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Observation of persistent spectral hole burning in CuBr quantum dots

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Persistent spectral hole-burning phenomenon in CuBr quantum dots embedded in glass was observed. The spectral hole and the sideband holes were made together with the redshift of the absorption spectrum in proportion to the logarithm of the laser fluence and were preserved for more than 8 h at 2 K. They were erasable by the temperature rise or by the light exposure. Electron trapping at the surface of the dots and hole tunneling into traps in the glass host is the most probable origin of the persistent spectral hole-burning phenomenon in CuBr quantum dots.

Nanometer-size semiconductor crystals, abbreviated to semiconductor nanocrystals, are known as zero-dimensional quantum dots.¹⁻³ Their optical properties have been characterized by the quantum confinement effect, and the lowest excited states show blueshifts depending on their size. 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 – 10^6 atoms. A 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 structure and 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.

However, this natural consideration has been treated lightly. Semiconductor quantum dots have been generally treated as spherical- or cubic-shaped dots isolated from surrounding materials for the calculation of the fundamental and nonlinear optical properties.^{2,3} Afterwards, interaction between dots and surrounding materials was taken into account as the effects of traps, surface states, etc., for the interpretation of experimental results which cannot be explained by the theoretical treatment of the idealized quantum dots. The interaction is considered to induce the change of the dynamical or nonlinear optical properties of quantum dots, but is not considered to induce the fundamental absorption spectra of the quantum dots. As a proof of this statement, the generally accepted model of inhomogeneous broadening treats the size distribution of dots as the unique origin of inhomogeneity.

Let us consider molecular or ionic guests embedded in glass, crystal, or polymer hosts which are much smaller than the quantum dot system. We can naturally understand that guests consisting of small numbers of atoms 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.⁴ The PSHB phenomenon requires the existence of more than one energetically inequivalent ground state of the total system consisting of guest and matrix. Moreover, the relaxation among the ground states must be slower than the decay rate of any excited

state. This condition causes the persistency of the hole.

When spectrally narrow light excites the ensemble of semiconductor quantum dots having inhomogeneously broadened absorption bands, a spectral hole is formed at the position of the excitation photon energy in the absorption band. So far, spectral hole burning observed in quantum dots has been believed to be transient. Nevertheless, CdSe and CuCl quantum dots embedded in glasses and crystals show the PSHB phenomena.^{5,6} Similarly, we may be able to find other kinds of quantum dots which show the PSHB phenomenon. The observation of the phenomenon requires additional inhomogeneous broadening for quantum dots coming from the various ground-state configurations of the dot-matrix system. In this sense, the concept for the inhomogeneous broadening of quantum dots should be drastically changed. In this paper, we present an experimental observation of the PSHB of CuBr quantum dots embedded in glass, and consider the mechanism of the phenomenon.

The samples studied are CuBr nanocrystals in potassium aluminoborosilicate glass.⁷ The mean size of the nanocrystals was measured by small-angle x-ray scattering and was 3.6 nm in radius. The sample was directly immersed in superfluid helium or mounted on the cold finger of the temperature variable cryostat. A spectrally narrow dye laser with DPS dye pumped by a Q-switched Nd³⁺:YAG (yttrium aluminum garnet) laser was used as a pump source, and a halogen lamp was used as a probe source. The spectral width of the dye laser was 0.014 meV. The transmittance spectrum was measured by using an optical multichannel analyzer in conjunction with a 25-cm monochromator. For the hole-filling experiment, another halogen lamp was used with a set of interference filters.

Figure 1(a) shows the inhomogeneously broadened absorption spectrum of the sample. The average radius of the CuBr nanocrystals was 3.6 nm. The spectrum has a pronounced peak at 3.073 eV which is higher than the $Z_{1,2}$ exciton energy of bulk CuBr by 109 meV. The blueshift is consistent with the previous data of CuBr quantum dots which were interpreted by the donorlike exciton model.⁸

After the center of the $Z_{1,2}$ exciton absorption band of the sample was excited by 9000 shots of dye laser pulses

with an energy density of $5 \mu\text{J}/\text{cm}^2$, the absorption spectrum was changed, as is displayed in Fig. 1(b). The absorption spectral change $-\Delta\alpha d$ is defined as the difference in the absorbance of the sample from that of the virgin sample. This spectral change is long preserved. The upper spectrum in Fig. 1(b) shows the spectral change at 2 min after the laser exposure was stopped. The spectral change was found to decrease in proportion to the logarithm of time between 2 and 100 min, and does not decrease substantially at 50 min. At 2 K, we observed that the spectral hole was preserved for more than 8 h after the excitation. The persistent spectral change is the sharp peak of a main spectral hole marked by \bullet and satellite holes marked by \blacksquare which are superimposed on the broad wavy structure (\circ). The wavy structure is well approximated by the first derivative of the absorption spectrum. This means the occurrence of a small redshift of the absorption spectrum. If the derivative of the absorption spectrum is subtracted from the observed spectral change, satellite holes are on the induced absorption structure at the higher-energy side of the main hole. We consider the induced absorption structure comes from a photoproduct.

With the change of the pump photon energy, energy positions of the main hole and the satellite holes change. The energy separation between the main hole and the satellite holes (1, 1', 2') does not change with the change of the pump photon energy, and is equal to the optical phonon energy or twice the size of it, so that the satellite holes 1, 1', and 2' are optical-phonon sidebands. The energy separation between the main hole and the satellite holes 2 and 3 changes with the change of the pump photon energy, and their change is interpreted by the energy

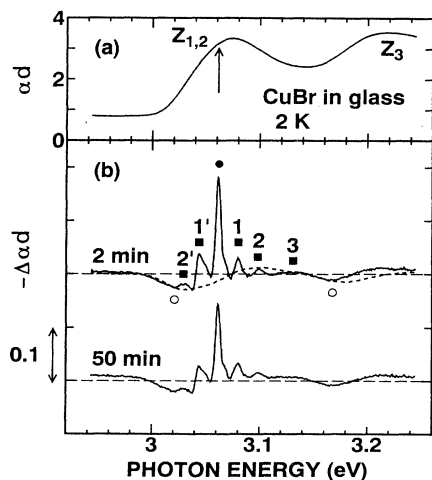


FIG. 1. (a) Absorption spectrum of a virgin sample, CuBr nanocrystals (the average radius is 3.6 nm) embedded in glass. (b) The absorption spectral change of the sample after the spectrally narrow laser exposure (9000 shots of dye laser pulses with the pump photon energy of 3.061 eV, and an excitation energy density of $5 \mu\text{J}/\text{cm}^2$). Long-dashed lines show the zero base, and the short-dashed line shows the derivative of the absorption spectrum (a).

separation between size-quantized levels of anisotropic multicomponent $Z_{1,2}$ excitons. This observation suggests that PSHB spectroscopy can be applicable to precise optical measurement of size-dependent quantum dots by laser marking.

The hole depth and the amplitude of the wavy structure increase in proportion to logarithm of the laser fluence, as is shown in Fig. 2. The logarithmic dependence holds for more than four decades of the fluence. The logarithmic hole growth has been observed in molecules in organic glasses and color centers in crystals, and is explained by a model which assumes the broad distribution of the burning rate.⁹ This model is based on tunneling through the potential barrier with distributed barrier height and thickness. The model assumes that the burning rate is proportional to $\exp(-\lambda)$ and that the tunneling parameter λ is rather uniformly distributed. Similarly, the hole burning in CuBr quantum dots is considered to take place via tunneling through a potential barrier with a broadly distributed barrier height and thickness.

The hole structures and the wavy structure are erasable by the temperature rise. Figure 3 shows the absorption change of the sample after the temperature cycle between T_b and T . First, the absorption spectrum of the virgin sample was taken at the burning temperature T_b . The sample was exposed by 9000 shots of dye laser pulses with an energy density of $5 \mu\text{J}/\text{cm}^2$ at T_b . The temperature of the sample was raised to T and maintained for 5 min. After that, it was cooled down to T_b . Then the absorption spectrum was measured and the difference spectrum was obtained. Even if we prolong the annealing time up to 60 min, the difference spectrum changes little. With the increase of annealing temperature, the hole depth and the amplitude of the wavy structure is reduced similarly. At the lower part of Fig. 3, both of them are plotted as a function of temperature.

The thermal hole filling is explained by the thermally activated barrier crossing mechanism.¹⁰ The rate of this

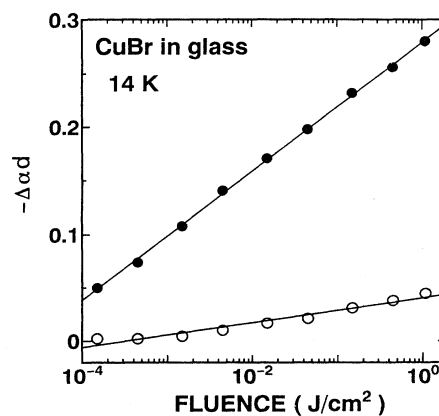


FIG. 2. Solid circles show the hole depth as a function of the laser fluence. Open circles show the maximum amplitude of the wavy structure. Both data are taken by changing the exposure time with the excitation energy density of $5 \mu\text{J}/\text{cm}^2$.

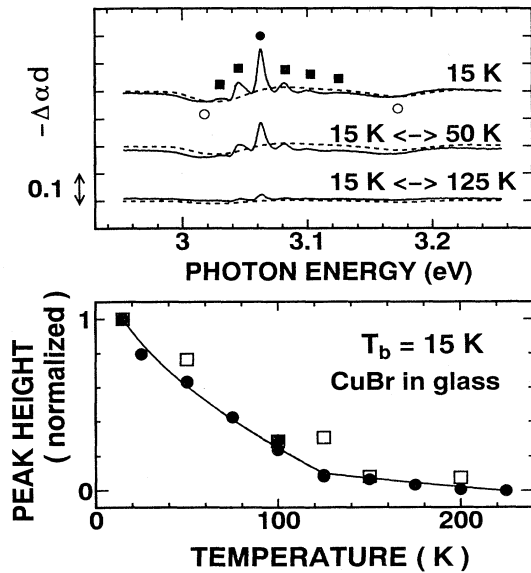


FIG. 3. The upper figure shows the persistent spectral change remaining after the temperature cycle. The hole was burned at 15 K. The lower figure shows the normalized hole depth (solid circles) and the normalized amplitude of the wavy structure (open squares) as a function of the annealing temperature. The solid line is the fit of the hole depth by the expressions shown in the text.

mechanism is represented by $\nu = \nu_0 \exp(-V/kT)$, where ν_0 is the frequency factor whose order is given by $kT/h \approx 10^{11} - 10^{13} \text{ s}^{-1}$, and V the potential barrier. During the holding time t at the annealing temperature T , the hole is filled if the condition $\nu t > 1$ holds. Therefore the hole is filled if $V < kT \ln(\nu_0 t)$. From the rather uniform distribution of the tunneling parameter, we assume that the distribution of the potential barrier $P(V)$ is represented by $P(V) \propto 1/\sqrt{V}$ with a maximum barrier height V_{\max} .¹⁰ The normalized hole depth observed after the temperature cycle between T_b and T can be calculated by

$$\int_{kT \ln(\nu_0 t)}^{\infty} P(V) dV / \int_{kT_b \ln(\nu_0 t)}^{\infty} P(V) dV.$$

This expression gives the functional form of $(1 - \sqrt{kT \ln(\nu_0 t)/V_{\max}}) / (1 - \sqrt{kT_b \ln(\nu_0 t)/V_{\max}})$ for $kT \ln(\nu_0 t) < V_{\max}$. The experimental results shown in Fig. 3 are well fitted by this expression, if we consider two distributions of potential barriers. In fact, fitting by the expression $0.7 (1 - 0.089\sqrt{T}) / (1 - 0.089\sqrt{T_b})$ for $T < 125$ K, plus $0.3 (1 - 0.067\sqrt{T}) / (1 - 0.067\sqrt{T_b})$ for $T < 225$ K, gives a good result. The obtained maximum barrier heights for two distributions are 0.36 and 0.65 eV.

The hole structures are also erasable by the broad-band light exposure. The light-induced hole-filling spectrum is shown in Fig. 4. Hole filling takes place even when the transparent region of the CuBr absorption spectrum is excited, as is shown in Fig. 4(a). As low as 1.2 eV, broad-band infrared light erased the hole. The hole-filling efficiency depends on the photon energy, and decreases monotonously with the decrease in the photon energy. The erased spectrum almost returns to the spec-

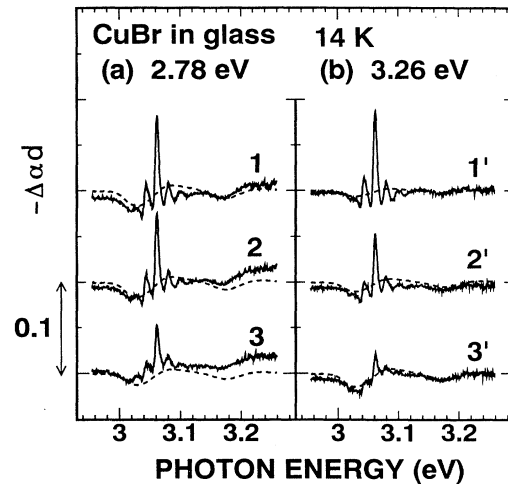


FIG. 4. Light-induced hole-filling experiments for case (a), in which the erase light energy, 2.78 eV, is below the absorption edge of the CuBr quantum dots, and for case (b), in which the erase light energy, 3.26 eV, is above the absorption edge. The spectral width of the erase light is 0.07 eV. Exposure times for spectra 1(1'), 2(2'), and 3(3') are 0, 120, and 3000 s, respectively. Dashed lines show the derivative of the absorption spectrum.

trum of the virgin sample, when the erase light is below the absorption edge of the CuBr quantum dots. On the other hand, when the absorption band of CuBr dots is excited by the broad-band light, it causes hole filling more efficiently than the below-absorption-edge light, but the persistent wavy structure coming from the redshift of the absorption spectrum is more enhanced, as is seen in Fig. 4(b).

The observation of the PSHB phenomenon, hole persistency, and thermal-annealing and light-induced hole filling, is confirmed in this way in CuBr quantum dots embedded in glass. The following is the most probable scenario of the observed PSHB phenomena. Photoexcited exciton in a CuBr dot is localized somehow, and an electron is trapped at the surface of the dot. A hole escapes from the dot, tunnels through the potential barrier in glass, and is trapped at the H_1^+ center in the glass host.¹¹ The potential barrier height between CuBr quantum dots and traps in glass is considered to be broadly distributed, and the maximum heights 0.36 and 0.65 eV are reasonably less than the difference in the energy gaps of CuBr and glass.¹² An exciton bound to an ionized donor or an ionized acceptor is a well-known problem in analogy with the problem of H_2^+ . In the case that the mass ratio of electron to hole, m_e^*/m_h^* , is less than 0.4, the exciton is bound to an ionized donor but is not bound to an ionized acceptor.¹³ From the values of $m_e^* = 0.28m_0$ and $m_h^* = 1.4m_0$,¹⁴ $m_e^*/m_h^* = 0.2$ holds, so that the exciton is not bound to an electron trapped at the surface of dots. In this case, Coulomb interaction in the dots causes the blueshift of the exciton energy, which results in hole burning and induced absorption at the high-energy side. This explains the observed main hole

and the associated induced absorption at the higher-energy side. Spatially separated electrons and holes apply the local electric field to CuBr dots and cause the quantum-confined Stark effect. The effect gives the redshift of the exciton structure. Not only photoexcited dots but also nonphotoexcited dots feel the electric field because of the long-range character of the Coulomb field. The ensemble of dots shows the quantum-confined Stark shift. Therefore, the redshift of the inhomogeneously broadened absorption spectrum is observed.

The spectral hole and the redshift of the absorption spectrum behave similarly in Figs. 2, 3, and 4(a). Now we can clearly understand these observations on the photoionization model. The only difference is observed in Fig. 4(b). When the erase light energy is below the absorption edge of CuBr dots, trapped holes are excited and recombine with electrons localized at the interface of dots. This process erases both the burned hole structures and the wavy structures coming from the redshift of the absorption spectrum, because the photoionized dots return to deionized dots. On the other hand, the broad erase light above the absorption edge of CuBr dots may deionize the burned dots but ionize many unburned dots. The former process fills the burned hole and reduces the redshift. However, the latter process fills the burned hole, gives the photoproduct which fills the hole burned previ-

ously, and increases the redshift, because the trapped carrier density increases.

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

There are several reports about long-lived spectral change¹⁵⁻¹⁷ and the Stark effect¹⁸ in semiconductor quantum dots. The observed spectral change is the broadening of the inhomogeneously broadened absorption spectra, similar to the redshift of them observed in this paper, and is not the hole burning. Although the spectral changes were due to the broadening of the absorption spectra, they were explained by the trapped-carrier-induced quantum-confined Stark effect on the basis of their similarity to the Stark effect data^{15,17} or the simulated result.¹⁶ In CuBr quantum dots, on the other hand, we observed the small redshift of the $Z_{1,2}$ exciton absorption spectrum. We feel there remains an unresolved question about the spectral change of quantum dots induced by the Stark effect. Further study is necessary to resolve the question.

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