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Pressure dependence of the band gaps in Si quantum wires

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The pressure coefficients a of interband transitions in (001) silicon wires are calculated using a plane-wave basis and carefully fitted empirical pseudopotentials. We find purely red shifts ($a < 0$).

Their magnitudes, as well as changes with wire sizes, can be interpreted in terms of the "truncated

conduction bands along the Γ -X line.

The pressure dependence of the photoluminescence (PL) from porous Si has recently been measured by a number of groups.¹⁻⁶ The results, summarized in Table I show the following trends.

(i) As the pressure increases above ~ 25 kbar the PL shifts to lower energies (red shift), with an average pressure coefficient of $a \sim -3$ meV/kbar. This value is more negative than the value for the indirect gap of crystalline Si (-1.41

wires are calculated here using the empirical pseudopotential method (EPM). All dangling bonds are tied up by hydrogen atoms. The Si-Si interatomic distances are taken from bulk Si, while the Si-H distance is that of SiH₄. The wire atoms are described by local pseudopotentials, simultaneously fit¹² to the Si bulk band structure and to the (001) surface potential function. Using this Si potential we then fit the hydrogen potential to reproduce the observed chemisorption-induced

TABLE I. Observed pressure coefficients a of photoluminescence energy in porous Si. Values in square brackets denote experiments in which the pressurizing liquid medium was alcohol.

Authors and Reference	$P=0$ peak (eV)	ΔP (kbar)	a_{wire} (meV/kbar)
Camassel <i>et al.</i> ^a	1.8	0-10	-1.1 to -3.2
Zhou <i>et al.</i> ^b	1.85	0-20	[+4.0 to +9.0]
Sood <i>et al.</i> ^c	1.68-1.80	0-70	-3 to -4
Zhao <i>et al.</i> ^d	1.74-1.86	0-26	[+6.2 to +6.5]
Zhao <i>et al.</i> ^d	1.74-1.86	≥ 30	[-2.8 to -4.1]
Ookubo <i>et al.</i> ^e	1.77	0-40	-3.0 to -5.0
Ryan <i>et al.</i> ^f	1.85	0-25	[+7.0]
Ryan <i>et al.</i> ^f	1.85	25-80	[-2.0]

^aReference 1.
^bReference 2.
^cReference 3.
^dReference 4.
^eReference 5.
^fReference 6.

we excite higher energy bands in a given wire size [compare * * * * *]. As the wire size increases, eventually approaching the bulk value, the pressure coefficient trends in the calculated wire pressure coefficients on porous Si (Table I) where the pressure coefficient is outside the range $a(\Gamma_5) = -1.4$ and $a(\Gamma_6) = +1$ of bulk values, our calculated result for the wire falls within the range of the calculated bulk values. These observations hold even when the uncorrected EPM's are used.

These trends in the calculated wire pressure coefficients

decomposed into bulk wave functions $\phi_{n,k^*}(\mathbf{r})$ of band index n and wave vector k^* :

$$k^* = \frac{j_x 2\pi}{a_0} (1, 1, 0); \quad k^* = \frac{j_y 2\pi}{a_0} (-1, 1, 0), \quad (2)$$

where the quantum numbers for bands $n \neq 1$ are:

$\langle \psi_i | \phi_{n,k^*} \rangle$ We find that the wire CBM is composed predominantly from bulk states in the first and second conduction bands ($n=5,6$), evaluated at k^* . For example, in a 8×8 wire, about 78% of the CBM comes from the two lowest bulk conduction bands at $k^* = 2\pi/a_0(0, 4, 0)$ while 90% of the valence band minimum (VBM) comes from the two highest bulk valence bands at $k^* = 2\pi/a_0(0, \frac{1}{4}, 0)$. Because the projection coefficients are not sensitive to the pressure, Eq. (1)

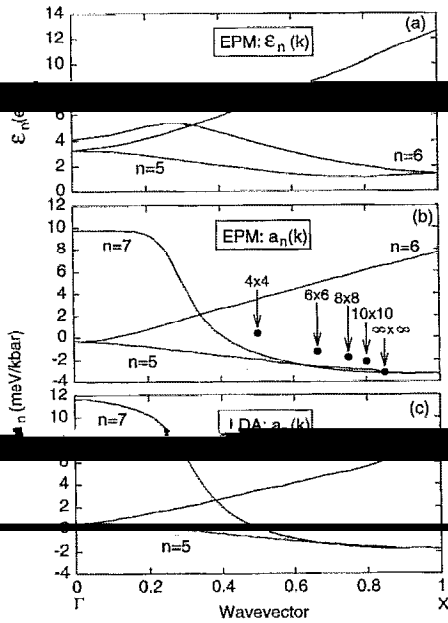


FIG. 1. (a) Calculated dispersions of three lowest bulk Si conduction bands obtained in the EPM; (b) calculated EPM pressure coefficients of the same three bulk bands; (c) same as (b) but using the LDA. The solid dots in part (b) denote the calculated pressure coefficients in the wires. Note how they

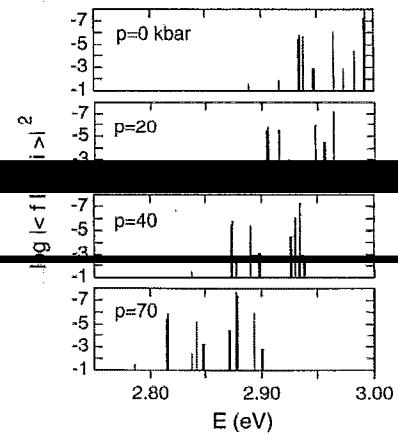


FIG. 2. Energy and pressure dependence of the diagonal matrix elements of

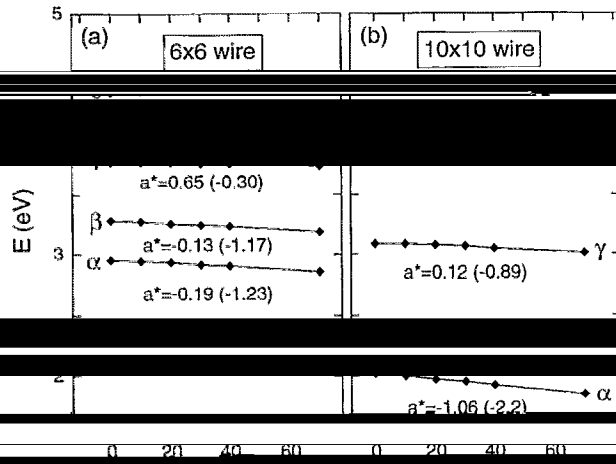


FIG. 3. Pressure dependence of the different groups of transitions ($\alpha, \beta, \gamma, \delta$) for the 6×6 (left) and 10×10 (right) Si wires. a^* are averaged arithmetic

its orientation, shape, and size. (v) Since higher energy *wire* bands ($\beta, \gamma, \delta, \dots$) are constructed from correspondingly higher energy *bulk* bands, their pressure coefficients are less nega-

Given the predicted off- Γ character of the wire CBM at ambient pressures,^{10–13} the analogy⁶ draw by Ryan *et al.*⁶ between porous Si and the direct gap GaAs under pressure clearly does not hold. The confusion arises, in part, because both Sanders and Chang¹⁰ and Buda *et al.*¹¹ have incorrectly

terize their λ -folded CBM. On the other hand, a molecular interpretation of the porous Si (e.g., siloxene) cannot explain a large positive β , either. It is possible that the confusion

that takes place in the pressure cell: Sood *et al.*^{3,17} noted that the conventional methanol–ethanol mixture used as a

alcohols as a pressure medium^{3,17} but not in experiments

we conclude that the predicted red shift is an intrinsic

effects, but that the red shift is not explained in these terms.

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We thus interpret the calculated red shift of (001)-oriented wires with [110] surfaces as a manifestation of the analogous bulk properties along the $2\pi/a_0(0,1,0)$ direction in the Brillouin zone. The value of k^* having the largest projection will be denoted k_{\max}^* . Analyzing our directly calculated wire wave functions, we find that as the wire size in-

$$\frac{\partial \epsilon_i}{\partial P} \cong \sum_n \sum_{k^*} |A_{n,k^*}^{(i)}|^2 \frac{\partial \epsilon_{n,k}}{\partial P}. \quad (3)$$

conclude the following: (i) The calculated pressure coefficients for the larger wires approach the bulk value $a(\Delta_{1c})$ at

approaches the CBM. (ii) The band edge pressure coefficients of small wires are less negative than $a^0(\Delta_{1c})$, since, by Eq. (3), the wire CBM represents a mixture of a few bulk states $|n, k^*\rangle$, most of which have $a_n(k^*) > a(\Delta_{1c})$ [Fig. 1(b)]. (iii) The fact that the observed wire pressure coefficients (Table I) are often most negative than the (observed) $a(\Delta_{1c})$ bulk value suggests either nonbulk (i.e., surface) or nonideality effects. (For example, the different compress-

shear that will split the wire VBM, pushing states further into

of our LDA-calculated pressure coefficients of bulk Si for off smaller in absolute value than $a(\Delta_{1c})$. Thus if the emission is caused by intrinsic quantum confinement, we expect a small