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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 [redacted] the wire energies and wave functions are studied. We find that the Si skeleton dominates the [redacted] measurements only if one assumes coexistence of quantum wires with quantum dots.

Much of the current debate on porous Si[1–4] centers on [redacted] emission. Recent experiments suggest that the emission [redacted] oxygen-coated Si and that the surface/volume ratio is as large as ~50% one wonders how the light-emitting entity [redacted] or also from other quantum objects, e.g., dots. We address [redacted] 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)×(−110) faces and square cross [redacted] tion is infinitely long. For a box we take[7] $L_z=\sqrt{2}L_x$. We use a direct band-structure approach, solving

[redacted]

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 [redacted] 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 [redacted] rated. 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 [redacted] urally removes the surface states. The empirical Si pseudopotential used was fitted to the bulk Si band structure and [redacted]

[redacted]

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

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

$$\chi^{\text{TC}}_{n,\mathbf{k}}(\mathbf{r})=N[u_{n,k_x,k_y,k_z}e^{ik(x+y)}+\alpha_1 u_{n,k_x,\bar{k}_y,k_z}e^{-ik(x-y)}$$

[redacted]

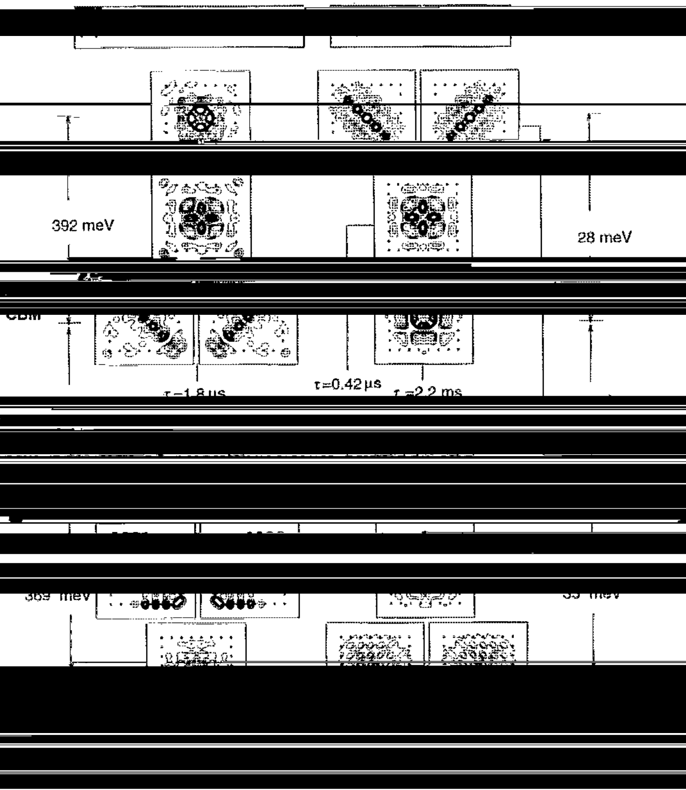
$$+\alpha_3 u_{n,\bar{k}_x,\bar{k}_y,k_z}e^{-ik(x+y)}]e^{ik_z z}, \qquad (3)$$

where $u_{n,\mathbf{k}}$ is the Bloch-periodic part of the bulk wave function, N is a normalization constant, and α_i are coefficients [redacted] lattice vectors $x=(1/\sqrt{2})(1,1,0)$ and $y=(1/\sqrt{2})(-1,1,0)$, are $\mathbf{k}_x=j_x(1,1,0)$; $\mathbf{k}_y=j_y(-1,1,0)$; (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, [redacted] wire space in the complete set of these "truncated crystal" (TC) basis functions $\{\chi^{\text{TC}}_{n,\mathbf{k}}\}$,

[redacted]

where $a_{n,f}(k_x,k_y)=\langle\psi_f^{\text{wire}}(\mathbf{r})|\chi^{\text{TC}}_{n,k_x,k_y}(\mathbf{r})\rangle$. We will use the projections $|a_{n,f}|^2$ to determine the identity of the directly [redacted] (n,k_x,k_y). Recall that in the effective-mass particle-in-a-box approach, the wire states are described in terms of [redacted]

[redacted]



[illegible] outer Si atoms.

Our results can be summarized as follows [illegible]

tions 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 [illegible] function is localized near the surface. Likewise, 70% of the conduction band minimum (CBM) comes from the lowest [illegible] states are qualitatively different from simple effective mass deviation [Eq. (5)] in that they represent interband coupling and off-Γ ($j\neq0$) 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.

(ii) *Hydrogen chemisorption changes the localization* [illegible]

band-gap wave function amplitudes $|\psi_f^{\rm wire}(x,y)|^2$, energy level separations, and radiative lifetimes for clean (a) and hydrogen-covered (b) 8×8 Si wire are shown. Three [illegible]

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 [illegible]

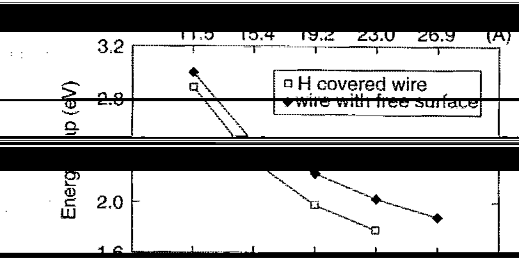


FIG. 2. Dependence of the band gap on the wire size. For the wire with free surfaces we consider only intrinsic states.

[illegible]

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 [illegible]

the intrinsic band gap. This reflects a combination of level [illegible] effective increase of wire size (thus, reduced confinement) [illegible]

(iv) *The emission spectrum to the states near the VBM* [illegible]

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

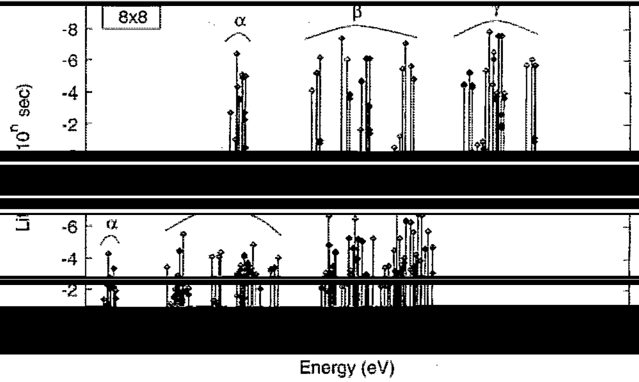


FIG. 3. Calculated radiative transition lifetime from the four highest VB states as functions of the transition energy.

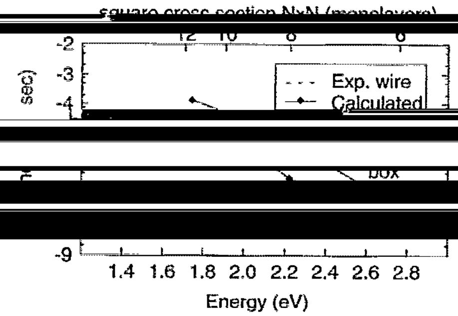


FIG. 4. Comparison of calculated (solid lines) lifetimes of quantum wires and quantum boxes with experimental *S*-band emission in porous Si (see [redacted]

[redacted]

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 calcu- [redacted] 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 [redacted] *quantum boxes.* Thus, the small photon energy region [redacted] the higher photon energy region could represent a larger contribution from boxes. This means that the "effective" [redacted]

[redacted] supported by the U. S. Department of Energy, under Contract No. DE-AC02-83-CH10093.

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[1] See many recent articles on porous Si in *Microcrystalline Semiconduc-* [redacted]

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

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[6] V. Petrova-Koch, T. Muschik, A. Kux, B. K. Meyer, F. Koch, and V. [redacted]

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

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

[9] Inside 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 [redacted] dom is not considered in the present calculation.