm)	*V* (nm)^3
GaN	0.3225	0.3225	0.5253	0.1893
GaN:Si	0.3213	0.3213	0.5253	0.1878

4. Properties of Ga(Si)N surface

4.1. Optimization of Ga(Si)N surface

The thickness of surface bilayer and the distance between bilayers of Ga(Si)N(0 0 0 1) and Ga(Si)N(0 0 0 $\bar{1}$) surfaces are obtained shown in Tables 2 and 3. After optimization, thickness of the outmost surface bilayer of Ga(Si)N(0 0 0 1) surface is increased by 2.28%, is bigger than undoped surface [22], that of subsurface bilayer is increased by 0.69%, and that of the third surface are increased by 0.69%, respectively (shown in Table 2). The influence of optimization on the thickness of surface bilayer weakens as the depth increase. The distances between the first and second surface bilayers of GaN(0 0 0 1) surface expands slightly comparing with the one of Ga(Si)N bulk-phase by 0.3%, those between the second and the third, between the third and the fourth subsurface bilayers expand only by 0.05%, shown in Table 3. The main reason is the existence of Si atom in the outmost surface layer, it is easier to lose electrons than Ga atom, the positive electricity in surface increase, dipole moment directing to outside is enhanced, this can be seen from the E-Mulliken population (shown in Table 4). The overlap population of Si-N is 0.53 small than that of Ga-N 0.55 in undoped surface, interaction of Si-N is smaller that that of Ga-N, so the expansion of the outmost atomic layer is large, although the atomic radius of Si is smaller than that of Ga. It can be seen that the doping of Si reduce the stress between layers [21,23]. After optimization, the angle among Si–N–Ga in the outmost surface decreases, Ga atoms is higher than Si atom, and its s, p, d states are enhanced, this agrees with experiment [24].

Ga(Si)N(0 0 0 $\bar{1}$) surfaces is N-terminated surface. Dipole moment directing to interior is formed for the outmost N atoms being negatively charged, this can be seen from the E-Mulliken population (shown in Table 4). The thickness of surface bilayer and the distance between bilayers of Ga(Si)N(0 0 0 $\bar{1}$) surface are compressed after optimization shown in Tables 2 and 3, the change of surface bilayers thickness is big especially. By comparison, we can see there are larger influence of optimization on the thickness and distance of bilayers of Ga(Si)N(0 0 0 $\bar{1}$) than those of Ga(Si)N(0 0 0 1) surface. The morphology of Ga(Si)N(0 0 0 $\bar{1}$) surface has changed largely after optimization, the surface integrity is worse, therefore, it can get better crystal quality in Ga(Si)N(0 0 0 1) surface.

4.2. Work function of Ga(Si)N polar surface

For the semiconductors, work function means the minimum energy needed by electron to escape from semiconductor bottom to external; it is expressed by [25]:

$$\Phi = E_{vac} - E_f \quad (1)$$

where E_{vac} is vacuum level, E_f is the systematic Fermi level.

The surface work function of Ga(Si)N(0 0 0 1) surface calculated by us is 3.204 eV, is smaller than the one of undoped surface 4.2 eV [22]. For the number of electrons loosed by Si atoms is more than that loosed by Ga atoms, this makes N atoms charge increase than undoped surface, dipole moment directing to outside is enhanced, Ga(Si)N(0 0 0 1) surface is more favorable for electron escape, it can be explained by the E-Mulliken population (shown in Table 4). The surface work function of GaN(0 0 0 $\bar{1}$) surface is 6.313 eV, is bigger than that of Ga(Si)N(0 0 0 1) surface, for the dipole moment directing to interior going against the electron escape.

4.3. Band structure and density of states for Ga(Si)N surface

Fig. 3(a) and (b) shows our results for the band structure and density of states calculations of optimized clean Ga(Si)N(0 0 0 1) surface, in which the dashed line represents the Fermi level. In