THE PERSISTENT SPECTRAL HOLE-BURNING IN GLASSES WITH SEMICONDUCTOR NANOCRYSTALS

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Abstract

The persistent spectral hole-burning was observed in exciton bands of CdSe and CuCl nanocrystals doped in glass matrices. The peculiarities of hole-burning are explained on the base of photophysical model of persistent spectral hole burning. The burned holes show the distinct phonon structure which can be attributed to the vibrations on the semiconductor/dielectric boundary. The phonon structure in the $z^3$ exciton band of CuCl nanocrystal in borosilicate glass matrix is characterized by phonon energy 0.001 eV and calculated Debye-Waller factor $\alpha < 0.5$.

INTRODUCTION

The non-linear optical properties of semiconductor microcrystals in dielectric matrix (SMDM) were detected rather long ago. Last time SMDM attracted an additional interest because of the theory prediction of the non-linear optical property enhancement due to size effect [1]. Besides size, the high microcrystal symmetry is the essential condition of the "giant" optical non-linearity of SMDM. Therefore, the words "'quantum dots, zero dimension structures, etc." became main key words of the recent year publication works. However, the legitimacy of the quantum dot approach in reference to real SMDM is questionable.

The recent investigations [2,3] show an unsoundness of zero dimensional approach in reference to the semiconductor nanocrystal optical nonlinearities. It turned out that just a configuration of the nanocrystal/dielectric environment system determines the non-linear optical response in the many spectral hole-burning experiments. New for semiconductor nanocrystals, so-called persistent spectral hole-burning (PSHB) pretends to be the one of the main model of their optical properties even at room temperature and at short-lived processes. New approach has an advantage of PSHB high resolution spectroscopy and permits to get the new possibilities for investigation of SMDM in glasses.

To clarify the role of nanocrystal/dielectric boundary on the process of hole burning of SMDM in glass matrices we investigate the non-linear optical response in these systems and analyse phonon structure of burning hole.

EXPERIMENTAL SETUP AND RESULTS OF MEASUREMENTS
The samples were; CdSe and CuCl microcrystals doped into glass matrices on the base of GeO$_2$ and SiO$_2$-B$_2$O$_3$ respectively. The measurements were carried out with a narrow band dye laser as a pump beam source and a dye cell as a probe beam spectrally broad source. The both light sources were pumped by Q-switched Nd$^{3+}$:YAG laser. The pulse duration was 5 ns and the maximum repetition rate was 30 Hz. Additionally the special chopper is used to provide the second time delay between pump and probe beams. The chopper blocked in turn pump and probe beams. Optical spectra was recorded with an optical multichannel analyser combined with a monochromator. The average size of semiconductor microcrystals was estimated by small-angle X-ray scattering measurements.

Under the usual pump-probe method, when the both pump and probe beams pass through the sample simultaneously, the well known nonlinear response has been recorded. The samples showed the high nonlinear sensitivity, sharp the spectral burned holes and increasing absorption of neighboring off-resonance spectral regions (fig.1 (b)).

![Fig.1](image)

**Fig.1.** Linear (a) and differential absorption (b, c) spectra of the CdSe microcrystals embedded in GeO$_2$ glass. The average radius is 2.4 nm. The spectra (b) and (c) were measured for time delays of 0 and 33 ms, respectively. The pump photon energies corresponding to spectra 1 (1') , 2 (2') and 3 (3') are 2.287 eV, 2.214 eV and 2.138 eV respectively.

**Fig. 2.** Linear (a) and differential absorption (b) spectra of the CuCl microcrystals embedded in borosilicate glass. The average radius is 2.5 nm. The delay times corresponding to spectra 1, 2, 3 and 4 are 0 s, 0.1 s, 0.5 s and 1.4 s respectively. Pump photon energy is 3.237 eV.

On the fig 1 (c) is shown the differential absorption spectra recorded with the chopper under 33 ms delay between pump and probe beams. It almost completely reproduce those in fig. 1 (b). The further investigation showed that spectral burned holes were stable at low tempera with life times from 1.5 s for CdSe to hours for CuCl. The hole formation is accompanied by the growth of one or two antiholes in the neighboring off-resonance spectral region (fig.1). Therewith the burned
holes show the distinct phonon structure that can clearly see in the long-lived differential absorption spectra of CuCl samples (fig. 2).

These results show clearly an unsoundness of the generally accepted approach of the quantum dot optical non-linearities for the present media. Instead, so-called persistent spectral hole-burning (PSHB) phenomenon seems to be a suitable candidate for explaining these results [4].

MICROSCOPIC MODEL AND ANALYSIS OF EXPERIMENTAL RESULTS

As distinct from the high-symmetry quantum dot model, PSHB uses the concept of the microcrystal-matrix configuration. PSHB model assumes an additional inhomogeneous broadening even for an ensemble of the same microcrystals due to the existence of more than one energetically inequivalent ground states of the total microcrystal-matrix system. The spectrally narrow laser irradiation change the ground state configuration by the transition through the excited state (fig. 3). This changing of configuration leads to the decrease of the ground state population of the resonant transition. Also the neighboring off-resonance states population is increased (so-called photophysical model). Photophysical bleaching is accompanied by the absorption increase at the neighboring frequencies, which is not the absorption from the excited states but so-called antiholes. Decay time of PSHB is mainly due to the relaxation among the ground states, but not the relaxation of excited states. The full decay time of non-linear response depends on the excited state relaxation and the relaxation among ground states. In order to PSHB phenomenon appreciably manifests itself, the relaxation among the ground states should be slower the decay rate of any excited state. It can be seen that the antihole depth value depends on their spectral position in the absorption spectrum (fig. 1). The antiholes are the deepest near the absorption peak and at the high-energy side of it, where absorption is fairly large. The antihole on the low-energy side of the burned hole becomes small as the pump photon energy decreases. The antihole disappears if coincides with the transparency area. According to the photophysical persistent hole-burning approach, the main behavior is clearly understood [4]. The antihole depth correlates with the ground state density and, therefore, the spectral area of the antihole is restricted by the absorption band.

Fig. 3. Schematic representation of photophysical mechanism of persistent hole-burning phenomenon. The ground state levels are represented as the potential energy wells for the explanation of the origin of persistency. Absorption spectrum before (solid line) and after (dashed line) the excitation by spectrally narrow laser beam.

To understand the photophysical mechanism of PSHB is necessary to determine the factor which allow to stabilize electronic system in new configuration (fig. 3). Obviously in this process
must participate electron and lattice systems. The information about electron-phonon interaction can be received from the shape of burning hole. For that reason we investigate the distinct phonon structure of persistent burned hole in the $z_3$ exciton band of CuCl nanocrystals (fig. 2) and calculate the Debye-Waller factor. The line shape function of one absorption center can be expressed as: $I(\omega-\omega')=\alpha \delta(\omega-\omega') \cdot (1-\alpha) \cdot p(\omega-(\omega'+\Delta))$, where $h\omega'$ is the energy of zero phonon transition; $\delta$, $p$ are normalized zero phonon line and phonon wing; $\Delta$ is phonon energy; $\alpha$ is the Debye-Waller factor which is determined by electron-phonon coupling strength $S$, $\alpha = \exp(-S)$. Taking into account the distribution $N(\omega)$ of absorbed centers on absorbed frequency $\omega$ we can write the following expression for the burned hole shape after irradiation time $t$ at laser frequency $\omega_i$ (5):

$$
H_t (\omega) = \int_N(\omega') \cdot \exp(-ct \cdot I(\omega - \omega')) \cdot I(\omega - \omega') d\omega',
$$

(1)

where $c$ depends from laser intensity and matrix element of electron transition. To compare the results of calculation with experiment is more convenient to consider the differential spectra $HD$ as the difference between absorption spectra without laser excitation and $H_t$ (absorption spectra after laser radiation).

$$
HD_t (\omega) = \int [N(\omega') \cdot (1 - \exp(-ct \cdot I(\omega - \omega'))) \cdot I(\omega - \omega') d\omega',
$$

(2)

In the limit of saturation (shape of the hole does not change during irradiation) and assumptions that $\delta$ and $p$ line shapes are approximated by Gaussian and $N(\omega)$ is constant in the spectral region from hole to antihole, we can rewrite (2) in the following form: $HD=$

$$
= N \cdot [\alpha \cdot F((\omega_x + 3\Gamma_0 - \omega)/\Gamma_0) - F((\omega_x - 3\Gamma_0 - \omega)/\Gamma_0) +
+ (\alpha - 1) \cdot F((\omega_x + 3\Gamma_0 - \omega + \Delta)/\Gamma_1) - F((\omega_x - 3\Gamma_0 - \omega + \Delta)/\Gamma_1)] +
+ \alpha \cdot F((\omega_x + 3\Gamma_1 - \omega - \Delta)/\Gamma_0) - F((\omega_x - 3\Gamma_1 - \omega - \Delta)/\Gamma_0)] +
+ (\alpha - 1) \cdot F((\omega_x + 3\Gamma_1 - \omega)/\Gamma_1) - F((\omega_x - 3\Gamma_1 - \omega)/\Gamma_1)],
$$

(3)

$$
F(x) = 1/2 \cdot \text{erf}(x/\sqrt{2}),
$$
where $\Gamma_0$ and $\Gamma_1$ are the widths of the zero phonon line and phonon wing. The $3\Gamma$ in (3) is connected with the fact that Gaussian takes noticeable meaning only in region from $-3\Gamma$ to $+3\Gamma$. The first and the last terms in (3) determine the central peak of burned hole (fig. 4).

The second term determines the phonon wing and the third determines the pseudo phonon wing. In the assumption that peaks are not overlapped we have the following relative intensities in maxima:

\[
\begin{align*}
1, & \quad \omega = \omega_t \\
\alpha_1, & \quad \omega = \omega_t - \Delta \\
(\alpha - 1) \cdot F(3\Gamma_0 \Gamma_1), & \quad \omega = \omega_t + \Delta
\end{align*}
\tag{4}
\]

The estimations fulfilled with using (4) showed that the Debye-Waller factor reached the meaning $\alpha < 0.5$ ($S > 0.6$) for CuCl nanocrystals in borosilicate glass. The difference in energy between phonon line and phonon wing is 0.001 eV. This low energy phonon differs from phonons of bulk CuCl crystal ($TO = 0.021$ eV, $LO = 0.026$ eV) and can be attributed to vibration on the boundary of CuCl nanocrystals and the host matrix. The noticeable electron-phonon coupling means that exciton formation is accompanied by deformation of the atomic lattice. Such deformation can be explained in the assumption that exciton interacts with local states of defects on the nanocrystal/glass boundary.

**CONCLUSION**
We have demonstrated the persistent spectral hole-burning phenomenon in semiconductor microcrystals doped into dielectric matrix, specially, the photophysical mechanism of hole-burning. The differential absorption spectra of CdSe and CuCl microcrystals measured by pump-and-probe method keep the burned hole at least more then one second at liquid helium temperature. In all cases, the positive part of differential absorption spectrum, indicating the bleaching around the pump frequency, is accompanied by darkening of one or two spectral parts. These spectral parts are conserved for a long time too and are not caused by the generation of new (multipartical) states. The shape of burning hole is determined by low energy phonons on the nanocrystal/glass boundary.

The experimental results showed that the general accepted model of quantum dots can not be used directly even as a rough approximation for many cases of semiconductor microcrystal laser spectroscopy. PSHB phenomenon detected in semiconductor nanocrystals in glasses on the one hand gives new instrument for semiconductor structure investigations and on the other hand proposes a new class of media for an application-oriented investigations.

REFERENCES