Available online at www.sciencedirect.com
ScienceDirect
Materials Science and Engineering C 27 (2007) 1386–1389
MATERIALS SCIENCE & ENGINEERING C
www.elsevier.com/locate/msec

Confined electrons and holes in Si nanocrystals: Theoretical modeling of the energy spectrum and radiative transitions

I.N. Yassievich [a,*], A.S. Moskalenko [a,b], A.A. Prokofiev [a]

[a] *Ioffe Physico-Technical Institute of RAS, 26 Polytechnicheskaya, 194021 St. Petersburg, Russia*
[b] *Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

Received 4 May 2006; accepted 8 September 2006
Available online 19 October 2006

Abstract

We construct the theory of carriers confined in spherical Si quantum dots with finite energy barriers for electrons and holes in the framework of Luttinger Hamiltonian for holes and taking into account the strong anisotropy of the conduction electron effective mass in Si. As a boundary condition for the electron and hole wave functions we use continuity of the wave functions and the current at the boundary of the nanocrystals. We apply this theory for the case of the SiO_2 matrix surrounding Si quantum dots. We show that for experimentally relevant quantum dots energy spacings between neighbouring electron and hole levels are of the order of hundreds of meV. Therefore the relaxation of excited electrons and holes is damped.

Theoretical calculations of probabilities of various radiative transitions are presented.

Keywords: Confined carrier; Silicon nanocrystal; Radiative transition

1. Introduction

The material composed of Si nanocrystals dispersed in SiO_2 matrix is a subject of big interest in various optoelectronic applications [1,2]. In order to understand the processes with participation of carriers confined in the nanocrystals, one should know their energy spectrum and wave functions. Here we present the theoretical modeling based on the envelope function approximation taking into account strong anisotropy of conduction band energy spectrum and the complex structure of the valence band in Si. The finite energy barriers at the boundary between Si and SiO_2 are accounted for using the Bastard boundary conditions [3,4]. The advantages of our method in comparison with *ab initio* methods based on the density functional theory [5–7] are that we can calculate not only the ground state of the confined carriers but also excited ones. Furthermore our theory can be applied to a broad range of nanocrystal sizes. We are not limited to nanocrystals with a small number of atoms. The other point is that the calculation of various excitation and de-excitation processes involving confined carriers using the wave functions, which we find, remains transparent.

2. Electron and hole states

The conduction band of bulk Si has six equivalent minima in the first Brillouin zone at points $\pm\vec{k}_{0,z} = (0,0,\pm 0.85)k_x$, $\pm\vec{k}_{0,y} = (0,\pm 0.85,0)k_x$, and $\pm\vec{k}_{0,x} = (\pm 0.85,0,0)k_x$, where $k_x = 2\pi/a$ and $a = 0.543$ nm is the lattice constant of Si [8]. The minima are situated in the neighbourhood of the six X-points (there are three non-equivalent X-points). The conduction band is doubly degenerate at each of the X-points, which is a consequence of the fact that Si lattice has two atoms in the elementary unit cell and the origin can be chosen at the center of any of them. Assuming the Bloch amplitudes not changing in the neighbourhood of X-point one can write the wave function of one of six equivalent ground states of electrons in the nanocrystal as

$$\psi_v^e = \xi^e(\vec{r})u_{cv}e^{i\vec{k}_{0v}\vec{r}} \qquad (v = \pm x, \pm y, \pm z), \tag{1}$$

* Corresponding author. Tel.: +7 812 292 8574; fax: +7 812 292 1017.
E-mail address: Irina.Yassievich@mail.ioffe.ru (I.N. Yassievich).

0928-4931/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2006.09.011

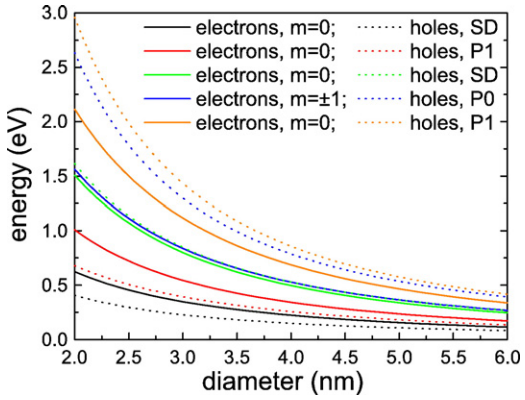

Fig. 1. Dependence of the energy levels of electrons and holes on the nanocrystal diameter. The value of the magnetic quantum number m for electrons and the wave function symmetry for holes are shown near the corresponding lines.

where u_{cv} is one of two Bloch amplitudes of bulk electron at X-point in the Brillouin zone, which corresponds to the lower conduction band at the $\vec{k}_{0v}$ point.

Let us consider an electron in the valley having minimum at k_{0z}. Its envelope wave function ξ^e inside the nanocrystal satisfies Schrödinger equation for a free electron with anisotropic effective mass: $m_z=m_{\|}=0.916m_0$, $m_x=m_y=m_{\perp}=0.19m_0$ with m_0 being the electron mass in vacuum. For description of electrons in SiO_2 (outside the nc) we assume a simple isotropic band with effective mass equal to m_0. The barrier energy $U_e=3.2$ eV is used for boundary Si/SiO_2 [9]. We use Bastard type boundary conditions implying that the envelope wave function ξ and the velocity density $\xi^*\hat{v}\xi$ are continuous across the boundary [3,4].

We have calculated the electron energy levels and the corresponding envelope wave functions numerically. The dependence of the energy levels on the nc size is depicted in Fig. 1. The dependence of the electron envelope wave functions on the distance from the nanocrystal centrum is shown in Fig. 2 for $d=2$ nm (such a small diameter is chosen for demonstration in order to resolve better the tunnelling tails of the envelope wave functions).

For description of the valence band states in Si we use generalization of the Luttinger Hamiltonian [10,11] in the limit of vanishing spin-orbit coupling, which is justified for Si. Holes wave functions can be found as eigenfunctions ψ_{FM} of the square $\hat{F}^2$ of the full angular momentum operator $\hat{\vec{F}}=\hat{\vec{L}}+\hat{\vec{J}}$ ($\hat{\vec{L}}=-i\vec{r}\times\hat{\partial}_{\vec{r}}$) and its projection $\hat{F}_z$ onto the axis z. The operator of "internal hole spin" $\hat{\vec{J}}$ is operator acting on the Bloch amplitudes. In our approximation $J=1$. In order to find hole states with the lowest quantization energies it is sufficient to look at states with $F=0$ and $F=1$. It is convenient to choose basis of the Bloch amplitudes space in the form of spherical components [12] $u_0=Z, u_{\pm}=\mp\sqrt{1/2}(X\pm iY)$ of the corresponding functions $X=yz$, $Y=xz$, and $Z=xy$, of the representation $\Gamma_{25'}$.

For $F=0$ there is one type of hole states with the envelope wave function

$$\psi^P_{00}(r,\theta,\varphi)=R^P_0(r)\sum_{m1,m2}C^{00}_{1m_1 1m_2}Y_{1m_1}(\theta,\varphi)u_{m_2}, \qquad (2)$$

where $R^P_0(r)$ is the radial part of the envelope wave function, $Y_{nm}(\theta,\phi)$ are spherical harmonics, and $C^{jm}_{j_1m_1j_2m_2}$ are Clebsh–Gordon coefficients [12].

For $F=1$ there are two types of hole states determined by the envelope wave functions ψ^{SD}_{1M} and ψ^P_{1M}, which are degenerate in M=−1, 0, 1:

$$\psi^{SD}_{1M}(r,\theta,\varphi)=R^S_1(r)Y_{00}(\theta,\varphi)u_M + R^D_1(r)\sum_{m1,m2}C^{1M}_{2m_1 1m_2}Y_{2m_1}(\theta,\varphi)u_{m_2}, \qquad (3)$$

$$\psi^P_{1M}(r,\theta,\varphi)=R^P_1(r)\sum_{m_1,m_2}C^{1M}_{1m_1 1m_2}Y_{1m_1}(\theta,\varphi)u_{m_2}. \qquad (4)$$

The form of envelope wave functions given by Eqs. (2), (3), and (4), is well-known and was used in the past for description of impurity states in semiconductors [13].

In case of holes the rigorous formulation of the boundary conditions for the boundary between Si and SiO_2 in the framework of the envelope function method is not a trivial task and generally has to be investigated in comparison with experiment and numerical methods. In this paper we take into account that the main contribution to the valence band states is usually given by p-orbitals and the corresponding effective

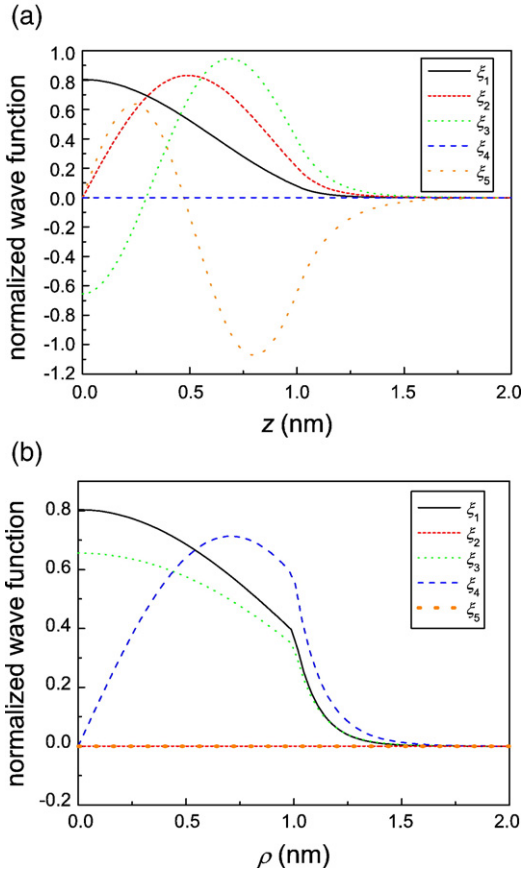

Fig. 2. Electron wave functions in dependence on the cylindrical coordinates z and ρ for the five lowest electron levels of a nanocrystal with diameter of 2 nm. The wave function ξ^e_4 of the fourth level with magnetic number $m=\pm1$ has also an angular dependence $e^{im\phi}$.

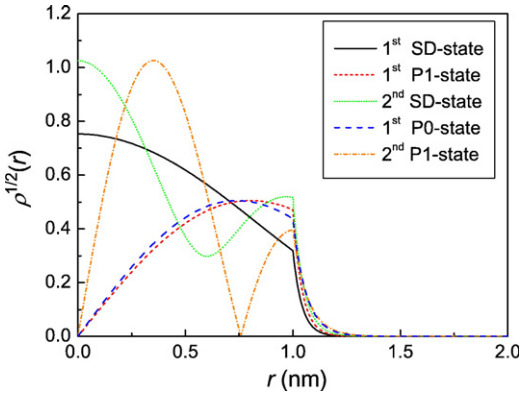

Fig. 3. Square root of the radial hole density in dependence on the distance from the nanocrystal centrum for five lowest hole with levels F=0, 1 of a nanocrystal with diameter of 2 nm.

mass is pretty large. Therefore, for description of hole states outside the Si nanocrystal we use the same Luttinger Hamiltonian but with parameters corresponding to an isotropic effective mass being equal to $5m_0$. In such a case the wave functions of holes are similar to (2), (3), and (4), and one can formulate Bastard type boundary conditions for the relation of hole wave functions inside and outside the nanocrystal. The barrier energy U_h=4.3 eV has been used for holes [9].

The calculated dependence of hole energy levels on the nanocrystal radius and their types are presented in Fig. 1 together with the electron levels. The dependence of the square root of the radial hole density on the distance from the nc centrum is shown in Fig. 3 for d=2 nm and several lowest hole levels with F=0, 1.

3. Excitonic shift

The Coulomb interaction leads to the decrease of the ground state energy of an electron–hole pair. In order to calculate this energy correction we take into account that for the ground states and low excited states electrons and holes are to the high extent localized inside the nc. Only a small part of the carrier probability density penetrate outside the nc even in the case of small nc's with $d\sim2$ nm. We estimate energy correction due to Coulomb interaction of confined carriers using the wave functions of infinite barrier dot. The effect of the increase of the effective distance between the electron and hole due to the probability density tails penetrating outside the nanocrystal is in counteraction to the decrease of the effective dielectric constant. In the case of the electron and hole being at the lowest quantization levels the energy correction is [11]: $V_C^{e1,h1}=-1.54e^2/(\kappa_{Si}R_{nc})$, where κ_{Si} is the dielectric constant of Si and it has been taken into account that the surrounding material has an approximately three times smaller dielectric constant than Si. For carriers in excited states the numerical factor changes: for example, it equals to 1.17 (when the electron is in the first state and the hole is in the second), to 1.29 (when the electron is in the second state and the hole is in the first), and to 1.01 (when both the electron and the hole are in the second states).

The dependence of the exciton ground state energy on the size of nanocrystal is presented in Fig. 4. For comparison, the experimental data obtained from photoluminescence spectra [14–19] are shown too.

4. Radiative transitions

We have produced the calculation of the probabilities P_r of radiative recombination assisted by emission of an optical transverse phonon (with energy 57.5 meV) as well as longitudinal one (55.3 meV). These channels of radiative transitions dominate in bulk Si. The calculations have been produced for electron–hole pairs localized in various space quantized states. The results of calculations for the ground exciton state ($P_{r,gr}$) are presented in Fig. 5. The probabilities of radiative transitions involving excited states P_r have similar dependences on nanocrystal size being of the same order of magnitude (e.g. for transition from the second electron state to the first hole state $P_r=0.8P_{r,gr}$). In Fig. 5 the result of calculations of direct (zero-phonon) radiative transition for the ground exciton state is presented as well. Such transition becomes possible for

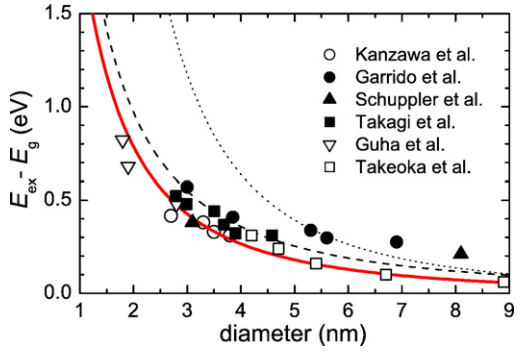

Fig. 4. Dependence of the exciton ground state energy as a function of diameter of nanocrystal (solid line). Dashed line shows the same energy without exciton shift taken into account. Dotted line represents ground exciton energy for infinitely high energy barriers. For comparison, the experimental data obtained from photoluminescence spectra [14–19] are presented.

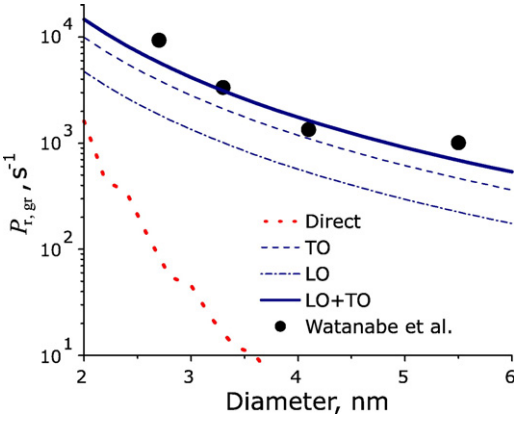

Fig. 5. Calculated probabilities $P_{r,gr}$ of radiative transitions between ground electron and hole states: assisted by emission of a TO-phonon (dashed line), an LO-phonon (dash–dot line) and their sum (thick solid line) as well as probability of direct (zero-phonon) transition (dot line), as functions of nanocrystal diameter. Experimental points [20] are shown as well.

confined carriers but one can see that the oscillator strength is noticeably less for the dots with diameter larger than 2 nm.

5. Conclusions

We have constructed the theory of confined carriers in Si quantum dots in SiO_2 matrix. We have calculated the energy levels as functions of the dot diameter and found that the energy spacings between neighbouring electron and hole levels are of the order of hundreds of meV for experimentally relevant quantum dots. Therefore the energy relaxation of excited electrons and holes is damped as well as Auger processes because they should be assisted by multiphonon processes. It is reasonable to suppose that the wide spectrum band observed in photoluminescence is originated by radiative transitions of "hot" carriers, i.e. carriers in excited states.

Acknowledgments

This work was financially supported by grants of Russian Foundation for Basic Research, NWO-RFBR, INTAS, Russian Academy of Sciences, Russian President Grant for Leading Scientific Schools. AAP also acknowledges support by Dynasty Foundation.

References

[1] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, F. Priolo, Nature 440 (2000) 408.
[2] A. Polman, Nat. Mater. 1 (2002) 10.
[3] P. Yu, M. Cardona, Physics and Material Properties, 3rd ed. Springer, 2002.
[4] E.L. Ivchenko, G.E. Pikus, Superlattices and Other Heterostructures, Springer, 1997.
[5] B. Delley, E.F. Steigmeier, Phys. Rev., B 47 (1993) 1397.
[6] M.V. Wolkin, et al., Phys. Rev. Lett. 82 (1999) 197.
[7] C.S. Garoufalis, A.D. Zdetsis, S. Grimme, Phys. Rev. Lett. 87 (2001) 276402.
[8] A. Dargys, J. Kundrotas, Handbook on Physical Properties of Ge, Si, GaAs and InP, Science and Encyclopedia Publishers, Vilnius, 1994.
[9] V.A. Burdov, JETP 94 (2002) 411.
[10] V.N. Abakumov, V.I. Perel, I.N. Yassievich, in: V.M. Agranovich, A.A. Maradudin (Eds.), Modern Problems in Condensed Matter Sciences, vol. 33, Elsevier, Amsterdam, 1991.
[11] A.S. Moskalenko, I.N. Yassievich, Phys. Solid State 46 (2004) 1508.
[12] A.R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton University Press, 1957.
[13] A. Baldereschi, N.O. Lipari, Phys. Rev., B 8 (1973) 2697.
[14] Y. Kanzawa, T. Kageyama, S. Takeda, M. Fujii, S. Hayashi, K. Yamamoto, Solid State Commun. 102 (1997) 533.
[15] B. Garrido Fernandez, M. Lopez, C. Garcia, A. Perez-Rodrigues, J.R. Morante, C. Bonafos, M. Carrada, A. Claverie, J. Appl. Phys. 91 (2002) 798.
[16] S. Schuppler, S.L. Friedman, M.A. Marcus, D.L. Adler, Y.-H. Xie, F.M. Ross, T.D. Harris, W.L. Brown, Y.J. Chabal, L.E. Brus, P.H. Citrin, Phys. Rev. Lett. 72 (1994) 2648.
[17] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, T. Nakagiri, Appl. Phys. Lett. 56 (1990) 2379.
[18] S. Guha, B. Qadri, R.G. Musket, M.A. Wall, T. Shimizu-Iwayama, J. Appl. Phys. 88 (2000) 3954.
[19] S. Takeoka, M. Fujii, S. Hayashi, Phys. Rev., B 62 (2000) 16820.
[20] K. Watanabe, M. Fujii, S. Hayashi, J. Appl. Phys. 90 (2001) 4761.