Electron transport of nanotube-based gas sensors: An *ab initio* study

Arta Sadrzadeh, Amir A. Farajian, and Boris I. Yakobson[a)]
*Department of Mechanical Engineering and Materials Science and Department of Chemistry,
Rice University, Houston, Texas 77251, USA*

The effect of physisorption of NO_2 gas molecules on quantum transport properties of semiconducting carbon nanotubes is studied using *ab initio* calculations and Green function formalism. The results show that the conductance change is mainly due to the electric dipole moment of NO_2. It is also shown that upon exposure of nanotube to different concentrations of gas, the common feature is the shift in conductance toward lower energies. This suggests that physisorption of NO_2 will result in a decrease (increase) in conductance of *p*-type (*n*-type) nanotubes with Fermi energies close to the edge of valence and conduction band. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2829609]

The utilization of semiconducting single-walled carbon nanotubes (S-SWNTs) as electrochemical sensors has attracted much attention in the past few years, perhaps because it is one of the closest applications of nanoscience to commercial arena.[1] It is particularly intriguing because detecting molecules at such low concentrations (~ 1 ppb) had not been achieved previously by other electrical sensors.[2] Following the original report of Kong *et al.* on detecting the gaseous molecules NO_2 and NH_3,[3] several experiments have been performed, mostly reconfirming the effect.[2,4,5] There have been some theoretical investigations as well on the mechanism of adsorption and binding energies of such molecules on SWNTs.[6–10] However, a theoretical account for the effect of such adsorption on quantum conductance is still lacking.

This letter is an attempt to fill the gap between the theory and experiment in explaining the observed change in electric conductance of a S-SWNT as a result of exposure to different concentrations of NO_2 gas molecules. We calculate such conductance change for a (10,0) SWNT. The computations were based on Green function formalism for conductance, in conjunction with density functional theory (DFT) calculation of electronic structures. For conductance calculations, TARABORD code[11] was used. DFT computations were performed using GAUSSIAN 03 package.[12] Generalized gradient corrected exchange and correlation functionals BLYP (Refs. 13 and 14) and 3-21G basis set were used for all electronic structure calculations. The initial relaxed structure for nanotube was obtained by Hartree-Fock approximation and 6-31G (d,p) basis set. The corresponding relaxed structure for NO_2 was obtained by MP2/6-31G (d,p).

There are several reports on the adsorption mechanism of NO_2 on SWNTs.[6–10] These results are mostly based on DFT calculation of the relaxed position of the molecule on the nanotube. The binding energies and the distances between the molecule and the nanotube, reported for adsorptions on a (10,0) SWNT, are in the range of $0.3-0.8$ eV and $2-3$ Å, respectively,[6–10] and correspond to physisorption. The results also show that within the same method, binding energies are not too sensitive to the orientation of the molecule or the position at which it is attached to the nanotube (difference in binding energies is of order of $k_B T$ at room

temperature). Noting this fact, we use one of the relaxed geometries with the lowest binding energy within local spin density approximation (LSDA)[10] for calculation of conductance. In this configuration, the nitrogen atom is located on top of a carbon atom and NO_2 molecule is parallel to the tangent plane to the nanotube, as shown in Fig. 1. Our calculations show that the main features in conductance change are the same for different orientations of the adsorbed molecules,[15] therefore, the conclusions drawn later are applicable for those orientations as well. We consider three different surface coverages (SCs), with a distance of 2.7 Å between the nitrogen and the underlying carbon. It is useful to parameterize the SC by the number of NO_2 molecules per hexagon (θ). Therefore, the three cases in Fig. 1 correspond to $\theta=2.5\%$ (a), 5% (b), and 10% (c). Surface coverage is obviously proportional to the gas concentration. The values used here for θ are chosen to lie in the range of experimental conditions, based on the relation[16]

$$\theta = \frac{P}{\nu_0 \sqrt{2\pi m k_B T}} e^{E_B/K_B T}, \qquad (1)$$

where P is the pressure, ν_0 is the attempt frequency (10^{12} s^{-1}), m is the mass of the molecule (NO_2), T is the temperature, and E_B is the binding energy. For $P=5$
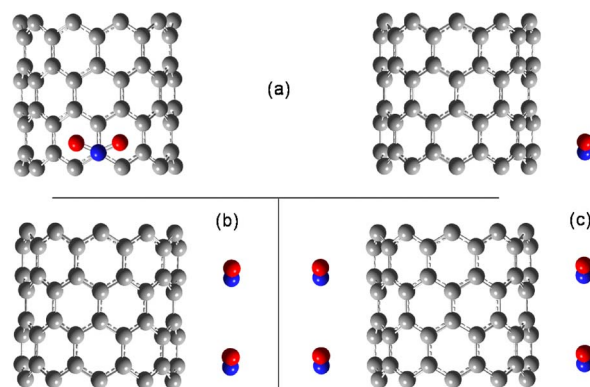

FIG. 1. (Color online) (a) Front (left) and side views of the NO_2 molecule adsorbed on a (10,0) SWNT at the lowest surface coverage (SC) with one molecule per two unit cells of the nanotube ($\theta=2.5\%$). (b) Medium SC (one molecule per unit cell, $\theta=5\%$). (c) High SC (two molecules per unit cell, $\theta=10\%$).

a)Electronic mail: biy@rice.edu.

$\times 10^{-3}$ Pa and room temperature,[10] we get $\theta = 0.1\%$ (14.5%) for LSDA (LDA) value of the binding energy $E_B = 0.5$ eV (0.62 eV). It should be noted that Eq. (1) is valid when the adsorption sites are mostly free.

In order to calculate the conductance of the nanotube, we need the *ab initio* calculation of the Hamiltonian and overlap matrices (in atomic orbital basis) for the conducting channel and for each principal layer of the semi-infinite source and drain contacts, as well as the corresponding coupling matrices between them.[11,17] A principal layer consists of the minimum number of nanotube unit cells such that each layer interacts only with its nearest neighboring layers. The contacts here are periodic extensions of the conducting channel, i.e., S-SWNT with adsorbed NO_2 molecules. These matrices are needed to calculate the self-energies of the contacts ($\Sigma_{D,S}$), as well as the Green function of the channel (G), which in turn will be used in Landauer-Buttiker formula for current[18]

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E,V)[f_S(E,V) - f_D(E,V)]dE. \qquad (2)$$

Here, $f_{D,S}$ are Fermi-Dirac functions of the contacts, V is the drain-source voltage, and $T(E,V)$ is the transmission probability[18,19]

$$T(E,V) = Tr(\Gamma_D G \Gamma_S G^\dagger), \qquad (3)$$

where

$$\Gamma_{D,S} = i(\Sigma_{D,S} - \Sigma_{D,S}^\dagger). \qquad (4)$$

Conductance as a function of carrier energies and bias voltage will be

$$C(E,V) = \frac{2e^2}{h} T(E,V). \qquad (5)$$

We calculate conductance at zero temperature and zero bias voltage. Correspondingly, in the actual case of lightly doped S-SWNT at low temperature and low bias (compared to the band gap), the area under the conductance curve from $E_f - (eV/2)$ to $E_f + (eV/2)$ gives the current by Eq. (2) (the Fermi-Dirac term will be zero outside this energy range).

Two unit cells of (10,0) SWNT are sufficiently large to be considered as a principal layer. Therefore, DFT computations were performed for a relatively large hydrogen-terminated nanotube (consisting of seven unit cells), before and after NO_2 adsorption. Then, Hamiltonian and overlap matrix elements corresponding to the middle four unit cells (i.e., two principal layers) were extracted. The (identical) diagonal blocks were used as corresponding matrices for the conducting channel and each layer of the contacts. The off-diagonal blocks form the coupling matrices between the channel and initial layer of each contact, as well as the coupling between adjacent layers in contacts.[11,17]

The density of states (DOS) and conductance plots for different concentrations of adsorbed NO_2 molecules are shown in Fig. 2. For pristine nanotube, we observe a gap of 0.98 eV between the valence and conduction bands, which is in good agreement with well established reports [e.g., generalized gradient approximation (GGA) result $E_g = 0.88$ eV (Ref. 20)].

Adsorption of NO_2 molecules results in additional van Hove singularities in DOS. One can easily identify two such peaks, which are common for all SCs: one around
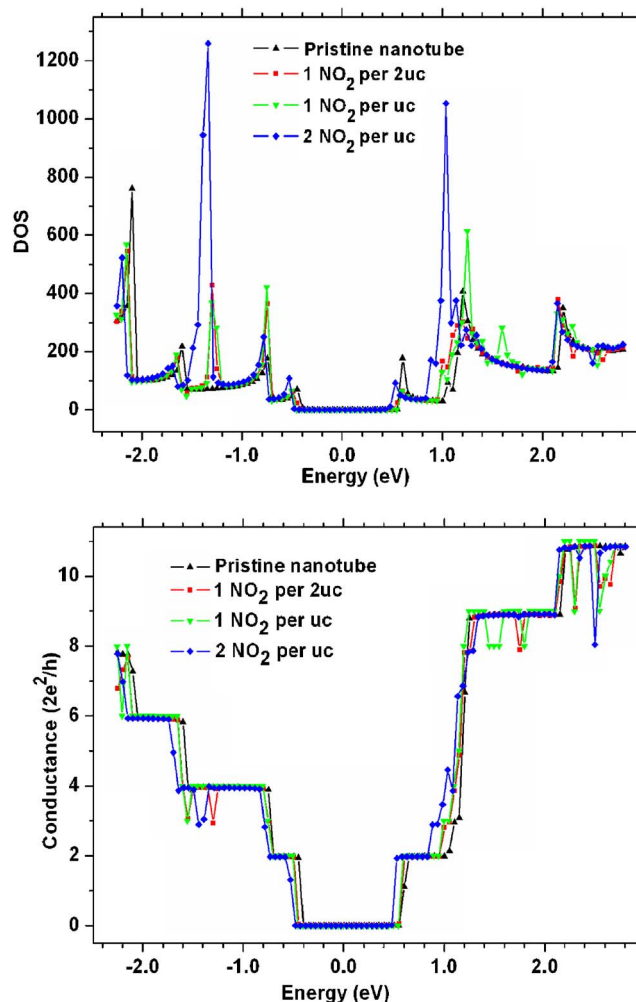

FIG. 2. (Color online) DOS (top) and conductance (bottom) as a function of energy of carriers, for different SCs.

$E = -1.4$ eV and the other around $E = 2.5$ eV. Both of these peaks correspond to drop of conductance. To our understanding, this is due to broken rotational symmetry around the NT axis after NO_2 adsorption, which in turn results in widened interband spacing responsible for the appearance of additional peaks and conductance drop.

The interesting feature here is the shift of conductance drops toward lower energies with increase of concentration. We can see the same effect in the conductance steps at usual van Hove singularities of S-SWNT. In Fig. 3, we show this shift with a higher resolution, around the bottom of conduction band. This shift in energy is due to the perturbation induced by the electric field of the NO_2 molecules on the nanotube, which can be estimated by average of electrostatic energy of carbon atoms in one unit cell of the nanotube in presence of NO_2 field (using Mulliken atomic charges).

Recalling that for small bias voltages, current is the area under the conductance curve within a small energy range around Fermi Energy, we expect a decrease (increase) of current for *p*-type (*n*-type) S-SWNTs with Fermi energies close to top (bottom) of the valence (conduction) band. Here, by *p*-type or *n*-type, we refer to doping before NO_2 adsorption, which is due to substrate or functionalization of the nanotube. From Fig. 3, we can also see that the device turn-off gate voltage (negative for *n*-type and positive for *p*-type S-SWNTs) decreases (increases) for *p* (*n*)-doped nanotubes, as concentration increases.
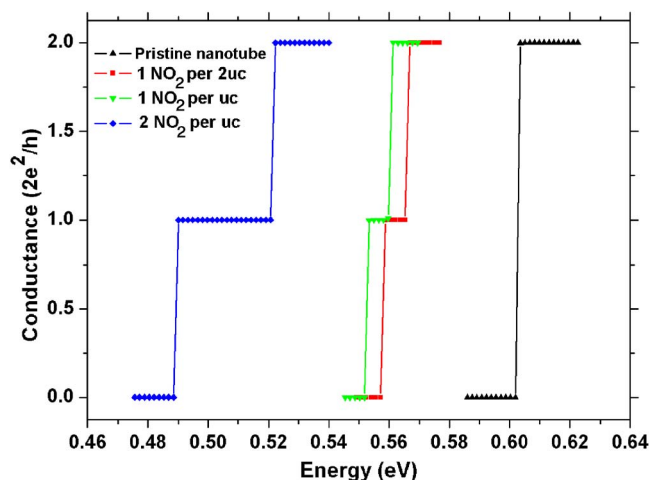
FIG. 3. (Color online) The shift in conductance towards lower energies at the minimum of conduction band. The shift increases with concentration.

The electron charge transfer from the tube to the molecule is small ($\sim 0.01e$, based on GGA calculations). Such charge transfer would lower the Fermi energy of the tube a few millielectron volts, depending on the initial Fermi level of the tube before NO_2 adsorption (this estimate is based on the change of the area under DOS curve up to Fermi level, caused by a charge transfer of $\sim 0.01e$). This change in Fermi level is very small. As a result, the effect of charge transfer, which would be the reverse of NO_2 dipole effect, is negligible.

Both the current and the turn-off gate-voltage change explained above (based on the theory) are in odds with reported experimental results.[2,3,5] In experiments, the mechanism of NO_2 detection is far from obvious. In a recent paper, Zhang *et al.* propose that detection is due to changes at the interface between the nanotube and the electrodes, and not to the molecules adsorbed directly on the nanotube surface.[21] Earlier, Peng *et al.* suggested that the effect is not due to adsorption of NO_2 but rather NO_3 molecules, which are formed by chemical reactions between NO_2 molecules, allowed by low diffusion barrier between adsorption sites around the nanotube.[10] The reason for the above proposal is that the experimental value for recovery time at room temperature (~ 12 h) is much larger than what the theory suggests (a few seconds, based on the calculated binding energies).[10]

In the original paper by Kong *et al.*,[3] the authors offer a different explanation (other than direct adsorption on the nanotube surface) for the current change upon exposure to NH_3 molecules. They attribute the effect to either binding of the gas molecules to hydroxyl groups on the SiO_2 substrate or interaction of NH_3 molecules and S-SWNT through other species (e.g., preadsorbed oxygen species on the nanotube). The reason for such an explanation was the belief that there was no affinity between NH_3 molecule and SWNT (this differs from some independent calculations results[6,7]).

Given the ambiguity in the reason for the current change, we can see that a different scenario for NO_2 detection in reported experiments (other than adsorption on the tube) is quite possible. Indeed, as we show here, such direct adsorp-

tion would result in an opposite effect on current change in extrinsic S-SWNTs.

In conclusion, based on quantum conductance calculations, we show that for *p*-type (*n*-type) nanotubes with Fermi energies close to usual S-SWNT van Hove singularities, direct adsorption of NO_2 molecules should result in decrease (increase) of current under small drain-source biases. This is due to the shift of conductance curve to lower energies as a result of adsorption. This shift is more significant for higher concentrations. We argue that this effect is due to relatively strong electric dipole moments of the gas molecules, which induce localized electric dipoles on the tube and as a result, lower the energy of the bands. We show that such a shift in energy decreases (increases) the turn-off gate voltage of the device for *p* (*n*) type S-SWNTs. We must add that the fact that DFT methods usually underestimate band gaps does not change our conclusions since they are based on the shift of the bands and not absolute value of the gap. Also, all our calculations are spin polarized with energy difference of less than 0.026 eV between spin-up and spin-down at the edge of valence and conduction bands. The plots are reported for spin-up values of energy, but since spin polarization effect is less than conductance steps shift (0.043 eV for lowest concentration), it does not change the conclusions (spin effect becomes less significant for higher concentrations).

[1] P. G. Collins and P. Avouris, Sci. Am. **288**, 62 (2000).
[2] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, and H. Dai, Nano Lett. **3**, 347 (2003).
[3] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, Science **287**, 622 (2000).
[4] J. Suehiro, G. Zhou, H. Imakiire, W. Ding, and M. Hara, Sens. Actuators B **105**, 398 (2005).
[5] X. Liu, Z. Luo, S. Han, T. Tang, D. Zhang, and C. Zhou, Appl. Phys. Lett. **86**, 243501 (2005).
[6] H. Chang, J. D. Lee, S. M. Lee, and Y. H. Lee, Appl. Phys. Lett. **79**, 3863 (2001).
[7] J. Zhao, A. Buldum, J. Han, and J. P. Lu, Nanotechnology **13**, 195 (2002).
[8] K. Seo, K. A. Park, C. Kim, S. Han, B. Kim, and Y. H. Lee, J. Am. Chem. Soc. **127**, 15724 (2005).
[9] S. Peng and K. Cho, Nanotechnology **11**, 57 (2000).
[10] S. Peng, K. Cho, P. Qi, and H. Dai, Chem. Phys. Lett. **387**, 271 (2004).
[11] A. A. Farajian, R. V. Belosludov, H. Mizuseki, and Y. Kawazoe, Thin Solid Films **499**, 269 (2006).
[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.* GAUSSIAN 03, Revision B.03. (Gausian, Wallingford, CT, 2004).
[13] A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).
[14] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[15] A. A. Farajian, A. Sadrzadeh, O. V. Pupysheva, and B. I. Yakobson (unpublished).
[16] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994), 13
[17] M. P. Lopez Sancho, J. M. Lopez Sancho, and J. Rubio, J. Phys. F: Met. Phys. **14**, 1205 (1984).
[18] S. Datta, *Electron Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995), 102
[19] H. M. Pastawski, Phys. Rev. B **44**, 6329 (1991).
[20] G. Sun, J. Kurti, M. Kertesz, and R. H. Baughman, J. Phys. Chem. B **107**, 6924 (2003).
[21] J. Zhang, A. Boyd, A. Tselev, M. Paranjape, and P. Barbara, Appl. Phys. Lett. **88**, 123112 (2006).