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Formation and Decay of Excitons and Biexitons Excited in CdSe/CdS/CdZnS Colloidal Quantum Dots

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***Abstract*— The kinetics of a strongly nonequilibrium state of electrons and holes excited in quantum dots by a long laser pulse in the p-states are studied using the time-resolved photoluminescence. Three bands of the transient photoluminescence spectra were identified, and the ignition and decay of each of them was investigated. The complex picture of the time evolution of the bands is explained by the fast processes of cascade intraband relaxation and the Pauli exclusion principle. The durations of formation and decay for each of the photoluminescence bands are determined.**

Keywords*— *quantum dots; photoluminescence; exciton; biexciton; binding energy

I. INTRODUCTION

Multiexciton states in semiconductor quantum dots (QDs) with two or more excited electron-hole (e-h) pairs play an important applied role in such devices as lasers, photodetectors, solar cells, light-emitting diodes, and photon-pair sources [1-6]. Owing to the enhanced interaction of charge carriers under conditions of quantum confinement, multiexcitons in QDs are scattered mainly through a nonradiative Auger process, and effective photoluminescence (PL) can be realized only by single excitons [1,7]. In the simplest two-exciton case, the biexciton in the ordinary CdSe QD can emit a photon during its subnanosecond Auger lifetime [8], which is much shorter than the radiation lifetime of tens of nanoseconds for the remaining single exciton. This transient presence of biexcitons is not pronounced in time-integrated (or *cw*) PL spectra and necessitates the use of ultrafast spectroscopic techniques and high-sensitivity experiments to detect their fundamental optoelectronic properties, such as PL lifetimes, spectral positions, and binding energies [9-15].

The relaxation kinetics of two, three, and four e-h pairs in CdSe QDs were studied in [1] using femtosecond transient absorption spectroscopy. It was shown that the relaxation cascades are mediated by Auger processes. The studies of ultrafast PL of colloidal CdSe/ZnS QDs were carried out in [10]. A new transient emission band red shifted by about 10–30 meV relative to the band-gap luminescence was extracted. The authors attributed it to the neutral biexciton with very short measured lifetimes (100 ps for QD radius of 3.5 nm), in agreement with transient absorption studies of the two e-h pairs in [1]. The bands associated with the radiative decay of the single exciton, biexciton, and triexciton in the transient spectra of time-resolved PL were clearly observed in [11] for CdSe QD in hexane. The detailed study of the multiexcitonic effects in CdSe QDs, based on the energetics, the lifetimes, and the pump-power dependence of the various emission bands was presented in [12,13]. All measurements in [10-13] were performed at room temperature. We also draw attention to works [14-17] on this issue. As shown in [10,11,13], the positions of the exciton and biexciton bands do not depend on the pump power indicating that each of them is due to the emission from QDs in the well-defined one- and two-particle states.

To explain the time evolution of the system, the following scenario was expected. Initially, the sample is excited by an ultrashort laser pulse, so that in a selected QD some quantity of e-h pairs with the energy much higher than the QD energy gap is generated. For example, in [11] a pulse of 300 fs at 400 nm was used. After that, the system is left to itself (without any external influence). At the next stage the electrons and holes relax to the lowest states on a picosecond time scale [18-22] due to the fast intraband Auger-like and phonon emission processes. Then, at the third stage, a relatively slow process of recombination of e-h pairs occurs within a time interval from several tens of picoseconds to ten nanoseconds. This final stage of the time evolution of the system can be described by a simple set of coupled rate equations [11] and reflects in the time-resolved kinetics of PL studied in [10-13].

After rapid intraband relaxation, a quasi-equilibrium state is established in the sample. In different QDs from one (exciton) to several (multiexciton) e-h pairs can be excited, depending on the excitation intensity. Their

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number in the selected QD is described by the Poisson statistics [18]. The Poisson distribution is valid if the probability of generating the e-h pair in a QD is independent of the number of e-h pairs already existing in it [23]. Therefore, it is applicable for the case of ultrashort pulse excitation well above the PL band edge and makes it possible to supplement the set of rate equations by the initial conditions [11].

The population of the QD states can change very rapidly, and a high time resolution is needed to study its dynamics. Therefore, in the experiments [10-13] ultrashort laser pulses and high-resolution measuring equipment were used. In this paper we report that the PL from biexciton states in QD may be observed by more modest measuring means and with laser pulse, whose duration is comparable with the lifetime of biexcitons and far exceeds the intraband relaxation time.

II. Main Results

The time-resolved PL triggered by a ~30 ps long exciting pulse centered at the time 154 ps was investigated. The use of long pulses allows one not only to trace the decay of multi-exciton complexes, but also to study the process of their formation and, thus, to give a more complete picture of the physical processes occurring in the system. In addition, in contrast to [10-13], in order to achieve a fast relaxation to the lowest state, we excite electron-hole pairs by a laser directly near the p-states.

We obtained from the spectrogram with ~50 ps resolution the temporal trace of PL in the main (low-energy) spectral range. The entire process of the PL decay can be conventionally divided into three consecutive stages (I,II, and III) characterized by the different rates of the intensity decrease. We will assume that this difference is associated with sequential processes; in each of them the decay of a spectral component is accompanied by the excitation of the other, lower-lying energy state. However, unlike these works, we will not assume a single- or multi-exponential character of the decay, expecting that while some states are depleted, the filling of others may increase, and their decay will begin later. Therefore, the total radiation from these states will not have a simple form of decreasing exponents in the entire studied PL region.

The fitting function for the time-integrated PL spectrum can be decomposed into two Gaussian functions and a constant part that takes into account the noise background. The first of these functions, associated with the radiation from the *s*-states of electrons and holes, has a maximum at 1.98 eV and a full width at half maximum of the peak ~100 meV. The second function, associated with radiation from the *p*-states, significantly overlaps the first one and has a maximum at 2.1 eV and a width of ~340 meV. A strong overlap of the spectral bands occurs due to the inhomogeneous broadening associated with the size dispersion of the QDs. Since the radiation of biexcitons is a fast transient process, the time-integrated PL spectrum does not contain any information about their presence. However, they can be detected by studying transient spectra at different points in time. This would make it possible to determine such parameters of biexcitons as the binding energy, excitation and decay times.

We obtained a series of transient PL spectra extracted at different delays relative to the center of the exciting laser pulse using a 50 ps integration window. The asymmetric fitting function can be presented as a sum of three Gaussian components $F_i \exp\left(-\left(\varepsilon-\varepsilon_i\right)^2/\gamma_i^2\right)$ centered at $\varepsilon=\varepsilon_i$ ($i=x,xx,xxx$) and some background constant F. We associate the broad peak in each transient PL spectrum described by the Gaussian function with a maximum at $\varepsilon_{xxx}=2.1$ eV with the radiative recombination of e-h pairs in p-states. It quickly disappears, but since its width is large, it also appears in the time-integrated spectrum. The high peak at $\varepsilon_x=1.98$ eV makes a major contribution to the time-integrated spectrum. We associate it with the decay of single excitons. And, finally, we explain the peak at $\varepsilon_{xx}=1.92$ eV, which first arises and then disappears, as the decay of biexcitons [11]. This peak is relatively low and is strongly overlapped by the other peaks; therefore, we can say that *biexcitons hide behind excitons*. The binding energy $2\varepsilon_x-\varepsilon_{xx}$ of two excitons in the biexciton is 60 meV.

Comparing the spectral dependences we see that the parameters of the fitting function change with time. To find out how this occurs, let us study the temporal dependences of the amplitudes of Gaussian functions and their widths. The corresponding results are shown in Figs. 1 and 2.

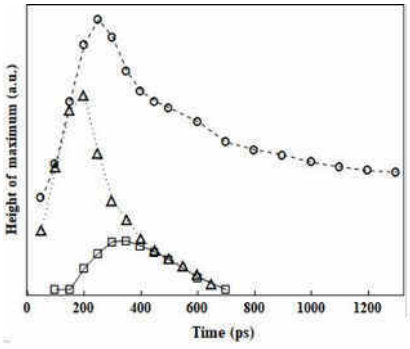

Figure 1. The temporal dependence of the height of the maximum of the fitting function at $\varepsilon=\varepsilon_x$ (circles), $\varepsilon=\varepsilon_{xx}$ (squares), and $\varepsilon=\varepsilon_{xxx}$ (triangles).

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As can be seen from Figs. 1 and 2, the laser pulse excites radiation, mainly from the *p*-states of electrons and holes, that occurs in a wide energy range and reaches a maximum value at 200 ps. Simultaneously, radiation appears from the *s*-states. It has an almost unchanged spectral range and reaches a maximum at 250 ps. The emission of biexcitons appears with even greater delay and much slower. Its growth ceases at 350 ps when two previous PL bands are already significantly reduced. The spectral range where this radiation occurs also does not almost change. Starting from 350 ps the decay of triexcitons is accompanied by the decay of biexcitons within ~140 ps. The decrease of radiation from single excitons within this time interval slows down. After 700 ps only a very slowly decreasing emission of single excitons occurs that can be described by a simple exponential curve. Using the exponential function for fitting only at times greater than 700 ps we obtain a value of ~10 ns for the decay time of a single exciton.

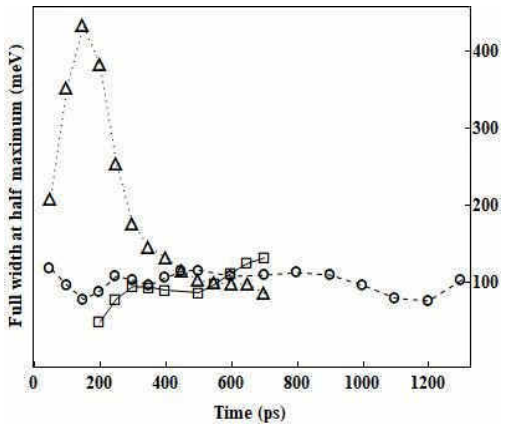

Figure 2. The temporal dependence of the width of the maximum of the fitting function at $\varepsilon = \varepsilon_x$ (circles), $\varepsilon = \varepsilon_{xx}$ (squares), and $\varepsilon = \varepsilon_{xxx}$ (triangles).

We assume that all microscopic processes occurring in the system can be divided into fast and slow ones. The accuracy of the measurements does not allow us to follow the fast processes, but we can take into account the results of their actions. These processes involve an Auger-like scattering of the electron by the hole and subsequent intraband relaxation of the scattered hole with emission of phonons. This sequence of processes leads to the fact that e-h pairs excited by a laser pulse near the $1P_e$–$1P_{3/2}$ state convert into e-h pairs in the lowest $1S_e$– $1S_{3/2}$ state. Moreover, due to the described mechanism of intraband relaxation the creation of pairs in the *s*-states may continue even after the end of the action of the laser pulse if this is allowed by the filling of the $1S_e$–$1S_{3/2}$ states of the e-h pairs in accordance with the Pauli Exclusion Principle. The number of pairs in *p*-states at this time decreases. This explains the behavior of the curves in Fig. 1 within the time interval from 100 to 200 ps.

If there is only one e-h pair in the *s*-states, then taking into account the Coulomb interaction, we can speak about the formation of an exciton. If the number of e-h pairs in this state reaches a maximum value equal to two, we can speak about the formation of a biexciton. In this terminology, the appearance of the second pair in the state where one pair is already present automatically means the disappearance of both pairs (or two excitons) and the formation of a biexciton. The second pair, like the first one, can quickly transit to the *s*-state from the *p*-state as a result of fast intraband relaxation. In this case, the appearance of a biexciton means the disappearance of one pair from the *s*-state and one pair from the *p*-state. The corresponding behavior of the curves in Fig. 1 manifests itself within the time interval from 200 to 350 ps where the ignition of the biexciton band of PL is accompanied by a rapid decrease in both the radiation from the single excitons and the emission from the e-h pairs in the *p*-states.

By the time of 350 ps, the generation of biexcitons seems to reach saturation, and their decay begins. We can consider the annihilation of any constituent e-h pair of the biexciton as a decay of the biexciton resulting in the creation of an exciton and a photon. The remaining pair can also annihilate; this means a radiative decay of the exciton. Another channel for the biexciton's decay is associated with an Auger-like interband process where the annihilating e-h pair transfers its energy to an electron or hole of the second e-h pair. We see that the biexciton and exciton decay processes are slower than those indicated for the formation of excitons and biexcitons. Note, that the decay of the biexciton PL band in the interval from 350 to 700 ps is accompanied by almost the same decay of other bands. In our opinion, this also indicates the saturation of biexciton states. Electrons and holes in the *p*-states *do not hasten* to radiatively recombine, but wait for the opportunity to stay in a lower energy state.

Thus, the stage I of the PL decay corresponding to the peak is the shortest and fastest; it has the widest spectrum and is associated with the recombination of electrons and holes from the *p*-states. The stage II located at the foot of the peak is characterized by complex processes associated with both the formation and decay of biexcitons, as well as the slowing down of the decay of triexcitons and single excitons. And, finally, the slowest stage III located in the tail of the dependence is associated with the radiative decay of single excitons.

III. CONCLUSION

We excited electrons and holes near the energy of the p-states expecting to get their fast relaxation in one step. However, the obtained results are very different from those previously presented in [10-13], where the

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excitation was high in the energy zone. We managed to trace not only the disintegration of the main PL bands, but also their ignition.

This gives evidence that taking account of the Pauli Exclusion Principle plays a significant role in the description of the temporal evolution of the system. An external pulse can excite only six e-h pairs in the *p*-state, while the *s*-states are ready to accept only two. Therefore, the pair conversion from the *p*- to the *s*-state does not occur until the *s*-state is at least partially vacant. The results presented by us show that in our case the Poisson distribution cannot be used as an initial condition for the rate equations at any fixed point in time. And the rate equations themselves cannot be linear, since one should take into account such a phenomenon as the saturation of the state of Fermi particles.

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