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Tight-binding description of disordered nanostructures: an application to porous silicon

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Abstract

We present the calculations of the coefficient of light (photo) absorption in porous silicon (por-Si) using the supercell tight-binding sp^3s^* model, in which the pores are columns digged in crystalline silicon. The disorder in the pore sizes and the undulation of the silicon wires are taken into account by considering nonvertical interband transitions. The results obtained for 8- and 32-atom supercells show a strong dependence on the pore morphology, i.e., the absorption coefficient changes with the shape and size of the silicon wires even at constant porosity. The absorption spectrum of this model for por-Si is defined by the interplay between the decrease in the indirectness of the material (connected to the absorption processes assisted by the scattering on the pores), which effectively reduces the direct gap, and the increase of the gap due to the quantum confinement. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Porous silicon (por-Si) thin films have been under intense study since the discovery of efficient visible luminescence [1–3]. In spite of the lack of agreement about the detailed microscopic mechanism of the luminescence (for a recent review see Ref. [4]), it is generally accepted that quantum confinement in nanometer-sized Si wires plays a key role in the optical properties of this material.

One approach to model por-Si is to consider finite-sized crystalline Si (c-Si) clusters, as quantum wires [5,6] and dots [7,8]. This way allows to understand many effects in por-Si, like the widening of the band gap and the recombination phenomena, but within this approach one misses the fact that the electron states still remain extended. In particular, the energy spectrum of a cluster is discrete while experimentally the absorption exhibits a broad band. Another method to model the electronic structure of por-Si [9] is to use a Si supercell periodically repeated in space. Such calculations are difficult to perform in a first-principles framework, but they become rather feasible in the tight-binding scheme, similar to the sp^3s^* used for crystalline semiconductors [10].

The goal of this work is to use such a tight-binding supercell model to calculate the absorption coef-

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ficient in por-Si. In the general case, it is convenient to choose a cubic cell, i.e., a cell containing 8, 32, 128, etc. Si atoms. To simulate por-Si, one column of Si atoms (in the [001] direction) is removed and the produced dangling bonds are saturated with hydrogen. In the case of an eight-atom supercell, we only remove the central atom, which results in a 12.5% porosity. Then this unit cell is periodically repeated in space. The resulting band structure was described in Ref. [9]. Clearly, this model does not contain any disorder, and the electronic states can be characterized by the wavevector ***k***. This wavevector, however, is restricted to a Brillouin zone (BZ) which is smaller than the c-Si one. Such approach can be clarified if one considers a 'zero-porosity' (c-Si) case. Then, in the supercell method, the bands are in fact folded to some reduced reciprocal space. An example is shown in Fig. 1, where the eight-atom cubic supercell band structure (Fig. 1b) is compared to the classical two-atom fcc one (Fig. 1a). For instance, one can notice how the lowest energy X-state in the valence band for the two-atom scheme becomes the Γ-state in the cubic eight-atom one. When a pore is introduced in the supercell (Fig. 1c), the band structure remains qualitatively similar to Fig. 2b (see [9]), but the bands are shifted, the gap increases, and, for low-symmetry pores, the band degeneracies are removed. Note, the substantial increase in the band gap, seen from the comparison of Fig. 1b and c, which we will hereafter refer to as the effect of the quantum confinement. Interesting that it happens mainly due to the shift of the valence bands.

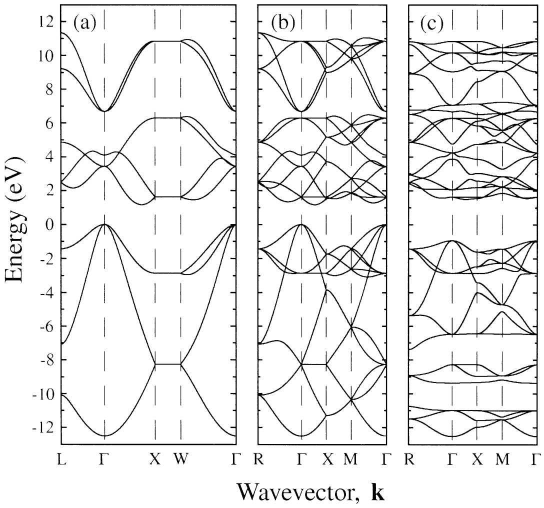

Fig. 1. The two ways to show the band structure of crystalline silicon: (a) the traditional Brillouin zone for the fcc lattice, corresponding to two-atom primitive cell, and (b) a reduced Brillouin zone for the cubic lattice with eight-atom supercell, and (c) the band structure of por-Si in an eight-atom supercell with one (central) atom removed (12.5% porosity).

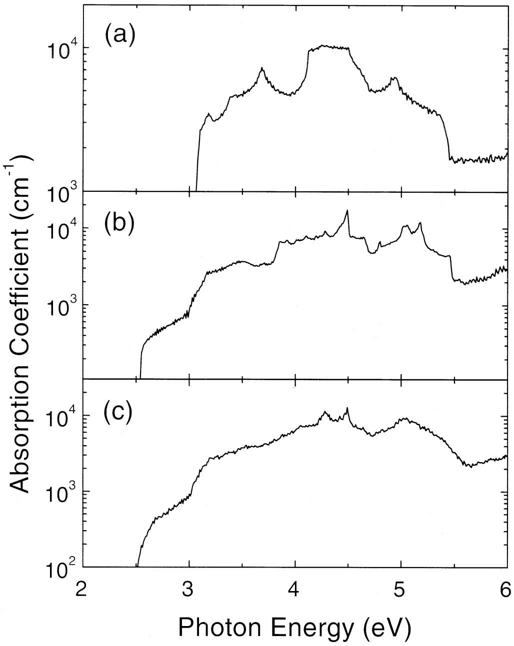

Fig. 2. Showing the frequency dependence of the absorption coefficient calculated for the eight-atom supercell: (a) the crystalline Si case (no pore), (b) without the central Si atom (12.5% porosity) obtained without disorder, and (c) the same structure as (b), but with an optical window (see text).

2. Discussion

To evaluate the absorption coefficient of the material one needs to calculate the matrix elements of the electron velocity operator **v** between the valence $|v,\boldsymbol{k}\rangle$ and conduction $|c,\boldsymbol{k}'\rangle$ band Bloch states, $\langle c,\boldsymbol{k}'|\mathbf{v}|v,\boldsymbol{k}\rangle$ (e.g., Ref. [11]). In the tight-binding scheme this could be done by making use of the commutation relation $\mathbf{v} = (i/\hbar)[H,r]$ and expanding the Bloch functions over the local Si orbitals $|\boldsymbol{R}j\mu\rangle$, e.g.,

$$|v,\boldsymbol{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \sum_{\mu j} A^{v}_{j\mu}(\boldsymbol{k}) |\boldsymbol{R}_{j\mu}\rangle . \qquad (1)$$

Here $\boldsymbol{R}$ are the Bravais vectors giving the positions of the supercells, j enumerates silicon 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 matrix elements between the atomic orbitals.

There are two approaches in the literature to evaluate $\langle \boldsymbol{R}'j'\lambda|\boldsymbol{r}|\boldsymbol{R}j\mu\rangle$. One, by Koiller, Osorio and Falicov (KOF) [12,13], has been used to study direct to indirect band gap transition in $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ alloys, while the other, used by Selloni, Marsella and Del Sole (SMD) [14] has been widely applied to study silicon and surface optical properties. 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 ($\boldsymbol{R} = \boldsymbol{R}'$ and $j = j'$) one has

$$\langle \boldsymbol{R}j\lambda|r|\boldsymbol{R}j\mu\rangle = (\boldsymbol{R} + \boldsymbol{u}_j)\delta_{\lambda\mu} + d_{\lambda\mu}, \qquad (2)$$

where $\boldsymbol{u}_j$ gives the position of the jth atom in the supercell, and $d_{\lambda\mu}$ is the intra-atomic matrix element, which is independent of $\boldsymbol{R}$, j and is nonzero only for $\mu \neq \lambda$. Within the KOF approach, the polarizability of a free atom is considered to be much smaller than that of the corresponding semiconductor [15], and only the first term of Eq. (2) 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. (2). For Si the nonzero matrix elements $d_{\mu\nu}$ in Eq. (2) are $\langle s|x|p_x\rangle = 0.27$ Å and $\langle s^*|x|p_x\rangle = 1.08$ Å. In our calculations of the absorption coefficient we allowed for both contributions.

The supercell model, as we already mentioned, does not contain any disorder, and in such framework only vertical in $\boldsymbol{k}$-space (conserving momentum) dipole transitions are optically allowed. In reality, however, the pores in por-Si are neither exactly parallel nor periodic columns, and there is an undulation in the diameter of the silicon wires. It can be shown [16] that *small* disorder can be incorporated in the above scheme. It results in the possibility of nonvertical interband transitions, giving thus a significant enlargement of the optically active $\boldsymbol{k}$-zone. More precisely, the δ-function describing the momentum conservation law for the dipole transitions, $\delta(\boldsymbol{k} - \boldsymbol{k}')$, is replaced by a 'weighting' function $\Delta(\boldsymbol{k} - \boldsymbol{k}')$. The last is also normalized to one, but has a finite width l^{-1}, which could be referred to as an 'optical window'. The value of l is a typical dephasing length of an electron in a smooth, quasi-classical random potential produced by the disorder. It can be shown that such a description is valid for large l; in particular, l should be much greater than the column width. In the following, we present the absorption spectra of the por-Si supercell model, which were calculated both with and without optical window, as indicated.

The frequency dependence of the absorption coefficient for eight-atom supercell is shown in Fig. 2. Fig. 2a represents the c-Si case (no pores), while Fig. 2b and c correspond to the supercell with one atom removed (12.5% porosity). The results shown on Fig. 2b were obtained for the perfect case (vertical transitions only), and Fig. 2c shows the data calculated with the step-like weighting function, $\Delta(\boldsymbol{k} - \boldsymbol{k}') = 2l$, when $|k_i - k_i'| \leq (2l)^{-1}$ at all $i = x,y,z$, and $\Delta(\boldsymbol{k} - \boldsymbol{k}') = 0$, otherwise, for $l = 10\ a/\pi$ (a is the lattice constant). This shape of the weighting function was chosen for simplicity. It is seen from comparison of Fig. 2b and c that the account for nonvertical transitions results mainly in an overall smoothing of the absorption spectrum, but does not produce substantial qualitative changes.

The most interesting feature seen in Fig. 2 is the appearance of the low-frequency shoulder (between 2.5 and 3.0 eV) on the absorption spectrum of the porous material. The direct optical absorption (without phonon assistance) is absent in this region in the c-Si case. Note that, referring to the band structure in the reduced Brillouin zone (Fig. 1b), one should have in mind that the dipole matrix element for the transition to the lowest Γ state in the conduction band is zero. This state is not a true Γ state but a linear combination of the states on the boundary of the original Brillouin zone, coming from the folding, and the apparent decrease in the energy difference between the direct and indirect band gaps is obviously fictitious in the c-Si case. However, when the

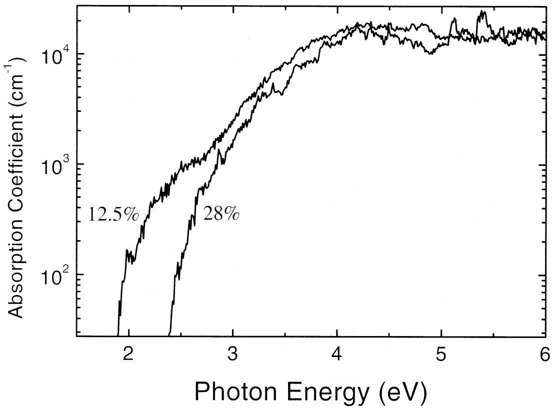

Fig. 3. The absorption spectra calculated for the 32-atom supercell with a four-atom pore (12.5% porosity) and a nine-atom pore (28.125% porosity).

pore is introduced in the supercell, the supercell becomes the *primitive* cell for the material, the matrix element is no longer zero, and the indirectness of por-Si is substantially smaller than that of c-Si. In general, the band structure of the supercell model for por-Si is defined by the competition between the above decrease in the direct band gap (from the band folding), and the increase of the gap due to the quantum confinement. The confinement is big for the eight-atom supercell and the red shift of the direct gap is greatly suppressed, but still the fundamental absorption starts at lower frequencies for por-Si than for the crystalline Si. Note also that in the case of small porosity this shift can be interpreted as a result of umklapp processes when the optical transitions in Si are accompanied by the Bragg scattering on the superlattice of the introduced pores.

These arguments are further illustrated in Fig. 3, which shows the absorption spectra for 32-atom supercell model with two porosities: 12.5% (four atoms removed) and 28.125% (nine atoms removed). The calculations were done with the same optical window as in Fig. 2c. First we note that even for the same 12.5% porosity, the 8- and 32-atoms supercells exhibit different onset of the absorption spectrum (cf. Fig. 3 with Fig. 2c). The onset is shifted to the low-frequency region in the case of the 32-atom model, because it presents a smaller quantum confinement (in other words, in the 32-atom case there are bigger but more separated pores, to preserve the same porosity). In second place, it is seen from Fig. 3 that the increase of the porosity results in the blue shift of the absorption edge, again due to the increase in confinement.

3. Conclusion

We presented the absorption spectra calculated using the supercell model, with 8- and 32-atom primitive cells, which simulates porous silicon, including, in a semi-phenomenological way, the effects of disorder. The absorption spectrum and, in particular, its fundamental edge is defined by a compromise between two opposite effects: (i) quantum confinement, which widens the band gap, and (ii) the optical absorption assisted by umklapp scattering on the superlattice of digged pores, which decreases the indirectness of the material and reduces the direct gap. In spite of a red shift of the absorption edge, it still happens at higher energies than those observed experimentally. To reproduce the por-Si absorption in the 1–2 eV region, one needs to use bigger cells, e.g., 128 atoms (the next cubic cell). These calculations are currently in progress.

Acknowledgements

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