Tunnel migration in ensembles of silicon nanocrystals doped with phosphorus.

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Abstract. A comparative study of radiative recombination and tunnel migration in ensembles of P-doped Si nanocrystals embedded in wide-band dielectric matrix is performed. We have found the migration process to be strongly suppressed at donor concentration exceeding some critical value. At the same time, the radiative recombination rate gradually rises as the concentration increases. This essentially enhances the radiative-channel efficiency in the photoluminescence process.

1. Introduction
Improvement of luminescent properties of various silicon-based structures remains up to now a challenge for modern optoelectronics. Because of indirect band gap of silicon, light emission turns out to be suppressed or completely forbidden in such structures. This drawback is partially overcome in Si nanocrystals due to the Heisenberg uncertainty relations and phonon assistance. An observation of visible-range emission from silicon nanocrystals [1] confirms this fact.

As a means to improve the emittance of silicon crystallites, doping with phosphorus was proposed. It has been shown experimentally that the doping can increase photoluminescence intensity by several times at certain conditions [2]. This rise of the photoluminescence intensity is a consequence of interplay between radiative and nonradiative processes. In the present paper, we analyze an effect of one of the most efficient nonradiative processes – tunneling of excited carriers from one quantum dot to an adjacent one – on light emission of an ensemble of highly and homogeneously P-doped Si nanocrystals. For this purpose, we estimate the rates of the radiative interband recombination and electron tunneling in Si nanocrystals doped with phosphorus. The calculations were carried out within the framework of envelope function approximation for spherical quantum dots.

2. Results and discussion
Coulomb interaction of the excited electron with the phosphorus ion plays a crucial role in the recombination process. The Coulomb field in a nanocrystal consists of two parts [3]: the long-range part; and the short-range microscopic part usually named the central-cell field [4]. The short-range part was determined by Pantelides and Sah [5] using microscopic dielectric function.

Determination of the electronic structure of a P-doped silicon crystallite also exhibits a key role of the short-range field in the electron state formation [6]. In particular, in the conduction band, the
spinless ground state (being sixfold degenerate in an undoped dot) splits due to the short-range field similarly to bulk Si into a singlet with the lowest energy, and doublet and triplet.

It should be noted that, phonon-assisted and no-phonon donor-induced transitions individually contributes to the total recombination rate $\tau^{-1}_R$. The phonon-assisted radiative transitions are, in fact, independent of doping [7]. Their rate $\tau^{-1}_0$ remains almost constant as function of phosphorus concentration $n_D$ in the dot. On the contrary, the donor-induced transitions are essentially intensified as $n_D$ increases. As was shown earlier [8], the central-cell potential of the phosphorus ions embedded in Si nanocrystal efficiently mixes electronic states of $X$ and $\Gamma$ bands. Such a mixing produces a partially direct radiative transition enhanced by the quantum confinement effect, which causes rising the rate.

The results of our calculations of radiative rates [8] are presented in Fig. 1. As seen, at donor concentrations $n_D$ greater than approximately 1% (1 P atom per 99 Si atoms), $\tau^{-1}_R$ is much greater than the radiative rate $\tau^{-1}_0$ in undoped nanocrystal ($n_D = 0$) for all dot sizes. This means that the donor-induced transitions become much faster than the phonon-assisted ones. This effect is more pronounced for bigger crystallites. For instance, at $n_D = 2\%$, the donor-induced transitions have the rates 1–2 orders of magnitude greater than the rates of the phonon-assisted transitions as the dot radius increases from 1 to 3 nm, respectively.

Let us now consider the tunnel migration of excited carriers. After laser pumping, electrons from the lowest energy level in the conduction band of one quantum dot can either relax into the valence band of this dot with photon emission or tunnel into the adjacent nanocrystal with phonon assistance occupying there the level with close energy. Similarly, the holes can tunnel from the upper level in the valence band onto the energy level in the valence band of a neighboring nanocrystal.

We consider two nanocrystals with radii $R_1$ and $R_2$, and assume the first nanocrystal to be less than the second one, i.e. $R_1 < R_2$. The distance between the dots, equal to the minimal distance between their edges, is $L$. Denote the wave functions of $k^{th}$ stationary state in the first and the second isolated nanocrystals as $\Psi^{(1)}_k$ and $\Psi^{(2)}_k$, respectively. Then, taking into account a weak tunnel connection between the nanocrystals, it is possible to construct the wave functions of the carriers in the double-dot system as a superposition of $\Psi^{(1)}_k$ and $\Psi^{(2)}_k$. In particular, one can formally write the wave functions of the initial, and the final electron (or hole) states in the form:

$$\Psi_{IF} = A_k^{(1,F)}\Psi^{(1)}_k + B_k^{(1,F)}\Psi^{(2)}_k.$$  \hspace{1cm} (1)

Here, $A_k^{(1,F)}$ and $B_k^{(1,F)}$ are the expansion coefficients, and the Einstein convention was used when summing over $k$. Suppose, for definiteness, that initially (before tunneling), the electron mainly populates the first nanocrystal (i.e. $A_k^{(1)} \gg B_k^{(1)}$), and has the energy approximately equal to $E_i$ that is
the energy of the ground state in the first isolated nanocrystal. On the contrary, in its final state (after tunneling), the electron mainly occupies the second nanocrystal. Correspondingly, in this case $A_k^{(f)} \ll B_k^{(f)}$, and the electron energy is close to the energy $E_{2n}$ of some $n$th stationary state in the conduction band of the second nanocrystal. Note that, we suppose $E_1$ to be greater than $E_{2n}$. In the opposite case the tunneling is strongly suppressed, as was also pointed out by Roman and Pavesi [9].

Evidently, similar treatment can be performed for hole tunneling.

Tunneling with phonon emission is defined in the first order of the perturbation theory by the rate

$$
\begin{align*}
\tau_{nm}^{-1} &= \frac{2\pi}{\hbar} \sum_{i=1,2} \sum_{q_i} \left| \langle \Psi_f | U^{(i)}_{i|q} | \Psi_i \rangle \right|^2 \delta_{L} \left( E_i - E_{2n} - \hbar \nu_i(q) \right). \\
&= \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2}.
\end{align*}
$$

Here, $U^{(1,2)}_{i|q}$ stands for the operator of the electron interaction with $\ell$th and $q$th phonon mode in the first, or in the second, crystallite. Because of homogeneous broadening, we have replaced standard Dirac delta-function by the Lorentz function

$$
\delta_{L} (x) = \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2},
$$

with semi-width $\gamma$ which is about 10 meV according to Allan and Delerue [10]. It is worth noting that, the Lorentz function allows one to violate the energy conservation under the tunnel transition. Nevertheless, the difference $E_{1} - E_{2n}$ for the nanocrystals with radii ranging within 1 – 3 nm can achieve 0.2 – 0.3 eV. In this case, the single-phonon process turns out to be inefficient for compensation this difference to within $\gamma$. As a result, instead of the Fermi golden rule in the form given by Eq. (2) we have to treat the electron-phonon interaction in the second order of the non-stationary perturbation theory. Results of our calculations for undoped and doped nanocrystals are presented in Fig. 2 and Fig. 3, respectively.

**Figure 2.** Tunnel rates of the electrons (solid lines) and holes (dots) in undoped nanocrystal as functions of the distance between the edges of the nanocrystals. The emitting nanocrystal has the radius $R = 1.5$ nm. The radius $R_1$ of the accepting nanocrystal equals (from top to bottom): 1.6 nm; 1.9 nm; 2.2 nm. Dashed line represents the radiative recombination rate in the emitting nanocrystal [7].

**Figure 3.** Electron tunnel rates as functions of the donor concentration $n_D$ at the distance $L = 0.5$ nm between the edges of the emitting and accepting P-doped nanocrystals. Radius of the emitting nanocrystal $R_1 = 1.5$ nm. Radii of the accepting nanocrystals are indicated in the figure. Dashed line represents the radiative recombination rate in the emitting nanocrystal according to [8].

It is seen in Fig. 2, that in the mean, after averaging oscillations caused by the resonant tunneling,
the migration rate quickly (exponentially) drops as the distance between the nanocrystals increases. However, if \( L \) is less than some distance \( L_0 \) depending mainly on the difference \( R_2 - R_1 \), the tunnelling turns out to be much faster than the radiative electron-hole recombination (dashed horizontal line) in the first nanocrystal.

As has been already mentioned, phosphorous doping leads to the partial degeneracy removal in the electron spectrum. As a result, the energy level has more homogenous distribution in the conduction band that effectively reduces the difference \( E_1 - E_{2a} \). This, in turn, leads to some initial rise of the tunnel rate with increasing \( n_0 \), as shown in Fig. 3. However, further increase of the phosphorus concentration sharply reduces the tunnel rate. In the accepting nanocrystal, electrons (emitted from the donors) populate the lowest levels in the conduction band and block tunneling of the ground-state electron (which could participate in the radiative transition) from the emitting nanocrystal if the Fermi level in the accepting nanocrystal turns out to be higher than the ground-state energy level in the emitting nanocrystal. Tunneling with increasing energy is strongly suppressed by temperature factor like \( \exp(-\Delta E/kT) \) while more probable tunneling with decreasing energy is forbidden due to the Pauli principle. As a consequence, the tunnel rate sharply drops when the phosphorus concentration achieves some critical value defined by the difference in sizes of the emitting and accepting nanocrystals.

For comparison, we have depicted in Fig. 3 the radiative recombination rate in Si nanocrystal with radius 1.5 nm as a function of the phosphorus concentration. It is seen that, at concentrations exceeding a certain value, the radiative recombination rate becomes greater than the migration rate.

The tunnel rates for holes are rather less than, or of the same order as, the ones for electrons, which is explained by the higher potential barrier for holes compared to the one for electrons [11]. In the valence band, phosphorus doping results, in fact, only in a common shift of the energy levels without their splitting and degeneracy removal. Therefore, the migration rates of holes shown in Fig. 2 remain almost invariable with varying phosphorus concentration.

3. Conclusion

Thus, doping with phosphorus can be an essentially positive factor from the point of view of improving emittance of silicon nanocrystals. First, doping accelerates the radiative interband recombination. Second, doping blocks one of the most efficient nonradiative channels – tunnel migration of excited electrons. Both these factors should enhance the photoluminescence intensity of Si nanocrystal ensembles.

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