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In-plane impedancemetric ammonia sensing of solution-deposited, highly semiconductor-enriched single-wall carbon nanotube submonolayer network gas sensors

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ABSTRACT

We present the impedancemetric operation of ammonia gas sensors based on drop-deposited, 99% semiconductor-enriched single-walled carbon nanotube networks. Impedance spectroscopic data for these devices exhibit a complex impedance over a range of frequencies (0.5 Hz to 300 kHz) and are well fit with a proposed equivalent electrical circuit model. The effect of NH_3 on the high-frequency arc resistance is described by a linear law at all NH_3 concentrations, indicating the possibility of utilizing the impedance spectra as the main sensing signal. The impedancemetric operation mode demonstrates a sensitivity of 3.70%/ppm at 3.6–41.4 NH_3 concentration, which is equivalent to an improvement in sensitivity of 2.1 times compared to conventional direct current (dc) measurement. Furthermore, impedancemetric sensing is much less susceptible than conventional dc to noise problems in the very low frequency or dc due to ionic contamination or dissociated NH_3 molecules.

1. Introduction

The rapid development of carbon nanotube (CNT)-based devices for chemical sensing, since pioneer works by Kong et al. [1] and Collins et al. [2] in 2000, has until recently attracted intensive research interest, because they show unique performance that cannot be achieved using conventional solid-state sensor technologies, due to CNT's unique physicochemical properties. A number of sensors for detection of analytes related to environmental monitoring, medical diagnostics, and food safety and security have been developed using individual CNTs [3,4], randomly oriented CNT networks [5,6], vertically or horizontally aligned CNT films [7,8], or polymer/CNT composites [9–11] as sensing elements. Especially, CNT networks are increasingly being used for chemical sensors because they are amenable to mass production and show a highly sensitive response to their chemical environment. Although significant progress has been made in exploring CNT networks as chemical sensors, at this point, there is still some ongoing controversy with regard to the underlying sensing mechanisms [12–20].

SWCNT network sensors have two basic modes of operation: conductance-based and capacitance-based detection. The resistive sensors detect the target gas by changing electrical conductance due to charge transfer effect and/or the Schottky barrier modulation at the metal–CNT contact [12–18]. In the CNTFET network, on the other hand, the gate capacitance is affected by both dielectric polarization and charge transfer upon exposure to analyte molecules, but the charge contribution is less than 10% [19,20].

Whichever sensing mechanism is actually responsible for a CNT sensor's operation, it is extremely important to form an electrically percolating network of only semiconducting single-walled carbon nanotubes (s-SWCNTs) for high sensitivity since only the resistance of s-SWCNTs can be significantly modulated by the absorbed molecules. In a normal CNT random network, approximately one-third of the tubes show metallic behavior and two-third have semiconducting properties. This heterogeneity makes it difficult to understand the sensing mechanism, because of the formation of Schottky barriers and isotype heterojunctions at metallic–semiconducting and semiconducting–semiconducting nanotube crossings, respectively [21,22].

In recent studies, we found that the dominant sensing mechanism is highly dependent on the semiconducting/metallic nanotube ratio within SWCNT network films (see Fig. S2 and Fig. 3). The most important aspect to note is that the 90% semiconducting single-walled carbon nanotube devices show a pure resistance, while the 99% devices exhibit a complex impedance and have a much higher sensitivity than the 90% devices, although

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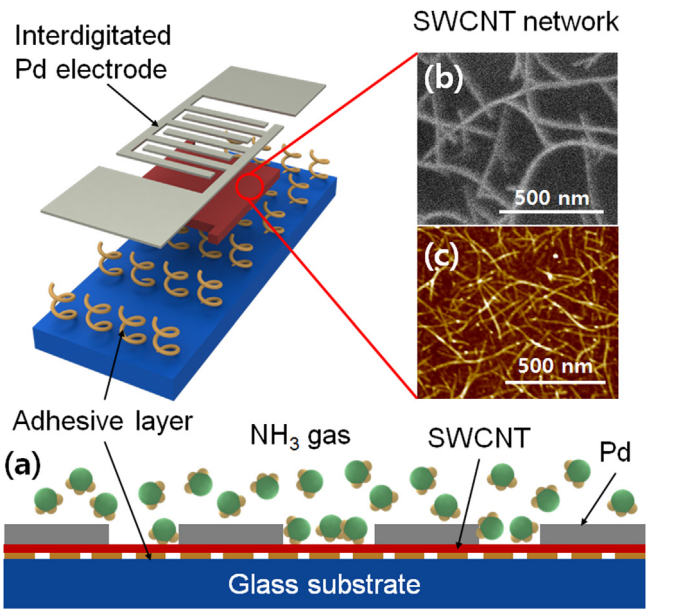

Fig. 1. (a) Schematic of the SWCNT NH_3 gas sensor geometry. (b) SEM and (C) AFM images of 99% semiconductor-enriched SWCNT networks. The SWCNT networks were solution-deposited on the glass substrate. Pd was evaporated on the SWCNT network and the interdigitated electrodes were patterned by lift-off.

the same electrode metal contacts and identical fabrication processes are employed. These results may be due to several factors. The electrical characterization of CNT-based gas sensors is usually performed using a constant direct current (dc) voltage. However, dc measurement cannot clearly reveal the sensing properties of a heterogeneous network of semiconducting and metallic nanotubes.

To overcome this deficiency, we employ impedance spectroscopy, rather than the conventional dc measurements, at frequencies between 0.5 Hz and 300 kHz to extract the complex impedance of a solution-deposited 99% s-SWCNT network sensor with interdigitated electrodes for a better understanding of the ammonia (NH_3) gas sensing mechanism. Impedance spectroscopy is a well-established technique for the measurement of material properties and interfaces, and chemical processes, but is recently growing in interest for use in chemical and biological sensors [23–25]. Impedancemetric measurements give relevant information in three variables: the real and imaginary components of the impedance and the frequency. The most important advantage of these ac methods is to obtain details about specific contributions to electrical conduction or polarization arising from different sources through their electrical analogs, whereas dc measurements show only the overall effect of these contributions. An independent separation of the different contributions to the sensor response is of significant importance to model and understand the sensing mechanism and thereafter to improve the performance of SWCNT network sensors.

2. Experimental

Fig. 1 illustrates a schematic of the SWCNT network gas sensor. The sensor consists of interdigitated palladium electrodes (Pd-IDEs) on top of the SWCNT network deposited on a 4-in. glass wafer. The IDEs provide a large sensing surface on the thin small SWCNT gap. First, the glass wafer surface was treated with oxygen plasma (50 W, 20 sccm, 5 min) to make it hydrophilic and then modified with poly-L-lysine by solution casting (0.1% w/v in H_2O) for 10 min to form amine-terminated adhesion [26–28] followed by rinsing with DI water. The nanotube networks were subsequently deposited by dropping 99% semiconductor-enriched

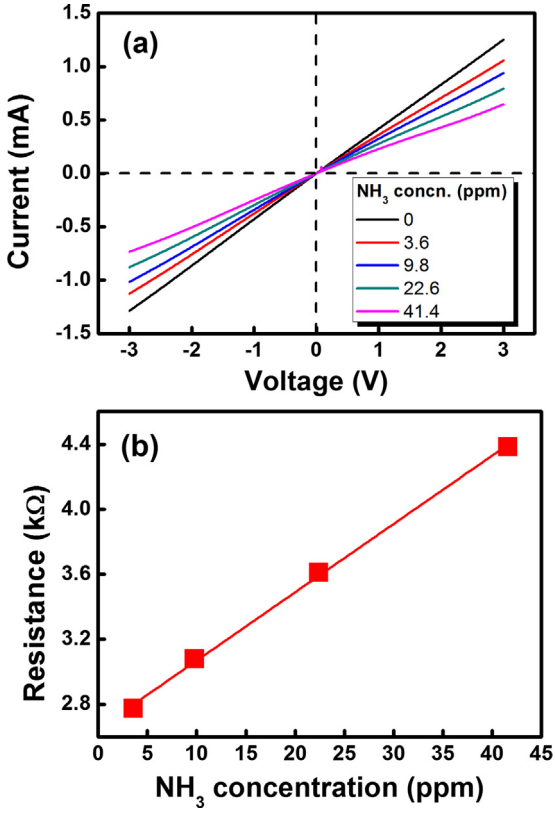

Fig. 2. (a) Two terminal dc current–voltage curves measured before and after exposure to different NH_3 gas concentrations for 99% s-SWCNT devices. The supply voltage, V was increased in a positive (or negative) direction at a rate of 100 mV/s. (b) The dc resistances as a function of NH_3 concentration.

SWCNT solution purchased from Nanointergris, Inc. (USA) without any densification or purification and dried for 2 h followed by rinsing with isopropyl alcohol. Next, for the interdigitated electrode and contact pad, a 30 nm-thick palladium was evaporated on top of the SWCNT network by a thermal evaporation system and patterned by lift-off with optical lithography using negative photoresist. For comparison, the 90% s-SWCNT network sensor was produced using an identical fabrication process.

Field emission scanning electron microscope (FE-SEM) and atomic force microscopy (AFM) systems were used to inspect and record the topography, showing submonolayer networks of SWCNTs, as shown in Fig. 1(b) and (c). The SWCNT sensing layer is too thin, and the underlying substrate surface is thus partially exposed.

3. Results and discussion

Fig. 2(a) shows the typical dc current (I)–voltage (V) characteristics measured before and after exposing the SWCNT network to different NH_3 concentrations for 10 min at room temperature, with the calculated resistance at a bias voltage of 1 V. Before the gas exposure, the I–V data exhibit a very linear ($R^2 = 0.9999$) and symmetric behavior, indicating that good ohmic Pd–SWCNT contacts had been achieved for 99% s-SWCNT devices. Reliable ohmic contacts between the CNT film and metal electrode are expected to confirm that the observed resistance change is mainly from the CNT film without influence from the contacts [29–31]. Such barrier-free two-terminal SWCNT devices have I–V characteristics more similar to highly resistive devices since the transport is not limited by the contacts. The resistance value obtained from the curve slope is 2.4 kΩ and includes the wiring and contact resistances as well as the SWCNT network resistance, which is the dominant part of the