A microscopic model for the dielectric function of Ge quantum wires

P.Alfaro, R.Vazquez, I.Lobota, A.E.Ramos*, M. Cruz-Irisson

Seccion de Estudios de Posgrado e Investigacion, ESIME-Culhuacan,
Instituto Politecnico Nacional, Av. Santa Ana 1000,
C.P. 04430 Mexico, D.F., Mexico
*Instituto de Investigaciones en Materiales, UNAM, Mexico,
D.F., 04510, Mexico

Free-standing, infinitely long, and homogeneous quantum wires of square cross section are considered using the chessboard-like supercell model. The optical transition properties of Ge nanocrystals are studied by means of an sp^3s^* semiempirical tight-binding approximation. The calculations have been carried out for light polarized in the [100] direction, i.e., perpendicular to the wire alignment. Dependence of the imaginary part of the dielectric function on the quantum confinement is presented within two different schemes: intra-atomic and interatomic matrix elements, which are applied and compared. The principal results show that although the intra-atomic matrix elements are small in magnitude, the interference between these terms and the interatomic matrix elements contributes about 25 % of the total absorption. Thus, it appears that a quantitative treatment of nanostructures may not be possible (in general) without the inclusion of intra-atomic matrix elements.

Свободно-стоящие однородные квантовые проволоки квадратного поперечного сечения рассматриваются с применением шахматной модели ячейки сверхрешетки. Оптические переходные свойства нанокристаллов германия исследуются с помощью полуэмпирического приближения сильной связи sp^3s^*. Расчеты выполнены для света, поляризованного в направлении [100], т.е. перпендикулярно выстраивание проволоки. Зависимость мнимой части диэлектрической функции от квантового ограничения представлена в рамках двух различных схем: внутриатомных и межатомных матричных элементов, которые сопоставлены между собой. Основные результаты показывают, что, хотя внутриатомные матричные элементы имеют малую величину, вклад интерференции между этими термами и межатомными матричными элементами в суммарное поглощение составляет приблизительно 25 %. Таким образом, оказывается, что количественное рассмотрение наноструктур, в общем, невозможно без включения внутриатомных матричных элементов.

One-dimensional structures with nanometer scale diameters, such as nanotubes and nanocrystals, offer great possibilities for testing and understanding fundamental concepts about the roles of dimensionality and size in, for example, optical, electrical, and mechanical properties and for applications ranging from probe microscopy tips to interconnection in nanoelectronics. The synthesis of crystalline semiconductor nanowires, such as Ge, holds considerable technological prom-ise for device application and for improving the optical properties of this indirect gap material but is difficult to carry out.

There are many reports of a strong visible PL in Ge nanocrystals prepared by several methods [1-3]. In all the cases, the PL maximum is above 2 eV quite independently of the nanocrystal size (2 to 15 nm). These results cannot be explained by a simple quantum confinement effect [4]. However, Takeoka and co-workers [5] have observed a size-dependent PL in the near infrared re-

gion which is close to the band gap of bulk Ge (0.66 eV at 300 K) and which seems more compatible with the quantum confinement model. In addition, it has been suggested that the radiative recombination in Ge nanocrystals could be fast because of the small energy difference between the indirect gap and direct gap of Ge [3] (0.14 eV between Γ and L conduction band minima).

A lot of theoretical work has been carried out on the band structure and on the behaviour of the excitons in such nanoscale structures [6]. On the other hand, investigations concerning the dielectric function are sparse. This is due to many factors. Experimentally, it is not easy to separate the dielectric function of one phase from a multiphase material such as porous silicon [7], and theoretically, it is very difficult to calculate the dielectric function, since the number of atoms to be considered is usually large and it is time-consuming to use the state-of-art ab initio methods to obtain the dielectric function in a wide energy range and in high resolution. A main attraction to consider the dielectric function is that it contains information about the different phases of the multiphase material and also the possible deviation from perfect phase, like strain, disorder, confinement, and surface effects [8].

In spite of the lack of agreement about the detailed microscopic mechanism of the luminescence, it is generally accepted that quantum confinement in nanometer sized Ge wires plays a key role in the optical properties, similarly to the case of porous silicon. The aim of the present work is to calculate, optical properties of Ge structures such as hydrogen-terminated Ge quantum wires similar to porous Si, using an accurate and efficient microscopic electron structure method. We take into account both intra-atomic (local) and interatomic (nonlocal) matrix elements of r. The imaginary part of the dielectric function is obtained through the one-particle tight-binding (TB) eigenvectors and eigenvalues, and using k-points in the irreducible wedge of the Brillouin zone. However, by eliminating the intra-atomic matrix elements, one obtains a TB model that is not valid in the TB limit of isolated atoms. Thus, although the model should provide a reasonable description of interatomic description between extended states, one has less confidence in its ability to describe localized states, which may be important at surfaces or interfaces. Below, a theoretical model is proposed capable of addressing this problem. Then, the calculation results of imaginary part of the dielectric function are presented. Finally, some conclusions are drawn.

In this work, we employ a semiempirical TB model of the electron structure that, by construction, reproduces the correct band gap of bulk Ge in the limit of infinite supercell size. As we are interested in describing the band structure modifications around the gap, the minimum basis capable of describing an indirect band gap along the L direction is the sp^3s^* one. We have used the parameters of Vogl, Hjalmarson, and Dow [9], which reproduce an indirect gap in bulk crystalline Ge. One point of this method is that it makes it possible to investigate the properties of large supercells while avoiding the computation difficulties involved in the first-principle method.

We employ a chessboard-like supercell model of crystalline Ge wires along the direction [001] (z axis). The cross-section of the narrowest wire considered is illustrated in Fig. 1, where nine 8-atom supercells are represented, each one is a cube of $a = 5.65$ Å side with translational symmetry in the z direction; a 32-atom supercell is built by joining four such cubes in the XY plane, resulting in a structure with parameters $a_x = a_y = 2a$ and $a_z = a$. We suppose that the nanostructures have the same lattice structure and the same interatomic distance than bulk Ge and that all the dangling bonds are saturated with hydrogen atoms. For simplicity, we suppose that there are no hydrogen-hydrogen interactions. The hydrogen atoms are used to simulate the bonds at the wire surface and sweep surface states out of the fundamental gap. We assume that the H-saturated dangling bonds on the surface of the cluster have the natural H–Ge bond length.

The on-site energy of the H and Ge–H orbital interaction parameters are taken to be $E_H = 0.205$ eV, $ss\sigma_{Ge–H} = -3.618$ eV, and $sp\sigma_{Ge–H} = 4.081$ eV, respectively, which are obtained by fitting the energy levels of GeH$_4$ calculated in Local Density Approximation [10]. We solve for the electronic states by diagonalizing the TB Hamiltonian directly.

To obtain optical constants from this model, it is necessary to evaluate also the dipole matrix elements (or oscillator strength). Within the TB method, there exist various approaches to the calculations. As a starting point, we repeat the derivation of the TB momentum matrix elements following the line of [11]. The real (ε_1) and
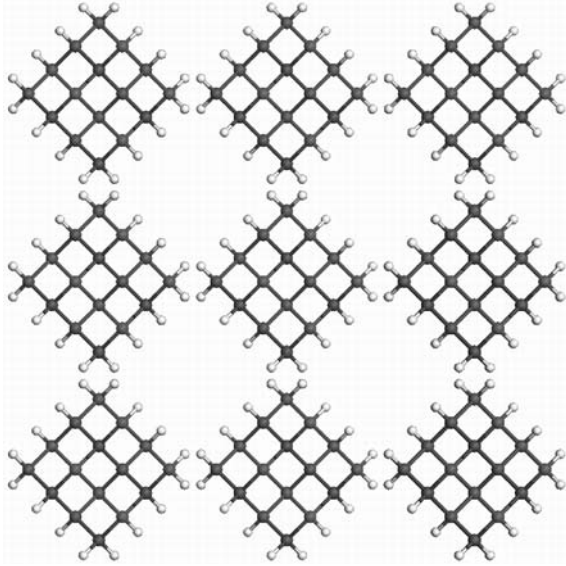
Fig. 1. A 32-atom chessboard-like supercell.

imaginary (ε_2) parts of the dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) are related by the Kramers-Kroning dispersion relations and ε_2 can be calculated as

$$\varepsilon_2(\omega) = \tag{1}$$
$$= \frac{2\pi^2 \hbar e^2}{m\omega V} \sum_{c,\mathbf{k}'} \sum_{v,\mathbf{k}} f_{v\mathbf{k},c\mathbf{k}'} \cdot \delta\left[E_c(\mathbf{k}') - E_v(\mathbf{k}) - \hbar\omega\right],$$

where the oscillator strength is given by

$$f_{v\mathbf{k},c\mathbf{k}'} = 2m \frac{|\langle c,\mathbf{k}'|\mathbf{e} \cdot v|v,\mathbf{k}\rangle|^2}{E_c(\mathbf{k}') - E_v(\mathbf{k})}. \tag{2}$$

In the above expression, $|v,\mathbf{k}\rangle$ and $|v,\mathbf{k}'\rangle$ represent the valence and conduction states [with energies $E_v(\mathbf{k})$ and $E_c(\mathbf{k}')$, respectively]; $\mathbf{e}$ is the polarization vector; v, the electron velocity operator; and $\mathbf{k}$, the wave vector. The integration is carried out over the whole Brillouin zone. In the TB scheme, the Bloch functions in Eq.(1) are linear combinations of atomic orbitals $|\mathbf{R}j\mu\rangle$, e.g.,

$$|v,\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{Rj\mu} e^{i\mathbf{k} \cdot (R + \mathbf{u_j})} A_{j\mu}^v(\mathbf{k}) |\mathbf{R},j\mu\rangle. \tag{3}$$

Here, $\mathbf{R}$ are the Bravais vectors defining the position of the supercell; j enumerates atoms within the supercell; μ identifies the atomic orbital; $\mathbf{u}_j$ is the position of a specific atom in the supercell; N is the number of supercells. The matrix elements of the electron velocity in Eq.(1) can be expressed, applying the definition $v = i/\hbar[\mathbf{H},r]$, via the matrix elements of the electron coordinate $\mathbf{r}$.

There are two approaches in the literature to evaluate $(\mathbf{R}'j'\lambda|r|\mathbf{R}j\mu$: that by Koiller, Osorio and Falicov (KOF, nonlocal approach) [12] and the other by Selloni, Marsella and Del Sole (SMD, local approach) [13]. In both cases, the overlapping of orbitals is supposed to be small and the interatomic matrix elements are neglected. Between the orbitals belonging to the same Si atom ($\mathbf{R} = \mathbf{R}'$ and $j = j'$),

$$(\mathbf{R}j\lambda|r|\mathbf{R}j\mu) = \left(\mathbf{R} + \mathbf{u_j}\right)\delta_{\lambda\mu} + d_{\lambda\mu}, \tag{4}$$

where $d_{\lambda\mu}$ is the intra-atomic matrix element, which is independent of $\mathbf{R}$, j and also is nonzero only for $\mu \neq \lambda$. Within the first approach (KOF), the polarizability of a free atom is considered to be much lower than that of the corresponding semiconductor, and only the first term of Eq.(4) is considered. In contrast, the second approach (SMD) 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 $d_{\lambda\mu}$ in Eq.(4) are $(s|x|p_x) = 0.2$ Å and $(s^*|x|p_x) = 1.0$ Å. In our calculations of the imaginary part of the dielectric function, we allowed for both contributions.

For the imaginary part of the dielectric function (ε_2), the calculations have been carried out for light polarized in the [001] direction, i.e, perpendicular to the wire alignment. Fig. 2 shows the variation of $\varepsilon_2(\omega)$ for crystalline germanium as a function of the photon energy, for both local and nonlocal approaches (solid line). Also, for comparison, the experimental results by Aspnes and Studna [14] are shown in Fig. 2 (dashed line). The position of the low energy peak is just slightly overestimated while its intensity is underestimated. Both these effects can be explained by neglecting the exciton effects in the calculation of the optical spectrum. This differences can be attributed to the limits of the sp^3s^* first-neighbor TB parametrization which fails to describe correctly the dispersion of the conduction band.

To analyze the dependence of $\varepsilon_2(\omega)$ on the wire width, d, one has to perform calculations on large supercells, where the width can be changed progressively. For simplicity sake, we have calculated only for the 32-
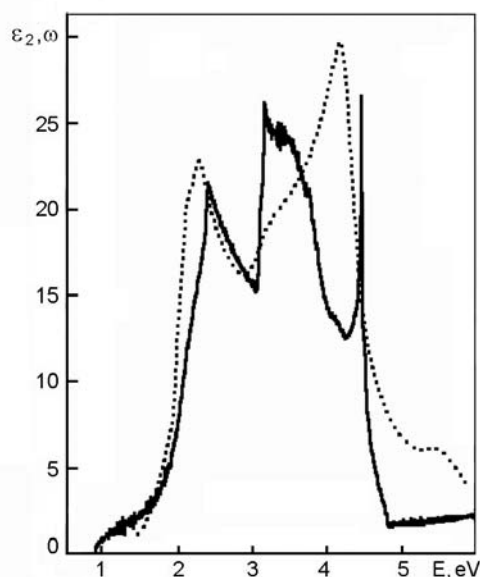
Fig. 2. Comparison between the theoretical optical spectrum of bulk Ge (solid line) obtained within sp^3s^* TB approximation and the experimental spectrum (dashed line) obtained from [14].
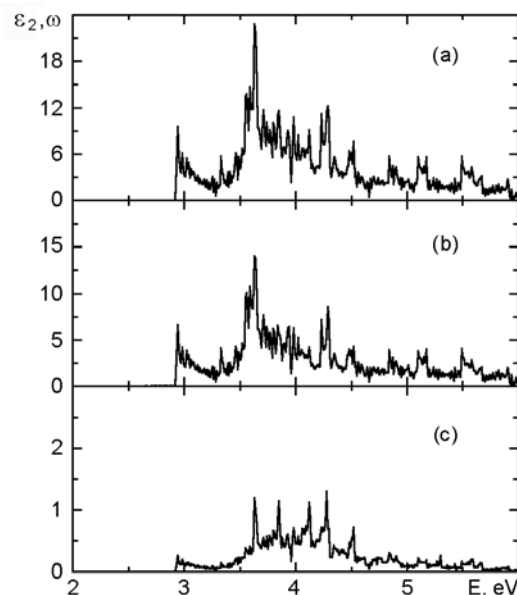

Fig. 3. Imaginary part of the dielectric function vs the photon energy for the 32-atom chessboard-like supercell. The results of the both contributions (nonlocal and local) are presented in (b) and (c), respectively, and (a) show both schemes, local (SMD) plus nonlocal (KOF).

atom chessboard-like supercell (Fig. 1). The results of the contribution provided by local and nonlocal schemes are presented in the Fig. 3(c) and Fig. 3(b), respectively. When we take into account the two approaches [Fig. 3(a)], the energy gap is 2.52 eV. These two schemes consider rather different contributions. While the nonlocal scheme emphasizes the importance of the bulk involvement, in the local work the atomic contributions are relevant. The energy spectrum is characterized by very flats mini-bands, and some of those do not possess dispersion at all. It results in a lot of peaks in the absorption spectrum as shown in Fig. 3.

The principal results show that, although the intra-atomic matrix elements are small in magnitude, the interference between these terms and the interatomic matrix elements contributes about 25 % to the total absorption. Thus, it appears that a quantitative treatment of nanostructures may not be possible (in general) without the inclusion of intra-atomic matrix elements.

Thus, we have shown that optical properties of surface-hydrogenated germanium nanocrystals can be calculated within a simple microscopic quantum-mechanical semiempirical tight-binding approach. Our results agree qualitatively with those obtained from experimental data. Small discrepancies do not change the conclusion that the confinement could be at the origin of germa-

nium nanocrystals luminescence. In this model, it is clear that we are simplifying enormously the surface description, ignoring other possible saturators and surface reconstruction

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Мікроскопічна модель діелектричної функції квантових дротів Ge

П.Альфаро, Р.Васкес, І.Лобода, А.Е.Рамос, М.Крус-Іріссон

Вільно стоячі однорідні квантові дроти квадратного перерізу розглянуто з застосуванням шахової моделі комірки надгратки. Оптичні перехідні властивості нанокристалів германію досліджено з використанням напівемпіричного наближення сильного зв'язку sp^3s^*. Розрахунки виконано для світла, поляризованого в напрямі [100], тобто перпендикулярно простяганню дроту. Залежність уявної частини діелектричної функції від квантового обмеження представлено в рамках двох різних схем: внутрішньоатомних та міжатомних матричних елементів, які зіставлено один з другим. Основні результати свідчать, що, хоча внутрішньоатомні матричні елементи мають незначну величину, внесок інтерференції між цими термами та міжатомними матричними елементами у загальне поглинання складає приблизно 25 %. Таким чином, виявляється, що кількісний розгляд наноструктур, загалом кажучи, є неможливим без урахування внутрішньоатомних матричних елементів.