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Photoluminescence of CdS nanoparticles suspended in vacuum and its temperature increase by laser irradiation

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Abstract

We report here photoluminescence of CdS nanoparticles suspended in vacuum. The CdS nanoparticles, whose size distribution was bimodal having peaks at 11.3 and 43.1 nm, were produced by the gas-evaporation method and the nanoparticle beams were formed within the rarefied inert-gas flow. The band-edge emission and surface luminescence of the CdS nanoparticles, whose surfaces were completely free from adsorption, reaction or contamination with their surroundings, were observed. As the excitation intensity increased, the band-edge emission shifted to lower energy and the surface state luminescence shifted to higher energy. These energy shifts in the photoluminescence spectra as functions of excitation intensity were interpreted as an internal temperature rise of the CdS nanoparticles suspended in vacuum, and the internal temperature of the CdS nanoparticles was evaluated by means of photoluminescence. It was found that the nanoparticles suspended in vacuum were heated by much weaker laser irradiation than the bulk surface due to the large surface-to-volume ratio.

1. Introduction

The optical properties of semiconductor nanoparticles or quantum dots have been studied by many researchers in the last decade. The greatest interest in semiconductor nanoparticles is in the unique behaviour of an electron–hole pair (exciton) confined in finite size. In the semiconductor nanoparticle, whose size is comparable to the effective Bohr radius of the

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exciton, the absorption edge is blue-shifted and the electronic band structures are transformed into discrete states as the result of the quantum confinement effect [1–4]. In particular, evidence of the quantum confinement effect for Cd-chalcogenide nanoparticles, for example deposition films [5, 6], nanoparticles embedded in GeO₂ glasses [7, 8] and colloidal nanoparticles [9–11], has been reported since the initial stages of research on the quantum confinement effect. These semiconductor nanoparticles are expected to be a novel material for optoelectronic devices. On the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size (surface effects). In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size. Therefore, the decay of an exciton at the surface states will influence the qualities of the material for an optoelectronic device. Moreover, the surface effects enhance the chemical reaction occurring on the surface of nanoparticles, such as photocatalysis [12]. Although the surface states or the interface states influence the intrinsic optical properties of nanoparticles, they have frequently been studied only on the nanoparticle whose surface was terminated or contaminated with its surroundings. On the other hand, the optical properties of nanoparticles whose surfaces are completely free have not been investigated enough experimentally.

Gas phase condensation in rarefied inert gas atmospheres, for example gas evaporation [5, 6, 13], laser ablation [14, 15], free jet expansion [16, 17], etc, are powerful methods for producing nanoparticles of various semiconductors. The nanoparticles produced by these methods have a fresh surface and keep their innate structure as long as they stay in the inert gas atmosphere. Previously, we reported the photoluminescence of a CdSe nanoparticle beam [18]. The CdSe nanoparticles were produced by a gas evaporation method and then the nanoparticle beam was formed in an inert gas flow. The CdSe nanoparticle whose surface was completely free dissociated under the very weak irradiation of a laser whose photon energy was much higher than the band gap energy.

In this paper, we report the photoluminescence spectra of CdS nanoparticles suspended in vacuum by means of a nanoparticle beam. A band-edge emission and surface luminescence were observed from the CdS nanoparticle beam excited by a laser and the peak energies shifted with an increase in the excitation power. The surface luminescence of CdS nanoparticles whose surface is completely free will be compared with that of a CdS nanoparticle deposition film. The excitation intensity dependent photoluminescence of CdS nanoparticles is discussed in terms of the internal temperature rise and the distribution of carriers at surface states.

2. Experimental details

The details of the apparatus have been reported elsewhere [18]. In this paper, a brief description of the experimental procedures is given. The apparatus is composed of a nanoparticle generation chamber and a beam formation and optical measurement part. The nanoparticles are produced by the gas evaporation method in the nanoparticle generation chamber which is equipped with a Knudsen cell as the evaporating device and is able to introduce inert gas. In order to produce CdS nanoparticles, the Knudsen cell was heated up to 750 °C in an inert gas atmosphere at a pressure of about 900 Pa. The nanoparticles produced were introduced into the beam formation and optical measurement part through a collimator (nozzle) of 7 mm diameter by differential pumping. A nanoparticle beam was then formed with the inert gas flow inside a quartz glass tube. The nanoparticle beam was irradiated in the quartz glass tube part with the 457.9 nm line of an argon-ion laser. The laser beam, which was perpendicular to the nanoparticle beam, was focused on 0.5 mm diameter about 50 cm downstream from the Knudsen cell. The mean exposure time was estimated to be about 0.5 ms. Photoluminescence

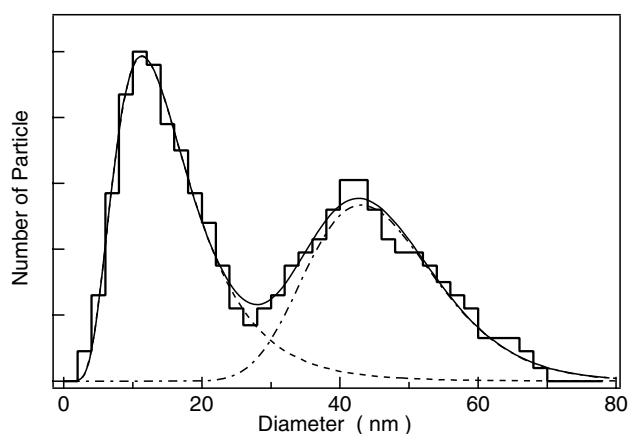


Figure 1. Size distribution of the beam composed of CdS nanoparticles. The full curve represents the best fit to the data using two log-normal functions whose peak sizes are 11.3 and 43.1 nm, respectively. Each log-normal function is represented by broken curves.

spectra of the CdS nanoparticle beam were measured using a single polychromator system equipped with a cooled MOS linear image sensor unit as a detector. Reflected and scattered laser light from the beam was eliminated by a holographic notch filter installed in front of the incident slit of the polychromator.

CdS nanoparticles were characterized by Raman scattering measurement and transmission electron microscopy (TEM). CdS nanoparticles were deposited either on Si wafers for Raman scattering and photoluminescence measurement or on electron microscopic grids for TEM. Raman scattering spectra of the nanoparticle deposition film were measured in the back scattering geometry using a triple-pass polychromator system (Jasco TRS600) equipped with a charge-coupled device (Photometrics TK-512CB) cooled by liquid nitrogen. The excitation light for Raman scattering was the 457.9 nm line of an argon-ion laser and the power was set at less than 3 W cm^{-2} . Raman scattering and photoluminescence of the deposition film was measured in air. The structure and shape of the CdS nanoparticles were observed by TEM (JEOL JEM-200CX).

3. Results and discussion

3.1. Characterization of CdS nanoparticle beam

Figure 1 shows the size distribution of the CdS nanoparticles composing the beam. The size distribution was bimodal. In many cases of the gas condensation method, it is known that the size distribution has a log-normal function shape. As shown by the full curve in figure 1, the size distribution was successfully fitted by two log-normal functions and it was found that the peak positions were 11.3 and 43.1 nm, respectively. According to the TEM observation, the first peak at 11.3 nm was composed of the primary particles and the population is greater than the second peak at 43.1 nm. The second peak is attributed to the coalescence of the primary particles.

Figure 2 shows typical Raman spectra of the CdS nanoparticle deposition film and the bulk crystal. There are two peaks at 301 and 601 cm^{-1} . The Raman frequencies of these peaks correspond to the 1-LO and 2-LO phonon modes of the bulk crystal, respectively. The 1-LO peak of the deposition film is asymmetric and has a tail at the low frequency side. The

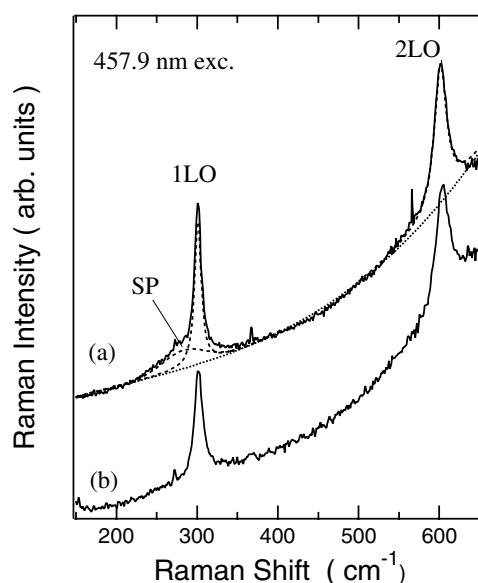


Figure 2. Raman spectra of the (a) CdS nanoparticle deposition film and (b) CdS bulk crystal. The Raman frequencies, 301 and 601 cm^{-1} , correspond to the 1-LO and 2-LO phonon mode of the bulk crystal, respectively. The 1-LO phonon peak and a surface phonon (SP) peak for the deposition film were fitted with a Lorentzian and a Gaussian function, respectively. The broken curve represents the best fit. The SP mode of the CdS nanoparticles is located at 284 cm^{-1} .

1-LO mode and the tail were decomposed by fitting with a Lorentzian function at 301 cm^{-1} and a Gaussian function having a peak at 284 cm^{-1} , respectively. The low frequency tail was assigned to a surface phonon mode [19] that appears with a decrease in the particle size [20]. The linewidth of the 1-LO peak is as narrow as that of bulk CdS, and there are no Raman spectra related to sulfur nanoparticles or clusters. Therefore, the crystallinity of the CdS nanoparticles composing the beam is as good as that of the bulk crystal.

3.2. Photoluminescence of CdS nanoparticle beam

Figure 3 shows the photoluminescence spectra of a CdS nanoparticle beam in comparison with that of a CdS nanoparticle deposition film and a bulk crystal. When the nanoparticle beam was excited with an excitation power of 5 mW (figure 3(a)), a sharp emission band at 2.44 eV and a broad emission band at 1.72 eV were observed. These emission bands were successfully fitted with Gaussian functions, as shown by the full curves in figure 3. The sharp emission band of the nanoparticle beam coincides with a photoluminescence peak at 2.45 eV of the bulk crystal. The peak energy of this emission band is slightly lower than the band-gap energy of the bulk crystal (2.50 eV at room temperature) and is regarded as a radiative recombination of an electron–hole pair trapped shallowly at donor–acceptor states in the CdS nanoparticle, which is referred to as ‘band-edge emission’. The peak energy of this band-edge emission of the CdS nanoparticle does not show a noticeable blue shift in comparison with the bulk crystal. The quantum confinement effect on the electron–hole system in CdS nanoparticles has been studied [4, 5, 7, 8]. The transition from a weak ‘exciton confinement regime’, in which the centre-of-mass motion is confined weakly in the nanoparticle, to a strong ‘individual particle confinement regime’, in which the exciton is squeezed, occurs at the particle size R

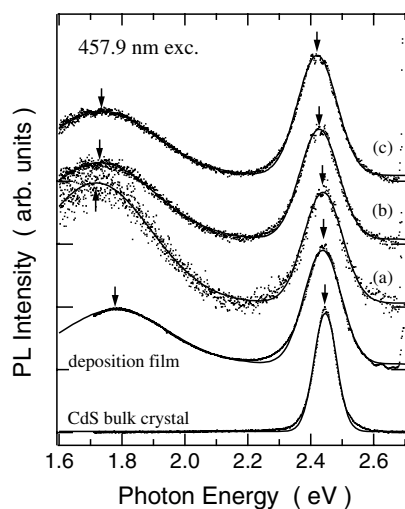


Figure 3. Typical photoluminescence spectra of a CdS nanoparticle beam excited with an excitation power of (a) 5, (b) 25 and (c) 50 mW. Photoluminescence spectra of the CdS bulk crystal and nanoparticle deposition film are also shown. A band-edge emission and surface luminescence were observed at about 2.45 and 1.7 eV, respectively, in (a). The full curves represent the best fit to the data using two Gaussians.

in $2a_B^* \leq R \leq 4a_B^*$, where a_B^* is the effective Bohr radius of the exciton [4]. The particle size in this paper is in an intermediate region between these confinement regimes, so that the electronic states remain as the three-dimensional characteristics of the bulk crystal and the band-gap energy does not increase noticeably.

On the other hand, as shown in figure 3, the intensity of the broad emission band at 1.72 eV was almost the same as the intensity of the sharp emission band at the excitation power of 5 mW, though the broad emission band was not observed from the bulk crystal. This broad peak is considered to be due to the recombination of the exciton deeply trapped at the defect states localizing on the surface of the nanoparticle, frequently referred to as 'surface luminescence' [7, 8, 21]. The surface luminescence was also observed in the case of the deposition film. In comparing the surface luminescence between the nanoparticle beam and the deposition film, the peak energy for the nanoparticle beam was lower than that for the deposition film by about 0.02 eV, as shown in figure 4. An energy shift or quenching of the surface luminescence induced by surface modifications has been reported [21, 22]. However, to the best of our knowledge, the surface luminescence of the nanoparticle whose surface is completely free has never been reported. In this work, adsorption of gas species in air or connection of nanoparticles may increase the transition energy of the surface state of the deposition film.

The photoluminescence spectra of a CdS nanoparticle beam excited with a power of 25 and 50 mW are also shown in (b) and (c), respectively, of figure 3. As the excitation power increases, the peak energy of the band-edge emission shifted slightly to lower energy and the intensity of the surface luminescence decreased relative to that of the band-edge emission. These excitation power dependent spectral changes in the photoluminescence of the CdS nanoparticle beam are discussed in the following sections.

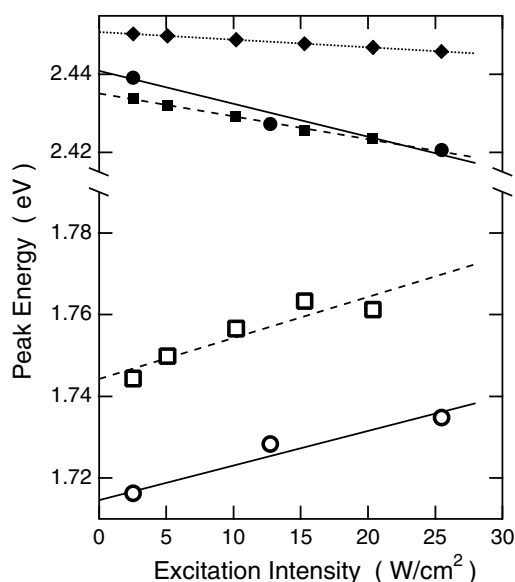


Figure 4. Changes in the peak energies of band-edge emission (●), surface luminescence (○) of a CdS nanoparticle beam and band-edge emission (■), surface luminescence (□) of a CdS nanoparticle deposition film and band-edge emission of bulk crystal (◆) with excitation intensity.

3.3. Dependence of band-edge emission on excitation intensity

The peak energy of the band-edge emission of the CdS nanoparticle beam is plotted as a function of the excitation intensity in figure 4 (●). The excitation intensity dependencies of the peak energies of the deposition film and the bulk crystal are also shown in figure 4. The peak energy of the band-edge emission shifts to lower energy with an increase of the excitation intensity in all the cases. In the photoluminescence measurements of II–VI compounds under high excitation intensity, some high-density excitation phenomena, such as photodarkening, high-density exciton effects, etc, have been observed [23]. However, the excitation intensities in our study are much smaller than those inducing high-density excitation phenomena. Our excitation intensity dependencies of band-edge emission are explained by the rise in the internal temperature of the nanoparticles. Generally, the thermal expansion of the lattice constant brings about the decrease in the band-gap energy. We measured the photoluminescence of the deposition film with an excitation intensity of 2.5 W cm^{-2} at temperatures ranging from 300–370 K. As the temperature rises, the peak energy of the band-edge emission shifts to lower energy. The peak energy of the band-edge emission at 300 K coincides with that of the nanoparticle beam excited with an excitation power of 2.5 W cm^{-2} , which is the lowest excitation intensity in this work. According to this agreement of peak energies, it was found that the internal temperature of the CdS nanoparticle beam was cooled to room temperature at about 50 cm downstream from the Knudsen cell.

The red shift of the band-edge emission with an increase of the excitation intensity is considered to be due to the decrease of the band gap energy with a rise in the internal temperature of the CdS nanoparticle. The energy shift $-\Delta E_{BE}$ of the band-edge emission is plotted as a function of the excitation intensity in figure 5. We estimated the rise in the internal temperature of the nanoparticles composing the beam to be about 33 and 55 °C for the excitation intensities of 13 and 25 W cm^{-2} , respectively, using the temperature coefficient

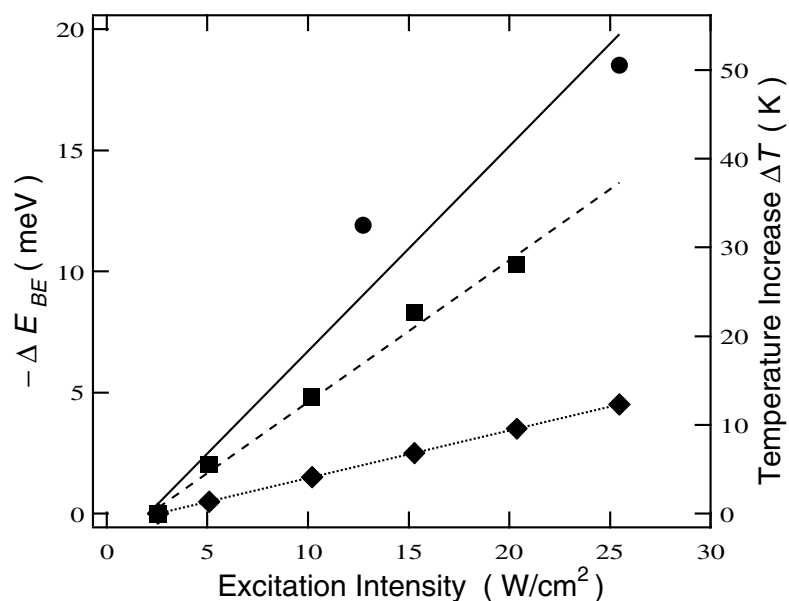


Figure 5. Excitation intensity dependence of the energy shift of the band-edge emission $-\Delta E_{BE}$ of the CdS nanoparticle beam (●), CdS nanoparticle deposition film (■) and bulk crystal (◆). The right axis indicates the temperature rise corresponding to $-\Delta E_{BE}$ induced by laser irradiation.

of the band gap for bulk CdS: 0.366 meV K^{-1} [24]. The right axis of figure 5 indicates the temperature rise corresponding to the red shift induced by laser irradiation. The temperature rise of the nanoparticles is larger than that of the bulk crystal. This large temperature rise can be understood by the surface-induced nonradiative recombination of the carriers confined in the nanoparticle. Some of the carriers in semiconductors decay nonradiatively with multiphonon emission and some energy in the excited electronic state converts into lattice vibrations. The free carrier in the nanoparticles is captured by the surface states very rapidly (\sim ps), and some kinds of surface states are the dominant centres of nonradiative recombination. Therefore, as the surface-to-volume ratio increases with a decrease in particle size, the energy of the carriers will be converted efficiently into thermal energy by surface-induced nonradiative recombination. Juršėnas *et al* [25] reported that the decrease in the carrier density in CdS nanoparticles is urged by the surface-induced nonradiative recombination with a decrease of the particle size. On the other hand, in the case of the bulk crystal, the electronic and vibrational energy diffuse to the inside of the crystal, so that the temperature rise at the irradiated spot is restrained.

The temperature rise of the nanoparticle beam is slightly larger than that of the deposition film, though the size distribution of both the nanoparticle beam and the deposition film is assumed to be identical. The nanoparticle suspended in vacuum confines the carriers perfectly inside itself and the internal temperature is easy to raise by laser irradiation. In the case of the deposition film, the diffusion of the energy owing to the connectivity of nanoparticles in the deposition film or cooling by air restrains the rise of the internal temperature less effectively as compared with the nanoparticle beam. It is found that the CdS nanoparticle with a completely free surface could be heated by much weaker laser irradiation than the bulk surface and the temperature rise can be evaluated by means of photoluminescence measurements.

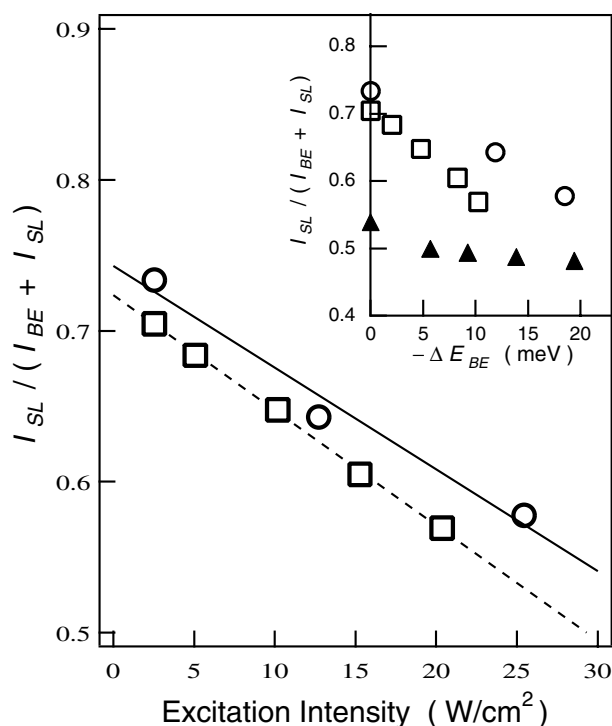


Figure 6. Excitation intensity dependence of relative intensity $I_{SL}/(I_{BE} + I_{SL})$ of the CdS nanoparticle beam (O) and deposition film (□), where I_{SL} and I_{BE} are the integrated intensities of surface luminescence and band-edge emission, respectively. These relative intensities are plotted as functions of the energy shift of the band-edge emission $-\Delta E_{BE}$ induced by the internal temperature rise in the inset of figure 6. The relative intensity of the nanoparticle whose temperature was raised just by heating (▲) is also plotted as a function of the energy shift of band-edge emission. Photoluminescence spectra of deposition film were measured at temperatures ranging from 300–370 K with an excitation intensity of 2.5 W cm^{-2} .

3.4. Dependence of surface luminescence on excitation intensity

The peak energy of the surface luminescence of the CdS nanoparticle beam is plotted as a function of the excitation intensity in figure 4 (O). The peak energy of the surface luminescence shifts to higher energy with the increase in excitation intensity. As mentioned above, we confirmed the fact that the internal temperature of the nanoparticles increased with excitation intensity. The rise in the internal temperature causes the blue shift of the surface luminescence of the CdS nanoparticle. The carriers trapped at the surface states are redistributed to the higher energy part in the surface states by thermal energy due to the rise in internal temperature. Therefore the peak energy of the surface luminescence increases. A similar temperature dependence of surface luminescence was observed for CdS microcrystals [5] and CdSe quantum dots [8]. Additionally, the band filling effect may also contribute to the blue shift of the surface luminescence. As shown in figure 3, the intensity of the surface luminescence decreases relative to the increase in excitation power in comparison with the intensity of the band-edge emission. Figure 6 shows the excitation intensity dependence of relative intensity $I_{SL}/(I_{BE} + I_{SL})$, where I_{SL} and I_{BE} are the integrated intensities of surface luminescence and band-edge emission, respectively. The relative intensities are also plotted as functions of the energy shift of the band-edge emission $-\Delta E_{BE}$ induced by the internal temperature rise

in the inset of figure 6. The relative intensity of surface luminescence decreases drastically with the increase in excitation intensity. However, as shown by the inset, there is a weak correlation between the relative intensity of the nanoparticle whose temperature was raised just by heating and the energy shift of band-edge emission. These results suggest that the excitation intensity dependence of the relative intensity is mainly due not only to the internal temperature rise but also to band filling of the low-density surface states with an increase in carrier density. As mentioned above, the surface states trap free carriers very rapidly (\sim ps) and become occupied when the carrier density increases with excitation intensity because of the rareness of the surface state and the long lifetime (\sim μ s) of carriers trapped at the surface state [26]. After the surface states are filled with carriers, direct recombination of free carriers becomes predominant due to its short lifetime (\sim 100 ps) [26, 27], and then the relative intensity of band-edge emission increases. This excitation intensity dependence of the relative intensity supports an incidence of band filling on the surface state. Such an excitation intensity dependence of surface luminescence was observed for CdS_xSe_{1-x} [26] nanoparticles doped glasses kept at low temperature. Therefore, the blue shift of the surface luminescence with the increase in excitation intensity is considered to be due to the redistribution of carriers to higher surface states because of the internal temperature rise and the band filling effect.

4. Summary

For the purpose of observing the optical properties of CdS nanoparticles having a free surface, we measured the photoluminescence spectra of CdS nanoparticles by means of a nanoparticle beam. The band-edge emission and the surface luminescence of CdS nanoparticles whose surface was completely free were observed. The band-edge emission shifted to lower energy and the surface luminescence shifted to higher energy with an increase in excitation intensity. These energy shifts were explained by the internal temperature rise due to laser irradiation. The nanoparticle beam was heated easily by lower excitation powers than the deposition film and bulk crystal. In the case of CdS nanoparticles suspended in vacuum, surface-induced nonradiative recombination converts the energy of the carriers efficiently into thermal energy due to its large surface-to-volume ratio.

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