

Novel Properties of Silicon Nanowires Through Many Body Perturbation Theory: Giant Excitonic Exchange Splitting in Si Nanowires

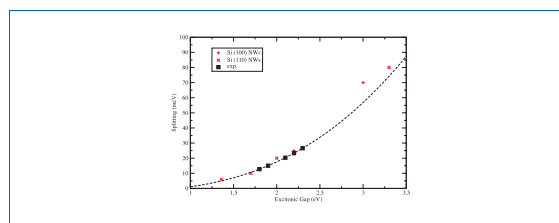
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In this work we have investigated by first-principle the size and doping dependence of the electron-hole exchange interaction in Si nanowires and how the excitonic optical properties can be tailored by n- and p-type doping. The pure Si-NWs are oriented along the (110) and (100) direction and have different diameter from 0.6 nm to 1.9 nm (1, 2), while for the doped one we fixed the orientation as (110) and the diameter as $d=1.1$ 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, maintaining a complete semiconductor character, as described already in other previous work on doped Si-NWs (3, 4).

The electronic properties for the relaxed ground state configuration have been calculated through the Density Functional Theory (DFT) scheme, by solving self-consistently the Kohn-Sham equations within the Local Density approximation (LDA) for the exchange-correlation potential (V_{xc}) and using plane waves and norm-conserving pseudopotentials (5) as implemented in the Quantum Espresso code (6). For what concerns the evaluation of the single-triplet splitting and of the excitonic properties, we use the Many Body Perturbation Theory to calculate both quasi-particle (QP) excitation energies within the perturbative G_0W_0 method (7) and the coupled e-h excitations by solving the Bethe-Salpeter equation (BSE) (7,8). This part of the work has been carried out through the Yambo code (9).

Concerning the exchange interaction, we have calculated singlet-triplet splitting Δ^{S-T} for several pure Si-NWs for different diameter size. In Fig. 1 the calculated Δ^{S-T} values, reported as a function of the excitonic gap, are compared with the splittings derived from the fit of the temperature dependence of the photoluminescence lifetime measured for Porous Si. We found a very good agreement with the experiment, as reported in (10). Moreover, since the excitonic calculations don't include any contribution due to the Franck-Condon shift, we can confirm that the two-level model suggested by Calcott (10) could explain the experimental data.

In Fig. 2 are shown the calculated optical many body absorption spectra for a pure Si-NW (black curve), for the same nanowire but n-doped with P impurity (red curve) or p-doped with B impurity (green curve), both with the presence of surface dangling bonds and for the codoped with P and B impurities (blue curve). In all the four spectra the wires present a semiconductor character. In Fig. 2 it can be seen that due to the presence of compensated impurities (the dopant charge is electrically deactivated) optical peaks appear below the 2 eV absorption edge of the undoped NW, thus demonstrating that the doping can in principle be used to tailor absorption and optical properties also at the nanoscale. These excitonic peaks can be related to the spatial localization of the e-h probability distribution: in doped Si-NWs we show that the exciton tends to localize around the impurity sites. In particular in the P-doped Si-NW in presence of a dangling bond, the excitonic length tends to reduce consistently with respect to the localization length in the other NWs. The different exciton length can affect also the Δ^{S-T} : a large e-h localization and overlap induce larger Δ^{S-T} with respect to other cases where the exciton is more delocalized along the wire axis. It follows that, while in the B (BP)-doped NW a splitting almost of the same (smaller) order (23 and 12 meV respectively) of that found in the pure Si-NW (20 meV) should be expected, since these cases have a similar exciton length, in the P-doped NW (where the localization is stronger), a larger Δ^{S-T} of 122 meV is found. This giant



excitonic exchange splitting, characterized by three orders of magnitude larger than in bulk Si, is related to the presence of the n-type impurity doped into the Si-Nw.

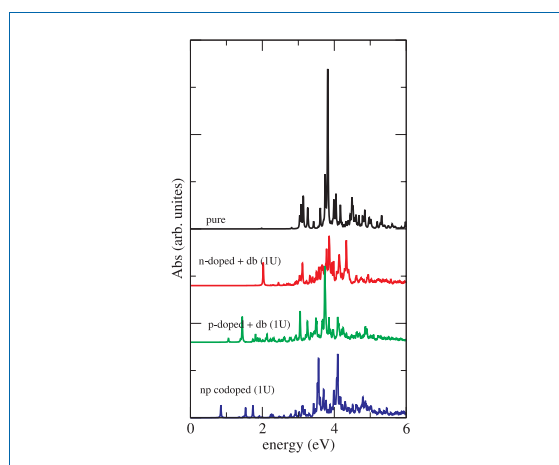


Fig. 1. – Experimental Δ^{S-T} for PSi (11, 10), as a function of the gap. Diagonal and vertical crosses: theoretical Δ^{S-T} for (100) and (110) Si-NWs. The dotted line is the fit of the experimental data, assuming an inverse power scaling behaviour.

Fig. 2. – 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. Red curve (second from top): for the same Si-NW but doped with P impurities and with the presence of surface dangling bonds. Green curve (second from bottom): as before but for B impurities. Blue 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.

The increase of the exchange interaction in quantum confined nanosystems is a general phenomena that can have profound effects on the nature of the emitting states (11, 12). A large Δ^{S-T} is expected to favour the optical gain for light emitted from the lowest energy state (the triplet exciton here) and therefore possible laser applications (13). In this regards it is worth to mention that in P-doped Si-NCs, an increase of the luminescence has been recently observed (14) which could be explained by the physics described here.

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