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Electronic band structure of high-index silicon nanowires

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We calculated the electronic properties of high-index free-standing silicon nanowires. $[11\bar{2}]$ nanowires are indirect semiconductors for diameters down to 0.8 nm; [110] wires have a direct band gap at the Γ-point, but the density of states is very small at the conduction band edge. Confinement arguments show that only [001] nanowires are expected to develop a direct gap with a large density of electronic states at the band edges for diameters in the nm range. The magnitude of the gap depends strongly on the wire growth direction, which is due to the different effective confinement length and effective masses for the ΓX-derived silicon states. Correcting for the extension of the wave functions we find our calculated energies to agree with recent scanning tunneling experiments.

Nanoscale semiconductor structures exhibit new physical properties. In silicon the dependence of its indirect band gap on confinement [1–10] is of great interest. Silicon is believed to develop a direct band gap in nanometer-size structures [4, 5, 10, 12], which is a necessary requirement for silicon-based optoelectronics. The electronic properties of silicon nanowires (SiNWs) were widely studied theoretically and experimentally. Calculations were performed on wires extending along the [001] direction [13–17] with only a few exceptions [18–20]. In practice, however, it is observed that free standing silicon nanowires grow along high-index directions like [110], [111], or $[11\bar{2}]$ [9, 21]. The question arises whether high-index silicon nanowires have direct band gaps as well.

In this work we present first-principles calculations of the electronic band structure and the density of states for two types of high-index silicon nanowires. We show that a direct band gap is only obtained in silicon if at least one of the ΓX-directions is perpendicular to the wire axis. A large electronic density of states at the Γ-point additionally requires confinement of the bands with a transverse effective mass, i.e., [001] silicon nanowires. We discuss the magnitude of the calculated band gaps and explain their dependence on the growth direction. We get excellent agreement with experiment after taking into account the penetration of the electronic wave function into vacuum.

We studied two types of SiNWs with hexagonal cross sections and an axis pointing in the [110] and the $[11\bar{2}]$ directions and compared the results with rectangular SiNWs extending along [001]. The silicon core of our [110] wire is shown in Fig. 1. For the $[11\bar{2}]$ wire we calculated four different diameters. The Si core of the largest wire with an average diameter of 1.7 nm, and the facets are show in Fig. 1(c) and (d), respectively. The three quadratic [001] SiNWs were formed of 8×8, 6×6 and 6×5 Si atoms in the unit cell. Dangling bonds were terminated with hydrogen atoms, see Table 1.

Ab initio calculations were performed using the SIESTA code [22] within the local-density approximation [23]. The core electrons were replaced by normconserving pseudopotentials in their fully seperable form [24]. A double-ζ, singly polarized basis set was used for the valence electrons [25]. The cutoff radii were 5.7 a.u. for the s and 7.1 a.u. for the p- and polarizing d-orbitals of silicon; the cutoff radius of

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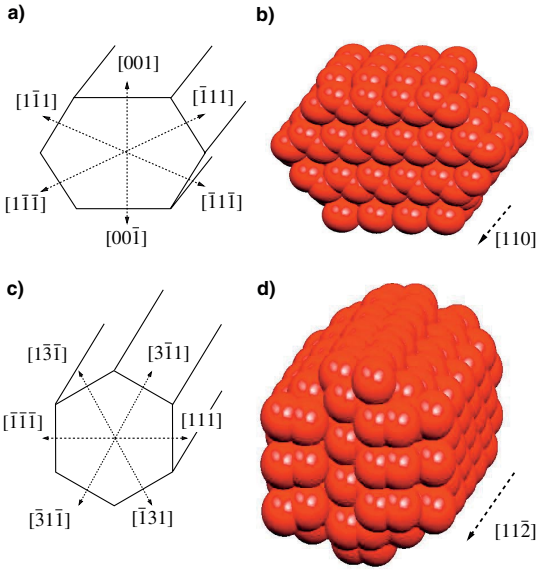

Fig. 1 (online colour at: www.pss-b.com) (a) Schematic view of a [110] SiNW with the facets indicated; silicon core (b) of the investigated wire with an average diameter $d = 2.25$ nm. (c) Schematic view and (d) the silicon core for the $d = 1.7$ nm [11$\bar{2}$] silicon nanowire formed of four (3$\bar{1}$1)-type and two (111)-type facets. The surfaces were terminated by hydrogen atoms (not shown).

the s-orbital in hydrogen was 5.6 a.u. The calculations were performed using periodic boundary conditions. Neighboring wires were separated by more than 7.3 Å; with this distance the interaction between two wires is strictly zero, because of the finite length of the atomic basis sets [22, 25]. Integrations in k-space along the wire axis were performed over 4 k-points. Real-space integrations were done in a grid with a cutoff of ≈ 160 Ry. We optimized the nanowire structures by a conjugate gradient minimization until all forces were below 0.04 eV/Å. Stress components along the wire axes were minimized with respect to the z-lattice constant. The deviations from the bulk lattice constant were found to be small (<1%). Then the band structure and electronic density of states (DOS) were calculated.

With this basis set and a k-point sampling of $8 \times 8 \times 8$ we found a lattice constant of 5.4390 Å for bulk Si in good agreement with experiment (5.425 Å). The LDA band gap of silicon was 0.524 eV. As usual, all LDA band structures and DOS were corrected by the scissors operator to match the experimental gap of 1.17 eV.

We first briefly explain why [001] Si nanowires are direct band gap semiconductors before turning to the high-index wires. [001] wires are unique among all possible nanowires, because their confinement plane contains four of the six equivalent X-point conduction band valleys of silicon [13]. Since the unit cell is enlarged in the wire, the conduction band minima are folded onto the Γ-point of the nanowire

Table 1 Parameters of the wires studied; the diameter d, defined as twice the average distance of the terminating hydrogen atom from the wire center, and the number of Si and H atoms per unit cell are given.

axis	d (nm)	Si	H
[001]	1.81	64	32
	1.36	36	24
	1.25	30	22
[110]	2.25	74	28
[11$\bar{2}$]	1.70	71	54
	1.53	54	42
	1.05	26	30
	0.82	14	18

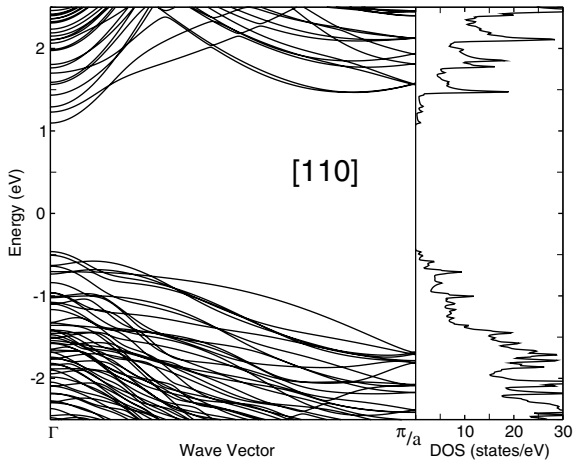

Fig. 2 Electronic band structure of the [110] wire ($d = 2.25$ nm) and the associated density of states (Gaussian broadening of 0.01 eV). The direct band gap lies at the zone center, providing only very few states. Energies were corrected using the scissors operator.

resulting in a direct band gap silicon nanowire. Changing the axis to a lower-symmetry direction always changes the confinement plane. As can be seen in Fig. 1 the [110] wire contains only one of the [001] directions in the confinement plane and the $[1\bar{1}2]$ none. The "useful" conduction band minima are thus less efficiently (or not at all) folded onto the Γ-point, rendering the high-index directions *a priori* less attractive from the optoelectronic point of view.

We discuss now the calculated band structures of our high-index wires. Figure 2 shows the calculated band structure and electronic density of states of the [110] silicon nanowire. As expected, we find a direct band gap for the [110] wire. The number of states in the minimum of the conduction band, however, is almost negligibly small. The influence on the band structure, in the energy gap region, by electronic states originating from Si–H bonds can be neglected since they are located far away from the band edges. Although the maximum of the valence band and the minimum of the conduction band are located at the Γ-point, the overall character of the [110] wire remains indirect. The DOS is small in the lowest conduction band states because of the large longitudinal masses in the confinement plane. The valleys with the 4.8 times smaller transverse mass, which would substantially contribute to the DOS, are not folded onto the Γ-point in the [110] nanowires. For quantum confinement of the transverse [001] valleys two of the Γ, X-directions have to be perpendicular to the wire axis. This can only be achieved for wires growing along the [001] direction.

The band structure and density of states of the $[1\bar{1}2]$ wire are shown in Fig. 3. Clearly, both from the band structure and the DOS the wire is an indirect semiconductor. The $[1\bar{1}2]$ wire is a prototype for other high-index nanowires where the growth axis is not perpendicular to the [100] direction like, e.g., the [111] direction. In these wires the minimum of the conduction band remains at the boundary of the wire Brillouin zone, see Fig. 3.

Having discussed the direct and indirect nature of the gap we now concentrate on the magnitude of the gap in the different nanowires. In Fig. 4 we plot the calculated gaps together with tunneling spectroscopy measurements on $[1\bar{1}2]$ wires and previous LDA calculations versus the inverse of the nanowire diameter [9, 13, 16][1]. The horizontal line is the low-temperature band gap of bulk silicon (1.17 eV).

The band gaps of the nanowires E_g are larger than the gap of silicon because of confinement. The magnitude of the band gaps shows a noticeable difference between the experimental and the calculated wire band gaps. In order to discuss the validity of our calculated band gaps we will evaluate the dependence of the band gap E_g on the wires diameter. The dependence on the diameter d can be described by

$$E_g = E_0 + \frac{C}{d^{\alpha}}, \tag{1}$$

[1] The diameters of the wires of Read et al. [13] were recalculated to coincide with our diameter definition. We made sure, that the determination of the diameters by Zhao et al. [16] agrees with our method.

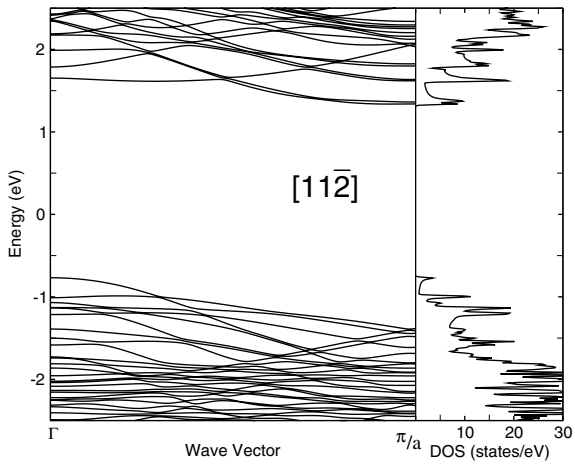

Fig. 3 Electronic band structure and density of states for the [11$\bar{2}$] wire (d = 1.7 nm). The indirect character of the nanowire is nicely pictured. Energies were corrected using the scissors operator.

as proposed by Delerue et al. [26], where d is defined as in Table 1. The diameter exponent $\alpha \approx 2$ for the experiment, but smaller for all calculations, see fits in Fig. 4 and Table 2.[2] An exponent of $\alpha = 2$ is also expected from the particle-in-a-box model [27] when the barrier height is infinite.

Theoretical determination of nanowire diameters are – in one way or the other – determined by taking the positions of the outmost Si atoms. The wire diameter is thus related to the atomic nuclei. We denote the diameter found by this procedure as d. Experimentally, the wire diameters are found, e.g., by scanning tunneling microscopy. The wire diameters are thus determined by the extension of the electron clouds, which we will call $\tilde{d}$. The difference between these two definitions becomes crucial if we consider a finite height for the confining barrier and thus a penetration of the electrons into the vacuum. Then, the confinement induced upshift deviates from the $1/d^2$ scaling when using the nuclei positions for the wire dimension. Conversely, if the extension of the electronic clouds is taken into account the upshift remains proportional to $1/\tilde{d}^2$. This is exactly the situation observed in Fig. 4.

We will now apply this idea to the calculated diameters of the [11$\bar{2}$] nanowires to see whether it explains the different exponents in the band-gap dependece on diameter in theory and experiment. We calculated the penetration depth, the length, for which the amplitude of the wave function has decayed to

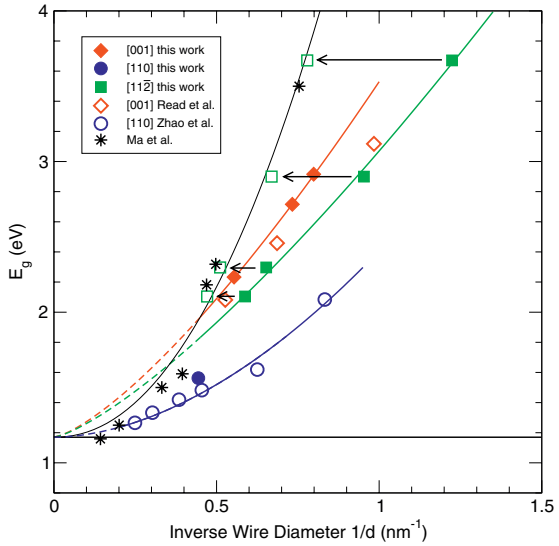

Fig. 4 (online colour at: www.pss-b.com) LDA band gaps calculated for [001] (filled red diamonds), [110] (filled blue circle) and [11$\bar{2}$] (filled green squares) wires. For comparison experimental band gaps of [11$\bar{2}$] wires by Ma et al. [9] as well as previous calculations by Read et al. [13] and Zhao et al. [16] are plotted. The solid horizontal line indicates the band gap of bulk silicon (1.17 eV). The black arrows indicate the diameter correction due to the particle-in-a-box model, see text.

[2] The difference between the measured and calculated band gaps in Fig. 4 is even larger than from what appears from Fig. 3C of Ref. [9]. In the reference the experiments on [11$\bar{2}$] wires were compared to calculations for [001] wires.

Table 2 The fit parameters of Eq. (1) for theoretical and experimental data of Fig. 4.

nanowire axis	α	$C \cdot$ nm (eV)
[001]	1.4	2.36
[110]	1.8	1.24
$[11\bar{2}]$	1.3	1.90
Ma et al. [9]	2.1	4.33

1/*e*, for a square well using the work function of Si (4.7 eV) as the barrier height and an effective mass $m^* = 0.2\,m_e$. In the diameter range considered here (1–2 nm) the finite-barrier correction leads to a diameter increase of ≈0.43 nm. Replacing d in Fig. 4 by $\tilde{d} = d + 0.43$ nm we find excellent agreement between experiment and theory for $[11\bar{2}]$ nanowires (see open green squares)[3]. This model thus gives an adequate correction of the geometric, i.e., balls-and-sticks derived, wire diameter to the quantum mechanical penetration of the wave function into vacuum.

For a given diameter the nanowire band gap depends strongly on the wire type. The [001] wire shows the largest and the [110] wire the smallest gap. This is due to the different contributions of the transverse and longitudinal effective masses. For a given diameter the [001] wire has the largest gap, because the [100] and [010] valleys are efficiently confined in the wire plane. The band gap of the [110] wire is the smallest due to the large longitudinal effective masses of the X conduction band valleys. In the $[11\bar{2}]$ silicon nanowire the minimum of the conduction band is at the boundary of the wire Brillouin zone, see Fig. 3. Because the Γ, X-directions are not perpendicular to $[11\bar{2}]$, the relevant confinement length for [001] related states is, in fact, larger than the wire diameter. For a rough estimate of the effective confinement length we take the sine of the angle between $[11\bar{2}]$ and the [100] direction as a lower limit, finding $d_{\text{eff}} \approx 1.1d$. In Fig. 4, replacing the calculated diameters for $[11\bar{2}]$ by the estimated d_{eff} shifts all points towards the (red) fit of the [001] wires by about 10%, bringing them to a near overlap. This confirms our analysis in terms of an effective confinement length, which explains why the band gap of a $[11\bar{2}]$ wire is smaller than the gap for a [001] wire of the same diameter.

In summary, we calculated the electronic band structures and density of states for high-index silicon nanowires from first principles. The band-gap character, direct or indirect, strongly depends on the crystallographic direction of the wire axis. Only wires with at least one axis perpendicular to the [100], [010], or [001] direction have the conduction band minimum at the Γ-point. The magnitude of the direct or indirect bandgap is due to quantum confinement. It depends on the direction of the wire axis and the wire diameter, which we explained by the effective masses and an effective confinement radius for the X valleys. Estimates of the penetration depth of the wave functions into vacuum yield a good agreement of experimental and theoretical diameter and gap values. Our results clearly show that high-index SiNWs fail to be promising candidates for light emitting devices.

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[3] Due to the inability of LDA to pecisely predict exited state energies, the calculated band gaps are underestimated, which in our calculations is corrected by the scissors operator. The recent calculations by Zhao et al. [16] suggest that this correction is not fully appropriate for silicon nanowires, due to the size dependent GW correction. We note that in Fig. 4 the green open symbols are slightly above the experimental fit (black line) for large diameters, whereas they fall below the line for small diameters. This may reflect the diameter dependence of the LDA correction.

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