Tight-binding calculations of SiGe alloy nanocrystals in SiO₂ matrix

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Abstract
In the empirical tight-binding approach we study the electronic states in spherical SiGe nanocrystals embedded in SiO₂ matrix. For the SiGe alloy and the matrix we use the virtual crystal approximation. The energy and valley structure of electron states is obtained as a function of Ge composition and nanocrystal size. Calculations show that the mixing of hot electrons in the nanocrystal with the electrons in wide band gap matrix is possible and this mixing strongly depends on the Ge composition in the nanocrystal.

Keywords: SiGe, quantum dots, tight-binding method

(Some figures may appear in colour only in the online journal)

1. Introduction

The SiGe alloy has the crystal structure similar to the bulk silicon and it is possible to grow the Si₁₋ₓGeₓ layers on the silicon substrate changing the content of Ge in the wide range from x = 0 (pure silicon) to x = 1 (pure germanium). This system is widely used in modern electronics: by changing the Ge content it is possible to switch the electronic band structure from bulk silicon to germanium. An important feature of Si₁₋ₓGeₓ material is high mobility and convenient, well-developed production technology. These properties have opened a way of using Si₁₋ₓGeₓ to manufacture different electronic devices: high-speed transistors [1], long-wave infrared detectors [2], solar cells based on SiGe p–i–n structures [3].

The use of silicon and germanium in optoelectronics is limited by the fundamental feature of their indirect band structure: the extrema of the conduction band are near the edge of the Brillouin zone, and the top of the valence-band is at the center of this zone. However, in nanocrystals (NCs), electrons and holes are localized and no longer have a definite (quasi) momentum due to the Heisenberg uncertainty principle. It stimulates the rapid development of technology, experimental, and theoretical work on the study of optical phenomena in silicon and germanium nanoparticles. There is a large number of reviews and monographs devoted to the successful application of silicon nanocrystals in SiO₂ matrix in optoelectronics, photovoltaics and medicine (see [4]).

In [5] the photoluminescence from spherical Si₁₋ₓGeₓ alloy nanocrystals with 4–5 nm diameter in SiO₂ matrix was studied as a function of the Ge content. The NC-Si₁₋ₓGeₓ samples were fabricated by the cosputtering of Si, Ge, and SiO₂ and postannealing at 1100°C. Recently, similar NCs prepared using the same technique were studied in details by spectroscopy and time-resolved spectroscopy [6, 7].

In the present paper, we develop the empirical tight binding (ETB) approach [8] for the modeling of electronic states and energy levels of SiGe nanocrystals embedded in SiO₂ matrix and present the results for Si₁₋ₓGeₓ nanocrystals with germanium content x in the range from x = 0 to x = 1. The distributions of the density of states in reciprocal and real space show the X–L valley transition as a function of Ge content and also show that excited electronic states with relatively small energy may strongly penetrate the SiO₂ matrix.

2. Virtual crystal approach for SiGe alloy

To simulate the alloy in empirical tight-binding (ETB), two approaches are widely used. First, one may consider the randomly chosen atom distribution within the structure and then average over realizations [9]. Second option is to use the virtual crystal approximation (VCA) which is the ETB parametrization of the averaged band structure of the alloy. Second approach has its limitations: It is valid only in the cases when...
one wants to neglect the effects due to the disorder in the alloy material. Recently it has been shown [10] that for the VCA in ETB it is not necessary to parametrize the alloy. At least for ternary alloys in the InGaAsSb and AlGaAs families the band structure of an alloy may be constructed from the ETB parameters of basic materials. Here we adopt the same procedure for the SiGe alloy. The parameters of the alloy are found from the parameters of Si and Ge: The lattice constant of the alloy is found as a linear interpolation between binaries (Vegard’s law). Then the parameters of $\text{Si}_1-x\text{Ge}_x$ alloy are found as a linear interpolation of ETB parameters of Si and Ge strained to the lattice constant of the alloy.

In [10] it is demonstrated that the accurate description of deformation potentials of binary materials is of critical importance. Then, the band structure of alloy will also be precise. The parametrization for bulk Si and Ge (as well as for SiGe bonds) which quantitatively reproduces all deformation potentials of the materials may be found in [11].

In the ETB we follow the procedure of [8] and construct the matrix elements of the tight-binding Hamiltonian using the standard procedure [12]. The parameters also depend on the strain: First, the transfer matrix elements of bulk Si and Ge are scaled due to the change of the lattice parameter following standard generalized Harrison law [8]

$$V_{m,ijk} = V_{m,ijk}^0 \left( \frac{d_m}{d_0^m} \right)^{n_{m,ijk}},$$

where $V_{m,ijk}^0$ and $d_m^0$ are the transfer parameters and lattice constant for the material $m$ (Si, Ge or SiGe), and $n_{m,ijk}$ is the power in generalized Harrison law, these parameters are taken from [11]. The lattice constant of the alloy is found from the linear interpolation

$$a_{\text{Si}_1-x\text{Ge}_x} = (1-x)a_{\text{Si}} + xa_{\text{Ge}},$$

(2)

The valence band offset (VBO) of the alloy depends linearly on $x$

$$E_{\text{VBO}} (\text{Si}_1-x\text{Ge}_x) = E_{\text{VBO}} (\text{Ge}) \cdot x,$$

(3)

where $E_{\text{VBO}} (\text{Ge}) = 0.68$ eV (see [11]).

In addition to the change of transfer matrix elements we also take into account the shift of orbital energies proportional to hydrostatic component of strain tensor

$$E_{m;\beta} = E_{m;\beta}^0 + \alpha_{m;\beta} 3 \left( \frac{d_m}{d_0^m} - 1 \right),$$

(4)

where parameters $\alpha_{\beta}$ ($\beta$ indexes the basis function of ETB) are also taken from [11]. The splitting of diagonal energies proportional to the off-diagonal components of the strain tensor introduced in [10, 11] is irrelevant to the construction of VCA alloy parameters and we do not discuss it here.

We check that the constructed ETB parameters of SiGe alloy are in a good agreement with the results obtained using the random alloy description which may be found in [11], see figure 1.

3. Virtual crystal approach for SiO_2 matrix

The simulation of $\text{Si}_1-x\text{Ge}_x$ alloy nanocrystals in SiO_2 by the tight-binding method is complicated by the fact that SiO_2 is an amorphous material. However, at the interface between SiO_2 and $\text{Si}_1-x\text{Ge}_x$ NCs, there is a large band offset for both types of carriers and, therefore, the electron and hole wave functions rapidly damp in the matrix. In this case, the role of disorder may be neglected and the most important factors are the general band structure of material surrounding nanocrystal and the boundary conditions between $\text{Si}_1-x\text{Ge}_x$ alloy and SiO_2. It opens the possibility to simulate SiO_2 as a virtual crystal [14]. We construct the virtual crystal with a band structure close to the band structure of $\beta$-cristobalite near the band gap edges,

**Figure 1.** Dependence of the band gap energy on the Ge mole fraction. In black solid line with dots we show the results of virtual crystal approximation (see section 2), in dots (green online) we show the results from [11]; in diamonds (red online) we show the experimental results [13]. Shaded area shows the Ge contents where the minimum of the conduction band lies in L valley.
following [15]. The $\beta$-cristobalite is the only polymorphous modification with a cubic lattice among SiO$_2$ crystals. We suppose that during the annealing process (which is is always one of the steps of the growth technology), the SiO$_2$ matrix in vicinity of Si (or SiGe) NCs forms the the structure similar to to the $\beta$-cristobalite. The tight-binding parameters were fitted to the band structure of $\beta$-cristobalite calculated using the density functional theory, see appendix. Note that in [15] another set of parameters has been used, fitted to rather old DFT calculations of $\beta$-cristobalite with significantly under-estimated band gap. As there is no strain of NCs in amorphous matrix, we set the lattice constant of the virtual crystal matching the lattice constant of the bulk Si$_{1-x}$Ge$_x$ alloy which forms the NC.

Figure 2 demonstrates the energy position of the band edges of the bulk silicon, virtual crystal SiO$_2$ and germanium. The virtual crystal ‘SiO$_2$’ is the direct band material with the band gap equal to 7.38 eV matching the value in $\beta$-cristobalite, the extrema of conduction and valence band lie in the $\Gamma$ point. Bulk silicon is the indirect-band semiconductor, with the 6 minima of the conduction band located between $\Gamma$ and X points of the Brillouin zone (the distance between minima and $\Gamma$ point is 0.85 of the $\Gamma$–X distance). Bulk germanium is also an indirect band semiconductor with 4 minima of the conduction band in L points. To consider the tunneling of electrons into the SiO$_2$ matrix, it is critical to reproduce exactly the energy positions of the edges of the conduction bands of the SiO$_2$ in X and L points. The distances from the top of the valence band at the point $\Gamma$ to the points X and L of the conduction band for the virtual crystal are 10.42 eV and 10.02 eV, respectively, which is close to values in $\beta$-cristobalite. We set the top of the valence band of the bulk silicon at the energy distance 4.5 eV above the top of the valence band in virtual crystal. This corresponds to the experimental data on the valence band offset between bulk silicon and amorphous SiO$_2$ according to [16].

From figure 2 it follows that the distance from the top of bulk Si valence band to bottom of conduction band of VCA SiO$_2$ in $\Gamma$ point is 2.88 eV and the distance between minimum of conduction band in bulk Si to bottom of conduction band of VCA SiO$_2$ in $\Gamma$ point is 1.71 eV.

Note that similar approach to model the virtual crystal with symmetry of Si for the description of SiO$_2$ matrix within the real-space pseudopotential technique has been proposed in [17], where the band gap of SiO$_2$ virtual crystal equal to 3.2 eV has been chosen to have a good agreement with experimental data on photoluminescence.
4. Results of modeling the SiGe nanocrystal in SiO₂

For convenience, in the calculations of electron and hole states in Si₁₋ₓGeₓ nanocrystals embedded in the SiO₂ matrix, we consider a cubic supercell of the virtual SiO₂ with a Si₁₋ₓGeₓ alloy nanocrystal in the supercell center (see figure 3). In calculations, we use the periodic boundary conditions to discard the effects at the SiO₂ surface and choose the supercell to be large enough to neglect the tunneling between neighboring NCs. The NC with diameter D is constructed by placing the SiGe ‘atoms’ inside the sphere with diameter D + 0.5 nm. Extra 0.5 nm are added to compensate for the interface effects, similar to [18].

First we check that the model of VCA SiO₂ matrix reproduces the band structure of Si NCs embedded in SiO₂ matrix. In figure 4 we show the dependence of the exciton energy localized in Si NCs as a function of NC diameter (line). To simplify the direct comparison with the experimental data, we take into account the Coulomb interaction using the empirical equation \( V_C = -3.08e^2/(\varepsilon_{Si} D) \) (here \( \varepsilon_{Si} \) is the dielectric constant of Si), following [23]. For comparison we show experimental data of the photoluminescence (PL) peak position at room temperature [19–21] (circles, diamonds and stars). Note that the photoemission in Si NCs is accompanied by the phonon emission to fulfill the momentum conservation rules, the main contribution is from the 60 meV optical phonon emission and the experimentally observed photoemission data is expected to be about 60 meV below the calculated indirect band gap. Also, we show the band gap as a function of NC diameter calculated in [18] (pentagons). We also show the experimental data of PL peak position in Si NCs passivated by hydrogen [22] (triangles) and the calculations using the pseudopotential method [17] (connected dots).

The energies of the ground states of electrons and holes as a function of NC diameter are presented in the inset in figure 4. In solid line we show the results obtained with current parametrization, in dashed line the results obtained in the same method, but the parameters of SiO₂ matrix taken from [15]. We also show the levels energy calculated using the pseudopotential method [24] (dotted line) and effective mass approach [23] (dash-dot line). As seen from
the comparison, all theoretical approaches give almost the same results for the NCs with diameter above 4.5 nm, when the tunneling into the matrix does not play any role. The calculations in the effective mass approach in [23] were carried out for the NCs with diameter above 2.5 nm because for smaller NCs this approach fails. The presence of the $\Gamma$ valley in the matrix which is just 1.71 eV above the bottom of the conduction band in bulk Si leads to the noticeable lowering of the quantum confinement energy for the NCs with diameter below 2.5 nm. There is no similar effect of the matrix for the hole states.

Results of calculation of the energy gap for Si$_{1-x}$Ge$_x$ nanocrystals with diameters = 2, 3, 4, 5 and 6 nm as a function of Ge content $x$ are presented in figure 5. The value of NC diameter corresponds to the pure silicon nanocrystal ($x = 0$). For the Si$_{1-x}$Ge$_x$ alloy nanocrystals we consider the NCs with the same number of atoms, as a result the actual diameter is larger by the factor $a_{\text{Si}_{1-x} \text{Ge}_x}/a_{\text{Si}}$.

5. Discussion

First of all, we note a good agreement between the detailed model of the SiGe alloy obtained as an averaged over the realizations of the random distribution of both atoms in a large supercell and the simple virtual crystal approximation. In addition to simplicity, the VCA allows for much easier analysis of the band structure behavior, as the bulk states do not need the extra procedure (unfolding, see e.g. [25]) to reveal the valley structure of the states. In particular, this allows one to unambiguously attribute the shoulder in figure 1 to the crossover between lowest $X$ valley in SiGe alloy with low Ge content to the lowest $L$ valley in SiGe alloy with high Ge content.

The detailed analysis of the SiO$_2$ band structure allowed us to construct the tight-binding parameters of the virtual crystal which reproduces all important features of the $\beta$-cristobalite band structure. This allows one to use the atomistic tight-binding to compute the states in relatively large nanocrystals with the account on the tunneling of the states in the matrix and the valley mixing. We stress that in this case the advantage of the tight-binding method is not the detailed description of the interface properties and/or the chemistry of the contact between SiGe and SiO$_2$ which is out of the scope of present paper, but the detailed quantitative description of the band structure of all materials in the full Brillouin zone and exact (within the model) account on the interaction between the states in different valleys.

Calculations show that the band structure of the SiGe alloy is qualitatively reflected in the structure of the states in nanocrystals. However, there are some changes. First, the position of $X$–$L$ crossover point is shifted towards high Ge content in small NCs, see figure 5. Second, for small NCs the band gap dependence on the Ge content is almost absent. This is explained by the opposed influence of the band gap change and the change of the effective mass. As a result, for intermediate size NCs the effect of the Ge content on the NC band gap is strongly suppressed, and the band gap for 2–3 nm size NCs is constant when the Ge content is within the range 0.0–0.85. We remind that the NCs in our calculations are nominally unstrained.
To resolve the valley crossing in more details, in figure 6 we show the energy of two first electron levels of in both L and X valleys as a function of Ge mole fraction for Si NCs with diameter 4 nm. It is clear that there is a simple levels crossing as a function of Ge composition, almost without the valley mixing. Note that the levels in X valley are 12 times degenerate and in L valley are eight times degenerate. This degeneracy is slightly lifted by the valley mixing by the inter-valley mixing. Note that the levels in X-valley are eight times degenerate. This degeneracy is slightly lifted by the valley mixing by the inter-valley mixing.

To trace the real space distribution of the wave function of hot electrons in more details, in figure 7 we show typical local density of states (LDOS) for few hot electron states in 3 nm diameter Si NCs (number of atoms in the NC is 1099). The calculations are performed in supercell with 10648 atoms (both Si and virtual atoms of SiO2 matrix), the size of the supercell \( L \approx 60 \, \text{Å} \) which is much larger than the NC diameter. In panels (a)–(c) we present respectively states with energies 2.8871 eV, \( E = 2.9203 \, \text{eV} \), and \( E = 2.8868 \, \text{eV} \). The state in panel (a) is well localized within the nanocrystal, the state in panel (b) is admixture of the state in NC and the state(s) in the matrix. The state in panel (c) is localized in the matrix and almost does not mix with the states inside the NC. All three types of states coexist in the structure. Note that these states have their energies in the interval of very dense density of states.

Also note that the electron states delocalized in the matrix in real structures will under most experimental conditions will be weakly localized by the Coulomb interaction with the hole inside NC forming type-II excitons.

To get the overall picture of electron and hole states, in figure 8 we demonstrate the local density of states for electron and hole states in real and k-spaces for nanocrystal with diameter 3 nm. From the local density of states (LDOS) it can be seen that the close position of the conduction band in the matrix leads to the strong penetration of the hot electron states in the matrix when the bottom of conduction band of the matrix is reached. The interesting feature of the tunneling into the matrix is that it is more ‘smoother’ for Ge nanocrystals. This can be seen in real-space LDOS. For the hot electron states in Si NCs states of types (a)–(c) (as indicated in figure 7) coexist in the range of energies above the bottom of conduction band of SiO2. For Ge NCs however, in addition to states of type (a) there are only states which are delocalized and have the maximum inside the nanocrystal, see figure 7(d). There are no states which are localized outside the Ge nanocrystals. This reflects the difference between the Si/SiO2 and Ge/SiO2 band alignment: in the former case, the minima of different valleys are located in different materials, while in the latter both materials have the bottom of conduction band in \( \Gamma \) valley.

In second column of figure 8 LDOS in k-space (for the details of calculations see [10]) shows that the states follow the band structure of the alloy. Distinct localization of the states near the k points of Brillouin zone corresponding to the position of \( L \) and \( X \) valleys for Ge NCs, and only \( X \) valleys for Si NC. Note that the contribution to the \( \Gamma \) valley for Si NCs is not from the Si itself, but due to states in the SiO2 matrix: the \( \Gamma \) valley in Si lies significantly above the maximum energy shown in this figure.

### 6. Conclusion

In conclusion, we have shown that the virtual crystal approximation in the framework of empirical tight-binding method for SiGe alloys and SiO2 is an effective and quantitatively correct approach. The calculations of electron states in SiGe nanocrystals in SiO2 matrix show reach valley structure of the states. For Ge-rich NCs we have demonstrated the importance of all three valleys and strong tunneling of excited electron states in the matrix. For Si-rich NCs, the states are predominantly X-valley, but the hot electron states after some threshold become delocalized and these delocalized states in the matrix and the states inside the NC are weakly mixed by the \( \Gamma-X \) mixing at the interface. This delocalization of hot electrons may be responsible for the photon cutting in silicon nanocrystals, which appears at the same energy range [27].

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### Appendix. Tight-binding parameters of SiO2 virtual crystal

To obtain the empirical tight-binding parameters of the virtual crystal representing the SiO2 matrix we fit the band structure of this material to the band structure of \( \beta \)-cristabolite calculated using density functional theory (DFT). DFT calculations were performed with the all-electron augmented plane wave \( \to \) local orbitals WIEN2K code [28]. Muffin tin radii of 1.78 and 1.1 were used for Si and O, respectively. The plane-wave expansion parameter RKMAX was 8.0. Screened hybrid exchange-correlational functional YS-PBE0 [29] (similar to HSE06 [30]) as implemented in WIEN2k has been used, for the integration over Brillouin zone we use \( 16 \times 16 \times 16 \) mesh in k-space and the reduced \( 4 \times 4 \times 4 \) k-mesh for the HF potential. The spin-orbit splitting is neglected. The comparison of the band structure obtained in DFT calculations with the fitted ETB parameters are presented in figure A1. The overall comparison is quite good. The main difference is the absence of the bands in the valence band originating from the oxygen states around \( 8 \, \text{eV} \), which is irrelevant for our problem. The description of the upper valence and lowerst
conduction bands is almost quantitative within the VCA with this set of parameters presented in table A1.

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