

Compensation Mechanism of Free Hole Carriers in N-Doped ZnSe

Masakatsu Suzuki, Takeshi Uenoyama and Akira Yanase*

Central Research Laboratories, Matsushita Electric Industrial Co., Ltd.,
Moriguchi, Osaka 570, Japan

*College of Integrated Arts and Science, University of Osaka Prefecture,
Sakai, Osaka 591, Japan

We have performed the energy band calculations for ZnSe compounds with N impurities using the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method. The compensation processes have been discussed from the point of view of the cohesive energy, the density of states and the charge density distribution. It was found that the pairing of two kinds of N atoms, a substitutional N atom and an interstitial N atom, causes the compensation of the free hole carriers.

I. Introduction

Practical p-type ZnSe has been realized by MBE growth using a plasma source for N doping¹ and these developments have led to the demonstration of II-VI laser diodes.^{2,3} However, an important and serious problem still remains. Although the grown ZnSe layers can contain N atoms over 10^{18} cm^{-3} , the free hole concentration is saturated at about 10^{17} cm^{-3} and abruptly decreases.⁴ It is necessary to clarify the microscopic mechanism of this saturation process, namely, the compensation of the free hole carriers. Recently, the total energy calculations have been performed for all native point defects in ZnSe.⁵ The result shows that native point defect concentrations are too low to cause compensation in stoichiometric ZnSe. Thus, we devote our attention to the behavior of N atoms.

In this paper, the electronic structure and the stability of the impurity complex involving two kinds of N atoms, a substitutional N atom and an interstitial N atom, are investigated by using the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method⁶. Then the compensation mechanism is discussed on the basis of the cohesive energy, the density of states and the charge density distribution.

II. Method

In the present calculations, the defects, such as a substitutional N atom at the Se site (N_{Se}), an interstitial N atom (N_{int}), are approximately introduced into

ZnSe with the supercell method, where the unit cell contains four ZnSe and N impurities. The energy band calculations have been performed within the local density approximation (LDA), using the Gunnarsson and Lundqvist form⁷. The 3d electrons of the Zn atom are treated as a part of the valence band. Inside the muffin-tin (MT) spheres, the angular momentum expansion is truncated at $l_{\text{max}} = 7$ for the wave functions. A set of the FLAPW basis functions is constructed within the criterion that $|\mathbf{k} + \mathbf{G}|_{\text{max}} = (2\pi/a) \times 5.5$ with $\mathbf{k}$ being a wavevector in the first Brillouin zone (BZ) and $\mathbf{G}$ being a reciprocal lattice vector. In the expansion of the full-potential, the plane waves are considered up to $|\mathbf{k} + \mathbf{G}|_{\text{max}} = (2\pi/a) \times 10.0$. In the iteration process, the charge density in the crystal has been determined self-consistently by using the meshed $\mathbf{k}$ points which bisect the symmetry lines in the irreducible BZ. The iteration process has been repeated until the calculated total energy of the crystal converges into less than 1 mRyd. The lattice parameter a and the all MT radii used in these calculations are, respectively, $5.6693 \text{ \AA}$ ⁸ and $0.21a$. We neglected the lattice distortion in the all cases. The density of states (DOS) has been calculated with a linearly energy-interpolated tetrahedron method^{9,10}. The cohesive energy has been calculated from the difference between the total energy for the crystal and the sum of the total energies for the neutral atoms in the ground state configurations of Zn ($4s^2$), Se ($4s^2 4p^4$) and N ($2s^2 2p^3$).

III. Results and Discussion

In Table I, the calculated cohesive energies are listed for the compounds with various kinds of N impurities. As for the position of a single N_{int} , we have performed the band calculations for two kinds of N_{int} positions. One is surrounded tetrahedrally by Zn atoms (Td(Zn)) and the other is surrounded by Se atoms (Td(Se)). The cohesive energy of the former, $E_c(N_{\text{int}}:\text{Td}(\text{Zn}))$, is larger by 0.064 Ryd than $E_c(\text{ZnSe})$. On the other hand, that of the latter, $E_c(N_{\text{int}}:\text{Td}(\text{Se}))$, is smaller by 0.013 Ryd than $E_c(\text{ZnSe})$. These results indicate that a single N_{int} prefers Td(Zn) site to Td(Se) site and that a $N_{\text{int}}:\text{Td}(\text{Se})$ is unstable impurity.

Next, we describe the results for the impurity complex. The calculations for the impurity complex, involving both a N_{Se} and a N_{int} , have been performed in order to examine the effect of excess N impurities in p-type ZnSe. Then, we suppose that a N_{int} locates not at Td(Se) site but at Td(Zn) site due to above result. We consider the two cases, which differ in the position of a N_{int} viewed from a N_{Se} . One is the nearest neighbor Td(Zn) site (Td(Zn)¹) and the other is the next nearest neighbor Td(Zn) site (Td(Zn)²). These positions of N atoms are shown in Fig.1. According to Table I, the sum of $E_c(N_{\text{Se}}, N_{\text{int}}:\text{Td}(\text{Zn})^{1(2)})$ and $E_c(\text{ZnSe})$ is larger by 0.065 (0.030) Ryd than the simple sum of $E_c(N_{\text{Se}})$ and $E_c(N_{\text{int}}:\text{Td}(\text{Zn}))$. The former sum corresponds to the case where a $N_{\text{int}}:\text{Td}(\text{Zn})$ is close to a N_{Se} and the interaction between them is taken into account. On the other hand, The latter sum corresponds to the case where a $N_{\text{int}}:\text{Td}(\text{Zn})$ is far away from a N_{Se} and the interaction is ignored. Thus, in this system, a N_{int} tends to locate near a N_{Se} and stably coexists with a N_{Se} . Then, $N_{\text{int}}:\text{Td}(\text{Zn})^1$ is more stable position than the $N_{\text{int}}:\text{Td}(\text{Zn})^2$. In short, a N_{int} is stabilized by pairing with a N_{Se} in p-type ZnSe.

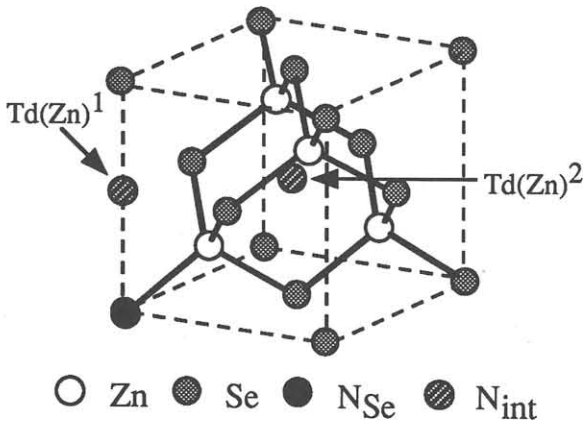


Fig. 1 Positions of N atoms in the ZnSe compound with both a N_{Se} and a N_{int} .

Table I Cohesive energies (in units of Ryd/unit cell) and electron numbers in each MT sphere (in units of electrons/atom) of the ZnSe compounds with various kinds of N impurities. N_{sub} and N_{int} stand for substitutional and interstitial N atoms, respectively. Td(Zn)¹⁽²⁾ stands for the compound with a N_{Se} and a $N_{\text{int}}:\text{Td}(\text{Zn})^{1(2)}$.

Defect	E_c	Zn	Se	N_{sub}	N_{int}
ZnSe	1.456	10.64	4.09		
N_{Zn}	1.457	10.65	3.99	4.77	
N_{Se}	1.158	10.57	4.08	4.85	
Td(Zn)	1.520	10.65	4.07		4.89
Td(Se)	1.443	10.65	4.06		4.97
Td(Zn) ¹	1.287	10.57	4.06	4.83	4.79
Td(Zn) ²	1.252	10.58	4.05	4.79	4.92

In the following, we discuss the compensation from the point of view of the DOS, the electron numbers in MT spheres and the charge density distribution. The partial DOS (PDOS) for the compound with both a N_{Se} and a $N_{\text{int}}:\text{Td}(\text{Zn})$ are shown in Fig.2, where the results for two different N_{int} positions (Td(Zn)¹, Td(Zn)²) are drawn together. Each PDOS contains the contributions arising from Se 4p, N_{Se} 2p and N_{int} 2p states in each MT sphere. In Table I, the electron numbers in each MT sphere are shown. In the first case, the N_{Se} 2p states are comparatively localized and

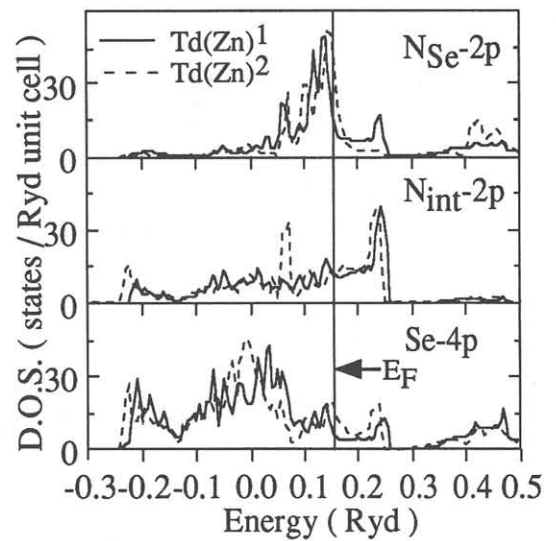


Fig. 2 Partial density of states at N and Se sites in the ZnSe compound with both a N_{Se} and a $N_{\text{int}}:\text{Td}(\text{Zn})$

close to the maximum of the valence band. According to Table I, the electron number around the N_{Se} with a $N_{int}:Td(Zn)^1$ is nearly equal to that around a single N_{Se} , which acts as an acceptor. On the analogy of a single N_{Se} , these states are acceptor states. On the other hand, the $N_{int}:Td(Zn)^1$ 2p states are comparatively localized and close to the minimum of the conduction band. These states are well hybridized with N_{Se} 2p states. According to Table I, the electron number around the $N_{int}:Td(Zn)^1$ is smaller than that around a single N_{int} and nearly equal to that around a single N_{Zn} , which acts as a donor. These facts indicate that these states are donor states and that the decrease of the electron number around the $N_{int}:Td(Zn)^1$ can be explained as the following process: electrons by a $N_{int}:Td(Zn)^1$ recombine with holes by a N_{Se} . Indeed, the acceptor states are almost occupied and the donor states are not occupied. Namely, the above recombination process corresponds to the self-compensation effect. Moreover, the valence charge density in (110) plane is shown in Fig.3. In the system where two different kinds of N atoms is pairing, there are some covalent charges between them. This covalency suppresses the increase of the intra-atomic Coulomb energy in the impurity atom site, in spite of the electron transfer from N_{int} to N_{Se} . In the second case, the shape of the PDOS is similar to that in the first case, but the Fermi level locates on the slope of the peak. As a result, the acceptor states becomes partially unoccupied and some hole carriers survive. Furthermore, the difference between the two

cases is explicitly shown in Table I. The electron number around a N_{Se} and $N_{int}:Td(Zn)^2$ in the second case are entirely different from those in the first case. Thus, the compensation does not occur.

IV. Conclusions

In order to clarify the saturation mechanism of the free hole concentration in N-doped ZnSe, we have performed the FLAPW band calculations for the ZnSe compounds with various kinds of N impurities and discussed the electronic structure and the stability of impurity complex. Consequently, we propose that the pairing of two kinds of N atoms, a N_{Se} and a N_{int} , is a suitable mechanism for the compensation of the free hole carriers in heavily N-doped ZnSe. To go into the more detail discussion, we shall expand the size of the supercell and consider the lattice distortion.

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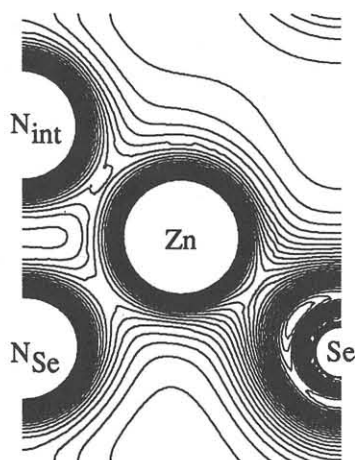


Fig.3 Valence charge density of the compound with both a N_{Se} and a $N_{int}:Td(Zn)$ in the (110) plane.

The contour unit is $0.005 \text{ e}/(\text{a.u.})^3$.