Electron carrier generation by edge dislocations in InN films; First-principles study

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abstract

Electronic structures of edge dislocations in InN films are studied using the first-principles calculation. We found that dangling-bond states of In atoms localized in the dislocation core are located above the conduction band bottom and thus supplies the electron carriers to the conduction band of bulk InN, in agreement with the experimental suggestion by Wang et al. (Appl. Phys. Lett. 90, 151901(2007)). Moreover, it is shown that the Fermi energy in the conduction band has the tendency to be pinned at the energy positions of N-related dangling-bond states.

1. Introduction

III-nitride semiconductors and their alloys are promising constituent materials for optoelectronic devices that cover a wide range of wavelength from the ultraviolet ($\sim 200\text{nm}$) to infrared ($\sim 2\mu\text{m}$) regions. Among these, due to the small band-gap of about 0.6 eV, InN plays an important role in the infrared regions. Moreover, because of the small effective mass around $0.12m_0$, InN is also expected as a material for a high-speed electronic device [1-4]. InN is often grown by Molecular Beam Epitaxy (MBE) and Metal-Organic Vapor Phase Epitaxy (MOVPE). Owing to the developments of crystal growth techniques, the crystal quality of grown InN films has made remarkable progress such as having atomic-order smooth and flat surfaces. However, it has long been observed that there always appear unintentional electron carriers even when one produces InN films with special cares. These carriers seem to occupy about 0.1 to 0.9 eV of the conduction band bottom [4,5], thus hindering the realization of p-type InN [5,6].

Unintentional carriers are believed to be created by defects such as atom vacancies because the lattice mismatch around 10 % always exists between the substrate and the grown InN layers in the present stage of crystal growth [6]. Recently, Wang et al. found

by performing the Hall measurement together with counting the number of dislocations in samples that the edge dislocations also produce a number of electron carriers, with the density over 10^{17}cm^{-3} [7]. Since dislocations often work as deep-level electron/hole traps and never produce carriers in conduction and valence bands of most semiconductors [8, 9], it is interesting to study whether dislocations can become donors in the case of InN films. However, to our knowledge, there have been no theoretical investigations of such possibility. In this work, we study electronic structures of InN edge dislocations and clarify the possibility of carrier generation by dislocations, using the first-principles theoretical calculations and comparing the results with those in cases of other semiconductors such as GaN and point defects like vacancies.

2. Model and Method

The atomic structures of edge dislocations in nitride semiconductors were first studied by Lei et al., using the empirical atomistic elastic model [9, 10]. They found that there exist three types of stable structures, which are schematically shown in Figs. 1(a) to 1(c). In this paper, we adopt these all and study their electronic structures. At the center of dislocation, they have five-and-seven-, eight-, and four-folded ring structures perpendicular to the c axis, respectively, contrary to the six-folded ring networks seen in bulk structure. Therefore, hereafter, we call these the 5/7, 8, and 4-ring dislocations. Though these dislocations have the same periodicity along the c axis as that of the hexagonal bulk system, they break the periodicity perpendicular to c , as seen in Figs. 1(a) to 1(c), which causes it difficult to adopt the conventional electronic-structure calculations using the periodic unit cells. To evade this difficulty, we use the repeated unit-cell systems that have a pair of dislocations with opposite directions in one unit cell. Such unit cell is shown in Fig. 1(d), for the case of 5/7-ring dislocation. This unit cell has 96 atoms and is periodic along any directions. The similar unit cells are adopted for 8 and 4-ring dislocations.

The atom positions and electronic structures of dislocations are calculated, using the standard first-principles total-energy method in the generalized gradient approximation (GGA) [11]. Vanderbilt-type ultrasoft pseudopotentials are adopted for both In and N atoms, where (5s, 5p, 5d) and (2s, 2p) electrons are treated as valence electrons [12]. The PBE form is used for the exchange-correlation potential [11]. The wavefunctions are expanded by plane waves with the energy less than 25 Ryd. All atomic positions and

unit-cell size are optimized until the forces on atoms become less than 10^{-2} a.u. The calculation is performed by the TAPP code [13]. The calculated lattice parameters of bulk InN are $a=3.57\text{\AA}$, $c/a=1.602$, and $u=0.378$, which all coincide the observed values with an error less than 1% [14, 15]. The other calculation details are described elsewhere [16, 17].

3. Results and discussion

We first consider the 5/7 dislocation, which calculated band structure is shown in Fig. 2(a), together with the Brillouin zone in the inset. The band structure of bulk InN is also shown in Fig. 2(b), where the similar size of unit cell is adopted to make a comparison easier. Note here that the bands, c1 and v1 in Fig. 2(b), are the lowest conduction and highest valence bands of bulk InN, respectively. The band-gap energy of bulk InN is 0.25 eV, which values is smaller than the experimental results of about 0.6 eV [18]. This occurs because the band gap is often underestimated by the calculations based on the density-functional theory (DFT) [19]. In case of Fig. 2(a), these c1 and v1 bands touch with each other around the Γ point, indicating some shrinkage of the band-gap energy around the dislocation. Most remarkable feature in this figure is the position of the Fermi energy, E_F ; E_F is located about 0.6 eV above the bottom of the lowest conduction band of bulk InN, c1. This result indicates that the electron carriers are generated in the conduction band, in agreement with the experiment [7, 14, 15].

In order to understand the origins of such electron carriers, we performed the wavefunction analysis of all band states. Figures 3(a) to 3(d) show the charge-density plots of electronic states at Γ , which are respectively denoted by c1, N1, N2 and In1 in Fig. 2(a). It is seen that the c1 state is a conduction-band state of bulk InN, thus being an anti-bonding state of In-s and N-s orbitals and extended over the system. The N1 and N2 states are respectively bonding and anti-bonding states of dangling bonds of N atoms that are located in the center of dislocation. On the other hand, the In1 state is the bonding state of dangling bonds of In atoms in the core region. Since these states are strongly localized around the dislocation, their bands show flat dispersions.

From these analyses, we obtain the overall feature of electronic structure of InN dislocation, which is schematically displayed in Fig. 4(a). In the dislocation core, there exist three-folded In and N atoms. Since these In and N atoms have dangling bonds and are nearest to the same kinds of atoms, they produce N-N and In-In dimer bonds to

stabilize the dislocation [8]. As seen in Fig. 4(a), the bonding state of N-N dimer, N1, is located about 0.3 eV below the valence-band top, while the anti-bonding one, N2, appears about 0.5 eV above the conduction-band bottom. On the other hand, the bonding and anti-bonding states of In-In dimer, In1 etc., are located much higher, at least 1 eV, above the conduction-band bottom. Since the dangling bonds of N and In atoms have 1.25 and 0.75 electrons, the N2 and In1 bands are originally occupied by 0.5 and 1.5 electrons, respectively. Reflecting the relative energy positions of these bands, the In1 band becomes donor band and supplies the electron carriers to the conduction band of bulk InN and the N2 N-N anti-bonding band as shown by the arrow. It should be noted here that the latter band is still occupied partially after such electron supply, which is contrary to the case of GaN shown below. As a result, the Fermi energy tends to be pinned at the energy position of the N2 band.

Then, we consider other types of dislocations. Figures 2(c) and 2(d) show the calculated band structures of 8 and 4-ring dislocations, respectively. Since the core of 8-ring dislocation also includes In and N dangling bonds, similar to the case of 5/7-ring dislocation, the In dangling bonds supply the electron carriers to the conduction band and the Fermi energy is located about 0.2 eV above the conduction-band bottom. On the other hand, there are no In and N dangling bonds in the core of 4-ring dislocation. However, due to the compressed atom configuration in the core region, the valence band states of N atoms localized around the core increase the energy about 0.25 eV above the conduction-band bottom and become the source of electron supply to the conduction band. In this way, though the origin of electron-carrier generation is different between 8 and 4-ring dislocations, all these dislocations also become the source of electron generation.

Here, we shortly comment on the formation energy of various dislocations. The calculated formation energies are 1.92, 2.30, and 2.23 eV/A for 5/7, 8, and 4-ring dislocations, respectively. The present calculation does not consider the elastic energy loss apart from the core region. However, since the difference of such energy is small between dislocations compared to that around the core [10], we expect that the 5/7-ring dislocation has the lowest formation energy.

It is interesting to consider whether the same scenario of carrier generation applies to other defects in InN and dislocations in other semiconductors. We first consider the N vacancy in InN. Figure 5(a) shows the band structures of N vacancy, which was

calculated using the 2*2*2 InN unit cell with a single vacancy. It is seen that the Fermi energy is located in the conduction band, thus the electron carriers appearing. This is because there are four In dangling bonds around the N vacancy and they supply electrons to the conduction band. In this sense, we can say that the generation origin of electron carriers is the same between dislocations and N vacancy.

Finally, we consider the dislocation in GaN. Figure 5(b) shows the calculated band structure of 5/7-ring dislocation in GaN. As seen in this figure, the Fermi energy is located in the fundamental band gap of InN and there are no electron carriers in the conduction band. This occurs because, as seen in Fig. 4(b), the flat bands made of N-N anti-bonding states are located deep in the fundamental band gap, the Ga dangling bonds supply electrons not to the conduction band but only to the N-N anti-bonding states as displayed by the arrow, and the latter states become fully occupied. Thus, the electron carriers never appear in GaN, being in good agreement with the observation [9]. The similar trend is also seen for dislocations in cubic semiconductors such as Si and GaAs [8].

4. Conclusion

Electronic structures of edge dislocations in InN films are studied using the first-principles calculation. By comparing to the cases of N vacancy in InN and dislocations in GaN, we have shown that the In dangling bonds around the dislocation core become the main source of electron carriers in the conduction band of bulk InN because the anti-bonding states originating from N dangling-bonds are located in the conduction band.

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Figure captions

Figure 1. Schematic pictures of dislocations in InN, viewed from the c direction. (a) 5/7-ring, (b) 8-ring, and (c) 4-ring dislocations. (d) Repeated unit cell used in the present calculation, for the case of 5/7-ring dislocation.

Figure 2. Calculated band structures of (a) 5/7, (c) 8, and (d) 4-ring dislocations in InN. (b) displays the band structure of bulk InN. c1 and v1 are the lowest conduction band and the highest valence band of bulk InN, respectively. N1 and N2 are bonding and anti-bonding states of N dimmer bonds, while In1 denotes the bonding state of In dimmer bonds. E_F is the Fermi energy position. The Brillouin zone is displayed in the inset.

Figure 3. Charge densities of electronic states at Γ of (a) c1, (b) N1, (c) N2, and (d) In1 bands shown in Fig. 2(b).

Figure 4. Schematic views of electronic structures of 5/7-ring dislocations in (a) InN and (b) GaN films. The vertical down arrows indicate the electron transfer from the In-dangling-bond states to the conduction band and the N-dangling-bond states.

Figure 5. Calculated band structures of (a) N vacancy in InN and (b) 5/7-ring dislocation in GaN.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5