PHYSICAL REVIEW B VOLUME 51, NUMBER 16 15 APRIL 1995-II

First-principles study of the compensation mechanism for nitrogen acceptors in ZnSe

Byoung-Ho Cheong
Department of Physics, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-ku, Taejon, Korea

C. H. Park
NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

K. J. Chang
Department of Physics, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-ku, Taejon, Korea
(Received 21 November 1994)

We present a mechanism for the compensation of N acceptors in ZnSe through first-principles pseudopotential calculations. In Se-rich conditions, the formation of N_2 molecules that are electrically inert neutralizes the acceptor activity, with the maximum acceptor density achievable with N dopants being about 10^{18} cm^{-3}, in good agreement with experiments. Going to Zn-rich conditions, the hole density is increased by an order of magnitude, suggesting a promising low-resistance *p*-type doping; however, a self-compensation still occurs due to a [100]-split interstitial N-N complex occupying a Se site, which behaves as a double donor.

In recent years wide-band gap II-VI semiconductors such as ZnSe are of growing interest because of its applications for blue-green light emitting and laser devices. Knowing for a long time that ZnSe can be doped *n*-type but not easily *p*-type, it was a breakthrough in using II-VI semiconductors for optoelectronic devices that ZnSe-based blue-green lasers emitting was demonstrated.[1] Although with Li, P, and As atoms as *p*-type dopants, free-carrier densities were generally found to be below 10^{17} cm^{-3}, low resistance *p*-type doping in ZnSe with acceptor concentrations as high as 10^{18} cm^{-3} was successfully achieved using a pure N source.[2–7] However, the actual N concentration was found to be larger by several times under high N concentrations, indicating that self-compensation is significant. Theoretically, it was indicated that the native point defects such as vacancies, interstitials, and antisites are not very important to explain the self-compensation of acceptors in stoichiometrically grown ZnSe.[8] From the first-principles pseudopotential calculations, Chadi and Chang showed that the difficulty with As and P dopants in achieving high hole concentrations is resulted from the bonding property of dopants with the surrounding host atoms, associated with large lattice relaxations inducing a localized hole state, whereas in the case of Li there exists a competition between substitutional and interstitial configurations.[9] Despite many theoretical studies,[9–11] the microscopic origin of the difficulty in achieving high hole concentrations above 10^{18} cm^{-3} with N as a dopant is not fully understood, and the maximum acceptor density achievable by such a doping process has not been successfully studied.

In this paper we present a mechanism for the self-compensation of N dopants in ZnSe. Calculating the formation energies for various N-related and native point defects, we obtain the maximum acceptor concentration of about 10^{18} cm^{-3} in Se-rich conditions, which is in good agreement with experiments. At higher N concentrations, the doping efficiency is significantly reduced due to the neutralization of the acceptor activity by a N_2 molecule which is electrically inert. In Zn-rich conditions, a doubly charged [100]-split interstitial N-N complex at a Se site is more stable than the molecular formation at an interstitial site, thus it leads to a compensation effect on N acceptors. However, we find the maximum acceptor concentration to increase by an order of magnitude, suggesting a promising low-resistance *p*-type ZnSe.

The total energy is calculated using the first-principles pseudopotential method and the Kleinman-Bylander type of fully separable pseudopotentials is used.[12,13] For the Zn pseudopotential, it is well known that the inclusion of the Zn 3*d* states in the core shell results in a poor description of bulk ZnSe.[14] However, we find that with partial core corrections[15] the bulk properties of ZnSe are well described; the lattice constant (a_0), the bulk modulus (B_0), and the pressure derivative of B_0 (B_0') are 5.680 Å, 63.2 GPa, and 4.17 for the Zn potential with partial core corrections only (Zn_{pcor}) and 5.677 Å, 68.9 GPa, and 4.59 for the Zn potential with the 3*d* electrons in the valence shell (Zn_{3d}), while experimental values[16] for a_0 and B_0 are 5.669 Å and 62.5 GPa, respectively. For major N-related defects within a supercell containing 18 atoms, we also test both the Zn_{pcor} and Zn_{3d} pseudopotentials and find the maximum errors in comparing relative formation energies and lattice relaxations to be less than 0.05 eV per N atom and 0.04 Å, respectively (see Table I). Since the 18 atom cell is not sufficient to get fully relaxed atomic configuration, we use a larger size of supercell containing up to 32 atoms and a higher kinetic-energy cutoff in the plane-wave expansion of wave functions.[17] Then, the calculated total energies are converged to within 0.1 eV per N atom. We achieve the energy minimization by the efficient modified-Jacobi relaxation method[18] and optimize the atomic geometry by calculating the Hellmann-Feynman forces. The Brillouin zone integration is per-

 ©1995 The American Physical Society

TABLE I. The bond lengths (d) and the relative formation energies ($\Delta E_D'$) of various N-related defects with respect to that of N_{Se}^- are compared for the Zn_{3d} and Zn_{pcor} pseudopotentials (see text), where E_D' is defined in Ref. 19. d and $\Delta E_D'$ are in units of Å and eV, respectively, and N_{Se}-N_i denotes a substitutional-interstitial N complex.

		Zn_{3d}	Zn_{pcor}
N_{Se}^-	d_{Zn-N}	2.04	2.05
	$\Delta E_D'$	0.0	0.0
$(N\text{-}N)_{Se}^{2+}$	d_{N-N}	1.04	1.04
	d_{Zn-N}	2.57	2.60
	$\Delta E_D'$	1.09	1.13
$(N_{Se}\text{-}N_i)^+$	d_{N-N}	1.03	1.03
	d_{N-Zn_1}	3.04	3.02
	d_{N-Zn_2}	2.82	2.80
	$\Delta E_D'$	1.36	1.30
V_{Se}^+	$d_{V_{Se}-Zn}$	2.19	2.20
	$\Delta E_D'$	1.24	1.28
N_{Zn}^+	d_{N-Se}	2.24	2.28
	$\Delta E_D'$	4.11	4.14

formed using two special k points. The formation energy for each charge state of a defect is expressed in terms of the total energy, the chemical potentials μ_i (i = Zn, Se, and N) of the constituent elements, and the electronic (or Fermi) energy (μ_e).[19] The stoichiometric condition of bulk ZnSe is controlled by varying the difference of the chemical potentials ($\Delta\mu = \mu_{Zn} - \mu_{Se}$) in the range $-\Delta H \leq \Delta\mu \leq \Delta H$, where ΔH denotes the heat of formation for bulk ZnSe and is calculated to be 1.59 eV, in good agreement with the measured value of 1.69 eV.[20] The total N concentration [N] in bulk ZnSe can be controlled by treating the N chemical potential μ_N as a variable, while in thermal equilibrium with the N gas phase μ_N is related to the partial pressure of the gas phase in experiments. Here, instead of using the partial pressure, we work with the N chemical potential to determine [N] because it can be directly calculated from first-principles.[10] Then, the maximum N concentration is achieved when the N chemical potential reaches its maximum value. It was shown that p-type ZnSe can be grown successfully by N radical doping using a radio-frequency or an electron cyclotron resonance plasma source.[2–7] Because of the failure of N doping using a normal N_2 gas,[2,3] we decide to use the maximum value for μ_N, which is higher by about 1.5 eV than the limit derived by N_2 molecules, assuming that equal amounts of N_2 molecules in the ground and excited states are in the N gas phase;[3] the energy of an excited N_2 molecule in the $^3\Sigma_u^+$ state is higher by 3.09 eV per N atom than that of the ground state ($^1\Sigma_g^+$).[3,6,21] This choice of the maximum N chemical potential also corresponds to the formation of a condensed phase such as N_2 in a void.[10] Then, for a given temperature and $\Delta\mu$, the equilibrium defect concentrations and μ_e are determined by the charge neutrality condition.[19]

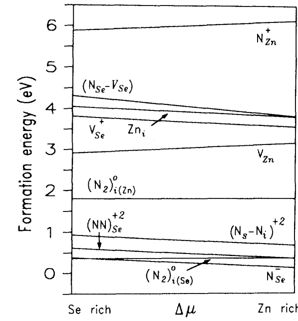

FIG. 1. Defect formation energies as a function of $\Delta\mu$ in p-type doping ($\mu_e = 0.1$ eV). $\Delta\mu$ varies from -0.5 eV (Se-rich) to 0.5 eV (Zn-rich).

We examine various defects including substitutionals (N_{Se} and N_{Zn}), interstitials (N_i, Zn_i, and Se_i), vacancies (V_{Zn} and V_{Se}), and N-N complexes. In Fig. 1, the formation energies of these defects are plotted as a function of $\Delta\mu$, which varies from Se-rich to Zn-rich condition; $\Delta\mu$ is chosen to vary from -0.5 eV to 0.5 eV, because the ratio of the Se partial pressure to the Zn pressure is limited to the values of 0.5–2.0 in most experiments, indicating that $\Delta\mu$ is not severely biased from the stoichiometric condition.[2–6,22] In this case, the Fermi energy which affects the formation energies of defects is set 0.1 eV in p-type doping and the N chemical potential is chosen such that the [N] concentration becomes an order of 10^{18}–10^{19} cm^{-3}. However, more accurate Fermi energy for each value of μ_N can be determined by the charge neutrality condition, as described earlier. As illustrated in Fig. 2, the most prominent defects are found to be a substitutional N_{Se}^- acceptor, a neutrally charged N_2 molecule at an interstitial site, and a [100]-split interstitial N-N complex at a Se site [denoted as $(N\text{-}N)_{Se}$], in which the N-N bond is aligned along the [100] direction, while the other defects are extremely low in defect concentration. For a substitutional N_{Se}, we find that the broken-bond configuration with C_{3v} symmetry which was suggested to be stable for dopants such as As and P is unstable by 0.34 eV per N atom with respect to the fourfold-coordinated structure.[9] In the T_d-

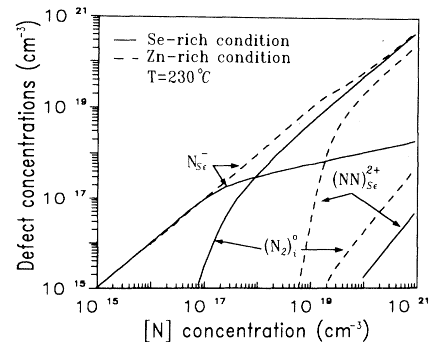

FIG. 2. Defect density vs N concentration for N_{Se}^-, N_2, and $(N\text{-}N)_{Se}^{2+}$ in Se-rich ($\Delta\mu = -0.5$ eV) and Zn-rich ($\Delta\mu = 0.5$ eV) conditions at 230 °C.

symmetry structure, the energy levels associated with the N s and p orbitals lie at about -10.1 and -0.8 eV, respectively, below the valence-band maximum (VBM). Thus, the hole state which is the highest valence band state of the supercell has a large suppression of density on the N atom, and its density is mostly distributed among the acceptor neighboring Se atoms, consistent with previous calculations.[11] The broken-bond configuration is found to be metastable only if the defect state is in a positively charged state, i.e., no barrier between the substitutional and interstitial sites for the neutral and negatively charged states. In the metastable state, both the N acceptor and the nearest [111] Zn atom are displaced by 0.86 and 0.79 Å, respectively, from their substitutional sites towards the interstitial region, forming an sp^2-like configuration with the bond angles of 119.7° and 119.6°. Then, the nonbonding N p_z orbital induces a localized hole state[9] at 0.14 eV above the VBM. Because of the small ionic radius for the N atom, the acceptor neighboring Zn atoms exhibit substantial relaxations of 0.44 Å towards the N_{Se}^- acceptor with the N-Zn bond length of 2.01 Å. A substitutional N occupying a Zn site behaves as a donor and exhibits similar relaxations of 0.42 Å for the nearest neighbors. However, because the formation energy of a N_{Zn}^+ is higher by 5.9 eV than for the N_{Se}^- acceptor, the concentration of N_{Zn}^+ is negligible.

For a N_2 molecule located at the interstitial tetrahedral site of the Zn atom, the N-N bond length is calculated to be 1.05 Å, which is slightly larger than the calculated value of 1.03 Å for a free N_2 molecule in vacuum, while this value is rather smaller than the measured bond length of 1.09 Å.[20] Our calculations show that the molecular formation is less stable in ZnSe than in vacuum because its formation energy is higher by 1.7 eV per atom. In ZnSe, the Zn atoms surrounding the N_2 molecule are relaxed towards the molecule only by 0.03 Å because of the weak interactions between the N and Zn atoms. Thus, an interstitial N_2 molecule is electrically inert. With the analysis of the angular momentum decomposition of the electron energy levels for an N_2 molecule, all the occupied states such as the $ss\sigma$, antibonding $ss\sigma^*$, doubly degenerated $pp\pi$, and $pp\sigma$ states, which are also occupied in a free molecule,[23] are found to lie in the valence band. When we consider an interstitial position of the Se atom, the formation energy of the N_2 molecule is increased by 1.5 eV. We examine the formation of N_2 molecules at the substitutional sites and find that a [100]-split interstitial N-N complex occupying a Se site is most stable among various complexes. The $(N\text{-}N)_{Se}$ complex has the N-N bond length of 1.04 Å, similar to that for an interstitial N_2 molecule. Although each N atom of a N-N complex occupying a Se site is bonded to two nearest Zn atoms, the interactions between the complex and nearest Zn atoms are extremely weak because the N-Zn bond lengths of 2.60 Å are larger by about 0.60 Å than that for a substitutional N_{Se}^-. In bulk ZnSe, since each Zn atom with two valence electrons forms four bonds with the nearest Se atoms, it contributes half of electrons per bonding. Thus, when a N-N complex is formed at a Se site, two valence electrons from the nearest Zn atoms are almost in a nonbonding state which becomes a double

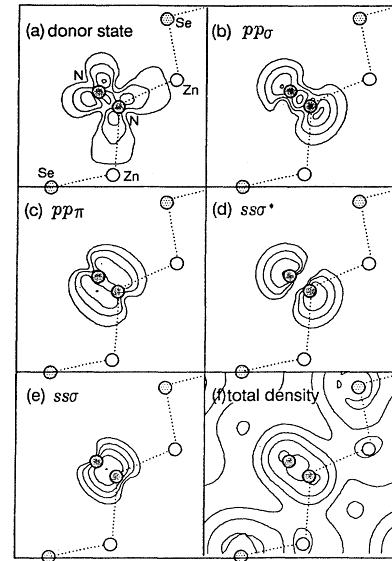

FIG. 3. Contour plots of the electron charge densities on the (110) plane for (a) the donor state, (b)–(e) the occupied molecular states, and (f) the total valence state of a $(N\text{-}N)_{Se}$ complex.

donor state. In fact, we find the double donor state of the $(N\text{-}N)_{Se}$ complex to lie at 0.12 eV above the conduction band minimum and be mainly composed of the Zn p-orbitals as shown in Fig. 3, while the other occupied states are similar to those for an interstitial N_2 molecule.

In the interstitial region, the N atomic species may exist and increase the acceptor concentration because it behaves as an acceptor. However, since its formation energy is higher by 5.3 eV per N atom than for a molecule, the molecular formation is more probable. For primary native point defects, previous theoretical studies showed that a Se vacancy and a Zn interstitial are the most dominant native defects in ZnSe.[8] We find that their formation energies are generally higher than those for the N-related defects, thus the compensation effect of these native defects on N_{Se}^- acceptors is not expected, which is consistent with the previous calculations.[8] It was suggested that a V_{Se}-N_{Se} complex may compensate for acceptors in N-doped ZnSe.[24] However, since the formation energy of a V_{Se}-N_{Se} complex is higher by 3.5 eV than for a N_{Se}^- acceptor, the acceptor compensation by such a substitutional-vacancy complex is not likely to occur.

Investigating the variations of defect concentrations with the chemical potentials of Zn and Se, we find that the maximum acceptor density achievable with N dopants and the principal mechanism for the compensation of N_{Se}^- acceptors strongly depend on $\Delta\mu$. In Fig. 2, our calculated defect concentrations in thermal equilibrium are plotted as a function of N concentration in both Se-rich ($\Delta\mu$ = -0.5 eV) and Zn-rich ($\Delta\mu$ = 0.5 eV) conditions at 230 °C to follow the experimental growth conditions.[5–7] In Se-rich conditions, the defect density of N_{Se}^- acceptors increases monotonically with the N concentration up to 10^{17} cm^{-3}. In the high doping regime, the stable compensating donors are the N_2 molecules located

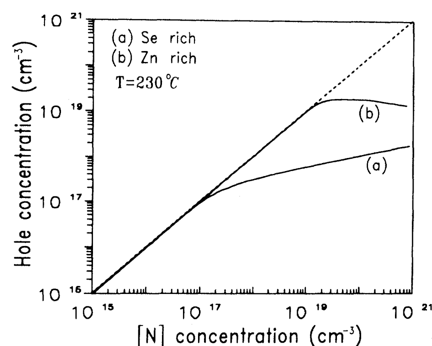

FIG. 4. Acceptor density vs doped N concentration in (a) Se-rich and (b) Zn-rich conditions at 230 °C. Dashed and solid lines represent uncompensated and compensated carrier densities, respectively.

at the interstitial tetrahedral sites, thus the hole compensation is mainly caused by the N_2 molecules which are electrically inert, while that of $(N\text{-}N)^{2+}_{Se}$ complexes is four to five orders of magnitude smaller. For N concentrations ranging from 10^{18} to 10^{21} cm^{-3}, the acceptor density is found to increase very slowly with a maximum concentration of about 2×10^{18} cm^{-3} (see Fig. 4), which agrees well with experimental measurements.[5–7] Experiments showed that N free radicals produced by a radiofrequency plasma source are effectively incorporated into bulk ZnSe, however, the N doping efficiency tends to decrease even if high pressures in the radical source are employed to increase the N concentration.[4–7] Such an observation agrees well with our results because experimental environments under high N pressures may result in the recombination of N_2 molecules by collisions, thus it reduces the electrical activity of N acceptors.

When the stoichiometric condition is changed to the Zn-rich condition, more Zn interstitials or Se vacancies are expected to be created. However, since these native point defects are still higher in energy, the Se vacancies are likely to be occupied by either a substitutional N or a N-N complex because these defects reduce the formation energy. As going to the Zn-rich condition, the formation energies of the N^-_{Se} acceptor and the $(N\text{-}N)^{2+}_{Se}$ complex decrease more rapidly than for the interstitial N_2 molecule. Hence, we expect higher acceptor densities by Zn-rich conditions. The Fermi level is found to decrease with increasing the N concentration, thus substitutional N acceptors can be neutrally charged if the Fermi level is below 110 meV, which is the acceptor level from the valence-band maximum. We find the Fermi level to be below 110 meV for N concentrations exceeding 10^{19} cm^{-3}. However, the density of neutral substitutional N defects is found to be two orders of magnitude smaller than that of N^-_{Se} acceptors. As illustrated in Fig. 2, the defect densities for the N^-_{Se} and $(NN)^{2+}_{Se}$ complex are significantly enhanced in the region of high N concentration, while the density of N_2 molecules is reduced by four orders of magnitude. Because of the increased stability of the N^-_{Se} acceptor, the maximum acceptor density is increased up to 1.8×10^{19} cm^{-3} as shown in Fig. 4. However, with the further increase of the N doping concentration, the acceptor density still decreases due to the compensation effect of doubly charged $(N\text{-}N)_{Se}$ complexes, while a neutral N_2 molecule is a dominating cause for self-compensation in Se-rich conditions. Our results that high acceptor concentrations are achievable in ideal stoichiometric or Zn-rich conditions are strongly supported by recent experiments.[4,25,26]

In conclusion we have suggested a mechanism for the self-compensation of N acceptors in ZnSe. From the dependence of the maximum acceptor density achievable with N dopants on the electronic and atomic chemical potentials, we predict that a doping efficiency is enhanced as going from the Se-rich to the Zn-rich condition.

This work was supported by the CMS at Korea Advanced Institute of Science and Technology and by the Ministry of Science and Technology.

[1] M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheong, Appl. Phys. Lett. **59**, 1272 (1991).

[2] R. M. Park, M. B. Troffer, C. M. Rouleau, J. M. DePuydt, and M. A. Haase, Appl. Phys. Lett. **57**, 2127 (1990).

[3] K. Ohkawa, T. Karasawa, and T. Mitsuyu, J. Cryst. Growth **111**, 797 (1991).

[4] S. Ito, M. Ikeda, and K. Akimoto, Jpn. J. Appl. Phys. **31**, L1316 (1992).

[5] J. Qiu, J. M. DePuydt, H. Cheong, and M. A. Haase, Appl. Phys. Lett. **59**, 2992 (1991).

[6] T. Ohtsuka and K. Horie, Jpn. J. Appl. Phys. **32**, L233 (1993).

[7] Z. Yang, K. A. Bowers, J. Ren, Y. Lansari, J. W. Cook, Jr., and J. F. Schetzina, Appl. Phys. Lett. **61**, 2671 (1992).

[8] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blöchl, and S. T. Pantelides, Phys. Rev. B **45**, 10 965 (1992).

[9] D. J. Chadi and K. J. Chang, Appl. Phys. Lett. **55**, 575 (1989); D. J. Chadi, *ibid.* **59**, 3589 (1991).

[10] C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Phys. Rev. B **47**, 9425 (1993).

[11] K. W. Kwak, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. B **48**, 17 827 (1993).

[12] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[13] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[14] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).

[15] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[16] *Semiconductors. Physics of II-VI and I-VII Compounds*, edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. b (Springer, Berlin, 1982).

[17] We use kinetic energy cutoffs ranging from 25 to 30 rydberg for the Zn_{pcor} pseudopotential and the supercells containing up to 32 atoms, while a cutoff energy of 64 rydberg is used for the Zn_{3d} potential and the supercell with 18 atoms.

[18] C. H. Park, I.-H. Lee, and K. J. Chang, Phys. Rev. B **47**,

15 996 (1993).
[19] J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993).
[20] *Handbook of Chemistry and Physics*, 73th ed., edited by R. C. Weast (CRC, Boca Raton, 1992).
[21] T. Nakao and T. Uenoyama, Jpn. J. Appl. Phys. **32**, 660 (1993).
[22] W. Xie, D. C. Grillo, R. L. Gunshor, M. Kobayashi, G. C. Hua, N. Otsuka, H. Jeon, J. Ding, and A. V. Nurmikko, Appl. Phys. Lett. **60**, 463 (1992).
[23] P. W. Atkins, *Physical Chemistry*, 4th ed. (Oxford University Press, Oxford, 1990), p. 397
[24] J. Simpson, S. Y. Wang, I. Huksson, H. Stewart, S. J. Adams, K. A. Prior, and B. C. Cavenett, J. Cryst. Growth **127**, 327 (1993).
[25] K. Morimoto, J. Cryst. Growth **117**, 111 (1992).
[26] S. Matsumoto, H. Tosaka, T. Yoshida, M. Kobayashi, and A. Yoshikawa, Jpn. J. Appl. Phys. **32**, L229 (1993).