Joint density of states of nanostructures:
an application to porous silicon

M. Cruz[1]**, M.R. Beltrán**[*2]**, C. Wang**[2]**,** and **J. Tagüeña-Martínez**[3]

[1] ESIME-Culhuacan, IPN, Av. Santa Ana 1000, 04430 México, D.F., México
[2] Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, 04510, México, D.F., México
[3] Centro de Investigación en Energía, UNAM, A.P. 34, 62580 Temixco, Mor., México

In this work the electronic interband transitions in porous silicon are studied. The calculation is performed using a supercell model with a tight-binding Hamiltonian, where an atomic-orbital sp^3s^* basis set is used. The pores are modelled as empty columns, digged in a crystalline silicon structure, and then passivated with hydrogen atoms. The effects of disorder in porous silicon are considered by introducing a random perturbative potential into the Hamiltonian, which produces non-vertical interband transitions in the reciprocal space. Such transitions occur in an interval inversely proportional to the electronic localization length. Finally, a comparative analysis of the optical absorption coefficient is performed by means of vertical, non-vertical transition, and the joint density of states (JDOS).

1 Introduction

The luminescence phenomenon observed in porous silicon (por-Si), at room temperature, has generated great interest in the last decade. As it is well known that crystalline silicon possesses an indirect gap which impairs an efficient radiative recombination. The importance in comprehending the optical properties of por-Si goes beyond pure science and goes well into the technology field. Much experimental and theoretical effort has been devoted and many conjectures have been proposed as to the origin of its visible emitting light [1]. Nevertheless, nowadays there is still controversy on the origin of this phenomenon.

The optical spectra of a semiconductor is determined by its electronic structure. In particular the optical absorption provides us with information from the optical dipolar transition matrix, which is fundamental in the phenomenon of luminescence. The absorption coefficient is calculated by means of the interband transitions between states from the valence and the conduction bands. We have chosen the semi empirical tight binding technique, which posses the virtue of being less intensive from the computational point of view than ab-initio techniques, and more complex geometry structures can be tackled. A supercell model has been used in which porosity and pore morphology can be studied, while maintaining connectivity, as in the experiments.

We assume a periodically distribution of pores and then we introduce a random perturbative potential in the original Hamiltonian, simulating the disorder present in real samples. The main effect of this random potential is the localization of the wave functions, and as a consequence of this, a relaxation in the wave vector **k** selection rules. This in turn produces an optical broadening of the optical active zone.

When the localization length l is much bigger than the wave vector, $l >> k^{-1}$, the effect of the disorder can be included by means of non-vertical interband transitions within the reciprocal space formalism.

[*] Corresponding author: e-mail: mbeltran@servidor.unam.mx, Phone: +52-55-5622 4634, Fax: +52-55-56161251

These non-vertical transitions have an important contribution within an interval (optical window), inversely proportional to the localization length [2]. Such optical window can take different forms such as quadratic or Gaussian functions.

In the next section we explain the supercell model (Fig. 1) and its application to the calculation of the absorption spectra. We then present results of the absorption coefficient and some conclusions.
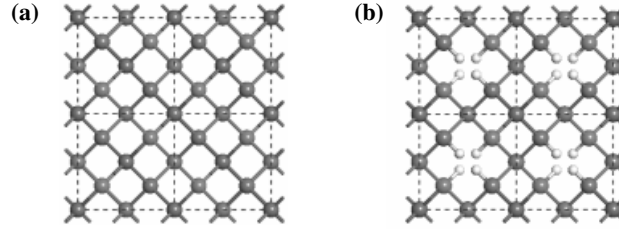
Fig. 1 Representation of four 8-atom supercells of **(a)** c-Si and **(b)** por-Si, both seen from the [001] direction. Each supercell is a simple cubic of side $a_0 = 5.431$ Å. The pore surface in **(b)** is saturated with hydrogen atoms (white spheres).

2 Theory

A minimal sp^3s^* orbital basis set is used which reproduces the silicon indirect 1.1 eV gap in the $\Gamma - X$ direction for c-Si. The pores are modeled by means of columns of atoms removed in the [001] direction from inside each supercell. This model follows the experimental evidence, that the [001] direction is favored during the etching process of por-Si [3]. It is well known that this material presents a great surface principally passivated by means of hydrogen atoms [4]. The dangling bonds produced when removing silicon atoms will be saturated with hydrogen atoms as a first crude model of the inside por-Si surface. We are aware of ignoring other possible saturators such as oxygen and the proper surface reconstruction. In Fig. 1(b) four 8-atom silicon supercells are represented, with one atom columnar pore in each one, saturating dangling bonds with hydrogen atoms. The parameters used in this calculation are described in Ref. [5]. The optical absorption coefficient (α) is given by [6]:

$$\alpha(\omega) = \frac{4\pi^2 \hbar e^2}{ncm^2 \omega V} \sum_{\mathbf{k}_\nu, \mathbf{k}_c} \left| \langle \mathbf{k}_\nu | \mathbf{e} \cdot \mathbf{p} | \mathbf{k}_c \rangle \right|^2 \delta\left(E(\mathbf{k}_c) - E(\mathbf{k}_\nu) - \hbar\omega \right), \tag{1}$$

where n is the refraction index, c is the velocity of light in the vacuum, $\mathbf{e}$ is the light polarization vector, V is the volume, $\mathbf{p}$ is the linear momentum of electrons, $|\mathbf{k}_\nu\rangle$, and $|\mathbf{k}_c\rangle$ are the states in the valence and the conduction band respectively. In the linear combination of atomic orbital approximation (LCAO) the Bloch states are described as $|\mathbf{k}\rangle = \sum_{i,\mu} e^{i\mathbf{k}\cdot\mathbf{R}_i} a_{i,\mu}(\mathbf{k}) |i,\mu\rangle$, where i is the site index and μ identifies the orbital, in such way that the dipolar matrix in Eq. (1) can be expressed as:

$$\langle \mathbf{k}_\nu | \mathbf{e} \cdot \mathbf{p} | \mathbf{k}_c \rangle = \sum_{i,j,\mu,\nu} e^{i(\mathbf{k}_c \cdot \mathbf{R}_j - \mathbf{k}_\nu \cdot \mathbf{R}_i)} a_{i,\mu}^c(\mathbf{k}_\nu) a_{j,\nu}^c(\mathbf{k}_c) \mathbf{e} \cdot \langle i\mu | \mathbf{p} | j\nu \rangle. \tag{2}$$

The dipolar matrix elements in Eq. (2) can be rewritten in terms of the operators of the Hamiltonian (*H*) and of the electron position (**r**), using the commutation relation $\mathbf{p} = \frac{im}{\hbar}[H, \mathbf{r}]$. Besides, if the orbital superposition between different atoms is small when compared with the corresponding intra-atomic terms we obtain:

$$\langle i\mu | \mathbf{p} | j\nu \rangle = \frac{im}{\hbar} \sum_\lambda \left(\langle i\mu | H | j\lambda \rangle \langle j\lambda | \mathbf{r} | j\nu \rangle - \langle i\mu | \mathbf{r} | i\lambda \rangle \langle i\lambda | H | j\nu \rangle \right),$$

The matrix element of the position operator is given by: $\langle i\mu|\mathbf{r}|i\lambda\rangle = \delta_{\mu\lambda}\mathbf{R_i} + \mathbf{d}^i_{\mu\lambda}$, where $\mathbf{d}^i_{\mu\lambda} = \langle i\mu|\mathbf{r'}|i\lambda\rangle$ and $\mathbf{r'} = \mathbf{r} - \mathbf{R}_i$. When $\mu = \lambda$, by symmetry arguments, $\mathbf{d}^i_{\mu\lambda} = 0$. Within sp^3s^* models, the non zero matrix elements $\mathbf{d}^i_{\mu\lambda}$ of c-Si are: $\langle s|x|p_x\rangle = 0.27$ Å and $\langle s*|x|p_x\rangle = 1.08$ Å [7].

The absorption coefficient can be estimated by means of the joint density of states (JDOS), which assumes that the elements of the electric dipolar matrix (Eq. (2)) do not depend on the transition initial and final states, this is to say that they are constant. In this way $\alpha(\omega)$ is proportional [6] to the integrated density of states (DOS) of the valence band $n_v(E)$, and the DOS of the conduction band $n_c(E)$:

$$\alpha(\omega) \propto JDOS(\hbar\omega) = \int dE \, n_v(E) n_c(E + \hbar\omega), \qquad (3)$$

where $\hbar\omega$ is the photon energy.

In the next section we will compare the optical absorption coefficient calculated with the two procedures previously explained in Eqs. (1) and (3).

3 Results

The calculations have been performed in an 8-atom supercell with polarized light in the X-direction. Fig. 2(a) shows the optical absorption spectra of c-Si, while Figs. 2(b), 2(c) and 2(d) correspond to those of por-Si. With regards to the methodology employed, the results shown in Figs. 2(a) and 2(b) have been obtained by means of the vertical interband transitions using 1,030,300 $\mathbf{k}$ wave vectors in the reciprocal space, while 2(c) has been calculated with 729 $\mathbf{k}_c$ and 1331 $\mathbf{k}_v$, non-vertical transitions, in according to Eq. (1). Fig. 2(d) has been obtained from the JDOS calculation, defined in Eq. (3).
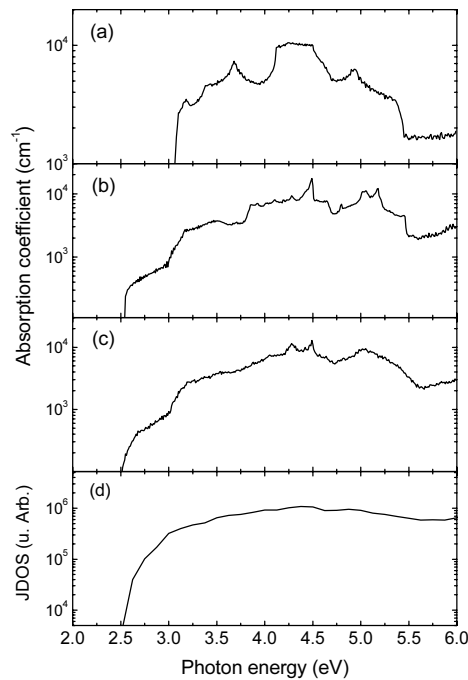
Fig. 2 Optical absorption spectra calculated in an 8 atoms supercell with light polarized in the X-direction (a) for c-Si, (b) for por-Si with only vertical transitions, (c) for por-Si with vertical and non-vertical transitions, and (d) for por-Si by means of the JDOS.

Notice that the spectra shown in Fig. 2(a) reproduces the characteristic 4.4 and 5.2 eV c-Si peak's [8]. The difference between Figs. 2(b) and 2(c) lies in that Fig. 2(b) has been obtained by means of only vertical transitions, while in Fig. 2(c) disorder has been included by means of non-vertical transitions. It can be observed that the introduction of disorder produces an approximate shift of 50 meV in the initial part of the spectrum. The form of the tail in both spectra cannot be attributed to the disorder, rather it is due to the supercell model itself, because in the case of por-Si the supercell becomes the unitary cell of the system. This new unitary cell reduces the optical gap with respect to the crystalline case and as a consequence new umklapp, $\mathbf{k}_c - \mathbf{k}_v = \mathbf{G}$ process occur, where $\mathbf{G}$ is a vector in the reciprocal lattice.

Finally, Fig. 2(d) shows the JDOS, which is proportional to the absorption coefficient, $\alpha(\omega)$ (see Eq. 3). As we can see, the peaks get softened while the mean features in Figs. 2(b) and 2(c) are still preserved, *i.e.*, Figs. 2(b-d) show the characteristic 3 eV shoulder of por-Si [**9**]. It is important to emphasize that the calculated spectra form the JDOS is equivalent to take all the possible (vertical and non vertical) interband transitions, with equal probability.

4 Conclusions

Por-Si is a complex material in which quantum confinement and disorder are two of its most important characteristic features. The effect of quantum confinement is considered within the supercell model. Despite the disorder is difficult to treat within the conventional techniques, such as the potential coherent approximation (CPA). The random potential introduced through the non-vertical transitions in this work provides us a simple way to simulate the disorder in por-Si. The results obtained are comparable with the experimental data available [9]. It is observed that the disorder produces a shift in the absorption coefficient border of approximately 50 meV, besides the form of α(ω) is smeared. The low frequency tail comes from the fact that the pores produce an almost direct band gap, due to the existence of new states through umklapp process.

We have shown that a simple quantum mechanical treatment with a perturbed tight binding Hamiltonian is capable of reproducing the most important characteristics in por-Si. Currently further studies are carried out to quantify the statistical weight associated to each non-vertical transition, which depend on the specific random potential introduced in the Hamiltonian.

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