

RADIATION SPECTRUM OF HOT EXCITONS IN Si NANOCRYSTALS

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The self-trapped exciton state (STE) is very important for the dynamics of hot excitons in photoexcited silicon nanocrystals embedded in a SiO₂ matrix. This fact has been recently confirmed by the experimental data obtained by the femtosecond pump-probe spectroscopy technique in Amsterdam University. In this work we have studied the energy exchange between the exciton localized in the STE state and the hot exciton in the core of silicon nanocrystals and have shown that it determines the dynamics of the energy distribution of the hot excitons. Using the Monte-Carlo we have simulated the energy distribution of excitons in the time interval 10–100 ps after excitation. Thus the model of formation of the distribution of hot excitons in silicon nanocrystals is developed and the fast formation of the wide energy distribution is demonstrated. The form of the photoluminescence spectrum almost directly corresponds to the energy distribution of excitons in a silicon nanocrystal at a given moment. In the result we have found the relaxation times of hot excitons equal to 100 ps and the inner quantum efficiency of the ultrafast photoluminescence of about 0.1%. These values are close to the experimentally observed ones.

Keywords: silicon nanocrystals, 'hot' electrons, energy relaxation

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1. Introduction

Silicon nanocrystals (SiNCs) is a popular object of investigations due to their efficient photoluminescence (PL) at room temperatures in the visible optical range. This property makes Si NCs promising for application in optoelectronics and medicine [1].

There are two bands observed in the Si NCs photoluminescence spectrum: the first band in the 'red' region and the second one in the 'blue' region. The red band has the slow decay time (about 100 μ s) and is characterized by a blue shift with decreasing of the Si NCs size. The light emission is originated by the radiative recombination of confined excitons in the ground state. The blue photoluminescence band is characterized by ultrafast decay times (10–100 ps) and it is assigned to the radiative emission of hot nonequilibrium carriers [2, 3]. The scientific group from Amsterdam University [4] have observed the red shift of this band with decreasing the Si NC

size, which has been presented as the evidence of the direct-band radiative transitions of the hot excitons in Si NCs.

There are two problems: (i) why the typical relaxation time (about 100 ps) of the 'blue' band is longer by two orders of magnitude compared to that of bulk silicon; (ii) what is a mechanism, which leads to a so fast formation of the blue band in the wide energy region (2.2–2.7 eV) during 1–10 ps after excitation. In the paper [5] the role of the nanocrystal shell in ultrafast carrier emission dynamics has been investigated for the Si NCs in the SiO₂ matrix. In that work an important role of the interface has been demonstrated.

In the current paper we present the model of formation of the distribution of hot carriers in silicon nanocrystals, occurring due to the energy exchange between the shell state and the core. By the Monte-Carlo simulation we have demonstrated the fast formation of a wide 'blue' band and have obtained

the relaxation time close to the experimentally observed one.

We study dynamics of the exchange between self-trapped exciton (STE) state on the Si NCs surface and the nanocrystal core. In Section 2 we describe the STE model and in Section 3 we show the way it leads to a wide distribution of hot excitons in the picosecond time interval. In Section 4 we discuss the form and the inner quantum efficiency of the blue photoluminescence band.

2. Self-trapped exciton model

In studying the dynamics of hot charge carriers by the method of femtosecond pump–probe spectroscopy, de Boer et al. [6] found that the surface self-trapped exciton states related to the Si–O bond play the key role in the dynamics of the hot carriers. In order to describe the physical processes caused by the self-trapped excitons, the single-mode Huang–Rhys model has been used [7, 8]. In this work we use the same model with one vibration frequency ω .

The system of the Si–O bond vibration plus an exciton is described by using the adiabatic potential scheme in the space of the configuration coordinate Q and the total energy E . In Fig. 1 three adiabatic potentials are presented. The adiabatic vibration potential 1 corresponds to the vibration potential of our system around the equilibrium position ($Q = 0$) and an exciton is absent. The adiabatic potential 2 corresponds to the presence of the exciton in the ground state in the core of Si NC. The gap between the origins of potentials 1 and 2 is the energy of the “free” exciton in the ground state (E_{exc}).

The potential 3 corresponds to the case, when the exciton is captured in the STE state. The origin of the adiabatic potential shifts to Q_0 at the energy E_{STE} due to the interaction between the exciton and the local vibration. The difference between the energies of potentials 3 and 2 is determined by the thermal excitation energy ϵ_T for the transition of the exciton localized at the ground state in the Si NC to the STE state: $\epsilon_T = E_{\text{STE}} - E_{\text{exc}}$. In the work [6] it has been shown that E_{STE} does not vary with changing of the nanocrystal size. In Fig. 1 the dotted line represents potential 4 that corresponds to the hot exciton in the nanocrystal core (hot “free” exciton) with energy E_{exc} (the excitation energy). In Fig. 1 the horizontal bold lines signify the vibration levels in the corresponding potential, the vibration energy of the ground level is $\hbar\omega/2$.

The exciton is born in the core of the Si NC at high energy level E_{exc} after the absorption of energy of a light pulse. In this moment the vibration of the Si–O bond is in the ground level. The total en-

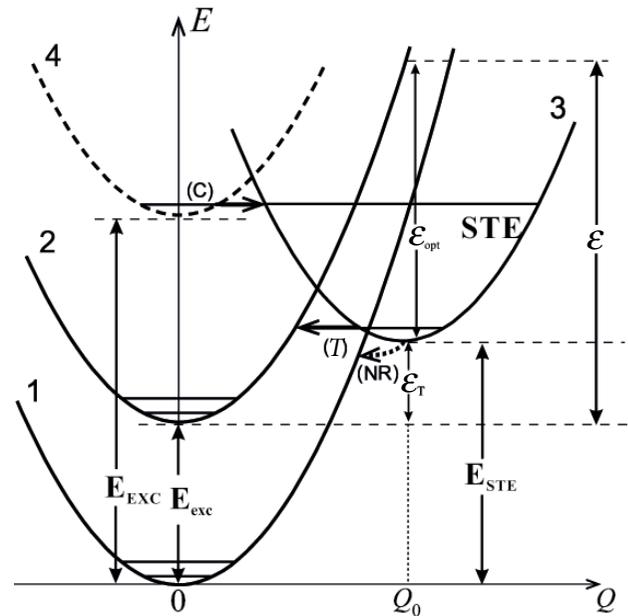


Fig. 1. The configuration scheme of the adiabatic vibrational potentials within the framework of the Huang–Rhys model [8].

ergy of the system is $E = E_{\text{exc}} + \hbar\omega/2$. From the core of the nanocrystal the exciton has the probability to tunnel to the surface STE state. In this process (arrow (C) in Fig. 1) a part of the exciton energy transforms to the vibration energy of the Si–O bond, i. e. the energy of the exciton changes from E_{exc} to E_{STE} and the Si–O vibration transits from the ground vibration level to the high level with energy $\hbar\omega/2 + E_{\text{exc}} - E_{\text{STE}}$. The inverse process is also possible: the exciton can come back from the surface STE state to the Si NC core from different vibration energy levels, including the ground level (arrow (T) in Fig. 1). Also there is a significant possibility of nonradiative recombination of the exciton in the STE state at the ground vibration level (arrow (NR) in Fig. 1). Estimations of the probabilities of these processes have been done in work [8].

3. Dynamics of hot excitons energy distribution

The process of the capture of the “free” hot exciton with the energy E_{exc} from the nanocrystal into the STE state at the high vibration level is continued by the relaxation to the ground vibration state assisted by emission of local phonons. However, at each vibration energy the return (the STE exciton to “free” exciton) process is possible. The total energy of the system is always conserved, but part of the vibration energy transforms into the exciton energy. The reverse process is also possible, so we have a variety of the exchange

processes between the “free” exciton state and the STE surface state during relaxation.

In Fig. 2 the configuration scheme of the silicon nanocrystal of 2.5 nm size with the surface self-trapped exciton state is presented. The curve (G) presents the adiabatic potential $U_G(Q)$ corresponding to the absence of an exciton in a nanocrystal, (1) corresponds to the adiabatic potential for the exciton in the ground state, (2)–(12) are the adiabatic potentials of “free” excitons in various excited states in a nanocrystal, and the shifted parabolic curve is the adiabatic potential for the surface self-trapped exciton. We assume that for Si NC with a diameter of 2.5 nm the origins of the STE state and the ground state of the nanocrystal have the same energy, $\varepsilon_T = E_{STE} - E_g = 0$ (Fig. 2) and the optical excitation energy is equal to 2.75 eV [6].

Both the “free” excitons and STE can go down to a lower vibration level in the same adiabatic potential after the emission of the local phonon $\hbar\omega$ with the probability W_{ph} . On the other hand, “free” excitons can also loose their energy due to the interaction with Si NC phonons. The process can be described as a transition from one parabolic potential to another one with lower minimum energy (Fig. 2), which is characterized by the probability W_{rel} . We determine the gap between two neighbour potentials equal to the energy of the local phonon $\hbar\omega$ for the Si–O bond,

that is 140 meV. The most efficient transitions between the STE state and the Si NC core are the transitions between states with the same energy. In [9] it has been shown that in Si NC after phonon absorption hot electrons and holes in the ground state are born. Using this result we consider the exciton transitions proceeding due to the hot electron tunneling. Thus the exciton transition probability is given by the production electron tunneling probability (w_e) and the overlap integral of corresponding vibration wave functions.

In this paper we present the Monte-Carlo simulation for the nanocrystal with a diameter of 2.5 nm. In the framework of our approximation, moving of each electron has been considered separately. We have chosen a minimal time interval, in that we calculate a chance of the transition of the exciton to an other electron state or at the vibration level equal to 10^{-14} seconds. For every possible state of exciton a numerical interval from 0 to 1 has been taken and divided proportionally to the transition and relaxation probabilities from this state. We supposed that in the first moment, immediately after excitation, electron is captured in the STE state at a high vibration level corresponding to the total exciton energy of 3.57 eV (see Fig. 2). At each time step a random number from 0 to 1 has been generated and the electron

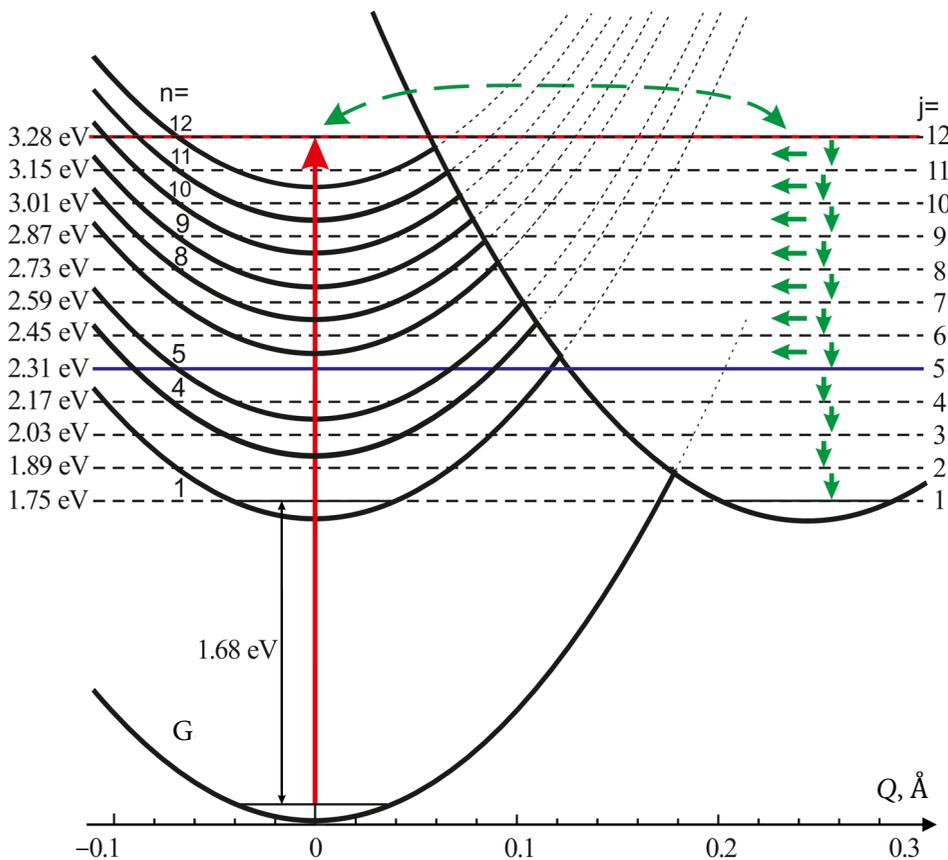


Fig. 2. The configuration scheme of hot carriers relaxation in Si NCs within the framework of the Huang–Rhys model.

has or has not transited to the position of this random number in the numerical interval. Thus, using random numbers and choosing values of relaxation probabilities we have found the electron position in any time moment. After reiteration of this procedure many times we obtained a spectral distribution of hot excitons in the nanocrystal after different time delays. Each reiteration means a new electron is injected into the system and the process starts from the beginning.

The results are presented in Fig. 3. We assumed the probability of the local phonon emission W_{ph} is equal to 10^{12} 1/s. The probability of the electron tunneling w_e is taken equal to 10^{11} 1/s as in work [6]. The value of W_{rel} is accepted to be 10^{-10} by using the results of work [6], where the energy relaxation of the core exciton has been studied. On the y axis the number of excitons, which are in the excited states in the nanocrystal, is presented; on the x axis there is the energy of the states.

In the first moment after the excitation all excitons are in highly excited states in the Si NC core, but after 30 ps, there is a broad band of spectral energy distribution with the maximum near 2.8 eV. Some excitons are already relaxed to the ground states. After

60 ps the number of relaxed carriers is significantly enhanced and the maximum of the band shifts by 200 meV to the lower energy region. Most excitons reach the ground state after 100 ps.

Thus, the results obtained demonstrate that the exchange process between the surface STE state and states in the nanocrystal leads after 30 ps to the broad energy band of exciton energy distribution and most excitons are relaxed to the ground state after 0.1 ns.

4. Spectrum distribution and efficiency of the hot photoluminescence

The excitons pumped to the high energy state release their energy through the phonons of the Si NC core or transit to the STE state. Also the radiative recombination is possible. The quantum efficiency of the radiative transition from each exciton state in the Si NC core is defined as

$$\eta = \frac{\tau_{\text{nonrad}}}{\tau_{\text{nonrad}} + \tau_{\text{rad}}}, \quad (1)$$

where τ_{rad} and τ_{nonrad} are radiative and nonradiative lifetimes of the excitons, respectively.

In [10] the radiative time of the hot exciton in Si NCs embedded in the SiO_2 matrix was estimated as $\approx 10^{-8}$ – 10^{-7} s, that is in two orders of magnitude longer than the time of the exciton relaxation, obtained in the current work. According to this fact the efficiency of radiative emission of the hot exciton can be about 0.1%. This result is in agreement with the experimental estimation of the hot photoluminescence inner efficiency obtained in [4].

There are the variety of the radiative lifetimes for the exciton energy states, but we believe that exciton energy distribution plays the dominant role in the formation of the hot exciton light emission band.

5. Conclusions

Using the Monte-Carlo method we have demonstrated the role of the energy exchange between silicon nanocrystal states and the surface STE state in fast formation of a wide distribution of hot carriers in Si nanocrystals during 10–100 ps after excitation. The model of formation of the distribution of hot excitons in silicon nanocrystals is developed and fast formation of the wide ‘blue’ band is demonstrated. We have obtained the relaxation times of the hot excitons close to the experimentally observed decay time of ultrafast photoluminescence. Thus we have demonstrated that the typical relaxation time

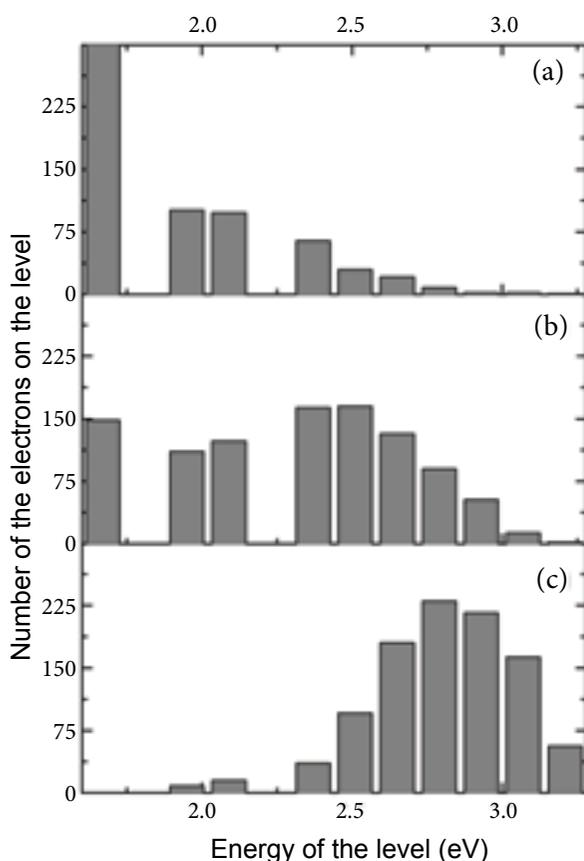


Fig. 3. Electron distribution after (a) 100 ps, (b) 60 ps and (c) 30 ps after excitation.

of the ‘blue’ band is about 100 ps due to exciton transitions between the surface state and the Si NC core during the relaxation. This mechanism also leads to very fast formation of the blue band in the wide energy region 2.2–2.7 eV during 1–10 ps after excitation.

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KARŠTUJŲ EKŠITONŲ SILICIO NANOKRISTALUOSE SPINDULIUOTĖS SPEKTRAS

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