Theoretical modeling of excitation and de-excitation processes of Er in SiO$_2$ with Si nanocrystals

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Abstract

We construct the theory of carriers confined in Si quantum dots with finite energy barriers for electrons and holes in the framework of the multiband effective mass theory. We apply this theory for theoretical modeling of the excitation of erbium inside and outside of Si nanocrystals in SiO$_2$ matrix due to the Auger process induced by the recombination of a confined electron–hole pair as well as the intraband transitions of "hot" confined carriers. Auger de-excitation processes of the Er^{3+} ion leading to the quenching of erbium luminescence are discussed as well.

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1. Introduction

The material composed of Si nanocrystals dispersed in SiO$_2$ matrix doped by Er is a subject of big interest in Si photonics because it has been shown that photo- and electroluminescence of Er$^+$ ions in SiO$_2$ can be effectively sensitized here [1]. However, till now understanding the mechanism of energy transfer from Si nanocrystals to Er ions is incomplete. In order to understand the processes with participation of carriers confined in nanocrystals, one should know their energy spectrum and wave functions. Previously, we have developed the theory of Auger excitation induced by recombination of electron–hole pairs confined in Si nanocrystal for Er ions in Si dots (inside the dots and near the boundary), where the barrier height has been considered as infinite for carriers and the tunneling phenomena have been taken into account as a weak perturbation [2]. Such an approach is valid for relatively large Si nanocrystals in SiO$_2$ suitable only for a small fraction of the nanocrystals under experimental investigation.

Here, we construct the theory of carriers confined in Si quantum dots with finite energy barriers for electrons and holes in multiband effective mass approximation. The finite energy barriers at the boundary between Si and SiO$_2$ are accounted when using the Bastard boundary conditions. The advantages of our method in comparison with ab initio methods based on the density functional theory [3] are that we can calculate not only the ground state of the confined carriers but also excited ones. We have found that the calculated energy spacings between neighboring electron and hole levels are of the order of hundreds of meV for experimentally relevant quantum dots [4]. Therefore, the energy relaxation of excited electrons and holes is damped as well as Auger processes because they should be assisted by multiphonon processes. Thus, one should take into account the Auger excitation of Er ions due to intraband transitions of confined "hot" carriers too. The other advantage of our approach is that the calculation of various excitation and de-excitation processes involving confined carriers using the wave functions, which we have found, remains transparent. We apply the theory constructed for theoretical modeling of the excitation of Er inside and outside of Si nanocrystals situated in SiO$_2$ matrix due to the Auger process induced by the recombination and the transition between space quantization levels of confined carriers. The theoretical consideration of various Auger de-excitation processes of the excited Er

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ion leading to the quenching of Er luminescence has been fulfilled.

2. Auger excitation of Er ion due to the recombination of a confined electron–hole pair

Let us consider the excitation of Er^{3+} ion by electron–hole pair recombination. In accordance with our calculations and existing experimental data the ground energy of an exciton in the nc is in the range 1.2–1.7 eV for the nc's under experiment [5–7]. Therefore, such excitons can effectively transfer energy exclusively to Er^{3+} ions being in the second $^4I_{11/2}$ excited state (energy of transition to the ground $^4I_{15/2}$ state $\Delta_{02} = 1.24$ eV) or in the third $^4I_{9/2}$ excited state (transition energy $\Delta_{03} = 1.55$ eV). Electron–hole pairs being in the excited states can lead to transitions involving higher multiplets of the Er^{3+} ion. The energy conservation in the transfer process is provided by phonon emission. Thus, the electron transition is accompanied by a multiphonon transition with participation of local phonons of the Er-ion vibration or the optical phonons associated with Si dots.

In this case, the excitation of the 1.5 μm luminescence of erbium radiative transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ should be considered as two step process with characteristic time τ_{eff} equal to sum of two: (i) time τ_1 of Er^+ excitation in higher excited state and (ii) time τ_2 of relaxation to state $^4I_{13/2}$. The relaxation time τ_2 is of the order of 2 μs in SiO_2, and the observed excitation time cannot be shorter.

To get the time τ_1, we have calculated the probability of Auger recombination. It can be written in the following way:

$$W_{\mathrm{tr}} = \frac{2\pi}{\hbar} \sum_{f'} \overline{|M_{ff',vM}|^2}$$
$$\times \sum_N J_T(N)\delta(E_{\mathrm{ex}} - \Delta_{ff'} - N\hbar\omega), \qquad (1)$$

where $\hbar\omega$ is the phonon energy, N is the number of emitted phonons, $\Delta_{ff'}$ is the energy of transition between the initial state in the ground $^4I_{15/2}$ multiplet of the Er^{3+} ion and the excited state in one of the upper multiplets. $J_T(N)$ is the phonon factor calculated in the model of two shifted parabolic potentials [8] depending on the Huang–Rhys factor S, the phonon energy $\hbar\omega$ and temperature (see Fig. 1). Index f' in Eq. (1) enumerates all possible final states of the 4f-electron having wave functions $\psi_{f'}$. The bar over the square of absolute value of the electron transition matrix element $M_{ff',vM}$ means averaging over initial states f of the 4f-electrons of the Er^{3+} ion being in the ground state with wave functions ψ_f, states of the confined electron numerated by $v = \pm x, \pm y, \pm z$, and states of the confined hole numerated by $M = -1, 0, 1$. For details of the carrier functions and energy levels see Ref. [4].
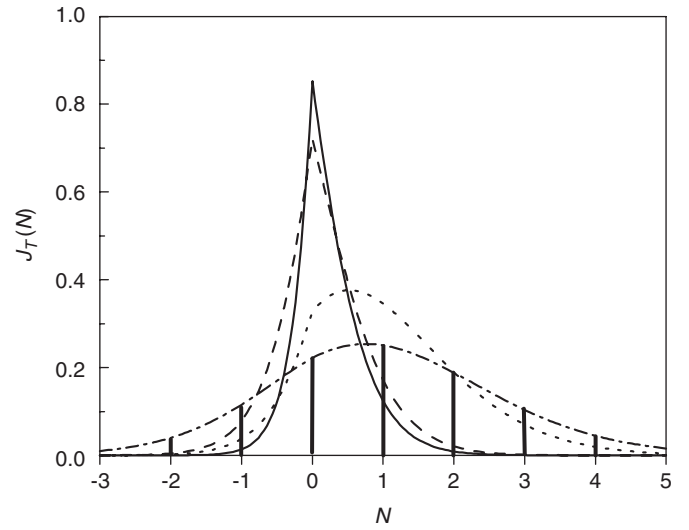

Fig. 1. Phonon factor $J_T(N)$ corresponding to the model of two shifted parabolic potentials at room temperature ($T = 300$ K). Solid line corresponds to parameters used in this paper (Huang–Rhys factor value $S = 0.1$, phonon energy $\hbar\omega = 60$ meV); $S = 0.1$, $\hbar\omega = 20$ meV for dashed line; $S = 1$, $\hbar\omega = 60$ meV for dotted line; and $S = 1$, $\hbar\omega = 20$ meV for dash-dot line.

General expression for the electron transition matrix element is given by

$$M_{ff',vM} = \int d^3r_1 \int d^3r_2 [\psi_v^e(\vec{r}_1)]^* \psi_M^h(\vec{r}_1)$$
$$\times V_C(\vec{r}_1 - \vec{R} - \vec{r}_2)\psi_f^*(\vec{r}_2)\psi_{f'}(\vec{r}_2), \qquad (2)$$

where the Coulomb interaction accounting for the time and spatial dispersion of the dielectric constant $\kappa(q, \omega)$ reads:

$$V_C(\vec{r}_1 - \vec{R} - \vec{r}_2) = \frac{4\pi e^2}{V} \sum_{\vec{q}} \frac{1}{\kappa(q,\omega)q^2} e^{i\vec{q}(\vec{r}_1 - \vec{R} - \vec{r}_2)}. \qquad (3)$$

Here V is normalization volume, $\vec{R}$ is the position of the center of the Er^{3+} ion, $\vec{R}, \vec{r}_1$ are counted from the center of the nanocrystal, $\vec{r}_2$ is counted from the center of the Er^{3+} ion.

Crucial for the evaluation of the electron matrix element are the calculation of the overlap integral between electron and hole Bloch amplitudes with the factor $e^{i\vec{q}\vec{r}_1}$ and the calculation of the integral $\langle f|e^{-i\vec{q}\vec{r}_2}|f'\rangle$ taking into account restrictions, which these integrals impose on the transferred wave vector $\vec{q}$. Depending on the position of Er^{3+} ion relative to the nanocrystal, different contributions can play the leading role.

2.1. Short-range Coulomb contribution

The absolute value of the transferred wave vector is around $k_{0s} = 1.15 k_X$ ($1/k_{0s} = 0.075$ nm) for the Er^{3+} ion situated inside the nanocrystal or at a very small distance away from the nanocrystal [9]. So the interaction has a contact character, i.e. it is determined by values of the electron and hole wave functions at position $\vec{R}$ where Er^{3+}

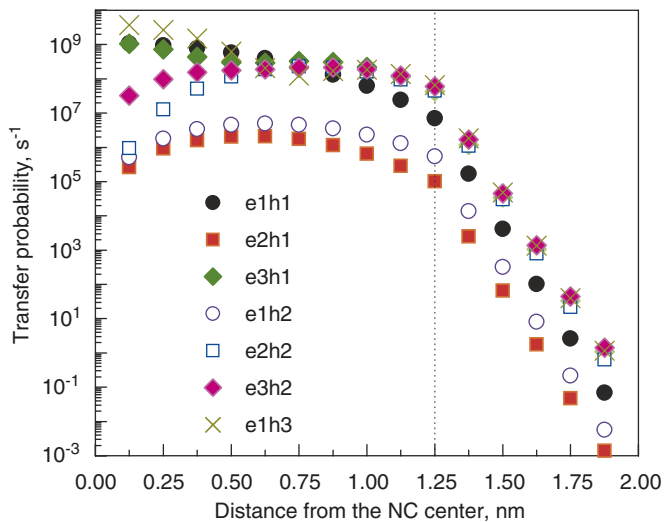Fig. 2. Transition probability for nanocrystal size $d = 2.5$ nm. Huang–Rhys factor value $S = 0.1$, phonon energy $\hbar\omega = 60$ meV, temperature $T = 300$ K.

ion is situated. The result of calculation of the transition probability is presented in Fig. 2. The exact value of the phonon energy and Huang–Rhys factor S are not known for the material considered here. We have used value $S = 0.1$, which is in accordance with experimental values obtained for Er^{3+} ions fluorozirconate glass [10], and $\hbar\omega = 60$ meV for the phonon energy, which is close to the one of optical phonon in Si.

2.2. Dipole–dipole contribution

If Er ion occurs at a distance $R \gg r_{nc}$, the Coulomb operator in (2) transforms to the dipole–dipole interaction:

$$\hat{V}_{dd} \equiv \frac{e^2}{\kappa_{eff} R^3} \left(\vec{r}_1 \vec{r}_2 - 3 \frac{(\vec{r}_1 \vec{R})(\vec{r}_2 \vec{R})}{R^2} \right). \quad (4)$$

In this case we can also neglect the size of space localization of confined carriers comparing to R. So the expression of the probability of transition in dipole–dipole approximation can be reduced to

$$W_{tr}^j = \frac{8\pi}{3} \frac{1}{\hbar^2 \omega} \frac{e^4}{\kappa_{eff}^2 R^6} d_{ex}^2 d_{0j}^2 J_T(N_j). \quad (5)$$

Averaged matrix elements d_{0j} of radius corresponding to the Er^{3+} ion transition from the ground (0) to excited state (j) as well as d_{ex} for transition of confined exciton can be expressed via the corresponding oscillator strengths. The calculation leads to the result that the transfer rate of the dipole–dipole transfer process given by Eq. (5) does not exceed $10\,s^{-1}$ for the considered nanocrystals.

In result, we have found out that dipole–dipole excitation is not effective. The Auger excitation assisted by recombination of confined excitons can take place as contact process only, i.e. only for Er inside Si nanocrystals or practically on their boundaries. The excitation goes to

the second or higher excited state and the observed excitation time of the $1.55\,\mu m$ luminescence cannot be shorter than the time of relaxation of Er ion.

3. Auger excitation of "hot" confined carriers

The "hot" electron–hole pairs (electrons in the levels up to fifth and holes in one up to fourth) could be created by optical pumping with photon energy of 2.75 or 2.42 eV which is often used in experiments. "Hot" carriers created could not have fast energy relaxation to the ground exciton state because one-phonon processes are impossible and transitions controlled by electron–electron interaction should be assisted by multiphonon processes. Thus, the energy relaxation via Auger excitation of Er ions directly to the first excited state (the transition energy of 0.8 eV) becomes possible. The process is similar to impact excitation by hot carriers in bulk silicon, but here the process should be assisted by multiphonon transition to take away the excess energy. Our estimations show that the effective excitation takes place for Er ions which occur at the distance of the order of nc radius and the time of excitation is in the range 0.1–10 μs. It should be noted that under high pumping when several e–h pairs are created per one nc, several Er that occur in the close vicinity can be excited.

For example, we present in Fig. 3 the probability of Er excitation to the first excited state in result of a confined hole transition from the third to the first space quantized level.

4. Auger de-excitation processes

However, fast luminescence quenching should take place if there are confined carriers due to the reverse process, that
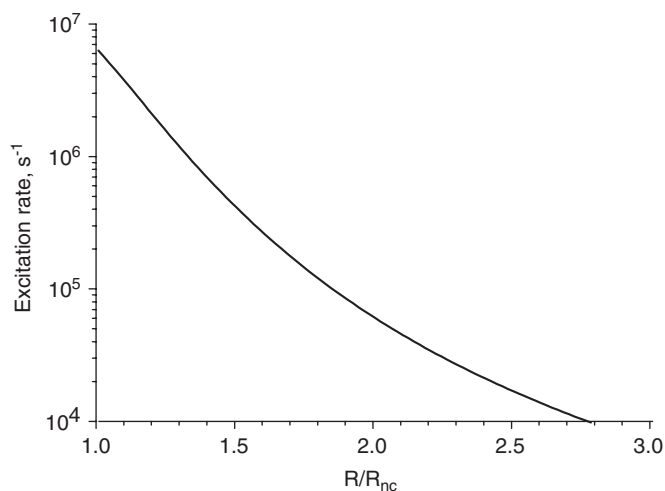

Fig. 3. The probability of erbium excitation due to confined hole transition from the third to the first quantized energy level versus distance from the centrum of nanocrystal, normalized to the radius of quantum dot. Huang–Rhys factor $S = 0.1$, nanocrystal size $d = 2.5$ nm, phonon energy $\hbar\omega = 60$ meV, temperature $T = 300$ K.

is, the Auger de-excitation process in which a carrier transits from the low energy level to the higher one. We obtained the characteristic time of this process in the range of $0.1–10\,\mu s$.

If after these fast processes there is only one e–h pair remaining in nc, another excitation process (i.e. the Auger excitation due to the recombination of confined electron–hole pair) occurs and Er ion gets excited with a long life time.

One can expect an Er^{3+} ion inside nanocrystal to be accompanied by a donor center similar to the one in bulk silicon. In such a case one may observe the fast quenching of Er luminescence by another process involving an extra electron, which can take away the energy of the excited Er^{3+} ion.

5. Conclusions

Auger excitation of an erbium ion due to recombination of a confined electron–hole pair is a two step process: first, erbium is excited to a higher excited state, and then it should relax down to the first excited state. Calculations show that such a process can be fast only for ions situated inside the nanocrystal or just at its boundary.

Direct erbium excitation into the first excited state can be caused by Auger energy relaxation of a "hot" confined carrier. It is shown that this process can be fast for ions situated up to the distance of the order of nanocrystal size from its centrum. More than one erbium ions can be excited if there are more than one electron–hole pair in the nc.

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