

First-principles optical properties of silicon and germanium nanowires

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Abstract

In this work we study the optical properties of hydrogen-passivated, free-standing silicon and germanium nanowires, oriented along the [100], [110], [111] directions with diameters up to about 1.5 nm, using ab-initio techniques. In particular, we show how the electronic gap depends on wire's size and orientation; such behaviour has been described in terms of quantum confinement and anisotropy effects, related to the quasi one-dimensionality of nanowires. The optical properties are analyzed taking into account different approximations: in particular, we show how the many-body effects, namely self-energy, local field and excitonic effects, strongly modify the single particle spectra. Further, we describe the differences in the optical spectra of silicon and germanium nanowires along the [100] direction, as due to the different band structures of the corresponding bulk compounds.

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1. Introduction

In recent years many efforts have been spent on the development of experimental techniques to grow well defined nanoscale materials, due to their possible applications in nanometric electronic devices. Indeed the creation of nanowire field effect transistors (NW-FET) [1–5], nano-sensors [6,7] atomic scale light emitting diodes (LEDs), lasers [8,9], has been possible due to the development of new techniques which give the possibility to control the growth processes of nanotubes, nanowires and quantum dots. Of particular importance, among the different atomic scale systems experimentally studied, are nanowires. Being quasi-one-dimensional structures, they exhibit quantum confinement effects such that carriers are free to move only along the axis of the wire. Further the possibility to modify their optical response as a function of their size has become

one of the most challenging aspect of recent semiconductor research. Because of their natural compatibility with silicon based technologies, Silicon nanowires (SiNWs) have being extensively studied and several experiments have already characterized some of their structural and electronic properties [2,6,10–13]. Recently, it has been possible to fabricate, for example, single-crystal SiNWs with diameter as small as 1 nm and lengths of a few 10s of micrometers [6,14–16]. Photoluminescence [17–19] data revealed a substantial blueshift with decreasing size of nanowires. Further scanning-tunneling spectroscopy data [16,19] also showed a significant increase in the electronic energy gap for very thin semiconductor nanowires, explicitly demonstrating quantum-size effects. Germanium nanowires (GeNWs), which can be synthesized using a variety of techniques [10,11,20], are particularly interesting due their high carrier mobility: in fact, GeNW based-devices such as NW-FET [21], solar cells and nanomagnets [22], have been characterized or envisaged [23]. It has also been shown recently that GeNWs could be used in optoelectronic components fabricated within silicon based technology [24].

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Despite such clear device potential, relatively few ab-initio calculations of optical properties beyond the one-particle approach have been performed [25,26] so far in order to clarify the experimental evidences and investigate the potential applications of such nanoscale materials. In fact, the theoretical panorama is essentially based either on ab-initio calculations [27–30], which neglect the electron–hole Coulomb interaction effects (which instead it is expected to play an important role due to the reduced dimensionality of such a systems) or within effective mass approximation (EMA) calculations [31] and semi-empirical approaches [32,33]. Moreover, the overwhelming majority of the papers refer only to Si nanowires.

2. Theoretical background

Here we calculate the optical properties fully accounting for the electron–hole interaction by solving the Bethe–Salpeter equation (BSE). In this section, we aim to resume very briefly the three-step computational procedure used. A more extended description about the Green’s function theory for the calculation of band structures and optical properties is given in the paper by Del Sole et al., in this volume. In short, through a DFT-LDA calculation [34,35], with the use of norm-conserving pseudopotentials [36,37], the geometrical structure of the relaxed ground state configuration of each wire has been obtained, solving self-consistently the one-particle Kohn–Sham equations [38]. Then, the eigenvectors and eigenvalues of the Kohn–Sham equation are considered as a first approximation to the true electronic wavefunctions and can be used to obtain the dielectric function according to the independent particle picture or IP-RPA (independent particle-random phase approximation) level as a sum over independent contributions from valence-conduction band pairs. In a second step the one-particle excitation energies are obtained. The DFT-LDA eigenvalues are corrected by solving the quasi-particle equation within the GW approximation [39,35]. This equation is formally similar to the Kohn–Sham equation but in place of the local, energy independent exchange correlation DFT potential, the self-energy operator (which is non hermitian, non local and energy dependent) appears. The calculated quasi-particle energies (i.e. the excitation energies) are the output of this part of the calculation and with the full dielectric matrix, calculated within the random phase approximation (RPA) at the DFT level, they are used as an input for the third step, which is the solution of the two particle Bethe–Salpeter equation, that describes the electron–hole pair dynamics [40].¹ Using the GW

corrected energies instead of DFT-LDA eigenvalues the dielectric matrix can be calculated in an independent quasi-particle picture (GW-RPA) [41].

3. Optical gaps in SiNWs and GeNWs: quantum confinement and anisotropy effects

In this section, we will describe the electronic properties of hydrogen passivated, free standing silicon and germanium nanowires oriented along the [100], [111] and [110] directions with diameters ranging from about 0.4–1.2 nm.² In particular, we will show the dependence of the electronic gap on both wire’s size and orientation (such behaviour will be ascribed to the quantum confinement effect). Further, in some of the studied wires, self-energy corrections will be included, by means of the GW method, in order to have an appropriate description of the excited states.

Concerning the electronic minimum gap (which is direct or quasi-direct in all the studied wires, see Refs. [25,26,35] for details) at the DFT level, as it is shown in Fig. 1, we find that it decreases monotonically with the wire’s diameter; in particular, for the smaller wires studied it varies from 2.7 (2.1) eV, in the [110] direction, to 3.9 (4.0) eV, in the [100] direction for Si (Ge)NWs. Such values, which are much bigger than the electronic bulk indirect gap, clearly reflect the quantum confinement effect. This effect, which has been recently confirmed in STM experiments [16,19], is related to the fact that carriers are confined in two directions being free to move only along the axis of the quantum wires. Clearly we expect that increasing the diameter of the wire, such effect becomes less relevant and the electronic gap will eventually approach the bulk value (see Fig. 1).

Another aspect that is interesting to note concerns the dependence of the DFT gap on the orientation of the wire, indeed, for each wire size the following relation holds: $E_g[100] > E_g[111] > E_g[110]$ (see Fig. 1). As it has been pointed out in Ref. [25] it is related to the different geometrical structure of the wires in the [100], [111], and [110] directions. Indeed the [100], [111] wires appear as a collection of small clusters connected along the axis, while the [110] wires resemble a linear chain. So we expect that quantum confinement effects are much bigger in the [100], [111] wires, due to their quasi zero-dimensionality, with respect to the [110] wires. Further, as it can be seen from Fig. 1, the orientation anisotropy reduces with wire’s width and it is expected to disappear for very large wires when the band gap approaches that of the bulk material.

¹ In our calculations we have used a supercell approach in order to simulate the one-dimensional structure of Si–Ge NWs. Carefull convergence tests have been performed on the size of the cell in order to be sure that the presented results do not depend on the wire–wire distance. Clearly the introduction of a Coulomb cut-off would guarantee a faster convergence (i.e., convergence on a smaller cell), although, if the cell is big enough, our results are the same as the ones that would be obtained with the inclusion of the cut-off in long range tail of the Coulomb potential.

² The effective width is defined as the wire cross-section linear parameter, following the definition of Ref. [30]. Nevertheless it must be underlined that this definition of the wire’s size is somehow ambiguous, indeed in the literature larger diameters are reported for wires with the same number of atoms in the unit cell, of the ones studied here. This is due to the fact that different definitions of the wire’s radius exist [33] and that in some cases the average distance among the external hydrogen atoms is taken into account.

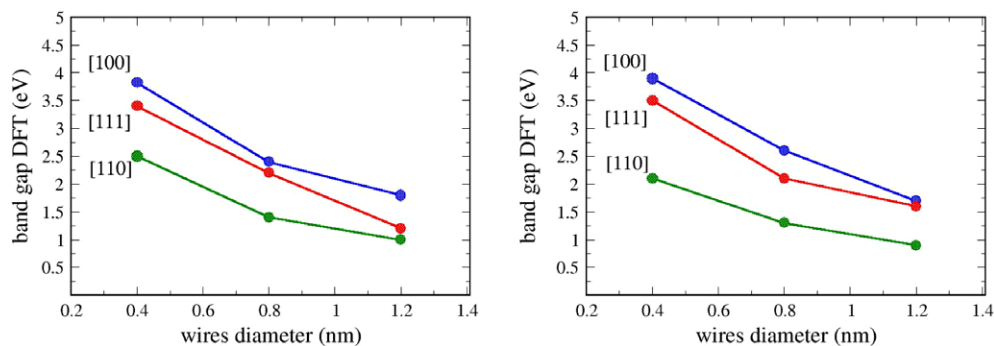


Fig. 1. Scaling of the DFT-LDA gap in SiNWs (left) and GeNWs (right) as a function of wires' size and orientation.

Table 1

DFT-LDA electronic gaps in SiNWs and GeNWs are reported, respectively, in the third and fourth column, quasi-particle gaps are reported for GeNWs in the fifth column

Wire size (nm)	Wire orient	Si E_g^{DFT}	Ge E_g^{DFT}	Ge E_g^{GW}
0.4	[100]	3.8	3.9	6.1
	[111]	3.4	3.5	5.4
	[110]	2.5	2.1	4.5
0.8	[100]	2.4	2.6	4.0
	[111]	2.2	2.1	
	[110]	1.4	1.3	
1.2	[100]	1.8	1.7	3.1
	[111]	1.2	1.6	
	[110]	1.0	0.9	

All values are in eV.

Most of the results presented in Table 1 do not take into account self-energy corrections, which are necessary in order to describe, in a proper way, the one-particle excited states. In the last column of Table 1, we report the GW corrected band-gaps, for the smallest GeNWs in the [111], [110] directions, and for all the [100] GeNWs. A complete discussion about this part can be found elsewhere [25,42]. We can see (Table 1, fifth column) that the effect of the GW correction is an opening of the DFT-LDA gap, by an amount which is much bigger than the corresponding

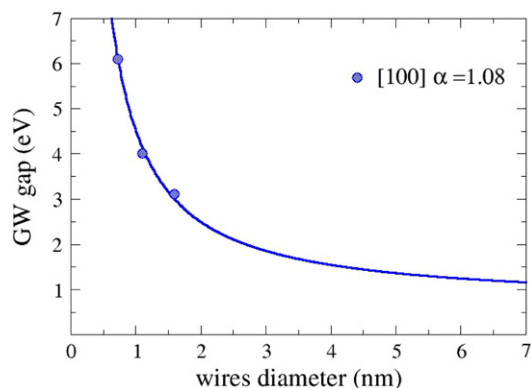


Fig. 2. Scaling of the GW gap in [100] oriented GeNWs as a function of wires' size. Note that in order to determine the scaling law, we have considered effective widths which included external hydrogen atoms.

correction in the bulk. Furthermore, it has to be noted that such corrections are also size and orientation dependent.

Fitting the GW band-gaps (Table 1, fifth column) with a function of $E_{g,\text{bulk}} + \text{const} \times (1/d)^\alpha$, where $E_{g,\text{bulk}}$ is the GW bulk gap value, and α is the scaling index (the fit is presented in Fig. 2), we have found $\alpha \simeq 1.1$, which is smaller than $\alpha = 2$ predicted in simple EMA models.

4. Optical properties of SiNWs and GeNWs

In Section 5 of the present paper, we aim to point out the importance of the many-body effects on the optical response of some of the studied nanowires. A more detailed description of these effects, depending on the size and the orientation of the NW, can be found in Refs. [25,42]. In Fig. 3, we report the theoretical optical absorption spectra of the Germanium and Silicon wires (grown along the [100] direction and with diameter of about 0.8 nm), for light polarized along the wires axis. In the top panels, the spectra calculated at the RPA one-particle level, but including self-energy corrections, are shown; while, in the bottom panels, the corresponding spectra obtained including the excitonic effects, are reported. Comparing the top and bottom panels, it is clear that strongly bound excitons, of more than 1 eV, are present. Moreover, we aim to underline an important difference between silicon and germanium wires: in fact, already at the GW level (top panels) a large oscillator strength near the onset of optical absorption is found only in the case of GeNWs and not in the case of SiNWs. With the inclusion of the excitonic effects (bottom panels) we see that an important transfer of the oscillator strength below the electronic gap appears and a strong optical peak comes out in the visible range for the 0.8 nm GeNW, but not for the 0.8 nm Si NW (see Fig. 3). This different behaviour between the Ge and Si nanowires is related to the different character of the conduction band minima (CBM) in the two cases. These CBM are obtained through the folding of the bulk energy bands on the wires axis; whereas in Si the CBM retain mainly the original indirect character of the absolute band minimum along the [100] direction [26,42], in the case of Ge, there is an important mixing between direct and indirect character, owing to the fact that the CBM at Γ in bulk Ge is only few meV higher than

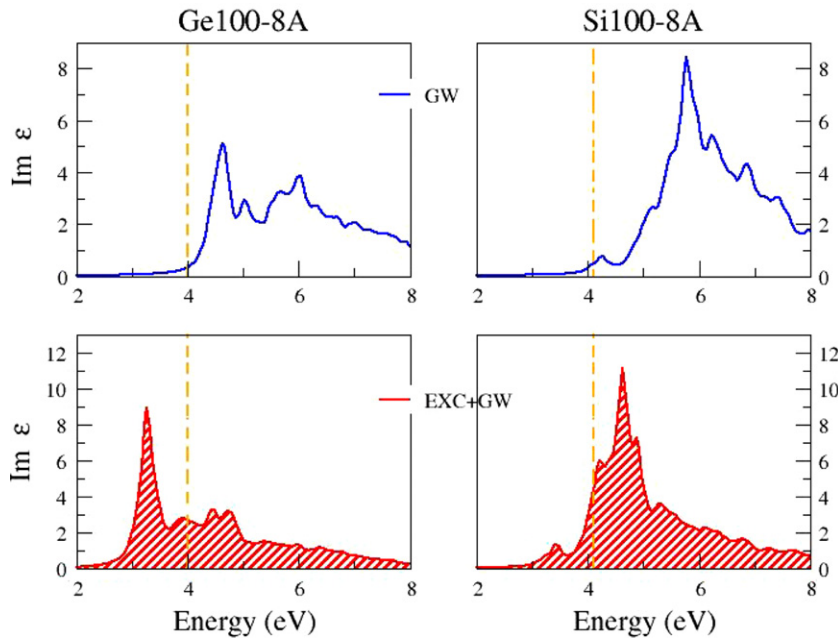


Fig. 3. Imaginary part of the dielectric function of [100] oriented GeNWs (left panels) and SiNWs (right panel) with diameters of 0.8 nm. First row shows optical spectra at the GW level, the second row shows the spectra obtained including excitonic effects. The dashed line represents the GW electronic gap.

the absolute CBM along the [111] direction. It is worthwhile to note that a similar finding has been obtained comparing the optical spectra of silicon and germanium nanodots [43]. We underline that the calculated excitonic peak is expected to move to lower energies with increasing NW diameter, thus covering fully the visible energy range.

5. Conclusions

In this paper, we have presented the electronic and optical properties of Silicon and Germanium NWs, focusing on the role played by the electron–hole interaction effects. Indeed we have shown how many-body effects, namely self-energy, local field and excitonic effects, strongly modify the single particle spectra. We have also shown the dependence of the optical properties, not only on the wires diameter, but also on wires' orientation; such highly anisotropic behaviour has been explained in terms of the different geometrical structure of wires grown with different orientation. Finally the comparison of the optical spectra of SiNWs and GeNWs with diameters of the order of 0.8 nm, demonstrates that GeNWs have a strong oscillator strength at lower frequencies with respect to SiNWs. This means that nanometric GeNWs, having the main absorption peak in the visible range, could be probably more efficiently applied in optoelectronic nanoscale devices.

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