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Giant excitonic exchange splitting in Si nanowires: First-principles calculations

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The size and doping dependence of the electron-hole exchange interaction in Si nanowires is investigated from first principles. In pure Si nanowires we found excitonic exchange splittings in very good agreement with the experimental results for porous silicon. For *n*-doped Si nanowires a giant singlet-triplet splitting, three order of magnitude bigger than in bulk silicon, is predicted as due to the dramatic enhancement of the electron and the hole probability of being in the same place at the same time.

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Physical properties at the nanoscale can be starkly different from those in the bulk.[1] Silicon nanowires (Si-NWs) have made an impact in applications in fields as diverse as electronics, photonic, sensing, biology, and photovoltaics.[2,3] Compared to nanotubes, they have the undoubted advantage of being compatible with the current silicon-based technology, and of having the electronic properties which, in principle, can be tailored by changing their thickness, orientation, surface morphology, and doping.[4–6] Furthermore Si-NWs are assumed to be the main building blocks of porous silicon (PSi).[4]

Despite the large number of experimental and theoretical investigations, the origin of the visible photoluminescence (PL) in PSi, is still controversial: it is not clear if it is due to quantum-confined excitons or to the presence of interface states near the surface.[7] In particular the reason for the emission versus absorption energy shift has been lively debated.[8–11] A two-level model based on the electron-hole (e-h) exchange interaction has been advanced as responsible for the temperature dependence behavior of PL in PSi.[12] This interaction creates low-lying triplet states which can be populated nonradiatively after an optical excitation in the singlet state and, thanks to the spin-orbit interaction which mixes the pure triplet character, luminescence with long lifetime; thus, the origin of the absorption-emission shift can be linked to the excitonic exchange splitting.

Regarding the doping, experiments have shown that Si-NWs can be doped either *p*- or *n*-type[13,14] and even codoped,[15] with the possibility of basic functional device applications such as solar cells and nanoelectronic power sources.[16] The main theoretical effort has been dedicated, up to now, to the influence of doping on the electronic and transport properties of Si-NWs,[17–22] while an analysis of the dependence of the optical features, is still missing.

The aim of this work is twofold: first we calculate the singlet-triplet exciton splitting (Δ^{S-T}) of pure Si-NWs of different size and orientation and show how, as expected for confined systems such as also nanodots,[23] it strongly increases reducing the NW diameter. Then we analyze how the doping influences this physical quantity and the excitonic and optical properties. Interestingly, for n-doped Si-NW, we predict a giant singlet-triplet splitting of the order of 100 meV, as being due to the dramatic enhancement of the e-h localization, being in the same place at the same time.

The electronic and optical properties of the Si-NWs are obtained within an *ab initio* approach based on density functional theory (DFT) (Refs. 24 and 25) and, many-body (MB) Green's functions perturbation theory.[26,27] The pure Si-NWs are oriented along the [110] and [100] directions and have different diameter from 0.6 to 1.9 nm,[28,29] while regarding the effect of doping, we fixed the orientation as [110] and selected the diameter $d=1.1$ nm. In particular we focus on few geometrical configurations of the dopants and we report results for one codoped and two single-doped cases, the latter in the presence of a surface dangling bond in the unit cell. In this way, all the considered NWs have a fully occupied top valence state, mantaining a complete semiconductor character. The same notations and definition of the cell size of Ref. 17 are used here, moreover we address the reader to Refs. 30 and 31 to have more information about the ground-state properties of these and other doped nanowires.

As a first step, the relaxed ground-state configuration has been obtained for all the Si-NWs by solving self-consistently the Kohn-Sham equations within a DFT local density approximation approach using plane waves and norm-conserving pseudopotentials.[32,33]

Then, the quasiparticle (QP) excitation energies, formally the poles of the one-particle Green's function, are obtained within the perturbative G_0W_0 method[26] and allow a successful description[28,29,34,35] of the electronic gaps measured with scanning tunnel microscope.[37] Finally the optical properties are calculated by solving the Bethe-Salpeter equation (BSE) where the coupled e-h excitations are fully taken into account.[26,27,38] As shown in the literature, the solution of this equation results from an eigenvalue problem of the excitonic Hamiltonian,

$$(\epsilon_{ck}-\epsilon_{vk})A^{\lambda}_{vck}+\sum_{v'c'k'}(K^{d}_{vck,v'c'k'}+2K^{x}_{vck,v'c'k'})A^{\lambda}_{v'c'k'}=E^{\lambda}A^{\lambda}_{vck},$$

Where E^{λ} and A^{λ}_{vck} are the excitonic eigenvalues and eigenfunctions, $\epsilon_{ck}-\epsilon_{vk}$ are the QP transition energies, $K^{d}_{vck,v'c'k'}$ is

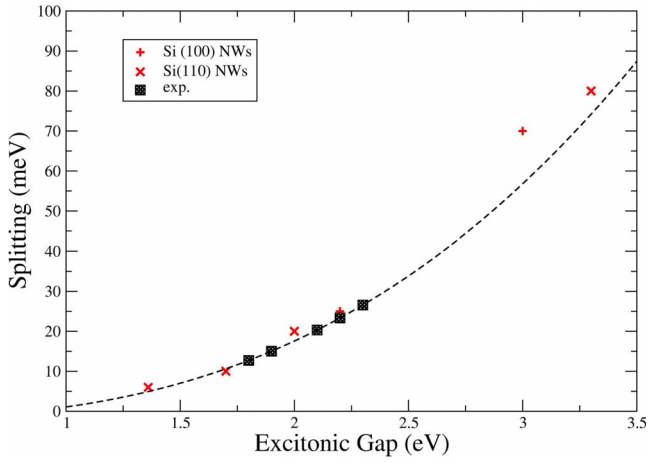

FIG. 1. (Color online) Experimental Δ^{S-T} for PSi (Refs. 9 and 12), as a function of the gap. Vertical and diagonal crosses: theoretical Δ^{S-T} for [100] and [110] Si-NWs, respectively. The dashed line is the fit of the experimental data, assuming an inverse power scaling behavior.

the direct attractive e-h interaction, $K^x_{vck,v'c'k'}$ is the exchange repulsive e-h interaction. When the spin-orbit term is negligible, the BS Hamiltonian can be solved separately for spin-singlet and spin-triplet excitons, where in the latter case, only K^d remains in the interacting kernel of the BS equation.[38] Then the singlet's energy increases due to the (repulsive) e-h exchange interaction, while the triplet exciton is lower in energy, due to the lack of this term. Δ^{S-T} depends from the entity of K^x. In other words, in the used scheme, the MB problem is transformed into a two-particle effective Hamiltonian, where the MB effects are taken into account by the screened e-h interaction and by the e-h unscreened exchange.

In the usual assumptions of the BSE derivation,

$$K^d_{vck,v'c'k'} = -\int drdr' \psi^*_{ck}(r)\psi_{c'k'}(r)W(r,r')\psi_{vk}(r')\psi^*_{v'k'}(r'),$$

where W is the static screened Coulomb interaction, while

$$K^x_{vck,v'c'k'} = \int drdr' \psi^*_{ck}(r)\psi_{vk}(r)V(|r-r'|)\psi_{c'k'}(r')\psi^*_{v'k'}(r'),$$

where V is the bare Coulomb potential. It is clear from the latter equation that the exchange term is larger when the e-h overlap is larger. Of course, such overlap is expected to be stronger in low dimensional structures than in bulk solids.

In Fig. 1 we plot, as a function of the gap, Δ^{S-T} of the lowest exciton in Si-NWs of different size and orientation. These values are compared with the splittings derived from the fit of the temperature dependence of the PL lifetime measured for PSi, as reported in Ref. 12. As mentioned in Ref. 8, it is worth remembering that these kinds of measurements do not include any contribution from a possible Franck-Condon shift, but determine directly the energy splitting under equilibrium conditions between the slow and fast initial states of the PL. The agreement between theory and experiment is very good: the experimentally observed enhancement of Δ^{S-T}, with respect to the bulk value of 0.15 meV, is well reproduced by the theoretical excitonic calculations without any adjustable parameter.

In the past, Martin *et al.*,[9] by means of semiempirical calculations, made a similar comparison between the PL data of PSi and the excitonic exchange splitting of spherical, ellipsoidal and undulating ellipsoidal (to simulate wires with varying diameter) Si nanocrystallites of different size. Their calculated values were smaller by a factor of 3–5 with respect to the experimental ones and for this reason they concluded that the two-level model suggested by Calcott[12] could not explain the experiments, thus to explain the data they proposed the presence of a Franck-Condon shift. The present first-principles calculations reach an opposite conclusion. The origin of this improvement can be certainly attributed to the high accuracy reachable with a complete *ab initio* approach in the description of the electronic states and of the dielectric screening of a system in a confined geometry. The importance of a robust description of the effective dielectric function for a correct analysis of the excitonic exchange splitting has been also underlined in the case of Si-NCs.[10,11] Moreover it has been demonstrated that the Franck-Condon shift strongly depends on size and dimensionality[30,39–42] and, in particular, is negligible for Si-NWs, owing to the presence of quantum confinement effects in only two directions.

Figure 2 illustrates the possibility to tailor, with doping, the optical response of a thin Si-NW. Here are reported the optical-absorption curves for a pure Si-NW (black upper curve), for the same nanowire but *n*-doped with *P* impurities (cyan curve, second from top) or *p*-doped with *B* impurities (red dashed curve, second from bottom), both with the presence of surface dangling bonds,[17] and for the codoped, with *P* and *B* impurities (blue dot-dashed curve, lower). All the four wires have a semiconductor character and in the three lower curves, the appearance of optical peaks around and below 2 eV, due to the presence of impurities related states, is evident.

These spectra are obtained by fully describing in an *ab initio* manner the e-h dynamics: the different character of the excitons is at the base of the observed optical behavior. This is clearly confirmed by looking (see Fig. 3) at the calculated e-h probability distribution associated with the lowest energy excitons (indicated by the arrows in Fig. 2). Looking at the side views (right), while the exciton localization is similar in the pure and BP-doped Si-NW (with an estimated exciton length of about l_{exc}=40 Å, instead of l_{exc}=42 Å), a clear reduction of the exciton length is visible in the B and P-doped (in presence of dangling bonds) NWs (with l_{exc}=30 Å and l_{exc}=16 Å, respectively). At the same time, the top views (left) show how the e-h localization changes in the NW section. While fixing the hole position (black cross) the probability to find the electron is completely delocalized over the section in the pure NW, it becomes more localized when impurities are introduced. Nevertheless the probability to find the electron and the hole near each other, increases only in the *n*-doped NW, while in the codoped and *p*-doped NW the hole (cross) and the electron (violet isosurface) are mainly localized in different places of the NW section. In fact with doping we are changing the character of the states near the gap: in the codoped NW, *B*

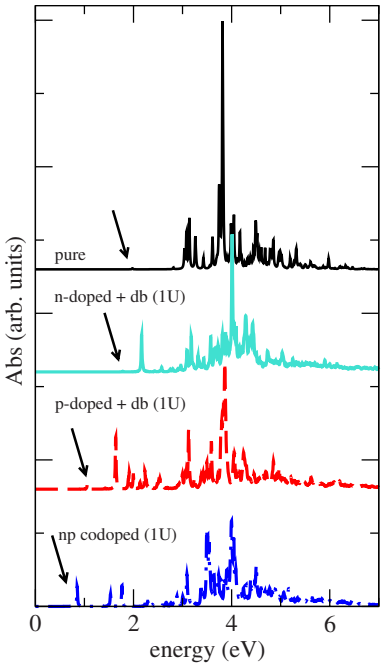

FIG. 2. (Color online) Optical absorption spectra for light polarized along the NW axis, obtained including the e-h interaction. Black curve (top): for a pure, H-terminated, Si-NW oriented along the [110] direction and with $d=1.1$ nm. Cyan curve(light gray; second from top): for the same Si-NW but doped with P impurities and with the presence of surface dangling bonds. Red dashed curve (gray, second from bottom): as before but for B impurities. Blue dot-dashed curve (bottom): for the same Si-NW but doped with both P and B impurities. The black arrows indicate the position of the lowest energy excitons.

(P) impurities introduce a new occupied (unoccupied) band on top (bottom) of valence (conduction) band of the pure Si-NW; in P (B) doping, the lowest unoccupied (highest occupied) band is due the P (B) impurities, while the highest occupied (lowest unoccupied) band is mainly due to the presence of the surface dangling bonds. In the n-doped NW, the lowest electron and highest hole states, are closer in energy to the empty and filled bands of the pure Si-NW, respectively (as can be seen looking at Fig. 7 of Ref. 17 and at the QP gaps reported in Tab. 1 of this work) and can strongly hybridize with them when solving the BSE. Furthermore, in the n-doped NW, (see Fig. 7 of Ref. 17) the highest occupied band associated with the surface dangling bonds presents a very strong localization along the wire axis. These facts contribute to a large e-h localization and overlap, and induce a larger Δ^{S-T} with respect to the other cases, as reported in Table I. It is worth to mention that a large splitting is not limited to the lowest exciton: an even larger splitting (about twice) has been observed focusing on the first intense optical peak (at 2.1 eV) of the n-doped wire. Summarizing, we can say that the different exciton localization induces changes in Δ^{S-T}: while in the B (BP)-doped NW, a splitting of the same order (smaller) of that found in the pure Si-NW should be expected, in the P-doped NW, a larger Δ^{S-T}, should be found. This is exactly the behavior we have found, as shown in the fourth column of Table I. Notably Δ^{S-T}, in the n-doped NW, remains very big also halving the dopant concentration (see the third row) showing that the e-h localization is more linked to the kind of impurities than to their concentration. Furthermore, in the first two columns of Table I, the pronounced dependence of the optical and electronic gap from doping is visible, while from the third column, we can see how the quasiparticle corrections are only weakly dependent on the doping.

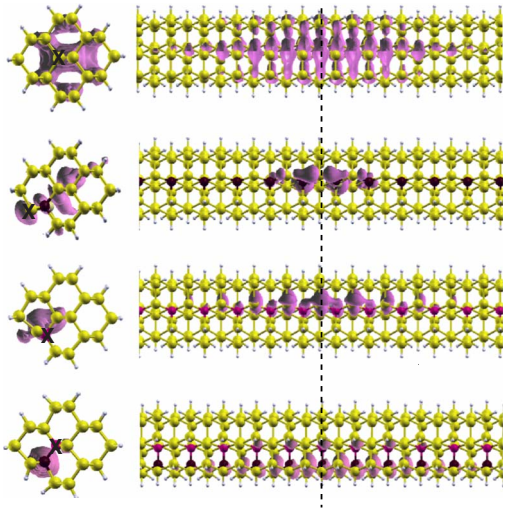

FIG. 3. (Color online) Geometrical structure of $d=1.1$ nm Si [110] wires with the same order from top to bottom of Fig. 2 Yellow/light grey spheres represent Si atoms, black (magenta/grey) spheres P (B) impurities, white spheres H atoms used to saturate the dangling bonds. The violet/grey isosurface gives the probability distribution $|\psi_{exc}(r_e,r_h)|^2$ for finding the electron when the hole is in a given position, indicated by the black crosses and by the dashed line. This position has been chosen in each case near the maximum of the charge distribution of the highest occupied state.

The increase in the exchange interaction in quantum-confined nanosystems is a general phenomena that can have profound effects on the nature of the emitting states.[43,44] A large Δ^{S-T} is expected to favor the optical gain for light emitted from the lowest energy state (the triplet exciton here) and therefore possible laser applications.[45] In this regard it is

TABLE I. Excitonic, QP gaps and corrections (in eV) are reported in the first, second and third columns respectively, while the e-h exchange splittings (in meV) are shown in the fourth column. First row: values calculated for pure Si-NW. Second row: for P doped Si-NW but in presence of a dangling bond in the unit cell. Third row: as before but halving the impurities concentration. Fourth row: doped with B impurity and with the presence of dangling bond. Fifth row: doped with B and P impurities. NW's orientation and size are fixed: [110] and $d=1.1$ nm.

Wire	E_{gap}^{exc}	E_{gap}^{QP}	ΔE^{QP}	Δ^{S-T}
pure	2.0	3.3	1.8	20
n-doped+1 db (1U)	1.7	3.1	1.8	122
n-doped+1 db (2U)	1.7	3.2	1.8	107
p-doped+1 db (1U)	1.1	2.3	1.7	23
np codoped (1U)	0.8	2.1	1.8	12

worth to mention that in *P*-doped Si-NCs, an increase of the luminescence has been recently observed[46] which could be explained by the physics described here.

In conclusion we have studied the excitonic exchange splitting in Si-NWs by using *ab initio* approaches including many-body effects. For pure Si nanowires our results are in excellent agreement with the experimental porous silicon data, confirming that their PL is due to localized quantum-confined excitons in crystalline Si-NWs. Most interestingly, by tailoring the optoelectronic properties of the confined Si nanowires with doping, a giant excitonic exchange splitting, three orders of magnitude larger than in bulk Si, has been found in *n*-doped Si-NWs. Finally we have demonstrated the possibility to tailor by doping the optoelectronic properties of thin Si nanowires.

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