

Optical Properties of Porous Silicon: A First-Principles Study

F. Buda, J. Kohanoff, and M. Parrinello

IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

(Received 9 June 1992)

We show that first-principles electronic structure calculations of silicon wires with diameters up to ~ 1.5 nm support the idea that quantum confinement and surface effects are responsible for the luminescence in porous silicon. Instead of the indirect gap of crystalline bulk silicon, the band structure of these wires exhibits a direct gap at $k=0$. The imaginary part of the dielectric function, polarized in the direction of the wire, shows a peak in the visible range. The dependence of this feature on wire size is analyzed and correlated to experimental luminescence spectra.

PACS numbers: 78.55.Hx, 73.20.Dx, 78.65.Gb

The discovery that highly porous silicon (PS) could efficiently emit visible light at room temperature [1] has generated an enormous interest in this material in view of its possible use for optoelectronic applications fully integrated in silicon structures. Since then, extensive experimental efforts have been carried out to characterize the microstructure of PS [2] and the stability and the origin of the luminescence [3,4] using a broad variety of techniques. It is now quite widely accepted that the microstructure of highly porous silicon can be characterized by an array of tiny Si wires in which the crystalline order is preserved. Indeed, transmission electron images have been obtained [2] which show (001)-oriented silicon columns as narrow as 2 nm. Furthermore, no feature related to the existence of an amorphous region has been observed in Raman scattering spectra [4]. The surface of the quantum wire turns out to be hydrogenated as a consequence of the electrochemical etching process in a HF solution [1]. The electron paramagnetic resonance signal combined with infrared transmission spectra [3] shows a luminescence degradation as a result of the oxidation of the surface, with a concomitant increase in the density of silicon dangling bonds. This observation indicates that the efficiency of the luminescence in PS is closely related to the H termination. In view of these results the interpretation that the luminescence arises from the presence of Si-O-H compounds in PS seems unlikely [5]. All these experimental findings strongly suggest that the origin of the luminescence should be traced back to the existence of quantum-size crystalline structure (quantum wires) in PS.

Our work is based on these experimental facts and gives a semiquantitative, theoretical picture of the quantum-size effects in PS. We present first-principles electronic structure calculations of silicon quantum wires with diameters up to about 1.5 nm using density-functional theory (DFT) within the local-density approximation (LDA) for the exchange-correlation energy [6]. The silicon dangling bonds at the surface are passivated by hydrogen atoms. Under these conditions, the resulting band structure shows a direct gap at $k=0$, as opposed to the indirect gap of bulk crystalline silicon. We show that

the imaginary part of the dielectric function $\epsilon_2(\omega)$ (related to the absorption coefficient), for the external field polarized in the direction of the axis of the wire, exhibits a peak in the range of visible light. We study the dependence of this peak on the size of the wire and correlate this with the luminescence peak seen experimentally. The electronic states responsible for this feature in $\epsilon_2(\omega)$ of a Si wire cannot be identified with any bulklike state of *c*-Si.

We consider (001)-oriented crystalline silicon wires whose cross section has the shape of a square with rounded corners. Hydrogen atoms passivate all the dangling bonds at the surface of the wire, the result being the presence of both monohydride and dihydride complexes [7]. The shape has been chosen in such a way as to avoid Si-H₃ complexes at the surface and to reduce the sharpness of the corners as much as possible. Periodic boundary conditions (PBC) have been applied in the $\langle 001 \rangle$ direction to represent an infinite wire. We expand the Kohn-Sham orbitals in plane waves (PW) using an energy cutoff of 12 Ry. The use of PW expansion forces PBC in all directions. However, we have chosen the size of the box in the orthogonal plane large enough such that the interaction between neighboring wires is negligible. We performed calculations on systems of different sizes and used these results to make a tentative extrapolation for larger quantum wires. We have considered three quantum wires of side length $d=0.76, 1.14,$ and 1.56 nm. The largest supercell contains 77 silicon atoms and 36 hydrogen atoms. Only the valence electrons have been treated explicitly. The interaction between the valence electrons and the core electrons plus nuclei has been described by a fully nonlocal pseudopotential for Si which includes up to d components [8(a)]. In order to remove the $1/r$ singularity of the H potential we have used a local pseudopotential which reproduces the Si-H bond rather accurately [8(b)]. The ground-state self-consistent electronic density and the optimized geometrical structure were obtained using a Car-Parrinello-like method [9]: We have minimized the LDA functional relative to the ionic positions and the electronic orbitals using a steepest-descent method. The main effect of the atomic relaxation is an overall expan-

sion. The amplitude of the relaxation approximately follows an r^2 law where r is the distance of the atom from the center of the wire. The largest relaxations observed are $\sim 0.15 \text{ \AA}$.

In Fig. 1 we present the band structure computed for the silicon quantum wire 1.14 nm wide. The conduction electronic states have been computed using the self-consistent electronic density obtained for the $k=0$ point [10]. We have considered six independent k points in the $\langle 001 \rangle$ direction where the translational symmetry holds. A direct gap of 1.84 eV appears for $k=0$. This is qualitatively different from the well-known indirect gap of bulk crystalline silicon of 1.17 eV with the conduction band edge lying along the Δ direction close to the boundary point X [11]. The presence of an indirect gap in Si and other elements that crystallize in the diamond structure has been rationalized on the basis of group-theory arguments and perturbation theory [12]. Thus, it is not surprising that in a reduced-symmetry situation the indirect gap disappears. Of course, this result makes, by itself, the probability of radiative recombination much higher in PS than in bulk c -Si, since no phonon of appropriate momentum is needed in the hole-electron recombination process. The dependence of the energy gap (E_g) at $k=0$ on the width of the wire is presented in Fig. 2. From simple particle-in-a-box arguments one expects E_g to vary proportionally to $1/d^2$, where d is the side length of a quantum wire with a square cross section

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{v,c} \int_{\text{BZ}} \frac{2d\mathbf{k}}{(2\pi)^3} |\langle \psi_{c\mathbf{k}} | \mathbf{e} \cdot \mathbf{p} | \psi_{v\mathbf{k}} \rangle|^2 \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega]. \quad (1)$$

Here the sum is over all the valence and conduction states whose energy is E_v and E_c , respectively. \mathbf{p} is the momentum operator and \mathbf{e} is the polarization vector. In the presence of nonlocal pseudopotentials, expression (1) should be corrected. Such corrections are known to be small and will be neglected here [15].

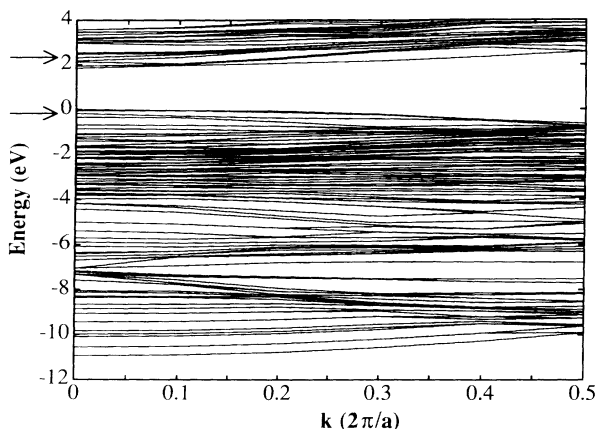


FIG. 1. Band structure of a ~ 1 -nm-wide silicon quantum wire along the one-dimensional Brillouin zone. The top of the valence band has been chosen as zero of the energy scale. $a = 5.43 \text{ \AA}$ is the length of the supercell along the $\langle 001 \rangle$ direction. The arrows indicate the electronic states involved in the largest dipole matrix element responsible for the side peak in ϵ_2^{\parallel} (see text).

[13]. From our results, there turns out to be a slightly more complicated dependence on d . In fact these three points, together with the indirect gap of bulk c -Si in LDA for $d \rightarrow \infty$, can be fitted with a function containing a linear and a quadratic term in $1/d$.

It is well known that the single-particle energy spectrum calculated within LDA severely underestimates the Si energy gap [11]. However, LDA reproduces its average spectral features qualitatively well [14]. Since here we are primarily interested in semiquantitative issues, we have not tried to go beyond LDA and assume that qualitative trends are correctly described by our approach. In the same spirit we have not tried to calculate photoluminescence (PL) spectra. These are in fact affected by a variety of complex phenomena such as relaxation processes, impurity scattering, and excitonic interactions. We have instead studied dipole matrix elements. This allows us to obtain information directly on absorption and photoluminescence excitation (PLE) spectra and indirectly on the relevant radiative PL processes. Quantitative description of the latter must include the above-mentioned processes, which is beyond the scope of the present investigation.

The transition matrix elements can be directly related to the imaginary part of the dielectric function $\epsilon_2(\omega)$, which is in turn related to the absorption coefficient at a given frequency ω . The basic expression of $\epsilon_2(\omega)$ in terms of the band structure and the dipole matrix elements is the following [12]:

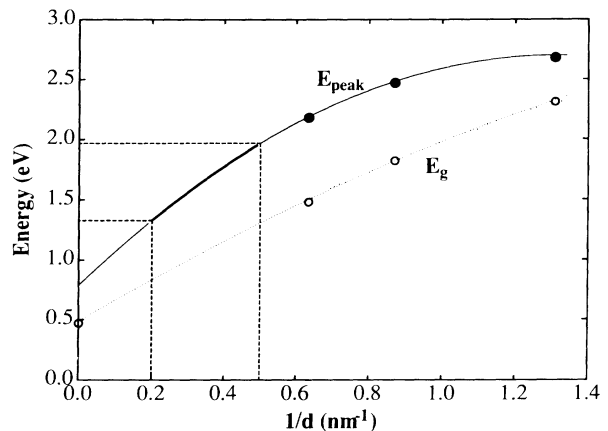


FIG. 2. Energy gap (E_g , open circles) and peak position of the ϵ_2^{\parallel} (E_{peak} , solid circles) vs the inverse side length of the quantum wire. The solid line is an extrapolation of E_{peak} to larger sizes. The region between 2 and 5 nm has been made thicker to indicate the range of the experimental data. The dotted line is a fit for the energy gap.

We will consider only frequencies lower than 3.5 eV which roughly cover the visible spectrum. Given the highly anisotropic nature of the system, we will consider separately the component of $\epsilon_2(\omega)$ along the direction parallel to the axis of the wire, $\epsilon_2^{\parallel}(\omega)$, and the one in the orthogonal plane, $\epsilon_2^{\perp}(\omega)$. The first quantity is shown in Fig. 3 for three different sizes. In the inset we compare $\epsilon_2^{\parallel}(\omega)$ and $\epsilon_2^{\perp}(\omega)$ for the largest wire. $\epsilon_2^{\parallel}(\omega)$ has a side peak at low frequencies which is absent in $\epsilon_2^{\perp}(\omega)$. While the position of the high-frequency peak in $\epsilon_2^{\parallel}(\omega)$ and $\epsilon_2^{\perp}(\omega)$ does not change with the system size, the position of the side peak is a strong function of d . This reflects the fact that the main peak is essentially due to bulklike excitations, while the side peak is a wire-related feature. This interpretation is strengthened by the observation that for bulk silicon $\epsilon_2(\omega)$ has a peak at a similar frequency. The intensity of the peak in $\epsilon_2^{\perp}(\omega)$ approaches that of the main peak in $\epsilon_2^{\parallel}(\omega)$ as the size increases (not shown in the figure). The behavior of this side peak as a function of the size is qualitatively similar to the behavior of the luminescence spectrum measured in PS as a function of increasing porosity of the sample [1].

We focus now on the study of the peak representing the new feature of the optical properties of quantum wires. In Fig. 2 we study its position as a function of $1/d$. As for the energy gap, these three points can be represented with a function containing a linear and a quadratic term in $1/d$ which is also shown in the figure. We have enlarged the portion of the extrapolation in the range between 2 and 5 nm, i.e., the range of the quantum wires observed in PS [2]. The predicted position of the optical peak in this range is $1.4 \text{ eV} < E_{\text{peak}} < 2.0 \text{ eV}$, which is compatible with the photoluminescence peak observed in PS [1,16].

The origin of the side peak in $\epsilon_2(\omega)$ can be traced back to the existence of a particular dipole matrix element

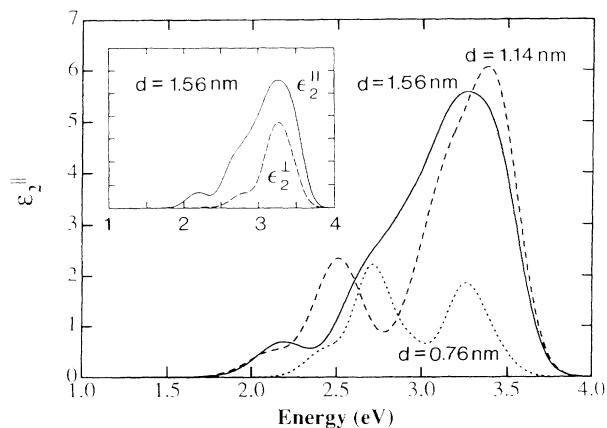


FIG. 3. Imaginary part of the dielectric function polarized in the direction of the wire ϵ_2^{\parallel} for three different values of the side length of the quantum wire: $d = 1.56 \text{ nm}$ (solid line); $d = 1.14 \text{ nm}$ (dashed line); $d = 0.76 \text{ nm}$ (dotted line). Inset: The same curve for $d = 1.56 \text{ nm}$ (solid line) compared to ϵ_2^{\perp} (dashed line).

which is at least 1 order of magnitude larger than the others in the same range of frequencies. The electronic states involved in this matrix element have some common features which are independent of the size of the wire. In Fig. 4 we show a cut of the charge density associated with the (a) valence and (b) conduction states responsible for the peak at 2.2 eV in the quantum wire 1.56 nm wide. The figure shows a top view of a 1-Å-thick slice of the wire. As a general feature the valence state involved in this matrix element lies just below the top of the valence band and its charge distribution is characterized by decaying to zero towards the center of the wire. The conduction state is located about 0.7 eV from the bottom of the conduction band. An interesting feature of the probability distribution associated with this state is the presence of helicoidal structures in the wire direction. In Fig. 4(b) these helices appear as ellipses pointing to the edges of the square. These states appear to be a peculiar characteristic of the quantum wires.

From first-principles calculations we have shown that the luminescence in porous silicon can be explained in

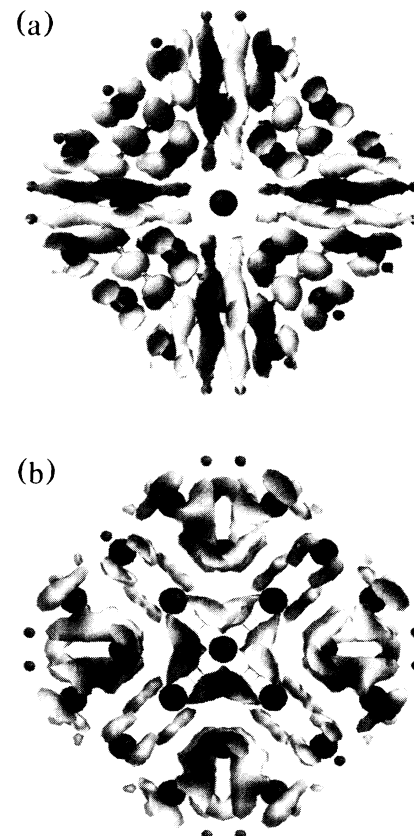


FIG. 4. Charge distribution of the (a) valence state and (b) conduction state involved in the largest dipole matrix element responsible for the side peak in ϵ_2^{\parallel} . Shown is a top view of a 1-Å-thick slice of the largest quantum wire studied. The charge contour corresponds to $0.003 \text{ electron}/\text{\AA}^3$. The Si and H atoms are also drawn by spheres of different dimension.

terms of silicon quantum wires with hydrogenated surfaces. The first important feature is that, unlike bulk *c*-Si, the systems studied here show a direct gap at the center of the Brillouin zone. The most striking result is the existence of a peak in the imaginary part of the dielectric function which is absent in the $\epsilon_2(\omega)$ of bulk *c*-Si. This peak appears only if the light is polarized in the direction of the wire, a fact that should be observed experimentally. The behavior of this optical feature as a function of the size can be put in close correspondence to the behavior of the luminescence peak observed in PS. The extrapolation of our data to thicker quantum wires covers the energy range at which PS emits. We have shown that the electronic states responsible for this feature are typical of the quantum wire and cannot be associated to any bulklike state.

From the experience with *c*-Si we would guess that we are underestimating E_g and, consequently, the frequency of the optical peak in $\epsilon_2(\omega)$, but it is difficult to quantify the errors. However, since the wave functions are expected to be reasonably well described in LDA [17,18], the dipole matrix elements should be correctly computed in this work. It would be interesting to compare the results contained in this work to a theory more accurate in describing excitation energies and optical properties (e.g., calculation of the self-energy operator in the *GW* approximation [17]).

We thank F. Bassani for helpful discussions. H. Salemink is gratefully acknowledged for critically reading the manuscript.

[1] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

[2] A. G. Cullis and L. T. Canham, *Nature (London)* **353**, 335 (1991).

[3] M. A. Tischler, R. T. Collins, J. H. Stathis, and J. C. Tsang, *Appl. Phys. Lett.* **60**, 639 (1992).

[4] R. Tsu, H. Shen, and M. Dutta, *Appl. Phys. Lett.* **60**, 112 (1992).

[5] M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, *Solid State Commun.* **81**, 307 (1992).

[6] For a recent review see, R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).

[7] The importance of silicon dihydride in porous silicon has been very recently addressed by C. Tsai *et al.*, *Appl. Phys. Lett.* **60**, 1700 (1992).

[8] (a) G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982); (b) P. Giannozzi (unpublished).

[9] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985); for a recent review see, G. Galli and M. Parrinello, *Computer Simulation in Materials Science*, edited by M. Meyer and V. Pontikis, NATO ASI (Kluwer Academic, Dordrecht, The Netherlands, 1991).

[10] We have checked that an improved sampling of the Brillouin zone does not change significantly the band structure.

[11] Note that within LDA the indirect gap of *c*-Si is underestimated to give $E_g = 0.48$ eV. See, e.g., M. T. Yin and M. L. Cohen, *Phys. Rev. B* **26**, 5668 (1982).

[12] See, e.g., F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, 1975).

[13] V. Lehmann and U. Gösele, *Appl. Phys. Lett.* **58**, 856 (1991).

[14] We have computed the imaginary part of the dielectric function for bulk *c*-Si and found a good qualitative agreement with experiment. All the features are well reproduced in intensity but slightly shifted in frequency.

[15] S. Baroni and R. Resta, *Phys. Rev. B* **33**, 7017 (1986); S. Baroni (private communication).

[16] X. L. Zheng, W. Wang, and H. C. Chen, *Appl. Phys. Lett.* **60**, 986 (1992).

[17] M. S. Hybertsen and S. G. Louie, *Phys. Rev. Lett.* **55**, 1418 (1985).

[18] Z. H. Levine and D. C. Allan, *Phys. Rev. Lett.* **63**, 1719 (1989).

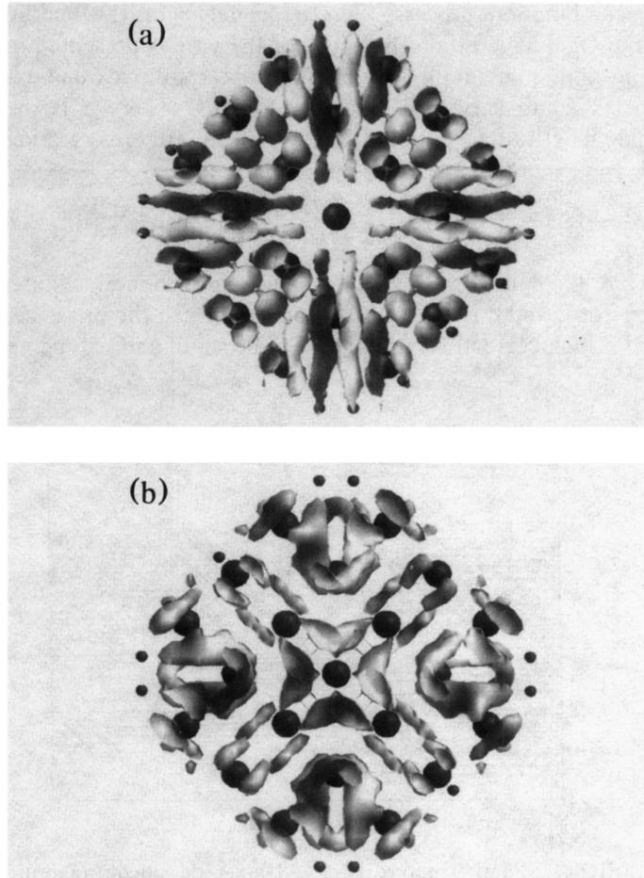


FIG. 4. Charge distribution of the (a) valence state and (b) conduction state involved in the largest dipole matrix element responsible for the side peak in ϵ_2^{\parallel} . Shown is a top view of a 1-Å-thick slice of the largest quantum wire studied. The charge contour corresponds to 0.003 electron/Å³. The Si and H atoms are also drawn by spheres of different dimension.