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Abstract. We developed an apparatus that enables us to perform optical measurements of nanocrystals suspended in vacuum. CdSe nanocrystals were produced by a gas evaporation method, and nanocrystal beams were then formed using an inert-gas flow with differential pumping. We measured photoluminescence spectra of the nanocrystal beams with excitations of various photon energies and powers. For a low excitation power, edge emission of the CdSe nanocrystal beam was observed. With increase of the laser power, Raman lines of Se dimers emitted due to the photodissociation of CdSe nanocrystals were observed. It was found that the thresholds of the excitation laser fluence for the photodissociation of CdSe nanocrystals were much smaller than the thresholds of laser fluence for the laser-induced emission of Se atoms from bulk CdSe. The electronic process is dominant in the photodissociation of CdSe nanocrystals whose surfaces are completely free. We suggest that the effective supply of carriers confined in nanocrystals to the surface state, and the excitations of the completely free surface state induce the photodissociation of nanocrystals by excitation with much weaker irradiation than is required for dissociation of the bulk surface.

1. Introduction

In recent years, nanocrystals of semiconductors, which have various properties different from those of the corresponding bulk materials because of the confinement of the systems, have attracted many researchers. As the diameter of a nanocrystal decreases, and carriers are gradually confined in the nanocrystal in a quantum fashion, the electronic band structure of the bulk is transformed to more discrete electronic states, and the transition energy shifts higher [1–8].

There are electronic surface states of semiconductors in which the lattice periodicity is broken. The surface is the 'stage' at which sublimation, desorption, adsorption, chemical reactions, etc, occur. In addition, at the surfaces of nanocrystals, there are defects, dangling bonds, and bonds with bond lengths longer than those for the bulk, which leads to surface softening. Such a surface softening induces a decrease of the melting points. The surface of a nanocrystal is more important as regards its properties than the bulk, because smaller nanocrystals have larger surface-to-volume ratios. In the case of CdS and CdSe nanocrystals, there is surface luminescence, which is considered to be due to recombination of carriers trapped deeply at localized states on the surface of the nanocrystal [3, 4, 6, 8]. Moreover, the intensity of the surface luminescence becomes dominant over that of the edge emission

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with the decrease of the size [3, 4]. In general, the surface of a nanocrystal is active, and interacts with the surrounding matter strongly. Many scientists have been investigating electrical and optical properties of nanocrystals prepared by various methods such as gas evaporation, co-sputtering, laser ablation, doping in glass, and the colloidal method. The forms of the samples vary with the method of preparation. For example, nanocrystals can be embedded in various matrices such as glasses, polymers, zeolites, porous glasses, and gels. They can also be deposited as granular films or covered with micelles. Thus the condition of a nanocrystal surface is strongly dependent on the surroundings. Therefore, the variation of the condition of a nanocrystal surface with decrease of particle size plays an important role in its properties. Spanhel *et al* [7] have reported that the intensity of the green luminescence of CdS colloid depends upon the pH values of the solution, and Hässelbarth *et al* [8] have exhibited that the fluorescence spectra of CdS colloids change with the addition of nitromethane or methylviologen. In the case of CdSe nanocrystals embedded in GeO_2 glass, Tanaka *et al* have reported an anomalous temperature dependence of the surface luminescence energy, and it has been necessary to consider the influence of the matrix in discussions of the intrinsic optical properties of nanocrystals [3].

In order to investigate the intrinsic optical properties that nanocrystals possess originally, the optical measurements should be carried out for nanocrystals suspended in vacuum. For molecules and clusters, many researchers have measured their optical properties by means of cluster beam. However, because of the experimental difficulties, just a few experiments involving optical measurements for nanocrystals with diameters of hundreds of Å and completely free surfaces have been reported. Mochizuki *et al* [9] have reported the extinction spectra of some semiconductor nanocrystals. To the best of our knowledge, photoluminescence spectra for that kind of nanocrystal have never been reported. The photoluminescence of semiconductor nanocrystals would be of interest, since photoluminescence is sensitive to those surface states.

In this paper, we introduce an apparatus that enables us to measure photoluminescence spectra of nanocrystals suspended in vacuum. We show the photoluminescence spectra of CdSe nanocrystal beams. With increase of the laser power, Raman lines of Se dimers emitted from the nanocrystals appeared. We report the change of the photoluminescence spectrum of the CdSe nanocrystal beam, and the appearance of Raman lines of Se dimers with increase of the excitation power, as evidence of the photodissociation phenomena of CdSe nanocrystals whose surfaces are completely free. We discuss the electronic process of the photodissociation of CdSe nanocrystals. We suggest that the confinement effect of carriers in nanocrystals, and the excitation of the completely free surface state induce the photodissociation of nanocrystals via excitation with much weaker photon irradiation than is required for dissociation in the case of the bulk surface.

2. Experimental procedure

We have developed an apparatus for the purpose of making optical measurements of nanocrystals suspended in vacuum. A general schematic view of the system is shown in figure 1. The apparatus is composed of two main parts: the nanocrystal generation part, and the beam formation and optical measurement part. The nanocrystals are produced by a gas evaporation method in the nanocrystal generation part, which is equipped with a Knudsen cell as the evaporating device and is able to introduce inert gases. The Knudsen cell consists of an inner cell and an outer cell which are made of boron nitride; the outer one is for shading radiation. The inner cell has a cylindrical aperture in its side, 2 mm in diameter, and a tungsten heater. The temperature of the inner cell is measured by a
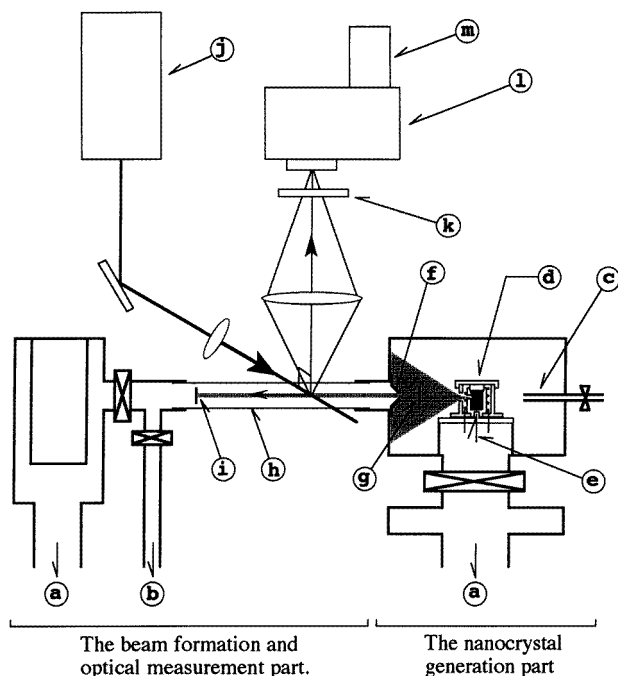
Figure 1. A general schematic view of the system: (a) an oil diffusion pump; (b) a rotary pump; (c) inert-gas injection; (d) the Knudsen cell; (e) the thermocouple; (f) the collimator; (g) the shutter; (h) a quartz glass tube; (i) the substrate; (j) the Ar-ion laser; (k) the holographic notch filter; (l) the polychromator; and (m) the cooled MOS linear image sensor.
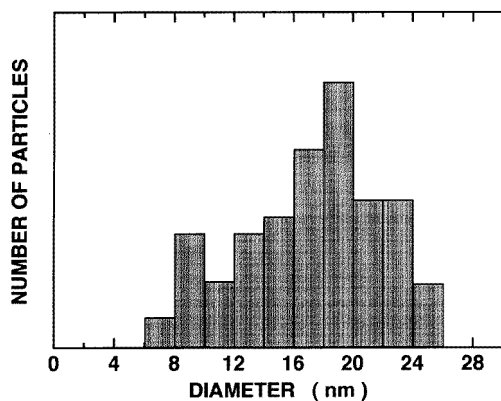
Figure 2. The size distribution of the CdSe nanocrystals composing the beam.

thermocouple. At first, CdSe bulk materials in the Knudsen cell are degassed at 300 °C under 1×10^{-6} Torr for a few hours. Then, in order to produce nanocrystals, the Knudsen cell is heated up to 850 °C in an atmosphere of inert gas over a pressure range from 1×10^2 to 1×10^4 Pa. The nanocrystals produced are introduced into the beam formation and optical measurement part through a collimator (nozzle) of 7 mm diameter by differential pumping. The distance between the Knudsen cell and the collimator is about 30 cm. A nanocrystal

beam is then formed with an inert-gas flow inside a quartz glass tube of 35 mm internal diameter and about 50 cm length. The density and the spread of the beam depend on the inert-gas pressure in the nanocrystal generation part, and the pressure difference between the nanocrystal generation part and the beam formation and optical measurement part. A higher pressure in the nanocrystal generation part tends to lead to the formation of a denser beam, and a larger pressure gradient at the collimator makes the beam spread more. The most suitable gas pressure for forming a dense beam varies with the choice of inert gas. A smaller-mass-number inert gas needs higher pressure. We could continue to produce the CdSe nanocrystal beam, approximately 15 mm in diameter, from the collimator to the end of the quartz glass tube by selecting argon gas and keeping the gas pressure constant, within the range from 1×10^2 to 1×10^3 Pa. The formation of beams could be observed by the naked eye under illumination.

We measured photoluminescence spectra of CdSe nanocrystal beams in the quartz glass tube part using a single polychromator (Jasco CT-25C) system with a cooled MOS linear image sensor unit (Hamamatsu C4834-02) as a detector. Some lines of an Ar$^+$ laser and a Kr$^+$ laser were used to excite the nanocrystal beams. The laser beam which was perpendicular to the nanocrystal beam was focused to a spot 500 μm in diameter. Reflected and scattered laser light from the beams was eliminated by a holographic notch filter installed in front of the incident slit of the polychromator, to avoid stray light in the polychromator that might have caused problems in the measurements of weak photoluminescence components. All of the photoluminescence spectra shown in this paper have been corrected for the character of the sensitivity of the measurement system by making measurements with a halogen standard lamp.

In order to characterize the nanocrystals in the beam, the nanocrystals were deposited either on Si wafers for Raman scattering measurement or on electron microscopic grids for transmission electron microscopy (TEM) of the lower part of the beams.
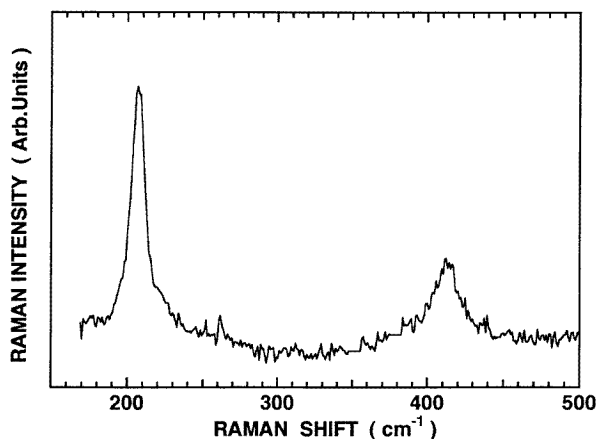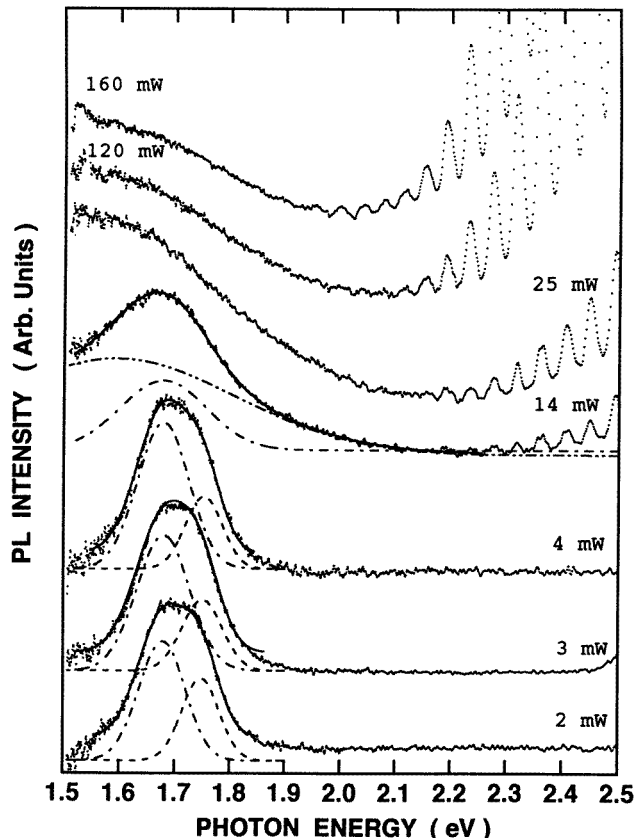

**Figure 3.** The Raman spectrum of the CdSe nanocrystal deposited film.

3. Results

We formed a CdSe nanocrystal beam at the evaporation temperature $T_K = 850$ °C and at the argon-gas pressure $P_{Ar} = 800$ Pa. We analysed the shapes and size distributions of the

Figure 4. Typical photoluminescence spectra of a CdSe nanocrystal beam excited by the 488.0 nm line of an Ar^+ laser (indicated by dots). The solid lines represent best fits to the data obtained using two gaussians. Each gaussian component is indicated by dashed lines.

nanocrystals by TEM imaging. The nanocrystals were almost spherical. We estimated the average nanocrystal size to be 17 nm from the size distribution of the CdSe nanocrystals, as shown in figure 2. It appears that there is a 1LO phonon peak at 207 cm^{-1}, and a 2LO phonon peak at 414 cm^{-1} for CdSe, but no phonon peaks of the selenium chain (230 cm^{-1}) or ring (250 cm^{-1}) in the Raman spectrum of the deposited films, as shown in figure 3. The linewidth (FWHM) of the 1LO peak is about 10 cm^{-1}, which is as narrow as that for bulk CdSe. Therefore, we ascertained that the beams were composed of only CdSe nanocrystals, without selenium molecules, and that the crystallinity of the CdSe nanocrystals was as good as that of bulk CdSe. Figure 4 shows typical photoluminescence spectra of a CdSe nanocrystal beam which were obtained with various excitation powers of the 488.0 nm line of an Ar^+ laser. When the excitation power is lower than about 10 mW, a broad peak is observed at 1.7 eV. With the excitation power higher than 14 mW, many narrow peaks appear in the high-energy region, and the broad peak at 1.7 eV is overwhelmed by a peak at below 1.5 eV, which seems to be new. We carried out the same experiments for various excitation energies, i.e., 457.9 nm, 476.5 nm, and 514.5 nm, of the Ar^+ laser and the energy 647.1 nm of a Kr^+ laser. Whenever we chose any of the three lines of the Ar^+ laser, we obtained similar spectral changes with excitation power to those described above.
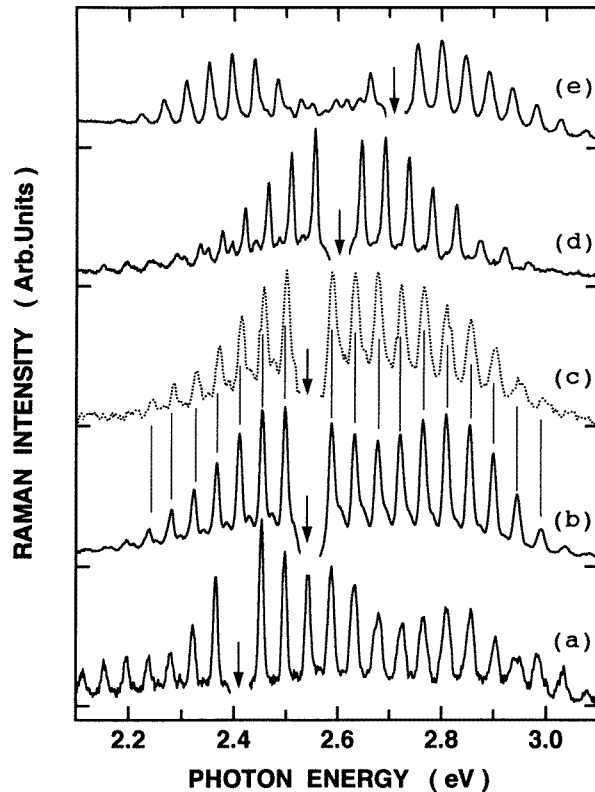
Figure 5. Photoluminescence spectra of a CdSe nanocrystal beam excited strongly by the (a) 514.5 nm, 170 mW, (b) 488.0 nm, 160 mW, (d) 476.5 nm, 75 mW, and (e) 457.9 nm, 60 mW lines of an Ar^+ laser, and (c) photoluminescence spectra of a Se cluster beam excited by the 488.0 nm line. The excitation energies are indicated by arrows in the figure. The peak energies of spectrum (b) and spectrum (c) coincide.

As shown in figure 5, many narrow peaks were also observed in the region in which the energy is higher than the excitation energy. Also, the envelopes of the peaks varied with the excitation energy. We formed a Se cluster beam at $T_K = 400\ °C$ and $P_{Ar} = 400$ Pa. We show the spectrum of the Se cluster beam excited strongly by the 488.0 nm line in figure 5(c). Comparing the Se cluster beam (c) and the CdSe nanocrystal beam which was excited with the same energy (b), we see that all of the peak energies coincide. All of the peaks align over almost the same energy interval from the excitation energies. The peak intervals are evaluated as approximately 44 meV for all of the spectra excited by the four lines. This value is in good agreement with the 355.8 cm^{-1} (44.1 meV) vibrational energy of the Se dimer on about the 15th vibrational energy level [10–12]. We regarded the series of peaks as Raman lines of Se dimers.

To discuss carefully the spectral changes with excitation power, we fitted the broad peak at 1.7 eV with two gaussians as shown in figure 4. The higher peak at 1.75 eV is regarded as edge emission. The peak energy is a little higher than that of bulk CdSe: 1.74 eV at room temperature, because the exciton is confined in the nanocrystals, whose average diameter corresponds to an 'exciton confinement region' [5]. The lower one at 1.68 eV is considered to be due to recombination of the carriers trapped shallowly at Se^+ vacancies [13] in the
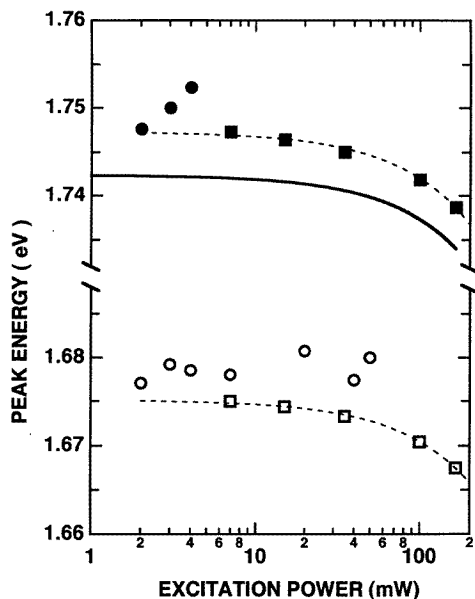
Figure 6. Changes in the peak energies of the edge emission (●), emission at Se^+ vacancies (○) of the CdSe nanocrystal beam and edge emission (■), and emission of Se^+ vacancies (□) of the CdSe nanocrystal deposited film and edge emission of bulk CdSe (solid line) with excitation power.

nanocrystal. The peak energies are plotted in figure 6 as functions of the excitation power together with those of bulk CdSe (solid line) and the CdSe deposited film (represented by the symbols ■ and □). The peaks of both the bulk and the deposited film shift toward lower energies with increase of the excitation power. This observation can be explained in terms of the narrowing of the band gap due to the increase of the internal temperature of the nanocrystals induced by laser irradiation. We estimated the temperature rise of the nanocrystals to be 6 °C for the excitation power 50 mW using the temperature coefficient of the band gap for bulk CdSe: 0.363 meV K^{-1} [13]. On the other hand, the edge emission and the Se^+-vacancy emission of the nanocrystal beam do not show red-shifts with increase of the excitation power. The results suggest that the internal temperature rise of CdSe nanocrystals suspended in vacuum is trivial for excitation powers up to 50 mW.

In the case of excitation at 647.1 nm, as shown in figure 7, there were no remarkable changes in the spectra, except for a slight red-shift of the edge emission peak, despite the strength of the excitation power.

4. Discussion

The excitation power dependence of the photoluminescence spectra of CdSe nanocrystal beams can be explained as follows. The disappearance of the edge emission band at 1.75 eV and the appearance of many sharp peaks for excitation powers higher than 14 mW are caused by the emission of Se dimers from CdSe nanocrystals. Although Cd atoms must be emitted simultaneously [14], we cannot detect such atomic species by Raman scattering.

The mechanism of emission of atoms composing nanocrystals induced by photo-excitation is of great interest. Some experiments involving laser-induced desorption or
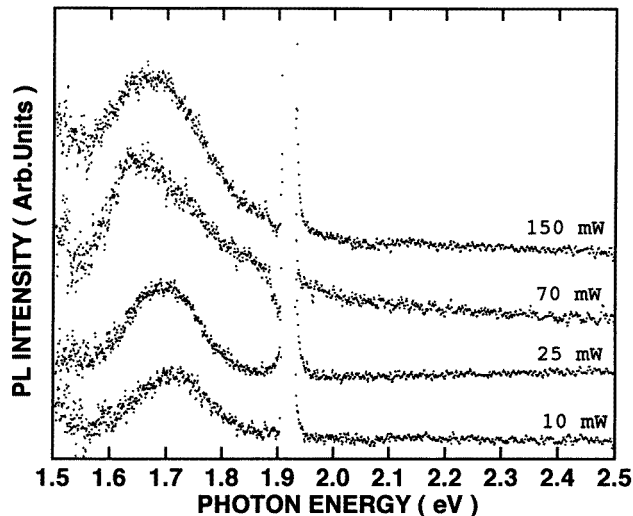
Figure 7. Typical photoluminescence spectra of a CdSe nanocrystal beam excited by the 647.1 nm line of a Kr$^+$ laser.

laser ablation from the bulk surface of II–VI compounds [14–16] have been performed, and some explanations have been given. Two major factors as regards laser-induced desorption or laser ablation have been suggested. One is the thermal factor: heat produced by the non-radiative transition of carriers excited by photons melts the local surface region. The other is the non-thermal factor: excited carriers induce the emission of surface atoms electronically. In the case of laser-induced emission from the bulk surface of II–VI compounds, it was reported that the emitted species did not simply obey the Maxwellian distribution, and the translational temperatures characterizing the distribution are lower than the melting points [14, 15]. It is thought consequently that multisteps including electronic processes and thermal processes are associated with laser-induced emission of surface atoms of II–VI compounds. Though it is very difficult to evaluate the internal temperature of a nanocrystal suspended in a vacuum, we estimate that the internal temperature is almost room temperature by comparing the value of the band-gap energy observed at photoluminescence in low-power excitation with that of bulk CdSe. As mentioned already in the previous section, the internal temperature rise of a CdSe nanocrystal suspended in a vacuum with increase of the excitation power is very small. This suggests that the thermal factor in laser-induced emission of a nanocrystal can be smaller than that of the corresponding bulk.

In figure 8, the threshold excitation power for the emission of Se dimers from CdSe nanocrystals is shown for each excitation photon energy. In this diagram the symbol □ is plotted when the edge emission peaks of CdSe nanocrystals are observed and the symbol ● is used when a series of Raman lines of Se dimers is observed. The excitation powers were reduced to excitation laser fluences that are given as numbers of photons per cm^2 and per mean exposure time. The mean exposure time t was evaluated using the velocity of the beam V and the laser spot size D, from $t = D/2V$. We estimated t to be about 0.5 ms by using the values $D = 500$ μm and $V = 50$ cm s^{-1}. Figure 8 shows that the threshold excitation laser fluence depends upon the excitation energy. Nakayama reported a similar photon energy dependence of the threshold laser fluence for laser-induced emission of Se atoms from bulk CdSe [14]. In his report, the yield of the emitted species from the bulk
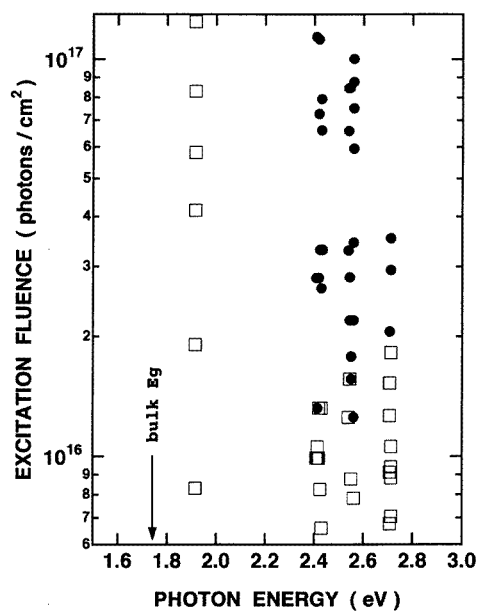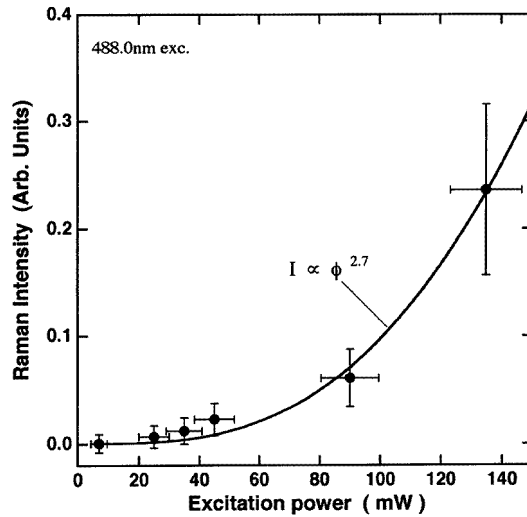
Figure 8. The excitation energy dependence of the threshold excitation fluence of the laser-induced emission of Se dimers from a CdSe nanocrystal beam. The symbol □ is used when the edge emission peaks of CdSe nanocrystals are observed, and the symbol ● is used when a series of Raman lines of Se dimers are observed.

surface irradiated by a 10 ns pulse of a laser was measured by means of the time of flight (TOF). Our threshold excitation laser fluence of 1.5×10^{16} photons cm^{-2} at 514.5 nm is only a tenth of the magnitude of Nakayama's threshold excitation laser fluence of 1.28×10^{17} photons cm^{-2} at 510 nm. Since Raman scattering measurements are less sensitive than TOF ones for detecting emission of species, a Se dimer is likely to be emitted from CdSe nanocrystals with an even smaller photon density than the value estimated above from the Raman scattering.

We think that the large surface-to-volume ratio makes the nanocrystals easy to dissociate by weak laser irradiation. Firstly, because of the increase of the surface-to-volume ratio with nanocrystallization, the absolute area of the surface at which sublimation occurs increases drastically. The excited electrons in nanocrystals decay through either non-radiative or radiative recombination. The non-radiative recombination would bring about lattice heating, which results in sublimation. However, we did not observe a rise of the internal temperature. Thus non-thermal processes become important for understanding our results. Various non-thermal models of the laser-induced desorption or laser ablation mechanism have been proposed for bulk solid [17]. In the case of solids with strong electron–lattice coupling, it was proposed that self-trapping of excitons distorts the lattice, and that this results in the emission of surface atoms [17]. In the case of solids with weak electron–lattice coupling, such as CdSe, Itoh and Nakayama [18] suggested that a localized pair of two holes at the same site is formed by an Anderson negative-U interaction [19] in dense electron–hole plasma, which contributes to a mutual approach caused by the screening of the Coulomb repulsion force between two holes, and induces the emission of surface atoms from the bulk. However, in our CdSe nanocrystal, the density of electron–hole plasma would not be enough to screen the repulsion force effectively, because our threshold excitation laser flux

of 3.0×10^{19} photons cm^{-2} s^{-1} at 514.5 nm is only a millionth of Nakayama's threshold excitation laser flux of 1.28×10^{25} photons cm^{-2} s^{-1} at 510 nm.

Figure 9. The excitation power dependence of the Raman intensity of a Se dimer. The intensity of the first-order Stokes Raman line of the Se dimer is plotted as a function of the excitation power.

Some kinds of relaxation of the bonding at the surfaces of nanocrystals occur: for example, extension of the bond length, dangling bonds, adatoms, kinks, and vacancies. These lead to the formation of surface states peculiar to nanocrystals. They would work as trapping sites. In radiative recombination processes of the nanocrystal, some of the excited carriers—probably holes—are quickly trapped at surface states, and then recombine with long lifetimes [20], and the others directly recombine inside nanocrystals as edge emission. The surface states have a limited number of trapping centres, so they are rapidly saturated with carriers [21]. The supply of a second hole trapped at the same centre will weaken the soft bonding of the surface atoms further. This further softening of bonds leads to the emission of Se dimers and Cd atoms. The intensity of the first-order Stokes Raman line of the Se dimer is plotted as a function of excitation power in figure 9. As shown in figure 9, the Raman intensity I_R increases as a superlinear function of the excitation power ϕ. The relationship of the Raman intensity I_R and the excitation power ϕ can be expressed as $I_R \propto \phi^m$. The power index m is about 3 in our experiments. Provided that the Raman intensity is proportional to the excitation power, because the excitation is not too strong, the Raman intensity I_R is given as the following function of the excitation power ϕ and the number of emitted Se dimers Y: $I_R \propto Y\phi$. Therefore, the number of emitted Se dimers Y is expressed as a superlinear function of the excitation power ϕ: $Y \propto \phi^{m-1}$. We have found that the number of Se dimers emitted from CdSe nanocrystals depends superlinearly on the excitation power, and that the power index is about 2. It has been reported that the excitations of surface defect states by the trapping of holes induce the emission of surface atoms effectively, and that there are superlinear dependences with power indices 2–6 of the emission yields on the laser fluence in bulk GaP and GaAs [22–24], and Hattori *et al* explained the power indices as representations of the multiplicity of the excitations of surface defect states [22]. On the other hand, in the case of laser ablation induced by dense

electron–hole plasma, it has been reported that the power index is larger than 10 [22, 24]. Therefore, the power index 2 for CdSe nanocrystals in this work corresponds to the former model in which the excitations of surface defect states induce the emission of surface atoms. We think that the threshold laser powers in this work are needed to saturate the surface states with one hole per trapping centre, and the additional excitations induce the emission of Se dimers. Whereas most of the carriers excited near the surface region of the bulk solid diffuse into the inside, carriers excited in nanocrystals would continue to be provided to the trapped states of the surface, because of the confinement effect of nanocrystals. This would be why CdSe nanocrystals with completely free surfaces can be dissociated by much weaker photon irradiation than is required to dissociate the bulk surface.

In the case in which the emission of constituent atoms is prevented by the environment— for example, in the deposition films of CdSe nanocrystals—the localized surface states are filled with carriers, and thus the radiative or non-radiative decay of excited electron–hole pairs is dominant. Non-radiative decay raises the internal temperature.

In summary, we have developed an apparatus which enables us to produce nanocrystals with free surfaces for the purpose of investigation of the photon–nanocrystal interaction. We have measured photoluminescence spectra of CdSe nanocrystals suspended in vacua by means of forming nanocrystal beams. The CdSe nanocrystals are dissociated, and emit Se dimers as a result of much weaker laser irradiation than is required to dissociate the bulk. This process does not involve an internal temperature rise in the nanocrystals. In the case of photodissociation of CdSe nanocrystals, the dense trapped holes at the surface play a more important role than the thermal effect.

Acknowledgment

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