Correlation between Cu+-ion instability and persistent spectral hole-burning phenomena of CuCl nanocrystals

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Semiconductor nanocrystals have attracted considerable attention not only because of their unique properties but also because of applicability to nonlinear optical devices. For the investigation of the size-dependent properties of nanocrystals, it is ideal to fabricate a well-defined single-sized nanocrystal. However, nanocrystal size is difficult to control in many preparation methods, so that the samples have size distribution and then the absorption bands are inhomogeneously broadened.

Hole-burning spectroscopy is a powerful tool to extract individual and intrinsic information, i.e., information of certain-sized nanocrystals, from the inhomogeneously broadened absorption band. The hole-burning phenomena in the nanocrystal systems were considered to be caused by the absorption saturation of photoexcited carriers, so that the hole spectra had been expected to disappear within a few nanoseconds.

Recently, there have been many reports on persistent spectral hole-burning (PSHB), long-lived hole-burning, or photoinduced absorption-spectral change phenomena of various semiconductor nanocrystals. The spectral holes persist for more than a few microseconds or even several hours. Understanding of the mechanism of the PSHB phenomena is indispensable for the understanding of nanocrystals but still poor: The PSHB phenomena were considered to be caused by carrier trapping or photochemical reactions. However, further study is necessary for the understanding of the mechanism.

Ab initio calculations predict that structural instabilities occur in zinc-blende cuprous halides, CuCl, CuBr, and CuI and cause Cu$^{+}$-ion related defects at low temperatures. Such instabilities are expected to induce anomalous phenomena by light irradiation, e.g., persistent photoconductivity in Si-doped GaAs (‘‘DX centers’’). However, there is no experimentally strong evidence of the instabilities in CuCl, and whether the instabilities occur or not is now under discussion.

In this paper, we have investigated a typical sample that exhibits the PSHB phenomena, CuCl nanocrystals embedded in a NaCl crystal, by using the laser-induced spectral-change and temperature-cycle experiments. The experimental results show that the PSHB phenomena can be explained by the two-level-system (TLS) model, in a way analogous to dye molecule-glass systems. The results also indicate that there are two types of TLS’s in the samples. We also found correlations between the PSHB phenomena and photoluminescence spectral changes of excitons in CuCl nanocrystals and of Cu$^{+}$ dimers in a NaCl crystal. The spectral changes can be triggered by photoinduced Cu$^{+}$-ion displacements in CuCl nanocrystals and in a NaCl crystal.

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FIG. 1. Persistent spectral holes of CuCl nanocrystals embedded in a NaCl crystal at 2 K. (a) Absorption spectra before (dash-dotted line) and after (solid line) the laser exposure; (b) absorption-spectral change measured at 2 min (dotted line) and 20 min (solid line) after the burning laser is stopped. The main hole (●) and satellite holes (▲, △, ■, and □) are clearly observed. The mean radius of the nanocrystals is 3.5 nm. The burning photon energy, the energy density, the pulse duration, the pulse repetition, and the excitation period are 3.245 eV, 33 μJ/cm², 5 ns, 30 Hz, and 3 min, respectively.

The hole structures are erasable by the temperature rise. Figure 2 shows (a) absorption spectrum, (b) hole spectra after various temperature cycles, and (c) the hole area plotted as a function of the cycling temperature. This experimental sequence is as follows: At first, the spectral holes are burned at certain temperature \( T_b \), and the hole spectrum is measured; after cycling through the elevated temperature (cycling temperature) \( T \), the hole spectrum is measured again at \( T_b \). The experimental cycling-temperature dependence of hole filling is well expressed by the thermal activation model across distributed barrier height. The rate of this model is expressed by \( \nu = \nu_0 \exp(-V/kT) \), where \( \nu_0 \) is the frequency factor which is the order of \( 10^{11} \, \text{s}^{-1} \) and \( V \) the potential barrier height. During the holding time \( t \) at the temperature \( T \), the hole is filled if the condition \( \nu t > 1 \) holds. Therefore,
the hole is filled, if $V < kT \ln(\nu_0)$. Moreover, we assume that the distribution of the potential barrier height $P(V)$ is expressed by $P(V) \propto 1/\sqrt{V}$ with a maximum barrier height $V_{0,\text{max}}$. The annealing temperature-dependent hole area have been fitted by the functional form of $[1 - V/kT \ln(\nu_0)/V_{0,\text{max}}][1 - \sqrt{kT_0 \ln(\nu_0)/V_{0,\text{max}}}]$ for $kT \ln(\nu_0) < V_{0,\text{max}}$ in the case of the potential barrier height $P$. Here, $\ln(\nu_0)$ is the logarithm of the product of the attempt frequency ($\nu_0$) and the holding time ($t$), and is given by $32-35$. We tried to fit the expression to the experimental results and estimated the maximum barrier height $V_{0,\text{max}}$ between the TLS. Two components are necessary to account for the data. The maximum barrier height is $140-160$ meV for $T < 50$ K and $400-420$ meV for $T > 50$ K. The absorption-change spectra abruptly varied after the temperature cycles above 50 K, as displayed in Fig. 2(b). After the temperature cycles above 50 K, the large wavy structures coming from redshiftlike spectral changes almost disappear, and antiholes, induced absorption adjacent to the spectral hole [$\Delta$ in Fig. 2(b)], appear. Antiholes are important signs that the PSHB phenomena are photophysical, e.g., local-environmental changes around the nanocrystals. After the temperature cycles above 150 K, the spectral hole almost disappears. These observations prove the coexistence of two kinds of TLS’s in the sample. The cycling temperature dependence is almost independent of the energy positions of the burned holes.

We found correlations between the absorption spectral changes showing PSHB phenomena and PL spectral-changes of excitons and Cu$^+$ dimers. Figures 3(a), 3(b), and 3(c) show absorption, absorption-change spectra, and PL spectra after the laser irradiation with the 3.492-eV excitation energy, respectively, at 2 K. The excitation source was the third harmonic of the output of the Q-switched Nd$^{3+}$:YAG laser. This experimental sequence is as follows: At first, absorption spectrum before the laser exposure is measured. Next, the band-to-band excitation of the sample is started and, during the first 10 s of exposure, PL spectrum is measured. After the sample is exposed for a certain time (300 or 3000 s, in this experiment), the laser exposure is stopped, and then the absorption spectrum is measured. After that, the PL spectrum is measured again. The PL-data accumulated time is 10 s.

In this case, the absorption-change spectra show the wavy structures coming from redshiftlike spectral change and the bleaching of the $Z_3$-exciton absorption band but do not show spectral holes. This is because the band-to-band transition occurs under the pump photon energy. Laser irradiation induces not only absorption-spectral changes but also PL-spectral changes. At first, PL peak energy was at the $Z_3$-exciton absorption peak energy ($\bullet$). With an increase of the laser irradiation time, another PL peak ($\times$) grew and the absorption spectrum was modified. Moreover, we found that the peak of the PL spectra ($\times$) in the well-irradiated sample is at almost the same energy position as the lowest-energy peak of the absorption-change (O). Using the nanocrystal samples with various mean radius, we determined the relations between the $Z_3$-exciton absorption peak energy (O), the lowest-energy peak of the absorption-change (O), and the peak energy of the PL spectra ($\times$). The results are plotted in Fig. 3(d). With the decrease of the $Z_3$-exciton absorption peak energy (O), i.e., the increase of the mean radius of the nanocrystals, the lowest-energy peak of the absorption-change (O), and the peak energy of the PL spectra ($\times$) are correlated with $I_1$ centers, namely, Cu$^+$-ion vacancies in CuCl nanocrystals and resultant charge instability of the nanocrystals.

Moreover, we found that the PL spectra as well as the absorption-change spectra change with an increase of cycling temperatures: After the temperature cycles above 50 K, the absorption spectral changes, i.e., wavy structures coming from redshiftlike absorption change, almost disappear. This observation is consistent with the abrupt spectral change ob-
observed at 50 K, as shown in Fig. 2(b). Simultaneously, the PL spectrum returned to the spectra observed before the intense laser irradiation. This can be explained by considering that \( I_1 \) centers, namely, \( \text{Cu}^{2+} \)-ion vacancies, and resultant charge instability were reduced by thermal activation.

PL spectral changes triggered by \( \text{Cu}^{+} \)-ion displacements are observed not only in CuCl nanocrystals but also in a NaCl crystal. Figure 4 shows PL spectra at around 2.1 eV in CuCl nanocrystals embedded in a NaCl crystal. The sample was the same as used in Figs. 1–3. The PL band in Fig. 4 is ascribed to \( \text{Cu}^+ \) dimers in a NaCl crystal since the PL lifetime (50 \( \mu \)s), the bandwidth (0.2 eV), and the peak position (2.1 eV) are consistent with those of \( \text{Cu}^+ \) dimers at low temperatures reported in Refs. 16–18. It is reasonable to expect that CuCl nanocrystals are surrounded by \( \text{Cu}^+ \) dimers since the nanocrystals are formed by aggregation of \( \text{Cu}^+ \) ions.\(^9\) At 25 K, the PL ascribed to \( \text{Cu}^+ \) dimers decreases its intensity with the increase of the laser irradiation time, as shown in Fig. 4(a). Moreover, after the PL spectra of the dimers are sufficiently changed by the intense laser irradiation, the PL intensity increases with the increase of the cycling temperature and quickly recovers when the cycling temperature exceeds 150 K, as shown in Fig. 4(b). These observations can be explained by photodissolution of \( \text{Cu}^+ \) dimers and thermal aggregation of \( \text{Cu}^+ \) monomers. The phenomena are considered to occur via the ion-exchange between \( \text{Na}^+ \) and \( \text{Cu}^+ \) ions, similar to \( \text{Cu}^+ \) ions in \( \text{Cu}^+ \)-doped \( \text{Na}^+ \)-\( \text{Al}^3+ \)-alumina.\(^7\)

The cycling-temperature dependence of recovery of the PL and absorption spectra is correlated with the return movement of \( \text{Cu}^+ \) ions in CuCl nanocrystals and in a NaCl crystal to the previous sites after the temperature cycles above 50 and 150 K, respectively. The cycling-temperature dependence of the PL spectral change due to the movement of \( \text{Cu}^+ \) ions coincides with that of the PSHB phenomena.

Here, it should be noted that the potential barrier heights obtained from the temperature-cycling experiments in the PSHB phenomena are almost consistent with those for \( \text{Cu}^{1+} \)-ion displacements in CuCl and NaCl crystals obtained from \textit{ab initio} calculations: from the temperature-cycling experiments, potential barrier heights were estimated to be 140–160 and 400–420 meV; from \textit{ab initio} calculations, potential barrier heights are estimated to be 120 (Ref. 4) and 180 meV (Ref. 5) for \( \text{Cu}^{1+} \)-ion displacements between on- and off-center sites in bulk CuCl, and to 160–870 meV for a formation of a \( \text{Cu}^{1+} \) site in NaCl crystals via \( \text{Na}^+ \)-\( \text{Cu}^{2+} \) ion exchange.\(^7\) Thus, barrier heights of 140–160 meV obtained from the temperature-cycling experiments corresponds to those for \( \text{Cu}^{1+} \)-ion displacement in CuCl nanocrystals, and the barrier heights of 400–420 meV those for \( \text{Cu}^{1+} \)-ion displacement in NaCl crystals.

Observed facts suggest the strong correlation between the \( \text{Cu}^+ \) displacements and the PSHB phenomena. Although we cannot explain the persistent spectral-change quantitatively, we speculate a possible PSHB mechanism as follows. Laser irradiation on the samples induces two types of \( \text{Cu}^+ \) displacements: one occurs in CuCl nanocrystals and the other in a NaCl crystal. These processes result in photodissolution of \( I_1 \) centers in CuCl nanocrystals and photodissolution of \( \text{Cu}^{1+} \) dimers in a NaCl crystal. The photodissolution of \( I_1 \) centers and resultant charge instability forms new absorption band at the lower-energy side of the \( Z_3 \)-exciton absorption band, and then reduces the \( Z_3 \)-exciton absorption band. At the same time, the \( \text{Cu}^{1+} \)-ion displacement can affect the \( Z_{1,2} \) excitons. The \( \text{Cu}^{1+} \)-ion displacement forms a new absorption band at the lower-energy side of the \( Z_{1,2} \)-exciton absorption band, and then reduces the \( Z_{1,2} \)-exciton absorption band, like the \( I_1 \) center. This is a possible origin of the large wavy structure coming from the redshiftlike absorption change and some spectral hole. On the other hand, the photodissolution of \( \text{Cu}^{1+} \) dimers to \( \text{Cu}^{2+} \) monomers around nanocrystals induces local-environmental changes, e.g., the change of the number of carriers trapped in matrix defects, or/and local-distortional change caused by the \( \text{Cu}^{2+} \)-\( \text{Na}^+ \) exchange around the nanocrystals. The environmental changes probably perturb the excitons in nanocrystals. This is a possible origin of antiholes and some of spectral hole. Thus, the absorption changes due to the \( \text{Cu}^+ \) displacements inside and outside of the nanocrystals simultaneously occur under the laser exposure. When the cycling temperature is below 50 K, most of \( \text{Cu}^+ \) ions in CuCl nanocrystals and a NaCl crystal will not return to the sites before the intense laser irradiation. When the cycling temperature is above 50 K, most of \( \text{Cu}^+ \) ions in CuCl nanocrystals return to the previous sites, and then \( I_1 \) centers and charged exciton bands disappear: wavy structures and some of the spectral hole disappears. On the other hand, \( \text{Cu}^+ \) ions in a NaCl crystal do not return because the potential barrier is higher. As a result, only the spectral change attributed to the \( \text{Cu}^+ \) displacements in a NaCl crystal remains, and then the abrupt spectral changes, i.e., antiholes are observed [spectrum C in Fig. 2(b)]. The spectral change vanishes after the temperature cycles above 150 K.

In conclusion, we have reported on the PSHB phenomena of CuCl nanocrystals embedded in a NaCl crystal. The experimental results show that the PSHB phenomena can be explained by two types of TLS’s. The PSHB and PL
spectral-change phenomena can be triggered by photoin-
duced Cu$^{+}$-ion displacements in CuCl nanocrystals and a
NaCl crystal.

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