

Photoluminescence properties of single CdSe quantum dots in ZnSe obtained by self-organized growth

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 L171

(<http://iopscience.iop.org/0953-8984/10/10/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 16:14

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Photoluminescence properties of single CdSe quantum dots in ZnSe obtained by self-organized growthM Y Shen[†], T Goto[†], E Kurtz[‡], Z Zhu[‡] and T Yao[‡][†] Department of Physics, Tohoku University, Sendai 980, Japan[‡] Institute for Materials Research, Tohoku University, Sendai 980, Japan

Received 17 November 1997, in final form 5 December 1997

Abstract. The photoluminescence of single CdSe quantum dots in ZnSe grown by molecular beam epitaxy and that of the same system grown by atomic layer epitaxy were investigated. The spectral diffusion and on/off behaviour of single CdSe quantum dots were observed, and the spectral diffusion range was only about 1 meV. The spectral peak shifting became quicker as the temperature rose. The spectral change from blue-shift to red-shift (or vice versa) was much quicker than that found in CdSe quantum dots synthesized as colloids. The phenomena are qualitatively explained by a Stark effect which originated from an Auger ionization process. The spectral diffusion may be a common property among single quantum dots.

Because of their fundamental properties and their potential applications, quantum dot systems have been intensively investigated. The properties of such systems are governed by the properties of each single quantum dot. The luminescences of single quantum dots have more potential to reveal intrinsic properties, because the luminescence of a dot ensemble is normally obscured due to the averaging of a large number of dots. It is especially valuable when the intrinsic dot dynamics is sensitive to the local environment. Although atom-like sharp photoluminescences of single quantum dots at low temperatures have been observed in a GaAs/AlGaAs system [1], an InAs/GaAs system [2], a CdSe/ZnSe system [3], and a system of CdSe nanocrystallites synthesized as colloids [4, 5], the detailed profiles differ from each other. The spectral shift of the emission energy and on/off behaviour are found only in single CdSe nanocrystallites synthesized as colloids. Thus there is a potential limitation on optical devices based on such CdSe nanocrystals, for which fast response time and high luminescence efficiency are crucial [5]. But the investigation of single quantum dots may uncover the difficulties to be overcome in order to fulfil applications needs, and also show the fundamental properties of a single micro-system which is sensitive to the local environment. In this work, we investigate single CdSe quantum dots in ZnSe, which is similar to an InAs/GaAs system obtained by self-organized growth. We found that the spectral peak shifted more quickly when the temperature rose and/or when the excitation light power increased. The spectral change from blue-shift to red-shift (or vice versa) was much quicker than that found in CdSe quantum dots synthesized as colloids [4]. The spectral diffusion range was more than ten times smaller than that found in CdSe quantum dots synthesized as colloids. The spectral diffusion may be a common property among single quantum dots.

The sample system of single quantum dots studied in detail was grown by molecular beam epitaxy (MBE). The CdSe quantum dots were obtained in a similar fashion to InAs quantum dots on GaAs [2]. A ZnSe buffer layer of 120 nm thickness was grown onto

(100) GaAs at 300 °C. The quantum dots were formed after deposition of about three monolayers (ML) of CdSe using elemental sources under Cd-rich conditions at 300 °C. The island formation was clearly indicated by a transition from a streaky two-dimensional (2D) RHEED (reflection high-energy diffraction) pattern to a typical spotty 3D pattern. To obtain a higher uniformity of dots, two quantum dot sheets were stacked with a ZnSe spacer of 12 nm and a cap layer of 50 nm. The total thickness of the structures was kept below 200 nm to avoid relaxation of the barrier material. The other sample of single quantum dots was prepared by the method of growing a ZnSe layer using MBE, while growing the CdSe layer by atomic layer epitaxy (ALE). The above two samples have the same photoluminescence properties as single quantum dots. In the following, we only give the photoluminescence results for the former sample grown by MBE. More details of the method of sample preparation are given separately [6].

The cw photoluminescence (PL) spectra were obtained by using an Ar⁺-ion laser which was in power control mode in order to keep the laser light intensity at the sample surface constant. The laser beam was first 'cleaned' by a prism and an aperture, and then focused through a microscope objective lens onto the sample mounted in an Oxford microscope cryostat. The laser light spot diameter was about 1 μm and the power density was about 1 kW cm⁻² on the sample surface. The PL signal was collected through the same microscope objective lens, dispersed by a triple monochromator and detected by a charge-coupled device (CCD) cooled by liquid nitrogen.

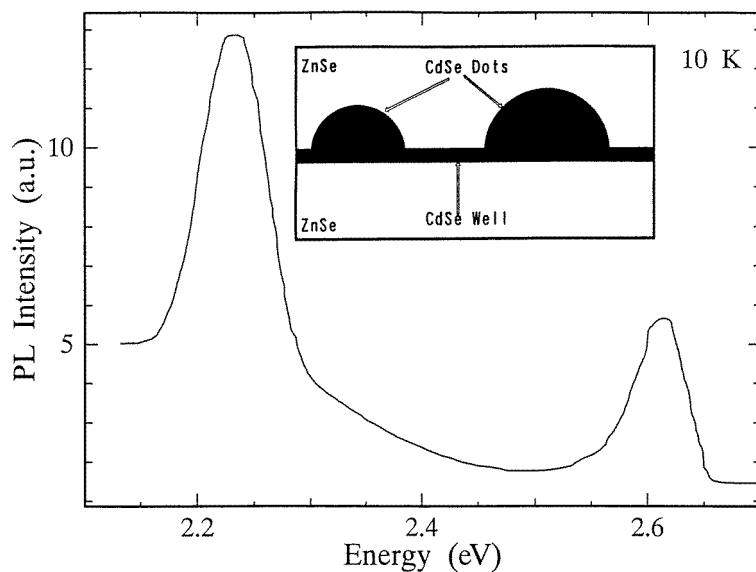


Figure 1. The conventional photoluminescence spectrum of the sample studied in this work excited by 325.0 nm light at 10 K. Inset: a schematic diagram of the structure of the samples grown by MBE and ALE.

Figure 1 shows a conventional photoluminescence spectrum of the sample studied excited by 325.0 nm light at 10 K. The inset in the figure shows the structure of the CdSe dots and well, covered by ZnSe layers. The peak at about 2.6 eV arose from the two-monolayer CdSe well. The peak at about 2.23 eV was considered to be due to the luminescence of the CdSe dots.

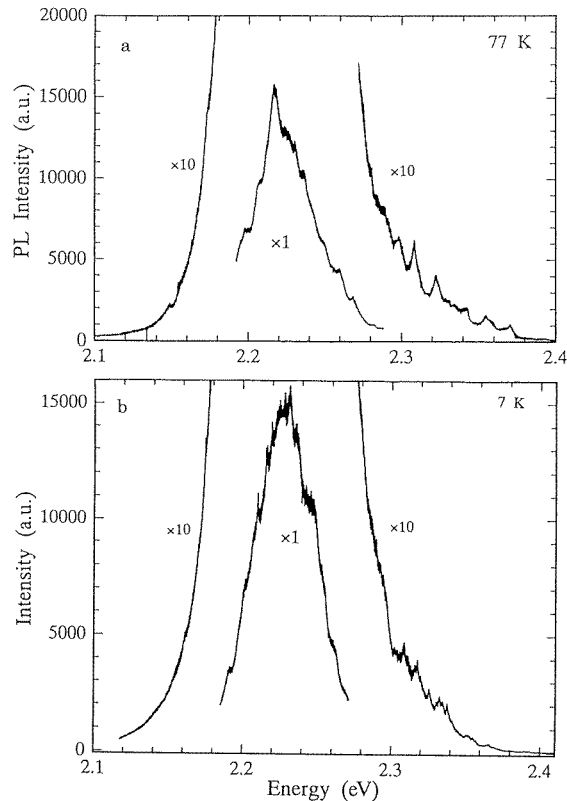


Figure 2. The microscopic photoluminescence spectrum of the sample excited by 476.5 nm light, (a) at 77 K with a four-second integration time, and (b) at 7 K with a one-second integration time. The laser light power density was 5 kW cm^{-2} on the sample surface, and the spectral resolution was 0.1 meV.

In the experiment, we used a 476.5 nm (2.602 eV) laser line of an Ar^+ laser in order to resonantly excite the excitons in the two-monolayer well, and then transferred the excitons to the dots. In this way, excitation in the ZnSe layers could be prevented, and thus influences from defects in the ZnSe layers could be avoided. Figure 2(a) shows the microscopic photoluminescence of the sample excited by the 476.5 nm light at 77 K with a four-second integration time. The luminescence spectrum consisted of many small peaks. These peaks were considered to be due to the luminescences of single CdSe quantum dots. Figure 2(b) shows the microscopic photoluminescence of the sample excited by the 476.5 nm light at 7 K with a one-second integration time. The luminescence spectrum consisted of many small peaks sharper than those shown in figure 2(a) obtained at 77 K.

Figure 3 shows two consecutive four-second-integration spectra expanded over a smaller energy range on the higher-energy side of the main structure of figure 2(a) at a given position of the sample obtained at 77 K. The time interval between the two spectra was four seconds. Notice that the spectral shape changes significantly as time goes on. Figure 4 shows a series of one-second-integration spectra on the high-energy side of the main structure of figure 2(b) obtained at 7 K. The time interval between two consecutive spectra was 15 seconds. Sharp peaks (for example the peak labelled A) with FWHM less than 1 meV are clearly shown in figure 4. From this figure we can see that the energy of the sharp peaks shifts and the intensity changes with time. We also found that, as the exciting light power decreases, the peaks became sharper (this is not shown in this article). These findings were similar to those found with CdSe quantum dots synthesized as colloids [4], but the peak energy shifts were random here, and the spectral change from blue-shift to red-shift (or vice versa) was

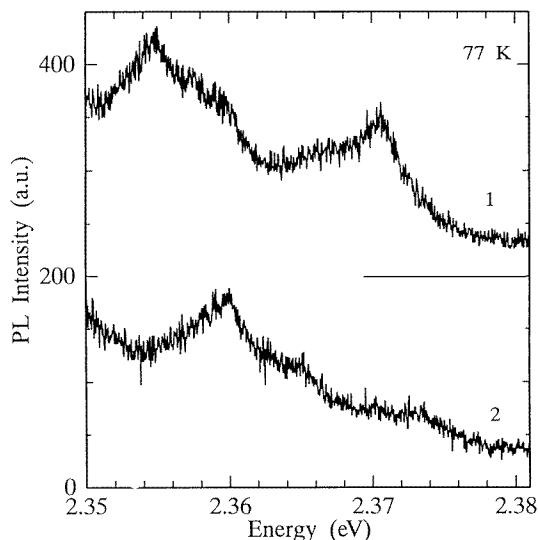


Figure 3. Two consecutive four-second-integration spectra on the high-energy side of the main structure in figure 2(a) at a given position of the sample at obtained 77 K, with excitation by 476.5 nm laser light. The laser light power density was 5 kW cm^{-2} , and the time interval between the two spectra was four seconds. The spectral resolution was 0.1 meV.

one order of magnitude quicker here. In addition, the spectral diffusion range was only about 1 meV, which was much smaller than that ($>10 \text{ meV}$) found in reference [4]. Notice that the speed of the shift increases as the temperature rises.

In the experiment, we found that the energy of the sharp peaks in figure 4 changed with a jump when the position of the sample was slowly moved. That is to say, when the position of the sample was slowly moved, peak A disappeared suddenly, peak B or C became stronger or disappeared, or another peak appeared suddenly. The sharp peaks are position dependent. We also found that when the size of the laser light spot was large (for example, $10 \mu\text{m}$), the sharp peaks disappeared in the broad spectral band in figure 2. These features are strong evidence that the observed sharp spectral peaks originated solely from single CdSe quantum dots. There is no other reasonable explanation for these experimental results. Considering that the measured spectral width of a single CdSe dot is about 1 meV and the width of the broad band in figure 2 is about 300 meV, the number of CdSe quantum dots can be estimated to be much smaller than one thousand in a probe spot of diameter $1 \mu\text{m}$.

Spectral diffusion leads to a measurable luminescence linewidth of a single quantum dot at low temperature. This spectral diffusion was first observed in single-molecular spectra [7]. The spectral diffusion and the on/off behaviour may be caused by changes of (1) temperature, (2) the stress field, (3) the magnetic field, (4) many-body effects, and/or (5) the electric field. The spectral diffusion at about 1 meV corresponded to a temperature change of less than 3 K, estimated from the band-gap temperature coefficient. With such small temperature changes, the PL intensity change could not be as large as that shown in figure 4. Thus the temperature effect could not lead to the observed phenomena. Likewise, in the present experiment, the changes in the stress field and the magnetic field were negligible. Thus the changes in the stress field and the magnetic field also could not lead to the observed phenomena. The many-body effects occur when a dot is highly excited, and there are many photogenerated carriers in the dots. In this case the optical properties will differ

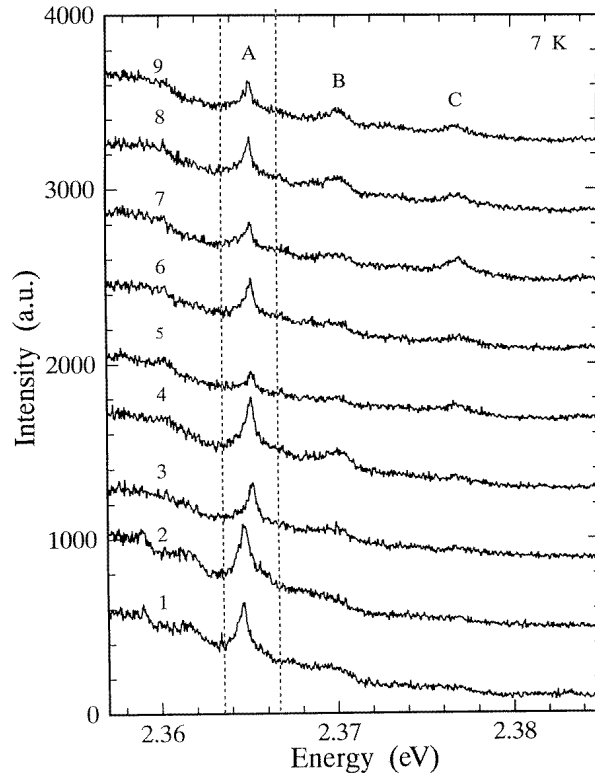


Figure 4. A series of one-second-integration spectra on the high-energy side of the main structure in figure 2(b) at a given position of the sample obtained at 7 K, with 476.5 nm laser light. The laser light power density was 5 kW cm^{-2} , and the time interval between two consecutive spectra was 15 seconds. The spectral resolution was 0.1 meV. The two vertical dotted lines were drawn as references for looking at the spectral shifts. The peaks labelled A, B and C may result from different single CdSe dots.

from those of a slightly excited dot. The lifetime of this effect is less than a nanosecond. However, the excitation in the present experiment was low, so not many carriers could be generated in a dot, and the phenomena could be observed on a seconds timescale. Thus the many-body effect cannot explain the observed spectral diffusion and the on/off behaviour. A change in the electric field around each dot may have been the cause of the observed phenomena. The spectral diffusion and the on/off behaviour of single microcrystallites have been qualitatively explained as due to a Stark effect [4]. The Stark effect results from a possible Auger ionization process that may be a cause of the photodarkening effect in microcrystallites [5, 8]. We have recently proved the existence of an Auger ionization process in CdTe nanocrystallites through photocurrent and photoluminescence experiments [9]. Therefore, we use the Stark effect and Auger ionization models to qualitatively explain the observed spectral diffusion and the on/off behaviour in the present work. After an electron (or a hole) leaves a quantum dot, the photogenerated electron and the hole in the dot will be influenced by the electric field created by the free electron in the vicinity of the dot. When the free electron (or hole) is recaptured by the dot, the electric field no longer has any influence on it. The migration of the free electron (or hole) outside the ionized dot is very important. The thermal energy of the free electron (or hole) becomes

larger than the trapping energy of some trapping centres as the temperature rises. Then, the electron (or hole) migrates easily, and thus goes back to the dot quickly as temperature rises. Therefore, the shift of the luminescence peak energy becomes quicker as the temperature rises from 7 K to several tens of K, as observed in figures 3 and 4. As the temperature rises, changes in the local environment occur more quickly. Consequently, at 77 K each individual peak in figure 3 was much wider than each peak obtained at 7 K in figure 4, and the two consecutive spectra of figure 3 were likewise different in shape. The fact that the change from the spectral blue-shift to a red-shift (or vice versa) was much quicker than that found in CdSe nanocrystallites synthesized as colloids [4] can be understood on the basis of the fact that the matrix outside the CdSe dots in our sample was ZnSe, while that in reference [4] was organic material. The migration of the free electrons outside the dot may have been quite different in the two cases. A free electron may have moved more easily in the ZnSe than it did in the organic material in reference [4]. The sample structure of the present CdSe dot system was very similar to that of the InAs dot system in reference [2], but spectral diffusion was not observed in InAs dots. This may have resulted from the fact that the photodiode measurement system in reference [2] was not able to detect a small spectral shift. If Auger ionization is an inevitable process, spectral diffusion may be a common property among single quantum dots.

In summary, we have presented photoluminescence data for CdSe quantum dots in ZnSe grown by the molecular beam epitaxy method. The atom-like photoluminescence line spectrum of single CdSe dots was observed. The photoluminescence spectral diffusion and the on/off behaviour of single CdSe quantum dots were observed. The spectral peak shift became quicker as the temperature rose or the excitation light power increased. The spectral change from blue-shift to red-shift (or vice versa) was much quicker than that found for CdSe quantum dots synthesized as colloids. The spectral diffusion range was more than ten times smaller than that found for CdSe quantum dots synthesized as colloids. These phenomena were qualitatively explained in terms of Auger ionization of the photogenerated electrons and the Stark effect due to electrons trapped outside the dots. Spectral diffusion may be a common property among single quantum dots.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

- [1] Brunner K, Bockelmann U, Abstreiter G, Walther M, Bohm G, Trankle G and Weimann G 1992 *Phys. Rev. Lett.* **69** 3216
Grundmann M *et al* 1995 *Phys. Rev. Lett.* **74** 4043
- [2] Marzin J-Y, Gerard J-M, Izrael A, Barrier D and Bastard G 1994 *Phys. Rev. Lett.* **73** 716
- [3] Flack F, Samarth N, Nikitin V, Crowell P A, Shi J, Levy J and Awschalom D D 1996 *Phys. Rev. B* **54** R17 312
- [4] Empedocles S A, Norris D J and Bawendi M G 1996 *Phys. Rev. Lett.* **77** 3873
- [5] Nirmal M, Dabbousi B O, Bawendi M G, Macklin J J, Trautman J K, Harris T D and Brus L E 1996 *Nature* **383** 802
- [6] Kurtz E, Zhu Z and Yao T 1998 to be published
- [7] Moerner W E 1994 *Science* **265** 46
Trautman J K, Macklin J J, Brus L E and Betzig E 1994 *Nature* **369** 40
- [8] Chepic D I, Efros Al L, Ekimov A I, Ivanov M G, Kharchenko V A, Kudriavtsev I A and Yazeva T V 1990 *J. Lumin.* **47** 113
- [9] Shen M Y, Oda M, Yokouchi T, Koyama S and Goto T 1998 to be published