

Excitons in germanium nanowires: Quantum confinement, orientation, and anisotropy effects within a first-principles approach

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Within a first-principles framework we show how many-body effects crucially modify the electronic and optical properties of free-standing Germanium nanowires. The electron-hole binding energy and probability distribution are found to depend on both wire size and orientation. Moreover, we observe an almost complete compensation of self-energy and excitonic effects for some of the analyzed quantum wires, which we explain as being due to their clusterlike atomic structure.

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Nanostructuring of semiconductors is an alternative means of developing devices. The huge efforts made toward 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, the possibility of tuning the optical response of nanosized materials by modifying their size has become one of the most challenging aspects of recent semiconductor research.¹ Among the different nanostructures, nanowires have recently attracted a lot of interest. Being quasi-one-dimensional structures, they exhibit extreme quantum confinement effects such that charge carriers are free to move only along the wire. Germanium nanowires (GeNWs), which can be synthesized using a variety of techniques,^{2–5} are particularly interesting due to their high carrier mobility: In fact, GeNW based-devices such as field-effect transistors, solar cells, and nanomagnets, have been characterized^{6,7} or envisaged.⁸ It has also been shown recently that GeNWs can be grown on silicon substrates [in particular, on the vicinal Si(111) surfaces^{9–11}]. Photoluminescence has also been observed.¹² In principle, therefore, GeNWs could be used in optoelectronic components fabricated within silicon-based technology, where the ultimate goal is the reduction of device size down to the nanoscale for higher device density.

In spite of such clear device potential, little theoretical study has been carried out on GeNWs, in contrast to their silicon counterpart.^{13,14} Research has instead been focused on quantum dots,¹⁵ quantum wells,^{16,17} and Si-Ge/Sn-Ge superlattices.^{18,19} With regard to GeNWs, only a single recent *ab initio* study of their electronic and optical properties has been performed, although this work considered ideal wires (without geometry optimization), and adopted a single-particle approach.²⁰

However, quantum confinement is known to strongly modify optical response through the influence of excitonic effects.²¹ In this paper, we examine the influence of these effects on the optical response of GeNWs through first-

principle calculations beyond the one-particle approach. We find that both the exciton binding energy and the *e-h* probability distribution depend not only on the effective size of the wire, but also on its orientational structure. The presence of bulges and kinks in the wire is shown to result in a stronger intensity, larger binding energy, and reduced spatial size for the exciton: The size L of the electron-hole probability distribution depends on the orientation growth by the relation: $L[100] < L[111] < L[110]$ (see Fig. 1). In particular, we find the strongest overlap of the electron-hole wave function (see bottom part of Fig. 1) and an excitonic binding energy close to 2 eV in the [100] GeNW (of width 0.4 nm). This value is particularly significant when compared with typical binding energies of ~ 1 eV obtained for semiconducting carbon nanotubes of comparable effective width,^{22,23} where the overlap is limited to the two-dimensional nanotube wall. Furthermore we find significant cancellation of self-energy and electron-hole interaction effects (as seen from the onset of the optical spectrum) in the wires which, resembling a string of small clusters, have a quasi-zero-dimensional character.

Free-standing, infinitely long, and homogeneous hydrogen-passivated GeNWs with effective widths²⁵ d of 0.4, 0.8, and 1.2 nm and different growth orientation (along [100], [110], and [111] directions), are considered. A schematic representation of the smallest wires is given in Fig. 1. As is usual for hydrogenated nanowires, no dangling-bond-like states appear within the band gap region for all the GeNWs oriented along the three directions.

The density functional theory–local-density approximation (DFT-LDA) electronic structures have been obtained with a plane-wave code,²⁶ using well tested norm-conserving pseudopotentials for Ge and H (Ref. 27) and an energy cutoff of 30 Ryd. An 8 k -point sampling of the Brillouin zone (BZ) has been used in the calculation of the geometrical structures for all wires. For the electronic and optical properties, a doubling of the k mesh is only needed for the [110] oriented wires. Self-energy and excitonic calculations were converged

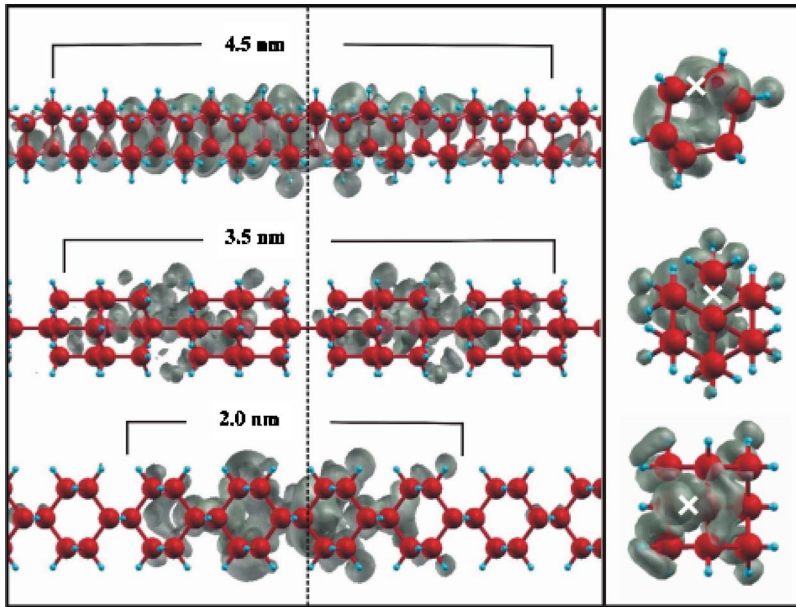


FIG. 1. (Color online) Geometrical structures of the 0.4 nm Ge wires in the [110] (top), [111], and [100] (bottom) directions shown from the side (left) and from the top (right). Large spheres represent Ge atoms; small spheres are hydrogen atoms used to saturate the dangling bonds. The gray isosurface (Ref. 24) gives the probability distribution $|\psi_{exc}(r_e, r_h)|^2$ for finding the electron when the hole is fixed in a given position (the e - h localization length L is reported for each wire). The hole positions lie on the dashed line in the left panel and are represented by the white crosses in the right panel

with respect to the energy cutoff and number of bands; moreover, a careful convergence of all results with respect to the cell dimension has been tested. Full geometrical relaxation of all atoms in the wires was allowed: Our calculations show that atomic relaxation, which yielded a small expansion of the most external atoms but no change along the longitudinal direction, causes minor modifications to the wire band structures and optical spectra. All the reported results refer to the fully relaxed systems.

At the DFT-LDA level we find that a clear direct gap is induced at Γ due to quantum confinement effects²⁰ in the [110]-oriented wires. However, the [111] and [100] wires are characterized by an indirect fundamental gap, even though there is a very small difference between direct and indirect gaps. Furthermore, all the DFT-LDA band gaps show a dependence on the wire orientation and size (see the results reported in the third column of Table I). The presence of indirect gaps in GeNWs is at variance with the case of SiNWs, where direct band gaps at Γ were found for [100], [110], and [111] oriented wires.^{14,28,29} This difference is a consequence of confinement effects on the conduction band

TABLE I. DFT-LDA electronic gaps (third column), quasiparticle gaps (fourth column), GW corrections (fifth column), excitonic binding energies (sixth column). All values are in electronvolts.

Wire size	Wire orient.	E_g^{DFT}	E_g	$\Delta E_g(\text{GW})$	E_B
0.4 nm	[110]	2.1	4.5	2.4	1.2
	[111]	3.5	5.4	1.9	1.6
	[100]	3.9	6.1	2.2	1.8
0.8 nm	[110]	1.3			
	[111]	2.1			
	[100]	2.6	4.0	1.4	0.8
1.2 nm	[110]	0.9			
	[111]	1.6			
	[100]	1.9			

minima, that have different locations in the two bulk semiconductors: In Si they occur in the [100] directions about 80% of the way to the zone boundary; in Ge, however, they lie along the [111] directions centered on the midpoints of the hexagonal zone faces. Nevertheless a similar behavior for the orientation anisotropy of the electronic gaps (with the following relation: $E_g[100] > E_g[111] > E_g[110]$) has been found both in GeNWs and in SiNWs.^{20,30,32} This can be explained in terms of the geometrical connectivity of the three different wires: From Fig. 1 it is evident that the [111] and [100] wires appear as a collection of small clusters connected along the axis, while the [110] wires resemble a linear chain.

In order to have an appropriate description of the one-particle excited states we avoid (for all NWs with $d=0.4$ nm and for the [100] NW's with $d=0.8$ nm) the DFT-LDA approximation by including, self-energy corrections³³ by means of the GW method. The main result at this level are openings of the band gap by amounts much larger than the corresponding correction in the bulk compound and which are also size dependent. Since the self-energy corrections are weakly dependent on the k point and energy band, we use an average scissor operator for each wire (see Table I, fifth column). For the size scaling of the quasiparticle band gap we find a dependence on the wire width which is consistent with that recently obtained in the [110] SiNWs.^{14,31,32} Moreover, we observe an appreciable wire orientation dependence of the self-energy correction in the smallest wires.

Coming to the optical properties, we wish to underline here that, for one-dimensional systems, first-principles calculations of excitonic effects through the solution of the Bethe-Salpeter equation (BSE),³⁴ have been considered, until now, only for carbon nanotubes^{22,23} and molecular organic chains,^{35,36} but not for the case of nanowires. As we discuss in the following, subnanometer nanowires show peculiar behavior, which are essentially due to their different atomic arrangement and to the multisubband nature of the electronic structures. In Fig. 2 we report the imaginary part of the dielectric function for light polarized along the axis (left panel) and perpendicular to it (right panel) for the 0.4 nm Ge [110].

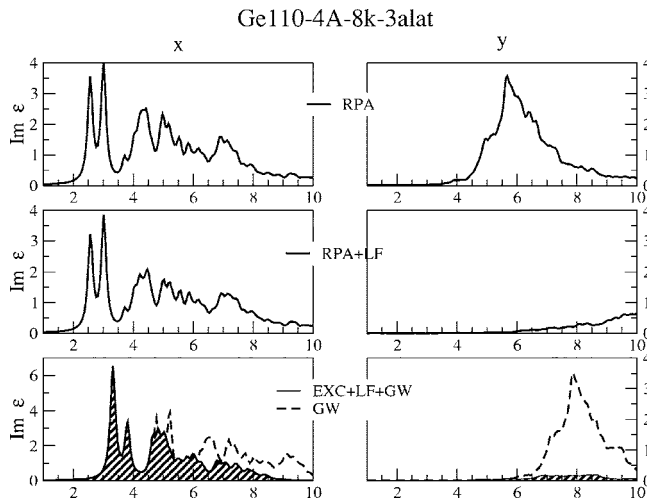


FIG. 2. Imaginary part of the dielectric function of [110] GeNWs (0.4 nm). Left panels: light polarized along the wire axis (x); right panels: light polarized perpendicularly to this axis (y). The reader should note the different scale of the vertical axes in the panels.

The first row of figures shows the optical spectra obtained at the random-phase approximation (RPA) level and reveal an important polarization dependence.²⁰ The second row illustrates how the dielectric response is modified by taking into account the inhomogeneity of the system [RPA and local field (RPA+LF)]. Similar to other one-dimensional systems, such as carbon nanotubes^{23,37} and silicon nanowires,³⁸ when local field effects (or equivalently, the depolarization effect³⁹) are included, we find an important intensity reduction for perpendicular light polarization (right panel) which renders the wire almost transparent below 8 eV, while a small change of the optical spectrum for light polarized along the wire axis (left panel) is observed. This anisotropic phenomenon has been observed experimentally in the optical absorption of carbon nanotubes,⁴⁰ in the photoluminescence spectra of porous silicon⁴¹ and in the optical gain in silicon elongated nanodots,⁴² it is interesting to test it in GeNWs.

The third row of each panel reports the absorption spectra when self-energy corrections alone (GW) and when self-energy, local-field, and excitonic effects (GW+LF+EXC) are taken into account. Again we see that the effect of the electron-hole interaction on the optical properties strongly depends on the light polarization. In fact, for light polarized perpendicular to the axis, the GW+LF+EXC spectrum is rather similar to the RPA+LF curve, whereas for light polarized along the growth axis, a big transfer of the oscillator strength to the low energy peaks is observed together with a reduction of the Sommerfeld factor above the electronic gap (as predicted in simplified models⁴³). In the left panel, it can be observed that the excitonic effects reverse the relative intensities of the first two peaks with respect to the one-particle optical spectrum and blueshift them by about 1 eV. In particular we note that the excitonic binding energy (1.2 eV, see last column of Table I) and the excitonic spatial size ($L \approx 4.5$ nm, see Fig. 1) in this wire are comparable to those observed in carbon nanotubes.^{22,23} This similarity is due to the atomic structure of the [110] wires which resembles that of a nanotube (see top view of Fig. 1). Nevertheless, the

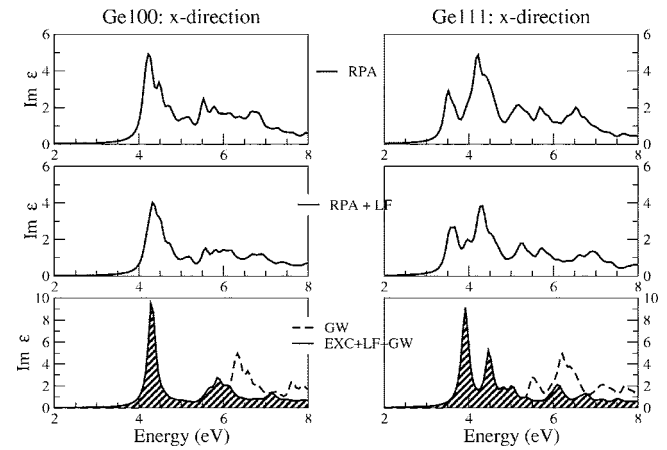


FIG. 3. As Fig. 2, but only for light polarized along the wire axis, for [100] (left panel) and [111] (right panel) GeNWs (0.4 nm).

optical spectrum of the [110] NW, as well as those of the other wires, shows a richer structure than that of nanotubes (NTs) and one-dimensional organic chains, due to the complex multisubband character of their electronic structures.

Similar observations may be made for the wires oriented along [111] and [100]. Reported in Fig. 3 are the $\epsilon_2(\omega)$ spectra, calculated within the different approximations. Since the depolarization effect is again responsible for the almost complete transparency for light polarized perpendicular to the wire axis, only the optical spectra for light polarized along the wire axis are shown in this figure. The main difference at the RPA level with respect to Fig. 2 occurs in the positions of the absorption peaks, which are shifted toward higher energies (both in [111] and [100] wires). On the other hand, two important features are evident when the e - h interaction is taken into account. With respect to the [110] orientation, we observe a much stronger transfer of the oscillator strength to the low energy peak, and second, an almost complete compensation (for both the absorption onset and the energy position of the peaks) of self-energy and excitonic contributions. This compensation has not been observed in other one-

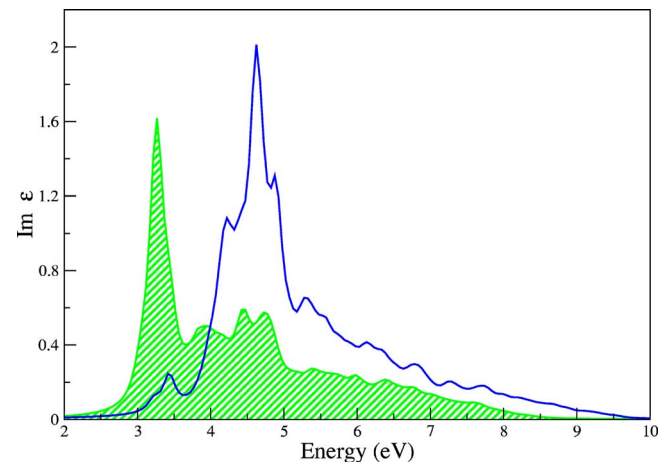


FIG. 4. (Color online) Imaginary part of the dielectric function of the [100] GeNW (0.8 nm) (dashed area) and [100] SiNW (0.8 nm) (solid line) for light polarized along the wire axis (x).

dimensional (1D) systems, but it has been predicted theoretically by Delerue *et al.*⁴⁴ and by Porter and coworkers⁴⁵ in zero-dimensional nanomaterials. In fact, the particular geometrical arrangements of the [111] and [100] 0.4 nm wires, which resemble a string of small atomic clusters connected along the wire axis, can again explain the particular observed behavior.⁴⁶

Finally, we point out that a larger oscillator strength near the onset of optical absorption is found in GeNWs (as well as in Ge nanodots⁴⁷) with respect to SiNWs, due to the Γ character of the first conduction band.^{14,32} We see in fact that a strong excitonic peak appears in the visible range for the 0.8 nm GeNW, but not for the 0.8 nm Si NW (see Fig. 4). This excitonic peak is expected to move to lower energies with increasing NW diameter.

In conclusion, we have studied within first principles the electronic structure and optical properties of subnanometer GeNWs, showing the crucial role played by the electron-hole interaction. By avoiding the effective mass approximation, we highlight the effect of the different geometrical structures of nanowires of different orientation on the optical spectra: In some cases the wire is made of connected clusters, while

in other cases it resembles a nanotube. Very large excitonic effects, different in the two cases, have been calculated that clearly depend on the orientation and symmetry of the nanowires. With respect to NTs of comparable diameter, we find larger exciton binding energies and oscillator strengths, due to the larger overlap of electron and hole wave functions inside the wire. With respect to both nanotubes and organic chains, a richer structure of optical spectra, due to the complex multisubband structure, is found. Finally, we stress that GeNWs show strong optical absorption at lower frequencies than SiNWs, with the main peak occurring in the visible range for a diameter of 0.8 nm (or greater). Hence, GeNWs of nanometer diameter have the potential to become efficient and tunable, small sized, strongly polarized light absorbers, and emitters in the visible range.

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