

Identity of the light emitting states in porous silicon wires

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We present empirical pseudopotential calculations of the electronic structure of [001] silicon quantum wires, aiming at identification of the states that couple radiatively to the valence-band maximum. We find that the near-gap wave functions differ qualitatively from effective-mass depictions. Instead, they can be described as off- Γ bulk states. The effects of H chemisorption on the wire energies and wave functions are studied. We find that the Si skeleton dominates the measurements only if one assumes coexistence of quantum wires with quantum dots.

Much of the current debate on porous Si^{1-4} centers on emission. Recent experiments⁵⁻⁷ suggest that the emission originates from the Si skeleton rather than from “extrinsic” states. Given the nanoscale size of the hydrogen- or oxygen-coated Si and that the surface/volume ratio is as large as $\sim 50\%$, one wonders how the light-emitting entity or also from other quantum objects, e.g., dots. We address structure of clean versus hydrogen-covered silicon wires and silicon boxes.

We have calculated the band energies, transition matrix element, and radiative lifetimes of [001] Si quantum structures with $(110) \times (-110)$ faces and square cross sections, ranging from 4×4 to 14×14 monolayers. The wire is infinitely long. For a box we take⁷ $L_z = \sqrt{2}L_x$. We use a direct band-structure approach, solving

$$[-\frac{1}{2}\nabla^2 + V^{\text{wire}}(\mathbf{r})]\psi_f^{\text{wire}}(\mathbf{r}) = \epsilon_f^{\text{wire}}\psi_f^{\text{wire}}(\mathbf{r}), \quad (1)$$

where the wire potential $V^{\text{wire}}(\mathbf{r})$ is constructed as a superposition of atomic pseudopotentials. Equation (1) is solved by imposing artificial periodic boundary conditions on the wire straddled by N_v layers of vacuum. This transforms Eq. (1) into a Bloch-periodic band-structure problem with

waves. We use a sufficiently large wire-wire separation N_v so that the solutions become N_v independent. Effective-mass approximations are completely avoided. We consider wires with clean, unreconstructed free surfaces as well as hydrogen-coated wires where the dangling bonds are saturated. Since we are interested in the present discussion in understanding the electronic structure of *intrinsic*, bulklike states, we will not discuss the surface dangling bond states of the wire with free surface. Hydrogen chemisorption naturally removes the surface states. The empirical Si pseudopotential used was fitted to the bulk Si band structure and

states of hydrogen-covered Si (001), (110), and (111) surfaces.⁷ We use bulklike Si-Si distance 2.34 \AA , while the

computed from the dipole matrix elements of $\psi^{\text{wire}}(\mathbf{r})$

$$\frac{1}{\tau_R} = \frac{2\alpha\omega n}{3m_e^2 c^2} P_{ff'}, \quad (2)$$

where α is the fine structure constant, ω is the photon of light.

of a superposition of *bulk* states. To do so, we defined a set of *symmetrized bulk wave functions*

$$\begin{aligned} \chi_{n,k}^{\text{TC}}(\mathbf{r}) = N [& u_{n,k_x,k_y,k_z} e^{i\mathbf{k}(\mathbf{x}+\mathbf{y})} + \alpha_1 u_{n,k_x,\bar{k}_y,k_z} e^{-i\mathbf{k}(\mathbf{x}-\mathbf{y})} \\ & + \alpha_2 u_{n,k_x,\bar{k}_y,k_z} e^{i\mathbf{k}(\mathbf{x}-\mathbf{y})} \\ & + \alpha_3 u_{n,\bar{k}_x,\bar{k}_y,k_z} e^{-i\mathbf{k}(\mathbf{x}+\mathbf{y})}] e^{ik_z z}, \end{aligned} \quad (3)$$

where $u_{n,k}$ is the Bloch-periodic part of the bulk wave function, N is a normalization constant, and α_i are coefficients of norm one. The quantization conditions, for a wire with lattice vectors $x = (1/\sqrt{2})(1,1,0)$ and $y = (1/\sqrt{2})(-1,1,0)$, are $k_x = j_x(1,1,0)$; $k_y = j_y(-1,1,0)$; (in units of $2\pi/Na_0$, where N is the number of the atomic monolayers within the wire width L , a_0 is the bulk lattice constant), and j_x, j_y are integer quantum numbers. The directly calculated

wire space in the complete set of these “truncated crystal” (TC) basis functions $\{\chi_{n,k}^{\text{TC}}\}$,

$$\psi_{f,\Gamma}^{\text{wire}}(\mathbf{r}) = \sum_n \sum_{k_x,k_y} a_{n,f}(k_x,k_y) \chi_{n,k_x,k_y}^{\text{TC}}(\mathbf{r}), \quad (4)$$

where $a_{n,f}(k_x,k_y) = \langle \psi_f^{\text{wire}}(\mathbf{r}) | \chi_{n,k_x,k_y}^{\text{TC}}(\mathbf{r}) \rangle$. We will use the projections $|a_{n,f}|^2$ to determine the identity of the directly calculated wire states in terms of bulk Si bands at (n,k_x,k_y) . Recall that in the effective-mass particle-in-a-box approach, the wire states are described in terms of *bulk-like* Bloch function $u_{n,k}(\mathbf{r})$ and normalized

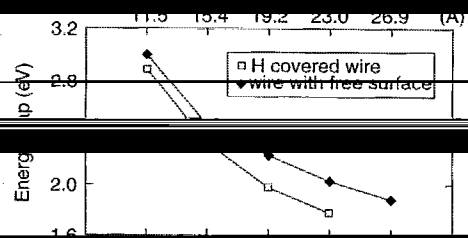
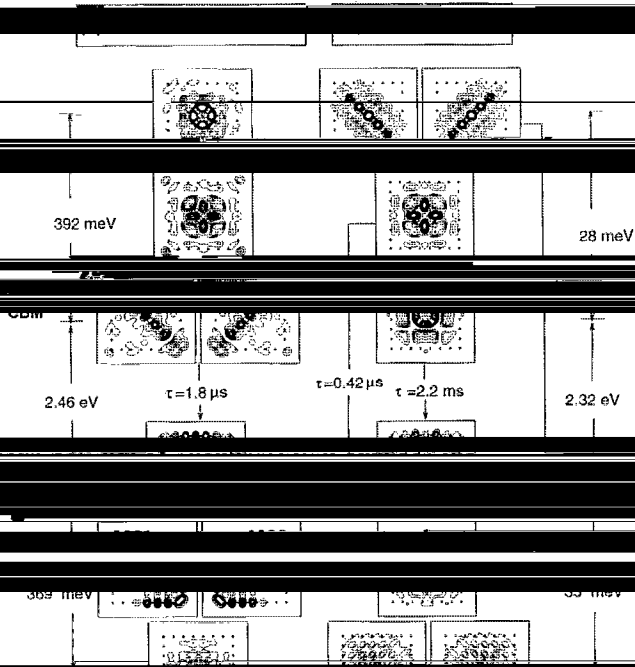


FIG. 2. Dependence of the band gap on the wire size. For the wire with free surfaces we consider only intrinsic states.

Third, the sparsely spaced levels near the VBM and CBM of the clean wire [see the four-level spread of 392 and 369 meV in Fig. 1(a)] give way to a tenfold denser level

the intrinsic band gap. This reflects a combination of level

effective increase of wire size (thus, reduced confinement)

(iv) The emission spectrum to the states near the VBM

of off- Γ bulk states, not effective masslike states: The projections of Eqs. (3) and (4) shows that 90% of the valence-band maximum (VBM) comes from coupling of the two highest valence bands ($n=3,4$) at the off- Γ k point

four highest VBs and four lowest CBs (Fig. 1) and is characterized by a slow average emission lifetime $\tau_{av} = [\sum_{i,f} N_{if} \sigma_{if}^{-1}]^{-1}$ of 0.35 μ s. This lifetime increase rapidly as the wire size increases (Fig. 4). The rather long lifetime

states are qualitatively different from simple effective mass variation [Fig. (5)] in that they represent interband coupling and off- Γ ($j \neq 0$) contributions. The fact that the VBM and CBM wire states project into bulk states of different wave vectors k (i.e., different j_x, j_y) proves conclusively that the band gap is *pseudodirect*, not direct.

emission of Calcote *et al.* The β band lies 0.6 eV above the α band (Fig. 2) and has faster transitions with $\tau = 21$

(ii) Hydrogen chemisorption changes the localization

band-gap wave function amplitudes $|\psi_f^{wire}(x,y)|^2$, energy level separations, and radiative lifetimes for clean (a) and hydrogen-covered (b) 8×8 Si wire are shown. Three points are noteworthy. First, we see that H chemisorption concentrates more of the VBM and CBM wave-function amplitude toward the interior of the wire. Thus, despite a large surface-to-volume ratio, the band-edge states are expected to reflect the properties of the Si skeleton rather

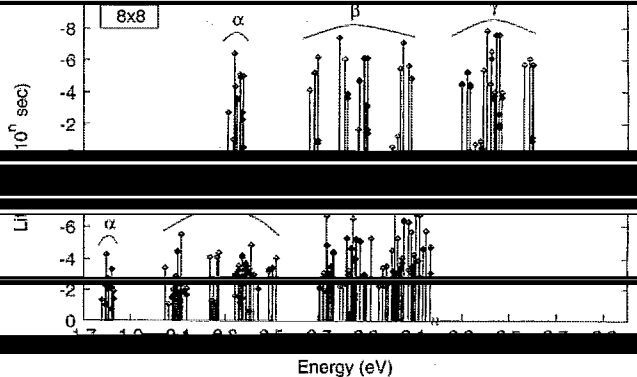


FIG. 3. Calculated radiative transition lifetime from the four highest VB states as functions of the transition energy.

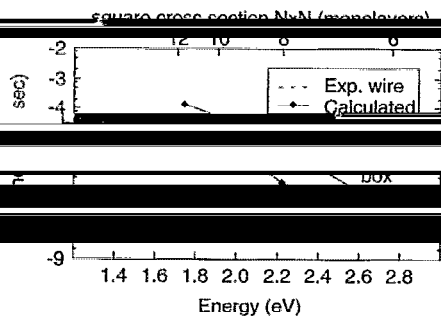


FIG. 4. Comparison of calculated (solid lines) lifetimes of quantum wires and quantum boxes with experimental S-band emission in porous Si (see

periment if a mixture of quantum dots and wires is postulated. Figure 4 shows that the calculated τ vs ϵ curve shows a faster increase of τ_R with size compared with the measured curve. This means that as size increases the calculated transition become forbidden (i.e., bulklike) faster than the measured one. This could be explained by assuming that porous Si is made of wires and boxes. In fact, it is reasonable to imagine that at the beginning of the etching process of porous Si one forms mostly thick wires, while after extended etching the wires thin down into linked-sausage shapes and eventually some of them break into quantum boxes. Thus, the small photon energy region

the higher photon energy region could represent a larger contribution from boxes. This means that the "effective" τ vs ϵ curve should consist of the mix contribution of is a better curve than for pure wires.

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¹See many recent articles on porous Si in *Microcrystalline Semiconductors: Materials Science and Devices*, edited by P. M. Foybat et al. (Mc

⁴P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumheada, *J. Phys. Condens. Matter* **5**, L91 (1993).

⁶V. Petrova-Koch, T. Muschik, A. Kux, B. K. Meyer, F. Koch, and V. Lehmann, *Appl. Phys. Lett.* **61**, 343 (1992).

⁷L. L. Wang and A. Zunger (unpublished).

⁸See reference inside the letter of A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott, and A. Qtiash, *Phys. Rev. Lett.* **69**, 1232 (1992).

⁹Inside α band, the band edge transition has a 2.2 ms lifetime and is 26 meV below the next transition. This happens to be close to the very slow transition of 3 ms with a 20 meV energy separation detected and designated as spin-triplet transition by Ref. 4, although spin-degree of freedom is not considered in the present calculation.