

Semiconductor quantum dots behave like molecules

著者	Masumoto Yasuaki
journal or publication title	AIP conference proceedings
volume	416
number	1
page range	45-52
year	1997-06-20
権利	(C)1998 American Institute of Physics.
URL	http://hdl.handle.net/2241/98325

Semiconductor Quantum Dots Behave Like Molecules

Yasuaki Masumoto

Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract. The persistent spectral hole burning (PSHB) phenomena were discovered in many kinds of nanocrystalline semiconductors, such as CdSe, CdS, CuCl, CuBr and CuI, embedded in crystals, glass or polymers. Hole burning in the luminescence spectrum was also observed. The observed PSHB phenomena are explained by the ionization of nanocrystals. The photoionization of nanocrystals takes place by tunneling through potential barriers with broadly distributed barrier height and thickness. The energy of photoionized nanocrystals is changed from the original energy and their new energies depend on the spatial arrangement of trapped carriers. Quantum confinement of carriers and resulting strong Coulomb interaction between confined carriers and trapped carriers cause the energy change.

Nanometer-size semiconductor crystals abbreviated to "semiconductor nanocrystals" are known as zero-dimensional "quantum dots" (1,2). They are much larger than atoms and molecules but are much smaller than bulk crystals. Both nanocrystals and clusters are called mesoscopic particles, but there is not a clear boundary between them. The system size of atoms, molecules, clusters and nanocrystals are displayed in Fig. 1. Electronic energies in atoms, molecules and small clusters can be calculated from the atomic approach, while those in large clusters and nanocrystals can be obtained from the energy band approach with effective mass approximation. In fact, optical properties of nanocrystals have been well characterized by the quantum confinement effect on band electrons and holes or excitons and the lowest excited states show blue shifts depending on their size. Figure 2 is the optical absorption spectra of semiconductor nanocrystals which show the quantum size effect of electrons and holes or excitons. In this sense, quantum dots are similar to other low-dimensional quantum structures, such as quantum wells and quantum wires. However, quantum dots are sharply different from quantum wells and quantum wires in the point that quantum dots are made of as small as $10^3 \sim 10^6$ atoms. Considerable fraction of atoms face the surface or the interface of quantum dots in the surrounding materials. Therefore, it is quite natural to consider that the electronic states of quantum dots should not be treated by themselves but should be treated together with the real surfaces or interfaces and the surrounding materials.

If the guest size is much smaller than the quantum dot system, such as molecular or ionic guests embedded in glass, crystal or polymer hosts, we can naturally

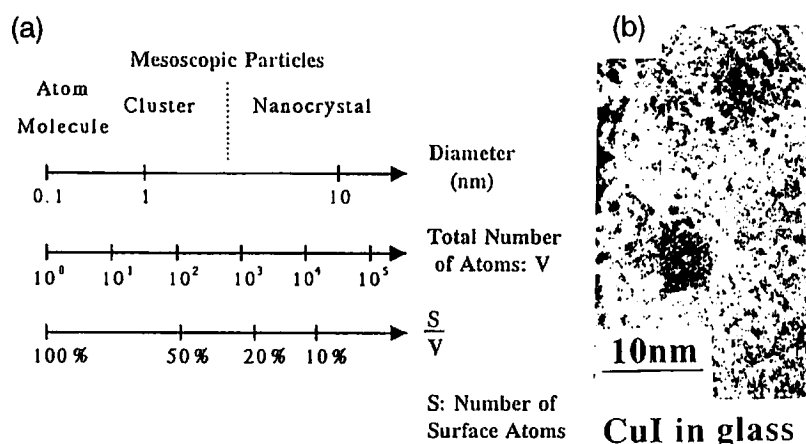


FIGURE 1. (a) Diameter, total number of atoms and its surface-to-volume ratio of atoms, molecules, clusters and nanocrystals. (b) Transmission electron microscope photograph of CuI nanocrystals embedded in glass is shown. The magnification is 300,000.

understand that guests are greatly influenced by the surrounding hosts and that the energy levels of the guest-host system are inhomogeneously broadened. Persistent spectral hole-burning (PSHB) phenomenon has been observed in a number of these materials (3). Various types of photophysical and photochemical processes, such as bond rearrangements in the host as well as proton or hydrogen rearrangements and photoionization in the guest, cause the PSHB phenomena. The PSHB phenomenon requires the existence of more than one energetically inequivalent ground states of the total system consisting of guest and host. Moreover, the relaxation among the ground states must be slower than the decay rate of any excited state for the persistency of the hole. Therefore, the PSHB phenomenon can take place in very small system, such as molecular or ionic guests embedded in glass, crystal or polymer hosts. We can characterize molecules as ones whose energy depends on the surroundings.

When the spectrally narrow light excites the ensemble of semiconductor nanocrystals having the inhomogeneously broadened absorption band, a spectral hole is formed at the excitation photon energy in the absorption band. Before the discovery of the PSHB phenomena of nanocrystals, inhomogeneous broadening is believed to come from the size distribution and spectral hole-burning observed in nanocrystals has been believed to be transient. Nobody considered the PSHB takes place in quantum dots. Nevertheless, recently the PSHB phenomena were discovered in many kinds of semiconductor nanocrystals embedded in crystals, glass or polymers (4-10). They are CdSe and CdTe nanocrystals in GeO_2 glass, CdSSe nanocrystals in glass, CdS nanocrystals in polymers, CuCl nanocrystals in glass and NaCl crystals, CuBr nanocrystals in glass and NaBr crystals and CuI nanocrystals in glass. The observation of the PSHB phenomena in many kinds of nanocrystals proves that PSHB

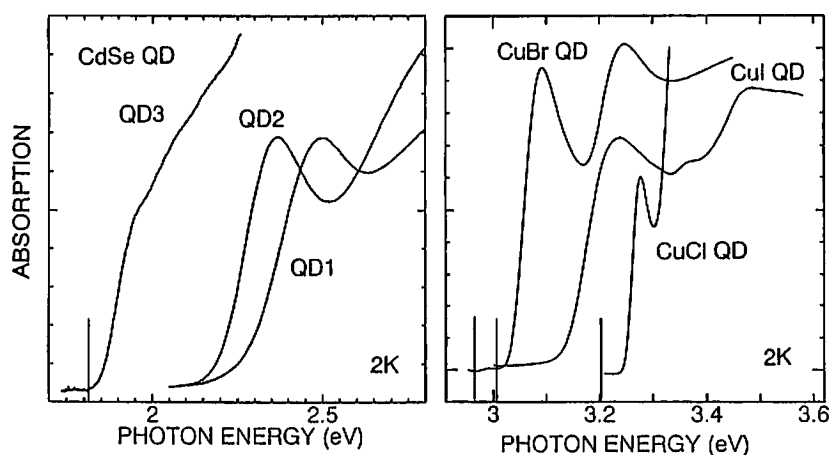


FIGURE 2. Absorption spectra of CdSe, CuCl, CuBr and CuI nanocrystals. The average radii of nanocrystals are as follows. CdSe QD1: 1.8 nm, CdSe QD2: 3.0 nm, CdSe QD3: 11 nm, CuCl QD: 1.8 nm, CuBr QD: 2.4 nm and CuI QD: 3.0 nm. Vertical long bars at 1.826 eV (CdSe), 3.2025 eV (CuCl), 2.964 eV (CuBr) and 3.06 eV (CuI) show the lowest exciton energy in bulk crystals. Absorption spectra show blue shift due to the quantum size effect.

phenomena take place widely in nanocrystals. The observation of the phenomenon requires the additional inhomogeneous broadening for the quantum dots coming from the various ground state configurations of the dot-matrix system. Semiconductor quantum dots behave like molecules in the sense that energy levels of quantum dots are greatly influenced by the surrounding host. The nanocrystals showing the PSHB phenomena are made of 10^3 - 10^4 atoms and much larger than ions, defects and molecules which showed the PSHB. Why the surrounding host seriously affects the energy of so large nanocrystals to induce the PSHB? It is the main aim of this paper to solve this question. In this paper, we introduce the experimental observation of the PSHB of nanocrystals, explain the mechanism of the phenomenon, and discuss the meaning of the phenomenon.

Figure 3(a) shows the absorption spectrum of CdSe nanocrystals embedded in GeO_2 glass. Three structures corresponding to A-exciton, B-exciton and C-exciton bands are indicated. Spectrum has a pronounced A-exciton peak at 2.19 eV which is higher than the band gap energy of bulk CdSe by 0.35 eV. The blue shift is the indication of electron and hole quantum confinement. This strong-confinement-model holds not only for CdSe nanocrystals, but also for CuI nanocrystals (9). Figure 3(c) shows the absorption spectrum of CuI nanocrystals embedded in glass. The absorption spectrum shows the $Z_{1,2}$ exciton structure whose energy increases with the decrease of the size. Besides the $Z_{1,2}$ exciton structure, the H_1 exciton structure of the hexagonal CuI nanocrystals was observed. Figures 4(a) and 4(c) show absorption spectra of CuCl nanocrystals embedded in glass and NaCl. The broad peaks indicated by Z_3 are due to the absorption of Z_3 excitons. These peaks show blue shifts compared

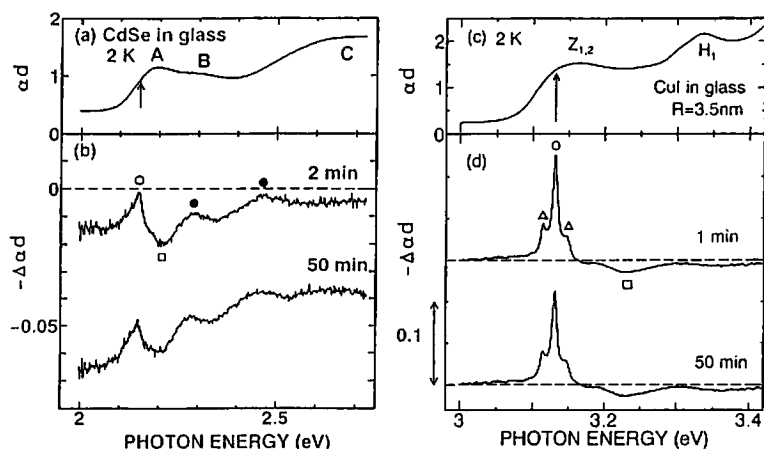


FIGURE 3. Observation of the persistent spectral hole-burning phenomenon in CdSe and CuI nanocrystals embedded in glass at 2 K. Both the samples belong to the strong confinement regime. The upper figures, (a) and (c), show the absorption spectrum of the virgin samples, CdSe ($R=2.4\text{nm}$) and CuI ($R=3.5\text{nm}$) in glass, respectively. The lower figures, (b) and (d), show the spectral change observed at 1 min or 2 min and 50 min after the burning laser exposure at 2.148 eV or 3.130 eV is stopped. [From Y. Masumoto et al., (7) and (9)]

Reprinted with kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

with that of bulk CuCl due to the exciton quantum confinement (1,11). The weak-confinement-model holds for CuCl nanocrystals.

In both strong and weak confinement regimes, the PSHB phenomena were observed. The PSHB phenomena in strong confinement regime were typically observed in CdSe nanocrystals in GeO_2 glass (5-7) and CuI nanocrystals in glass (9). The observation of PSHB phenomena in weak confinement regime are best demonstrated in CuCl nanocrystals in glass and a NaCl crystal (5-7). The PSHB phenomena are observed also in CuBr nanocrystals in glass (7,8). After the samples were excited by dye laser pulses, the absorption spectra of the samples were changed as are shown in Figs. 3(b), 3(d), 4(b), 4(d) and 4(b). This spectral change is preserved for long time at low temperature. At 2 K, we observed that the spectral holes were preserved for more than 8 hours after the excitation. These spectra show a main spectral hole (○), satellite holes (●) and an induced absorption structure (□) which are superposed on the photodarkened spectra [Fig. 3(b)]; a main spectral hole (○), phonon sideband holes (Δ) and an induced absorption structure (□) [Fig. 3(d)]; a main spectral hole (○), phonon sideband holes (Δ), satellite holes (●) or an antihole (□) which are superposed on the broad wavy structure (■) which is approximated by the first derivative of the absorption spectrum [Fig. 4(d)]; and a sharp spectral hole (○) and antihole (□) [Fig. 4(b)]. The first derivative of the absorption spectrum means the small red shift of the absorption spectrum. In the time regime ranging from minute to hour, the hole depth decays spontaneously in proportion to logarithm of

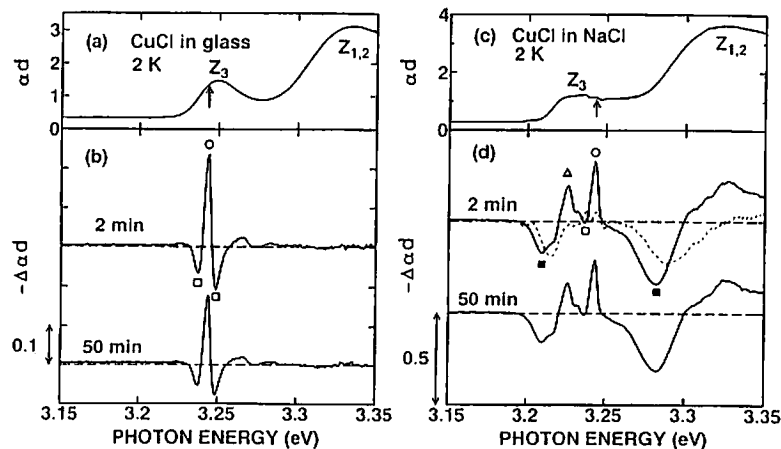


FIGURE 4. Observation of the persistent spectral hole-burning phenomenon in CuCl nanocrystals embedded in glass and NaCl. Both the samples belong to the weak confinement regime. The upper figures, (a) and (c), show the absorption spectrum of the virgin samples, CuCl ($R=2.5\text{nm}$) in glass and CuCl ($R=3.5\text{nm}$) in NaCl, respectively. The lower figures, (b) and (d), show the spectral change observed at 2 min and 50 min after the burning laser exposure at 3.245 eV is stopped. A short dashed line in figure (d) shows the derivative of the absorption spectrum (c). [From Y. Masumoto et al., (7)]

Reprinted with kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

time, indicating the broad distribution of spontaneous decay rates (7).

The PSHB phenomena require that the guests should be greatly affected by the surrounding hosts. The requirement tells us that the PSHB phenomena should depend on the size of nanocrystals strongly, and should disappear with the increase of the size. This conjecture was found to hold from the size-dependent PSHB experiments of CdSe nanocrystals in Ge_2O glass, CuCl nanocrystals in glass and CuBr nanocrystals in glass. The PSHB was hardly observed in CuCl nanocrystals in glass whose radii are larger than 10 nm.

To explain experimental data of the PSHB phenomena of nanocrystals, we consider the photoionization of nanocrystals and carrier trapping into the hosts as the mechanism to induce the PSHB phenomena (7,8). To derive this conclusion, similar behavior of the burned hole and the red shift in both burning and filling processes became a key point. The proposed mechanism to give rise to the PSHB phenomena is schematically shown in Fig.5. Photoexcited exciton in a nanocrystal is localized and an electron or a hole is trapped at the surface of the nanocrystal. A hole or an electron escapes from the nanocrystal, tunnel through the potential barrier in host and is trapped in host. The potential barrier height between nanocrystals and traps in host is considered to be broadly distributed. In the ionized nanocrystals, Coulomb interaction in the nanocrystals causes the blue or red shift of the exciton energy which results in the hole burning at the laser excitation energy and the induced absorption

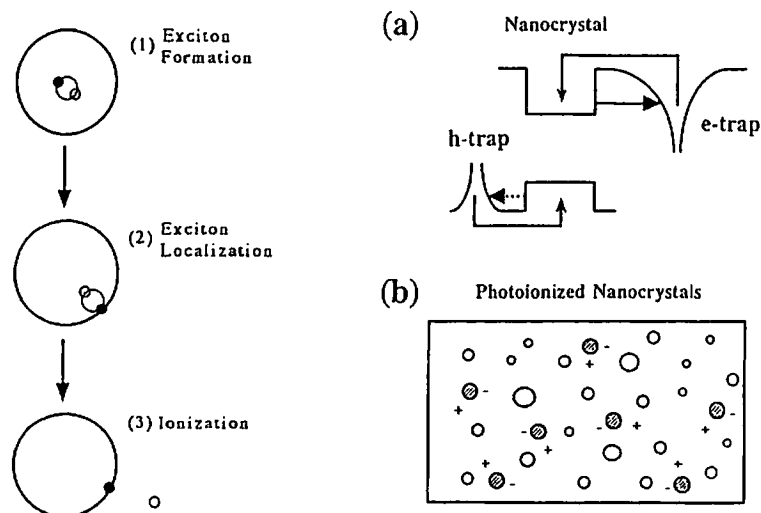


FIGURE 5. Schematic drawing of the proposed time sequence of exciton dynamics to account for the luminescence hole burning and the absorption hole burning. (a) Photoionization of nanocrystals takes place by the tunneling process. Photogenerated electrons or holes tunnel through barriers and are captured by traps in the host. Tunneling process is shown by solid and dashed arrow lines. Thermally annealing hole filling and light-induced hole filling processes are shown by shadowed arrow lines. (b) Schematic view of the photoionized nanocrystals and carriers in traps. Various configurations between photoionized nanocrystals and spatial charge distribution in the host give another inhomogeneous broadening which satisfies the requirement of the persistent spectral hole-burning.

Reprinted from *Journal of Lumin* 66 & 67 1-6 Y. Masumoto and T. Kawazoe, "Luminescence Hole Burning in Semiconductor Quantum Dots," pp. 144 © 1996 and *Journal of Lumin* 70 1-6 Y. Masumoto, "Persistent Hole Burning in Semiconductor Nanocrystals," pp. 393, 395 © 1996 with kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

at the high or low energy side. This explains the observed main hole and the associated induced absorption. Spatially separated electrons and holes apply the local electric field to nanocrystals and causes the quantum confined Stark effect. The effect gives the red shift of the exciton structure. Not only photoexcited nanocrystals but also non-photoexcited nanocrystals feel electric field because of the long range character of the Coulomb field. The ensemble of nanocrystals show the quantum confined Stark shift. Therefore, the red shift of the inhomogeneously broadened absorption spectrum is observed.

Photoionized nanocrystals and trapped holes are stable enough to give the PSHB at low temperature. There are many spatial arrangements for electrons and holes in both nanocrystals and glass. A variety of the spatial arrangements induce the additional inhomogeneous broadening of the absorption spectra of nanocrystals. The presence of the inhomogeneous broadening coming from the carrier distribution satisfies the requirement of the PSHB.

Unusual luminescence behaviors are observed simultaneously with the PSHB. They are luminescence elongation followed by the increase of the light exposure

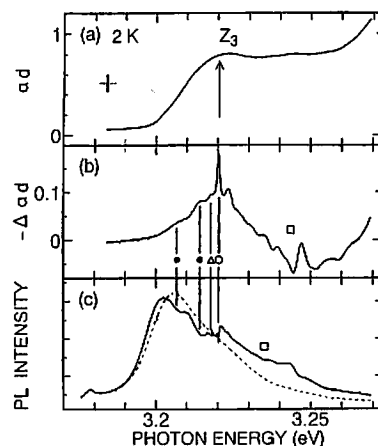


FIGURE 6. (a) Absorption spectrum of CuCl nanocrystals ($R = 3.0$ nm) embedded in a NaCl crystal at 2 K. An upward arrow shows the energy of the dye laser pulses. (b) Absorption spectral change of the sample exposed by the narrow-band dye laser at 3.220 eV. (c) Luminescence spectra before and after the sample is exposed at 3.220 eV. Luminescence spectrum was taken under the excitation at 355 nm with the excitation density of $0.5 \mu\text{J}/\text{cm}^2$, after the sample is exposed at 3.222 eV with the excitation density of $10 \mu\text{J}/\text{cm}^2$. [From Y. Masumoto and T. Kawazoe, (12)]

Reprinted from *Journal of Lumin* 66 & 67 1-6 Y. Masumoto and T. Kawazoe, "Luminescence Hole Burning in Semiconductor Quantum Dots," pp. 144 © 1996 and *Journal of Lumin* 70 Y. Masumoto, "Persistent Hole Burning in Semiconductor Nanocrystals," pp. 396 © 1996 with kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

which is observed in CuI nanocrystals in glass (9,12) and luminescence hole-burning observed in CuCl nanocrystals in NaCl crystals (12,13).

Figure 6(a) shows the absorption spectrum of CuCl nanocrystals embedded in a NaCl crystal. The Z_3 exciton absorption peak shows the blue shift of 20 meV from the bulk value. It corresponds to the blue shift of 3.0 nm-radius CuCl nanocrystals on the exciton confinement model (11). Luminescence spectra of the sample are shown in Fig.6(c). A dashed line displays the spectrum before the sample is excited by the narrow-band 3.220 eV laser pulses. The peak position of the luminescence is located at 3.206 eV, which is lower than the absorption peak of the Z_3 exciton, 3.223 eV. The luminescence spectrum shows a Stokes shift. This Stokes shift shows that the major part of the luminescence does not come from free excitons in nanocrystals. After the sample is excited by the narrow-band 3.220 eV laser pulses, the luminescence spectrum changes as is shown by a solid line in Fig.6(c). The luminescence spectrum shows a small hole (○), much larger satellite holes (●) which are observed at the low energy side of the burning laser energy and a phonon side-band hole (△). Simultaneously, the luminescence intensity increases at the high energy side of the burning laser energy (□). After the luminescence hole burning experiment, the absorption spectrum was taken and the absorption spectral change was obtained as shown in Fig.6(b). It consists of a main hole (○), satellite holes (●), phonon sideband holes (△), and an induced absorption structure (□).

The luminescence spectral change of Fig.6(c) and the absorption spectral change

of Fig.6(b) correlate with each other. In fact, a main hole, a phonon sideband hole, satellite holes and broad increased absorption or luminescence structure are observed in both the spectra at the same energy. The burning photon-energy dependence of the luminescence holes shows that the lower energy satellite holes in luminescence are ascribed to charged exciton complexes confined in nanocrystals (13). A negatively charged exciton is composed of two electrons and a hole, while a positively charged exciton is composed of two holes and an electron. They are formed from an electron or a hole remained in a photoionized nanocrystal and a photogenerated pair of an electron or a hole. We consider that the ionization of nanocrystals takes place via the exciton localization process and that the ionization causes the PSHB phenomena. Femtosecond pump-and-probe measurement gives us the fastest ionization time of excitons. It was found to be in an order of picosecond or tens of picosecond for CuCl nanocrystals in glass and CuBr nanocrystals in glass (14).

The energy of photoionized nanocrystals is kicked out from the original energy and their new energies depend on the spatial arrangement of trapped electrons and holes. Quantum confinement of carriers and resulting strong Coulomb interaction between confined carriers and trapped carriers are essential in the energy change. The long-range Coulomb interaction explains the reason why so large nanocrystals are affected by the surrounding host. Photoionized nanocrystals and trapped carriers are stable enough to give the PSHB at low temperature, because the thermal activation energy for trapped carriers is lower than the potential barrier for hole filling. There are many spatial arrangements for electrons and holes in both nanocrystals and host. A variety of the spatial arrangements induce the additional inhomogeneous broadening of the absorption spectra besides the inhomogeneous broadening produced by the size distribution. In this sense, semiconductor quantum dots behave like molecules, although quantum dots are much larger than molecules.

REFERENCES

1. A.I. Ekimov, A.L. Efros, and A.A. Onushchenko, *Solid State Commun.* **56**, 92 (1985).
2. A.D. Yoffe, *Adv. in Phys.* **42**, 173 (1993), and reference therein.
3. *Persistent Spectral Hole-Burning : Science and Applications*, edited by W. E. Moerner (Springer-Verlag, Berlin, Heidelberg, 1988).
4. See the review paper: Y. Masumoto, *J. Lumin.* **70**, 386 (1996).
5. Y. Masumoto, L.G. Zimin, K. Naoe, S. Okamoto and T. Arai, *Mater. Sci. Eng. B* **27**, L5 (1994).
6. K. Naoe, L.G. Zimin, and Y. Masumoto, *Phys. Rev. B* **50**, 18200 (1994).
7. Y. Masumoto, S. Okamoto, T. Yamamoto and T. Kawazoe, *Phys. stat. solidi (b)* **188**, 209 (1995).
8. Y. Masumoto, T. Kawazoe and T. Yamamoto, *Phys. Rev. B* **52**, 4688 (1995).
9. Y. Masumoto, K. Kawabata and T. Kawazoe, *Phys. Rev. B* **52**, 7834 (1995).
10. J. Qi and Y. Masumoto, *Solid State Commun.* **99**, 467 (1996).
11. T. Itoh, Y. Iwabuchi, and M. Kataoka, *Phys. status solidi B* **145**, 567 (1988).
12. Y. Masumoto and T. Kawazoe, *J. Lumin.* **66&67**, 142 (1996).
13. T. Kawazoe and Y. Masumoto, *Phys. Rev. Lett.* **77**, 4942 (1996).
14. T. Okuno, H. Miyajima, A. Satake and Y. Masumoto, *Phys. Rev. B* **54**, 16952 (1996).