From Si Nanowires to Porous Silicon: The Role of Excitonic Effects

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We show that the electronic and optical properties of silicon nanowires, with different size and orientation, are dominated by important many-body effects. The electronic and excitonic gaps, calculated within first principles, agree with the available experimental data. Huge excitonic effects, which depend strongly on wire orientation and size, characterize the optical spectra. Modeling porous silicon as a collection of interacting nanowires, we find an absorption spectrum which is in very good agreement with experimental measurements only when the electron-hole interaction is included.

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Nanostructuring of semiconductors is a means of developing new electronic and optoelectronic devices. The huge efforts made towards matter manipulation at the nanometer scale have been motivated by the fact that desirable properties can be generated just by changing the system dimension and shape. In particular, after the discovery of visible photoluminescence in porous silicon (PS) and in Si nanostructures [1–3], the possibility of tuning the optical response of Si nanosized materials by modifying their size has become one of the most challenging aspects of recent semiconductor research due to their natural compatibility with silicon based technologies [4]. In this realm, Si nanowires (Si-NWs) constitute an example of one-dimensional structures with remarkable size and orientation dependent absorption and photoluminescence properties. Thin Si-NWs down to about 1 nm diameter have been obtained with growth orientation along the [100], [110], [111], and [112] directions and with a very rich surface chemistry [4–9]. Furthermore, together with Si nanocrystals, Si-NWs are used to model the optical and photoluminescence properties of PS [10]. However, despite the large amount of experimental data available, our understanding of the electronic properties of Si-NWs and PS is still almost confined to single-particle calculations done with semiempirical methods [11] or with the *ab initio* density functional theory (DFT), usually within the local density approximation (LDA) [12]. As a result the measured electronic gaps for various Si-NWs are larger than the LDA gaps by almost 50%. More importantly, the role of the electron-hole (e-h) interaction, neglected within any independent-particle approach, is typically treated within the simple effective mass approximation (EMA) [13]. A similar scenario has been found in analogous one-dimensional systems [14], such as nanotubes [15–17] and molecular organic chains [18,19], where, through first-principles excited-states calculations, the optical spectra are now quantitatively explained in terms of strong excitonic effects in a confined geometry. On the other hand, the *ab initio* optical properties of Si-NWs and PS have been calculated up to now at the level of the random-phase approximation (RPA), i.e., within the independent-particle approximation [20,21].

There exists a complete collection of optical, electronic, and photoluminescence experimental results for Si-NWs and PS that needs a consistent and sound interpretation in terms of a parameter-free theory. This is the goal of the present Letter. We show that only a fully microscopic, *ab initio* theory that correctly includes self-energy corrections and excitonic effects, well beyond the DFT-LDA, correctly explains the size-dependent experimental gaps in Si-NWs. Moreover, we show that the present results reproduce the photoluminescence gaps and the optical absorption of PS, questioning the interpretation of its optical data only in terms of Si nanocrystals.

Calculation details.—We first compute the ground-state properties (atomic configurations and single-particle states) using the DFT-LDA of nine Si-NWs, with different sizes and orientations. As a second step, we include self-energy corrections in the GW (where G is the Green function and W is the screened Coulomb interaction) approximation [22] to obtain the quasiparticle (QP) energies, and finally we describe the excitonic effects by solving the Bethe-Salpeter equation (BSE) [23] in the Bloch-space representation [24].

In Fig. 1 we compare the QP electronic gaps with the experimental data obtained by Ma *et al.* [7] through scanning tunneling spectroscopy, for different Si-NWs (grown along the [112] and [110] directions) with diameters ranging from 1.3 to 7 nm [7]. All the experimental gaps, although 50% larger than the LDA values, fall within our [100] and [110] theoretical QP curves, which represent the two limiting cases in terms of quantum confinement effects [14]. By fitting the QP band gaps E_g with a function of the effective wire diameter d, $E_{g,\mathrm{bulk}} + \mathrm{const} \times (1/d)^{\alpha}$ (where $E_{g,\mathrm{bulk}}$ is the bulk gap value and α is the scaling exponent) we find orientation dependent values for α (see Fig. 1). These values are, in any case, smaller than 2, the value

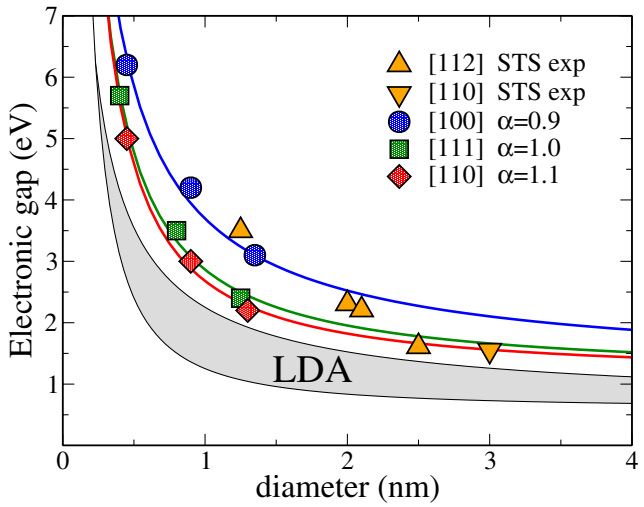

FIG. 1 (color online). QP gaps for [100] (circles), [111] (squares), and [110] (diamonds) Si-NWs as a function of wire size compared with experimental results (triangles) from scanning tunneling spectroscopy (STS), Ref. [7]. The gray region represents the LDA electronic gaps from [110] (bottom) to [100] (top) wires.

predicted in a simple EMA model which assumes infinite potential barriers, parabolic bands, and single band framework. The GW corrections have been calculated for three different wire sizes and for the [100], [111], and [110] orientations separately, showing a non-negligible orientation dependence. This can explain the discrepancy found for the [110] scaling exponent with the value reported in Ref. [21]. If now we compare, in Fig. 2, the Si-NWs QP

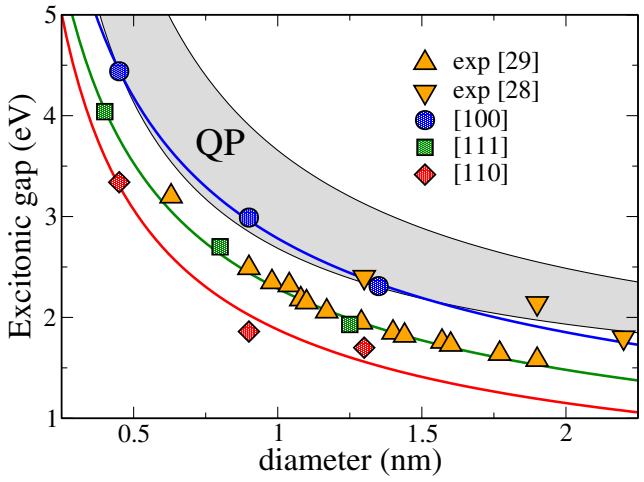

FIG. 2 (color online). Excitonic gaps for [100] (circles), [111] (squares), [110] (diamonds) Si-NWs, and experiments (triangles). Down- and up-pointing triangles correspond, respectively, to the photoluminescence data of Zhang and Bayliss [28] and Wolkin *et al.* [29] in PS samples. The gray region represents the quasiparticle electronic gaps, from [110] (bottom) to [100] (top) wires.

with the experimental photoluminescence gaps of PS we see that the QP gaps largely overestimate the experiment. This discrepancy cannot be entirely ascribed to the additional nanostructures that characterize PS. Indeed photoemission and x-ray absorption studies [28] show a progressive degradation in long range order on going from bulk Si to nanowires to porous silicon, indicating that PS is a sort of quantum sponge [3] mainly composed of a distribution of small interconnected nanowires of different size and electronic properties. Furthermore, although the overall structure of PS is related to the conditions of the sample preparation, several TEM studies have shown a preferential [100] orientation of the wirelike structures in PS obtained using (100) wafers [10]. Consequently the large discrepancy in Fig. 2 can be interpreted only in terms of the short-range interactions occurring between the electrons confined in the one-dimensional structure. Such interactions are described by the BSE as repeated QP collisions. Indeed, taking into account the effects of electron-hole interaction, the Si-NW excitonic gaps, corresponding to the lowest exciton with nonvanishing optical strength, are in excellent agreement with the photoluminescence experimental data from Refs. [28,29], as is shown in Fig. 2. Moreover, the data of Zhang and Bayliss [28], obtained with PS wires prepared by electrochemical anodization of Si(100) wafers, are in very good agreement with our [100] wire excitonic gaps. All the calculated excitonic gaps, which are size and orientation dependent, lie well below the QP gaps. The e-h interaction effect on the excitonic gap, shown in Fig. 2, is a consequence of the more general modification of the Si-NWs absorption spectra, given by the imaginary part of the dielectric function $\epsilon(\omega)$. This is shown in Fig. 3 where the QP-RPA $\epsilon_2(\omega)$ spectra are compared with the BSE results for the nine Si-NWs. The electron-hole interaction (solid curves) yields significant variations with respect to the one-particle spectra (dashed curves), with an important transfer of the oscillator strength to the low energy side. For the smallest wires, we observe that the correlated BSE spectra are characterized by intense peaks below the electronic gap (orange dashed arrows): bound excitons. Increasing the NWs size, we note a very smooth increase of the absorption near (or above) the electronic QP gap. Moreover, the rich structure of states, often characterized in the low energy side by the presence of excitons with small oscillator strengths, determines excitonic gaps (solid arrows) well below the optical absorption onset. The binding energy of these excitons, E_b, can be as big as 1.8 eV, which is very large if compared with bulk Si ($\sim$15 meV) or with carbon nanotubes [15,16] where $E_b \sim 1$ eV. Furthermore, the binding energy of the [100] wires comes out to be about 4 times larger than the value predicted within the EMA approach [13]. Using variable reaction pressure within a supercritical fluid solution-phase approach, Holmes *et al.* [6] were able to produce both [100] and [110] oriented Si-NWs. They ob-

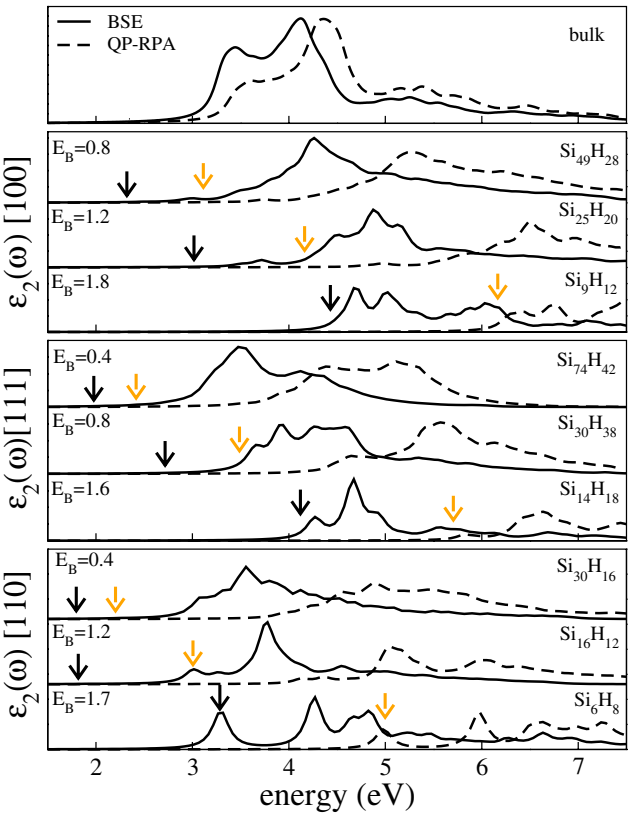

FIG. 3 (color online). BSE (solid lines) and QP-RPA (dashed line) optical absorption of [100] (second panel), [111] (third panel), and [110] (fourth panel) Si-NWs, for light polarized along the axis of the wire, compared with the corresponding spectra of bulk Si (first panel). In each panel the spectra for decreasing linear cross sections [36] ($l = 1.2$ nm, $l = 0.8$ nm, and $l = 0.4$ nm) are reported from top to bottom. The theoretical gaps are represented by the arrows: excitonic gap (solid arrow); electronic gap (orange dashed arrow). The first exciton binding energy, E_B, is reported in eV for any structure together with the wire atomic composition.

serve a blueshift of about 1 eV of the [100] absorption spectra if compared to the [110] spectra. This is in striking agreement with the result of Fig. 3, where the main BSE optical peaks of *all* the [100] are about 1 eV larger than the corresponding ones in the [110] direction. For [100] Si-NWs with $l = 1.2$ nm we find an excitonic gap (shown in Fig. 2) of $\simeq 2.4$ eV and an absorption onset of 3 eV (see the upper curve in the second panel of Fig. 3). These values and the consequent Stokes shift of 0.7 eV are in excellent agreement with the experimental data of Zhang and Bayliss [28].

In Fig. 2 we have shown how the excitonic effects yield an excellent description of the PS photoluminescence gaps. The question to answer is then: can we extend the encouraging agreement found for the PS excitonic gaps to the whole energy dependence of the $\epsilon_2(\omega)$ absorption spectrum? In order to answer this question, within our first-principles approach, we can model the PS as a collection of parallel wires of different size and with different wire-wire distance. As already demonstrated in other one-dimensional systems [30,31], the decrease of the interwire distance in the simulation cell substantially alters the optical properties. In particular, for light polarized perpendicular to the wire axis, the giant polarization effects (more than 90%) and the strong optical anisotropy observed in the visible-UV region for the isolated wires are considerably reduced. This is consistent with the recent results of Ma *et al.* [32] who have measured the polarization-dependent photoluminescence of highly oriented isolated Si-NWs finding a polarization ratio $\rho = [(I_{\|} - I_{\perp})/I_{\|} + I_{\perp})]$ of 94%, whereas in porous silicon usually this value is as large as 30% [33]. For light polarized along the wire axis, we observe instead a simultaneous reduction of the *e*-h interaction and of the QP gap correction, resulting in an almost unchanged position of the BSE optical threshold, if compared with the case of isolated wires (shown in Fig. 3). In Fig. 4 the experimental optical absorption spectrum of PS measured in Ref. [34] and the result of theoretical calculations, at the BSE and at the QP-RPA level, are reported. The agreement is excellent, with the experimental peak position and width very well described by the BSE calculation. On the contrary, the QP-RPA spectrum does not reproduce the experiment, missing the main absorption peak position by almost 1 eV. This result indicates that PS is better described as a collection of interacting Si-NWs of different size mostly oriented along the [100] direction, rather than as an ensemble of isolated nanostructures [35]. The collection of interacting Si-NWs representing the PS have been modeled as a Gaussian distribution (inset of Fig. 4) of wires with different diameter, oriented along the [100] direction. The scaling of the wire optical re-

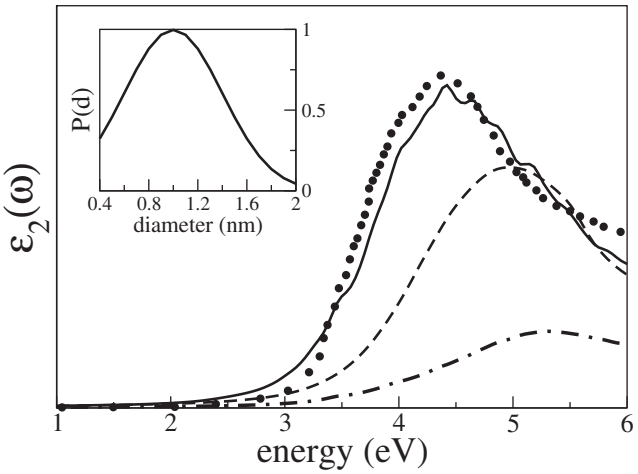

FIG. 4. BSE (solid line) and QP-RPA (dashed line) $\epsilon_2(\omega)$ of PS compared with the experiments (dots) [34]. The average contribution due to wire-wire interaction is also shown (dot-dashed line). In the inset is reported the Gaussian distribution of wires as a function of their diameters, as used in the described modeling of PS.

sponse, as a function of the diameter, has been calculated by fitting the size dependence of the dielectric function for the three wires studied in Fig. 3 and using an average wire-wire distance. The choice to consider only [100] oriented wires for the calculation of the PS absorption spectrum has been motivated by the experimental evidence [10,28] (indicating a dominance of [100] oriented nanostructures) by the fact that the main absorption peak, which is at about 4.5 eV in PS, is below 4 eV for [110] and [111] wires, as shown in Fig. 3.

In conclusion, we have performed a study of many-body effects on the electronic and optical properties of several Si-NWs with different size and orientation. The quasiparticle electronic and excitonic gaps agree well with the available experimental data. At the same time, the BSE absorption spectrum of PS, modeled as a collection of interacting nanowires, is found to be in very good agreement with the experimental evidence. Strong excitonic effects show up. This clearly demonstrates that a consistent and successful description of the electronic gaps and the optical and photoluminescence properties of Si-NWs and PS can be achieved only by including many-body effects.

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