Research Article

Study of the P-Type Doping Properties of ZnS Nanocrystals

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Received 24 April 2010; Accepted 11 July 2010

Academic Editor: Quanqin Dai

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The paper presents the study of p-type doping properties of ZnS nanocrystals (Ncs) using the local density approximation theory (LDA). Doping with single species of N, P, or As, ZnS nanocrystals are found to have a low-doping concentration and efficiency, which may be limited by the large expelling effect between Zn and impurity atoms and the compensation action from interstitial Zn_{int} atoms that can offer donor states to compensate the acceptors. To decrease the expelling and the compensation effect, composite dopants, such as N jointed with Ga, In, or Al, are applied to codope ZnS nanocrystals. As a result, ZnS nanocrystals in p-type with high doping density and efficient are completed.

1. Introduction

ZnS nanocrystals, with unique optical properties and a direct band gap of 3.68 eV at room temperature, have great potential applications in fabrication of short-wavelength light-emitting devices (LED) and blue injection-laser diodes (LD) [1–3]. To fabricate nanoscaled devices, semiconductor nanocrystals need to be doped in p-, n-types firstly. And the performance of devices depends on the doping types and doping concentration [4]. Doping with other special impurities, semiconductors will not only enhance their conductivity significantly but also exhibit many novel photoelectric properties [5–7]. For semiconductor nanocrystals, however, the doping concentration and steady are much low than that of the bulk materials. The volume of nanocrystals is so small that it limits the doping concentration and allows the doped impurities to easily escape from it.

Also, doping with other metallic ions, the photoelectric properties of ZnS nanocrystals will be widely adjusted and improved [8]. However, it is found that they are easily doped for n-type but hard for p-type [9]. This occurs because a Zn atom in ZnS very easily departs from its lattice site to become an interstitial Zn_{int} atom, which makes ZnS displaying an intrinsic property of n-type. On the other hand, from the point of system energy, n-type doping will low the system energy while p-type doping will raise

it based on the calculation of the first-principle. At the same time, Zn_{int} atoms will lift the lattice energy as well. Therefore, ZnS nanocrystals have more difficult in p-type doping [10, 11]. Now, this problem has become a large barrier for their practical use and delayed the development of new nanodevices. Many theoretical and experimental works have been done on the doping problems for ZnS nanocrystals, especially for p-type doping [12–14]. Although some succeeded, the doping concentration and steady still do not meet the requirement of devices. In the present study, we investigate the p-type doping properties of ZnS nanocrystals doped with single dopants of N, P, or As and composite dopants of N:Ga, N:In, or N:Al. Using the local density approximation (LDA) method, we study the activity and doping efficiency of all dopants, and discuss the doping mechanisms and the compensation properties based on the calculated density of states of ZnS. Finally, p-type ZnS nanocrystals with enhanced doping concentration and efficiency are realized.

2. Theoretical Model

2.1. Local Density Approximation Theory (LDA). According to Schrodinger equation in quantum mechanics,

$$H\Psi = E\Psi, \quad (1)$$

FIGURE 1: (a) A schema of ZnS structure. The red circles and blue spheres stand for Zn and S atom, respectively.

where, H is Hamiltonian operator, E is the system energy, and Ψ describes the state of the system with N electrons.

$$H = -\frac{1}{2}\nabla^2 - \sum_q \frac{Z_q}{|\vec{r} - \vec{R}_q|} + \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} dr' + V_{xc}(\vec{r}). \quad (2)$$

The density of state (DOS) $\rho(r)$ of electrons can be written as [1, 11]

$$\Psi_i^k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_g c_i^k(g) e^{i\vec{k}\cdot\vec{r}}, \quad (3)$$

$$\rho(\vec{r}) = \sum_i n_i \Psi_i^*(\vec{r}) \Psi(\vec{r}). \quad (4)$$

Equation (4) is a local-density approximation (LDA) of $\rho(r)$, by which the DOS of a doped ZnS cluster can be calculated.

2.2. Structure of ZnS and the Simulation Method. ZnS is characteristic of a zincblende structure with a lattice constant of 0.5046 nm, as shown in Figure 1. Four Zn atoms are located at the corners of a cube forming a tetrahedron; an S atom is positioned at the zenith of the tetrahedron. For p-type doping, S atom is substituted with either N, P, or As single dopants from Column V to offer more vacancy. To decrease the compensation effect from Zn_{int} atoms, the composite dopants of N:Ga, N:In, or N:Al are used to codope ZnS nanocrystals as well. For a comparison, the density of state (DOS) and the electronic structures of ZnS nanocrystals with and without doping were investigated using LDA method. In the simulation, we adopt a Von Barth-Hedin exchange correlation potential with the parameters used by Von Barth and Hedin [15]. Brillouin zone integration was carried out for 84-k points in an irreducible wedge and for 24-k points for doped crystals. For valence electrons, we employed p and d orbitals for Zn atoms and the outer most s and p orbitals for other atoms. From the calculated DOSs, we determined the valence bands, the impurity level and the doping concentration.

FIGURE 2: The density of state of ZnS nanocrystal without doping.

FIGURE 3: (a) DOS of ZnS nanocrystals doped with N atom; (b) DOS of N atom; (c) DOS of the undoped ZnS nanocrystals.

3. Results and Discussion

3.1. Single Doping. For undoped ZnS nanocrystals, the calculated DOS is shown in Figure 2, where energy is measured from Fermi level (E_F), thus the energy zero point is located on top of the valence band. As can be seen, there are three strong bands in the spectrum: the first one is from -6.5 eV to -5.0 eV with a strong character of d , mostly originating from the d state of Zn atoms; the second one is a sharp

FIGURE 4: DOS spectra of ZnS nanocrystals doped with P, and As atoms.

band located at -5.1 eV to -4.0 eV, mainly contributed by the $3p$ state S atoms; the third one in the range of -3 eV to 0 eV is just nearby the valence band, resulting from a strong hybrid interaction between S $2p$ and Zn $2s$ states. The hybrid interaction occurs because the $3s$, $3p$ states of S atoms overlap with $4s$ state of Zn atoms, leading to the s and p states of Zn atoms shifting to S sites, along with charges are transferred from Zn atoms to S atoms.

For N doped ZnS nanocrystals, the DOS spectrum is shown in Figure 3(a). For comparison, the DOSs of single N atom and the undoped ZnS are shown in Figures 3(b) and 3(c), respectively. Clearly, in addition to the three bands of the undoped ZnS, after doping a small narrow band at -0.1 eV appears on top of the valence band. The narrow band is introduced by N impurities, termed as an acceptor level. From the small band, we can estimate the relative doping density of N to be 10^{13} cm^{-3} . It shows that ZnS nanocrystals doped with single N have low doping concentration and efficiency. This may be caused by the expelling effect of holes between the valence band and N impurities. The expelling force will localize the state of N on top of the valence band, leading to N atoms hard to ionize. In addition, the doping efficiency is affected by the compensation action of Zn_{int} atoms, which gives rise to multi ionizations: the first and the second ionizing energies of Zn_{int} are 0.05 eV and 0.2 eV. They offer two donor states that can compensate the acceptors. Thus, the doping efficiency is not high.

FIGURE 5: A schematic of complex defects in ZnS structure, it involves two unit cells.

For P and As dopants, similarly, a narrow acceptor level is introduced on top of the valence band of ZnS, as shown in Figures 4(a) and 4(b), respectively. Also, because of the strong expelling interaction between $2p$ states of P or As and Zn atoms, the acceptor levels are localized nearby E_F level. Thus, the activity of the dopants is depressed, and the doping efficiency decreases as well.

For the doped structures of the three dopants, here referred to as N_s , P_s , and As_s , we found that N_s is quite different from those of P_s and As_s . An N_s atom is positioned at the center of the tetrahedron, and the structure remains symmetrical but its volume shrinks by 0.48 . P_s and As_s atoms shift to the bottom of the relaxed structures by 0.11 Å and 0.13 Å, respectively. The volume for P_s shrinks by 0.13 but for As_s is almost unchanged. The shifts for P_s and As_s cause some distortion in the relaxed structures, which low the symmetry of the doped structures. Thus, the structure of N_s doped ZnS nanocrystals is the most stable one.

For further increasing the doping concentration of single species, we found that the doping efficiency changes little, that is, the doping efficiency is not limited by the doping concentration but the expelling effect and the compensation action. The latter will become dominative as the doping concentration increases.

Zn atoms very easily deviate from the lattice sites to become interstitial Zn_{int} atoms, which may combine with dopants to form complex defects. For N-doped ZnS, the complex defect is denoted as $\text{N}_s\text{-Zn}_{\text{int}}$, where N_s means an N atom replacing an S atom in the structure. On the other hand, for heavily p-type doped ZnS nanocrystal, to achieve a stable structure some adjacent point defects may combine together to form complex defects as well, such as $\text{N}_s\text{-Zn-V}_s$, where N_s and V_s atoms are bonded through a Zn atom. We therefore have two complex defect models: $\text{N}_s\text{-Zn}_{\text{int}}$ and $\text{N}_s\text{-Zn-V}_s$. The latter is associated with two neighboring ZnS unit cells, as shown in Figure 5. These complex defects are different from the point defects. $\text{N}_s\text{-Zn-N}_s$ produces a deep acceptor level while $\text{N}_s\text{-Zn}_{\text{int}}$ forms a donor level in the band gap of ZnS, both play an important compensation action for p-type doping of ZnS, which makes the p-type doping of ZnS more complex [16, 17].

FIGURE 6: (a) DOS of ZnS nanocrystals codoped with N:In elements; (b) DOS of N atom; (c) DOS of In atom.

Above all, due to the expelling and compensation effects, single dopants in Column V cannot achieve the p-type doping for ZnS. The compensation effect is an inherent behavior of ZnS, which can be depressed at low doping concentration. From the point of energy view, the system energy falls with the expelling potential decreasing, and then the compensation is depressed as well. To achieve the p-type doping, therefore, it is necessary to enhance the activity of the acceptors and decrease the expelling effect.

3.2. Codoping. Yamamoto et al. [11] studied the p-type doping properties for ZnO with various dopants using LDA, and found that it could be achieved with ally dopants from Column III-V. ZnS will have a similar doping behavior to ZnO for both of them belonging to II-VI semiconductors. Hence, we apply the composite dopants, N:Ga, Al, or In, to codepo ZnS Ncs. Figure 6(a) gives the DOS spectrum for ZnS Ncs doped with N:In. As references the DOSs for single N and In elements are shown in Figures 6(b) and 6(c), respectively. Apparently, the DOS of the codoped ZnS is different from that of the single species. Besides the three bands originated from ZnS, a new band at -3.67 eV, closely to In site appeared. Moreover, the acceptor level on top of the valence band becomes much wider than that of the single species. The new band results from the strong interaction between N $2p$ and In $3s$ states, meaning a strong coupling action between N and In atoms. This coupling action just cancels the expelling effect between N $2p$ and Zn $3p$ states, and increases their orbitals hybridizing. The decreased expelling

FIGURE 7: (a) DOS of ZnS nanocrystals codoped with N:Ga elements. (b) DOS of ZnS nanocrystals codoped with N:Al elements.

lowers the system energy and the compensation effect; the relative doping concentration of N:Ga can be enhanced to 10^{16} cm^{-3} . As a result, the doping efficiency of N is improved.

For N:Ga and N:Al codopants, the DOSs are shown in Figures 7(a) and 7(b), respectively. Similarly, a small new band is located at -3.70 eV resulting from the interaction between N $2p$ and Ga or Al $3s$ states. And the acceptor levels on top of valence bands become wider as well. Apparently, the dopants of Ga, Al, or In play a role for activating single species than recombination centers. Among the three dopants, Ga shows the best doping efficiency. Finally, using the composite dopants of N with Column III elements, p-type ZnS with high doping efficiency is completed.

4. Conclusions

Using the LDA method, we investigate the p-type doping properties of ZnS nanocrystals doped with both single dopants N, P, or As and the composite dopants N:Ga, In, or Al. For single dopants, the doping efficient is not very high because of the strong compensation of interstitial Zn_{int} and the expelling potential between Zn atom and N impurity, which low the solid concentration in ZnS nanocrystals and restrain the active of the acceptors. For the composite dopants N:Ga, In, or Al, the expelling effect between N and Zn atoms decreases, and the concentration of N impurity is enhanced. Finally, p-type ZnS nanocrystal with high doping efficiency is achieved.

Acknowledgments

The research work was supported in part by the National Natural Science Foundation (nos. 60776004, 60976071) and the Scientific Project of Shaoxing City (no. 2009A21054).

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