Electronic Properties and Transport in Silicon Nanowires

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ABSTRACT

In a truly integrated silicon nanotechnology environment, it may be desirable to replace metallic inter-connects like Al, with silicon itself if adequate metallicity can be established. This motivated us to investigate the electronic properties of quasi one dimensional (1D) silicon nanowires. The standard pseudopotential density functional method was employed to obtain stable structural arrangements. Silicon manifested several stable 1D structures. The resultant electronic structures and charge densities for these 1D nanowires are presented. The results are promising since some of these nanowires, unlike bulk Si, do display adequate metallic behavior. For electronic transport through these wires, we provide an estimate for the value of quantum conductance using the maximum channel capacity arguments in the ballistic transport regime. The practical benefits must await until such nanowires can be fabricated, a task which is likely to be challenging.

Keywords: Nanowire, Silicon, Quantum conductance

1 Introduction

The semiconductor industry already manufactures chips in the 0.1 μm range. Further miniaturization [1] will require migration to the nanometer scale. Devices in the nanometer range pose many challenges [2] because of quantum mechanical effects. Due to the quantum effects, the transport in nanowires is no longer governed by Ohm's law. The fundamental work on quantized conductance in 1D systems is due to Landauer [3], and an excellent exposition has been given in a monograph by Datta [4]. An alternate way to understand the quantum conductance in nanowires, as a consequence of the Heisenberg uncertainty principle, has also been recently presented [5].

Research in nanoscience has led to successes such as the creation of stable gold monatomic chains suspended between gold electrodes [6], [7] and the measurement of quantized conductance in nanowires [8]. The pioneering work [9], [10] on metal-Si nanowire contacts established quantum conductance concepts in these systems of practical importance. Important results, using a parameterized tight-binding method, for the electronic properties of the stand alone Si nanowires have been published [11]. Nanowires of other elements using the first-principle methods have been studied. The calculations of Portal et al [12], Häkkinen et al [13], and Sen et al [14] gave important structural information for various 1D nanowires. Portal et al [12] showed that finite and infinite gold atomic chains energetically favor a planar zigzag structure with a bond angle of 131°. Häkkinen et al [13] found that a finite gold chain favors a dimerized state. In a comparative study [15] among gold, copper, calcium, and potassium infinite chains, it was found that these atoms all form planar zigzag structures consisting of equilateral triangles. Among these elements, Au was the only element to form another zigzag structure: the wide angle structure reported by Portal et al [12] with a bond angle of 131°. Similar work by Sen et al [14] on aluminum atomic chains also found the existence of two stable zigzag structures: an equilateral triangle and a wide angle structure with a bond angle 139°.

Here we employ a density functional based first-principles method to study the atomic and electronic structure of silicon atomic chains. With the recent success [16] in building diodes, transistors, and inverters using silicon nanowires, it is essential to understand stable structures and their properties. For the numerical work, we use the Vienna Ab-initio Simulation Package [17] (VASP), a software program that performs first-principles calculations using pseudopotentials and a plane wave basis set. A main claim of our study is the discovery of an equilateral zigzag Si nanostructure which is fairly stable and also displays metallic behavior. In fact, our findings are similar to the results reported [14] for the aluminum atomic chains. In what follows, we give details of the electronic structure and charge density to support our claim.

2 Calculational Details

We used density functional theory as implemented in the VASP code [17] to perform the simulations. To simulate the 1D structures we used a slab method, where the slab lattice vectors were set at 15 Å in the two dimensions orthogonal to the dimension in which the chain propagated. The x axis was taken to be along the chain and the z axis (y axis) is perpendicular to (in) the plane of the 1D structure. The wave functions were expressed by plane waves with the cutoff energy, \(|\mathbf{k} + \mathbf{G}|^2 < 275\ eV\). The Brillouin-zone (BZ) integration was performed with a Γ-centered Monkhorst-Pack scheme [18] using \((40 \times 1 \times 1)\) k points. The cutoff energy and the number of k points were varied to test for convergence and were found to converge within 2 meV for the reported values. We

3 Results and Discussion

We first studied a linear (L) periodic 1D Si nanowire for which the lattice vector, R, is the same as the nearest neighbor distance, d. The computed band structures for four different values of R are shown in Fig. 1. The zero of energy is set at the Fermi-level, $E_F$, determined by filling the bands with four electrons. There are four bands of interest around the Fermi level. The lowest lying $\sigma^*$-band arises from the $sp_\alpha$ hybrid, holds two electrons and is always occupied. The next two higher lying energy bands are doubly degenerate $\pi$-bands (having their origin in equivalent $p_y$ and $p_z$ orbitals) which cross $E_F$ at or below the mid-point ($M = 0.25 \frac{a}{\sqrt{2}}$) of the BZ. They can hold up to four electrons but actually hold two or less. The fourth band, $\sigma^*$ shows interesting variation when the lattice constant is changed. At $R = 2.0$ Å, this band is totally unoccupied. With increasing R, it starts to dip below $E_F$ near the zone edge, siphoning electrons from the $\pi$-bands causing these $\pi$-bands to cross $E_F$ at a $\mathbf{k}$ point between $\Gamma$ and $M$. At $R = 2.5$ Å, bands 1 and 4 become degenerate (Fig. 1(c)) at the BZ edge because the phase change makes the two $sp_\alpha$ hybrids identical. Our results are in excellent qualitative agreement with an earlier parametrized study [11]. Clearly, it is not possible for them [11] to calculate the optimized lattice constant. But that indeed is the parameter that determines the “observable” electronic structure and hence should be optimized using total energy.

Figure 1: Band structure of silicon linear (L) chain for different values of the interatomic distance, $d$ (a) 2.0 Å, (b) 2.2 Å, (c) 2.5 Å, and (d) 3.0 Å. The Fermi energy, labeled $E_F$, is indicated by the dotted line and the lattice translation vector $R = d$.

Our total energy calculations gave the optimized value of $R = d = 2.2$ Å for which the band structure is shown in Fig. 1(b). We note that the $\sigma^*$-band (4) is partly occupied.

This band and its movement w.r.t. $E_F$ play a significant role as we investigate other nanostructures of Si. We further conclude from Fig. 1(b) that a dimerizing Peierls distortion is not expected for the optimized L structure, since the $\pi$-bands do not cross $E_F$ at the middle of the BZ. This band structure is also consistent with that obtained by Mozos et al [9].

Figure 2: The calculated total energy $E$ of linear L₂, planar zigzags W and T, and parallel P infinite Si chains. Relevant structural parameters, bond length $d$, bond angle $\alpha$, and $s$ are shown for the various stable structures.

We next investigated other stable structures by allowing the nanowires to distort in the xy-plane. The variation of total $E$ (in eV) versus $s$ (in Å) for various structures: linear L₂ (two atoms per unit cell), planar zigzags W and T, and parallel P are shown in Fig. 2. Here $s$ is the horizontal distance (along $x$), between the two atoms in the primitive unit cell. To keep the number of atoms per unit cell to be the same in all these nanowires, we performed the calculations on the linear chain with an artificial doubled periodicity. This will facilitate in understanding of the band structure of various atomic chains. The total energy is measured relative to the energy of the free Si atom. A negative value indicates that the structure is stable. The cohesive energy $E_C = -E$. The cohesive energy of the optimized L₂ structure is found to be 3.4 eV/atom. and is well below the bulk value, as is the lattice constant. Also presented in Fig. 2 are the geometries and important structural parameters of the other stable

<table>
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</tr>
<tr>
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<td>4.4</td>
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Table 1: Structural Parameters and Cohesive Energies
Figure 3: Band structures of silicon chains: (a) L₂, (b) W, (c) T, and (d) P. The Fermi energy, \( E_F \), is indicated by the dotted line.

structures.

The plot reveals two stable zigzag quasi 1D structures as deduced from local energy minima in Fig. 2. As in the case of Au [12], [15] and Al [14] chains, two local minima for the zigzag geometry were found. The wide angle zigzag (specified as W) at the shallow minimum, has a bond length \( d = 2.2 \text{ Å} \) with \( \alpha = 117^\circ \) and \( s = 1.9 \text{ Å} \). The wide angle zigzag has the lower cohesive energy of the two stable zigzag structures with \( E_C = 3.8 \text{ eV/atom} \). Like the linear structure, the wide angle zigzag has only two nearest neighbors but it has a higher cohesive energy by \( \sim 0.4 \text{ eV/atom} \) due to stronger \( \sigma \) bonds.

The second zigzag structure (specified as T) with bond length \( d = 2.42 \text{ Å}, s = 1.24 \text{ Å} \) and bond angle \( \alpha \approx 61.6^\circ \) formed a near equilateral triangle. The equilateral formation has four nearest neighbors and a cohesive energy \( E_C = 4.4 \text{ eV/atom} \); about 0.6 eV/atom higher than that of the wide angle zigzag formation. This zigzag structure looks promising. The cohesive energy is high (4.4 eV/atom) and the inter-atomic distance (2.4 Å) is close to the bulk value. The P structure \( \alpha = 90^\circ \) is indeed intermediate in cohesive energy to W and T. Table 1 provides all the vital structural parameters of the stable structures. In general \( E_C \) increases with increasing coordination number and decreasing bond angle. The stable structures found in this study for silicon are similar to the structures found in the case of Al [14] despite the difference in the number of valence electrons. The enhanced bonding with puckering of the chains has been discussed by Harrison [21].

The band structures of various silicon "diatomic" chains, L₂, W, T and P are shown in Fig. 3. The BZ edge is located at 0.5 \( \frac{2\pi}{R} \) where \( R \) is the lattice translation vector length. The band structure of L₂ shown in Fig. 3(a) is simply obtained from folding the bands shown in Fig. 1(b) for the linear L chain. Thus at \( \Gamma \) the two lowest \( \sigma \) bands are followed by degenerate \( \pi \) bands (3 and 4) followed by partly occupied \( \sigma^* \)

Figure 4: Charge-density contour plots of: (a) linear L, (b) wideangle W, (c) near equilateral T, and (d) parallel P Si nanowires.
band. 5 lying closest to $E_F$. The band structure of $W$ shown in Fig. 3(b) can then be easily understood. As the bond angle departs from $\alpha = 180^\circ$, $p_y$ and $p_z$ orbitals become inequivalent lifting the degeneracy of the $\pi$ bands. The $\pi$ bands arising from in-plane $p_y$ orbitals dip below $E_F$ pushing the $\sigma^*$ band above $E_F$. The chain is semi-metallic since only a few states are present near $E_F$; the occupied and unoccupied bands touch each other only at one $k$ point.

The band structure of $T$ shown in Fig. 3(c) continues the trend seen in $W$. Namely the $\pi$ bands straddle $E_F$, the filled ones moving further below $E_F$ at the zone-center leading to better cohesion. There are four bands that cross $E_F$ and another band (5) lies just above $E_F$. From this electronic structure we obtain a maximum value of $3G_0$ (since one band crosses twice) for the quantum conductance, where $G_0 = 2e^2/h$. The maximum channel capacity per channel of $G_0$, follows [5] from Heisenberg’s uncertainty principle. The metallic behavior seen for this chain will be further evident from the charge density plots to be discussed below. The band structure for $P$ (Fig. 3(d)) is rather similar to $T$, but due to the lower cohesive energy, this chain is not favored.

The charge-density contour plots for nanowires $L$, $W$, $T$ and $P$ are shown in Fig. 4 in the $z = 0$ plane. The charge accumulation between the atoms for the $L$ structure is due to the formation of the directional bonds arising from the $sp_x$ hybrids. In the other structures, the contribution of $p_y$ continues to increase and the bonds become strong and directional. The charge density plot of the $W$ structure is similar to the plot of the $L$ structure and shows directional bonding among atoms, highly reminiscent of bulk Si. The system is semimetallic and hence not suited as a "metallic" nanowire. For the $P$ structure, $\sigma$ bonds along both $x$ and $y$ are revealed. The charge density plot of $T$ (Fig. 4(c)) shows significant charge delocalization as for the free electron metals. This chain sits in a sea of $\pi$ electrons delocalized over the entire chain. The electronic structure of this nanowire displays metallic behavior. If such metallic Silicon nanowires were to be fabricated, then one could achieve a major integration in nanotechnology.

4 Conclusion

We found that a near equilateral zigzag chain of silicon was most stable among the planar structures that were studied. Its metallicity is derived from a ‘sea’ of $\pi$-electrons which are delocalized over the entire chain. The chain gets its stability since the atoms are held together by strong $\sigma$-bonds formed from appropriate $sp$-hybrids. We will study the effect of doping these nanostructures. Fabrication of these quasi 1D structures and their placement on semiconducting surfaces without losing their metallic properties remains a challenge. If successful, it would considerably advance the field of nanoscience and the semiconductor industry.

REFERENCES