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A simple approach in fabricating chemical sensor using laterally grown multi-walled carbon nanotubes

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Abstract

In this work, we proposed a new process for fabricating chemical sensors employing multi-walled carbon nanotubes (MWNTs) as the active sensing element. The MWNTs were selectively grown between lateral sides of the catalytic metals on pre-defined Nb electrodes. Upon exposure to air or NH_3, the electrical resistance of the MWNTs is found to decrease or increase, respectively. The response time decreases and the sensitivity increases while measurement temperature and gas concentration increase. Though there are a few technical problems to be solved, our results show a promising technique for chemical gas sensor.
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1. Introduction

There are various types of sensor for detecting small concentrations of combustible or toxic gases in air. Among them, semiconductor gas sensors are particularly interesting because of their structural simplicity and low price. But a drawback of the conventional semiconductor gas sensors is their operation at elevated temperature (typically in the range 200–500 °C), which implies that power is required. Obviously, it would be desirable for many applications if the sensor could operate at room temperature, and a reduction of the power consumption and sensor size is a key goal for gas sensors [1,2]. Since carbon nanotubes (CNTs) have excellent electrical conductivity, mechanical strength and nanometer scale sizes, they have been intensively studied as molecular-scale device elements and components for nano-machines [3–7]. Especially gas adsorption in CNTs is an important issue for both fundamental research and technical applications. CNTs change their electrical resistance drastically when exposed to alkalis, halogens and other gases at room temperature, raising hopes for better chemical sensors, although the CNTs are exquisitely sensitive to so many things that they may not be able to distinguish one chemical or gas from another. Recently, it has been reported that CNTs sensor, based either on single-walled carbon nanotubes (SWNTs) or on vertically grown MWNTs, can be used to detect NH_3 and NO_2 at room temperature and their sensitivity was high. However, for electronic applications an additional effort was necessary to remove CNTs from the templates and disperse them onto pre-patterned electrodes [8–11].

In this work, we fabricated the chemical sensor employing laterally grown MWNTs as the active sensing element and measured their gas sensing behaviors using dc electrical resistance.

2. Experimental details

The CNTs based gas sensor was fabricated by conventional silicon processing [12–14]. The details of our process are as follows. (i) The SiO_2 layer was grown on the n-type heavily doped Si wafer by a conventional dry oxidation process at 1100 °C [Fig. 1a]. (ii) The Nb electrodes with a 100 nm thick were deposited by sputtering using Ar plasma, and then patterned by photolithography and plasma etching [Fig. 1b]. (iii) We patterned a catalyst region on the electrodes using a second photolithography step aligned to the electrodes. Catalyst and oxide were then deposited by sputtering into patterned region followed by liftoff in acetone, where top oxide layer is introduced as a barrier layer

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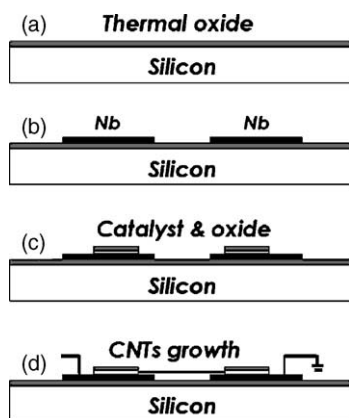
Fig. 1. Process flow for the fabrication of the resistive sensor using directly grown CNTs.

Fig. 2. SEM image of CNTs vertically grown on Co catalyst at 750 °C for 5 min under $C_2H_2/NH_3/Ar$.

for vertical growth and exposure gas, covering the top of the Co catalytic layer with a 100 nm thick [Fig. 1c]. (iv) Aligned MWNTs across the gap between the electrodes were grown in thermal CVD system with electrical feed-through. The CVD chamber temperature was rapidly raised to the process temperature of 750 °C within 10 min by halogen lamps after evacuation down to 10^{-2} torr. During the growth, a 3 V bias was applied across the Nb electrodes and the total pressure of the chamber was kept constant at 50 torr, while the total flow rate of process gases was maintained at 200 sccm (standard cubic centimeters per minute). For instance, the flow rate of the hydrocarbon source, C_2H_2 (acetylene), was 5 sccm and the remaining 195 sccm was for the carrier gases. After the CNT growth, the chamber was purged continuously with a mixture of H_2 and Ar until the chamber temperature reached room temperature [12,13].

To measure the dc electrical resistance R, the substrate were mounted in a test chamber with provisions for heating and cooling the sample and injecting different environmental gases. The chamber was purged continuously with Ar gas for 30 min. After the entire valves of reaction chamber were closed, the reaction gases were introduced in a hermetically sealed chamber for 3 sec. Argon was used as the carrier gas throughout the work. The NH_3 flow was varied from 25 to 500 sccm. The total flow was maintained at 500 sccm. When the ammonia concentration is translated into ppm, the concentration range of NH_3 in chamber was from 50 to 1000 ppm. Resistance measurements were performed under conditions of 100 mV [Fig. 1d]. All experiments were conducted with the same sensor. Prior to each measurement, the sensors were stripped of possible contaminating adsorbents by being baked at 150 °C for 2 h in an inert, flowing carrier gas.

3. Results and discussion

Fig. 2 shows a typical SEM image of vertically aligned CNTs. CNTs were grown on Co catalyst with a 10 nm thick at 750 °C for 5 min under $C_2H_2/NH_3/Ar$. As the size
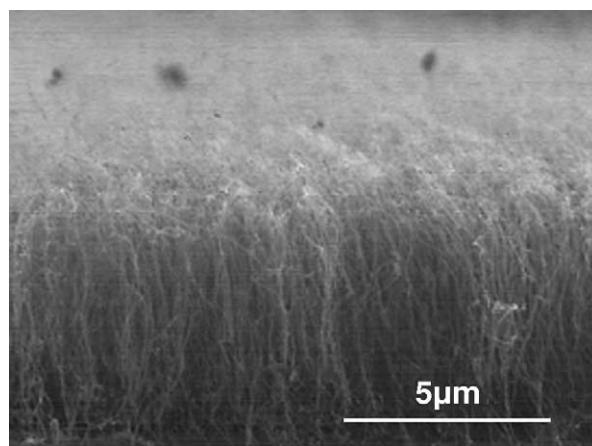
of the catalyst nanoparticles increases with the film thickness, the diameter of the CNTs increases linearly because the diameter of the catalyst tends corresponding to the inner diameter of the MWNTs. As mentioned in introduction, it was necessary to remove CNTs from the templates and disperse them onto pre-patterned electrodes for electronic applications.

For simple process, we experimentally present a direct nano-wiring of multiwalled carbon nanotubes between two parallel patterned electrodes under electric fields using thermal CVD. Fig. 3a shows photograph of a completed MWNT based gas sensor. The electrode pattern consists with seven pairs of arms (spacing gap between the arm ≈2 μm, arm width ≈50 μm) to provide large surface area for the sensor to interact with a gas. The CNTs were examined by field emission scanning electron microscopy (FESEM, Hitachi S4300). Fig. 3b show a typical SEM and TEM image of the laterally grown CNTs between Nb electrodes, respectively. The dark line in the center region of the images are aligned CNTs. The CNTs appear dark since they are electrically conducting, whereas the SiO_2 surface appears bright due to charging effects. The suspended MWNTs are very straight with little bending across the whole length and laterally aligned along the electric field. The reason for lateral align of CNTs is that the electric field directions between two electrodes. The electric field vector at the catalyst is nearly perpendicular to the substrate and upward. The electric field vectors are parallel to the substrate gradually in the middle of gap between the electrodes. The selectively grown CNTs form highly robust contacts. CNTs have a slightly wavy shape due to the increase of defects and the lower growth rate. We have carried out with several samples, and observed a reproducible though there is small arm-to-arm disparity in the density of CNTs. The average number of CNTs across the gap between the arms is about 3 per 10 μm. The CNTs are multi-walled CNTs with outer diameter range from 15 to 20 nm and consists of hollow compartments, looking like a bamboo.
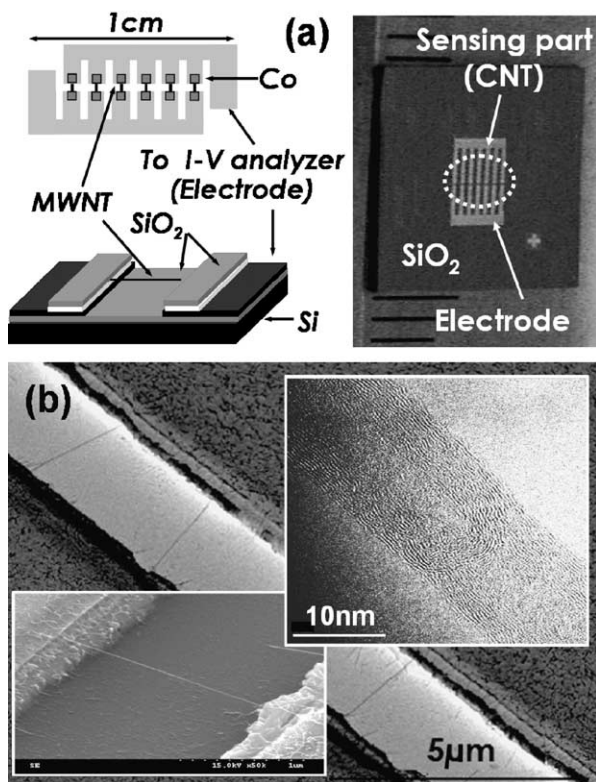
Fig. 3. (a) Photograph of completed MWNTs based chemical sensor (b) SEM image of aligned CNTs resting on SiO_2 surface after directed growth. The CNTs show clear alignment in the direction of the electric field. The insert shows TEM image of laterally grown CNTs.
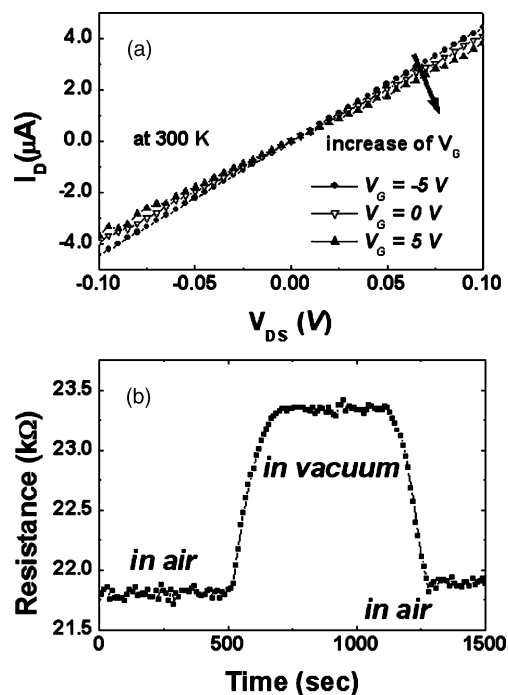

Fig. 4. (a) Typical drain current vs. drain-source voltage of three terminal CNTs device as a function of gate voltages and (b) electrical resistance of sensor by cycling chamber atmosphere from air to vacuum.

First of all, a control experiment was carried out with the same substrate and electrode structure. The electrical properties source-drain current (I_{DS}) versus source-drain voltage (V_{DS}), as a function of the gate voltages V_G for typical three terminal CNTs device are shown in Fig. 4a. The device approximates a voltage variable resistor reasonably well for small values of V_{DS} of ±100 mV with a two terminal resistance of 24 kR at $V_G = 0$ V. If the gate voltage is positive, the source–drain current decreases, and if the gate voltage is negative, it increases. These phenomena are signatures of hole-doped MWNTs acting p-type transistors like the semiconducting SWNTs [14]. In most cases, they show typical properties of metallic MWNTs that have no dependence on the gate voltage at room temperature. Gas sensing characterizations were conducted with the sample showing p-type semiconductor. We observed in situ measurement of electrical resistance by cycling chamber atmosphere from air to vacuum ($\leq 10^{-3}$ torr) at room temperature. The CNTs resistance is switched by 5–8 % as shown in Fig. 4b. Generally, using the as-formed CNTs without any further processing to fabricate CNTs electronic devices, the resulting devices are unipolar p-type. One of mechanisms to explain the p-type character of semiconducting CNTs is doping by the adsorption of atmospheric oxygen [9]. Therefore, as the sample was degassed in vacuum, R for CNTs increased.

We have observed resistance change at constant gas flow by cycling the purge gas from pure Ar to pure NH_3. Fig. 5a shows dynamic sensing response of the MWNT based sensor at room temperature upon exposure to NH_3 flow. Upon exposure to NH_3, the electrical resistance of the sensors is found to increase. This phenomenon can be explained by conventional p-type semiconductor theory. Upon exposure to electron-donor, electron charge transfer was found to be from the electron-donor to the p-type semiconductor. NH_3 may interact with MWNTs by replacing pre-adsorbed oxygen. Therefore, Exposure to electron-donating gases such as alcohol and NH_3, effectively shift the valance band of the nanotubes away from the Fermi level, resulting in hole depletion and increased resistance. The insert of Fig. 5a shows the response time to NH_3 content in Ar. The response time to 500 sccm NH_3 flow were ∼3 min. For the same sample, lowering the NH_3 flow to 25 sccm led to response time of ∼9 min [15,16]. It is evident that the sensitivity and resistance of the sensor increases almost linearly with the increase of the NH_3 flow from 25 to 500 sccm. Fig. 5b shows the temperature dependent of resistance change in 500 sccm NH_3 flow. The resistance change is defined as $[(R - R_o)/R_o] \times 100\%$, where R_o is the original resistance of the sensor and R is the resistance of nanotubes when exposed to NH_3. The sensitivity linearly increases with temperature. The sensitivity of the response to the gas molecule seems to be related to the amount of electron charge transfer and the nature of the surface interaction of the gas and CNTs. In our results, the small resistance change is due to the presence of
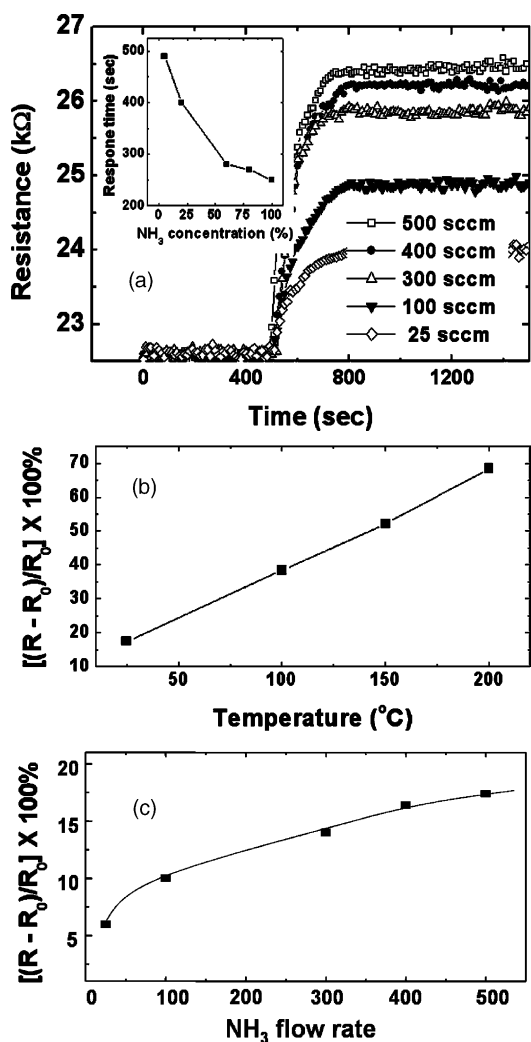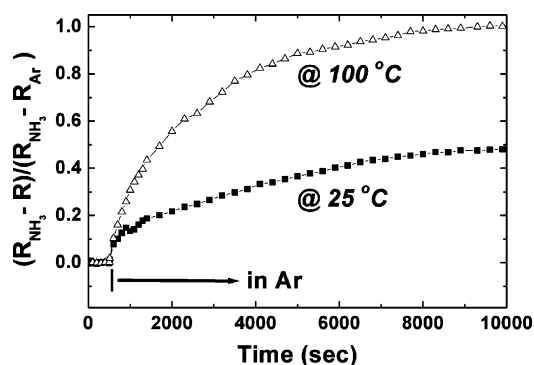
Fig. 6. Recovery time of sensor at 25 and 100 °C in Ar.

the recovery time of the sensor decreases as the temperature goes up.

To investigate the stability of senor, the sensor underwent five sensing cycles by repeating sensing and recovery. It can be found that the sensor does not have much sensitivity decay during the sensing cycles, which proves that the sensing characteristic of our sensor is repeatable.

4. Summary

We experimentally realized chemical sensor using MWNTs laterally grown between Nb electrodes. Upon exposure MWNT to air or NH_3, the electrical resistance of the MWNTs is found to decrease or increase, respectively. Our results show a promising technique for chemical gas sensor at room temperature. In order to realize better functions of the CNTs gas sensor, the modification of sensor structure and the interaction between gas and CNT should be investigated in future study.

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Fig. 5. (a) Resistance of sensor vs. time in a NH_3 flows. The insert shows the sensing response time to NH_3 content in Ar. (b) Temperature dependent of sensitivity of CNTs sensor in 500 sccm NH_3 flow. (c) NH_3 flows dependent of sensitivity of CNTs sensor when 600 s have passed since introduction of NH_3 gas.

semiconducting MWNTs dispersed among the predominant metallic MWNTs because CNTs grown by CVD generally are not a single character of metallic or semiconducting but include both types [17]. Fig. 5c shows the resistance change when 600 sec have passed since introduction of NH_3 gas for 3 sec. While the flow rate of NH_3 was below 100 sccm, the resistance change rate is relatively high in spite of the small change in NH_3 flow. We expect resistance change cannot increase significantly with further increase in NH_3 flow. We have not yet optimized the operating region that CNT act as a precise gas sensor.

Fig. 6 shows resistance change versus time after the pure NH_3 flow is replaced by pure Ar. We define abruptly the recovery time as the time of 90% total resistance change. The resistance of test sample was observed to slowly recover, and the typical recovery time was ~20 h. Heating the exposed sensor in Ar at 100 °C led to recovery in ~3 h. It can be found

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