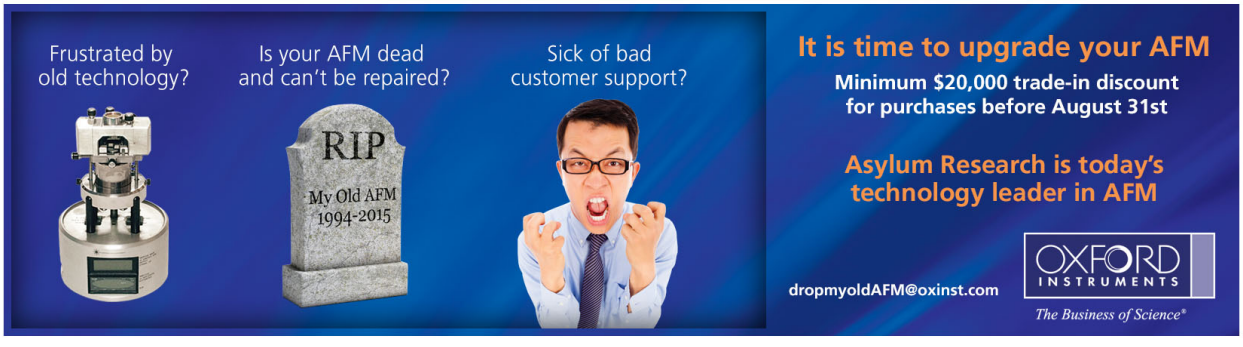
AIP | Applied Physics Letters

Pressure dependence of the band gaps in Si quantum wires

Chin-Yu Yeh, S. B. Zhang, and Alex Zunger

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 crystal model" which describes the wire conduction bands as linear combination of the lowest bulk 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 ± 0.06 meV/kbar)[7a] or that of amorphous Si (-2 ± 0.5 meV/kbar)[8].

(ii) In addition to the red shifts, Zhou *et al.*,[2] Zhao *et al.*,[4] and Ryan *et al.*[6] also find *at lower applied pressures* a blue shift, with pressure coefficients in the range of +4 to +9 meV/kbar. Ryan *et al.*[6] have interpreted the crossover from blue to red shift as a pressure induced direct-to-indirect transition in the wire. They supported this contention by pointing to the analogy with the pressure-induced direct-to-indirect transition in GaAs,[9] and by noting that previous calculations[10,11] predicted that Si quantum wires are direct gap systems at ambient pressures.

The results of Table I led different authors to diverging conclusions: Camassel *et al.*[1] concluded that their $a_{\text{wire}} \leq a_{\text{bulk}}$ "gives strong support to the quantum-size effects," while Sood *et al.*[3] concluded that their results $a_{\text{wire}} \ll a_{\text{bulk}}$ "do not support the suggestion of quantum size effects," and Ryan *et al.*[6] interpreted the change of sign of a_{wire} with pressure as "best described by the quantum confinement model."

Here, we report the results of direct empirical pseudopotential calculations on the pressure dependence of the band gap of hydrogen-saturated square Si quantum wires. We find that (i) there is no band gap blue shift at any of the wire sizes studied here. (ii) Our finding of pure red shifts shows that the wire behaves as an indirect gap material, not as a direct gap system.[6] This agrees with our previous zero-pressure calculation[12] that showed that the wire conduction band minimum (CBM) can be described as superposition of bulk states near the Δ_{1c} minimum. (iii) Our calculated a_{wire} is *less negative* than the indirect bulk value, in agreement with the fact that the wire CBM represents a mixture of several bulk states, many of which have less negative pressure coefficients than the CBM at Δ_{1c}.

We consider [001]-oriented Si wires with $(110)\times(\bar{1}10)$ square cross section, $N\times N$ monolayer wide. While wires with small cross sections (e.g., $N=5$) can be treated[13] by first-principles local density approximation (LDA), larger 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 states in hydrogen covered Si *surfaces*. The Schrödinger equation is solved in a supercell geometry using plane wave basis functions. The pressure coefficient of the band gap $a=\partial E/\partial P=-(V/B)(\partial E/\partial V)$ is computed from the volume derivative $\partial E/\partial V$, assuming $B=978.8$ kbar,[14] taken from bulk Si. Reference LDA calculations for bulk Si, employ nonlocal pseudopotentials and a 20 Ry cutoff energy.

We have first calculated the EPM pressure coefficients $a_n(\mathbf{k})$ for the three lowest conduction bands in bulk Si (with respect to the valence band maximum) along the wave vector $\mathbf{k}$ ranging from Γ to X. The results are shown in Fig. 1(a) (energy bands) and 1(b) (pressure coefficients) and are compared in Fig. 1(c) with the LDA results. We see that the EPM pressure coefficients $a_{\text{EPM}}(k)$ parallels the LDA results (i.e., a nearly constant shift) but are consistently somewhat more negative. Since LDA pressure coefficient agree consistently better with experiment than EPM results for most semiconductors,[15] we thus scale the EPM pressure coefficient as $a^*_{\text{EPM}}=\alpha\, a_{\text{EPM}}(k)+\beta$, and determine the parameters α and β by minimizing $|a^*_{\text{EPM}}(k)-a_{\text{LDA}}(k)|^2$ through a least-squares fit. This yields $\alpha=0.90$ and $\beta=0.92$ meV/kbar. The scaled EPM coefficients compare favorably with experiments (given in parenthesis), i.e., $a^*_{\text{EPM}}(X_{1c})=-2.03[-1.41 \pm 0.06$ (Ref. 7a)], $a^*_{\text{EPM}}(\Gamma_{15c})=0.65[1\pm 1$ (Ref. 7b)].

Our previous calculation on the electronic structure of Si wires at ambient pressures[12] showed that the states above the CBM can be grouped into "bands" (α,β,γ...), each separated from the others by pseudogaps. Figure 2 shows the calculated α-band spectrum (transitions between the four highest valence bands and four lowest conduction bands) of the 6×6 wire, as a function of pressure. We see (i) a pure red shift, and (ii) a weak decrease in average dipole matrix elements with pressure (e.g., from 4.5×10^{-2} to 4.1×10^{-2} as the pressure changes from $P=0$ to $P=70$ kbar). Figure 3 gives both the scaled and the unscaled pressure coefficients a^*_{EPM} (a_{EPM}) for bands α, β, γ, and δ in the 6×6 (11.5 Å), and the 10×10 (19.2 Å) wide wires. This shows that (i) the pressure coefficients become less negative (and eventually turn positive) as

 0003-6951/94/64(26)/3545/3/$6.00

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 $a^*(\Delta_{1c})=-1.90$ meV/kbar]. (iii) In contrast with experiments on porous Si (Table I) where the pressure coefficient is *outside* the range $a(X_{1c})=-1.4$ and $a(\Gamma_{15c})=+1$ 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 can be understood in terms of the "truncated crystal" model,[12] in which wire wave functions $\psi_i(\mathbf{r})$ are spectrally decomposed into bulk wave functions $\phi_{n,k^*}(\mathbf{r})$ of band index n and wave vector $\mathbf{k}^*$

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

Our previous work showed that the quantization of particle in a box is still valid, namely

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

where the quantum numbers for bands $n\neq 1$ are j_x, $j_y=0,1,2,...N$. Here, a_0 is bulk lattice constant and N represents the number of atomic monolayers. The expansion coefficients of Eq. (1) were calculated from the projections $\langle\psi_i|\phi_{n,k^*}\rangle$ 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 $k^*=2\pi/a_0(0,\frac{3}{4},0)$ 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)

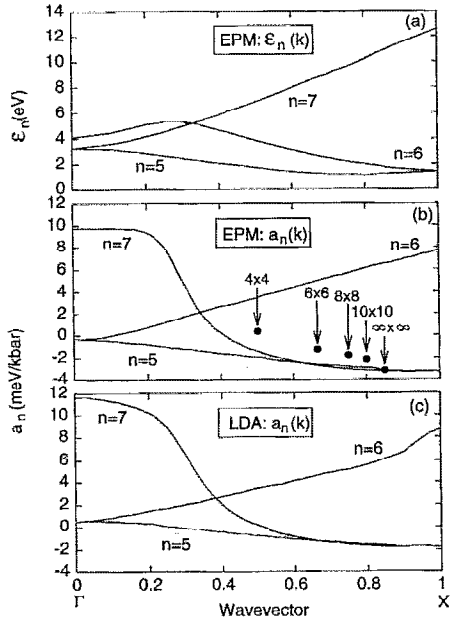


FIG. 1. (a) Calculated dispersions of three lowest bulk Si conduction bands obtained in the EPM, (b) calculated EPM pressure coefficients of the same three bulk bands; (c) same as (b) but using the LDA. The solid dots in part (b) denote the calculated pressure coefficients in the *wires*. Note how they approach the bulk value at $k\sim\Delta_{1c}$ as the wire size increases.

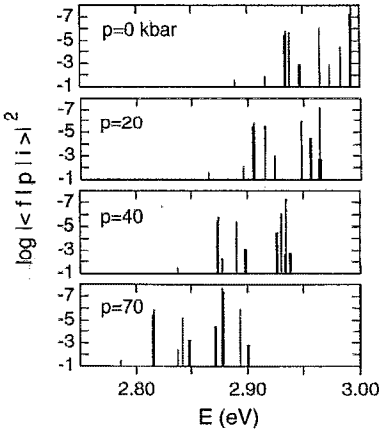


FIG. 2. Energy and pressure dependence of the dipole matrix elements of the lowest energy α band in a 6×6 Si wire.

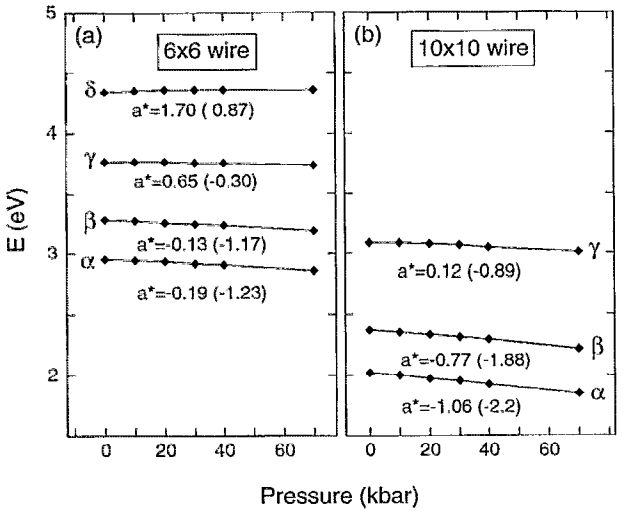


FIG. 3. Pressure dependence of the different groups of transitions ($\alpha,\beta,\gamma,\delta$) in the 6×6 (part a) and 10×10 (part b) Si wires. a^* are averaged arithmetically within each band. The unscaled EPM a values are given in the parentheses.

implies that the pressure coefficients of the wires are given by a sum over k^* [Eq. (2)] and n of the *bulk* pressure coefficients

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

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 increased, $k^*_{\max}$ moves towards the value $2\pi/a_0(0,0.85,0)$ at which bulk Si has its CBM [Fig. 1(a)]. These values are indicated in Fig. 1(b) by solid circles and vertical arrows. We conclude the following: (i) The *calculated* pressure coefficients for the larger wires approach the bulk value $a(\Delta_{1c})$ at the CBM (as expected by continuity arguments) since $k^*_{\max}$ 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 compressibilities of Si and the empty pours could create an effective shear that will split the wire VBM, pushing states further into the gap and increasing $|a|$.) (iv) For wires with different surfaces and different orientations, the pressure coefficients could have contributions off the bulk Γ-X line. Examination of our LDA-calculated pressure coefficients of bulk Si for off Γ-X directions near Δ_{1c} shows that they are all negative and smaller in absolute value than $a(\Delta_{1c})$. Thus if the emission is caused by intrinsic quantum confinement, we expect a small and negative pressure coefficient for porous Si regardless of 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 negative. In fact, the δ band had a *positive* pressure coefficient [Fig. 3(a)] since it is composed of states near the bulk $\Gamma_{2'c}$ state [see Fig. 1(b)].

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 used the term "direct" instead of "pseudodirect" to characterize 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.[1,16] It is possible[3,17,18] that the blue shift does not represent an intrinsic feature of Si wires but rather a pressure-induced size-reducing chemical reaction that takes place in the pressure cell: Sood *et al.*[3,17] noted that the conventional methanol–ethanol mixture used as a pressure-transmitting medium actually reacts with porous Si.[17] Blue shifts were indeed seen only in experiments using alcohols as a pressure medium[2,4,6] but not in experiments using inert fluids.[3,5,18]

We conclude that the predicted red shift is an intrinsic property of the Si wires, describable in terms of bulklike 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 Conference on the Physics of Semiconductors*, edited by Ping Jiang and Hou-Zhi Zhang (World Scientific, Singapore, 1992), p. 1463.
[2] W. Zhou, H. Shen, J. F. Harvey, R. A. Lux, M. Dutta, F. Lu, C. H. Perry, R. Tsu, N. M. Kalhhoran, and F. Nawavar, Appl. Phys. Lett. **61**, 1435 (1992).
[3] A. K. Sood, K. Jayaram, and D. V. S. Mathu, J. Appl. Phys. **72**, 4963 (1992).
[4] X.-S. Zhao, P. D. Persans, J. Schroeder, and Y.-J. Wu, Mater. Res. Soc. 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).
[10] G. D. Sanders and Y. C. Chang, Phys. Rev. B **45**, 9202 (1992).
[11] 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); L. W. Wang and A. Zunger, J. Phys. Chem. **98**, 2158 (1994).
[13] M. S. Hybertsen and M. Needles, Phys. Rev. B **48**, 4608 (1993).
[14] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **35**, 2161 (1964).
[15] K. J. Chang, S. Froyen, and M. L. Cohen, Solid State Commun. **50**, 105 (1984).
[16] S. Ernst, M. Rosenbauer, U. Schwarz, P. Deak, K. Syassen, M. Stutzmann, and M. Cardona, Phys. Rev. B **49**, 5362 (1994).
[17] J. M. Lauerhaas, G. M. Credo, J. L. Heinrich, and M. J. Sailor, J. Am. Chem. Soc. **114**, 1911 (1992).
[18] V. Petrova-Koch (private communication).