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 efficiency 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 lower 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,

\[ \hat{H}\Psi = E\Psi, \]  

(1)
where, $H$ is Hamiltonian operator, $E$ is the system energy, and $\Psi$ describes the state of the system with $N$ electrons.

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

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

$$\Psi^j_i(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \sum_g c_i^j(g) e^{i\vec{k} \cdot \vec{r}},$$

$$\rho(\vec{r}) = \sum_i n_i |\Psi^j_i(\vec{r})|^2.$$  \hspace{1cm} (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.

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
compensation action of Zn atoms, which gives rise to multi
acceptor level. From the small band, we can estimate the
narrow band is introduced by N impurities, termed as an
ionizations: the first and the second ionizing energies of Zn
are 0.05 eV and 0.2 eV. They o

Figure 4: DOS spectra of ZnS nanocrystals doped with P , and As
doped ZnS
P doped ZnS
Pure ZnS

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 additional 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 atoms, which gives rise to multi
ionizations: the first and the second ionizing energies of Zn
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.

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 dommative as the doping
concentration increases.

Zn atoms very easily deviate from the lattice sites to
become interstitial Zn\textsubscript{int} atoms, which may combine with
dopants to form complex defects. For N-doped ZnS, the
complex defect is denoted as N_S-Zn\textsubscript{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 N_S-Zn\textsubscript{V_S},
where N_S and V_S atoms are bonded through a Zn atom. We
therefore have two complex defect models: N_S-Zn\textsubscript{int} and N_S-
Zn\textsubscript{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. N_S-Zn\textsubscript{V_S} produces a deep
acceptor level while N_S-Zn\textsubscript{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].
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 codope 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 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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