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Hydrogen Sensing Characteristics from Carbon Nanotube Field Emissions

Changkun Dong,*[a] Haijun Luo,[a] Jianqiu Cai,[a] Fuquan Wang,[a] Yangyang Zhao,[a] and

Detian Li[b]

[a]Institute of Micro-nano Structures & Optoelectronics, Wenzhou University, Wenzhou, Zhejiang,

P. R. China, 325035

*Corresponding Author: dck@wzu.edu.cn

[b]Science and Technology on Vacuum & Cryogenics Technology and Physics Laboratory,

Lanzhou Institution of Physics, Lanzhou, Gansu, P. R. China, 730000

Abstract

An innovative hydrogen sensing concept is demonstrated based on the field emission from multi-walled carbon nanotubes, where the low emission currents rise in proportional to hydrogen partial pressures above 10^{-9} Torr. Experimental and first principle studies reveal that the sensing mechanism is attributed to the effective work function reduction from dissociative hydrogen chemisorption. The embedded Ni catalyst would assist both the hydrogen dissociation and work function reduction. This technique is promising to build miniature low cost hydrogen sensors for multiple applications. This work is valuable for studies of nano carbon-gas reaction mechanisms and the work function properties in adsorption related applications, including field emission, hydrogen storage, energy cell, and gas sensing.

Keywords: carbon nanotube, field emission, hydrogen, sensor, work function

Carbon nanotubes (CNTs) possess extraordinary mechanical, physical, chemical, and electronic properties. The unique hollow structures are sensitive to various adsorbents, benefiting greatly chemical and gaseous sensing applications.[1-3] Upon the exposure to gas molecules, the electrical resistances may vary dramatically resulting from the change of the charge carrier density. As the consequence, CNT chemiresistor sensors are developed to detect various species, including gas molecules,[4, 5] protein,[6] and chemical warfare agents.[7] Other techniques, such as capacitor and field effect transistor based structures, are also investigated for gaseous and bio sensing applications.[8-10]

Hydrogen sensing is critical in many scientific and industrial fields. However, it is commonly considered that pristine CNTs cannot detect H_2 because hydrogen molecule does not adsorb on the CNT surface effectively under room temperatures.[11,12] With the post-growth metallic treatments, nanotube based hydrogen sensors have been demonstrated, including the palladium decorated nanotube sensor,[13] the platium nano carbon sensor,[14] the conidial palladium nanotube array sensor,[15] and the Schottky barrier field-effect transistor.[16] Most research and development efforts focused on hydrogen detections in atmospheric pressure, but low pressure hydrogen sensing is important as well in many fields, such as petroleum distribution, space mission, low-emission fuel cells, vacuum electronic devices, and high vacuum measurement. Developments of low cost miniature hydrogen sensing techniques would be very attractive for such applications. Huang et al. showed a nanomechanical beam resonator hydrogen sensor working mainly in $10^{-5} - 10^{-4}$ Torr range.[17] Khalap

et al. developed a Pd-decorated single-walled CNT device, which is able to detect H_2 gas down to milliTorr range by amplifying the chemoresistive response.[18] Besides, the reaction mechanism and the work function properties with hydrogen adsorption is an important issue in CNT applications such as hydrogen storage, field emission, and gas sensing. In this report, a novel hydrogen sensing technique is demonstrated based on adsorption assisted field electron emission enhancement for multiwalled carbon nanotubes (MWNTs). Experiments and first principles study reveal that the sensing mechanism is attributed to the work function reduction from the dissociated hydrogen chemisorption.

The MWNT emitters are synthesized directly on Ni alloy Hastelloy substrates by chemical vapor deposition from acetylene and argon under 750 ℃. MWNTs grow on the substrate randomly with the film thickness of $1 - 2$ μm (Fig. 1a). The tube diameters are typically around 30 nm and can reach 45 nm with layers in fifties (Fig. 1b). Both open and capped tubes exist (Fig. 1c), and embedded catalyst particles of dimensions from sub-nanometer to over 10 nanometers could be found (Fig. 1d), confirmed by the EDEX analysis. The experiments are conducted in a turbo vacuum system, and a $10^{-9} - 10^{-10}$ Torr ultimate vacuum is reached before each test with baking the chamber under 350 ℃ for 10 hours. The diode setups, consisting of a MWNT cathode and a Si anode with the gap of 100 μm and the emitting area of 4×4 mm^2, are constructed to test the field emission behavior. The low gas adsorption/desorption performance makes the Si substrate a better candidate to achieve and maintain ultra-high vacuum comparing with metal anodes.

Figure 2 shows the field emission current-voltage (I-V) curves with the inset of

Fowler−Nordheim (F−N) plots. The F−N data in the first measurement cycle deviates

from the intrinsic line significantly, attributed to gas adsorptions on CNT surfaces.[19, 20]

After the surface cleaning by emission induced Joule heating,[21] the F−N data from the

third test fits best to the intrinsic F−N line. Even so, low current emissions are still

deviated from the F−N line, which is related to an emission assisted surface reaction

process.[22] In high emission current regime, field emissions are stable and follow the

intrinsic F−N feature well.

Experiments show that low emission currents could rise gradually under constant

emission fields, as shown in Fig. 3a. To study further the field emission behaviors in

different gas ambiences, the low current stabilities are investigated for three major air

components hydrogen, oxygen, and nitrogen respectively, as shown in Fig. 3b − 3d.

Each test starts from the intrinsic emission state after cleaning the CNT samples by

the high emission Joule heating (20 μA @ 8.4 V/μm) in 10^{-10} Torr vacuum for 2

minutes. After purging 1×10^{-8} Torr hydrogen into the system, the emission currents

increase by 220%, 128%, and 157%, respectively, in 10minutes under emission

voltages of 520 V, 540 V, and 560 V. After increasing hydrogen partial pressures, the

emission currents rise in faster rates. Under 1×10^{-7} Torr hydrogen pressure, the

emission currents increase by 745% (520 V), 456% (540 V), and 300% (560 V),

respectively. However, there are no significant differences between emission

variations in 10^{-8} and 10^{-7} Torr with nitrogen or oxygen exposures. Hydrogen

adsorption is identified as the key factor causing such low emission increases.

The responses of emission currents to three gases are further investigated in 10^{-9} ~ 10^{-5} Torr range. To maximize the emission enhancement effect, the tests are conducted in low emission regime, where the curents are in nano to sub-micron ampere level and may fluctuate seriously. To offset the fluctuations of the low emission currents, we average the currents taken at the end of every minute, counting on the starting value, during a N minute test to get a normalized current I_N: $I_N = \sum_{i=0}^{N} I_i / (N + 1)$, i. e., I_0 is the starting value and I_1 is the emission current at 1 min. Fig. 4a shows the relations between I_N and hydrogen partial pressures under the emission voltage of 520 V for the 5-minute and 10-minute tests. With increasing hydrogen partial pressures from 3×10^{-9} Torr to 1×10^{-6} Torr, normalized currents jump from 5.67×10^{-8} A to 4.63×10^{-7} A for the 5-minute test and from 1.44×10^{-7} A to 1.39×10^{-6} A for the 10-minute test, respectively. Both the hydrogen pressure and the exposure period influence the field emission significantly. Fig. 4b shows the I_N-pressure behaviors for three gases from the 5-minute tests under 540 V emission voltages, demonstrating clearly hydrogen sensing characteristics. Excellent sensing reproducibility is also illustrated from two separate groups of tests with hydrogen exposures. The data summation is effective to make this sensing technique reliable under fluctuated low current emissions.

The field emission performance is characterized by analyzing the F−N behaviors.[23] Figure 5 shows the F−N data, $\ln(I/V^2)$ vs. $1/V$, tested in the low emission regime with varying the hydrogen pressures from 10^{-9} Torr to 10^{-6} Torr. The F−N lines are obtained by linear fitting. The slope k of the F−N plot, where $k = -6.83 \times$

$10^7 \Phi^{3/2}/\beta$, can be used to evaluate the variation of the effective work function Φ, assuming the enhancement factor β constant. There is a clear trend of k decline with increasing the hydrogen pressures, and the effective work functions drop 21% (3×10^{-9} Torr), 33% (1×10^{-7} Torr), and 43% (1×10^{-6} Torr), respectively. The work function declines are significant, which is to be elaborated in this paper.

H$_2$ molecules are normally considered to physisorb on CNT surfaces,[24] and the exposures to H$_2$ do not influence the field emission properties obviously from most reports.[19, 25, 26] However, chemisorption may occur after the dissociation of molecular hydrogen from a energy input,[27-29] or by the hydrogen plasma treatment.[30, 31] We expect that both dissociated and ionized chemisorption could occur in the experiments. In the first aspect, hydrogen molecules initially physisorb on CNT surfaces. Under the low current emission, local emission site temperatures could be in 500 K level,[21] resulting in the hydrogen dissociations and chemisorption. Low current emission is the key factor to stabilize the chemisorption, because the hydrogen adsorbates could be desorbed under temperatures of above 600 K.[32] Additionaly, nickel containing catalyst particles distributed inside MWNTs could play role. With the participation of Ni, the reaction temperature between graphite carbon and hydrogen molecule to form chemical bonds could be reduced approximately from over 1300 K to 800 K.[22, 33] It is expected that catalyst particles facilitate the H$_2$ dissociation and chemisorption. In the second aspect, hydrogen ions can be generated from the electron impacts, and the ion production rates are proportional to hydrogen pressures and electron currents. Considering the low hydrogen gas densities and small electron currents, the

adsorption of hydrogen ions can be neglected comparing with the adsorption of molecular hydrogens. Thus, the dissociated chemisorption, possibly assisted with nickle catlyst, is regarded the key factor of the sensing characteristics. Besides, the dissociative chemisorption of hydrogen molecule under strong electric fields (0.005 a.u. $= 2.57 \times 10^9$ V/m and above) was also reported to the graphene sheet and BN sheet from the first principle studies.[34, 35] Our experiments are conducted under relative low electric fields, thus, this dissociative process may exist, but shouldn't play significant role. However, most reports investigated the effect of hydrogen adsorption beyond the low emission regime, where the local temperatures should be higher than 600 K. As the result, the dissociated chemisorption, if occurred, could not hold so as to enhance the field emissions.

Under the chemisorption between atomic or molecular hydrogen with carbon atom, a surface dipole is formed with the positive charge on the vacuum side because carbon is the more electronegative element. This dipole assists the extraction of electrons from the nanotube, resulting in the drop of the effective work function. This work function reduction has been investigated theoretically and experimentally for various carbon allotropes, and the increases of field emission currents from this reduction were also reported.[30, 31, 36] The work function shift $\Delta\Phi$ from the surface dipole layer can be evaluated from the relation:[37] $\Delta\Phi = 2\pi P_i N_S \theta$, where P_i is the dipole moment, N_S is the maximum number of adsorption sites per unit area, and θ is the fraction of filled ones. The steady rises of the emission currents are likely due to the continuous drop of the surface effective work function from the increase of the

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chemisorption coverage. The higher the pressure is, the larger the θ, leading to bigger

work functions drops, thus the hydrogen sensing effect.

The adsorption properties of hydrogen, nitrogen, and oxygen are further

investigated for capped (5, 5) single-walled carbon nanotubes (SWNT) based on the

density functional theory (DFT) by using the projector-augmented plane wave (PAW)

method[38, 39] implemented in the Vienna ab initio simulation package (VASP).[40, 41] The

SWNT consists of 90 carbon atoms capped with the half of a C60 structure and

dangled with 10 unsturated bonds at the other end. Fig. 6a illustrates the dissociation

and chemisorption of a hydrogen molecule on top of a 4-Ni atom embedded tube. Fig.

6b shows that the energy barrier for the dissociative chemsorption of H_2 is site related

and can be 0.26 ~ 0.71 eV lower on different layers after the Ni incorporation. The

work functions under different coverages of molecular and atomic hydrogen are

caculated for both pristine and Ni embedded SWNTs, as shown in Fig. 6c. After the

physisorption of molecular hydrogen, the work function is about same or slightly

higher than 4.89 eV for the pristine SWNT, and rises to 5.09 eV under the adsorption

of 5 hydrogen molecules. In contrast, the tube work function drops significantly after

the chemisorption of atomic hydrogen. With increasing the atomic hydrogen coverage

from one to thirty atoms, Φ drops gradually from 4.43 eV to 3.11 eV, in good

agreement with the sensing mechanism discussed above. The maximum work

function reduction of 37% is also in line with the F−N analysis from the experiments.

Furthermore, Ni embedding could cut down the work function by up to 5.0% for both

molecular and atomic adsorption, faciliating this sensing process.

The effects of oxygen and nitrogen exposures are mixed from different reports. Oxygen is normally unfavorable to field emission with the current degradation due to the surface C−O dipole or nanotube etching from chemical reactions.[19, 25, 42] Meanwhile, recoverable current degradation with oxygen exposure was reported for SWNTs,[25] and the first principles study showed that interactions between nonpolar oxygen molecules and carbon nanotubes could be weak, resulting in negligible influences by oxygen.[43] The same goes for nitrogen exposures. Emission currents could degrade owing to stronger electronegativity for nitrogen comparing with carbon atom.[26, 25] On the other side, the first principles investigation revealed that N_2 does not affect the field emission significantly because the Fermi level shift from N_2 adsorption is small.[42] Our simulation confirms that the work function increases slightly for most cases under N_2 or O_2 adsorption. Overall, the influences of adsorbates on field emission are balanced by multiple factors, including nanotube structure, field emission current, electric field, as well as defect and impurity. For MWNTs investigated in this work, we believe the weak O−C or N−C bindings dominate the oxygen (nitrogen)-carbon reactions in the low emission regime, which do not influence the emission obviously.

Several technical superiors favor practical device developments. Firstly, excellent sensitivity performance is demonstrated. Defining the sensitivity S as the ratio of the normalized current in hydrogen over that in vacuum, S is around 1.5 at low hydrogen pressure end and reaches 10 at high pressure end for 5-minute tests. The response time could be shortened greatly taking advantage of the high sensitivity

property, in addition to the optimizations of CNT growth and structure design. Secondly, the low current operation benefits applications in several aspects, including longer lifetime, lower power consumption, and less disturbance to surroundings. Thirdly, the sensor is only in minimeter dimension, and could be smaller, making it very easy to be integrated into various systems, including sealed vacuum electronic devices. Another advantage of this sensing technique is the quick recovery ability. A high current pulse of dozens of seconds is capable of cleaning the surfaces to restore the intrinsic field emission state.

In summary, by exploring the field emission behaviors in low emission regime for MWNT samples grown directly on catalytic substrates, an innovative low pressure hydrogen sensing concept has been demonstrated. The low emission currents rise steadily in hydrogen ambiences, and the rising rates are proportional to hydrogen partial pressures in a wide range. The reduction of the MWNT effective work function from chemisorption of atomic hydrogen on nanotube surfaces is considered the key factor for this sensing behavior from the first principles study. Features of simple setup, high sensitivity, and fast recovery make this technique attractive to build low cost miniature hydrogen sensors. This work is also valuable for the study of nano carbon-gas reaction mechanisms in adsorption related applications, including hydrogen storage, field emission, and gas sensing.

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