Working mechanism of a SiC nanotube NO_2 gas sensor*

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Abstract: The working mechanism of sensors plays an important role in their simulation and design, which is the foundation of their applications. A model of a nanotube NO_2 gas sensor system is established based on an (8, 0) silicon carbide nanotube (SiCNT) with a NO_2 molecule adsorbed. The transport properties of the system are studied with a method combining density functional theory (DFT) with the non-equilibrium Green's function (NEGF). The adsorbed gas molecule plays an important role in the transport properties of the gas sensor, which results in the formation of a transmission peak near the Fermi energy. More importantly, the adsorption leads to different voltage current characteristics of the sensor to that with no adsorption; the difference is large enough to detect the presence of NO_2 gas.

Key words: working mechanism; SiCNT; gas sensor; non-equilibrium Green's function
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1. Introduction

Gas detection plays an important role in industrial and environment monitoring. An adsorbed gas molecule can change the electronic structures and transport properties of semiconductors and results in variation of the voltage current characteristic of the semiconductor with the concentration of the target gas. This is the conventional working mechanism for most gas sensors. Bulk silicon carbide (SiC) is one of the typical semiconductor materials widely used in the fabrication of gas sensors for the detection of CO, NO_2, etc[1].

Since the discovery of carbon nanotubes (CNTs)[2], extensive studies have focused on the application of CNTs in sensors[3−5]. Prepared CNT sensors have advantages of low power consumption, fast response and easy recovery capability over the traditional bulk material sensors. The synthesized CNTs may be metal or semiconductor depending on their radius and chirality, which limits their application in gas sensors. The newly synthesized silicon carbide nanotubes (SiCNTs) overcome this disadvantage and are semiconductors[6,7]. The surface-to-volume ratio of the SiCNTs is higher than that of the bulk SiC materials. This indicates that SiCNTs are candidates for NO_2 detecting.

The working mechanism of the nanotube sensors is the basis of their modeling and design, which is rarely studied and hinders studies on the nanotube sensors. A method combining density functional theory (DFT) with the non-equilibrium Green's function (NEGF) has been successfully used in studies on the working principle of molecular devices[8−10]. In this paper, the working mechanism of the SiCNT NO_2 gas sensor is studied with the above method and the results are meaningful to the development of gas sensors.

2. Model and methods

The most fabricated nanotube gas sensors are realized with a single CNT or mesh of CNTs bridging between two metal electrodes. Charge transfer can occur between the gas molecule and the surface of the CNT, which results in variation of the current voltage characteristic of the CNT.

The stable configuration for NO_2 adsorbed to an (8, 0) SiCNT is the key problem for the modeling of an NO_2 gas sensor. Geometry optimization is performed with the CASTEP package, which has been successfully applied in studies of the O_2 molecule adsorbed to a zinc oxide (ZnO) nanotube[11] and CO adsorption on a titanium-coated CNT[12]. In the geometry optimization, the maximal force, stress and displacement were set to be 0.05 eV/ , 0.05 GPa and 5×10^{-4} . The local structure of an (8, 0) SiCNT with a NO_2 molecule adsorbed is shown in Fig. 1. The nearest distance between the molecule and the nanotube is 1.47 . At such distances, stable adsorption can be formed.

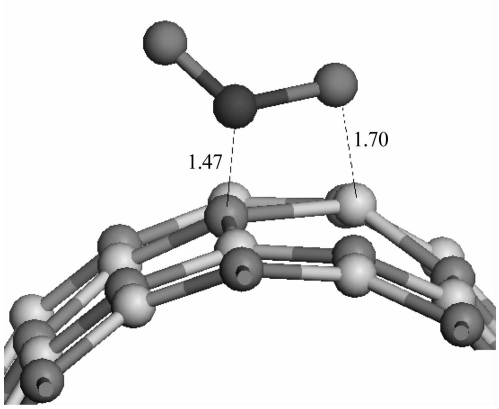

Fig. 1. Local structure of an (8, 0) SiCNT with a NO_2 molecule adsorbed.

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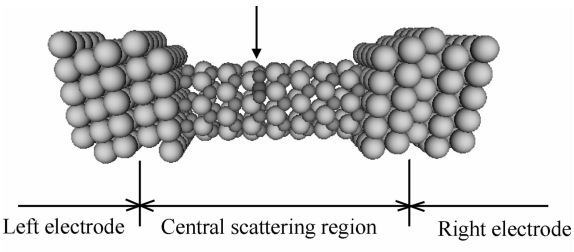

Fig. 2. A two-probe system of the SiCNT gas sensor.

A two-probe system of the SiCNT NO_2 gas sensor is established based on the above structure, which is realized with a finite (8, 0) SiCNT with a NO_2 molecule adsorbed coupled to two Au (111) electrodes via Au–C bonds (Fig. 2). It can be divided into the left semi-infinite electrode, the center scattering region, and the right semi-infinite electrode. The center scattering region consists of a finite (8, 0) SiC nanotube adsorbed NO_2 molecule and two (5×5) surface layers of the left and right electrodes. The electronic structures of the Au electrodes are considered to be the same as those of the bulk Au. Periodic boundary conditions were imposed in the directions parallel to the interface between the SiCNT and Au electrodes.

The mechanisms of the SiCNT NO_2 gas sensor modeled in Fig. 2 are studied with a method combining NEGF with DFT implemented in the TranSIESTA-C code and its latest version, Atomistix Toolkit 2.2 (ATK 2.2), which has been successfully applied to the study on the transport properties of CNT electron devices. A single zeta plus polarization (SZP) basis set was used for the valence electrons of all atoms. The core electrons of the system were modeled with the Troullier-Martins non-local pseudo-potential[13]. The generalized gradient approximation (GGA) was used to describe the exchange-correlation potential[14].

The transmission spectrum and the current- voltage characteristics are of great importance in the electronic transport properties of nanotubes gas sensors. The transmission spectrum means the probability for an electron with incident energy E to transfer from the left semi-infinite electrode to the right and is calculated by

$$T(E,V) = Tr[\Gamma_{\rm L}(E,V)G(E,V)\Gamma_{\rm R}(E,V)G^{\dagger}(E,V)], \qquad (1)$$

where $G(E, V)$ is the Green's function of the two-probe system, and $\Gamma_{\rm L/R}$ is the coupling matrix. The integral of the transmission spectrum yields the current through the system

$$I(V) = \int_{\mu_{\rm L}}^{\mu_{\rm R}} T(E,V)[f(E-\mu_{\rm L}) - f(E-\mu_{\rm R})]{\rm d}E, \qquad (2)$$

where $\mu_{\rm L} = -V/2$ ($\mu_{\rm R} = V/2$) is the chemical potential of the left (right) electrode.

3. Results and discussions

First, the equilibrium transport properties (no bias voltage applied) of the nanotube NO_2 gas sensor were studied.

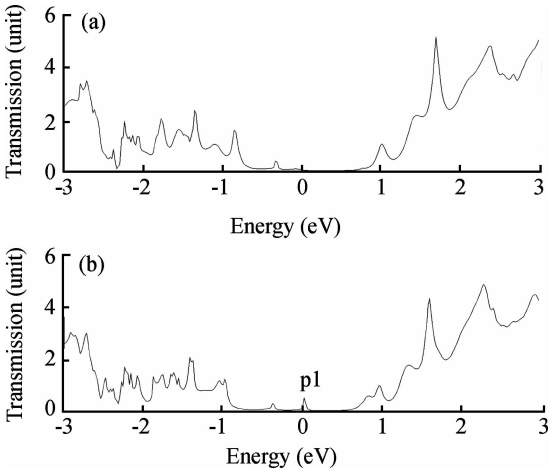

Fig. 3. Transmission spectra of the two-probe system for a NO_2 gas sensor with NO_2 adsorbed (b) and pure (a).

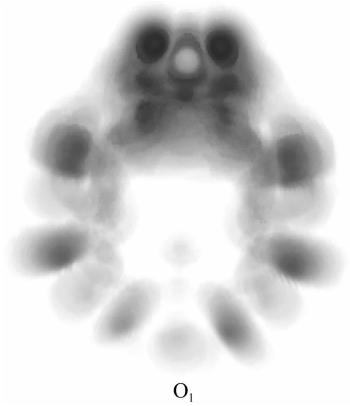

Fig. 4. Frontier orbital of the MPSH for the gas sensor.

The transmission coefficients $T(E)$ for the sensor as a function of the energies were plotted in Fig. 3. Comparing these two curves, we can see that a new transmission peak is formed at an energy of 0.04 eV.

The molecular projected self-consistent Hamiltonian (MPSH) can be achieved by projecting the self-consistent Hamiltonian onto the Hilbert space spanned by the basis functions of the central atoms. The eigenstates of the MPSH are associated with the poles of Green's function and roughly correspond to the peaks in the transmission spectrum[15]. To understand the peak in Fig. 3, we calculated two frontier molecular orbitals of the MPSH for the gas sensor.

The common feature of the orbital in Fig. 4 is that it has a high electron density in the vicinity of the NO_2 molecule. This means that charge transfer has happened and a stable adsorption is formed. Orbital O_1 is the lowest unoccupied molecular orbital (LUMO). The eigenvalue of this orbital is 0.025 eV, which formed transmission peak p_1 in Fig. 3(b).

Then the non-equilibrium transport properties of the NO_2 gas sensor are studied, in which the voltage current characteristic plays an important role. The current following through the two-probe system of the SiCNT sensor is calculated by the Landauer-Büttiker formula: $I(V) = \int_{\mu_{\rm L}}^{\mu_{\rm R}} T(E,V)[f(E-\mu_{\rm L}) - f(E-\mu_{\rm R})]{\rm d}E$, which is determined by the transmission probability $T(E,{\rm V})$ and the energy region

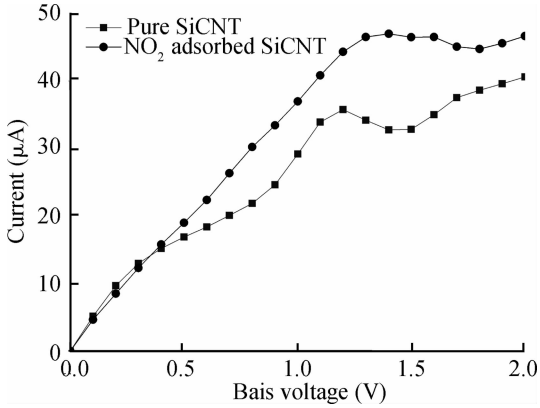

Fig. 5. Current voltage curve of the two-probe system for the SiCNT NO_2 gas sensor.

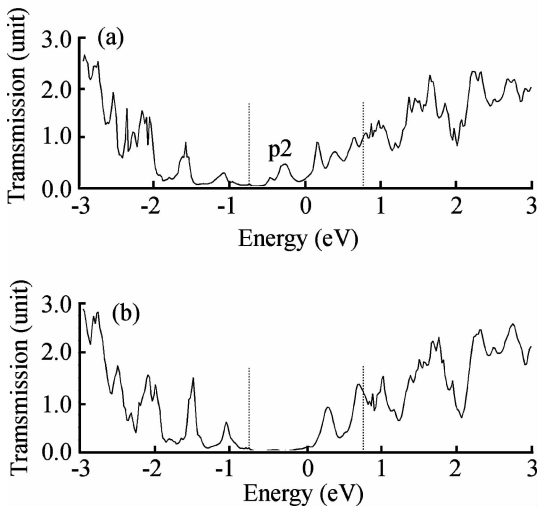

Fig. 6. Transmission spectra of the sensor with NO_2 adsorbed (a) and pure (b) under bias +1.5 V.

(or integral window) of the current integral. As the Fermi level is set to be zero, the integral window is $[-V/2, V/2]$. As the calculation of current is time-consuming work, the bias range is set from –2.0 to 2.0 V.

To find the influence of NO_2 gas molecule adsorption on the voltage current characteristic of the SiCNT, an *I*–*V* curve of the sensor with no NO_2 molecule adsorbed is also drawn in Fig. 5. From +1.1 V under positive bias, the difference between the *I*–*V* curves of the sensor with a NO_2 molecule adsorbed and that with none begins to increase. Under a bias of +1.5 V, the current of the sensor is about 1.5 times that with no gas molecule adsorbed, which is large enough for detecting the gas in application. In application, the concentration of the target gas is higher than that in our simulation and a more obvious result can be obtained.

The difference in the current of the sensor before and after NO_2 molecule adsorption can be achieved by comparing their transmission spectra under the same bias voltage. The transmission spectra of the sensor under the bias +1.5 V are calculated (see Fig. 6).

The current following through the two-probe system is determined by the transmission spectrum and the magnitude of the integral window. As the bias voltage is the same, the current depends on the transmission spectrum. The most obvious difference between the two transmission spectra is the appearance of the transmission peak p_2 in Fig. 6(a), which results in the change of the *I*–*V* characteristic. Comparing Fig. 6 with Fig. 3, we can see that the transmission peaks of the sensor with a NO_2 gas molecule move towards low energy. Transmission peak p_2 has a similar origin as p_1 formed by the adsorbed gas molecule. The variation of the current originates from the NO_2 gas molecule, which is the basis for further studies on the SiCNT gas sensor.

4. Conclusion

The working mechanism of a sensor is the foundation of its design and application. We studied the working mechanism of a SiCNT NO_2 gas sensor with a method combining NEGF with DFT. A model of the sensor is established based on an (8, 0) SiCNT with a NO_2 molecule stably adsorbed on its surface. The adsorbed NO_2 molecule plays an important role in the equilibrium transport properties of the sensor, which means that the SiCNT can be used to detect this gas. More importantly, the variation of the *I*–*V* characteristic caused by adsorption is large enough for detection. Our results are meaningful to studies on SiC nanotube gas sensors.

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