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Synthesis of colloidal Zn(Te,Se) alloy quantum dots

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Abstract

Colloidal Zn(Te₁₋ₓSeₓ) quantum dots (QDs), which are highly mismatched semiconductor alloys, were synthesized by the hot injection of an organometallic solution, and the composition and size dependence of their optical gap were studied together with the theoretical calculation using the finite-depth-well effective mass approximation. The optical gaps exhibited considerable negative deviation from the mole fraction weighted mean optical gaps of ZnTe and ZnSe, i.e. a large optical gap bowing was observed, similar to the bulk and thin-film alloys. The composition and size dependence of optical gaps agreed well with theoretically calculated ones employing a bowing parameter similar to that of the bulk alloys; therefore, the extent of the optical gap bowing in these alloy QDs is concluded to be the same as that in bulk and thin-film alloys. The optical gaps of Zn(Te₁₋ₓSeₓ) QDs with diameters of 3.5–5 nm, where x ~ 0.35, were close to the energy corresponding to green light, indicating that those QDs are very promising as green QD-phosphors.

1. Introduction

Colloidal semiconductor quantum dots (QDs) have attracted much attention as phosphors applicable in various next-generation light-emitting devices, such as light-emitting diodes, electroluminescence devices, and wavelength converters for back lights in liquid crystal displays (QD-LCDs) [1–7], because of their bright and narrow-band emission arising from exciton recombination [8]. The emission energy of QD-phosphors can be adjusted using the quantum size effect [8]; this is one of the most attractive features of QD-phosphors. Currently, CdSe is the most promising material as a QD-phosphor emitting green and red light. Because it is difficult to adjust the emission of CdSe QDs in the blue region using only the quantum size effect, alloying of CdSe or CdS with ZnSe or ZnS is also utilized [9–11]. Therefore, the alloying of semiconductor QDs has been one of the major topics in colloidal semiconductor QD research.

Generally, the energy band gap of an alloyed semiconductor is described by the mole fraction weighted mean of the energy band gaps of the constituent unalloyed materials. However, there are some alloy systems in which the energy band gap exhibits a significant negative deviation from the mole fraction weighted mean of the energy band gap. Such a phenomenon is usually observed in alloy systems consisting of materials having considerably different lattice constants and chemical features, such as an electronegativity of group V or VI elements in III–V or II–VI semiconductors, respectively, for example, Ga(As,N) [12, 13], Al(P,N) [14], Zn(Se,Te) [15–17], and Zn(Se,S) [18, 19]; therefore, the system is called a highly mismatched semiconductor alloy. The energy band gaps of these alloys exhibit much smaller energies than that of constituent unalloyed materials; for example, while the energy band gaps of pure ZnTe and ZnS are respectively 2.25 [20] and 3.83 eV [21], the minimum energy band gap in Zn(Se,T) alloys is 1.90 eV [18]. Such behavior is referred to as large band gap bowing and has intensively been studied experimentally and theoretically in bulk and thin-film alloys [18, 19]. In contrast, only a few studies on alloy QDs of systems exhibiting large band gap bowing have been reported so far, even though the large band gap bowing is expected to extend the emission energy region of QD-phosphors.
The Zn(\(\text{Te,Se}\)) system is one of the semiconductor alloy systems where large band gap bowing appears and solution syntheses of alloy QDs have been reported previously [22, 23]. However, the composition of the alloys previously reported was limited to very small composition range in Se-rich side, while the characteristic feature of this highly mismatched alloy system appears in Te-rich compositions, and the smallest band gap arising from the large band gap bowing in this alloys appears at around \(x = 0.35\) in Zn(\(\text{Te}_{1−x}\text{Se}_x\)) [15–17]. Consequently, the composition and size dependence of the optical properties in this highly mismatched semiconductor alloy QDs has yet to be clarified. Further, not only blue emission but also green emission is highly expected from Zn(\(\text{Te}_{1−x}\text{Se}_x\)) alloyed QDs because of the large band gap bowing according to the theoretical calculation [24].

In the present study, we successfully synthesized the colloidal Zn(\(\text{Te}_{1−x}\text{Se}_x\)) alloy QDs in a wide alloying range. The obtained QDs were characterized in terms of the development of alloying and composition- and size-dependent optical gap, together with the theoretical calculation of the optical gap. The optical gap bowing and the potential as a green QD-phosphor for these alloy QDs were discussed based on the composition- and size-dependent optical gap observed.

### 2. Methods

#### 2.1. Chemicals

Diethylzinc (\(\text{Zn(C}_2\text{H}_5)_2\) (ZnEt\(_2\)), 52 wt% Zn basis, Aldrich), anhydrous zinc acetate (\(\text{Zn(CH}_3\text{COO)}_2\) (Zn(ac\(_2\))), 99.99%, Aldrich), Se powder (99.99%, Aldrich), Te powder (99.997%, Aldrich), tri-n-octylphosphine ((\(\text{C}_8\text{H}_{17}\))\(_3\text{P}\) (TOP), >96%, Wako Pure Chemical Industry), oleylamine (\(\text{C}_{18}\text{H}_{35}\text{NH}_2\) (OLA), >98%, Aldrich), oleic acid (\(\text{C}_7\text{H}_{14}\text{COOH}\) (OA), 99%, Aldrich), 1-octadecene (\(\text{C}_{18}\text{H}_{36}\) (ODE), >90%, Tokyo Chemical Industry), n-hexane (\(\text{C}_6\text{H}_{14}\), >96%, Wako Pure Chemical Industry), chloroform (CHCl\(_3\), 99.8%, Wako Pure Chemical Industry), acetone (\(\text{CH}_3\text{COCH}_3\), 99.5%, Wako Pure Chemical Industry), toluene (\(\text{C}_6\text{H}_5\text{CH}_3\), 99.8%, Wako Pure Chemical Industry), and ethanol (\(\text{C}_2\text{H}_5\text{OH}\), 96%, Imazu Chemical) were used without further purification.

#### 2.2. Synthesis of colloidal Zn(\(\text{Te}_{1−x}\text{Se}_x\)) QDs

The synthesis of colloidal Zn(\(\text{Te}_{1−x}\text{Se}_x\)) QDs were performed using standard air-free techniques. The method is developed based on the synthesis method of ZnTe QDs previously reported [25]. A Te stock solution (TOP-Te) was prepared by dissolving 1.91 g of Te powder in 50 ml of TOP at 250 °C under an argon flow, yielding a yellowish and transparent solution. A Se stock solution (TOP-Se) was prepared by dissolving 1.18 g of Se powder in 50 ml of TOP at room temperature under a nitrogen atmosphere, yielding a colorless solution.

A total of 0.105 ml (1.0 mmol) of ZnEt\(_2\) was mixed with 3.33 ml of a mixture of TOP-Te and TOP-Se (1.0 mmol of a total amount of Te and Se), of which the mole fraction of TOP-Se in the TOP-Te and TOP-Se mixture, \(X_{\text{Se}}\), was varied dependent on the target composition of Zn(\(\text{Te}_{1−x}\text{Se}_x\)) alloyed QDs, and 0.56 ml of TOP at room temperature under a nitrogen atmosphere. The resulting source solution was loaded in a syringe with a capacity of 5 ml.

A total of 6.48 ml of OA and 20 ml of ODE were mixed in a flask, and the solution was degassed under vacuum at 120 °C for 30 min. After the solution was heated up to a predetermined temperature in the range of 250–310 °C under an argon flow, the source solution was injected into the OA and ODE mixed solution in the flask. Subsequently, the solution in the flask was cooled to a temperature 10 or 20 °C lower than the injection temperature and kept there to grow the alloy QDs; then, the solution was cooled to room temperature. Injection and growth temperatures and growth time for respective syntheses are summarized in table 1.

Because wurtzite-type QDs were formed from the above reaction in the case of \(X_{\text{Se}} = 1\), ZnSe QDs possessing a zincblende structure were prepared by the following procedures [26]: a Zn source solution was prepared by dissolving 18.3 mg of Zn(ac\(_2\)) in a mixed solution of 0.33 ml of OLA and 3.5 ml of ODE at 60 °C using a reciprocal shaker. A Se source solution was prepared by dissolving 63.2 mg of selenium powder in 2 ml of TOP at room temperature. Then, 1.5 ml aliquots of the Se source solution were mixed with the Zn source solution in a glass vial (10 ml capacity); then, the solution in the vial was placed in a 280 °C oil-bath for 9 min under an Ar flow. After that, the vial was quickly removed from the oil-bath and cooled to room temperature.

Powdered QDs were extracted from the as-synthesized colloidal solution as follows. A total of 1 ml of hexane and 3 ml of ethanol were added to 2 ml of the colloidal solution to aggregate the QDs. Aggregated QDs were isolated by centrifugation and decantation. The resulting powder was redispersed in 1 ml of hexane, and the QDs were again aggregated by the addition of 3 ml of ethanol. This was repeated several times, and the resulting wet precipitates were dried in a vacuum desiccator at room temperature.

#### 2.3. Characterization

The crystalline phases obtained and their lattice parameters were determined using powder x-ray diffraction (XRD) (Rigaku, RINT2500, Cu-K\(_{α}\) radiation). The average grain size, \(d\), was evaluated from the full-width at half-maximum (FWHM) of the 111, 220, and 311 diffractions of the zincblende structure using the Scherrer equation [27]:

\[
n = \frac{\beta}{\cos \theta}
\]

\(n\): the number of reflections, \(\beta\): the FWHM of the diffraction peak, \(\theta\): the Bragg angle.
\[ d = \frac{0.9 \lambda}{\beta \cos \theta}, \]  

(1)

where \( \lambda \) is the x-ray wavelength, \( \beta \) is the FWHM, \( \theta \) is the diffraction angle, and 0.9 is the shape factor. In bulk Zn(Te\(_{1-x}\)Se\(_x\)) alloys with a zincblende structure, it is known that the lattice parameters at a composition \( x \), \( a(x) \), of the alloys agree well with Vegard’s law \[28\], i.e. the mole fraction weighted mean lattice parameter of unalloyed ZnTe and ZnSe, is expressed by the following equation:

\[ a(x) = (1-x)a_{ZnTe} + xa_{ZnSe}, \]  

(2)

where \( a_{ZnTe} \) and \( a_{ZnSe} \) denote the lattice parameters of zincblende-type ZnTe (6.103 Å) \[29\] and ZnSe (5.669 Å) \[30\], respectively. Therefore, the chemical compositions, \( x \), of the alloy QDs were evaluated based on their lattice parameter, \( a(x) \), from the following equation:

\[ x = 14.06 - 2.30a(x). \]  

(3)

The chemical compositions of the alloy QDs were also determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES; SPS7800, SII Nanotechnology, Japan). High-resolution transmission electron microscopy (HRTEM) images were collected using a JEM-2010 microscope (JEOL, Japan), at an accelerating voltage of 200 kV. Samples were prepared by depositing dilute colloidal solutions of QDs in toluene on carbon-coated copper grids (200 mesh, EM Japan), and drying under vacuum at room temperature.

For optical absorption measurements, QDs extracted from the as-synthesized colloidal solution were dispersed in chloroform. This was loaded into a 10 mm-pathlength SiO\(_2\) glass cuvette, and spectra were recorded using a double beam spectrophotometer (U4100, Hitachi, Japan).

2.4. Calculation of optical gap of Zn(Te\(_{1-x}\)Se\(_x\)) QDs

The composition- and size-dependent optical gaps of the alloy QDs were theoretically calculated using the finite-depth-well effective mass approximation (EMA) calculation to discuss the experimentally determined optical gaps of the QDs. This calculation reproduces well the experimentally observed size-dependent optical gaps of various II–VI and III–V binary and I–III–VI\(_2\) ternary semiconductor QDs \[31−34\]. Detailed calculation procedures have been described elsewhere \[24, 32\]. The bulk energy band gaps of Zn(Te\(_{1-x}\)Se\(_x\)) alloys used in the calculation that exhibit large band gap bowing were obtained using the following equation:

\[ E_g = E_g(ZnSe) + (1-x)E_g(ZnTe) - b(1-x), \]  

(4)

where \( E_g(ZnSe) \) and \( E_g(ZnTe) \) are the energy band gaps of the unalloyed ZnSe and ZnTe, respectively, and \( b \) is the optical bowing parameter; specifically, \( E_g(ZnSe) = 2.72 \) eV \[35\], \( E_g(ZnTe) = 2.25 \) eV \[20\], and \( b = 1.45 \) eV \[15\]. In addition, a bold approximation regarding the effective masses of electrons and holes was introduced into the present calculation: The effective masses of respective alloys are calculated as mole fraction weighted mean effective masses of the two unalloyed compounds, i.e. the effective mass of the Zn(Te\(_{1-x}\)Se\(_x\)) alloy with composition \( x \) is expressed by the following equation:

\[ m''(x) = xm''(ZnSe) + (1-x)m''(ZnTe), \]  

(5)

Table 1. Synthesis conditions of colloidal Zn(Te\(_{1-x}\)Se\(_x\)) QDs.

<table>
<thead>
<tr>
<th>Composition of starting solution, ( X_{Se} )</th>
<th>Injection temperature/°C</th>
<th>Growth temperature/°C</th>
<th>Growth time min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>270</td>
<td>250</td>
<td>30</td>
</tr>
<tr>
<td>0.1</td>
<td>270</td>
<td>250</td>
<td>20</td>
</tr>
<tr>
<td>0.25</td>
<td>290</td>
<td>270</td>
<td>10</td>
</tr>
<tr>
<td>0.30</td>
<td>310</td>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>0.35</td>
<td>290</td>
<td>270</td>
<td>10</td>
</tr>
<tr>
<td>0.40</td>
<td>290</td>
<td>270</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1. Synthesis conditions of colloidal Zn(Te\(_{1-x}\)Se\(_x\)) QDs.
where \( m^*(\text{ZnSe}) \) and \( m^*(\text{ZnTe}) \) are the effective masses of unalloyed ZnSe and ZnTe, respectively; specifically, \( m_e^*(\text{ZnSe}) = 0.16 \) \([36]\) and \( m_e^*(\text{ZnTe}) = 0.09 \) \([37]\) for the electron and \( m_h^*(\text{ZnSe}) = 0.75 \) \([36]\) and \( m_h^*(\text{ZnTe}) = 0.6 \) \([37]\) for the hole were employed in the present calculations.

3. Results

3.1. Synthesis of colloidal Zn(Te\(_{1-x}\)Se\(_x\)) QDs

The solutions started to change color, from colorless to reddish brown, when the source solution was injected; the color darkened with increasing reaction time. All the reaction solutions after cooling to room temperature were clear and transparent (figure S1 in the supplementary data (stacks.iop.org/MRX/4/106501/mmedia)). Figure 1 shows powder XRD profiles of the powders synthesized from the reaction solutions with various \( x \). For \( x = 0 \), all the diffraction peaks observed were identified as those of ZnTe with a zincblende structure \([38]\), while the diffractions were considerably broadened because of their small crystal size. For \( x > 0 \), the diffraction peaks were also identified as those of zincblende-type phase, and no impurity phase formation was observed. With increasing \( x \), all the diffraction peaks indexed as 1 1 1, 2 2 0, and 3 1 1 diffractions shifted to higher 2\( \theta \) angle, indicating that the lattice parameter of the obtained phase decreased with increasing \( x \). This observation is consistent with the fact that the ionic radius of \( \text{Se}^{2-} \) (1.98 Å) is smaller than that of \( \text{Te}^{2-} \) (2.21 Å) \([39]\); hence, this indicates that the alloying of ZnTe with ZnSe was successfully developed in the obtained powders. Based on the XRD profiles in figure 1, the compositions of obtained alloys, \( x \), were determined from equation (3). The results are summarized in table 2, together with the composition determined from ICP-AES. The composition determined by XRD agreed well with that determined by ICP-AES; therefore, we employed the composition determined by XRD hereafter because it is easier to determine.

Figure 2 shows HRTEM images and particle size distributions obtained from the HRTEM images of Zn(Te\(_{1-x}\)Se\(_x\)) QDs. Although the dispersion of respective QDs is not excellent, it can be seen that the obtained QDs are approximately spherical in shape. Lattice fringes were clearly observed in the images; however, fringe breakages are observed in some places, indicating that some point-defects are involved in the QDs. Table 2 also summarizes the average particle diameters determined based on XRD and HRTEM. The average particle diameters determined based on XRD were \( 4.0 \pm 0.1 \) nm, which agree well with those determined based on HRTEM.

Figure 3 shows powder XRD profiles of Zn(Te\(_{0.61}\)Se\(_{0.39}\)) QDs synthesized under various conditions (table 1). While the diffraction angles are constant, indicating that the compositions of the alloy QDs are similar to each other, the broadening in the diffractions is dependent on the specimens. The size of QDs determined based on the XRD profiles are also indicated in figure 3. We successfully synthesized Zn(Te\(_{0.61}\)Se\(_{0.39}\)) alloy QDs with diameters in the range from 3.5 to 6.3 nm. Figure 4 shows HRTEM images and particle size distributions obtained from the HRTEM images of Zn(Te\(_{0.61}\)Se\(_{0.39}\)) QDs. The particle size distribution became broader with increasing
average diameter, as observed in HRTEM images; this situation is clearly indicated by the standard deviation, which increased from 0.6 nm for 3.4 nm QDs to 1.0 nm for 6.1 nm QDs.

### Table 2. Compositions determined by XRD and ICP-AES and average diameters determined by XRD and TEM of Zn(\(\text{Te}_{1-x}\)\(\text{Se}_x\)) alloy QDs synthesized from the starting solutions with various Se concentrations, \(x_{\text{Se}}\).

<table>
<thead>
<tr>
<th>(x_{\text{Se}})</th>
<th>(x) in Zn((\text{Te}_{1-x})(\text{Se}_x)) alloy QDs</th>
<th>Average diameter of alloyed QDs/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD</td>
<td>ICP-AES</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.10</td>
<td>0.11</td>
<td>0.137</td>
</tr>
<tr>
<td>0.25</td>
<td>0.28</td>
<td>0.334</td>
</tr>
<tr>
<td>0.30</td>
<td>0.38</td>
<td>0.411</td>
</tr>
<tr>
<td>0.35</td>
<td>0.41</td>
<td>0.458</td>
</tr>
<tr>
<td>0.40</td>
<td>0.48</td>
<td>0.514</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

#### Figure 2. HRTEM images and particle size distribution obtained from the HRTEM images of Zn(\(\text{Te}_{1-x}\)\(\text{Se}_x\)) QDs obtained. (a) \(x = 0\), (b) \(x = 0.41\), and (c) \(x = 0.48\). \(d_{\text{ave}}\) and \(\sigma\) denote average diameter and its standard deviation, respectively.

#### 3.2. Optical properties of colloidal Zn(\(\text{Te}_{1-x}\)\(\text{Se}_x\)) QDs

Figure 5(a) shows the optical absorption spectra of colloidal Zn(\(\text{Te}_{1-x}\)\(\text{Se}_x\)) QDs with diameters of 4.0 ± 0.1 nm. The absorption shoulder indicated by the triangles in the figure shifted to longer wavelengths with increasing \(x\) up to 0.38; then, it shifted to shorter wavelengths. Because the absorption shoulder corresponds to the optical
gap of QDs, i.e. the first exciton absorption, this observation clearly indicates that the optical gap of the alloy QDs exhibits large bowing, taking into account the fact that the sizes of the QDs are almost constant. Figure 5(b) shows the optical gap of the QDs with 4.0 ± 0.1 nm diameters as a function of the composition, x. Large optical gap bowing in these alloy QDs is clearly observed, and the observed optical gaps agree well with those obtained from theoretical calculation for QDs with 4.0 nm diameters (thick solid line in figure 5(b)) within 50 meV.

Figure 6(a) shows the optical absorption spectra of colloidal Zn(Te0.61Se0.39) QDs with diameters ranging from 3.5 to 6.3 nm. The absorption shoulder indicated by the triangle shows a continuous shift to longer wavelengths with increasing QD diameter because of the quantum size effect. The optical gaps obtained from figure 6(a) agree well with the calculated size-dependent optical gaps for Zn(Te0.61Se0.39) QDs shown in figure 6(b).

4. Discussion

In previous syntheses of Zn(Te,Se) alloy QDs, the alloying range was quite limited and only in the Se-rich range [22, 23]. Generally, the reactivity of group VI elements is significantly different and dependent on the kind of element; therefore, the alloying in a very small composition range might come from the difference in the reactivity between Te and Se source materials with the Zn source material in the reaction solution. In contrast, the alloying was successfully developed in a wide composition range by the present reaction, as clearly indicated by the peak shift in XRD (figure 1) and optical absorption spectra (figures 3(a) and (b)). When the zinc carboxylate or halide were used as Zn source materials in our preliminary trial, we encountered elemental Te precipitation, even though TOP-Te and TOP-Se, which have the same Te and Se source materials as in the present synthesis, were used. Therefore, the wide alloying of ZnTe and ZnSe in the present synthesis is thought to be the result of the use of ZnEt2 as a Zn source material, which may be highly reactive with both TOP-Te and TOP-Se at high temperatures. One might be concerned that the composition of the alloyed QDs, x, considerably deviates from the composition of the starting solution, XSe, as observed in previous studies because of the difference in reactivity between TOP-Te and TOP-Se; however, the compositions are sufficiently close to each other, as summarized in table 2, and the relationship between x in the alloy QDs and XSe in the starting solution is well described by the linear relationship shown in figure S2 in the supplementary data. In addition, the composition of the alloy QDs did not change, as shown in figure 3, when the growth conditions, such as reaction time and injection and growth temperatures, were changed, while the size of QDs varied depending on the condition. This indicates that the compositions of the obtained alloy QDs are highly homogeneous and the QDs are not compositionally graded. In terms of the quality of the QDs, HRTEM images in figures 2 and 4, in which lattice fringes are clearly observed, and optical absorption spectra in figures 5(a) and 6(a), in which the first exciton absorptions clearly appear as absorption shoulders, indicate that the QDs had some point defects but exhibited modestly good optical quality, even though they did not exhibit photoluminescence (PL) emission. Consequently, the present alloy QDs have sufficient quality to discuss the dependence of their optical properties on the composition and size.
The Zn(Te$_{1-x}$Se$_x$) alloy QDs synthesized in the present study exhibited sizes ranging between 3 and 6 nm in diameter. Taking the exciton Bohr radii of ZnTe (6.7 nm) and ZnSe (3.8 nm) into account [40], the quantum confinement effect sufficiently works on the electron and hole in the QDs. In fact, the observed optical gaps were larger than the energy band gaps reported for the bulk alloys, as shown in figures 5(b) and 6(b). According to a previous study of Zn(Te,Se) alloy nanowires (NWs) [41], of which the diameter and length were respectively \( \sim 10 \) nm and \( > 2.5 \) \( \mu \)m, large optical gap bowing was clearly observed, but the extent of bowing was slightly smaller than that observed in bulk alloys. Specifically, the bowing parameter \( b \) for the NWs was 1.26, while that for the bulk material was reported to be 1.45–1.5 [15, 17]. However, in the present QDs, the composition dependence of optical gaps for QDs with diameters of 4.0 ± 0.1 nm agreed well with that which appeared in the theoretically calculated one, in which the bowing parameter was assumed to be the same as that of the bulk alloys \( (b = 1.45) \), as observed in figure 5(b). This clearly indicates that the bowing behavior in the alloy QDs, including the extent of the bowing and composition that achieved the smallest gap, is the same as that in bulk alloys. In addition, with a constant alloy composition, the size-dependent optical gap was described well by the conventional EMA theory, as shown in figure 6(b). Thus, we conclude that no special quantum confinement features appear in these highly mismatched semiconductor alloy QDs; the composition dependence of the optical gap in the QDs is the same as that in the bulk material, and the quantum size effect is similar to that observed in simple compound semiconductors and Cd(Se,S) and Cd(Te,Se) alloys [24].

Although we introduced a bold approximation regarding the effective mass into the calculation, i.e. the effective mass of the alloy is assumed to be the mole fraction weighted mean effective mass of the two unalloyed compounds, the experimentally observed optical gaps were described well by this calculation, as shown in figures 5(b) and 6(b). The band gap bowing is a phenomenon arising from strong modulation of the valence and conduction band electronic structures; therefore, the effective mass of an electron or hole should not be described by a
mole fraction weighted mean of the two unalloyed compounds. Ghosh et al reported the bowing behavior of the electron effective mass, $m^*_{e}(x)$, in a Zn(Te$_{1-x}$Se$_x$) alloy system [42]. The deviation from $m^*_{e}(x)$ of the mole fraction weighted mean was $\sim 10\%$ at most. Although there unfortunately is no study of the hole effective mass, $m^*_h(x)$, in a Zn(Te$_{1-x}$Se$_x$) alloy system, the extent of bowing in $m^*_h(x)$ is expected to be larger than that in $m^*_e(x)$ because the
large band gap bowing in this alloy system originates from the strong modulation in the valence band electronic structure, where Te 6p and Se 5p states primarily contribute. The present theoretical calculation is not very sensitive to the effective mass used in the calculation; several tens % of difference in the effective mass results in almost the same optical gap within 50 meV. This implies that the deviation of the hole effective mass from the mole fraction weighted mean in the present alloys is expected to be not too large and may be several tens % at most.

Finally, we discuss the potential of the Zn(Te$_{1-x}$Se$_x$) alloy QDs as the green QD-phosphors. In previous studies synthesizing Zn(Te,Se) alloy QDs, the goal was to obtain non-toxic and Cd-free blue QD-phosphors exhibiting sufficient chemical stability [22, 23]. For the application of QD-phosphors in next-generation QD-LCDs, QD-phosphors emitting green and red light under the excitation of blue light from GaN-based LEDs are required [5–7]. As seen in figure 6(a), the optical gaps of Zn(Te$_{0.61}$Se$_{0.39}$) QDs with diameters of 3.5–4.7 nm that correspond to the composition exhibiting the smallest optical gap are at wavelengths between 485 and 524 nm. This leads to the emission of direct electron–hole recombination, i.e. exciton recombination, at 505–547 nm, assuming a Stokes shift of 100 meV. Therefore, green emission at 532 nm in next-generation displays described in the BT.2020 recommendation from the International Telecommunication Union [43] is expected to be achieved by the Zn(Te$_{0.61}$Se$_{0.39}$) alloy QDs with diameters of ~ 4 nm. Unfortunately, the present alloy QDs did not exhibit PL emission; however, this does not negate the potential of the alloy QDs synthesized by the present method as green QD-phosphors for the following reason: when point defects are involved in QDs, they frequently behave as radiative recombination centers and result in broad-band PL emission because of strong electron–phonon interactions at deep levels, as observed in CuInS$_2$-based QDs [34, 44] and previous Se-rich Zn(Te,Se) alloy QDs [22, 23]. QDs exhibiting such broad-band emission are not suitable as QD-phosphors. In contrast, the present alloy QDs did not exhibit any PL emission, including defect-related deep level emission. This implies that the electrons and holes experience non-radiative recombination at the surface of the QDs. Because it is well known that ZnTe is easily oxidized [45], the surface of the present Zn(Te,Se) alloy QDs was slightly oxidized and the oxidized surface might disturb PL emission. Therefore, passivating surface states is the key to realize PL emission from exciton recombination. For this purpose, fabrication of a core/shell structure, such as Zn(Te,Se)/ZnS, may be effective, as determined by many previous studies on CdSe-based QDs.

5. Conclusion

Colloidal Zn(Te$_{1-x}$Se$_x$) alloy QDs, which are highly mismatched semiconductor alloys, were synthesized by the hot injection of an organometallic solution, and their composition- and size-dependent optical gaps were studied together with theoretical calculation. Their optical gaps exhibited considerable negative deviation from the mole fraction weighted mean optical gaps of ZnTe and ZnSe, i.e. large optical gap bowing was observed, similar to bulk and thin-film alloys. The composition and size dependence was described well by the finite-depth approximation weighted mean in the present alloys is expected to be not too large and may be several tens % at most.

References

Growth


Asano H and Omata T 2017 Design of cadmium-free colloidal II–VI semiconductor quantum dots exhibiting RGB emission design of cadmium-free colloidal II–VI semiconductor quantum dots exhibiting RGB emission AIP Adv. 7 45309.


