



Optical Absorption in Porous Silicon

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Abstract. The optical properties of porous silicon (p-Si) are calculated from the electronic band structure obtained by means of an sp^3s^* tight-binding Hamiltonian and a supercell model, in which the pores are columns etched in crystalline silicon (c-Si). The disorder in the pore sizes and the undulation of the silicon wires are considered by the existence of a random perturbative potential, which produces non-vertical interband transitions, otherwise forbidden. A typical interval around each \mathbf{k} -vector (optical window), where non-vertical transitions make an important contribution, depends on the value of the disorder and its order of magnitude is given by l^{-1} , where l is the localization length. The calculated absorption spectra are compared with experiments, showing good agreement.

Keywords: porous silicon, optical absorption, theoretical modelling

The discovery of semiconductors has changed entirely the human's life. One of the important current lines of research in materials science and solid state physics is the study of porous semiconductors. In particular, many new effects take place in the nanostructured porous semiconductors where it is believed that quantum confinement plays a major role in their peculiar behavior. Porous silicon (p-Si) represents a very interesting, easily produced and non-expensive nanostructured porous semiconductor [1].

From a theoretical point of view, the study of optical properties starts with the calculation of the electronic band structure. This can be achieved mainly

by two possible approaches. First principle methods are very successful in treating small systems, such as idealized Si wire and dot structures [2]. However, semi-empirical or tight-binding calculations, less computationally intensive than first principle calculations, can consequently deal with larger and more complex structures. The use of phenomenological parameters in semi-empirical calculations could include many-body effects, otherwise extremely difficult to consider in first principle methods. Another advantage of the tight-binding approach is the possibility of treating different types of disorder such as local defects, alloys, quasi-crystals and amorphous systems. Several well known

techniques to treat disorder exist in the literature [3] virtual crystal approximation (VCA), average T-matrix approximation (ATA) and coherent potential approximation (CPA). These methods have played an important role in the understanding of many disordered materials though they are mostly appropriate for local disorder and, if self-consistency is included they become extremely computing demanding.

In this work, we extend a semi-empirical tight-binding supercell approach, capable of studying disordered and nanostructured porous media [4] to calculate the optical absorption by means of interband transitions between valence and conduction states. In this model, the pores in p-Si are produced by removing columns of atoms within a supercell of crystalline silicon (c-Si). The supercells are then periodically repeated in the space. The resulting band structure can be described using the Brillouin zone with respect to the supercell, and all valence and conduction band states are characterized by a wavevector \mathbf{k} . Obviously, in this idealized case only vertical in \mathbf{k} -space (conserving momentum) transitions are optically allowed. In reality, however, the columnar pores are neither parallel nor periodic. Furthermore, there is an undulation in the diameter of the silicon wires. In order to address the disorder, instead of using the conventional procedures, we introduce a new approach which includes a random perturbative potential to simulate the aleatory distribution of the carrier wave functions and then a relaxation of the \mathbf{k} -wavevector selection rule broadening the optically active zone. When the typical localization length l is much greater than the wavelength, $l \gg k^{-1}$, the disorder effect could be included by introducing non-vertical interband transitions. The typical interval around each \mathbf{k} -vector (optical window), where non-vertical transitions make an important contribution, is about the inverse of the localization length. These optical windows can take different shapes, like a squared function or $(a/l) \sin(l\Delta k/2)/\sin(a\Delta k/2)$ [5], where Δk is the change of the wavevector in the transition and a is the lattice constant.

We use a minimum basis capable of describing an indirect band gap along the x -direction, an sp^3s^* , with the parameters of Vogl et al. [6]. This gives a 1.1 eV gap in bulk crystalline silicon. Empty columns (pores) are produced by removing, in the [001] direction, columns of atoms within supercells. We saturate the pore surface with hydrogen atoms. The Si–H bond length is taken as 1.48 Å. The on-site energy of the H atom is

considered to be -4.2 eV, since the free H atom energy level, -13.6 eV, is so close to the s -state energy level of a free Si atom, -13.55 eV [7], therefore the on-site energy of H is taken to be the same as that of silicon, as in Ref. [8]. The H–Si orbital interaction parameters are taken as $ss\sigma_{\text{H-Si}} = -4.075$ eV, $sp\sigma_{\text{H-Si}} = 4.00$ eV, which are obtained by fitting the energy levels of silane [9].

The absorption coefficient ($\alpha(\omega)$) is defined as [7]

$$\alpha(\omega) = \frac{4\pi^2 e^2}{ncm^2\omega} \sum_{\mathbf{k}_v, \mathbf{k}_c} |\langle \mathbf{k}_v | \mathbf{p} \cdot \mathbf{e} | \mathbf{k}_c \rangle|^2 \delta(E(\mathbf{k}_c) - E(\mathbf{k}_v) - \hbar\omega), \quad (1)$$

where n is the refraction index of the porous media, c is the light speed, \mathbf{e} is the light polarization vector, \mathbf{p} is the electronic linear momentum, $|\mathbf{k}_v\rangle$ and $|\mathbf{k}_c\rangle$ are valence- and conduction-band eigenstates, respectively. The dipole matrix in Eq. (1) can be expressed as

$$\langle \mathbf{k}_v | \mathbf{p} | \mathbf{k}_c \rangle = \sum_{i, j, \mu, \nu} e^{i(\mathbf{k}_c \cdot \mathbf{r}_j - \mathbf{k}_v \cdot \mathbf{r}_i)} a_{i, \mu}^{v*}(\mathbf{k}_v) a_{j, \nu}^c(\mathbf{k}_c) \langle i\mu | \mathbf{p} | j\nu \rangle, \quad (2)$$

where the eigenstates are given by $|\mathbf{k}_v\rangle = \sum_{i, \mu} e^{i\mathbf{k}_v \cdot \mathbf{r}_i} a_{i, \mu}^v(\mathbf{k}_v) |i, \mu\rangle$, being i and μ site and orbital index, respectively. The dipole matrix elements in Eq. (2) may be rewritten in terms of the Hamiltonian (H) and the position (\mathbf{r}) operators, using the commutation relation $\mathbf{p} = (im/\hbar)[H, \mathbf{r}]$. If the overlapping of orbitals belonging to different atoms is small, one can neglect the interatomic dipole matrix elements, and

$$\langle i\mu | \mathbf{p} | j\nu \rangle = \frac{im}{\hbar} \sum_{\lambda} (\langle i\mu | H | j\lambda \rangle \langle j\lambda | \mathbf{r} | j\nu \rangle - \langle i\mu | \mathbf{r} | i\lambda \rangle \langle i\lambda | H | j\nu \rangle) \quad (3)$$

with the matrix elements of the position operator being given by

$$\langle i\mu | \mathbf{r} | i\lambda \rangle = \delta_{\mu\lambda} \mathbf{r}_i + \mathbf{d}_{\mu\lambda}, \quad (4)$$

where $\mathbf{d}_{\mu\lambda}$ is the intra atomic matrix element with $\mu \neq \lambda$. For c-Si the nonzero matrix elements $\mathbf{d}_{\mu\lambda}$ in Eq. (4) are $\langle s | x | p_x \rangle = 0.27$ Å and $\langle s^* | x | p_x \rangle = 1.08$ Å [10].

We have considered transitions between states of the valence and conduction bands, for x -direction polarized light. They are calculated in 8-atom supercells

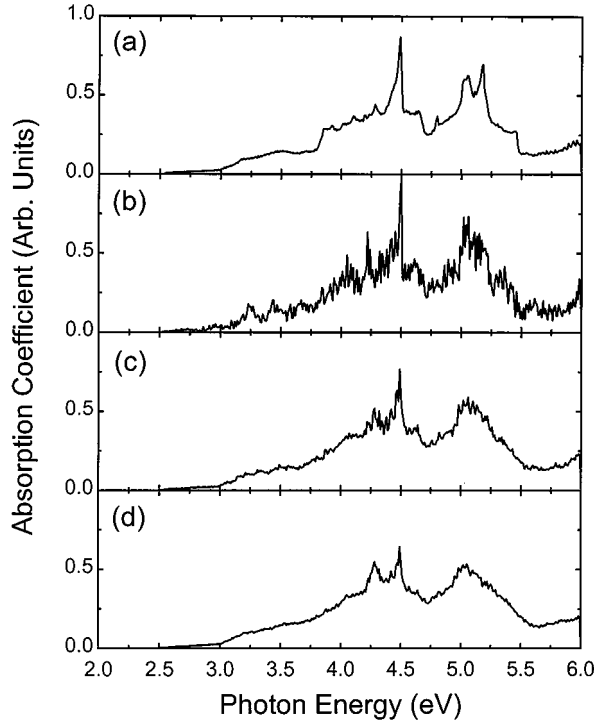


Figure 1. Absorption coefficient spectra calculated in an 8-atom supercell with a one-atom columnar pore, considering: (a) only vertical transitions; (b), (c) and (d) all possible transitions within squared optical windows of size: 1/20, 3/20, and 5/20 of the first Brillouin zone, respectively.

[4] with a 1-atom columnar pore saturated by hydrogen atoms. Figure 1(a) shows the absorption coefficient calculated with vertical interband transitions, i.e., $\mathbf{k}_i^c = \mathbf{k}_f^v$. The calculation has been performed using 1030300 \mathbf{k} -points in the first Brillouin zone. In Fig. 1 (b–d), the absorption coefficient spectra are shown for localization lengths of 145, 62, and 40 Å, respectively. These spectra have been calculated by considering non-vertical transitions, i.e., $\mathbf{k}_i^c \neq \mathbf{k}_f^v$, to include the disorder in p-Si, which is excluded by a conventional supercell model otherwise. For Fig. 1(b–d), the calculation has been performed with 729 \mathbf{k}_c -points in the whole first Brillouin zone, and with 27, 343, and 1331 \mathbf{k}_v -points, respectively, in squared and different sized optical windows conserving the spacing between \mathbf{k}_v 's. The size of the squared optical windows are defined by their respective localization lengths. In general, adding nonvertical transitions is a very lengthy calculation. Notice that Fig. 1(a) reproduces the shoulder at 3 eV and the main peaks at 4.4 and 5.2 eV of the absorption spectra of c-Si [11]. However, we observe a tail

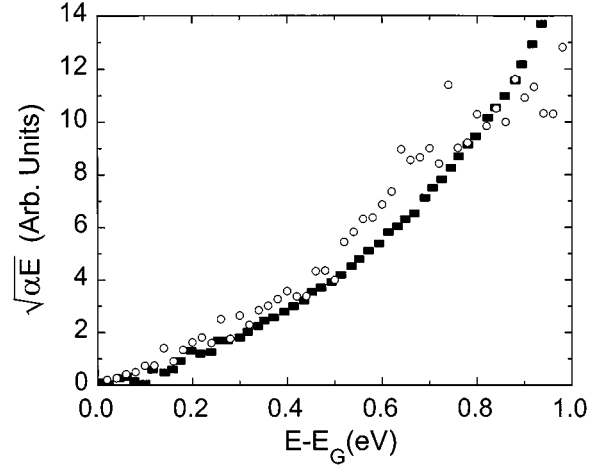


Figure 2. Absorption coefficient $\sqrt{\alpha E}$ (open circles) calculated from an 8-atom supercell with a one-atom columnar pore and by using a wide square optical window of the size of the whole first Brillouin zone, compared with Sagnes' experimental data (solid squares) for a p-type p-Si sample with 74% porosity.

between 2.5 and 3 eV, which is due to umklapp processes, $\mathbf{k}_c - \mathbf{k}_v = \mathbf{G}$, where \mathbf{G} is a reciprocal lattice vector of the lattice of etched pores. These transitions in c-Si are forbidden since they involve a big change of the momentum. After introducing the pores, the supercell becomes the *unit* cell for the material, and these transition can be thought as vertical transitions in the reduced Brillouin zone. From Fig. 1(b) through 1(d) one can observe a smoothing process of the spectra, as the amount of disorder increases, which is in agreement with experimental results [12].

The absorption coefficient could give interesting information on the nature of the band edge, related to the disorder present in a p-Si sample [13]. Figure 2 shows a comparison between the normalized absorption coefficient and the experimental data [14]. It is seen that the theory gives reasonably well the shape of the edge of the absorption spectrum, in spite that no d -orbital is considered, and that the porosity simulated by this supercell is 12.5% while the experimental data are obtained from 74% porosity samples.

In summary, we have shown that a simple microscopic quantum mechanical treatment, such as a phenomenological tight-binding technique, is capable of reproducing the essential features of the absorption coefficient of p-Si. The disorder in p-Si leads to non-vertical transitions in \mathbf{k} -space, moves the onset of the absorption (about 100 meV) and smooths the shape of the dependence of $\alpha(\omega)$. Furthermore, the

low-frequency tail comes from the fact that the pores effectively decrease the “indirectness” of the material. Note, however, that in other properties, like the recombination rate at low temperatures, non-vertical transitions can play a key role. The results on the radiative lifetime will be published elsewhere [5].

Certainly, porous silicon is a complex material, where the quantum confinement and the disorder are two of the most important features. The quantum confinement effect is considered within the supercell method. However, disorder is difficult to treat within the widely used theoretical techniques, such as CPA. The non-vertical transition approach discussed here provides us a non-conventional first-approximation tool to treat the disorder present in p-Si, that has the advantage of being simple to implement and gives reasonably good results.

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