First-principles calculation of positron states and annihilation parameters for group-III nitrides

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Abstract. We calculated theoretically positron states and annihilation parameters for V_{Ga,C} complexes in GaN. Positron lifetimes and Doppler-broadening S-W parameters were evaluated. The obtained results are compared other various types of defects in group-III nitrides. A random alloy In_{0.5}Ga_{0.5}N and its multilayer system together with GaN are investigated also. The results of the present study are expected to be useful for interpretation of experimental results on practical materials.

1. Introduction

Group-III nitrides are thought to be important and promising materials for various applications such as optoelectronics etc. Their properties and functions can be controlled by forming alloys and/or superlattices. For practical materials and devices, often, defects such as vacancies and dislocations play a critical role in their performances. We have been successfully applying the positron annihilation technique in characterizing defects for group-III nitrides [1]-[10].

In the present study, we calculated positron states and annihilation parameters for V_{Ga,C} complexes, which are thought to be closely related to photoluminescence, in GaN and compared with the previous results for various kinds of defects in AlN, GaN and InN. We also investigated a random alloy In_{0.5}Ga_{0.5}N. For the purpose of more realistic modeling of alloys, we have used the special-quasirandom-structure (SQS) approach [12, 13]. Distributions of Doppler S and W parameters as well as positron lifetimes for cation vacancies are evaluated. Positron states and annihilation parameters for a superlattice system In_{0.5}Ga_{0.5}N/GaN are also investigated.

2. Computational details

To calculate positron states and annihilation parameters in systems containing defects or in alloys, we used orthorhombic supercells which are equivalent to 4 × 4 × 2 hexagonal unit cells of the wurzite structure. As for the alloys, we utilized the special quasirandom structure (SQS) approach [12, 13], which provides realistic structural modeling for random alloys using periodic supercells. With this approach, two kinds of atoms are arranged so that pair-correlation functions become as close to those for an infinite random alloy as possible. Practically, an atomic arrangement, which gives the lowest Warren-Cowley parameter for several neighboring shells $\alpha_i = 1 - P_B(i)/x_B$, is chosen, where $P_B(i)$ is the probability of finding a B atom on the...
i-th nearest neighbor shell about an atom as the origin. In the present study, shells up to the 7-th are taken into account and the quantity $\sum_{i=1}^{7} \alpha_i^2$ should be minimized.

Electronic structures have been calculated with our computational code QMAS [14], which adopts the projector augmented-wave (PAW) method [15] and the planewave basis. As for the electronic exchange-correlation energy, we used the generalized gradient approximation [16]. Although lattice parameters can be determined with first-principles calculations, we used the experimental ones in the present study for convenience. Internal atomic positions were optimized with evaluating the Hellmann-Feynman force. Effects of the positron localization to atomic configurations were not considered. For each system, we assumed a neutral charge state. The planewave energy cutoff and the force convergence criterion were set to be 20 Ha and $5 \times 10^{-5}$ Ha/bohr, respectively. As for $k$-point sampling, we used the $\Gamma$ point only. Positron states were calculated with constructing the positron effective potential using core electron wavefunctions from isolated atom calculations and valence electron wavefunctions described in the PAW formalism [17]. With the resultant positron and electron wavefunctions, positron annihilation Doppler broadening spectra $\rho_{1D}(p_x)$ and positron lifetimes $\tau$ were calculated with the following equations:

$$\rho_{1D}(p_x) = \int \int \rho(p) dp_x dp_y, \quad \rho(p) \propto \sum_j \left| \int \psi_+(r) \psi_{-j}(r) \sqrt{\gamma (n_-(r))} \exp(-i p \cdot r) dr \right|^2,$$

$$1/\tau = \pi r_0^2 c \int n_+(r)n_-(r)\gamma(n_-(r))dr,$$

where $\psi_+$, $\psi_{-j}$, $n_+$ and $n_-$ are the positron wavefunction, the $j$-th electron wavefunction, the positron density and the electron density, respectively. $r_0$ represents the classical electron radius and $c$ is the speed of light. $\gamma$ is the enhancement factor. Here, we used the Borowski-Nieminen enhancement factor $\gamma(r_s) = 1 + 1.23r_s + 0.8295r_s\sqrt{\gamma} - 1.26r_s^2 + 0.3286r_s^2\sqrt{\gamma} + r_s^3/6$ [18], where $r_s = [3/(4\pi n_-)]^{1/3}$ is the density parameter, with a small modification to deal with semiconductors [19]. In analogy with the GGA enhancement factor [20], and to be consistent with the positron-electron correlation energy, we used the expression $\gamma_{sem} = 1 + (\gamma - 1)(1 - 1/\varepsilon_{\infty})$. $\varepsilon_{\infty}$ is the dielectric constant of the target system. Although it can be determined by first-principles calculations, we used the experimental values for convenience. For alloys, we used linearly-interpolated values. As for the positron-electron correlation potential, we used that proposed by Borowski and Nieminen [18]. It is also modified for semiconductors [19].

### 3. Results and discussion

In Table 1, calculated positron lifetimes for $V_{Ga}$ complexes in GaN together with the previous results for various kinds of defects in AlN, GaN and InN are listed. For example, the calculated lifetimes for the bulk and the Ga vacancy in GaN are 159.5 ps and 237.9 ps. They are in good agreement with the experimental values of 166 ps and 235 ps [21]. Positrons are not completely trapped at the N vacancy. Although these predicted lifetime values are already useful to distinguish defect species, so-called $S$-$W$ plots are more powerful for this purpose. In Fig. 1, an $S$-$W$ plot for bulk GaN and defects in GaN is shown. Systematic variations are observed in the two-dimensional space while the lifetime varies in the one-dimensional space. As for $V_{Ga}$-impurity complexes, the direction of variation differs depending on the impurity species. For several representative ones, ratio curves against the bulk are plotted in Fig. 2.

As for the $In_{0.5}Ga_{0.5}N$ alloy, the supercell used in the present study contains 128 atoms. Its lattice parameters and dielectric constant are given as average values of those for InN and GaN. There are 64 different cation sites. We made calculations for single vacancies on these sites. In Fig. 3, obtained $S$ and $W$ parameters are plotted. It is clearly shown that the $S$ parameter shows a significant variation while the $W$ parameter shows a smaller variation. We have found that the larger Ga concentration on the nearest 12 cation sites tends to bring the larger $W$ value.
et al. InN/GaN superlattice studied by Makkonen

This is due to the variation of the positron effective potential shown in Fig. 4 (b) and (c) as
not taken into account. It has been revealed that positrons are predominantly distributed in
along

Figure 1. S–W plot for GaN bulk and defects therein (S: –0.419 ∼ +0.419 a. u., W: ±(1.828 ∼ 3.688) a.u.).

We also investigated an In$_{0.5}$Ga$_{0.5}$N/GaN superlattice system. The $4 \times 4 \times 2$ In$_{0.5}$Ga$_{0.5}$N unit and the $4 \times 4 \times 2$ GaN unit are stacked along the wurtzite $c$ axis as shown in Fig. 4 (a). The unit cell of the superlattice system contains 256 atoms. The lattice parameters of the supercell perpendicular to $c$ are fixed to those of the GaN unit. As for the lattice parameter along $c$, it is set to $c$(In$_{0.5}$Ga$_{0.5}$N) + $c$(GaN), where $c$(In$_{0.5}$Ga$_{0.5}$N) and $c$(GaN) are the lattice parameters along $c$ for the units mentioned above. Thus, the Poisson effect in the In$_{0.5}$Ga$_{0.5}$N region was not taken into account. It has been revealed that positrons are predominantly distributed in a part of the GaN region, which is close to one type of the interfaces, as shown in Fig. 4 (a). This is due to the variation of the positron effective potential shown in Fig. 4 (b) and (c) as the planar average $\tilde{V}$ and the macroscopic average $\tilde{V}$. This is similar to the situation for an InN/GaN superlattice studied by Makkonen et al. [11]. The obtained $S$ and $W$ parameters are also plotted in Fig. 2. Naturally, it is close to the location of the plot for the GaN bulk.

Table 1. Calculated positron lifetimes (ps)

|        | AlN          | GaN          | InN          |
|--------|--------------|--------------|--------------|
|        | $(a, c) = (3.11, 4.98)$ Å, $\varepsilon_{\infty} = 4.7$ | $(a, c) = (3.189, 5.1625)$ Å, $\varepsilon_{\infty} = 5.5$ | $(a, c) = (3.385, 5.7029)$ Å, $\varepsilon_{\infty} = 8.4$ |
| bulk   | 165.3        | 159.5        | 175.8        |
| $V_{AI}$ | 244.6        | 237.9        | 256.8        |
| $V_{N}$    | 166.9        | 160.2        | 176.6        |
| $V_{AI}V_{N}$ | 253.0, 267.0 | 244.9, 245.7 | 258.4, 260.9 |
| $V_{AI}(V_{N})_{3}$ | 281.5        | 259.6        | 265.6        |
| $V_{AI}(O_{N})_{3}$ | 248.2        | 241.2        | 263.4        |
| $V_{AI}(O_{N})_{4}$ | 245.5        | 239.8        | 264.1        |
| $V_{Ga}$     | 230.7, 231.7 | 211.5        |              |
| $V_{Ga}(C_{N})_{3}$ | 203.9        |              |              |

Figure 2. Ratio curve for representative defects in GaN against its bulk.

Figure 3. S–W plot for a random alloy In$_{0.5}$Ga$_{0.5}$N bulk and defects therein.
4. Summary
The positron annihilation S and W parameters as well as the positron lifetime have been calculated for V_{Ga-C} complexes in GaN and been compared with other various types of defects in AlN, GaN and InN. They are expected to be useful in interpreting experimental results. A random alloy In_{0.5}Ga_{0.5}N was modeled with the SQS approach and the S, W and lifetime for cation vacancies were calculated and analyzed. An In_{0.5}Ga_{0.5}N/GaN superlattice system is also investigated. Modeling for practical materials is now possible. Calculations for In_{0.125}Ga_{0.875}N/GaN, which is closer to the situation of existing devices, are now in progress.

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