Structural and optical properties of CdSe nanostructures (nanoparticles, nanoparticle- and nanosheet-superlattices) fabricated using organic molecules as a template

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Abstract. Structural and optical properties of trioctylphosphine-oxide-capped CdSe nanoparticles in an wurtzite phase were investigated to obtain the size dependences of bulk modulus and deformation potential by X-ray diffraction and photoluminescence measurements under high pressure. The bulk modulus $B$ [GPa] and the deformation potential $\alpha$ [eV] were described as a function of the diameter $D$ [nm] of CdSe nanoparticles by $B = -110 \times (1/D) + 53$ and $\alpha = 5.13 \times (1/D) - 2.30$ in the pressure range to 3 GPa. Structural and optical properties of three-dimensional CdSe nanoparticle-superlattice and two-dimensional CdSe nanosheet-superlattices were also studied at ambient pressure and under high pressure. Enhanced interaction between nanoparticles in CdSe nanoparticle-superlattices, compared with CdSe nanoparticles dispersed in solution, was observed in their optical properties. For two-dimensional CdSe nanosheet-superlattices, two excitonic bands whose energy difference was much larger than that of bulk CdSe crystals were observed in optical absorption spectra. The energy of splitting between the two excitonic bands increased linearly with pressure. The observations indicate that the crystal field effect on the band mixing is enhanced significantly in the nanosheet-superlattice structure.

1. Introduction
Semiconductor nanostructures (nanoparticles (NPs), nanorods (NRs) and nanosheets (NSs)) exhibit unique size-dependent optical properties that are significantly distinguished from its bulk state. Especially, CdSe-related nanostructures have drawn much interest in viewpoints of both physics and optical applications due to their easily-tunable high efficient luminescence in the visible range by changing the nanoscale dimension [1, 2]. However, to our best knowledge, there have been few experimental works on the size dependences of bulk modulus and deformation potential of CdSe nanostructures.

A self-organized method using organic molecules as a template to form organic-inorganic hybrid superlattice (SL) has been utilized to fabricate CdSe nanostructures with controlled dimensionality [3, 4]. However, optical and electronic properties of organic-CdSe hybrid SL have not been studied sufficiently and therefore have not been fully understood.

In this study, we have studied the size dependences of high pressure properties, especially the bulk modulus and the deformation potential of TOPO (trioctylphosphine oxide)-capped CdSe NPs ranging from 2.8 to 5.4 nm in diameter. In addition, we have investigated structural, optical and electronic
properties of three-dimensional CdSe nanoparticle-superlattice (CdSe NP-SL) and two-dimensional CdSe nanosheet-superlattice (CdSe NS-SL) at ambient pressure and also under pressure to discuss effects of interaction between NPs and NSs on excitonic states by changing the distance between adjacent NPs and NSs, respectively, in the SL structures.

2. Experimental

TOPO-capped CdSe NPs with diameters $D$ ranging from 2.8 to 5.4 nm were prepared by a conventional hot-injection method [5]. The sizes of the prepared CdSe NPs were determined by using the relationship between the NP diameter and the lowest excitation energy obtained from optical absorption spectra in an UV-visible region [6]. The surface modification on CdSe NPs was also made by altering TOPO by HDA (hexadecylamine) to explore the effects of the surface states on the bulk modulus and deformation potential. After carefully purifying TOPO-capped CdSe NPs, X-ray diffraction (XRD) and photoluminescence (PL) were measured under high pressure to 9 GPa using a diamond anvil cell (DAC) with a 4:1 methanol-ethanol mixture as a transmitting medium. High-pressure XRD measurements were carried out at the BL-18C beamline (wavelength: 0.6198Å) at KEK-PF. PL spectra were measured under high pressure using the 442 or 325 nm line of a He-Cd laser as an excitation light source.

TOPO-capped CdSe NPs were arrayed three-dimensionally to form CdSe NP-SLs by a pressure-controlled solution-evaporation method as follows. TOPO-capped CdSe NPs were dispersed in the mixture of n-octane and 1-octanol (the ratio was 9:1). The dispersed solution was heated up to 80 °C, and then evacuated to 1 torr at the rate of 3 torr/min, and kept at 80 °C at 1 torr for two days to grow crystals of CdSe NP-SLs. SL structures were confirmed and their lattice parameters were determined by small angle X-ray scattering (SAXS; Rigaku, NANO-Viewer) for CdSe NP-SLs.

CdSe NS-SLs with alkylamine molecules acting as a barrier layer as well as a template were fabricated by a soft-colloidal template method [4]. Two-dimensional SL structures and their lattice parameters were examined by conventional XRD measurements.

Optical absorption and PL spectra of CdSe NP-SLs and CdSe NS-SLs were measured under hydrostatic pressure to 6 GPa using a DAC with either cyclohexene or a 4:1 methanol-ethanol mixture as a transmitting medium. Time-resolved PL measurements to obtain fluorescence life times were performed at ambient pressure using a streakscope with a spectrograph and a N$_2$ pulse laser (337 nm) for CdSe NP-SLs and a pico-seconds laser diode (375 nm) for CdSe NS-SLs as an excitation light source.

3. Results and discussion

3.1. Bulk modulus and deformation potential of CdSe NPs

High-pressure XRD patterns of TOPO-capped CdSe NPs exhibited an wurtzite structural phase below 3 GPa and recovered to the original ones after releasing to atmospheric pressure.

Figure 1. Calculated unit cell volumes of CdSe NPs with $D = 2.8$, 3.1 and 5.4 nm represented by △, ◇, ○, respectively, as a function of pressure. The dashed lines are the curves fitted to the data using equation (1).
pressure. We obtained the unit cell volume $V$ as a function of pressure $P$, as shown in figure 1, from high-pressure XRD data below 3 GPa, and then calculated the bulk modulus $B$ for CdSe NPs with $D =$ 2.8, 3.1 and 5.4 nm, as tabulated in table 1, by fitting $V$ using the Murnaghan’s equation of state;

$$P(V) = \frac{B}{B'} \left[ \left( \frac{V_0}{V} \right)^{B'} - 1 \right],$$

(1)

where $B'$ is the pressure derivative of $B$, and $V_0$ is the unit cell volume at atmospheric pressure. We found that the bulk modulus for CdSe NPs is much smaller than that of bulk CdSe crystals ($B = 53.0$ GPa [7]) and decreases as the size of NP decreases. We plotted $B$ as a function of $1/D$ in figure 2 and found that $B$ [GPa] decreases linearly with the inverse of $D$ [nm], as expressed well by $B = -110 \times (1/D) + 53$.

We observed a PL band originating from the excitonic (or HOMO-LUMO gap) emission which shifts linearly to higher energies with pressure in the low pressure region to 3 GPa. The pressure coefficient of the energy of the PL band is tabulated in table 1 and plotted as a function of $1/D$ in

| Diameter $D$ [nm] | Bulk Modulus $B$ [GPa] | Pressure Coefficient [meV/GPa] | Deformation Potential $\alpha$ [eV] |
|------------------|------------------------|-------------------------------|-------------------------------|
| 2.8              | 11.9                   | 14.4                          | $-0.38$                      |
| 3.1              | 21.6                   | 16                            | $-0.74$                      |
| 4.1              |                        | 21.3                          |                               |
| 5.4              | 29.4                   | 23.5                          | $-1.34$                      |

**Figure 2.** Bulk modulus as a function of $1/D$ for CdSe NPs. The open circles are from the present study, and the open triangles from Refs. [7, 8].

**Figure 3.** Pressure coefficient of PL peak energy and deformation potential as a function of $1/D$ for CdSe NPs. The open circles and triangles represent the pressure coefficients from the present study and from Refs. [7, 9], respectively. The solid circles and triangles represent the deformation potentials from the present study and from Ref. [10], respectively.
The size dependence of the pressure coefficient of the HOMO-LUMO gap for CdSe NPs can be understood in the light of the enhancement of mixing of electronic states at off-Γ points to that at Γ point in the Brillouin zone of bulk CdSe crystals by decreasing the size of NP. We found also that the Stokes shift increases with pressure, e.g. by 6 meV/GPa for the sample of $D = 2.8$ nm.

We estimated the deformation potential $a$ using the bulk modulus and the pressure coefficient of the energy of the PL band, as tabulated in Table 1. We found that the absolute value of deformation potential for CdSe NPs is much smaller than that of bulk CdSe crystals ($a = -2.3$ eV [10]) and decreases as the size of NP decreases. We plot $a$ as a function of $1/D$ in figure 3 and find a linear relationship between $a$ [eV] and $1/D$ [nm$^{-1}$], as expressed by $a = 5.13 \times (1/D) - 2.30$. It should be pointed out that the linear dependence of deformation potential on $1/D$ did not change by the surface modification by HDA, even though the pressure coefficient of the energy of the PL band depended on the surface ligands.

3.2. Structural and optical properties of CdSe NP-SLs

TOPO-capped CdSe NPs with $D = 2.3, 3.2, 3.7$ and $4.2$ nm were arrayed three-dimensionally by a pressure-controlled solution-evaporation method. We obtained small platelets of CdSe NP-SLs. The SAXS profiles shown in figure 4 exhibit broad, but appreciable, peaks originating from (1 1 1) and (2 2 2) diffraction peaks of simple cubic (SC) structures, providing confirmation of three-dimensional SL structures. We found that the lattice parameter of SC structure increased from 3.7 to 5.0 nm as $D$ increased from 2.3 to 4.2 nm. The result implies that the distance between the nearest surfaces of two adjacent NPs, $d_{NP}$, was decreased from 1.4 to 0.8 nm as $D$ increased from 2.3 to 4.2 nm.

After dispersed-CdSe NPs were arrayed three-dimensionally for CdSe NP-SL, the excitonic emission band in PL spectra was red-shifted and became asymmetric in lineshape, as shown in figure 5 for $D = 3.2, 3.7$ and $4.2$ nm. Here, the change in the energy of the PL band with $D$ for dispersed-CdSe NPs can be well explained by a quantum confinement model [11]. It should be noted that the red-shift of the PL band after arraying to three-dimensional SL structure depends on $d_{NP}$. Roughly speaking, the red-shift becomes larger as $d_{NP}$ decreases. The observation suggests that the energy transfer between NPs occurs in the SL structures and is promoted as $d_{NP}$ decreases.
Figure 6 shows the time-resolved PL intensity as a function of decay time for dispersed-CdSe NP (blue color) and CdSe NP-SL (red color) with $D = 3.5$ nm. We analyzed the data by curve-fitting to a first-order kinetics equation with two lifetimes (i.e. two exponential decay components) to evaluate an effect of interaction between NPs on the excitonic state. From the curve-fitting, the lifetimes were estimated to be 10.2 and 41.3 ns for dispersed-CdSe NP and 2.4 and 15.2 ns for CdSe NP-SL. The result implies that the exciton lifetime was shortened by one-fourth for the fast component and by one-third for the slow component after dispersed-CdSe NPs were arrayed to the SL structure. This is another evidence of enhanced interaction between NPs in CdSe NP-SLs as a result of the formation of SL structure.

Figure 7 shows the pressure dependence of the excitonic emission band in PL spectra for dispersed-CdSe NP (blue color) and CdSe NP-SL (red color) with $D = 4.2$ nm. With applying hydrostatic pressure, the PL peak of CdSe NP-SL increases in energy and becomes symmetric in lineshape. It is noteworthy that it becomes eventually almost identical in appearance with that of dispersed-NP around 6 GPa. We found that the peak energy of the excitonic emission band shifts linearly to higher energies with pressure to 3 GPa for both dispersed-CdSe NP and CdSe NP-SL. However, the pressure coefficient for CdSe NP-SL is larger by 10% than that for dispersed-CdSe NP.

3.3. Structural and optical properties of CdSe NS-SLs

Figure 8 shows the XRD patterns in the low angle region ($2\theta = 3 - 15^\circ$) for CdSe NS-SLs with hexylamine, octylamine, dodecylamine and oleylamine. The (0 0 $l$) diffraction peaks ($l = 2, 3$) were clearly observed, indicating a two-dimensional SL structure with the c-axis (the stacking direction of CdSe nanosheets and alkylamine layers) normal to the plane of flakes of sample. The observed diffraction peaks shift to higher angles with longer alkylamines used for the barrier layer as well as for the template. The lattice constant of the two-dimensional SL structure, i.e. the distance between adjacent CdSe nanosheets, was estimated and plotted in figure 9 as a function of the number of carbon atoms of the alkylamine used for CdSe NS-SLs.
We found that the distance between adjacent CdSe nanosheets in CdSe NS-SL varied linearly with the number of carbon atoms in the alkylamine. By interpolating the linear relationship to zero in the number of carbon atoms in figure 9, we estimated the thickness of a CdSe nanosheet to be 1.4 nm (corresponding to about 7 atomic layers) which is consistent with the result of high-resolution transmission electron microscopy observation of CdSe NS-SL with octylamine by Son and his coworkers [4]. Consequently, the thickness of an alkylamine layer (i.e. barrier layer) was found to vary from 1.0 to 3.1 nm by using different alkylamines in order of hexylamine, octylamine, dodecylamine, oleylamine. Our XRD data in the high angle region ($2\theta = 20 – 50^\circ$) revealed that the CdSe nanosheets have a slightly-distorted wurtzite structure. A previous work on selected-area electron diffraction measurements reported that the $c$ axis of the wurtzite structure is parallel and the $a$ axis perpendicular to the nanosheet [4]. Schematic structural image is sketched in figure 10 in aid of the findings by calculation using density fluctuation theory [4].

Optical absorption spectra of CdSe NS-SL with octylamine at ambient pressure and under high pressure are shown in figure 11. They exhibit two distinct sharp peaks originating from two excitonic states, $1_{hh-1_e}$ and $1_{lh-1_e}$, which are associated with heavy and light holes, respectively. The energy of splitting between the two peaks corresponds to the difference in energy between the heavy hole and the light hole in the valence band. We found that both $1_{lh-1_e}$ and $1_{hh-1_e}$ shift slightly to a higher energy with an increase in the thickness of barrier layer (i.e. the thickness of alkylamine layer) due to dielectric confinement of excitons. The energy of splitting between $1_{hh-1_e}$ and $1_{lh-1_e}$ at ambient pressure for CdSe NS-SL with octylamine is 186 meV at 5 K which is about 8 times larger than the energy difference between heavy and light holes at the $\Gamma$ point in the valence band of bulk CdSe crystals (25 meV at 4.2 K). The significant increase in the energy of splitting between heavy and light holes in CdSe NS-SL compared with that of bulk CdSe crystals can be explained with an increase in the crystal field effect by the quasi-cubic model of band mixing for wurtzite crystals [12] in addition to an exciton confinement effect in CdSe nanosheets.

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**Figure 8.** X-ray diffraction patterns of CdSe NS-SLs with hexylamine (C6-CdSe), octylamine (C8-CdSe), dodecylamine (C12-CdSe), oleylamine (C18-CdSe) in the low angle region. The Cu-K$\alpha$ line was used as an X-ray source.

**Figure 9.** Lattice constant of two-dimensional SL structure (i.e. distance between adjacent CdSe nanosheets) as a function of the number of carbon atoms of the alkylamine acting as the barrier layer as well as the template for CdSe NS-SLs.
As shown in figure 11, both the absorption peaks of $1_{hh}-1_{e}$ and $1_{lh}-1_{e}$ shift to higher energies with applying pressure to 6.5 GPa. It should be noted that any indications of a phase transition can be

![Figure 10. Schematic structural image of CdSs NS-SL with octylamine. Pink and green solid circles represent Cd and Se atoms, respectively, in CdSe nanosheets.](image10)

![Figure 11. Change in optical absorption spectra with pressure for CdSe NS-SL with octylamine.](image11)

![Figure 12. Change in PL spectra with pressure for CdSe NS-SL with octylamine. The 325 nm line (3.81 eV) of He-Cd laser was used as an excitation light source.](image12)

![Figure 13. Pressure dependences of energies of two optical absorption peaks, $1_{hh}-1_{e}$ (green solid circles) and $1_{lh}-1_{e}$ (blue solid circles), and PL peak (red solid circles) for CdSe NS-SL with octylamine.](image13)

As shown in figure 11, both the absorption peaks of $1_{hh}-1_{e}$ and $1_{lh}-1_{e}$ shift to higher energies with applying pressure to 6.5 GPa. It should be noted that any indications of a phase transition can be
realized in the pressure dependence of optical absorption spectra, while bulk CdSe crystals exhibit a structural phase transition from an wruzite to a rock salt structure at 2.7 GPa, which is accompanied by a significant change in an optical absorption spectra due to the direct-indirect band structural change. The pressure dependence of PL spectra of CdSe NS-SL with octylamine is shown in figure 12. The PL peak originating from the 1hh-1e exciton emission appears at 2.75 eV at ambient pressure and shifts to higher energies with pressure. We plot the energies of the two optical absorption peaks and the PL peak as a function of pressure in figure 13. All of them shift linearly with pressure to 3GPa. The pressure coefficients are 40 and 50 meV/GPa for the 1hh-1e and 1lh-1e absorption peaks, respectively, and 34 meV/GPa for the 1hh-1e exciton emission peak. The energy of splitting between 1hh-1e and 1lh-1e absorption peaks increases linearly with pressure and reaches 225 meV at 6 GPa. The observation indicates that the crystal field effect is enhanced significantly by applying pressure in CdSe nanosheets. Another interesting finding is that the Stokes shift, i.e. the difference in energy between the absorption and emission peaks of 1hh-1e exciton, increases linearly with pressure by 6 meV/GPa, suggesting that electron-lattice (or exciton-lattice) interaction is also enhanced with applying pressure in CdSe nanosheets. We have found that the fluorescence life time of 1hh-1e exciton emission band for CdSe NS-SLs decreases with increasing the thickness of alkylamine layers (i.e. barrier layer) by using different alkylamines, providing information about interaction of excitons between nanosheets. The details will be reported elsewhere.

4. Conclusion
We have studied the structural and electronic states of TOPO-capped CdSe NPs ranging from 2.8 to 5.4 nm in diameter under high pressure to explore the size dependences of bulk modulus and deformation potential. We found that a linear relationship between the bulk modulus and the size of NP as well as between the deformation potential and the size of NP below 3 GPa. We have also investigated the structural and optical properties of three-dimensional CdSe NP-SLs at ambient pressure and under high pressure to discuss effects of interaction between NPs on the excitonic states by changing the distance between adjacent NPs. Evidence of enhanced interaction between NPs in CdSe NP-SLs was obtained as a result of the formation of SL structure. For two-dimensional CdSe NS-SLs, two excitonic states, 1hh-1e and 1lh-1e, were observed. The energy of splitting between heavy and light holes was much larger than that of bulk CdSe crystals, and increased linearly with pressure, indicating that the crystal field effect on the band mixing of wruzite structure is significantly enhanced in the NS-SL structure.

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