



Optical matrix elements in tight-binding approach of hydrogenated Si nanowires

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ABSTRACT

The dependence of the imaginary part of the dielectric function on the quantum confinement within two different schemes: *intra-atomic* and *interatomic* optical matrix elements are applied and compared. The optical spectra of Si nanowires are studied by means of a semi-empirical sp^3s^* tight-binding supercell model. The surface dangling bonds are passivated by hydrogen atoms. The results show that although the *intra-atomic* matrix elements are small in magnitude, the interference between these terms and the *interatomic* matrix elements contributes with nearly 25% of the total absorption. Thus, a quantitative treatment of nanostructures may not be possible without the inclusion of *intra-atomic* matrix elements.

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1. Introduction

Silicon nanowires (SiNW) are especially attractive for their possible efficient integration in conventional Si-based microelectronics [1,2]; the interest is essentially related to the strong modifications of the basic properties of the material induced by space confinement, with remarkable effects on the optical properties. On the other hand, 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 nanoscale electronic devices. In particular, among the different atomic scale systems experimentally studied, are nanowires [3,4]. Being quasi-one-dimensional structures, they exhibit quantum confinement effects such that carriers are free to move only along the axis of the wire.

The calculations of the optical properties of these systems require knowledge of momentum matrix elements. Within the semi-empirical tight-binding (TB) approximation, these are not readily available since wave functions are expanded in an unknown basis. A solution to this problem is based on taking the k -space gradient of the TB Hamiltonian. This technique is only approximate since *intra-atomic* contributions are emitted. In this work, we study the dependence of the imaginary part of the dielectric function on the quantum confinement of SiNW within two different schemes: *intra-atomic* and *interatomic* optical matrix elements, which are applied and compared.

2. Model and theoretical approach

For modelling SiNW, we consider free standing, infinitely long and homogeneous wires of square cross-section with the wire axis along the [001] direction, and wire surfaces which correspond to (110) surfaces of bulk Si. Each surface dangling bond is saturated with a hydrogen atom having a H–Si bond length of 1.48 Å. The system has translational symmetry in the z -axis with period equal a lattice constant $a = 5.431$ Å. For SiNW with bigger cross-sections, Si atoms are added on (100) and (010) planes to obtain nanowires with larger width (d), conserving their square shapes. The minimal basis that reproduces the indirect band gap within the TB approximation is sp^3s^* . The parameters of Vogl et al. [5] are used, which reproduce an indirect-gap of 1.1 eV for bulk crystalline silicon (*c*-Si).

The on-site energy of the H and the Ge–H orbital interaction parameters are taken as $E_H = -4.2$ eV, $ss\sigma_{Si-H} = -4.075$ eV, and $sp\sigma_{Si-H} = 4.05$ eV, respectively. The last three parameters are obtained by fitting the energy levels of silane [6].

Having established a TB model, we proceed with the computation of the optical properties of the material. For the calculation of the imaginary part of the dielectric function, $\epsilon_2(\omega)$, we use the expression

$$\epsilon_2(\omega) = \frac{2\pi^2 \hbar e^2}{m_0 V} \sum_{c,k'} \sum_{v,k} f_{vk}^{ck'} \delta(E_c(k') - E_v(k) - \hbar\omega) \quad (1)$$

where the oscillator strength is given by

$$f_{vk}^{ck'} = 2m \frac{|(c, k' | e \cdot v | v, k) |^2}{E_c(k') - E_v(k)} \quad (2)$$

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In the last expression, $|v, \mathbf{k}\rangle$ and $|c, \mathbf{k}'\rangle$ are valence and conduction band Bloch states with energies $E_v(\mathbf{k})$ and $E_c(\mathbf{k}')$, respectively, \mathbf{e} is the polarization vector, \mathbf{v} is the electron velocity operator, and \mathbf{k} is the wave vector. In the TB approach, the Bloch functions in Eq. (2) are linear combinations of atomic orbitals $|\mathbf{R}j\mu\rangle$, e.g.,

$$|v, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}j\mu} e^{i\mathbf{k}(\mathbf{R}+\mathbf{u}_j)} A_{j\mu}^v(\mathbf{k}) |\mathbf{R}j\mu\rangle \quad (3)$$

Here, \mathbf{R} are the Bravais vectors giving the positions of the supercells, j enumerates Si atoms within the supercell, $\mu = s, p_x, p_y, p_z, s^*$ identifies the orbital, and N is the total number of supercells. Thus, it is necessary to know the position of matrix elements between the atomic orbitals. The matrix elements of the electron velocity in Eq. (2) can be expressed, by means of $\mathbf{v} = (i/\hbar)[H, \mathbf{r}]$, the matrix elements of the electron coordinate \mathbf{r} . In TB model, the basic hypothesis is to neglect the interatomic matrix elements of \mathbf{r} , since the overlapping of orbitals belonging to different atoms is supposed to be small. That is,

$$\langle \mathbf{R}'j'\lambda' | \mathbf{r} | \mathbf{R}j\mu \rangle = \{ (\mathbf{R} + \mathbf{u}_j) \delta_{\mu\lambda'} + \mathbf{d}_{\mu'\mu} \} \delta_{\mathbf{R}\mathbf{R}'} \delta_{j'j} \quad (4)$$

where the diagonal term is the position of the atom, and $\mathbf{d}_{\mu'\mu}$ is the *intra-atomic* dipole matrix elements (DME) between different orbitals ($\mu \neq \mu'$). Within the *interatomic* approach [7], the polarizability of a free atom is considered to be much smaller than that of the corresponding semi-conductor [8], and only the

first term of Eq. (4) is considered. In contrast, the second approach (*intra-atomic*) [9] considers the contribution to the dipole matrix element coming from different orbitals at the same atom, without neglecting the first term in Eq. (4). For Si, the nonzero matrix elements $\mathbf{d}_{\mu\mu'}$ in Eq. (4) are $\langle s|x|p_x \rangle = 0.27 \text{ \AA}$ and $\langle s^*|x|p_x \rangle = 1.08 \text{ \AA}$ [9]. In our calculations of the dielectric function, we allowed for both contributions. The calculations for ϵ_2 have been carried out for light polarized in the [100] direction, i.e., perpendicular to the SiNW alignment.

3. Results

In Fig. 1, the imaginary part of dielectric function, ϵ_2 , is plotted as a function an x -polarized photon energy for c-Si, where the open circles and lines correspondingly represent the experimental [10] and TB results.

It is seen that the theory (with both *intra-atomic* and *interatomic* DME) gives reasonably well the shape of the edge of the optical spectrum, in spite that no d -orbitals are considered. The position of the low energy peak and its intensity are underestimated. This can be attributed to the limits of the sp^3s^* first-neighbour TB parameterization, which fails to describe correctly the dispersion of the second conduction band.

Fig. 2 shows the variation of ϵ_2 as function of the photon energy, for the case of one SiNW with width $d = 0.57 \text{ nm}$, the energy spectrum is characterized by very flat minibands, and some of them do not possess dispersion at all. It results in the appearance of a lot of peaks in the absorption spectrum.

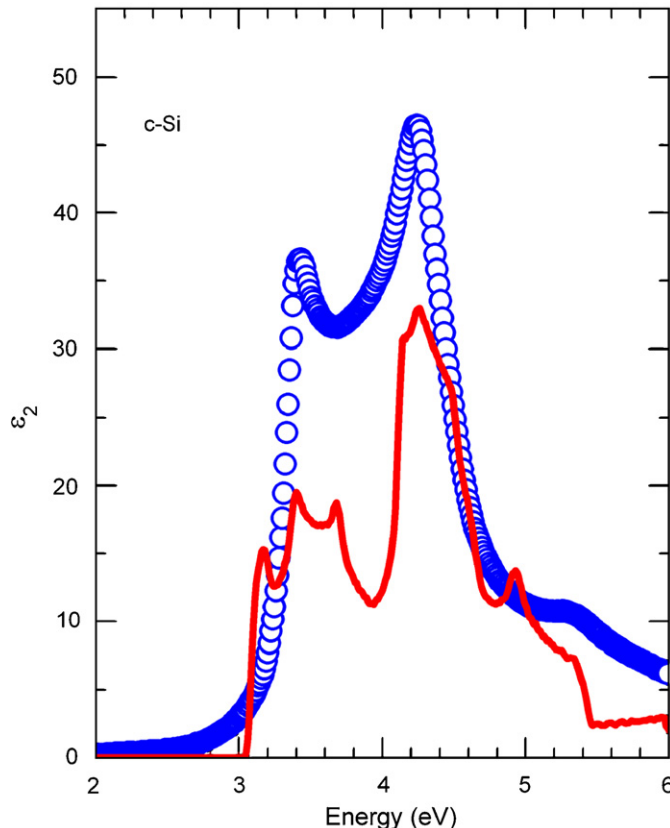


Fig. 1. ϵ_2 as a function of photon energy for c-Si. The solid line represents our results obtained from TB, and the open circles represent the experimental data [10].

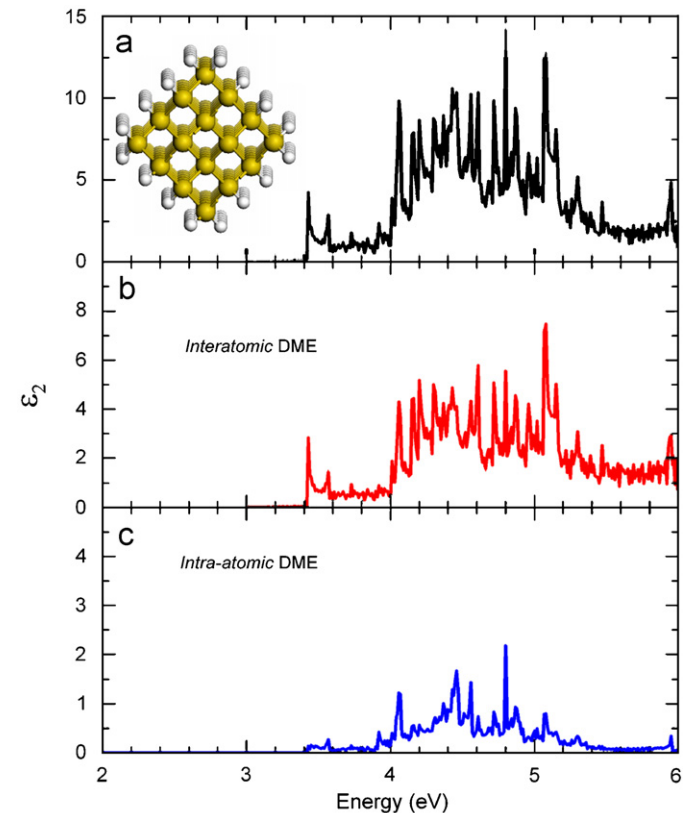


Fig. 2. ϵ_2 vs. the photon energy for SiNW with width of $d = 0.57 \text{ nm}$ (inset of (a)). The contributions given by *interatomic* and *intra-atomic* DME are presented in (b) and (c), respectively, and (a) show both schemes.

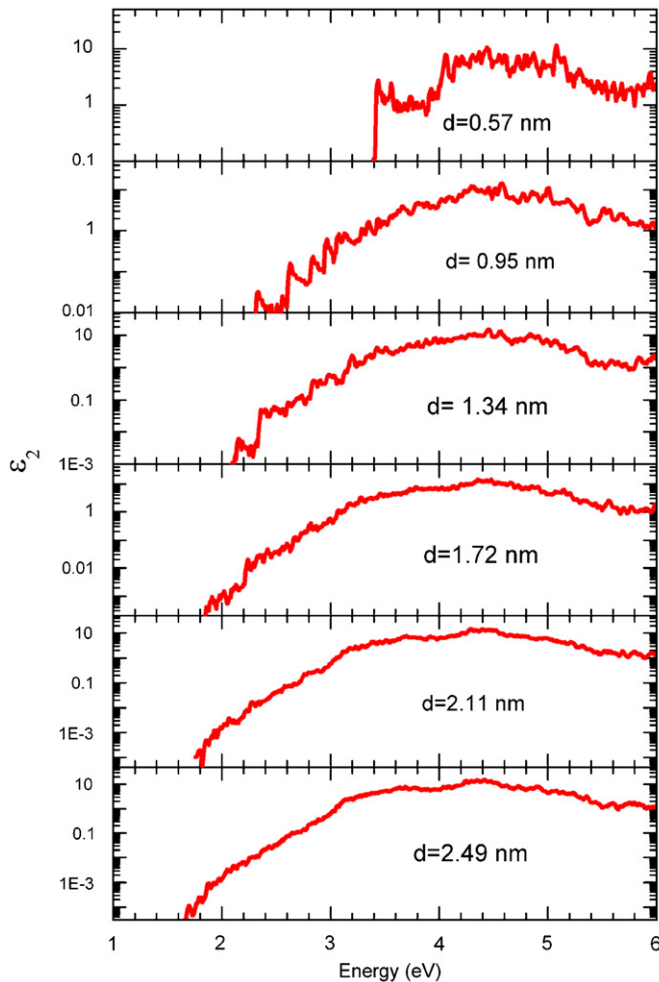


Fig. 3. Show the low-frequency tail of ϵ_2 as function of photon energy for SiNW with diverse widths d .

The results of the contribution given by *intra-atomic* and *interatomic* DME are presented in Figs. 3(b) and (c), respectively. Notice that, although the *intra-atomic* DME are small in magnitude,

the interference between these terms and *interatomic* DME contributes 25% of the total absorption.

To analyze the dependence of ϵ_2 on the width (d) of the SiNW, one has to perform calculations on big supercells, where the width can be changed progressively. Fig. 3 presents such dependence.

Notice the appearance of a low-frequency tail in the function ϵ_2 for SiNW when the width is increased. With a decrease of width, quantum confinement comes into a play and produces the blueshift of this tail. The calculations show a consistent asymptotical behavior to the crystalline limit when the width of wires enlarges.

4. Conclusions

In summary, we have studied from semi-empirical TB approximation, the imaginary part of the dielectric function of SiNW as function of their widths. We have shown that a simple microscopic quantum mechanical treatment, including interatomic and intra-atomic DME, is capable of reproducing the essential features of the dielectric function of c-Si. The calculations show that, in general, a quantitative treatment of nanostructures may not be possible without the inclusion of *intra-atomic* DME.

Acknowledgments

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