Different mechanism of capacitance change for gas detection using semiconducting and metallic single-walled carbon nanotubes

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ABSTRACT
Semiconducting single-walled carbon nanotubes (s-SWCNTs) with lower absorption energy of NO2 gas exhibited higher sensitivity than metallic SWCNTs. The result originated from quantum capacitance of s-SWCNTs, which was readily affected by charge transfer, whereas that of m-SWCNTs showed no change with even more transferred charges. However, m-SWCNT that were aligned polarize adsorbed gases on the surface by a local field that contributed the capacitance changes of m-SWCNT networks. This is a newly introduced detection mechanism of gas sensing using m-SWCNTs.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) have demonstrated superb responses to various gases due to the full utilization of a large surface area of exposed carbon that, as a consequence, facilitates direct interactions with foreign gases. In particular, the existence of π electrons on the SWCNT surface provides the best platform for sensors with reasonable adsorption energies and adsorption/desorption time [1,2]. Adsorption of gases in general involves changes in resistance, charge transfer, threshold voltage, dielectric constant, and capacitance [3–8]. For instance, a resistive-type gas sensor measures the conductance variation due to the charge transfer between CNTs and the target gases, whereas the change in dielectric constant cannot be measured directly with this approach.

Gas adsorption on CNTs has also been characterized by measuring the capacitance (C) [9–13]. Change in dielectric constant (ε) by the adhesion of gases with different ε on a sensing element, was reported to cause the capacitance change (∆C). More specifically, the capacitance change originates from both polarization of gases due to a strong local electric field (εL) and quantum capacitance (Cq) of the CNTs, although these effects compete with each other depending on the electrode geometries [14–16]. This is competing effect, together with dynamic behaviors in a capacitive-type sensor, is often advantageous in classifying and identifying target gases by simultaneously measuring both electronic and dielectric properties of the CNTs upon gas adsorption, as opposed to the resistive-type which measures only the electronic properties of the CNTs.

Analyses of the gas detection mechanism of SWCNTs have been made ambiguous by the presence of both metallic (m-) and semiconducting (s-) SWCNTs in the channel. Since m-SWCNTs in the channel are expected to exhibit different responses from those of s-SWCNTs, use of a single type of SWCNT is highly desired. The capacitive responses of gas sensors can be stemmed from both charge transfer and dielectric constant change, separate tests with only s- and m-SWCNTs are desired to differentiate the two effects—charge transfer and dielectric constant change between them, which has not yet been reported.

The purpose of this letter is to elucidate the underlying
detection mechanism of the SWCNTs using separated metallic and semiconducting SWCNTs as a channel. We were able to observe different origins of the capacitance change in the metallic channel from that in the semiconducting channel. A remarkable quantum capacitance change of approximately 2500% was observed in s-SWCNTs, originating from a change in the electronic structures near the Fermi level rather than to charge transfers. On the other hand, in the case of m-SWCNTs, no appreciable quantum capacitance variation was observed due to the constant density of states (DOS) near the Fermi level. Instead, the capacitance was increased slightly by the polarization of gases due to strong local electric field in the case of aligned m-SWCNTs. This mechanism does not depend on the electronic structure, but local alignment of SWCNTs, which enables metallic SWCNTs to be used for gas detection.

2. Experimental

Highly purified arc-discharge SWCNTs were dispersed and separated into metallic and semiconducting ones using density gradient ultracentrifugation (DGU) [17]. The purity of the separated SWCNTs was characterized using UV--vis-IR absorption spectroscopy, as shown in Fig. 1(a). The pristine SWCNTs exhibited van Hove singularity peaks both from m- and s-SWCNTs, which were positioned near 700 nm (M11) and 1000 nm (S22), respectively. Optical images of each solution are presented in Fig. 1(b). Suppression of M11 peak intensity in s-SWCNTs and of S11 peak intensity in m-SWCNTs clearly demonstrated the efficiency of the DGU separation. Two separated solutions were dispensed on the interdigitated electrodes (Cr (10 nm)/Au (50 nm)) with a gap of 2.5 μm by the two different methods of drop casting and dielectrophoresis. The voltage applied for dielectrophoresis was about 5–10 Vpp at 10 MHz. Images of the as-prepared devices, presented in Fig. 1(c) and (d), exhibited different distributions of SWCNTs networks, i.e., a random network from drop-casting and an aligned network from dielectrophoresis. Both m-SWCNTs and s-SWCNTs were aligned parallel to the direction of the electric field, independent of the metallicity, which contrasts with the results of a previous report [18]. After depositing SWCNTs, the device capacitance increased by 3–4 orders of magnitude. We were not able to control the uniformity of density of SWCNTs, but the device capacitance was quite consistent under the same deposition conditions. The Raman spectrum shows a clear G-band near 1590 cm⁻¹, as shown in Fig. 1(e). In addition, a broad fluorescent spectrum was also observed due to the presence of surfactant introduced during the process.

![Image](image_url)
separation process. After rinsing with methanol, the fluorescence band was removed, and a clear G-band near 1590 cm\(^{-1}\), a 2D-band near 2681 cm\(^{-1}\), and radial breathing modes (RBMs) near 187 cm\(^{-1}\) were present, indicating the formation of solid SWCNTs in the channel, as shown in Fig. 1(f).

To characterize the capacitance response of the sensor, the real \(Z_1\) and imaginary \(Z_2\) impedance was measured with a 2-terminal method using a potentiostat (Solartron 1287) and an impedance analyzer (Solartron 1260 FRA). The applied AC bias and frequency were 3 V\(_{\text{rms}}\) and 100 kHz, respectively. The parasite capacitances from cable, electrodes, gate oxide were examined using a blank sensor and suppressed below a detection level. The capacitance of SWCNTs was then derived based on an equivalent parallel RLC circuit \[ C = \frac{Z_2}{\omega (Z_1 + Z_2)} \], where \(\omega\) is the angular velocity. The capacitance of gas sensor varied depending on the deposition method, density, and metallicity of SWCNTs, i.e., under the same conditions of dielectrophoresis, m-SWCNTs generally showed a larger capacitance than s-SWCNTs. For DC resistance, the 2-point resistance was measured using a digital multimeter (Keithley 2000). Concentrations of all gases used in this study were fixed at 20 ppm.

3. Results and discussion

The capacitance increased rapidly with exposure to NO\(_2\) gas in the drop-casted s-SWCNTs channel (Fig. 2(a)), where the SWCNTs were randomly entangled with one another. The sensitivity \( \Delta C / C \) (\(\%\), \(=100 \times (C_f - C_i)/C_i\)), reached about 50% in the s-SWCNT channel and decreased slowly with desorption of the NO\(_2\) gas. The irreversible recovery indicated relatively strong adsorption binding of NO\(_2\) molecules to the CNT surface. The resistance decreased in a manner similar to that of the capacitance change (inset of Fig. 2(a)). On the other hand, in the m-SWCNT channel, neither appreciable capacitance or resistance changes were observed (Fig. 2(b)).

![Fig. 2. Capacitance (C) responses of (a) s-SWCNTs and (b) m-SWCNTs prepared with drop-casting and (c) s-SWCNTs and (d) m-SWCNTs prepared with dielectrophoresis. The inset of each figure shows resistance (R) changes measured with a Keithley 200 multimeter.](image)

Similar experiments were performed for the samples prepared by dielectrophoresis, where the SWCNTs were aligned preferentially in the direction of the applied field. After exposing s-SWCNTs to NO\(_2\) gas, the capacitance increased by 25 times with respect to an initial capacitance of s-SWCNTs (Fig. 2(c)), remarkably larger than previously reported values \[4\]. It is also interesting to note that the resistance decreased by only 2.5 times, implying that the origins of the increased capacitance \(\Delta C\) and decreased resistance \(\Delta R\) may be identical although their transduction coefficients to charge transfer would be different. Interestingly, in the case of an aligned m-SWCNT channel, the capacitance increased rapidly and became saturated, giving rise to a detectable sensitivity of approximately 3% (Fig. 2(d)), in a good contrast with that of the randomly oriented m-SWCNT channel. No appreciable resistance change was observed from m-SWCNTs. These distinctive behaviors observed from both different metallicity and degree of alignment of SWCNTs have never been observed before, and the underlying mechanism of these behaviors is still undetermined.

It has been reported that the adsorption of NO\(_2\) gas is more favorable for m-SWCNTs than for s-SWCNTs due to a stronger binding energy on m-SWCNTs \[20–22\]. Furthermore, m-SWCNTs show larger charge transfers from CNTs to NO\(_2\) molecules compared to those from s-SWCNTs to NO\(_2\) molecules \[23\]. Therefore, our observations of large capacitance changes in the s-SWCNTs and smaller changes in the m-SWCNTs cannot be explained by a simple charge transfer mechanism. This raises two fundamental uncertainties: (i) the source of the sensitivity difference between m-SWCNTs and s-SWCNTs if charge transfer is not a crucial factor and (ii) the effect of CNT alignment on the enhancement of capacitive sensitivity, particularly in m-SWCNTs.

In general, gas adsorption on the SWCNT channel involves charge transfer. However, this may not be the only cause of the observed sensitivity behaviors in s- and m-SWCNTs because m-
SWCNTs with a larger amount of charge transfer exhibited reduced sensitivity compared to that of the s-SWCNTs. The rationalization of this behavior can be hypothesized from the quantum capacitance of SWCNTs, which is correlated to the electronic DOS at the Fermi level. The quantum capacitance \( C_q \) can be expressed as \( C_q = \frac{dQ}{dV_o} \).

The charge density, \( Q \), in the semiconductor can be further written as, \( Q = q \int_0^\infty g(E) [f(E + E_g/2 + qV_o) - f(E + E_g/2 - qV_o)] dE \), where \( g \) is the magnitude of charge, \( g(E) \) is the DOS, \( f(E) \) is the Fermi-Dirac distribution function, \( E_g \) is the band gap, and \( V_o \) is the local electrostatic potential [24].

To understand the correlation between sensitivity and quantum capacitance, the DOSs of similar diameter CNTs, metallic (5.5) and semiconducting (13.0) SWCNTs with NO\(_2\) adsorption occurring on their surfaces, were calculated using the density functional theory (DFT) implemented by Quantum Espresso code [25]. Ultrasoft pseudopotentials were employed with the generalized gradient approximation (GGA) for exchange and correlation in the Perdew–Burke–Ernzerhof functional [26–28]. The super cell sizes of (5.5) and (13.0) nanotubes were chosen to be \( 25 \times 25 \times 9.84 \) Å and \( 25 \times 25 \times 8.52 \) Å, respectively. The Brillouin zone was sampled with a \( 1 \times 1 \times 4 \) irreducible Monkhorst-Pack k-point grid [29]. Our model structures were relaxed until the forces on the atoms were less than 0.025 eV/Å.

Fig. 3 shows the DOSs of (13.0) s-SWCNT and (5.5) m-SWCNT with and without NO\(_2\) gas. Because of the strong binding energy and electron affinity of the NO\(_2\) molecule to SWCNTs, charges are donated from SWCNTs to NO\(_2\). The amounts of charges transferred were 0.12 e for (13.0) s-SWCNT and 0.17 e for (5.5) m-SWCNT. As a consequence, the Fermi level was decreased by 0.6 eV for (13.0) s-SWCNT and located inside the valence band. At this new Fermi level, both NO\(_2\) and SWCNT states were observed, as indicated by the red line on the left panel of Fig. 3(a) (in the web version). The DOS of (13.0) s-SWCNT at the new Fermi level increased, contributing to the increment of quantum capacitance and electrical conductance as well after charge transfer. The density of states of the SWCNT itself was also modified upon NO\(_2\) adsorption, giving rise to the change in resistive sensitivity, as observed in the experiments. On the other hand, the effect of NO\(_2\) adsorption on m-SWCNT was quite different from that of s-SWCNT. The Fermi level was slightly decreased by 0.1 eV toward the valence band in the case of the (5.5) m-SWCNT with NO\(_2\) adsorption (Fig. 3(b)). The increase in DOS near the new Fermi level resulted from localized NO\(_2\) states, which have nothing to do with the change in the DOS of the carbon nanotube. As a consequence, the density of states of the (5.5) m-SWCNTs remained unchanged at the new Fermi level. This gave rise to no change not only in the quantum capacitance, but also in the resistance of the m-SWCNT channel, in good corroboration with experimental observations.

We next assessed the effect of SWCNT alignment. When the same m-SWCNTs used for drop-casting were aligned by dielectrophoresis, we observed a sensitivity increase of 3–8% (Fig. 2(d)), which was persistently observed over 50 samples. Since the quantum capacitance of m-SWCNT was neither changed by NO\(_2\) gas nor affected by the alignment, the enhanced sensitivity of m-SWCNTs was rather peculiar. In general, total capacitance is the sum of quantum capacitance, \( C_q \), and classical capacitance, \( C_d \). Since there is no change of DOS at \( E_F \) level, no change of quantum capacitance is expected from m-SWCNTs. Therefore, we consider only classical capacitance \( C_d \). The classical capacitance is calculated as \( C_d = \varepsilon_0/\varepsilon_r d \), according to Debye’s expression, \( \varepsilon_r = 1 + 4\pi N\epsilon_0 a_i + \mu^2/3k_BT \), where \( N \) is the number of molecules, \( a_i \) and \( \mu \) are the electronic polarizability and dipole moment of molecules, respectively, \( \varepsilon_0 \) is the Boltzmann constant, and \( T \) is the absolute temperature [30]. Therefore, \( C_d \) is affected by the local field, which is subject to the arrangement of SWCNTs between electrodes. The variation in dielectric constant particularly for polar molecules is dominated by orientation of molecules rather than their electronic polarization.

To study the polarization effect, m-SWCNTs were exposed to each gas until their capacitances were saturated by adsorption, as shown in Fig. 4(a). The bias voltage was then decreased to 0.5 V/μm (from 3 V/μm) and increased to 3.0 V/μm to monitor the capacitance change caused by the rotation of polar gases with respect to the applied field. In this scheme, we distinguished the effect of \( C_d \) from that of \( C_q \). The orientation polarization of NO\(_2\) gas at the edge of SWCNTs by a local electric field is schematically presented in Fig. 4(b). The capacitance curves in Fig. 4(c), normalized by the
initial capacitance ($C_0$), are presented as a function of electric field. At low field strength, the change in the capacitance was linearly proportional to the field, following Debye’s relationship, as shown in Fig. 4(b). At high field strength ($\mu E/kT >> 1$, the electrostatic energy of the dipole was much greater than the thermal energy), the capacitance increased almost exponentially, implying a contribution of nonlinear higher order terms, which is expressed by

$$\epsilon = 1 + 4\pi N(\mu^2E/3kT - \mu^4E^3/45k^2T^3 + 2\mu^6E^5/945k^3T^5 + \cdots)$$

[30]. Fitting the NO2 curve to this equation with higher orders well fitted the experimental data, as shown in Fig. 4(b). Here the capacitance change is expressed in the dielectric constant change, which is proportional to the dipole moment of the molecule, i.e., the higher is the dipole moment, the larger is the capacitance change.

However, the capacitance change with gases of different dipole moments did not follow this trend. For instance, as shown in Table 1, the dipole moment of the SO2 molecule is around 5 times higher than that of NO2, which is opposite the present observations. Another important parameter is $N$, which is the number of molecules in the system. Since the aligned SWCNTs simply promote molecular reorientation for those molecules which stay near the SWCNTs, the capacitance change is invoked from molecules near the SWCNT electrode. Therefore, $N$ can be defined as the number of molecules that are influenced by the local field of aligned SWCNTs.

This value then changes as the field strength increases. In particular, those molecules which are adsorbed on the CNT surface are most influential to the capacitance change. The number of molecules that are adsorbed on the CNT surface is strongly related to the adsorption energy. As shown in Table 1, the adsorption energies of the compounds follows the order NO2 > SO2 > NH3. This trend coincides with the capacitance changes observed in the experiments. Thus, our results support the idea that the observed capacitance in Fig. 2(d) was attributed to the polarization of NO2 gas adsorbed on the CNT surface due to induction by a strong local field of aligned m-SWCNTs.

It is possible in our measurements that the junction capacitance between SWCNT-metal electrodes may go into effect. However, the junction capacitance in an SWCNT-FET was observed to be negligible comparing to the one from the channel[35,36]. To see the effect of the junction capacitance, we annealed the sensor in a vacuum system at various temperatures to change the junction nature. Nevertheless, the phenomenon observed above sustained. This underlines that the capacitance change resulted from the interaction of NO2 to SWCNT channels, not to metal-SWCNT junction.

4. Conclusions

In summary, using aligned s- and m-SWCNT and drop casted s- and m-SWCNTs, we systematically analyzed the cause of capacitance variations. Although NO2 gases donate more charges to m-SWCNTs than s-SWCNTs, the larger capacitance change was observed from s-SWCNTs, rather than m-SWCNTs. Such a remarkable response of s-SWCNTs originated from a band structure whose DOSs are more subject to change at $E_F$, whereas those of m-SWCNTs were constant near $E_F$, resulting zero change of quantum capacitance after the charge transfer. In addition to the capacitance response invoked by electronic structures, the aligned SWCNTs gave rise to capacitance changes due to the polarization effect induced by the molecular reorientation. This provides m-SWCNTs with a mechanism to detect to polar gases, which has been known to be disadvantageous in gas sensing through a change in carrier concentration.
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References

[19] In a series equivalent circuit, the capacitance behavior was very similar to that of a parallel one, although magnitudes of the capacitance changes were reduced slightly.