Si-Nanotrees: Structure and Electronic Properties

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We investigate structure and electronic properties of branched silicon nanowires (or “nanotrees”) using large scale quantum mechanical simulations. Our calculations show that such structures are stable for underlying tetrahedral as well as cage-like cores making up the “stems” and “branches” of these nanotrees. Electronic structure analysis shows that the formation of “nanotrees” are accompanied by a narrowing of the HOMO–LUMO gap. This has important implications in their application in molecular devices due to the predicted enhancement in the conducting properties.

Keywords: Molecular Dynamics, Nanostructures, Silicon Electronics.

1. INTRODUCTION

Nanowires are increasingly becoming popular from scientific and technological perspectives. These wires can be grown from a variety of different materials and can even attain lengths approaching tens of micrometers. The current interest in silicon nanowires (Si-NWs) is mainly derived from their tremendous technological potential in nanoscale devices.1–4 One of the major advantages of these nanowires is that they afford tailoring of their electronic properties through selective doping. This property makes them a prime candidate for use in electronic industries where the miniaturization trend needs to be sustained for the foreseeable future. Tetrahedral wire-like structures have been theoretically investigated by various groups.5–10 More recently, structural predictions for small diameters Si-NWs were made by Menon and Richter11 and Marsen and Sattler.12

If two nanowires, one semiconducting and the other metallic, are connected, a hetero-junction is formed that will act like a rectifying diode. Experimentalists, in fact, have succeeded in creating a nanowire diode by joining two differently doped semiconductor nanowires.13–15 While such two terminal hetero-junctions have many uses, they still lack the versatility of the 3-terminal devices where the 3rd terminal could be used for controlling the switching mechanism, power gain, or other transist ing applications that are needed in any extended molecular electronic circuit. Nanowires containing branching structures, therefore, appear to be more promising in technological applications. Very recently, experimentalists working with semiconductor nanowires have reported the synthesis of branched nanowires.16 Furthermore, they have demonstrated that these tree-like nanostructures (“nanotrees”) can be formed in a highly controlled way. The high-resolution transmission electron microscopy (TEM) analysis showed that the branching mechanism gives continuous crystalline (monolithic) structures throughout the tree-like structures. Such structures can lead to the isolation of “Y-” and “T-junctions” of nanowires with tremendous potential in use as three-terminal devices.

Nanowires and nanotrees made of Si have the added advantage that they permit a natural extension of silicon technology to the nanoscale regime and allow a natural integration of nanoscale devices into traditional larger-scale silicon electronic technology. Si-nanowires have been synthesized by laser ablation of metal-containing Si.17 The resulting Si-nanowires are reported to consist of pure Si and have fairly uniform diameter. Further experimental analysis using electron diffraction and high-resolution transmission electron microscopy (HRTEM) suggested the nanowires to consist of an outer layer and a Si crystalline core.18, 19 Synthesis of nanowires of diameter as small as 1 nm has been reported recently.17 In the present work, we investigate the stability of branched nanowires (nanotrees) made of Si atoms using a quantum molecular dynamics method. While Si can exist in many crystalline phases, the most stable of them are all four-fold coordinated. They include the diamond and the clathrate phases.18, 19 Recent theoretical works have shown the Si-nanowires with the crystalline core consisting of the diamond or the clathrate types to be the most stable.20

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We, therefore, focus our investigations on Si-nanotrees whose "stem" and "branches" consist of Si-nanowires with diamond or clathrate type of inner cores.

2. TECHNIQUE

The theoretical method used in the present work is the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy\textsuperscript{18} that allows for full relaxation of covalent systems with no symmetry constraints. This method has been found to be very reliable in obtaining very good agreement with experiment for structural and vibrational properties of Si from dimer all the way to the bulk.\textsuperscript{18} The details of the technique can be found in Ref. [18]. Here we give a brief summary.

If the total energy $U$ of a system is known, the force $F_x$ associated with an atomic coordinate $x$ is given by

$$F_x = -\frac{\partial U}{\partial x}$$

The total energy is given by the sum:

$$U = U_{el} + U_{rep} + U_0$$

where $U_{el}$ is the sum of the one-electron eigenvalues $E_n$ for the occupied states:

$$U_{el} = \sum_{n=1}^{\infty} E_n$$

and $U_{rep}$ is given by a repulsive pair potential

$$U_{rep} = \sum_{i>j} \chi(r_{ij})$$

$U_0$ is constant that merely shifts the zero of energy.

In the non-orthogonal tight-binding scheme the characteristic equation for obtaining the eigenvalues is given by\textsuperscript{18}

$$(H - E_n S)C^n = 0$$

where $H$ and $S$ are the Hamiltonian and overlap matrices, respectively.\textsuperscript{18}

The Hellmann-Feynman theorem for obtaining the electronic part of the force is given by\textsuperscript{18}

$$\frac{\partial E_n}{\partial x} = C^n \left( \frac{\partial H}{\partial x} - E_n S^n C^n \right)$$

In the Slater-Koster scheme the Hamiltonian matrix elements are obtained from the parameters, $V_{ij}$, in terms of the bond direction cosines $l,m,n$.\textsuperscript{18,21} We take the parameters $V_{ij}(r)$ to decrease exponentially with $r$:\textsuperscript{18}

$$V_{ij}(r) = V_{ij}(d_0) e^{-\beta(r-d_0)}$$

where $d_0$ is the sum of the covalent radii of the pair of interacting atoms and $\alpha$ is an adjustable parameter. The scaling of the repulsive term (Eq. (4)) is also taken to be exponential:

$$\chi(r) = \chi_0 e^{-\beta(r-d_0)}$$

In the non-orthogonal scheme, the overlap matrix is calculated in the spirit of extended Hückel theory\textsuperscript{22} by assuming a proportionality between $H$ and $S$:\textsuperscript{18}

$$S_{ij} = 2 \frac{H_{ij}}{K H_{ii} + H_{jj}}$$

where $K$ is the non-orthogonality coefficient. The diagonal elements of $H_{ij}$, as in the orthogonal theory, are taken to be the valence $s$ and $p$ energies. The off-diagonal interatomic matrix elements are given in terms of the Hamiltonian matrix elements in orthogonal theory, $V_{ij}$, by

$$H_{ij} = V_{ij} \left[ 1 + \frac{1}{K} - S_{ij} \right]$$

where,

$$S_{ij} = \frac{(s_{s} - 2\sqrt{3} s_{sp} - 3 s_{pp})}{4}$$

is the nonorthogonality between $sp^3$ hybrids.\textsuperscript{18} The quantities $S_{ij}$, in turn, are determined from

$$(11) \hspace{1cm} S_{ij} = \frac{2 V_{ij}}{K (E_i + E_j)}$$

We take a simple exponential distance dependence in the nonorthogonality coefficient, $K$,

$$K(r) = K_0 e^{-\beta(r-d_0)^2}$$

Making use of all these terms, Eq. (1) can now be used to obtain trajectories of the particles for performing molecular dynamics simulations.

3. PARALLELING GTBMD SCHEME

For large scale simulations, GTBMD involve the following calculations at each time step:

- Obtaining Hamiltonian and the overlap matrices as parameterized analytical functions of inter-atomic distances.
- Computing the forces using the eigenvalues and eigenvectors.
- Moving the atoms to new positions.

The computational costs are dominated by those for solving the eigenvalue problem. The matrix dimension is number of basis times the number of atoms in the simulation. For models of interest with several thousand atoms, the matrix dimension $N$ is in the range 10,000 to 50,000. In each time-step of the simulation, the generalized eigenvalue problem has to be solved and a simulation typically involves nearly a thousand time-steps. An additional challenge is that the GTBMD requires at least $N/2$ eigenvalues as well as the corresponding eigenvectors at each time-step. The computational cost of one instance of the eigenvalue problem grows as $O(N^3)$. Consequently, for matrix dimensions of interest, the computational costs are prohibitive. Furthermore, storage demands also grow prohibitively. Such simulations are, therefore, not feasible
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We solve the generalized eigenvalue problem of the form $H\psi = \lambda S\psi$ in parallel using SCALAPACK. We used a cluster with 80 compute nodes where each node has a dual 2.4 GHz AMD processor with 8G main memory. The re-orthogonalization required for the eigenvector computation constitutes the bulk of the costs. These eigenvalue computations typically have the following three main steps:

(i) compute a tridiagonal matrix $T$ using orthogonal transformations and an orthogonal factor, $Q$;
(ii) compute all eigenvalues of $T$ and, (iii) compute eigenvectors of $T$ and then use $Q$ to compute eigenvectors of the original matrix.

**4. APPLICATIONS TO Si-NANOTREES**

We next present applications of the formalism to branched Si-nanowires or Si-"nanotrees." It should be noted that the nanowires synthesized in experiments are hydrogen covered, while the nanowires used in our simulations are made of pristine Si. The Si-nanotrees and stems considered in the present work consists of several thousand Si atoms. A fully quantum mechanical simulations for such large systems using the serial GTBMD method is computationally prohibitive. We, therefore, use the parallelized GTBMD method in Section 3.

We perform GTBMD simulations for the Si-nanowires at zero temperature. The nanowires are carved out from the most stable crystalline forms of Si so that their interiors resemble bulk Si. The relaxation process results in surface reconstruction common to bulk Si surfaces. We consider three different types of Si-nanowires; portions of which are shown in Figure 1. The largest diameter of these nanowires is $\approx 4$ nm. The total number of Si atoms in each of these nanowires range from 2000–2500. All these nanowires have a four-fold coordinated inner core surrounded by an outer surface of atoms with three-fold coordination. They belong to two general category; tetrahedral and clathrate (cage-like). The tetrahedral nanowire is denoted by Si(Td). The clathrate nanowires are further divided into two categories. The first has an inner core made of the Si clathrate structure consisting of a face centered cubic (fcc) lattice with a 34 atom basis. We denote this by Si(34). The other has as its inner core a Si clathrate structure consisting of a simple cubic (sc) lattice with a 46 atom basis, denoted by Si(46). All the structures shown in Figure 1 are fully relaxed without any symmetry constraints. The surface atoms of all these nanowires show reconstructions that lower the surface energy.

We next investigate the stability of "nanotrees" with stems and branches consisting of Si(Td), Si(34), and Si(46) nanowires. The total number of Si atoms in each of these nanowires range from 2500–3000. Each nanotree is constructed by attaching smaller diameter nanowire branches with cores that are identical to the stem in a such a way that all the tree structures have four-fold coordinated inner cores surrounded by outer surface of atoms with three-fold coordination. We then fully relax the resulting structures without any symmetry constraints. The atoms in the junction region are the most affected by the relaxation process as they move to relieve the strain. Portions of the relaxed structures are shown in Figure 2. The surface reconstruction, coupled with branching results in interesting junction regions. These regions appear smooth for Si(34) and Si(46) "nanotrees," while in the case of Si(Td) "nanotree" the junctions appear abrupt. This is understandable since the underlying cage-like arrangements of Si(34) and Si(46) structures allow seamless connection between stems and the branches. This is because the cage-like forms are more isotropic than the tetrahedral forms.

The branching also gives rise to interesting electronic properties. The "stems" are essentially finite length Si-nanowires that have core atoms with four-fold coordination, while the surface atoms have three-fold coordinations and show reconstructions that minimize the surface energies for these structures. Formation of branches induces additional strains on the surface atoms in the
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Fig. 2. Portions of Si-nanotrees with stems and branches made of tetrahedral (top), clathrate structure with 34 atom fcc unit cell (lower left), and another clathrate structure with 46 atom sc unit cell (lower right).

junction area resulting in the introduction of states in the electronic band gaps. This is illustrated in Figure 3 where we show the computed electronic densities of states (DOS) for “stems” and “nanotrees” of Si(Td). The electronic structure analysis is performed using a \( sp^3 \) tight-binding model\(^{25} \) that correctly reproduces the band gap for bulk Si in the diamond and clathrate phases. The DOS for the “stems” show a highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gap value of 0.57 eV which is smaller than that for the bulk diamond phase of silicon (1.1 eV). This is because of the presence of a significant number of three-fold coordinated unpassivated surface Si-atoms. Formation of “nanotrees” causes the creation of states in the HOMO–LUMO gap, narrowing the gap value to 0.16 eV. Furthermore, more states from the unoccupied levels are pulled in towards the Fermi level, \( E_F \) (shown as dashed line). This is expected to enhance conductivity due to more conduction channels being available. For small diameter pristine tetrahedral Si-nanowire, it is well-known that quantum confinement increases the gap. For large enough diameter, however, the gap is expected to approach that of the Si bulk. A systematic study of gap dependence on diameter and growth direction can be found in Ref. [26].

In summary, we have presented results for structure and stability studies using large scale quantum mechanical simulations of “nanotrees” made from Si and shown that such structures are stable. Electronic structure analysis shows that formation of “nanotrees” are accompanied by a narrowing of the HOMO–LUMO gap. This has important implications in their application in molecular devices due to the predicted enhancement in the conducting properties. The present work is supported through grants by NSF (ITR-0221916), DOE (00-63857), and US-ARO (W911NF-05-1-0372).

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Received: 26 April 2006. Accepted: 3 August 2006.