Preparation of ZnSe-ZnS alloy quantum dots by a hydrothermal method and their optical properties

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Abstract. We prepared colloidal ZnSe$_x$S$_{1-x}$ alloy quantum dots (QDs) and investigated their optical properties. ZnSe$_x$S$_{1-x}$ QDs were successfully prepared by a hydrothermal method, which was confirmed by the results of X-ray structural analysis. When the alloy composition was decreased from $x = 1$ to $0$, the absorption energy continuously shifted to the high energy side. Band-edge photoluminescence (PL) was the main PL band in ZnSe QDs, whereas only defect-related PL band was observed in ZnS QDs. The band-edge PL was clearly observed as the main PL band for $x = 0.52$ to $1$, which shifted to the high energy side by decreasing $x$.

1. Introduction

In semiconductor quantum dots (QDs), absorption and photoluminescence (PL) energies can be controlled by QD size owing to quantum confinement effect [1]. However, PL quantum yield (QY) in QDs having small sizes and high surface to volume ratio is usually low because of the influence of nonradiative recombination process and surface defects. Therefore, it is still a challenge to prepare semiconductor QDs having high PL QY in a wide energy range merely by controlling QD size. In alloy semiconductors, it is possible to control the band-gap energy over a wide range by changing alloy composition. Therefore, it is expected that optical properties of the alloy semiconductor QDs can be controlled not only by QD size but by alloy composition as well.

To date, hot-injection method is widely used not only for preparation of alloy QDs but for synthesis of various types of QDs as well, including II-VI and IV-VI semiconductors [2, 3]. DeGroot et al. succeeded in synthesizing ZnCdSe alloy QDs using the hot-injection method [4]. On the other hand, preparation of water-soluble QDs is necessary for the application of QDs in bioscience fields. The QDs synthesized by the hot injection method can disperse in water by ligand exchange [5]. Therefore, direct synthesis of water-soluble QDs having good optical properties is still an important issue even now. Cheng et al. synthesized water-soluble ZnCdTe QDs by a reflux method [6]. The alloy composition was controlled by changing the molar ratio of Zn$^{2+}$ and Cd$^{2+}$ in precursor solutions. In this study, ZnSe-ZnS (ZnSe$_x$S$_{1-x}$) alloy QDs those are cadmium-free, were prepared by a hydrothermal method. Because ZnSe$_x$S$_{1-x}$ QDs are an alloy of two wide band-gap semiconductors of ZnSe and ZnS, they can be expected to be applied as an optical functional material in the near ultraviolet region.

2. Experiments

ZnSe$_x$S$_{1-x}$ QDs were prepared by a hydrothermal method. First, solutions of ZnSe and ZnS as two precursors were prepared separately. The precursor solution of ZnSe or ZnS was prepared by mixing $N$-
acetyl-L-cysteine as a ligand, and Zn(ClO$_4$)$_2$·6H$_2$O as a Zn$^{2+}$ ion source, whereas NaHSe or Na$_2$S as a Se$^{2-}$ or S$^2$ ion source [7]. Then, a precursor solution of ZnSe$_x$S$_{1-x}$ was prepared by mixing ZnS and ZnSe precursor solutions having a molar ratio between 0 and 1. Finally, 10 ml of the precursor solution was transferred into an autoclave and heated at 200 °C using an oil bath to prepare QDs. We define $x'$ as the mixing ratio of ZnS and ZnSe precursor solutions.

To perform X-ray diffraction (XRD) measurements, multilayer structures of QDs were fabricated by layer-by-layer (LBL) assembly in which QDs and positively charged polyelectrolytes of poly(diallyldimethylammonium chloride) were alternately deposited [8]. The periodicity in the laminating direction was obtained from small-angle out-of-plane XRD measurements, and average diameter of QDs was estimated [8]. In addition, the actual alloy composition, $x$, was estimated from the analysis of wide-angle in-plane XRD measurements. Absorption and PL spectra were recorded using a JASCO V-650 UV/Vis spectrophotometer and a JASCO FP-8300 spectrofluorometer, respectively.

### 3. Results and discussion

Figure 1(a) shows the result of wide-angle X-ray structural analysis. For ZnS QDs ($x' = 1$), diffraction peaks were observed at 27.2°, 46.1° and 54.5°, which corresponds to the (111), (220), and (311) planes in ZnSe crystal of zincblende structure. However, for ZnS QDs ($x' = 0$), the signals corresponding to (220) and (311) planes are very weak, and only the diffraction peak corresponding to the (111) plane was clearly observed at 28.5°. Thus, the lattice constant was calculated using the Bragg's law based on the diffraction angle of the (111) plane in each QD sample. The actual alloy composition, $x$, was estimated on the basis of Vegard's law and is listed in Table 1. Figure 1(b) shows the result of small-angle out-of-plane XRD. The diffraction peak of ZnSe QDs ($x = 1$) was observed at 2.56°, indicating

**Table 1.** Lattice constant, alloy composition ($x$), and QD diameter of ZnSe-ZnS alloy QDs prepared for a reaction time of 60 min by heating precursor solutions having the mixing ratio ($x'$) of ZnS and ZnSe precursors.

| $x'$  | 0   | 0.2 | 0.4  | 0.6  | 0.8  | 1   |
|-------|-----|-----|------|------|------|-----|
| Lattice constant (nm) | 0.539 | 0.550 | 0.554 | 0.555 | 0.560 | 0.570 |
| $x$   | 0   | 0.36 | 0.52 | 0.58 | 0.76 | 1   |
| QD diameter (nm) | 3.0  | 3.1  | 3.3  | 3.3  | 3.3  | 3.5  |
that the ZnSe QD multilayers had a structural regularity with a periodicity of 3.5 nm in the lamination direction. The results of the prepared alloys are listed in Table 1.

Figure 2(a) shows absorption spectra of ZnSe0.76S0.24 QDs prepared for different reaction time. The absorption peak was red-shifted, by increasing the reaction time, indicating that the average QD size was increased. Similar results were obtained for QD samples having other alloy compositions. For each kind of alloy QDs, the QD size became the maximum at a reaction time of 60 min.

Next, we discuss the dependence of optical properties on the alloy composition in ZnSe0.76S0.24 QDs prepared for 60 min. Figure 2(b) shows absorption and PL spectra of ZnSe0.76S0.24 alloy QDs having x = 0, 0.36, 0.52, 0.58, 0.76, and 1. In the absorption spectra for x = 0 (x = 1), the absorption peak was observed on the higher energy side than the band-gap energy of 3.7 eV (2.7 eV) in the ZnS (ZnSe) bulk crystal, demonstrating the formation of ZnS (ZnSe) QDs. The absorption peak shifted to the high energy side by increasing the molar ration of ZnS, suggesting the increase in the band-gap energy. In PL spectra of alloy QDs having x = 0.58 to 1, the band-edge PL was observed as the main PL band, while defect-related PL was dominant in QDs having x = 0 to 0.52.

The alloy-composition dependence of the absorption energy was discussed subsequently. The band-gap energy of alloy semiconductors generally has a bowing characteristic with respect to the alloy composition. Ebina et al. reported that the x-dependence of the band-gap energy in a bulk crystal of ZnSe0.76S0.24, \( E_g(x) \), can be given by

\[
E_g(x) = E_g(ZnS) + [E_g(ZnSe) - E_g(ZnS) - b] \cdot x + b \cdot x^2 \tag{1}
\]

where a bowing parameter of \( b \) is 0.63 [9]. The solid curve in figure 3 represents the calculated result of \( E_g(x) \). The open circles denote the experimental results of the x-dependence of the absorption energy in ZnSe0.76S0.24 QDs, which was estimated from the energy minimum of the second-derivative spectrum. The x-dependence of the absorption is similar to that of the band-gap energy as shown by the solid curve. The large energy difference between them is caused by the quantum confinement effect.

The lowest exciton energy in II-VI semiconductor QDs is well explained by the electron-hole individual confinement model [10]. In alloy QDs, the effective mass of electrons and holes as well as the dielectric constant depend on the alloy composition. Thus, the exciton energy in a spherical alloy QD having a radius \( R \) and an alloy composition \( x \) is given approximately by [11]

\[
E(R, x) = E_g(x) + \frac{\hbar^2}{2\mu(x)} \left( \frac{\pi}{R} \right)^2 - 1.8 \frac{e^2}{\varepsilon(x)R}, \tag{2}
\]
Figure 3. Alloy-composition dependence of the absorption energy. Solid curve: Calculated result of $E_g(x)$. Open circles: Experimental results of the $x$-dependence of the absorption energy in ZnSe$_x$S$_{1-x}$ QDs. Open diamonds: Calculated results using equation (2).

where $\mu(x)$ and $\varepsilon(x)$ denote the $x$-dependence of the reduced mass and dielectric constant of the exciton, respectively. The open diamonds denote the calculated results of how the optical transition energy depend on $x$ of ZnSe$_x$S$_{1-x}$ QDs using equation (2). Because the detailed dependence of $\mu(x)$ and $\varepsilon(x)$ in ZnSe$_x$S$_{1-x}$ has not yet been clarified, we assume that $\mu(x)$ and $\varepsilon(x)$ vary linearly with $x$ between the values in ZnSe and ZnS bulk crystals. The value of $R$ obtained from the analysis of out-of-plane XRD as shown in Table 1 was substituted. The calculated results agree well with the experimental ones. These results demonstrate that the quantum confinement effects in ZnSe$_x$S$_{1-x}$ QDs can quantitatively explain the $x$-dependence of the absorption energy. In addition, alloy QDs of ZnSe$_x$S$_{1-x}$ can be successfully prepared by the hydrothermal method.

4. Conclusion

ZnSe$_x$S$_{1-x}$ alloy QDs were successfully prepared by the hydrothermal method. In the absorption spectrum of the sample prepared with $x = 0$ ($x = 1$), the absorption peak was observed on the higher energy side than the band gap energy of 3.7 eV (2.7 eV) in the ZnS (ZnSe) bulk crystal, demonstrating the formation of ZnS (ZnSe) QDs. By decreasing the alloy composition from $x = 1$ to 0, the absorption energy continuously shifted to the high energy side. Band-edge PL is the main PL band as shown in Figure 3, which shifted to the high energy side by decreasing $x$.

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