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Citation: Applied Physics Letters 64, 3545 (1994); doi: 10.1063/1.111219
View online: http://dx.doi.org/10.1063/1.111219
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/64/26?ver=pdfcov
Published by the AIP Publishing

Pressure dependence of the band gaps in Si quantum wires

Chin-Yu Yeh, S. B. Zhang, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 25 January 1994; accepted for publication 14 April 1994)

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 silane. The wire atoms are described by local pseudopotentials, simultaneously fit[12] to the Si bulk band structure and to the (001) surface work 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 *et al.*[a]	1.8	0–10	−1.1 to −3.2
Zhou *et al.*[b]	1.85	0–20	[+4.0 to +9.0]
Sood *et al.*[c]	1.68–1.80	0–70	−3 to −4
Zhao *et al.*[d]	1.74–1.86	0–26	[+6.2 to +6.5]
Zhao *et al.*[d]	1.74–1.86	≥30	[−2.8 to −4.1]
Ookubo *et al.*[e]	1.77	0–40	−3.0 to −5.0
Ryan *et al.*[f]	1.85	0–25	[+7.0]
Ryan *et al.*[f]	1.85	25–80	[−2.0]

[a]Reference 1.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.
[e]Reference 5.
[f]Reference 6.

we excite higher energy bands in a given wire size [compare a^*_α, a^*_β, a^*_γ, and a^*_δ for the 6×6 wire in Fig. 3(a)]. (ii) The pressure coefficient becomes more negative as the wire size increases, [eventually approaching the bulk value

ments on porous Si (Table I) where the pressure coefficient is *outside* the range $a(X_{xy})=-1.4$ and $a(\Gamma_{xy})=+1$ of bulk values, our calculated result for the wire falls *within* the range of the calculated bulk values. These observations hold even when the unscaled a_{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 $\mathbf{k}^*$

$$\psi_i(\mathbf{r})=\sum_{n}\sum_{k^*} A^{(i)}_{n,k^*}\phi_{n,k^*}(\mathbf{r}) \qquad (1)$$

Our previous work showed that the quantization of particle

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

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

$\langle\psi_i|\phi_{n,k^*}\rangle$ 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 $k^*=2\pi/a_0(0,\frac{1}{4},0)$ 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)

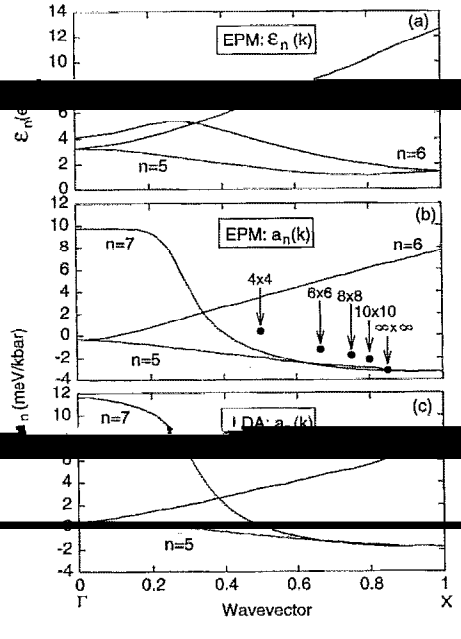

FIG. 1. (a) Calculated dispersions of three lowest bulk Si conduction bands obtained in the EPM. (b) calculated EPM pressure coefficients of the same three bulk bands; (c) same as (b) but using the LDA. The solid dots in part (b) denote the calculated pressure coefficients in the wires. Note how the

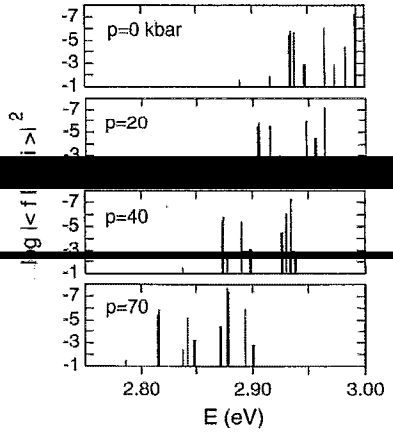

FIG. 2. Energy and pressure dependence of the dipole matrix elements of

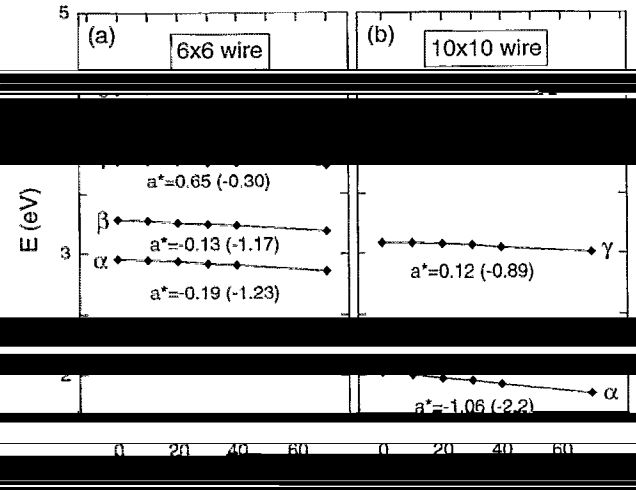

FIG. 3. Pressure dependence of the different groups of transitions ($\alpha,\beta,\gamma,\delta$) in (a) 6×6 (part a) and 10×10 (part b) Si wires. a^* are averaged arithmeti-

implies that the pressure coefficients of the wires are given

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

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-

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

its orientation, shape, and size. (v) Since higher energy *wire* bands (β,γ,δ...) 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 analogy[6] 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 Chang[10] and Buda *et al.*[11] have incorrectly

tenize their X-folded CBM. On the other hand, a molecular interpretation of the porous Si (e.g., siloxene) cannot explain a large positive b, either. It is possible that the blue

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[4,7,8] but not in experiments

We conclude that the predicted red shift is an intrinsic

effects, but that the blue shifts is not explainable in these terms.

We wish to thank V. Petrova-Koch for many helpful discussions. This work was supported by the Office of Energy Research (OER) [Division of Materials Science of the Office of Basic Energy Science (BES)], U. S. Department of Energy, under Contract No. DE-AC02-83-CH10093.

[1] J. Camassel, E. Massone, S. Lyapin, J. Allegre, P. Vicente, A. Foucaran, A. Raymond, and J. L. Robert, in *Proceedings of the 21st International Con-*

[3] A. K. Sood, K. Jayaram, and D. V. S. Mathu, J. Appl. Phys. **72**, 4963 (1992).

Symp. **283**, 127 (1993).

[5] N. Ookubo, Y. Matsuda, and N. Kuroda, Appl. Phys. Lett. **63**, 346 (1993).

[6] J. M. Ryan, P. R. Wamsley, and K. L. Bray, Appl. Phys. Lett. **63**, 2260 (1993).

[7] (a) B. Welber, C. K. Kim, M. Cardona, and S. Rodrigues, Solid State Commun. **17**, 1021 (1975). (b) E. Schmidt and K. Vedam, *ibid.* **9**, 1187 (1971).

[8] B. A. Weinstein, Phys. Rev. B **23**, 787 (1981).

[9] A. R. Goni, K. Strossner, K. Syassen, and M. Cardona, Phys. Rev. B **36**, 1581 (1987).

F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).

[12] C.-Y. Yeh, S. B. Zhang, and A. Zunger, Appl. Phys. Lett. **63**, 3455 (1993);

[13] M. S. Hybertsen and M. Needles, Phys. Rev. B **48**, 4608 (1993).

(1984).

[17] J. M. Lauerhaas, G. M. Credo, J. L. Heinrich, and M. J. Sailor, J. Am. Chem. Soc. **114**, 1911 (1992).