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Perturbation analysis on large band gap bowing of dilute nitride semiconductors

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ABSTRACT

Contrary to the conventional empirical law, band gap of the dilute nitride semiconductors decreases with increasing nitrogen concentration. In spite of a number of investigations, the origin of this "large band gap bowing" is still under debate. In order to elucidate this phenomenon, we investigate change of the band edge energy of GaN_xAs_{1-x} due to nitrogen by using the perturbation theory. We found that energy shift of the conduction band edge is arising from intervalley mixing between the Γ- and L-states and/or Γ- and X-states mainly induced by displacement of Ga atoms around nitrogen. The valence band edge state shows upward shift in spite of negative potential of nitrogen. These results are well understood from symmetry of the wavefunctions and the perturbation potential.

1. Introduction

The III–V compound semiconductors containing a small amount of nitrogen atoms are attracting much attention [1–7]. In addition to prospect for applications of devices such as infrared lasers and high efficiency solar cells [8–10], their properties largely different from those of other semiconductors also evoke much interest [11–13]. In particular, the large band gap bowing is an issue still under debate. Usually, band gap of a mixed compound is well described as a linear interpolation of the band gaps of the constituent materials. This empirical law is well satisfied, though a small deviation called band gap bowing is sometimes observed. Contrary to the empirical law, band gaps of some compounds such as GaNAs, GaInNAs, and GaNP become smaller with the N concentration. This phenomenon is treated simply as large band gap bowing. There are various models and theories to explain this phenomenon [14–16]. Analysis on the basis of the tight-binding theory [17,18], the empirical pseudopotential method [19–23] and the first principle calculations [24,25] have been carried out. In spite of these studies, its mechanism is still under debate.

In this paper, to elucidate the mechanism of the large band gap bowing, we carry out analysis on behavior of the band edge energies for a typical dilute nitride semiconductor GaN_xAs_{1-x} (GaNAs). For this purpose, we carry out perturbation calculations regarding the effects due to the nitrogen as a perturbation. In the next section, first, we show the model used in this study. Then, after evaluating matrix elements of the perturbation potential, we calculate reduction of the band gap. Finally, by making qualitative interpretation in terms of symmetry of the perturbation potential and the wavefunctions, we show how the reduction of the band gap by the introduction of nitrogen.

2. Perturbation analysis

2.1. Model

We consider an $N_d \times N_d \times N_d$ supercell of GaAs in which one of As atoms is replaced by a N atom. Since this supercell consists of $4N_d^3$ unit cells of the zinc blende structure, the nitrogen concentration is given by $x = 1/(4N_d^3)$. Introduction of the N atom brings about change in crystalline potential. We consider the following three factors: (i) shift of atomic potential from that of As to N, (ii) displacement of Ga atoms adjacent to the N atom, and (iii) displacement of As atoms on the second neighboring sites to the N atom. Then, the perturbation potential is given by

$$\Delta V(\boldsymbol{r}) = \Delta V^{(\mathrm{i})}(\boldsymbol{r}) + \Delta V^{(\mathrm{ii})}(\boldsymbol{r}) + \Delta V^{(\mathrm{iii})}(\boldsymbol{r}), \quad (1)$$

with

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$$\Delta V^{(\mathrm{i})}(\boldsymbol{r}) = [V_{\mathrm{N}}(\boldsymbol{r}-\boldsymbol{R}_I) - V_{\mathrm{As}}(\boldsymbol{r}-\boldsymbol{R}_I)], \tag{2a}$$

$$\Delta V^{(\mathrm{ii})}(\boldsymbol{r}) = \sum_j [V_{\mathrm{Ga}}(\boldsymbol{r}-\boldsymbol{\tau}-\boldsymbol{R}_j-\boldsymbol{\xi}_j) - V_{\mathrm{Ga}}(\boldsymbol{r}-\boldsymbol{\tau}-\boldsymbol{R}_j)], \tag{2b}$$

and

$$\Delta V^{(\mathrm{iii})}(\boldsymbol{r}) = \sum_{j'} [V_{\mathrm{As}}(\boldsymbol{r}-\boldsymbol{R}_{j'}-\boldsymbol{\eta}_{j'}) - V_{\mathrm{As}}(\boldsymbol{r}-\boldsymbol{R}_{j'})], \tag{2c}$$

where the superscripts (i)–(iii) correspond to the three factors noted above. That is, $\Delta V^{(\mathrm{i})}(\boldsymbol{r})$ denotes the potential shift from that of As to N, and $\Delta V^{(\mathrm{ii})}(\boldsymbol{r})$ and $\Delta V^{(\mathrm{iii})}(\boldsymbol{r})$ stem from the displacements of atoms adjacent to the nitrogen. In these equations, V_{N}, V_{As}, and V_{Ga} are atomic potentials of N, As, and Ga, respectively. For these atomic potentials, we used empirical pseudopotentials presented in [20,21]. The vector $\boldsymbol{R}_I$ ($\boldsymbol{R}_j$) indicates the location of a zinc blende unit cell, and $\boldsymbol{\tau} = (a/4, a/4, a/4)$ (a is the lattice constant) is a vector that indicates the position of a Ga atom within a unit cell. The displacements of atoms adjacent to the nitrogen are written as ξ_{j} and $\boldsymbol{\eta}_{j'}$ for the first neighboring Ga and the second neighboring As, respectively. The indices j and j' run through so that the vectors $\boldsymbol{R}_j + \boldsymbol{\tau} + \boldsymbol{\xi}_j$ and $\boldsymbol{R}_{j'} + \boldsymbol{\eta}_{j'}$ indicate the positions of the first neighboring four Ga atoms and the second neighboring 12 As atoms, respectively. We set $\boldsymbol{\xi}_j$ so that the Ga atoms approach toward the N atom by 0.38 Å. Similarly, $\boldsymbol{\eta}_{j'}$ was determined so that the second neighboring As atoms approach toward the N by 0.1 Å. These values were obtained from total energies evaluated by the first principle calculations using the CASTEP package [26].

2.2. Perturbation matrices and band gap reduction

Fig. 1 shows the energy band of GaAs calculated using the empirical pseudopotentials and plane wave basis functions. Using the wavefunctions of the bulk GaAs, we calculated a matrix element defined by

$$\Delta V_{n\boldsymbol{k},n'\boldsymbol{k}'} \equiv \langle \psi_{n\boldsymbol{k}} | \Delta V | \psi_{n'\boldsymbol{k}'} \rangle, \tag{3}$$

where $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ is the wavefunction of the bulk GaAs with a wavevector $\boldsymbol{k}$. The index n denotes the band as indicated in Fig. 1 where the highest valence band and the lowest conduction band are labeled $n = 3, 4$ and $n=5$, respectively. We note that the matrix elements were evaluated using wavefunctions normalized within the zinc blende unit cell. Thus, a factor $1/(4N_d^3)$ is necessary for the perturbation calculations so that the wavefunctions are normalized within the $N_d \times N_d \times N_d$ cell containing one nitrogen.

We show here that only a restricted number of $\boldsymbol{k}$-states are necessary for the perturbation calculation in the present model in which N atoms are periodically aligned. Since the perturbation potential in the present model has translational symmetry with a period $N_d a$ in all the x-, y-, and z-directions, the matrix element $\langle \psi_{n\boldsymbol{k}} | \Delta V | \psi_{n'\boldsymbol{k}'} \rangle$ must be unchanged when $\Delta V(\boldsymbol{r})$ is replaced by $\Delta V(\boldsymbol{r}-\boldsymbol{R})$ with a lattice vector of the supercell $\boldsymbol{R} = N_d a(n_1, n_2, n_3)$ with n_1, n_2, and n_3 integers. From this invariance and Bloch's theorem, the wavevectors $\boldsymbol{k}$ and $\boldsymbol{k}'$ in Eq. (3) must satisfy a relation $\boldsymbol{k} - \boldsymbol{k}' = (2\pi)/(N_d a)(n_x, n_y, n_z)$ with n_x, n_y, and n_z integers between $-N_d$ and N_d. In the present case where $\boldsymbol{k}'$ is Γ, $\boldsymbol{k}$ is given by

$$\boldsymbol{k} = \frac{2\pi}{N_d a}(n_x, n_y, n_z). \tag{4}$$

Therefore, the $\boldsymbol{k}$-states connected by the perturbation potential discretely distribute within the Brillouin zone with spacing depending on nitrogen concentration. In the inset of Fig. 1, we show such $\boldsymbol{k}$-states for $N_d=4$. Note that some points on the border are identical. For example, $(2\pi/a)(1, 0, 0)$ and $(2\pi/a)(-1, 0, 0)$ denote the same one $\boldsymbol{k}$-point. Hence, we excluded one of them from the calculations to avoid double counting, although both are left plotted in the figure. Excluding such points, we have $4N_d^3$ $\boldsymbol{k}$-points in the first Brillouin zone to be mixed due to the perturbation potential. There are 256 points for $N_d=4$ (2048 points for $N_d=8$) required for the calculations. These $\boldsymbol{k}$-points are the points that are folded onto the Γ-point of the Brillouin zone of the $N_d \times N_d \times N_d$ supercell.

In the upper panel of Fig. 2, we show $|\Delta V_{5\Gamma,n\boldsymbol{k}}|$ the matrix elements between the conduction band edge state (Γ-state of the 5th band) and various states. The solid- and dotted-curves are the

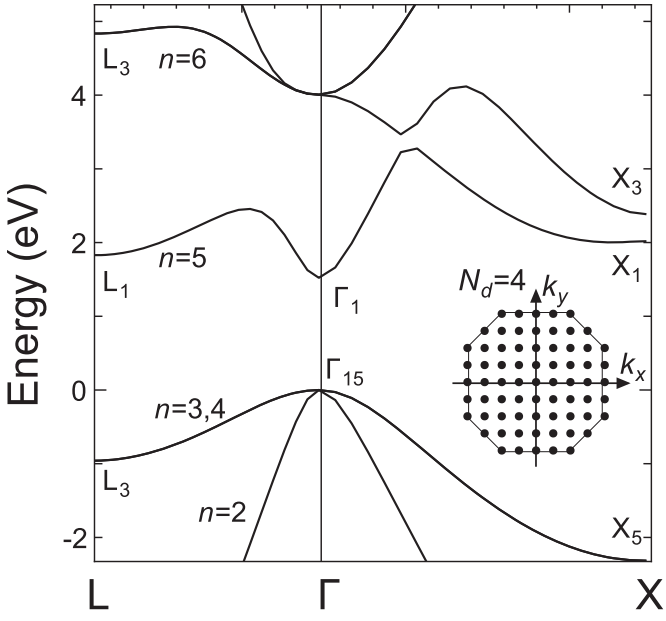

Fig. 1. The energy band of GaAs calculated using the empirical pseudopotentials [20,21]. Inset: reciprocal lattice vectors to be connected with one another by the perturbation potential of the present model for $N_d = 4$. Note that equivalent points are excluded in the following calculations though they are plotted in the figures.

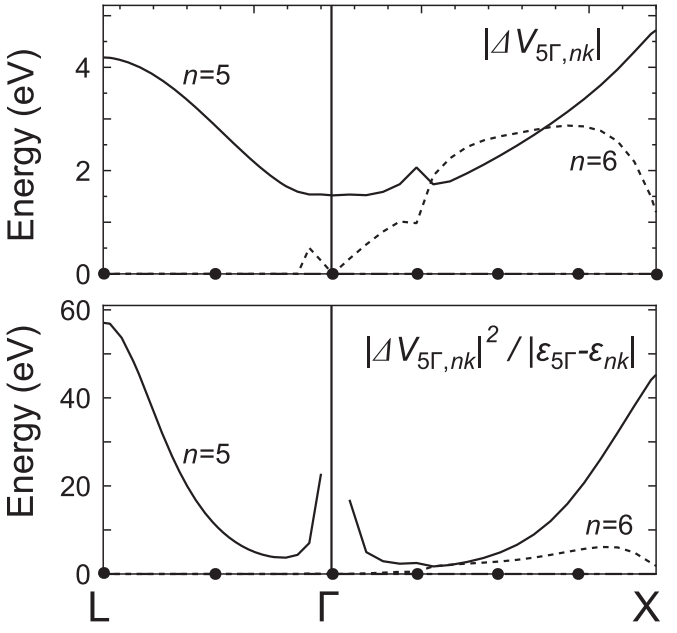

Fig. 2. Upper panel: absolute value of the perturbation matrix element between the conduction band edge state $(5, \Gamma)$ and band states $(n, \boldsymbol{k})$ as a function of wave vector $\boldsymbol{k}$ along the L–Γ–X line. Lower panel: square of the matrix element divided by the energy separation along the L– Γ–X line. The dots on the x-axis denote $\boldsymbol{k}$-states relevant to the calculations for $N_d=4$.