



Interaction of nucleobases with silicon nanowires: A first-principles study

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ABSTRACT

The interaction between the nucleic acid bases – adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U) – and a hydrogen-passivated silicon nanowire (SiNW) is investigated within the framework of density functional theory. The calculated binding energy of the nucleic acid bases with the SiNW shows the order: $G > A \approx C \approx T \approx U$. This suggests that the interaction strength of a hydrogen passivated SiNW with the nucleic acid bases is nearly the same-G being an exception. The electronic structure of the nucleobase-SiNW complex is used to further characterize the nature of the interaction showing that it is likely electrostatic in nature.

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1. Introduction

Silicon nanowires (SiNWs), with a diameter of ~ 10 nm are an interesting family of one-dimensional nanoscale materials [1] which can be seamlessly coupled with existing devices based on silicon [2]. Furthermore, the size and doping level of SiNWs can easily be controlled during the synthesis process [1,3,4], making them an attractive host material for the next generation of sensing devices at nanoscale [5–8]. The central idea is that a conductivity change can be detected as a response to variation of surface electric potential [9–11]. This scheme enables sensing applications of SiNW based field-effect transistors since the electric potential change induced by the binding of a target molecule to the surface of the semiconducting substrate is analogous to a change in the applied gate voltage.

Silicon prefers the so-called sp^3 tetrahedral coordination in a lattice. Unsaturated dangling bonds on the surface of a SiNW are highly reactive. As a consequence, SiNWs grown in experiments tend to be passivated [2]. The nature of the surface passivation is an important aspect in determining the properties of SiNWs, especially for those with smaller diameters. For example, hydrogen termination yields *p*-type characteristics of SiNWs [12] while phosphorus passivation is predicted to further increase the *p*-doping level in SiNWs [13]. In describing the interaction of a SiNW with an analyte molecule on its surface, as a SiNW would be used in a realizable sensor, the inclusion of a passivation layer is paramount.

In this Letter, we present the results of our first-principles study of a hydrogen passivated SiNW interacting with deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Since full scale quantum

mechanical calculations consisting of DNA-strands are prohibitively expensive, we begin with the nucleobases, the building blocks of the genetic macromolecules (DNA/RNA) to discover factors that play an important role in these kinds of interactions. We will consider the interaction of a passivated SiNW with adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U). Since the interaction of nucleobases with graphene [14] and metallic carbon nanotubes (CNTs) [15] is predicted to be dominated by the so-called van der Waals (vdW) forces, our focus will therefore be to identify the type of interaction for the case of SiNWs which are semiconducting in nature. It is expected that a complete understanding of the underlying physics and chemistry of the sensing mechanism of DNA would help in developing SiNW based biomolecular sensing devices.

2. Computational method

The local density approximation (LDA) of the exchange and correlation functional forms within density functional theory, as incorporated in the SIESTA program package was used [16]. We make use of Troullier-Martins type pseudopotentials [17] and double- ζ basis sets with polarization functions for all atoms in our electronic structure calculations. A minimum vacuum distance of 15 Å between neighboring system images was used. The *k*-space integration was done with a $1 \times 1 \times 4$ sampling grid. The calculated equilibrium configurations are fully relaxed, with residual forces smaller than 0.04 eV/Å.

It is noted that the LDA functional, due to a lack of the description of long-range dispersive forces is, in principle, not an optimal choice for calculating interaction energies of weakly-bonded systems consisting of nucleic acid bases. On the other hand, many-body perturbation theory, which is more suitable for describing long range forces, becomes prohibitively expensive for complex

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systems as considered here. Furthermore, the LDA-DFT level of theory gives almost the same equilibrium configuration as the GGA + vdW level of theory in systems like graphene interacting with the nucleobases [14,18]. A recent theoretical study has also examined the performance of density functional methods for H-bonded interaction energies in biomolecules including DNA and RNA base pairs [19]. It was concluded that these methods can yield reasonable values of binding energies in systems consisting of biomolecules. Thus, these conclusions give us confidence in the results obtained in the present study to be reasonably accurate in describing the interaction of the nucleic acid bases with SiNWs.

3. Results and discussion

3.1. Nucleobases

The total energy and optimized geometrical structure of the isolated nucleobases were found prior to the nucleobase-SiNW complex calculations. The bond lengths and bond angles of the optimized equilibrium structures for the nucleobases are in good agreement with earlier reported studies [20,21]. The calculated binding energy for each nucleobase at the LDA-DFT level of theory, defined as the total energy difference between the equilibrium configuration of the molecules and the isolated individual atoms, is 6.82, 6.76, 6.87, 6.83 and 6.76 eV for A, T, G, C, and U respectively.

3.2. Passivated silicon nanowires

In this Letter, a SiNW is constructed of [100] bulk silicon with a square cross section of dimension 14 Å (Figure 1). The surface dangling bonds are passivated with hydrogen [2]. Thus, all Si atoms are sp^3 coordinated as in bulk, with no dangling bonds on the surface of the SiNW. The resulting passivated SiNW is finite in the two dimensions of its cross-section, and infinite (periodic) in length.

In the optimized passivated SiNW, the bond distance between silicon and hydrogen atoms, R_{Si-H} , is 1.52 Å. At the core of the SiNW, the calculated silicon-silicon bond length, R_{Si-Si} , is 2.33 Å. The silicon-silicon bond is slightly shortened to 2.32 Å at the surface of the SiNW. The calculated bond lengths are in excellent agreement with the results of the GGA-DFT level of theory where R_{Si-Si} (core) and R_{Si-Si} (surface) were calculated to be 2.36 and 2.35 Å, respectively [22].

3.3. Nucleobases with SiNW

In calculations to obtain the equilibrium configurations, the nucleobases were allowed to approach one surface in a direction perpendicular to the axis of the nanowire. The plane of the hexagon/pentagon rings of the nucleobases is parallel to the surface of the SiNW. Unlike small -diameter carbon nanotubes (CNTs)

where the tube curvature has an effect on the binding energy [15], a SiNW has flat surfaces due to the passivating hydrogen atoms. In order to simulate an electronic environment resembling more closely the situation in DNA and RNA, the N atom of the base molecules linked to the sugar ring in a nucleic acid was terminated with a methyl group [14,15,23,24].

The equilibrium configurations (Figure 2) of the bioconjugated SiNW are obtained by a full optimization of the nucleobase-SiNW complex in which all atoms were free to relax. No significant changes in the bond lengths of the nucleobases are seen in the equilibrium configurations. Likewise, the surface bond lengths of the passivated SiNW remain nearly the same. Only a few passivating hydrogen atoms that are near an oxygen atom of the nucleobases experience perturbations (about 0.2 Å). The calculated distance between a nucleobase and SiNW is about 2.0–2.1 Å which is defined as the separation between the hexagonal ring-center of the molecule and the passivated surface.

Interestingly, the nucleobases show a slight tilt towards the underlying passivated surface with the estimated tilt angle being 2°, 17°, 12°, 5°, and 5° for A, C, G, T, and U, respectively in the equilibrium configurations. The tilt angle describes the orientation of the ring plane of the nucleobases and is defined as the angle between the base ring plane and the plane defined by frozen hydrogen atoms of the passivation surface layer of the SiNW. It appears that adenine which contains no oxygen atom yields a nearly parallel configuration to the surface. On the other hand, the presence of one or two oxygen atoms in other nucleobases can facilitate a weak $O \cdots H-Si$ interaction which seems to provide tilting of the nucleobases on the surface of SiNW. The nucleobases C and G are levered out-of-plane to a greater degree by their single oxygen atom, than are U and T which possess two distributed oxygen atoms that provide a level of counterbalance.

The interaction strength between a nucleobase and a SiNW can be characterized by the binding energy (E_b), defined as the total energy difference between the equilibrium configuration of the complex (Figure 2) and the isolated individual constituents (base molecules and SiNW). The calculated binding energy is 1.74, 1.72, 2.12, 1.64 and 1.53 eV for A, C, G, T and U, respectively. Thus, the guanine-SiNW complex exhibits a slightly higher binding energy than the other four bases, which show a similar binding strength. This is somewhat similar to nucleobases interacting with a semiconducting boron nitride nanotube (BNNT) [23], but significantly different from the case of nucleobases interacting with a metallic carbon nanotube (CNT) which follows the order of $G > A > T > C \sim U$ [15]. Since the E_b associated with CNTs was found to be correlated with the polarizability of individual bases, it was suggested that the interaction of nucleobases with CNTs was governed by a dispersion force like van der Waals which varies with the polarizability of the interacting entity [15]. For the case of BNNT, it was suggested that dispersive forces with a marginal

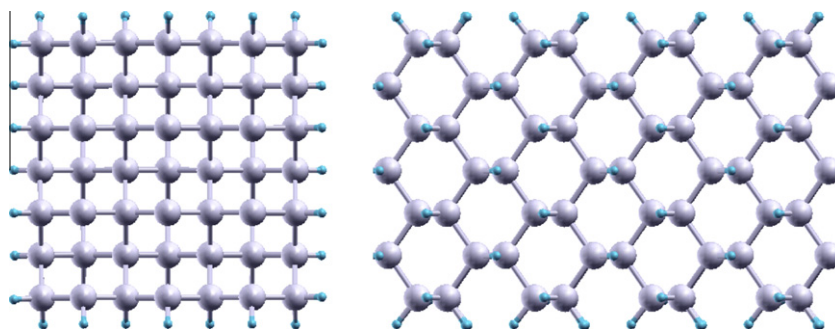


Figure 1. Hydrogen passivated SiNW (color online). Silicon: grey (grey), hydrogen: light blue (grey). Left: cross-section view. Right: top view of surface of wire (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

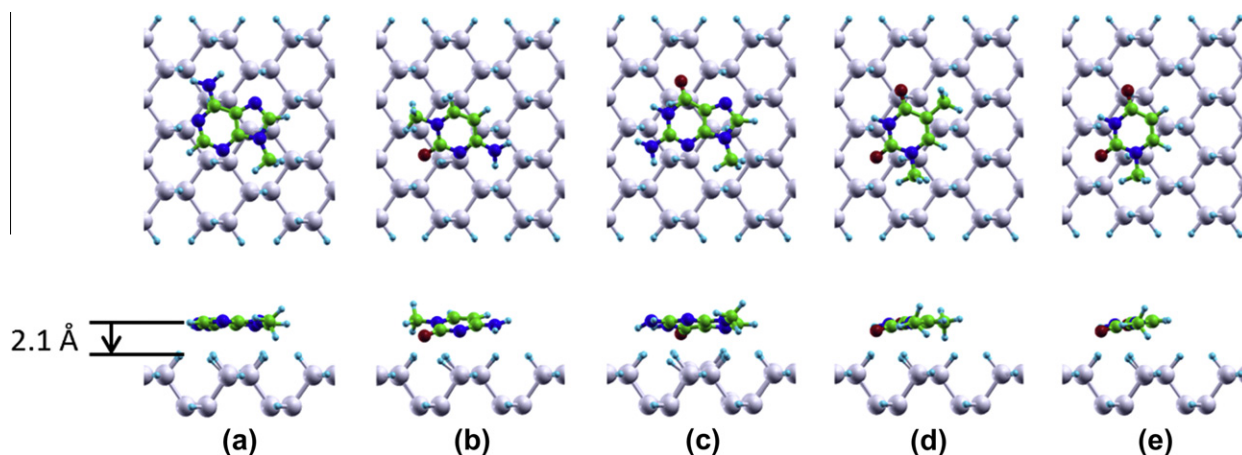


Figure 2. Top and side views of the equilibrium configurations of nucleobases interacting with a SiNW: (a) adenine, (b) cytosine, (c) guanine, (d) thymine and (e) uracil (color online). Silicon: grey (grey), hydrogen: light blue (grey), nitrogen: dark blue (black), carbon: green (dark grey), oxygen: red (black) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

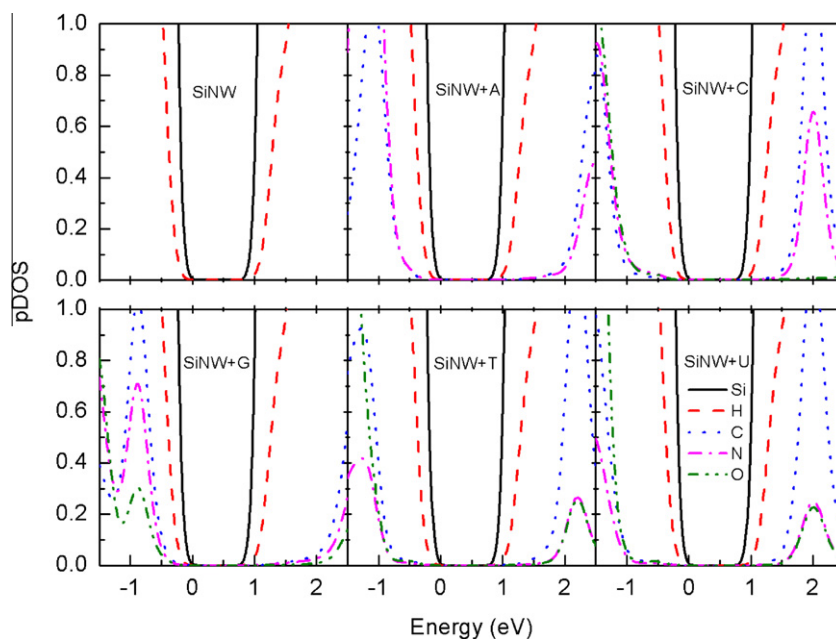


Figure 3. The calculated species-resolved projected density of states (pDOS) of pristine and conjugated SiNWs.

contribution from electrostatic forces provide for the stability of the bioconjugated complex [23].

Since the passivated SiNW have sp^3 -like bonding, we do not expect the van der Waals like dispersive interactions to play any role in the stabilization of the bioconjugated complex consisting of the passivated SiNW. Instead, a noticeable degree of charge transfer from the nucleobase to the passivated SiNW suggests the interaction to be dominated by electrostatic forces. Mulliken population analysis indicates the transfer of 0.3, 0.3, 0.4, 0.2 and 0.2 electrons from A, C, G, T and U, respectively to the passivated SiNW. On the other hand, charge transfer between a nucleobase and a CNT or a BNNT is much less significant [15,23]. The amount of charge transferred from a nucleobase to the SiNW also agrees with the rank order of the binding energy calculated for the complex. This is consistent with the results of a previous investigation which used classical molecular dynamics simulations on the nucleobases interacting with a Si (111) surface functionalized with alkyl-amine molecules. It was suggested that the interactions involving the ring

hydrogen bond donors and acceptors of the nucleobases mainly provide the stability of the bioconjugated complexes [24,25].

Figure 3 shows the calculated density of states (DOS) for the passivated SiNW which suggests it is semiconducting with a band gap of about 0.82 eV. The projected density of states finds both the valence band maximum and conduction band minimum to be associated with the Si atoms, thus reflecting the electronic structure of core of the SiNW [26].

For the cases of the conjugated SiNWs, there appears to be no change in the band gap values; the calculated gap is 0.80, 0.80, 0.79, 0.81 and 0.81 eV for A, C, G, T and U-conjugated SiNWs. As shown in Figure 3 the electronic states at the valence band maximum and conduction band minimum remain associated with the Si atoms of the wire of the nucleobase-SiNW complex. For each complex, the electronic states contributed by the nucleobase fall outside the gap; i.e., below the valence band maximum or above the conduction band minimum. This is in contrast to the case of nucleobase interactions with a semiconducting BNNT where a

mid-gap state appears representing a mixing of electronic states of the nucleobases and the BNNT [23]. In the case of BNNT, boron and nitrogen atoms are exposed to the external environment without any passivation, facilitating a direct hybridization of states between boron/nitrogen and nucleobases. In the present work, the silicon atoms are protected by the hydrogen passivation, leading to a much weaker interaction between nucleobases and silicon atoms. Thus, the interaction between the nucleobases and the passivated SiNW does not modify the semiconducting nature of SiNWs.

4. Conclusions

The interaction of the nucleobases with hydrogen passivated SiNW was investigated using a first-principles method based on density functional theory. The equilibrium configurations of the nucleobase-SiNW complexes have the nucleobases lying with their ring planes nearly parallel to the surface of the nanowire. The tilt of the C, G, T, and U nucleobases exhibits a weak $O \cdots H-Si$ interaction. Except for G, the base molecules exhibit almost similar interaction strengths with a SiNW. The magnitude of the calculated binding energy exhibits the following order: $G > A \approx C \approx T \approx U$. Charge transfer by each nucleobase in forming a nucleobase-SiNW complex also follows this trend. An examination of the density of states for a passivated SiNW and the nucleobase-SiNW complexes shows semiconducting behavior and that the band gap remains defined by states contributed by the Si atoms of the nanowire. No mid-gap states are created in forming the complexes. The calculated band gap of the passivated SiNW is essentially unchanged in the interaction. As such, the nature of bonding between a nucleobase and a hydrogen passivated SiNW is dominated by electrostatic interactions with the band gap of the complex defined by the passivated SiNW.

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