Strong confinement of PbSe and PbS quantum dots

doi: 10.1016/S0022-2313(99)00220-3

Journal of Luminescence 87-89 (2000) 491-493

Strong confinement of PbSe and PbS quantum dots

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We synthesized PbSe and PbS quantum dots in strong-confinement regime, and measured energy relaxation time by using pump-and-probe experiments. Energy relaxation time of PbSe dots in phosphate glasses showed clear correlation with the average radius. Smaller dots were shown to have shorter decay times. This dependence is ascribed to the relaxation to the surface of the dots.

PbSe, PbS, quantum dots, strong confinement

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1. Introduction

The electronic and optical properties of semiconductor quantum dots have recently attracted much attention due to their interesting physical nature and potential utility in applications. Most researches have been done in II-VI or III-V semiconductors. Compared to these materials, IV-VI semiconductors such as PbSe and PbS have larger exciton Bohr radius (46 nm for PbSe and 18 nm for PbS). Thus in PbSe or PbS quantum dots, we can expect large strong-confinement effect, which cannot be accessed in other materials. In addition, PbSe and PbS quantum dots can have absorption peak in the 1~2 μm range, which is important for telematiks and technology applications. In this paper, we report the synthesis of PbSe and PbS quantum dots, as well as decay-time measurements at room temperature. We present a clear dependence of the carrier lifetime against radius, and clarify the importance of the relaxation to the surface of the dots.

2. PbSe and PbS quantum dots

We fabricated PbSe or PbS quantum dots in phosphate glasses. The composition of the glass, P_2O_3-Ga_2O_3-ZnO-AlF_3-Na_2O, was used, since low glass formation temperature is preferred due to high volatility of the chalcogenides [1]. The glass batch including the semiconductor was melted around 1000℃. After the quenching, transparent pieces were annealed around 400℃ for several minutes or hours. The annealing led to brownish or black coloring of the glass samples. Average radius was controlled by the annealing temperature and duration.

Optical absorption spectra of PbSe quantum dots measured at room temperature are shown in Fig. 1. In addition to the lowest absorption peaks (full arrows), the spectra show second and third peaks (dashed arrows), which indicate relatively small size distribution of these

samples. Depending on the annealing conditions, the lowest peaks are located between 0.84 and 1.47 eV. These exciton transition energies correspond to average radius of (a) 3.2 nm, (b) 2.9 nm, (c) 2.5 nm, (d) 2.4 nm, (e) 2.2 nm, and (f) 2.0 nm, following the calculated results by using the envelope-function formalism [2] [3].

Figure 2 shows room temperature absorption spectra of PbS quantum dots. Spectra of (i) – (iv) are ones of PbS in phosphate glasses. Average radii are estimated to be (i) 10 nm, (ii) 6.0 nm, (iii) 3.0 nm, and (iv) 2.2 nm [2]. We tried also to synthesize PbS dots in poly(vinyl alcohol) PVA [4]. H_2S gas was injected into the distilled water containing PVA and $Pb(CH_3CO_2)_2$. Then the solution was dropped on a glass plate, and PbS quantum dots in PVA were obtained after the water was dried. Spectrum (v) shows their absorption spectrum. The peak at 2.12 eV corresponds to the radius of 1.3 nm, which was confirmed by the transmission-electron-microscope observation. Controlling the average radius of PbS dots in PVA was not successful.

The ratio of radii r evaluated for our PbSe and PbS quantum dots and Bohr radius a_B gives r/a_B ranging from 0.04 to 0.07 for PbSe, and from 0.12 to 0.6 for PbS in phosphate glasses (0.07 for PbS in PVA). Thus the set of the samples synthesized is suitable for the study of the quantum dots behavior in the strong confinement regime.

3. Energy relaxation in PbSe quantum dots

One of the possible applications of media embedded with quantum dots is based on using fast carrier lifetimes for the design of optical processing devices. However, the lifetime, especially at room temperature, is often determined by nonradiative carriers relaxation. The lifetime is subjected to “sample quality”, and it is not easy to control it. This situation somehow prevents systematic study necessary for designing the promising material. As a

way of overcoming the situation, we use the set of the PbSe quantum dots samples. In these samples, we demonstrate the systematic change of the lifetime, and clarify the importance of the relaxation to the surface.

We measured energy relaxation times by using pump-and-probe experiments. A regenerative amplifier of a titanium sapphire laser was used. For the pump beam, we used the second harmonics (3.1 eV). An optical parametric amplifier (the idler) was used to obtain the probe beam, which was resonant with the lowest exciton transition energy (full arrows in Fig. 1). The pump beam density at the sample surface was ~5 $\mu J/cm^2$, and the probe beam density was less than 1/10 of the pump. The time resolution was ~0.5 ps.

Figure 3 shows the differential transmission of PbSe dots at room temperature. The temporal profiles of (a)-(f) correspond to the samples shown in Fig. 1(a)-(f), respectively. Since the average radius is from (a) 3.2 nm (the largest) to (f) 2.0 nm (the smallest), smaller dots are found to show faster decays. The profiles can be fitted by two-exponential decays (see the figure and the caption). The shorter lifetime τ_1 decreases monotonically from (a) 25 ps to (f) 1 ps. The longer lifetime τ_2 is in the range of 30 ~ 1000 ps.

When we excited these samples by an argon ion laser (2.4 eV), exciton-related luminescence was observed between 12 K and room temperature. The Stokes shift was ~100 to ~300 meV. The luminescence is thought to be originated from the exciton localization at the surface [5]. The luminescence intensity at room temperature was decreased to ~1/10 of that at 12 K. This means the presence of the nonradiative process at room temperature.

There are several reports on differential transmission having two-exponential decays in quantum dots systems. Fast decays are often attributed to the relaxation processes of free carriers, and slow decays to that of trapped carriers. Considering the presence of

Stokes-shifted luminescence in PbSe dots, we assume that shorter decay times τ_1 are ascribed to free-carrier relaxation determined by the nonradiative decay and the transition to the luminescing surface state. Longer decay times τ_2 are assumed to be due to the relaxation of the surface states.

As for the shorter decay times τ_1 obtained in Fig. 3, we see clear correlation with quantum-dot radius. Smaller quantum dots have shorter decay times. This seems quite natural because smaller dots have larger surface/volume ratio. Among the samples with different average radius, we assume a constant surface thickness in which luminescing states and nonradiative centers are thought to be located. Smaller dots have larger surface/volume ratio. Then the shorter decay time is expected in smaller dots, and the obtained dependence of the decay time on the average radius can be understood by this consideration. Detailed studies are in progress.

We do not see clear correlation between dot radius and the longer decay times τ_2 which was ascribed to the relaxation at the surface. This can be expected, because the relaxation at the surface should not correlate with dot radius but with the surface "quality". However, relatively poorer reliability of longer decay components in Fig. 3 prevents us from further discussion here.

4. Conclusion

We fabricated PbSe and PbS quantum dots. The ratio r/a_B ranges from 0.04 to 0.6, which is in extremely strong confinement regime. In the set of PbSe dots with different average radius, energy relaxation times were measured by differential transmission. The smaller dots showed faster relaxation. This result is explained by the relaxation to the surface which occupies larger volume ratio in smaller dots.

Acknowledgements

T.O. acknowledges the Kurata Foundation, and A.L. thanks JSPS, for the financial support.

References

[1] A. Lipovskii et al., Appl. Phys. Lett. **71** (1997) 3406.

[2] I. Kang and F.W. Wise, J. Opt. Soc. Am. B**14** (1997) 1632.

[3] Ref. [1] reports that the radius r obtained from scanning transmission electron microscope is smaller than the calculation results, when $r < 3.5$ nm. However, because of the lack of experimental data connecting the radius with transition energy larger than 1.2 eV, we here use the calculated results tentatively.

[4] M.T. Nenadovic, M.I. Comor, V. Vasic, and O.I. Micic, J. Phys. Chem. **94** (1990) 6390.

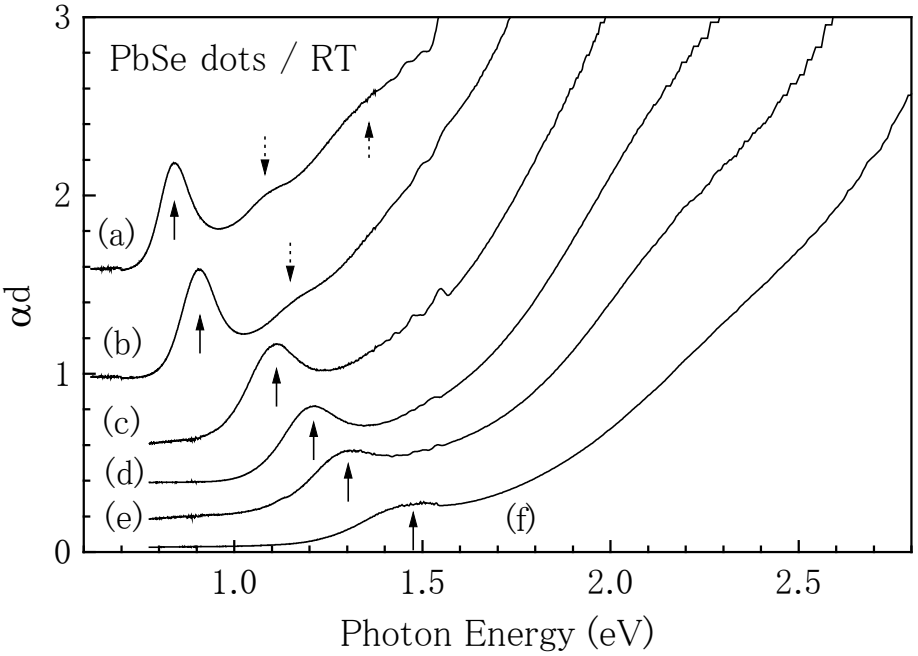
[5] M.G. Bawendi et al., Phys. Rev. Lett. **65** (1990) 1623.

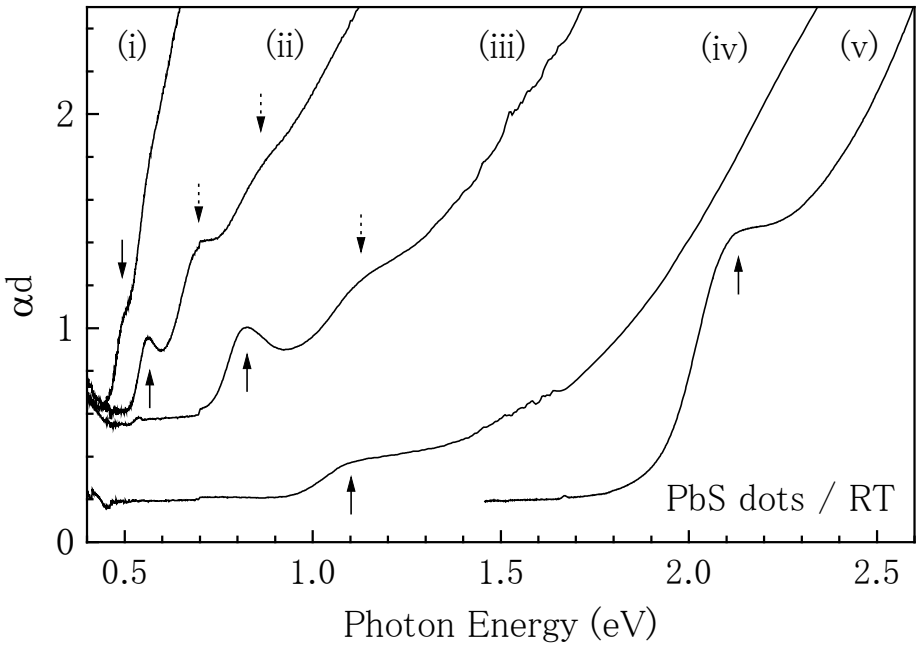
Figure captions

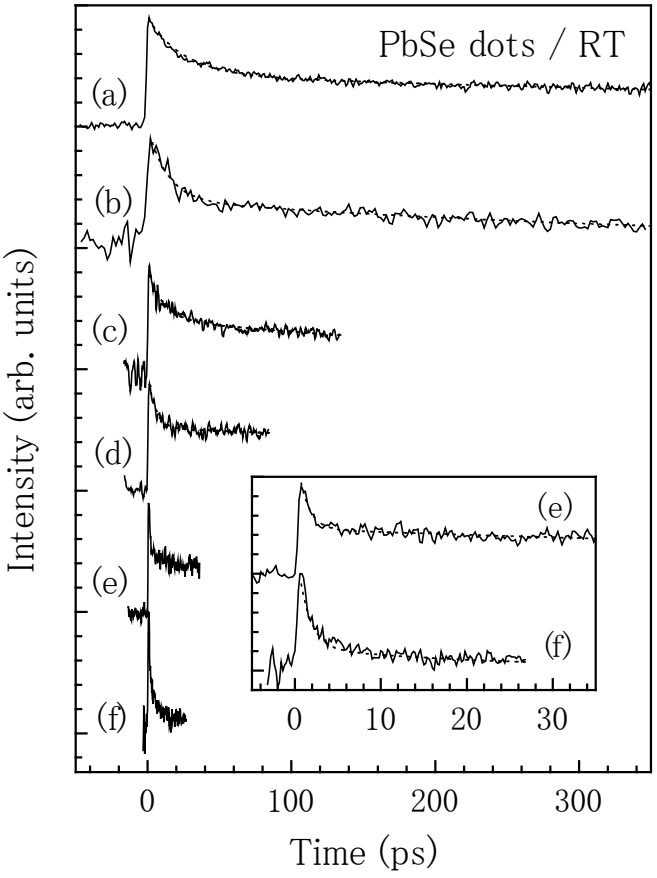
Fig. 1 Absorption spectra of PbSe quantum dots in phosphate glasses at room temperature.

Fig. 2 Absorption spectra of PbS quantum dots (i)-(iv) in phosphate glasses and (v) in PVA at room temperature.

Fig. 3 Temporal changes of differential transmission in PbSe dots at room temperature. The profiles (a)-(f) correspond to the samples in Fig. 1(a)-(f), respectively. Pump photon energy was 3.1 eV, and probe photon energy was tuned to the lowest exciton transition energy. The profiles can be fitted by two-exponential decays ($C_1 \exp(t/\tau_1) + C_2 \exp(t/\tau_2)$). The obtained decay times τ_1 and τ_2 are (a) 25 ps and 1000 ps, (b) 14 ps and 400 ps, (c) 11 ps and 400 ps, (d) 5 ps and 1000 ps, (e) 1 ps and 100 ps, and (f) 1 ps and 30 ps. Typical errors of τ_1 and τ_2 in the fitting procedures were ~20% and ~50%, respectively.


PbSe dots / RT
αd
Photon Energy (eV)
(a)
(b)
(c)
(d)
(e)
(f)
0
1
2
3
1.0
1.5
2.0
2.5


(i)
(ii)
(iii)
(iv)
(v)
αd
0
1
2
0.5
1.0
1.5
2.0
2.5
Photon Energy (eV)
PbS dots / RT


PbSe dots / RT
(a)
(b)
(c)
(d)
(e)
(f)
Intensity (arb. units)
0
100
200
300
Time (ps)
0
10
20
30