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Research Article

Low-Resistivity p-Type Doping in Wurtzite ZnS Using Codoping Method

Deng-Feng Li, Min Luo, Bo-Lin Li, Cheng-Bing Wu, Bo Deng, and Hui-Ning Dong

Department of Mathematics and Physics, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

Correspondence should be addressed to Deng-Feng Li; phyldf@gmail.com

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By using first principles calculations, we propose a codoping method of using acceptors and donors simultaneously to realize low-resistivity and high carrier concentration p-type ZnS with wurtzite structure. The ionization energy of single N_S can be lowered by introducing the III_{Zn}-N_S (III = Al, Ga, In) passivation system. Codoping method in ZnS (2N, III) has lower formation energy comparing with single doping of N since III elements act as reactive codopants.

1. Introduction

Wide bandgap semiconductors, such as ZnX (X = O, S, Se), have attracted attention due to their potential application in short-wavelength light-emitting devices. Unfortunately, the doping unipolarity, that is, it can be doped either p-type or n-type, but not both, impedes the implementation of the materials [1]. Earlier researches show that ZnS and ZnO are difficult to be doped as p-type due to asymmetric doping limitation [1–3]. In order to obtain low-resistivity p-type ZnS, single doping and codoping methods are studied. Nakamura et al. fabricate Li-doped ZnS by a low-pressure metal organic chemical vapor deposition technique [2]. They find that it is p-type conductivity, and the acceptor ionization energy is about 196 meV, which is larger than the calculated results of 155 meV by Gai et al. [3]. Gai et al. calculated ionization energies for possible single doping method to obtain p-type ZnS [3]. The result shows that N-doped ZnS is promised to be p-type, but the ionization energy is calculated to be 144 meV, which is still deep acceptor level.

In recent years, codoping method was suggested to solve the unipolarity of semiconductor [1, 4, 5]. P-type doping in ZnO is realized by codoping with N acceptors and Ga donors in the ratio of N : Ga = 2 : 1 [6, 7]. For p-type ZnS, experimental researches realize it by codoping with N and Li dual acceptors, and the hole concentration is measured to be 10^{18} cm^{-3} [8]. Theoretical investigations show that the codoping method of acceptor-donor-acceptor is more efficient than the single-doping method. They realize p-type ZnS by codoping with N acceptors and In or Al donors based on first principles calculations [9–11]. Codoping method makes the acceptor levels broaden and delocalize compared with the single doping of N. In addition, p-type ZnS nanocrystals can be obtained by codoping with N and Ga, In, or Al [12]. However, earlier researches about p-type ZnS with codoping method mainly focus on the density of state analysis. Quantifiable parameters, such as acceptor ionization energy and formation energy, are not presented. In addition, they have studied the zinc blende (ZB) ZnS. P-type ZnS with wurtzite (WZ) structure has not been investigated up to now. Therefore, the purpose of this study is to investigate p-type ZnS with WZ structure by codoping with N and Ga, Al, and In. Acceptor ionization energy, formation energy, and density of states are presented to analyze the effects of Ga, Al, and In codopant on p-type ZnS.

2. Calculation Method

We performed the calculations using the projector augmented wave method [13] within the generalization gradient approximation (GGA) [14], as implemented in the Vienna *ab initio* simulation (VASP) code [15]. 3*d* and 4*s* electrons of Zn are treated as valence electrons. The energy cutoff for the plane wave expansion sets with a 450 eV. For the Brillouin zone integration, we use Monkhorst-Pack special

k-points [16], equivalent to the $2 \times 2 \times 2$ mesh. Wurtzite supercells containing 96 atoms are used. For charged defect systems, a uniform background charge is added to maintain the global charge neutrality of the periodic system. All the geometries are allowed to relax until the Hellmann-Feynman force becomes less than 0.02 eV/Å. The optimized lattice constants for ZnS is $a = b = 3.85$ Å, $c = 6.29$ Å, which are in good agreement with the experimental values $a = b = 3.81$ Å, $c = 6.23$ Å.

The ionization energy of an acceptor with respect to VBM is calculated as follows [1, 17]:

$$\varepsilon(0/-) = \left[E(\alpha,-) - \left(E(\alpha,0) + \varepsilon_D^k(0)\right)\right] + \left[\varepsilon_D^\Gamma(0) - \varepsilon_{\mathrm{VBM}}^\Gamma(\mathrm{ZnS})\right], \quad (1)$$

where ε_D^k and ε_D^Γ are the defect levels at the special k-points (averaged by weights) and at Γ-point, respectively; $E(\alpha,-)$ or $E(\alpha,0)$ is the total energy of the supercell at charge state -1 or neutral for defect α; $\varepsilon_{\mathrm{VBM}}^\Gamma$ is the VBM energy of the host ZnS at Γ-point.

The formation energy of an isolated impurity α in charge state q is described as follows [1, 17]:

$$\Delta H_f(\alpha,q) = \Delta E(\alpha,q) + n_{\mathrm{Zn}}\mu_{\mathrm{Zn}} + n_{\mathrm{S}}\mu_{\mathrm{S}} + n_{\mathrm{A}}\mu_{\mathrm{A}} + qE_f, \quad (2)$$

where $\Delta E(\alpha,q) = E(\alpha,q) - E(\mathrm{ZnS}) + n_{\mathrm{Zn}}E(\mathrm{Zn}) + n_{\mathrm{S}}E(\mathrm{S}) + n_{\mathrm{A}}E(\mathrm{A}) + q\varepsilon_{\mathrm{VBM}}$. The n_i (i = Zn, S, and A) are the numbers of exchanged particles between the supercell, q is the defect charge state, μ_i is the chemical potential of constituent i referenced to elemental solid/gas with energy E_i. μ_{Zn} and μ_{S} in (2) are not independent but limited by the formation of stable ZnS compound, $\mu_{\mathrm{Zn}} + \mu_{\mathrm{S}} = \Delta H_f(\mathrm{ZnS})$, where $\Delta H_f(\mathrm{ZnS})$ is the formation enthalpy of solid ZnS.

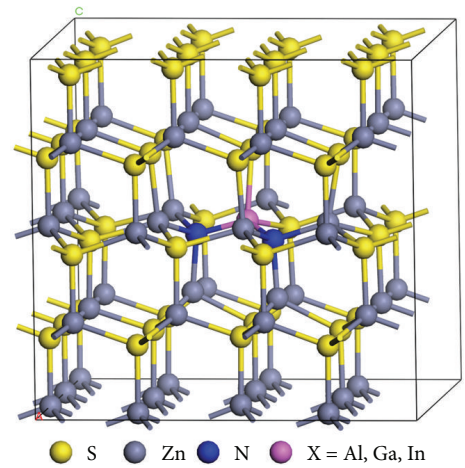

Figure 1: Schematic structure of codoping with N and X (Al, Ga, and In) in wurtzite ZnS.

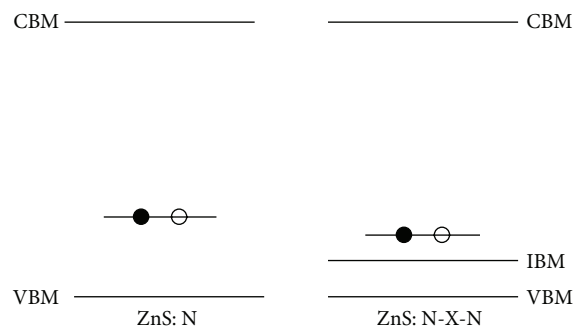

Figure 2: Schematic illustration of the energy level for single doping of N and codoping with N and X (Al, Ga, and In) in ZnS.

3. Results and Discussion

We firstly determine the most stable structure of codoped ZnS with N and group III elements (Al, Ga, and In) based on minimizing the total energy. For ZnS (N, III), we discuss two possible configurations. One configuration is $\mathrm{N_S}$-$\mathrm{III_{Zn}}$ pair occupied the nearest-neighbor sites and the other is a pair separated certain distance away. The result shows that the formation of the first case is energetically favorable. When another N atom is doped in the ZnS (N, III), total energy calculations show that the N atom also prefers to locate at the nearest-neighbor site, as shown in Figure 1. For the stable ZnS (2N, III), the bond length of N–Al, N–Ga, and N–In is 1.9 Å, 2.0 Å, and 2.2 Å, respectively, which is remarkably smaller than Zn–S bond length of pristine ZnS of 2.36 Å.

The calculated acceptor ionization energy and formation energy of codoping with N and III elements in ZnS are presented in Table 1. The acceptor ionization energy denotes the provided hole in ZnS, and the formation energy controls the dopant solubility, which is important for p-type doping of semiconductor. When only N atom is doped in ZnS, the ionization energy is 103.9 meV, which is smaller than that of N doping in ZB ZnS (144 meV). This suggests that N doping generates a deep acceptor level above the valence band. Fortunately, codoping with N and III elements in ZnS can remarkably reduce the ionization energy. Shallow acceptor level exists in ZnS, and the acceptor ionization energies of $\mathrm{Al_{Zn}}$-$2\mathrm{N_S}$ and $\mathrm{Ga_{Zn}}$-$2\mathrm{N_S}$ pairs are 40.1 meV and 37.5 meV, respectively. The lower ionization energy of codoping with N and III elements can be explained by Figure 2. ZnS (N, III) creates a fully unoccupied impurity band above the VBM. The N atom passivates the III elements to form the ZnS (N, III) passivated system. When excess N atoms are available, the impurity band is regarded as new VBM, and $\varepsilon_{\mathrm{VBM}}^\Gamma$ (ZnS) in (1) is replaced by the impurity band minimum (IBM). The acceptor transition occurs between the N energy level and the IBM rather than the original VBM. Thus, the ionization energy can be remarkably reduced.

The formation energies of $2\mathrm{N_S}$-$\mathrm{III_{Zn}}$ complex and single doping of N for ZnS in neutral charge state and at $\mu_i = 0$ in (2) are also shown in Table 1. The low formation energy suggests this defect has high carrier concentration. Our calculations reveal that the formation energy of $2\mathrm{N_S}$-$\mathrm{III_{Zn}}$ complex is smaller than that of single doping of N. This can be explained by the density of states (DOS) analysis. Figure 3 shows DOS of N-p state in ZnS (2N, Al) and ZnS (N). The DOS of the N atom in ZnS (2N, Al) is similar to that in ZnS (2N, Ga) and ZnS (2N, In), and we only present the representative result

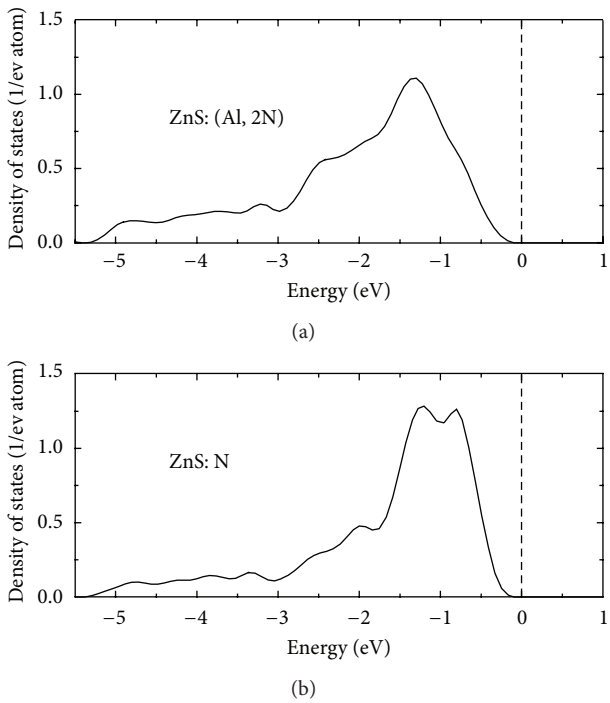

Figure 3: DOS of N-p states for (a) ZnS codoped with Al and 2N species and (b) ZnS doped with the N atom.

Table 1: Ionization energy $\varepsilon(0/-)$ and formation energy ΔH_f of defect complexes in ZnS.

	$2N_S$–Al_{Zn}	$2N_S$–Ga_{Zn}	$2N_S$–In_{Zn}	N_S
$\varepsilon(0/-)$ (meV)	40.1	37.5	44.1	103.9
ΔH_f (eV)	3.04	3.17	3.16	3.35

of ZnS (2N, Al). We observe that a narrow band forms near VBM in ZnS (N) due to the large electronegativity of N comparing with that of S. The localization of DOS for N atom results in high formation energy. Meanwhile, the N-impurity bandwidth in ZnS (2N, Al) is increased due to the interaction of N-p and Al-p orbitals, which indicates that the defect is easily formed. Therefore, we can see that the codoping using N as an acceptor and III elements (Al, Ga, and In) as reactive-codopant donor is very effective for materials design to obtain low-resistivity and high-concentration p-type ZnS.

4. Conclusion

In summary, our first principles calculations reveal that the codoping method with two acceptors and one donor is effective to realize low-resistivity and high carrier concentration p-type ZnS with WZ structure. The ionization energy of single N_S can be lowered by introducing the III_{Zn}-N_S passivation system due to the acceptor transition between the N level and the IBM rather than the VBM. The codoping method in ZnS (2N, III) has lower formation energy compared with single doping of N since III elements act as reactive codopants with N.

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