Moisture Assisted Electron Transport in Si-C Nanotubes: an *ab-initio* study

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ABSTRACT

We investigate the effect of moisture-adsorption on the electron transport properties in a (8, 0) semiconducting silicon-carbide nanotube (SiCNT) by applying self consistent non-equilibrium Green's function formalism in combination with density-functional theory to a two probe molecular junction constructed from moisture-adsorbed SiCNTs and gold (Au) electrodes. Results obtained by relaxing an H_2O molecule (water) over a (8, 0) SiCNT show that water molecule binds with SiCNT. The formation of Si-O bond (bond length ~ 1.95 Å) between the SiCNT and H_2O molecule was discovered. However, previous studies on H_2O adsorbtion in carbon nanotubes (CNTs) have shown the formation of C-H bond at the CNT surface. A different position and orientation of the H_2O molecule over SiCNT was also tried, however, the nearest silicon (Si) atom was still found as the favorable position resulting in Si-O bond formation. Bias voltage dependent current characteristic and transmission spectrum characteristic show an increase in current with applied bias resulting from the deloclaised orbitals. A comparative analysis based on the studies on defect free SiCNT and when bringing more than one H_2O molecule near the SiCNT surface is required to comment further on the conductivity in the moisture adsorbed SiCNTs.

Keywords: nanotube, SiCNT, adsorption, DFT, NEGF

1 INTRODUCTION

In the process of the growth of CNTs or SiCNTs, a variety of structural defects inevitably occur, which can affect their electronic properties [1] [2]. It is possible for CNTs or SiCNTs to absorb moisture and other contaminants during the fabrication process, which has drawn attention of researchers in recent years [3-6]. Adsorption of H_2O molecule over CNT surface has been investigated previously by [5] [6]. However, the adsorption of H_2O molecule over SiCNT surface is still an open question which this paper is attempting to address.

There have been very few theoretical studies on the interaction of water molecules with CNTs. In [5], it was reported that water molecule does not bind with CNT. The study lacked full relaxation of the water molecule over CNT and was limited to only one water molecule. Another study [6] addressed these limitations and performed a full relaxation of water molecule over carbon dimer and concluded that water molecule binds with CNT. It was found that carbon (C) atom in CNT binds with hydrogen (H) atom of water molecule. The C-H binding was reported to have an adverse effect on the conductivity of the CNT.

In an attempt to study the adsorption of water molecule over SiCNTs, a H_2O molecule was relaxed over the (8, 0) SiCNT surface. Surprisingly, the relaxation resulted in the formation of Si-O bond between silicon (Si) atom of SiCNT and oxygen (O) atom of water molecule. Different positions and orientations of the H_2O molecule over SiCNT were also tried, however, the nearest silicon (Si) atom was still found as the favorable position resulting in Si-O bond formation. This result is in contrast to water adsorption in CNTs [6] where carbon atom of CNT binds with hydrogen atom of water molecule (in SiCNT, silicon atom of SiCNT binds with oxygen atom of water molecule). We also investigate the bias voltage dependent current charateristic and transmission spectra of the water adsorbed SiCNT and found the increase in current due to the delocalization of orbitals at higher bias. A comparative study on defect free SiCNT and when bringing more than one H_2O molecule near the SiCNT surface is required to comment on the effect of moisture (water) adsorption on the overall conductivity of the SiCNT. This comparative study will be reported in future as it is time consuming and requires heavy computational resources.

2 MODEL AND METHOD

A relaxed structure of (8, 0) SiCNT with H_2O molecule over the SiCNT surface is shown in Fig. 1. This is a two probe geometry that consists of a left electrode, right electrode and a central region (scattering region). Si-C bond length of 1.78 Å [7] [8] and 1:1 Si-C ratio were considered in constructing this structure.

An (8, 0) SiCNT is semiconducting by nature hence it cannot be used as electrodes, as semiconducting leads will give no current. Unless the electrode is conducting, there will be no injection and hence no current. We used gold (Au) electrodes for building two probe geometry with (8, 0) SiCNT in the central region, gold electrodes have been used previously in studying the electronic properties of CNTs and SiCNTs by [9] [10] and also by [11] for doped SiCNTs. We have also used Au electrodes in our previous research works [1] [2]. Length dependency is neglected by

considering a minimal length segment of nanotube in the central region. The lengths of the central regions, screening layers and the Both left and right electrodes are made up of three 5 X 5 Au layers perpendicular to the nanotube axis, distance between the SiCNT and Au electrode is set as 1.6 Å [9], central region is of 8 periods (80 C and 80 Si atoms), screening layers are made of two 5 X 5 Au layers.

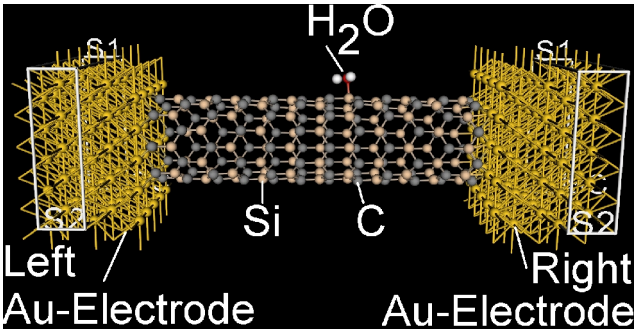

Figure 1: Two Probe setup: SiCNT is placed between (5x5x5) Au-electrodes with electrode-SiCNT spacing ~ 1.25 Å, Si-C bond length ~ 1.78 Å [1]. Adsorbed H_2O molecule is also shown over the SiCNT.

The above described two probe geometry is used for studying the transmission spectrum (Fig. 2), molecular orbitals (Fig. 3) and current-voltage characteristics (Fig. 4).

2.1 Simulation Parameters

To obtain transmission spectrum and *I-V* characteristics, self consistent calculation are performed on an *ab initio* based simulator called Atomistix [11] which uses density functional theory (DFT) and non equilibrium Green's functions formulations (NEGF) together for obtaining electronic transport properties of molecules and devices. More details about the method and software could be found in previous reports [12-15].

The simulation parameters were selected to provide accurate measurements as reported for CNTs [13-15] and are following: mesh cut-off energy was *400 Ry*, basis set was double zeta polarized with 0.001 Bohr radial sampling, exchange correlation functional was set to local density approximation (LDA) type with double zeta polarized (DZP) basis set, Brillouin zone integration parameters of electrodes are taken as (3, 3, 500). Electrode temperature was set to *1000 K* which makes the convergence easier; it has no effect on the overall measurement which was also verified at lower electrode temperatures. It is important to keep in mind about the uncertainty in the calculated LDA band gap as it is well known that the LDA underestimates the width of the band gap due to the self-interaction of the electrons. The above parameters were used by [1] [2] [16] and several others to obtain accurate results using LDA.

3 RESULTS AND ANALYSIS

Results describing the transport properties are presented in this section.

3.1 H_2O molecule binding with SiCNT

A water molecule is fully relaxed over SiCNT surface using Quasi-Newton geometry optimization methods until all residual forces on each atom are smaller than 0.05 eV/Å. Si-O bond (bond length ~ 1.95 Å) between silicon (Si) atom of SiCNT and oxygen (O) atom of water molecule was observed in the relaxed structure which was also verified at various position and orientation of the H_2O molecule over SiCNT.

3.2 Equilibrium and Non-Equilibrium Transport Properties

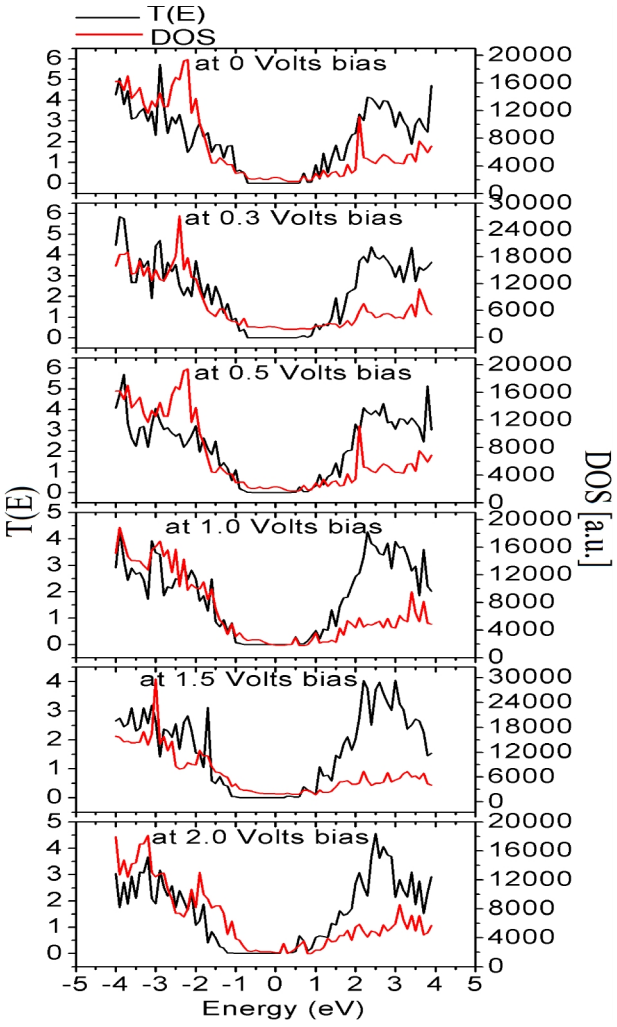

Fig. 2. Transmission spectrum T(E) and DOS in the bias range 0 to +2.0 V. Fermi level is set as 0 eV, as in [1]. T(E) follows DOS.

The transmission spectrum describes the probability for electron with incident energy (E) to transfer from the left electrode to the right electrode under applied bias voltage (V), described in the next section. Transmission spectrum T(E) is plotted in Fig. 2 by black curve, here the Fermi energy is set as 0 eV [1] [16], DOS is shown by red curve. The equilibrium transport properties (no bias voltage applied) of the SiCNTs are studied first. A perfect (8, 0) SiCNT is semiconducting in nature, a water adsorbed SiCNT is also semiconducting which is confirmed by the transmission gap (transmission coefficient is zero) around Fermi level for semiconducting tube,as shown in Fig. 2.

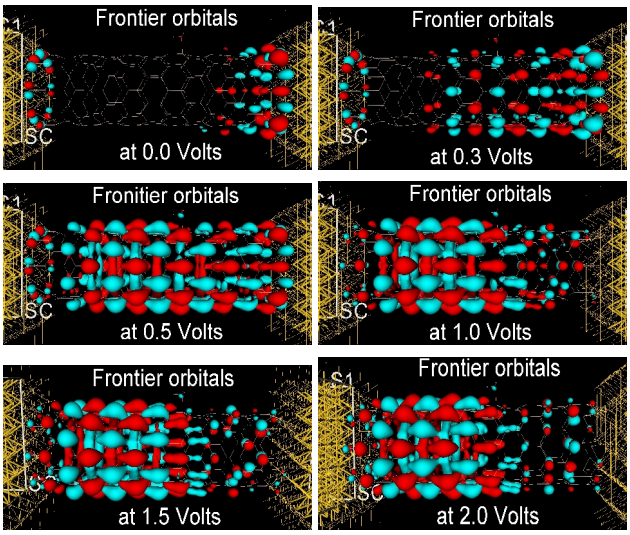

Fig. 3. Frontier orbitals of the MPSH (Molecular Projected Self-Consistent Hamiltonian) at different bias voltages.

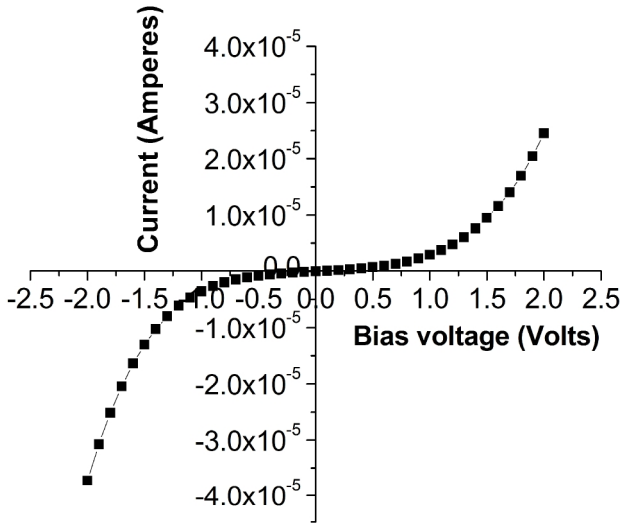

Fig. 4. I-V characteristics of H_2O adsorbed SiCNT. Rectification is negligible and NDR is absent.

The eigenstates of molecular projected self-consistent Hamiltonian (MPSH) are closely related to the poles of Green's function, which roughly corresponds to these peaks of the transmission spectrum in Fig. 2. These peaks are actually the new electronic states developed around the Fermi level, which play an important role in the formation of frontier orbitals (HOMO and LUMO). The localization of frontier orbitals is weakened with increase in bias voltage and more orbitals are seen to contribute to current with the increase in bias window, which could also be observed by comparing frontier orbitals (FO) at zero bias with the FOs at high bias in Fig. 3. From the analysis of Fig. 3, it is observed that FOs at low and high bias has contributions from H_2O molecule.

I–V characteristics of moisture-chemisorbed SiCNT in Fig. 4 show that both the currents under positive and negative bias voltages have an exponential growth and decay. Rectification observed is negligible as the current is seen to increase exponentially after a forward and reverse cut-in (threshold) voltage of ~0.5 volts. Also, the negative differential resistance (NDR) region seems to be suppressed in the bias range -2 to +2 Volts, which is due to the introduction of new electronic states around the Fermi level that enhances the conductivity. HOMO-LUMO shift at low and high bias voltages (see Fig. 5), which is due to the potential shift with applied bias and also due to the inclusion of LUMO in non-equilibrium density matrix which makes the spectrum shift more complex.

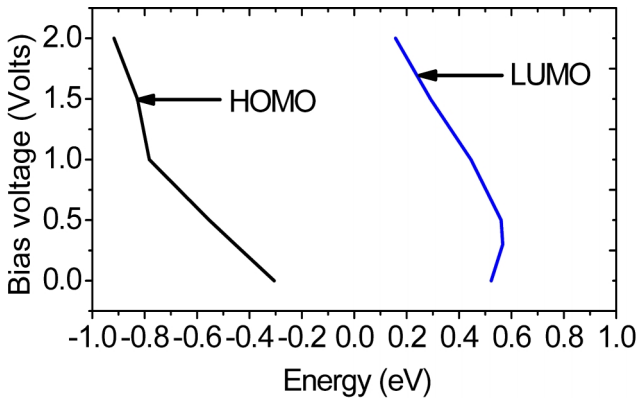

Fig. 5. HOMO-LUMO shift with applied bias.

4 CONCLUSION AND FUTURE WORK

Moisture adsorption in SiCNT is investigated. Full relaxation of H_2O molecule over SiCNT shows binding of H_2O molecule with SiCNT. Silicon atom of SiCNT participates in binding with oxygen atom of water molecule which is in contrast to water adsorption in CNTs where a carbon atom of CNT binds with hydrogen atom of water molecule. We also studied the effect of adsorption on electron transport properties using density functional theory

in combination with non-equilibrium Green's function and found the increase in current at higher bias voltages which is due to the delocalization of molecular orbitals at higher bias and due to an increase in the number of orbitals contributing towards the current. A comparative study on defect free SiCNT and when bringing more than one H_2O molecule near the SiCNT surface will be reported in future to investigate the effect of moisture (water) adsorption on the overall conductivity of the SiCNT.

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