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Ab initio study of the effect of water adsorption on the carbon nanotube field-effect transistor

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We perform density-functional calculations to investigate the effect of adsorbed water molecules on carbon nanotubes (CNTs). Noting that the H_2O molecule has much wider energy gap than the CNT, we find that the charge transfer between them is negligible. We discuss that several recent publications, which claimed a substantial electron transfer from the water molecule to the CNT, have been based on incautious interpretations of the Mulliken population analysis. We suggest that the effect of humidity on nanotube devices may be attributed to various indirect effects enhanced by water vapors, rather than the carrier generations by the physisorbed H_2O molecules. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2397543]

Since the carbon nanotube field-effect transistor (CNTFET) was demonstrated experimentally in 1998, there has been widespread effort to understand the underlying physics as well as to improve the device performance.[1–3] The characteristics of the CNTFET as a Schottky barrier transistor with a quasiballistic channel conduction may lead to an ultimately miniaturized electronic device.[4,5] The potential of the CNTFET as a highly sensitive gas sensor has been demonstrated.[6] The study of the adsorption effect on either the nanotube surface or metal-nanotube contact is still one of the most important subjects in the field.[7–9] The effect of adsorption should be investigated in detail for the further development of the CNTFET as a gas sensor as well as a nanoscale electronic device.[10–13]

The effect of water or humidity on the CNTFET performance has been investigated experimentally as well as theoretically, but still remains arguable.[14] In the transfer character measurement of the CNTFET, the hysteresis in I-V_g curves has been commonly observed. The charge trapping and detrapping in the adsorbed water molecules have been suggested as the underlying mechanism for such hystereses.[15] In addition, several literatures claimed that a substantial amount of electron transfer from the adsorbed water molecules to the nanotube, inducing a measurable electron doping in the semiconducting nanotube. In the present work, however, we show that such conclusion of the charge transfer between the H_2O molecule and the nanotube was based on the incorrect interpretation of computational results. Instead, we suggest that the experimentally measured humidity effect should be ascribed to some indirect effects of the water vapors. As an example we show that the OH ions adsorbed on the SiO_2 gate surface near the carbon nanotube generate trap levels, which could have substantial effect on the transport measurement.

For computation, we use the Vienna *ab initio* simulation package (VASP).[16,17] The generalized gradient approximation (GGA) in the form of the PBE-type parametrization[18] and the local density approximation (LDA) in the Ceperley-Alder form[19] are employed. The ionic pseudopotentials are described via the projector augmented wave,[20] and the cutoff energy for the plane-wave basis is set to 400 eV.

We first investigate the adsorption geometry of the H_2O molecule on the outer wall of the isolated semiconducting nanotube. In this calculation, along the axial direction twice the minimal unit cell of the zigzag nanotube (≈ 8.49 Å) is chosen as the unit cell. In the perpendicular direction to the nanotube axis, the unit-cell dimensions are chosen such that the interatom distances in the neighboring cells are larger than 10 Å. We note that previous studies[21,22] did not agree on the adsorption geometries of the water molecule on the carbon nanotube. In the present study, various adsorption sites, including the center of the hexagon, the bridge of the carbon-carbon bond, and the top of the carbon atoms, are explored to determine the optimal adsorption geometry.

Geometry optimizations converged to several adsorption geometries with little energy difference. Their energies and geometries show that the adsorption of H_2O is a mere physisorption. Two configurations with the lowest energies for the

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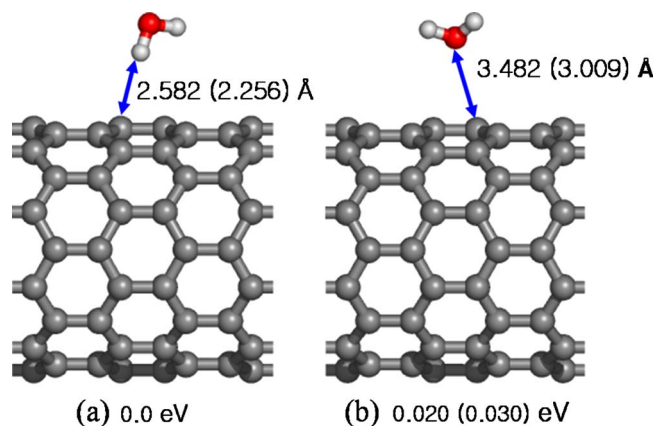[c)]Electronic mail: noejung@dku.edu

FIG. 1. (Color online) Two optimized geometries for the (10,0) carbon nanotubes with the adsorbed H_2O molecule. The hydrogen atom is directed to the bridge of the C–C bond in (a), and the oxygen atom is directed to the hexagonal center of the carbons in (b). The C–O and C–H distances and the total energy difference between the two geometries are shown. The results from the GGA and LDA calculations are written out of and in parentheses, respectively.

representative positions of water molecule are shown in Fig. 1. Between the optimized geometry where one hydrogen atom points toward the bridge of the C–C bond [Fig. 1(a)] and that where the oxygen atom is more attracted toward the center of the carbon hexagon [Fig. 1(b)], both the LDA and GGA calculations find that the former geometry is slightly more stable. It is noteworthy that the PBE functional, which is used in the present work, has proved to be accurate in the hydrogen-bonded systems.[23,24]

The electronic band structure of pristine (10,0) nanotube and that of the H_2O-adsorbed (10,0) nanotube are shown in Figs. 2(a) and 2(b), respectively. We note that the band structure near the top of the valence bands or bottom of the conduction bands is negligibly changed within the computational accuracy upon the molecular H_2O adsorption. The highest occupied molecular orbital (HOMO) level of H_2O molecule is located about 2.5 eV below the Fermi level of the carbon nanotube, as indicated by the blue leftward arrow in Fig. 2(b). The lowest unoccupied molecular orbital (LUMO) level of H_2O molecule sits at about 4 eV above the Fermi level, as denoted by the red arrow. We find that the LUMO-derived band is more or less dispersive. This should be attributed to the smallness of the supercell length, and the
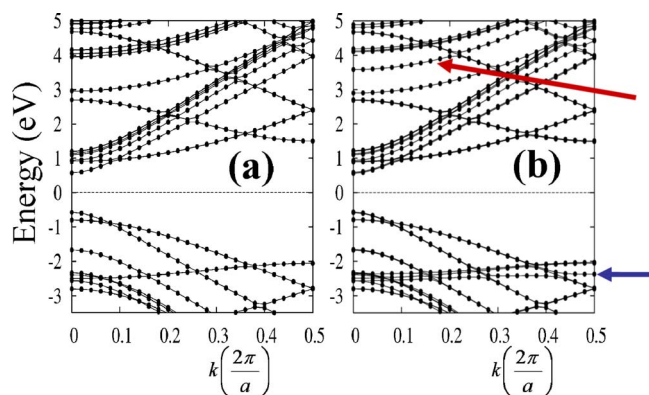

FIG. 2. (Color online) Electronic band structures for (a) the bare and (b) the H_2O-adsorbed (10,0) carbon nanotubes. The blue short arrow and the red long arrow indicate the HOMO and LUMO states of H_2O molecule, respectively.

TABLE I. Charge of the water molecule adsorbed on CNT calculated by various basis sets.

Method and basis set	$Q(H_2O)$ ($|e|$)
Ref. 14	+0.019
Ref. 21	+0.03
Ref. 22	+0.035
SZ (present work)	−0.004 39
SZP (present work)	−0.005 16
DZP (present work)	−0.000 89

resulting interactions of water molecule with its periodic images. Besides small splitting of the doubly degenerate nanotube bands near the HOMO level of H_2O molecule, there is no noticeable change in the nanotube electronic structure. This implies that the charge-transfer-induced doping is not a relevant mechanism of the physisorption of H_2O molecule.

Quite a few experimental and theoretical studies have considered the effect of humidity or water adsorption on the CNTFET.[14,15,21,22] A few of them claimed the electron transfer from the CNT to the adsorbed H_2O molecule based on the Mulliken population analysis. However, it is well documented in quantum chemistry textbooks that the Mulliken population analysis should be taken with caution because it is not unique and sensitively depends on the quality of basis sets.[25] A mere overlap between the tails of the molecular charges could result in a trace of charge transfer in the Mulliken charge analysis. However, if the adsorption states in a semiconductor induce a true charge transfer, it should be accompanied with electron depletion in the valence bands (hole doping) or electron accumulation in the conduction band (electron doping). Simple molecular physisorption may induce a small overlap between the tails of the overall charge densities. This could slightly affect the electronic structure deep in the valence bands, as shown in Fig. 2(b), but should have negligible effect on the electronic structure near the Fermi level.

For explicit demonstration, we calculate the Mulliken charge for the H_2O-adsorbed carbon nanotube at different levels of Gaussian basis sets. We use the SeqQuest program in which the contracted Gaussian basis sets for the corresponding PBE norm-conserving pseudopotentials are optimized for both molecules and bulk solids and thus more balanced than those for the standard quantum chemistry codes.[26] As noted in Table I, the calculated Mulliken charge transfer within our computational scheme indeed converges to zero as the completeness of the basis set increases, i.e., from the single zeta (SZ) and single zeta polarization (SZP) to double zeta polarization (DZP) level. This obviously indicates that the previously alleged charge transfer should have been cross-checked with variable basis sets.

To explain the humidity-induced hysteresis, instead of the direct charge transfer from the CNT to the neutral water molecule, we note that the actual CNTFET has various components, including metal electrode, metal-CNT interface, and the gate dielectric surface. The effect of water adsorption on such device parts could have substantial effect on the transport properties of the CNTFET. For example, the metal-CNT interface may have an increased chemical activity, and the molecule adsorption on the metal-CNT interface region could result in the modification of the Schottky barrier.
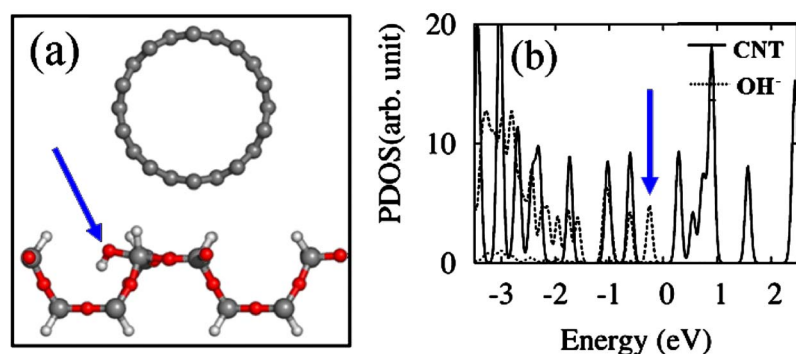
FIG. 3. (Color online) (a) Model for OH adsorption, indicated by an arrow, on the surface of the gate oxide (SiO_2) of the CNTFET. (b) The electronic structure for the geometry (a) with an additional electron. The partial densities for the carbon nanotube and OH are presented by the solid and dotted lines, respectively, with respect to the Fermi level of the CNT.

On the other hand, the accumulation of water layer on the gate oxide surface may help gathering of some ionic substances in the vicinity of the carbon nanotube. In this regard, we note that a previous study discussed the possibility of the concentration of OH ions on the SiO_2 surface.[15] In the present work, we investigate the effect of such ionic substances in terms of electronic structures. We first calculate the electronic structure of the OH-adsorbed SiO_2 surface near the carbon nanotube. We find that the weakly bonded neutral OH on the SiO_2 surface produces a half-filled molecular level at the Fermi level. Next, considering the same system with one additional electron, we obtain the optimized geometry for the CNT on the SiO_2 surface with an adsorbed OH^-, as shown in Fig. 3(a). The aforementioned half-filled OH level is occupied by the additional electron, as indicated by an arrow in Fig. 3(b). We thus conclude that the OH ions on the gate oxide surface near the carbon nanotube could be electron trap centers under an elevated gate voltage.

In summary, we performed density-functional calculations to investigate the effect of water adsorption on the performance of the CNTFET. We showed that the effect of doping by the simple physisorption of H_2O molecule is negligible. We noted that the alleged charge transfer between the H_2O molecule and the nanotube in previous literatures has been based on incorrect interpretation of the Mulliken analysis. We instead suggested that the effect of accumulated ionic substances via the help of water layer on either the gate oxide surface or the metal-CNT interface could be a more convincing scenario to explain the humidity-induced hysteresis.

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