Hypergolic fuel detection using individual single walled carbon nanotube networks

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Accurate and reliable detection of hypergolic fuels such as hydrazine (N_2H_4) and its derivatives is vital to missile defense, aviation, homeland security, and the chemical industry. More importantly these sensors need to be capable of operation at low temperatures (below room temperature) as most of the widely used chemical sensors operate at high temperatures (above 300 °C). In this research a simple and highly sensitive single walled carbon nanotube (SWNT) network sensor was developed for real time monitoring of hydrazine leaks to concentrations at parts per million levels. Upon exposure to hydrazine vapor, the resistance of the air exposed nanotubes (p-type) is observed to increase rapidly while that of the vacuum-degassed nanotubes (n-type) is observed to decrease. It was found that the resistance of the sample can be recovered through vacuum pumping and exposure to ultraviolet light. The experimental results support the electrochemical charge transfer mechanism between the oxygen redox couple of the ambient and the Fermi level of the SWNT. Theoretical results of the hydrazine-SWNT interaction are compared with the experimental observations. It was found that a monolayer of water molecules on the SWNT is necessary to induce strong interactions between hydrazine and the SWNT by way of introducing new occupied states near the bottom of the conduction band of the SWNT. © *2010 American Institute of Physics*. [doi:10.1063/1.3386513]

I. INTRODUCTION

Carbon nanotubes are known to exhibit extreme sensitivity toward changes in the local chemical environment and are believed to be due to the modification of their electronic structure in response to the interacting molecules. This chemical sensitivity makes them ideal candidates for integration into chemical sensors. Despite a wealth of experimental and theoretical investigations and accomplishments, several fundamental questions on nanotube-molecule interactions remain unexplained. These concerns must be addressed before carbon nanotubes are to be competitive with state-of-the-art solid-state sensor materials.

Accurate and reliable detection of hypergolic fuels is a vital component of missile defense systems, as the missile design involves a liquid fuel initiator [monomethyl hydrazine (MMH)—fuel; nitrogen tetroxide—oxidizer]. Hydrazine is a colorless liquid with an ammonia (NH_3) like odor. Its two main derivatives, MMH and dimethyl hydrazine are highly flammable and carcinogenic. Since they are widely used as propellants in satellites, missiles, and spacecrafts, the reaction with oxygen at room temperature can be very volatile. An early warning leak detection system capable of operating at low temperatures is needed to warn personnel of the potential toxic exposure and the dangers imposed by a possible explosion. A wide variety of detection techniques have been used in the detection of hydrazine[1–3] with electrochemical sensing being the most prominent. Devices using a conducting polymer[3] have also been fabricated and show sensitivity as low as 1 ppm of hydrazine. A change in the resistance of the sensor was detected, however, no recovery was possible limiting these sensors to a single use.

Semiconducting single walled carbon nanotube (s-SWNT) based sensors offer significant advantages over conventional metal-oxide-based electrical sensor materials in terms of sensitivity, room temperature operation, power consumption, and small sizes needed for miniaturization and construction of massive sensor arrays.[4]

Performance on pristine as well as functionalized SWNTs has demonstrated the detection of small gas molecules such as NO_2, NH_3, O_2, H_2, and others.[4–7] Detection sensitivities using SWNTs on the order of parts per million can be readily reached at room temperature, however, it requires a temperature of >300 °C for conventional metal oxide microfilm resistive sensors.

The nanotube-molecule interaction still lacks clear theoretical understanding and the exact nature of the chemical doping remains unclear. The pinning of the Fermi level at the impurity states generated by O_2 near the top of the valence band of the s-SWNT is believed to be responsible for the observed p-type behavior of the SWNTs.[6] However s-SWNTs with one section suspended across a trench found that the s-SWNT section bound on the SiO_2 substrate is p-type doped, and the suspended s-SWNT is undoped.[8] This raises the possibility that SWNT doping arises from an inter-

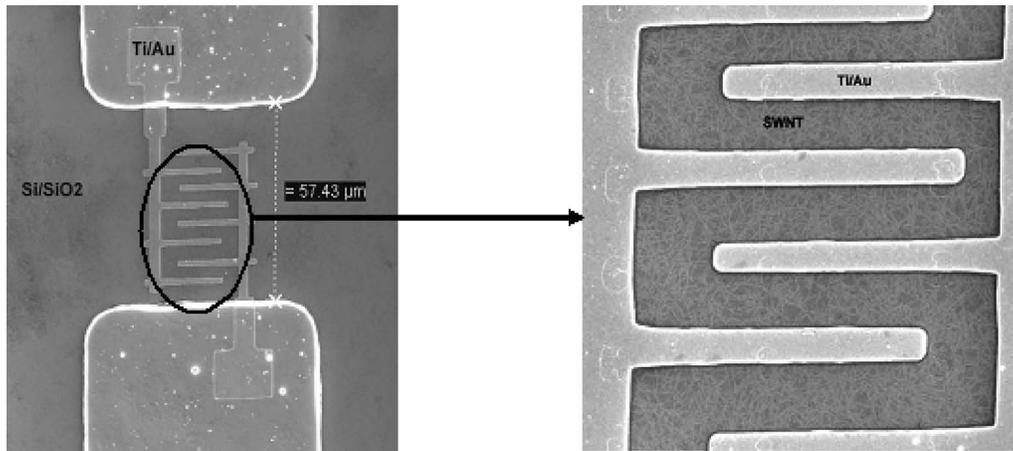a)Author to whom correspondence should be addressed. Electronic mail: gusuma01@louisville.edu.

FIG. 1. SEM images of SWNT network with IDE used in this study for hypergolic fuel detection.

action with the SiO$_2$ substrate. For solution-processed SWNTs on Au electrodes, annealing produced n-type field effect transistors (FETs), and exposure to O$_2$ restored p-type operation, interpreted as due to changes in metal work function.[9] However, the origin of n-type behavior in the annealed FETs remains unclear, so a complete picture is lacking. It has been found that the exposure of an individual s-SWNT based FET device to dry N$_2$, O$_2$, or He does not alter the low conductance state, while exposure to humid air immediately causes a change to the high conductance state, suggesting that water is necessary for doping.[10] It has been found theoretically that hydrazine or ammonia interaction with SWNTs do not cause any noticeable change in the SWNT band-structure to support any charge transfer. Recently charge transfer between diamond and an electrochemical redox couple in an adsorbed water film has been shown to pin the Fermi level in hydrogen-terminated diamond.[11] This effect is a more general phenomenon and influences the properties of other semiconductors such as semiconducting SWNTs when the band lineup between the ambient and electronic states in the semiconductor is appropriate. These observations are explained by electron exchange between the oxygen electrochemical redox couple in an adsorbed water film and electronic states in the semiconductor. The change in the electrochemical potential which is a function of the *p*H value under acidic and basic conditions can explain the observed charge transfer effects from donor and acceptor agents.

In this work we studied the hydrazine sensing response to chemical vapor deposition (CVD) grown individual SWNT-networks with interdigitated electrodes (IDE) fabricated using electron beam and photolithography. The sensor measurements were performed under three different conditions such as:

(i)   Dynamic sensing for predetermined parts per million levels by continuous flow of dry nitrogen and intermittent flow of hydrazine in nitrogen.
(ii)   Sensor was annealed under high vacuum in a closed reactor before exposure to hydrazine vapor at varying pressure levels at room temperature and 5 °C.
(iii)   Sensor was annealed under high vacuum in a closed

reactor and exposed to hydrazine diluted in argon to a predetermined parts per million level within a mixing gas bag at room temperature.

For each of these measurements the recovery response was also studied. Transport measurements were also performed on individual SWNT devices in FET configuration to better understand the adsorption properties.

Theoretically we have explored the electronic structure of SWNTs with direct interactions to various molecules such as ammonia and hydrazine as well as those mediated by water molecules.

The use of SWNT networks in the sensor study eliminates the problems encountered by the individual nanotube sensor assembly and its associated conductivity variations, while maintaining the sensitivity of the semiconducting nanotubes.

II. EXPERIMENTAL

A film of randomly oriented SWNTs was synthesized on a Si/SiO$_2$ (silicon/silicon-dioxide) substrate by CVD using Fe nanocatalysts similar to earlier work.[6] Following the synthesis of SWNTs, electrical contacts are fabricated using Ti/Au (titanium/gold) IDE using the electron beam lithography technique and Ti/Au contact pads by photo-lithography technique. The scanning electron microscopy (SEM) image of the device is shown in Fig. 1.

We have performed sensor measurements under static conditions, where the sample is positioned in an enclosed quartz reactor inside a tube furnace. The reactor is connected to a turbo molecular pump for easy evacuation and has provisions for gasses and liquid chemicals. The pressure was measured using a barometer. The parts per million level dilution of gasses were accomplished by mixing the respective gas under test with dry nitrogen to the desired parts per million level inside a mixing chamber using two well calibrated mass flow controllers. For dynamic sensing studies, dry nitrogen with a calculated cubic centimeter per minute at STP level was bubbled through hydrazine. For static sensor studies, the desired parts per million level was accomplished by
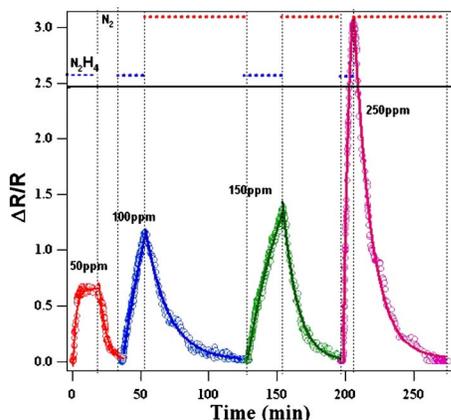
FIG. 2. (Color online) p-type SWNT network response to exposure of hydrazine diluted to the desired concentration in nitrogen. The recovery (downward exponential) is achieved with a pure dry nitrogen flow.

FIG. 3. Energy band diagram of SWNTs with the chemical potentials corresponding to relevant reduction-oxidation couple for varying pH values.

injecting a calculated volume of hydrazine using a calibrated syringe into a mixing bag consisting of a known volume of the dilute gas (dry nitrogen).

III. RESULTS

Experimental results on parts per million level hydrazine sensing under dynamic conditions are discussed first. N_2 was used as the dilution gas and mixtures ranging from 50 to 250 ppm were exposed to the device. The relative response $\Delta R/R_0$ for the device was recorded with each exposure. Here the R_0 is the initial resistance of the device before the hydrazine exposure and ΔR is the change in the resistance due to the exposure. Once the resistance was found to be saturated, hydrazine was turned off and only the N_2 flow was maintained. N_2 washes the hydrazine away and the resistance of the device was recovered. The recovery response is also recorded. Figure 2 shows the response with respect to time for both exposure and recovery.

From Fig. 2 it can be seen that upon exposure to different parts per million levels of hydrazine the resistance of the device increases and recovers back to its original value when flushed with N_2. Both adsorption and desorption are found to be exponential, with time constants for adsorption being few minutes and shorter compared to that of desorption. The sensitivity is found to be more than 70% for 50 ppm. Despite various efforts by several groups, the interaction of NH_3 with SWNTs remains controversial. The p-type SWNT-FET has been shown to induce two orders of magnitude change in electrical conductance upon exposure to a flow of 1% NH_3 at room temperature,[4] and believed that a charge transfer of electrons from NH_3 to SWNTs was responsible for the observed change. On the other hand, theoretical calculations on isolated defect-free nanotubes have predicted that NH_3 molecules should physisorb to the tube wall without significant change in the band structure.[12] Bradley *et al.*[13] found that vacuum-degassed nanotube-FETs were insensitive to NH_3 and suggested that for NH_3 gas to be detected in the FET response, the NH_3 must first dissolve in a H_2O monolayer which forms on the nanotube-FETs under ambient laboratory conditions. In the light of electrochemically mediated charge transfer mechanism, the observed resistive response can be
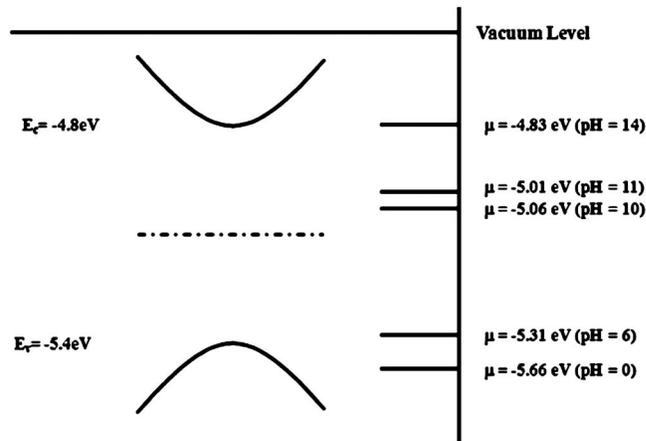
understood on the basis of differences in the chemical potentials of the redox couple of the ambient in the presence of hydrazine and the Fermi energy of the p-type SWNTs similar to the enhanced conductivity seen in the hydrogen terminated diamond.[11] The air exposed SWNTs are known to be p-type with work function of 5.1 eV, electron affinity of 4.8 eV, and ionization potential of 5.4 eV (i.e., band gap of 0.6 eV).[14–16] The chemical potential corresponding to the redox couple in the presence of aqueous hydrazine (pH=11) is calculated to be −5.01 eV according to the electrochemical reaction, $O_2+2H_2O+4e^-=4OH^-$ so it lies above the Fermi level of the p-type SWNT and expected to be closer to the valence band maximum as shown in Fig. 3. Therefore, one expects the redox couple to act as a donor to p-type nanotubes and undergoes a charge transfer from the aqueous hydrazine to the SWNT and the majority carrier holes get depleted resulting in an increase in the resistance of the device. Once the hydrazine is flushed off with dry N_2 the resistance recovers to its initial state.

The resistive response of the device is consistent with the amount of hydrazine present and exhibits a linear response as shown in Fig. 4. This can be understood in terms of the monolayer coverage of the nanotube surface being not complete by the gas molecules within the range of parts per
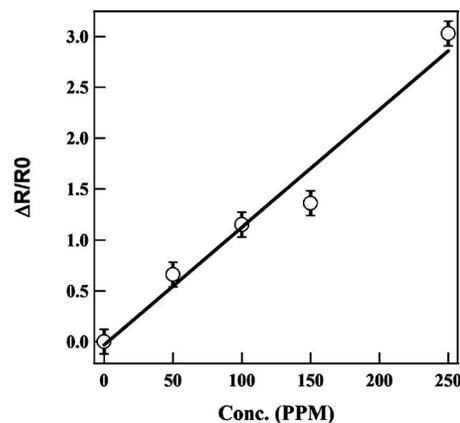

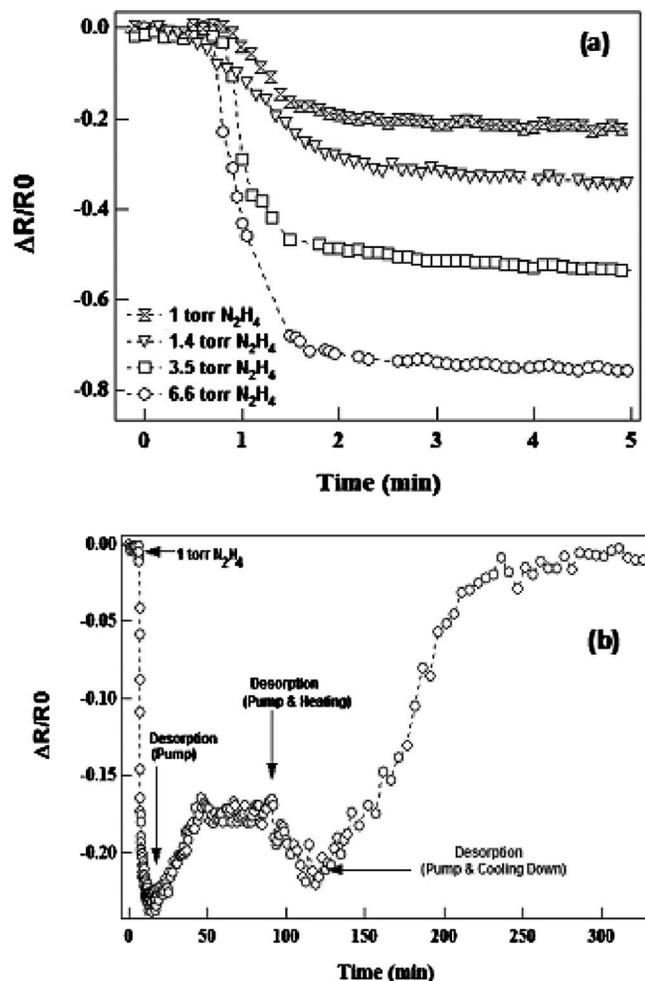FIG. 4. Sensor response vs concentration of hydrazine for a p-type SWNT network.

FIG. 5. (a) Sensor response vs time (minutes) for an annealed (n-type) SWNT network for varying pressure. (b) Resistive response of the n-type sensor upon exposure to 1 torr of hydrazine followed by desorption brought on by pumping. Pumping alone can only partially recover the resistance of the network, saturation is seen in the mid region from ~50–100 min. By heating to 150 °C at t~100 min the resistance is seen to temporarily decrease followed by an accelerated desorption process as the device cools.

FIG. 6. n-type sensor response vs concentration of hydrazine.

million levels studied. A saturation of the response is expected after complete monolayer coverage is reached.

To better understand the molecule-SWNT interaction, a series of experiments were performed under controlled environments of constant pressure and temperatures. A set of room temperature experiments were performed on a vacuum annealed device subjected to 150 °C annealing under a pressure of $<10^{-7}$ torr and then cooled to room temperature. It is known that once the O_2 is removed, the SWNT sample behaves as an n-type semiconductor as seen in earlier works.[5–7,9,17] The device was then exposed to different pressures of hydrazine vapor with the saturated vapor pressures in the range of 1–7 torr and the response $\Delta R/R_0$ of the device was recorded. Figure 5(a) shows the monotonic device response to various hydrazine vapor pressures.

When the resistance of the device has reached saturation, desorption was attempted through vacuum pumping on the device. The initial recovery response with pumping alone was found to be slow and it was necessary to heat the sample t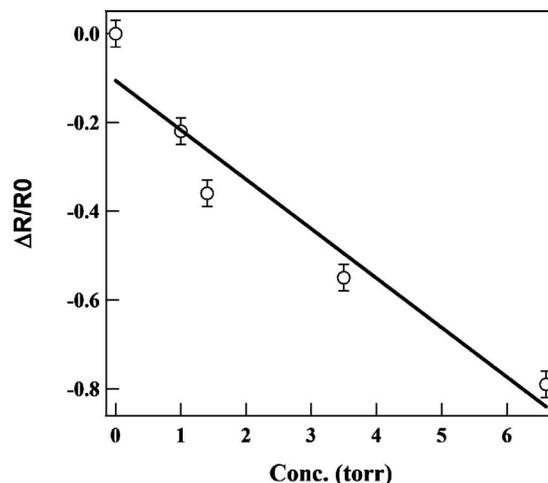o 150 °C for complete recovery. Desorption kinetics are shown in Fig. 5(b). It is clear that only a partial recovery is possible by pumping alone. Heating under vacuum enhances the desorption kinetics. It is worth noting the intrinsic temperature dependence of the SWNTs during heating and cooling.

Since the vacuum degassed SWNTs behave as n-type semiconductors the Fermi level of the SWNTs lie closer to the conduction band. As seen earlier the electrochemical potential of the redox couple corresponding to the pH value of aqueous hydrazine lies closer to the conduction band of the SWNT. From Fig. 5(a) it can be seen that the device exhibits a negative response in contrast to the positive response shown by the device when exposed to ambient air. Again the charge transfer occurs from aqueous hydrazine to the SWNTs but this time increasing the majority carrier electrons and hence increasing conductivity of the SWNT device.

The resistive response of the device shows linear dependence with the saturated vapor pressure of hydrazine as shown in Fig. 6. Again the complete monolayer coverage is not achieved at the highest concentration tested at room temperature.

To expedite the recovery of the resistance of the vacuum degassed device; the device was initially vacuum pumped and then simultaneously exposed to UV light at 340 nm. It has been seen in earlier work by Chen *et al.*[18] that UV light exposure promotes the desorption kinetics of adsorbed gas molecules (photo induced desorption). As seen in Fig. 7(a), once the device was exposed to UV light during pumping, the resistance of the device recovered much more rapidly than the sample subjected to pumping alone. It can also be seen that when the UV light is turned off the rate of desorption decreases and the device resistance recovers slowly. Multiple sets of UV light exposure were conducted on the device during the recovery of the resistance of the device. This is shown in the Fig. 7(b) with arrows.

Next the hydrazine-SWNT interaction was studied at low temperature. The device was cooled down to 5 °C using a temperature controlled ice bath while being degassed and the change in the resistance was recorded. The device was then exposed to different pressures of hydrazine vapor and the change in the resistance of the device was recorded as
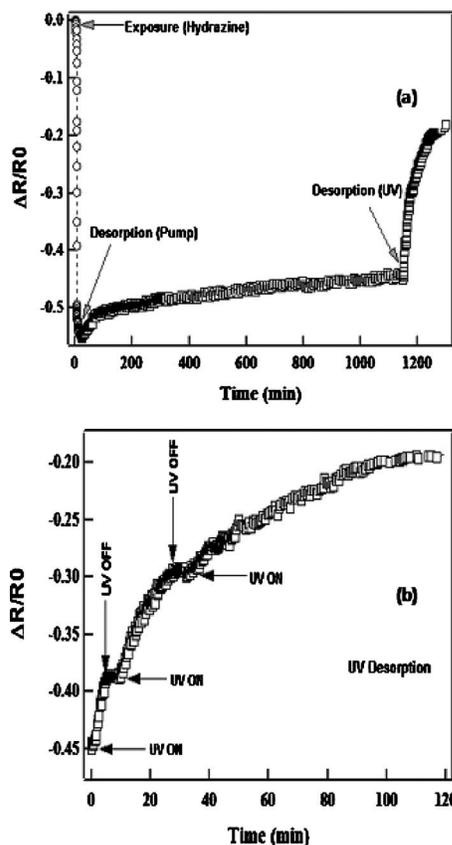
FIG. 7. (a) Resistive response of the n-type sensor upon exposure to 3.5 torr of hydrazine followed by desorption brought on by pumping. The desorption rate can be greatly increased by adding UV exposure as seen at t∼1200. (b) Desorption response of hydrazine to intermittent UV exposure with constant pumping.

FIG. 8. (a) Sensor response vs time (minutes) for an annealed (n-type) SWNT network for varying pressure. (T∼5 °C). (b) Sensor response vs concentration of hydrazine for a n-type SWNT network.

shown in Fig. 8. Similar negative resistive response was observed with an enhanced sensitivity as compared to when the device was operated at room temperature. The response is seen to saturate for higher exposures due to enhanced adsorption and slower desorption (in the dynamic situation) at lower temperatures.

In order to investigate the detection limit of the device, the degassed device at room temperature was exposed to parts per million levels of hydrazine under static conditions and the resistive response was measured. Argon is used as a dilution gas in this case. Results are shown for 100 and 1000 ppm levels of hydrazine in Fig. 9. It can be inferred from the results that hydrazine down to 500 ppb level can be easily detected when the signal to noise ratio is compared in the data for the measured concentrations with high enough sensitivity.[19] Similar value for the detection limit was obtained using the data shown in Fig. 2.

To further understand the mechanism of sensing for hydrazine and ammonia the gate dependence measurements were performed on the individual s-SWNTs FET device with a silicon substrate used as a back gate. Gate voltage (V_{gs}) is swept from −10 to 6 V and the conductivity is measured. The device showed a p-type behavior on the as grown SWNTs and n-type behavior for the vacuum (P < 10^{-6} torr) annealed device. This behavior is shown in Fig. 10.

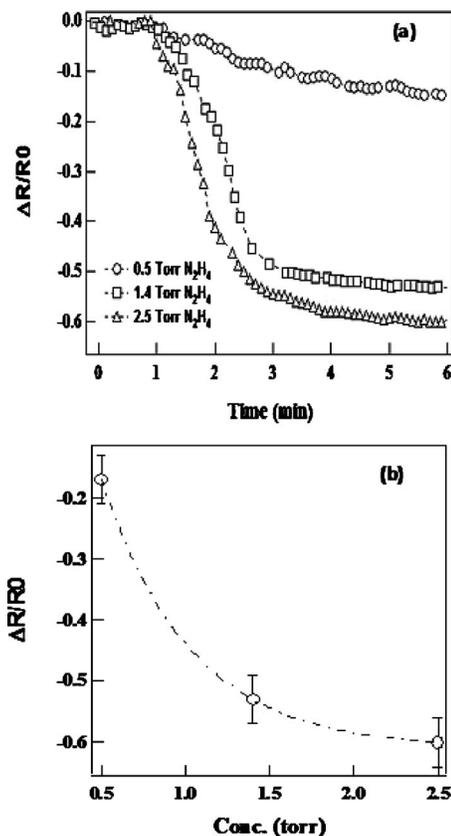The vacuum annealed SWNT sample was exposed to 1

torr of N_2H_4 vapor and 760 torr of NH_3 at room temperature. Gate dependence measurements were performed on the device once the device resistance was found to be saturated. From Fig. 10 it can be seen that for both N_2H_4 and NH_3, the conductivity of the sample was increased which supports the negative response seen earlier in the vacuum annealed sensor device. The ratio of the I_{on}/I_{off} was found to be 720 for N_2H_4 and 379 for NH_3 which also confirms that the device is more sensitive to N_2H_4 than to NH_3. It is also seen that the Turn ON (threshold) voltage shifts further negative from −2 to −4 V for N_2H_4 (1 torr) and −2 to −6 V for NH_3 (760 torr)
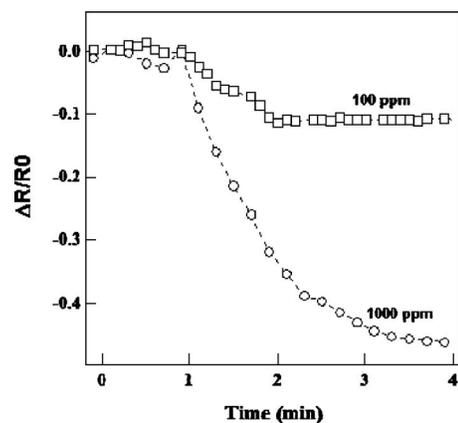

FIG. 9. n-type sensor response vs time (minutes) for parts per million level of hydrazine diluted in nitrogen.
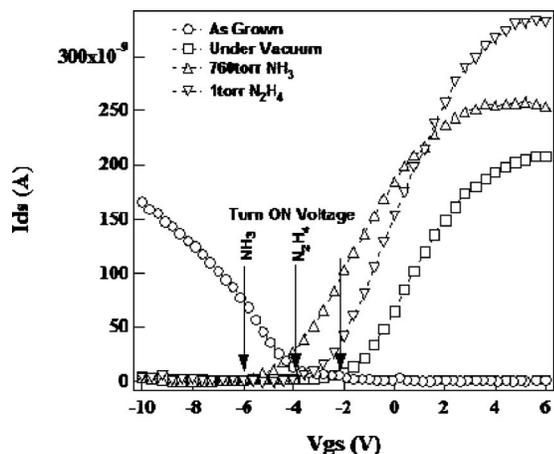
FIG. 10. FET characteristics (source-drain (I_{ds}) current vs gate voltage (V_{gs})) of an individual SWNT for as grown, vacuum annealed, and hydrazine exposed device. The threshold voltages are shown by downward arrows.

as shown by the down pointing arrows. This confirms a charge transfer occurring between the aqueous N_2H_4 and aqueous NH_3 with SWNT.

To shed light on the n-type behavior of the tube when exposed to the N_2H_4 molecule, we have carried out the electronic band structure calculations using the density functional theory based simulation method, referred as VASP.[20,21] The electronic band structure of the zigzag SWNT (8, 0) was studied in four cases:

(i)   The pristine tube.
(ii)   The tube with a hydrazine molecule adsorbed on its surface.
(iii)   The tube covered with a water film.
(iv)   The tube covered with the water film and a hydrazine molecule adsorbed on its surface near the water film.

The results of the four tests cases are shown in Fig. 11. The pristine tube has a gap of ~0.65 eV showing semiconductor behaviors [Fig. 11(a)]. Comparing to the pristine tube, we found that the band structure of the SWNT with the hydrazine adsorption is practically unaltered [see Fig. 11(b)]. The states associated with N_2H_4 are found in the valence and the conduction bands, and no new energy levels are introduced near the bottom of the conduction band to generate an n-type behavior.

When a H_2O film is covered on the tube, the gap is reduced to ~0.3 eV (i.e., more states are created by the H_2O film in the gap region), as shown in Fig. 11(c). When a N_2H_4 molecule is added to the surface near the H_2O film we found that there are occupied states associated with N_2H_4 located near the bottom of the conduction band, representing an n-type behavior for the system [see Fig. 11(d)] at finite temperatures. In order to further delineate the role of water and how its interaction with N_2H_4 alters the band structure of the SWNT, we have compared the results for the tube covered with almost a monolayer of H_2O film with corresponding results for the tube covered with fewer H_2O molecules. We found that the interaction between N_2H_4 and the water molecules in the latter case is not strong enough to introduce
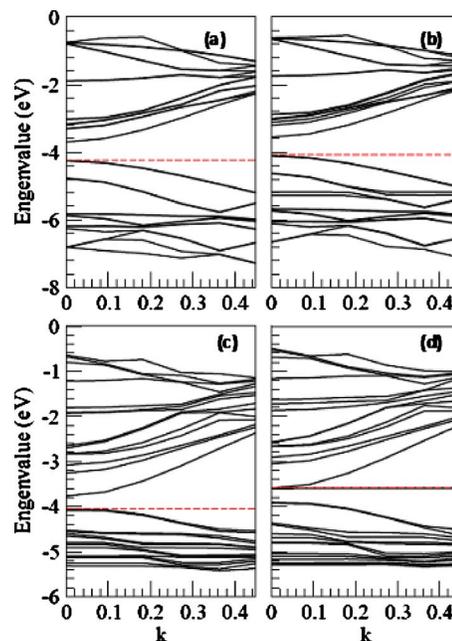

FIG. 11. (Color online) The calculated electronic band structures of (a) the pristine tube (8, 0), (b) a N_2H_4 molecule adsorbed on the tube (8, 0), (c) the pristine tube (8, 0) covered with water film, and (d) a N_2H_4 molecule adsorbed on the tube (8, 0) covered with water film. The red dashed line in each plot is the corresponding Fermi energy. The k points are along the tube axis.

occupied states near the bottom of the conduction band. From these studies, it is evident that with the addition of a monolayer of water molecules on the SWNT, strong interactions among H_2O, N_2H_4, and the SWNT are induced, and new occupied states are introduced near the bottom of the conduction band that lead to an n-type behavior. This finding is consistent with our experimental observation.

IV. CONCLUSION

Based on the data of the p-type and n-type SWNT device's response to hydrazine it can be concluded that s-SWNTs can be used for hydrazine sensing at room temperature and lower temperatures. Thin films of randomly oriented SWNTs were synthesized on a Si/SiO_2 substrate by CVD using Fe nanocatalysts. The change in the resistance of the film is found to be exponential, with time constants for adsorption being a few minutes and shorter compared to that of desorption. The detection limit for SWNT network sensor is estimated to be ~500 ppb.

From the experimental study and the theoretical calculations it can be seen that the presence of a water film around the surface of the SWNTs is necessary for the charge transfer from N_2H_4 to s-SWNTs. The charge transfer mechanism is supported by desorption of N_2H_4, which requires additional energy like heat or UV light. This desorption allows for the s-SWNT sensors to be reused by "resetting" their resistance, via, nitrogen flow, vacuum pumping, heating, and/or UV light exposure.

The gate dependence transport study also showed a significant shift in the "Turn ON" voltage during the adsorption of N_2H_4 by n-type SWNT which also supports the charge transfer mechanism.

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