

Hole-filling of persistent spectral holes in the excitonic absorption band of CuBr quantum dots

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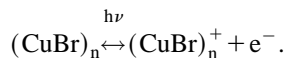
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Persistent spectral-holes (p-SH) are burned in the $Z_{1,2}$ excitonic band of CuBr nanocrystals by a pulsed laser excitation. The annealing of p-SH is studied by three types of hole-filling (HF) experiments: (i) the spontaneous HF, (ii) thermally-induced HF, and (iii) the laser-induced HF. Results are compared to the well developed theory of the persistent spectral hole-burning (p-SHB) in the system of molecules in amorphous matrices. Both p-SHB and HF phenomena can be explained within the framework of a photochemical reaction like the photoionization of nanocrystals. The potential application of p-SHB to the frequency-domain optical data storage is discussed. © 1997 American Institute of Physics. [S0003-6951(97)00906-6]

The low-temperature persistent spectral hole-burning (pSHB) in semiconductor nanocrystals (NCs), observed for the first time two years ago by Masumoto *et al.*,¹ represents an interesting and surprising effect in such a material (The term “persistent” means that the laser-induced absorption changes last for a significantly longer time than any excited state in a material). The inhomogeneously broadened excitonic absorption band can be nearly arbitrarily formed within about 10%–20% of the original absorption. We can imagine a number of interesting applications for such an extraordinary phenomenon, not only the frequency-domain optical data storage as proposed by Masumoto,² but also some optical devices³ like narrow band filters etc. Prior to such speculations, however, we must know more about the p-SHB effect in semiconductor NCs. The effect of hole-filling (HF), especially i.e., the annealing of “persistent” spectral hole,⁴ has to be considered.

We represent here the first results on the laser-induced hole-filling of persistent spectral holes (p-SH) in the excitonic absorption band of small CuBr NCs. The study is completed by measurements of the spontaneous HF and thermally induced HF. Our results are compared with the experiments of Masumoto's group⁴ and the potential applications are discussed.

Generally, two types of spectral hole-burning mechanisms are distinguished: photophysical (or nonphotochemical) and photochemical processes.⁵ Since in our material the persistent spectral changes show an induced absorption (product absorption) well separated from the excitonic absorption band,⁶ the mechanism is supposed to be photochemical. It will be discussed in detail in a separate paper. For the moment we will consider a photoionization of small NCs to be an appropriate mechanism of the photochemical reactions taking place in CuBr NCs



A photon absorbed by a NC creates an exciton, which can be localized on the surface of the NC and is then dissociated. An electron escapes the NC and is trapped in the glass matrix around the NC. In such a way the reaction product is stabilized. Saturation of accessible trapping centres leads to a backward reaction—the return of an electron to the ionized NC; an equilibrium between the product and the educt is established. In this case, the observed p-SHB effect reaches its saturation.

The experimental setup is based on a pulsed nanosecond XeCl-excimer laser serving as a pump source for a dye-laser (with PBBO dye in dioxane solution as active medium). The spectral width of the laser emission is less than 0.12 meV full width at half maximum (FWHM). Absorption changes are tested with the spectrally broad superradiance of a laser-dye solution excited by a part of the source laser emission. Probe and pump pulses are focused on to the sample surface such that they coincide in space and time. This allows one to perform not only persistent SHB, but transient SHB experiments as well, which are described in detail elsewhere.⁶ The test pulses are dispersed in a single grating 3/4 m monochromator and are detected by an optical multichannel analyzer connected to a computer.

The experiments are performed at low temperatures, the samples being mounted inside a continuous flow cryostat (CF 1204 of Oxford Instruments) which allows one to adjust the temperature between 4 and 300 K.

The CuBr NCs have been grown in a borosilicate glass matrix using a diffusion controlled process. The semiconductor concentration in the matrix is about 1%. We study a set of five samples made of glass containing CuBr NCs of different mean radius, i.e., of 12, 9.5, 5.1, 3.8, and 2.8 nm. We should note, that narrow-band persistent as well as transient SHB are observed only in the two samples containing the smallest NCs. (The NC mean radius of 2.8 or 3.8 nm approaches the Bohr radius of excitons which is about 1.2 nm in the bulk CuBr.) In the following we will present only results obtained with these two samples.

Spontaneous hole-filling (p-SH relaxation). By spontaneous HF we denote every changes of p-SH without any

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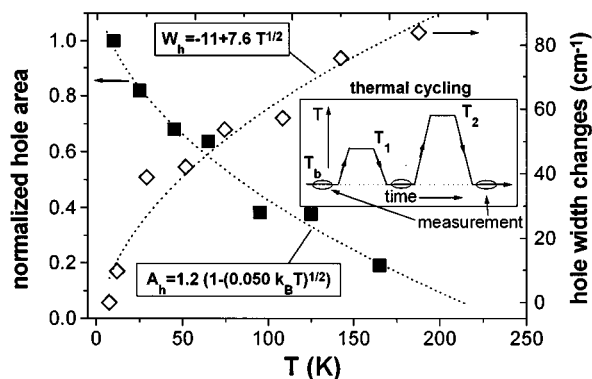


FIG. 1. Spontaneous HF: (a) The persistent spectral hole measured for three different delays τ after the burning. (b) Semilogarithmic plots of a hole area (full squares) and a hole width (open circles) vs. relaxation time.

intentional external perturbations such as heating or exposition by light. We can speak also about the relaxation or annealing of the p-SH. For molecular systems in a glass matrix, the p-SH relaxation obeys a logarithmic time evolution. The process is explained by tunnelling relaxation from a photo-product state to the educt. The distribution of the tunnelling parameters (and consequently of the relaxation rates) is very large because of the amorphous nature of the glass matrix.

In CuBr NCs, we also observe a slow logarithmic temporal recovery of the hole parameters. The decrease of the area of a central part of hole [zero-phonon hole (ZPH)—for the shape of a typical hole see Fig. 2(a)] is about 4% after 30 min of relaxation. The broadening of the ZPH is also non-negligible and increases logarithmically with relaxation time.

Thermally-induced hole-filling (HF). Thermally-induced HF is usually studied by applying a so called thermal cycling procedure. The sample with p-SH burned at low temperature T_B is heated up to a certain temperature, there maintained for several minutes (in our case 5 min) and is then re-cooled to T_B . The remaining p-SH after such a temperature cycle is compared with the original hole (see inset in Fig. 1). The cycling is repeated with still higher temperatures until the hole is completely erased.

The theory of thermal filling was developed by Köhler *et al.*^{7,8} for molecular systems in glasses. The area of holes depends on the cycling temperature as $\sim [1 - \sqrt{(\alpha k_B T / V_{0\max})}]$, where $V_{0\max}$ is the maximum barrier height, and α is a constant. The value of the parameter α is estimated from the maximum barrier height which can be crossed at a temperature T , $V_0 = k_B T \ln(\nu_0 t)$ (t being the experimental time scale about 100 s), ν_0 is the activation frequency of the order of 10^{11} s^{-1} . The parameter α is given by $\ln(\nu_0 t)$, whose value is of the order of 30. A broadening of the ZPH is often called “spectral diffusion.” This is caused by a structural relaxation of the matrix surrounding the molecules, which can have a rich temperature dependence, but at very low temperatures a tunnelling is dominant (giving rise to a linear dependence of the hole width on temperature). For higher temperatures a thermally activated process of relaxation occurs and the hole width increase with $T^{3/2}$.

Our experimental results obtained by the thermal cycling procedure are summarized in Fig. 1. The integrated area of the ZPL hole fits well the dependence derived by Köhler and

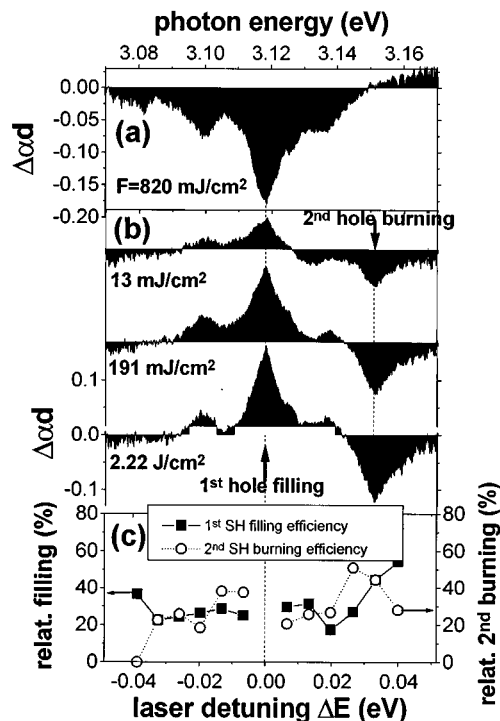


FIG. 2. Laser-induced HF: (a) The p-SH at 3.118 eV before filling. (b) Changes of the first spectral hole after the second burning at 3.151 eV for three fluences 13, 191, and 2220 mJ/cm². (c) The second hole-burning (open circles) and the hole-filling of first hole (full squares) as a function of laser detuning ΔE (the second burning fluence is 38 mJ/cm²).

co-workers. We found $\alpha/V_{0\max}$ to be 0.05, which give us the maximum barrier height $V_{0\max} = 600 \text{ meV}$ (if $\alpha = 30$). On the other hand the temperature dependence of the hole width does not obey the variation expected for molecular systems in glass. The broadening is supralinear with temperature, and it can be approximated by a square root dependence. We suppose this to be a consequence of the proximity of the important phonon sidebands (caused by a strong exciton-phonon interactions⁵) and their thermally induced changes which are not considered in the above mentioned model.

Laser-induced hole-filling. In order to study laser-induced HF, we have applied the following procedure: A p-SH is burned at a wavelength of 397.5 nm (3.118 eV). Then, the dye-laser is tuned off at the second wavelength and the spectral changes induced by excitation at this new wavelength is measured. We thus observe simultaneously the filling of the first p-SH and a burning of the second p-SH at the new laser wavelength. After each burning-filling cycle, the sample is slightly shifted in order to have a virgin sample for a next cycle.

In Fig. 2, we show the first (original) spectral hole [Fig. 2(a)] burned by exposition of 820 mJ/cm². The central part of the figure [Fig. 2(b)] shows the absorption changes of the original hole induced by the laser when tuned to the second photon energy for three expositions of 13, 190, and 2220 mJ/cm². It means that positive and negative parts of curves represents the filling of original hole and the burning of the second hole, respectively.

In order to represent the dependence of the HF on the laser detuning ΔE from the original position, we plot the relative primary hole filling and the relative second hole

burning for exposition of 38 mJ/cm^2 (bottom part of the Fig. 2). Relative means that the hole depths are compared with the depth of the original hole before its filling. We can see that the relative filling of the first hole is about 25% through almost all the studied range of ΔE . For the highest ΔE ($> 35 \text{ meV}$), it starts to grow significantly. The burning of the second p-SH has nearly the same value as the filling of the first one, but for big negative ΔE , it falls down to zero. There are just two values of ΔE which show a specific relation between relative filling and new burning. They correspond to the position of the high- and low-energy side bands of the original hole. For $\Delta E = -20 \text{ meV}$, the second hole burning coincides with the low-energy side band (the pseudo-phonon wing³) of p-SHB, and the second holeburning has a minimum value for this detuning. On the other hand, for $\Delta E = 20 \dots 30 \text{ meV}$ [position of high-energy side-band (phonon-wing) of the p-SHB], the secondary burning has a strong maxima. This is exactly the most favourable detuning value to perform optical data storage in the frequency-domain (i.e., to burn several p-SHs for one position of laser spot on a sample). We have chosen a detuning of about 20 meV and try to burn a sequence of four p-SHs. Results are sketched in the Fig. 3. The HF is still relatively efficient and causes a smoothing of all existing holes during the subsequent burnings. Finally, the four holes have depths of only about 2% of the sample absorption. All holes can be erased by illumination with the laser tuned on the low-energy side of the excitonic absorption band.

It is clear that a system consisting of CuBr NCs in a glass matrix is not suitable for a frequency-domain optical data storage. Special samples made from organic molecules in a polymer matrix have much better properties. The main inconveniences of semiconductor NCs (regardless to the need of cooling to low temperatures and the use of complicated laser equipment) which one should have in mind are: (i) large widths of p-SHB means that one cannot burn more than four or five holes even in relatively large inhomogeneously broadened absorption bands, and (ii) the strong exciton-phonon interaction, which causes the broadening of holes and the growth of a pronounced structure of side bands.

The HF phenomenon can be explained within the framework of the photochemical mechanism as a backward reaction. If we excite new NCs by the second burning (unchanged by first burning) new electrons are injected into the matrix and they can be captured by the previously ionized NCs. Consequently, the primary hole is erased and the second one is burned into the absorption spectrum.

Comparing our results to those of Masumoto's group,⁴ we find the following. (i) *Spontaneous HF*: The recovery of p-SHs observed in Ref. 4 is also logarithmic but much faster than in our case. (ii) *Thermally-induced HF*: Masumoto *et al.* used a combination of two distributions of barriers to fit the thermal recovery of holes. The reason for this complicated treatment is not clear. They did not discuss spectral diffusion at all. (iii) *Laser induced HF*: In Ref. 4, only the filling of p-SH by broad-band light exposure is shown and the monotonous decrease of filling efficiency with decreasing photon energy is mentioned. The frequency-domain optical data storage experiment in CuCl NCs reported by Masumoto and

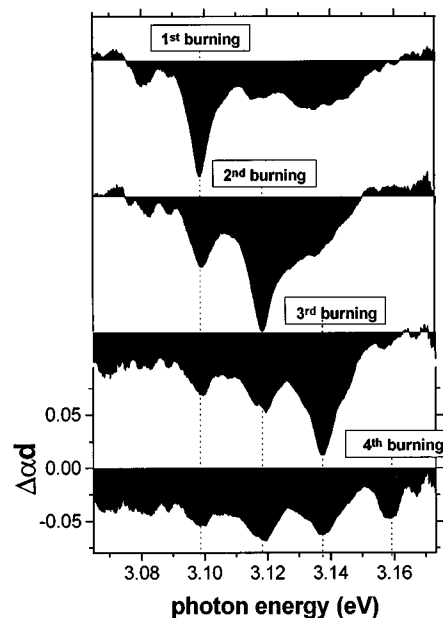


FIG. 3. Optical data storage in the frequency-domain: Four spectral holes burned in one place of the sample. The laser detuning ΔE between two subsequent burnings is 19 meV .

co-workers^{2,4} is comparable to our results on CuBr NCs, but in contrast to our opinion, it is claimed to be promising.

In conclusion, we show three different types of HF phenomena in small CuBr NCs embedded in borosilicate glass: a spontaneous HF, a thermally induced HF, and a laser-induced HF as they are observed. The p-SHB process seems to have a photochemical origin, namely the ionization of NC. The erasing of p-SH with time and by temperature cycling experiments is well described by the theory developed for organic molecules in amorphous matrices. From this comparison we deduce a value of the maximal barrier between product and educt of our photochemical reaction. Laser-induced HF experiments allow us to find the most favourable value of laser detuning ($\Delta E \sim 20 \text{ meV}$) for optical data storage experiments. Due to a strong exciton-phonon interaction and the always present HF effects, however, CuBr NCs in a glass matrix is not a perspective material for this application. Nevertheless, the rare possibility of changing arbitrarily the absorption spectrum of a material up to about 20% of its original absorption can be interesting for other types of applications.

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