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Lattice deformation in silicon and germanium nanocrystals

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We present a theoretical study of lattice deformation and its influence on the electronic states and the optical transitions in Si and Ge nanocrystals covered by hydrogen. The lattice of Si and Ge nanocrystals has been optimized by Merck molecular force field method. The semiempirical tight-binding computer simulation has shown that the lattice optimization reduces effective energy band gap in silicon nanocrystals and increases it in germanium nanocrystals. This is similar to the effect of the hydrostatic compression of bulk Si and Ge. The sketch of the state density distribution in k-space is presented. It demonstrates the orbital-valley mixing, that appears due to space-quantization and lattice deformation influence.

1 Introduction Study of silicon nanocrystals (NCs) is a rapidly developing area of research with a number of promising applications for optoelectronics and photovoltaics [1]. Germanium nanocrystals has got less attention, while they also have some advantages, such as lower formation temperature [2], which allows for advanced band engineering. Modeling silicon and germanium nanocrystals properties can provide some additional information about quantum-size effects in indirect band semiconductors [3–5].

The validity of the band structure concept in Si NCs a few nanometers in size for the electron states has been analyzed for surface passivation by (OH), (H), and (CH3) groups by using the local orbital DFT code FIREBALL [6]. The results obtained Ref. in [6] have shown that the relaxation of Si atoms in the core region is negligible and, therefore, the Si NC core has very similar atomic structure as bulk Si.

Here, we present the theoretical study of the effect of small lattice deformation on the electronic states and the optical transitions in Si and Ge NCs covered by hydrogen. Such boundary conditions are commonly used in the tight binding model and correspond to the free-standing Si NCs [7].

2 Relaxed Si and Ge nanocrystals The original structures in the simulation are the quasispherical polyhedron Si and Ge nanocrystals with the same lattice structure as bulk semiconductors. On the base of the molecular dynamics by using Merck molecular force field method (MMFF) [8], which is integrated into Gaussian program [9], we have found the optimized structure of the Si and Ge NCs. The MMFF is an universal method, which performs well for a wide range of organic chemistry calculations. Here, we present the results of the simulation of Si and Ge nanocrystals consisting of 6, 8, and 11 atomic layers plus one surface layer of hydrogen, which are of 1.8, 2.5, and 3.6 nm in diameter, respectively. The length of a bond depends on the distance from the central atom as well as on the direction of the bond.

The results of the computer simulation of interatomic distances in relaxed silicon and germanuim nanocrystals are shown in the Fig. 1a and b, respectively. Bond lengths are 2.35, and 2.45 Å in bulk Si and Ge, respectively. The presented results show about 2% decrease of the interatomic distance compared to the bulk material. One can expect, the effect of the relaxation to be similar to the effect of the hydrostatic pressure, that leads to the band gap decrease in bulk Si and, contrary, its increase in bulk Ge [10].

3 Electron states in relaxed nanocrystals To calculate the states of confined carriers, we use the $sp^3d^5s^*$ empirical tight binding approximation with the nearest neighbor interactions following to [11] and taking into account the spin–orbit interaction for both Si and Ge nanocrystals. This technique, being restricted to the nearest neighbors, is suitable to analyze the electron states in small nanocrystals.

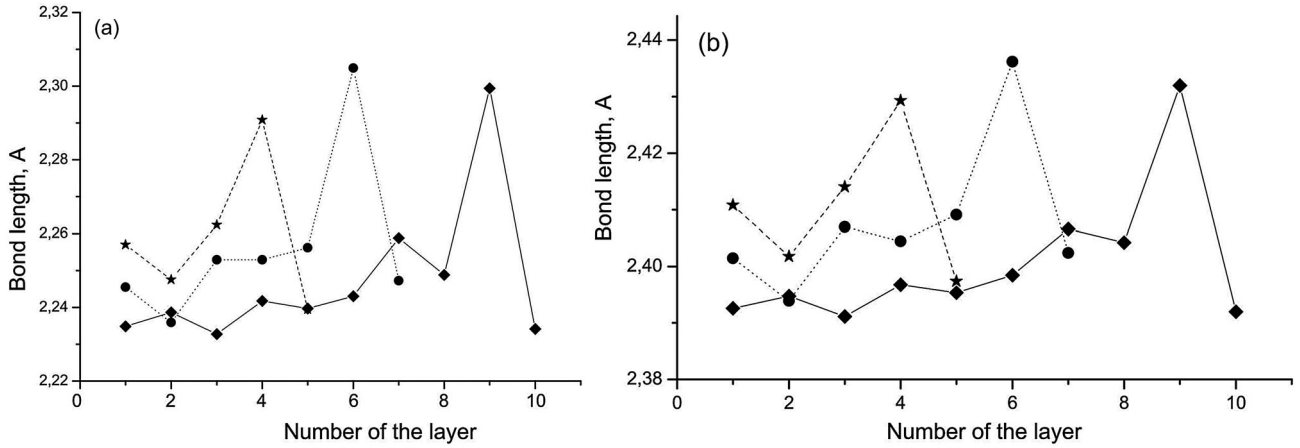


Figure 1 Interatomic distances in relaxed Si (a) and Ge (b) nanocrystals of diameters 1.8 (dashed line), 2.5 (dotted line), 3.6 (solid line) nm as functions of the layer number: layer 1 corresponds to the nearest layer to the central atom, the last (surface) layer is passivated by hydrogen atoms.

Parameters have been taken from Ref. [11] for Si–Si and Ge–Ge interactions and from Ref. [12, 13] for Si–H and Ge–H interactions, correspondingly.

To investigate the effect of lattice deformation on electronic states of the nanocrystal we used the results from Ref. [11]. The authors generalized Harrison's law [14] for tight-binding interatomic integrals ijk:

$$ijk(d) = ijk(d_0) \cdot \left(\frac{d}{d_0}\right)^{n_{ijk}}, \quad (1)$$

where ijk is the tight-binding parameter for interactions between k, i and j atomic wave functions, $n_{ijk}(d_0)$ is the

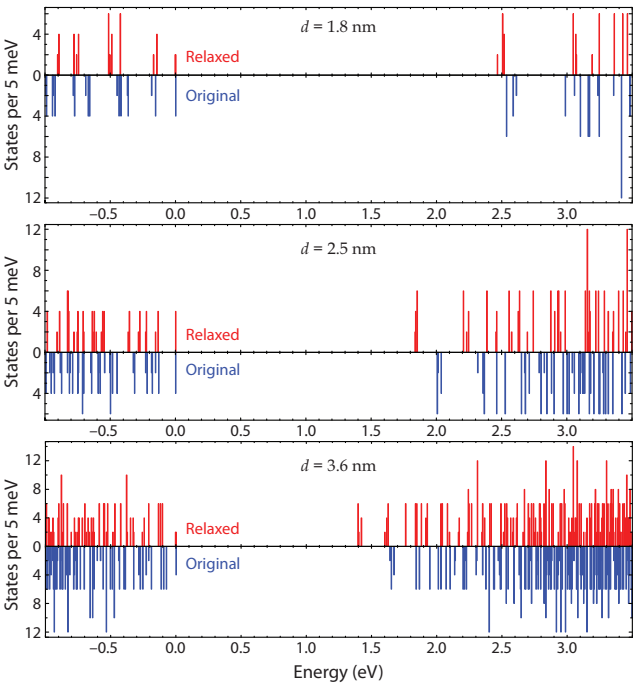


Figure 2 Density of states in Si nanocrystals of 1.8, 2.5, 3.6 nm diameters calculated by tight-binding method. Top lines (red online) for the relaxed nanocrystals, bottom (blue online) for the original structure. The energy of the valence band top state is taken equal to zero.

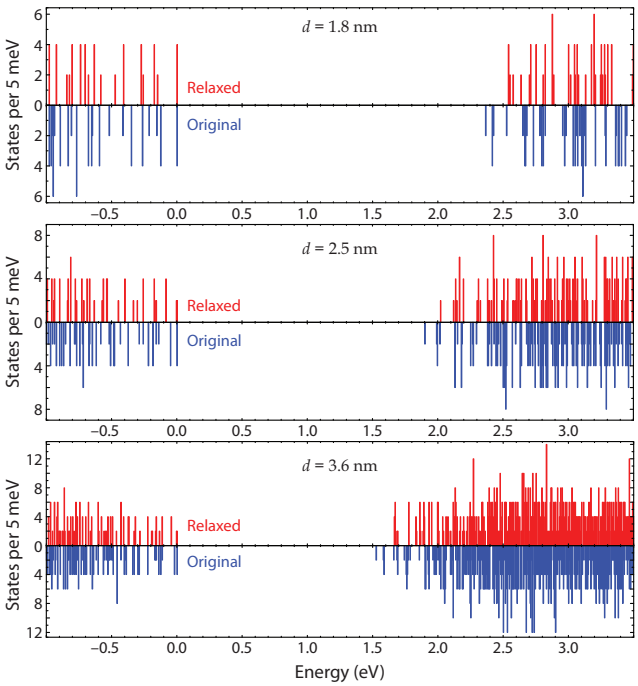
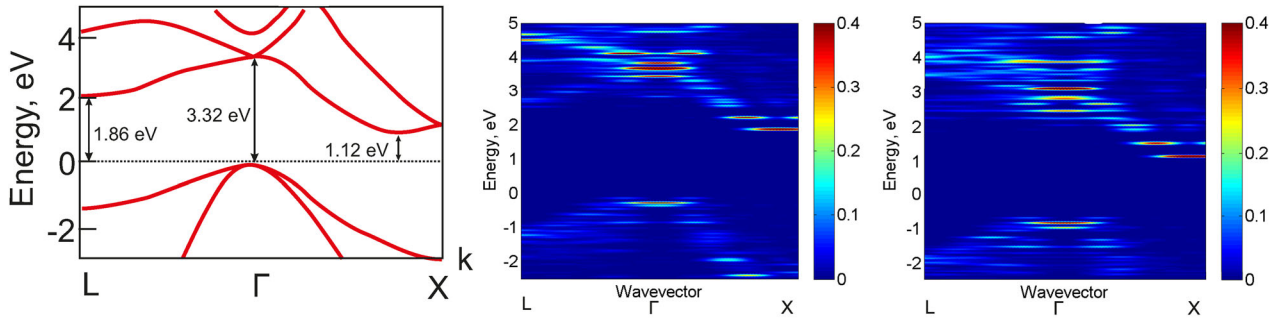


Figure 3 Density of states in Ge nanocrystals of 1.8, 2.5, 3.6 nm diameters calculated by tight-binding method. Top lines (red online) for the relaxed nanocrystals, bottom (blue online) for the original structure. The energy of the valence band top state is taken equal to zero.



a) Silicon band structure b) NC Si 2.5 nm original c) NC Si 2.5 nm relaxed

Figure 4 The scheme of the state density in the k-space for the original (b) and relaxed (c) Si nanocrystal of 2.5 nm diameter. Brighter lights correspond to the higher density in accordance with the scale shown to the right of the picture. The red color is the state with 0.4 of the highest density, the blue color corresponds to zero density. The band structure of bulk Si is shown in panel (a). The zero energy in subfigures (b, c) is corresponding to the top of the valence band of bulk silicon.

parameter characterizing the location of functions i and j in the atomic nucleus, d is the distance between neighbor atoms in the relaxed nanocrystal, d_0 is the distance between neighbor atoms in bulk silicon or germanium. We take into account atom shifts only for the Si–Si and Ge–Ge bonds.

The calculated densities of the electronic states in the conduction and valence bands for relaxed and original Si and Ge nanocrystals are presented in Figs. 2 and 3, respectively. In the figures, the energy of the valence band top state is taken equal to zero. The deformation leads to decrease of the energy gap for the silicon nanocrystals, to increase of it for the germanium nanocrystals and it also leads to the splitting of some states, which are degenerate in original nanocrystals.

To clarify the change in the structure of electron states induced by the space quantization and the shift of atoms in relaxed nanocrystals, we present the sketch of the state density distribution in k-space, calculated by the method [15], for original and relaxed Si NC of diameter 2.5 nm in Fig. 4 and Ge NC of the same size in Fig. 5. The energy band structure of bulk Si and Ge are presented in Fig. 4a and Fig. 5a.

In relaxed nanocrystals, the top valence band and minimum of the conduction band are dramatically shifted down, but energy gap is changed nondramatic compared with the original nanocrystal (see Figs. 2 and 3). One can see this effect for Si and Ge nanocrystals of 2.5 nm size on the Figs. 4 and 5.

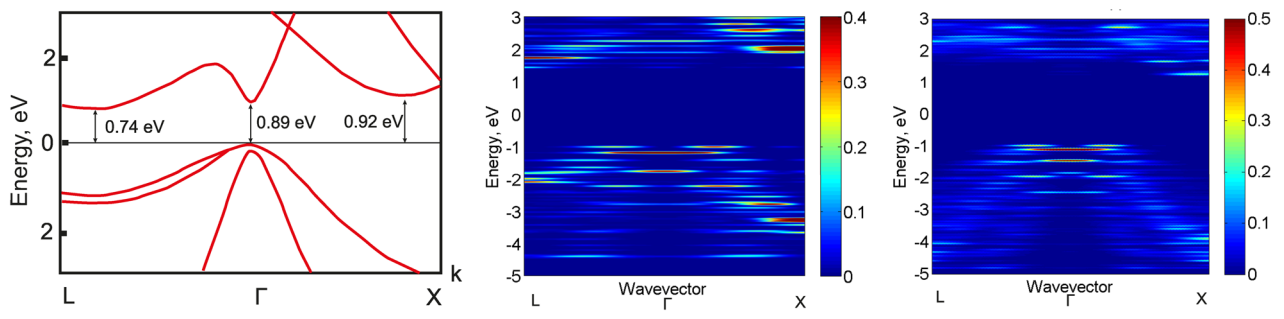
The structure of the state density in k-space reflects the band structure of corresponding bulk semiconductors. Presented figures demonstrates the effect of the orbital-valleys mixing for electron states in nanocrystals due to the space quantization. The mixing effect is the most significant for the germanium nanocrystals, because the energy positions of the minima of valleys L, Γ, and X are closed to each other in germanium.

4 Optical transitions Here, we proceed to the analysis of the lattice deformation effect on the phononless optical transitions in Si NCs.

The rate of spontaneous radiative recombination of an electron in state e with a hole in state h is given by

$$\frac{1}{\tau_{\rm rad}} = \frac{4\epsilon_0 \langle h|r|e\rangle F^2 n_{\rm out}(\hbar\omega)^3}{3\hbar c^3}, \qquad (2)$$

where $\hbar\omega$ is photon energy, $F = 3n_{\rm out}^2/n_{\rm in}^2 + 2n_{\rm out}^2$ is the local field factor ($n_{\rm in}$ and $n_{\rm out}$ are refractive indices of media inside



a) Germanium band structure b) NC Ge 2.5 nm original c) NC Ge 2.5 nm relaxed

Figure 5 The scheme of the state density in the k-space for the original (b) and relaxed (c) Ge nanocrystal of 2.5 nm diameter. Brighter lights correspond to the higher density in consideration in accordance with the scale shown to the right of the picture. The red color is the state with 0.4 of the highest density, the blue color corresponds to zero density. The band structure of bulk Ge is shown in panel (a).

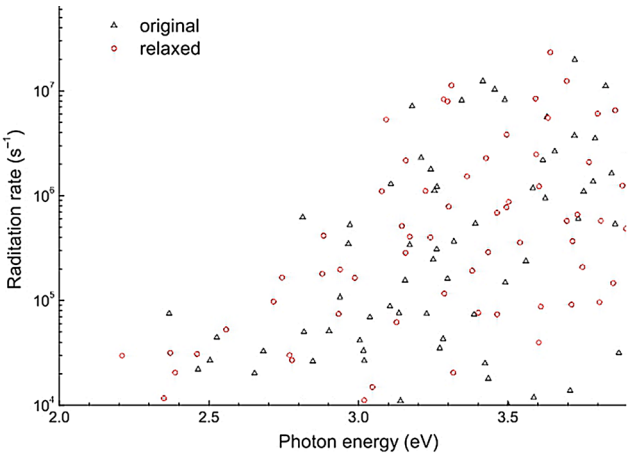


Figure 6 The rate of the radiative recombination of a hot electron with a hole in the ground state in the silicon nanocrystal of 2.5 nm diameter as a function of the energy of a photon emitted.

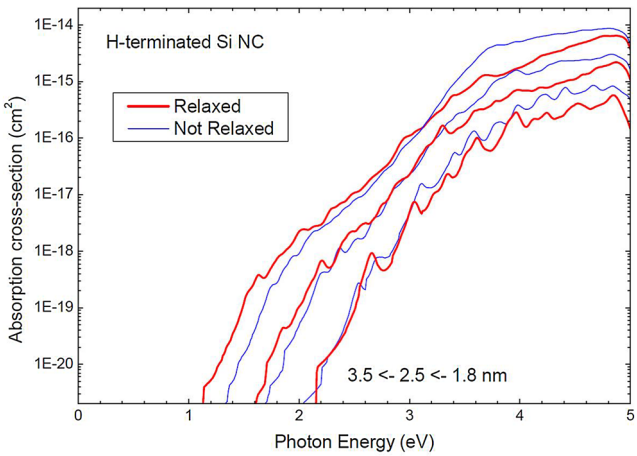


Figure 8 Absorption cross-section for the relaxed (red online) and original (blue online) Si nanocrystals of 1.8, 2.5, 3.6 nm diameters at different photon energies.

and outside the NC, respectively) [16]. As was discussed in the previous section, the lattice deformation influences on electron states, and, consequently, produces some changing in the radiative recombination rates. The calculated rate of radiative recombination of hot electrons with the hole situated in the ground state is presented in Fig. 6 for relaxed and non-relaxed Si nanocrystals of 2.5 nm diameter as a function of photon energy.

There is a fast energy exchange between a hole and an electron situated in the same NC. We produce calculations of the radiative recombination rates of an electron-hole pair as function of a photon energy emitted, taking into account that energy can be deviated by arbitrary way between a hot electron and a hot hole. The result of the calculation is presented in Fig. 7 only for transitions, when the recombination rate of direct transition is more than 10^4 1 s^{-1}. When the energy of electron–hole pair <2 eV, the probability of direct radiative transition don't compete with radiative transition assisted by phonons. The radiative recombination of the electron and the hole situated in the ground states is the phonon assisted process for Si nanocrystals with diameter > 2 nm [17].

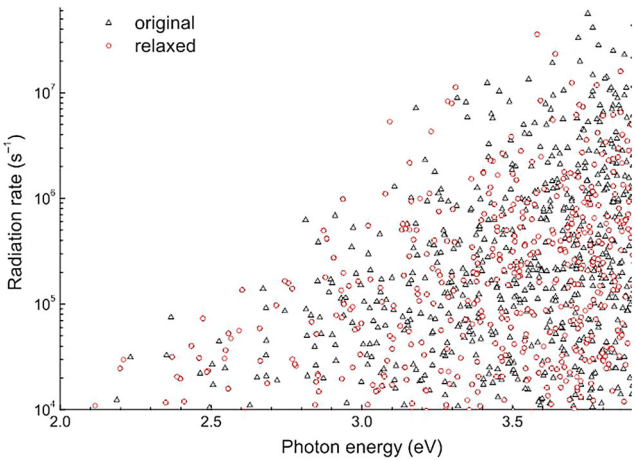


Figure 7 The rate of the radiative recombination of electron–hole pairs in the silicon nanocrystal of 2.5 nm diameter as a function of the energy of a photon emitted.

The calculation results of the absorption cross-section for the direct optical transitions as a function of the photon energy for three sizes of nanocrystals with and without deformation is presented in Fig. 8. One can see that the main effect of the deformation is the shift of the energy edges for the direct optical transitions.

5 Conclusions We have studied the effect of the lattice deformation in Si and Ge nanocrystals by using molecular dynamics method and effect of this deformation on their optical and electronic properties. It has been found that the decrease of the interatomic distance compared to the bulk material is about 2%. Computer simulation has shown that the lattice deformation leads to the decrease of the band gap for silicon nanocrystals and to the increase for germanium nanocrystals, similar to the effect of hydrostatic compression.

The change of the orbital-valley mixing due to the lattice deformation has been demonstrated in Si and Ge NCs.

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