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A novel single wall carbon nanotubes-based sensor doped with lithium for ammonia gas detection

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To deposit SWCNTs (single wall carbon nanotubes) on substrates and evaluate their gas sensing properties, a pair of interdigitated electrodes was made by sputtering Au on Si/SiO_2. SWCNTs were first doped with lithium by heating with $LiNO_3$ and HNO_3 for 12 h. Then SWCNTs-lithium doped was well-dispersed in dimethylformamide (DMF). By using electrophoresis and applying a DC voltage, the SWCNTs were forced to deposit between the two electrodes. The deposited SWCNT on the electrodes were heat treated at 350 °C for 5 h. with Ar to eliminate the DMF adsorbed layer. The electrical response of this sensor has been measured by exposing the films to NH_3 (500 ppm) at different operating temperatures between 25 °C to 280 °C. The response to NH_3 has been found to be a maximum at around 150 °C and a high sensitivity of 34% was achieved.

Key words: SWCNT, Electrophoresis, Interdigitated electrode, Gas sensor.

Introduction

Since Iijima first discovered carbon nanotubes, the past two decades [1, 2] have witnessed significant progress in both carbon nanotube synthesis and information revealing the electrical, mechanical, and chemical properties of the nanotubes. Nanotubes have great potential to be used as nano-scale electronic devices such as field effect transistors, single-electron transistors, and nano-scale p-n junctions. In addition, carbon nanotubes are becoming promising candidates in sensors [3-8]. Dai and co-workers were the first to demonstrate that semiconducting single-wall carbon [9] nanotubes act as rapid and sensitive chemical sensors at ambient temperature. They found that the conductivity of the semiconducting SWCNTs changed rapidly by several orders of magnitude upon exposure to ammonia. Theoretical studies have also predicted significant changes in the electronic properties of carbon nanotubes caused by gas adsorption. These results provide the motivation of applying carbon nanotubes as gas sensors to detect ppm concentrations of gases [2, 5, 10].

It seems that alkali metals form intercalation compounds with all sp^2-bonded carbon materials [11]. These intercalation compounds are of basic interest. In this study we report the electrochemical intercalation of lithium into raw carbon nanotubes. The relatively large porosity of carbon nanotubes compared to graphite induced a high irreversible storage of Li [12-14]. The idea of doping carbon nanotubes has been attractive since it allows controlling their surface properties [15]. Then in this paper, demonstration of a simple SWCNT-lithium doped sensor platform with extended application to the sensitive detection of gas molecules is reported. In this platform, SWCNTs-lithium doped form a network on interdigitated electrodes using an electrophoresis process, providing a large enough density of SWCNTs for sensor performance. To form a good dispersion, the SWCNTs were dispersed in dimethylformamide (DMF).

The behavior of this sensor was observed by exposing it to 500 ppm of ammonia gas. The effect of temperature was also investigated on the sensitivity, response and regeneration times.

Experimental

A pair of interdigitated electrodes was fabricated using a conventional photolithographic method with a finger width of 50 μm and a gap size of 100 μm. The interdigitated electrode fingers were made by e-beam evaporating of 200 nm Au on a layer of 100 nm silicon dioxide (SiO_2) thermally grown on top of a silicon wafer (Fig. 1).

The raw single wall carbon nanotubes were purchased. Their diameter is 5 nm and the length is 10 μm with 95% purity (Aldrich). The ends of the nanotubes always appear to be capped. The caps have a polyhedral shape with sharp corners. The nanotube samples were used without further purification. The carbon nanotubes were opened and filled with lithium compounds by suspending 0.4 g nanotubes in 20 g of super purity-grade concentrated nitric acid containing 0.5 g of lithium nitrate and refluxing in an oil bath at 140 °C for

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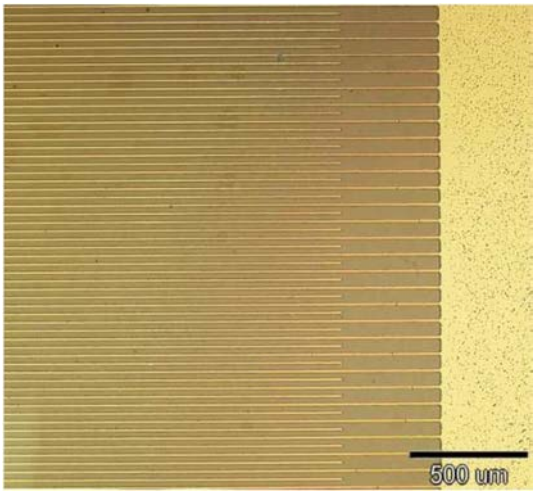

Fig. 1. Interdigitated electrode of Au on SiO_2 substrate.

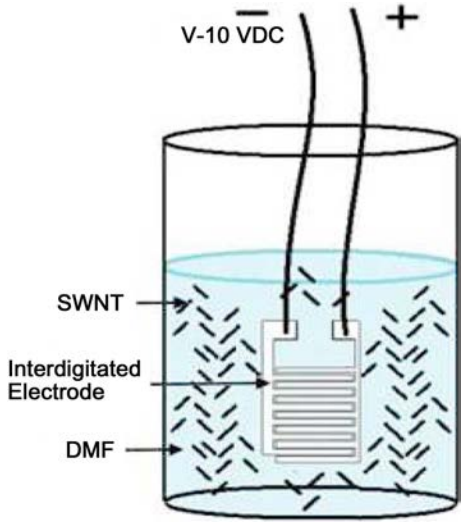

Fig. 2. General scheme of the electrophoresis deposition process in the DMF solution.

12 h. The suspension was allowed to settle and the solution was removed. In order to remove HNO_3 completely, after washing with distilled water and drying at 100 °C overnight, the resulting insoluble black product was then heated at 70 °C for 3 h. Tubes containing a lithium compound were obtained.

Powder X-ray diffraction (XRD) measurements were carried out with a Cu K_α source (RigakuRINT-2000). Data were collected between 10 ° and 80 ° with a scan speed of 1 ° $minute^{-1}$. Atomic absorption spectroscopy (AAS) analysis was carried out to measure the Li^+ ion concentration in the remaining solution. Finally, Raman scattering spectra were taken.

Dispersion experiments were carried out using purified SWCNTs-lithium doped. 1 mg SWCNTs-lithium doped was then sonically dispersed in dimethylformamide (DMF) of 40 ml for 2 h to form a suspension. DMF is known to generate a stable dispersion of carbon nanotubes. The DMF was chosen to untangle the SWCNT bundles because the amide group could easily attach to the surface of nanotubes, providing a uniformly suspended solution of SWCNTs in DMF [6].

The general scheme of the electrophoresis deposition process, used for the sample preparation, is shown in Fig. 2. To deposit the SWCNTs-lithium doped onto the substrates, electrophoresis was carried out in the DMF solution produced. The interdigited electrodes were placed in the solution and a constant DC voltage in the range of 7-10 V was applied to the electrodes. The SWCNTs-lithium doped was deposited between the fingers of the electrodes. The deposited film was dried for 5 h at 350 °C in a vacuum to desorb the DMF adsorbed layers.

After the device fabrication, the sample was placed in a gas testing chamber with a 2 l capacity. The concentration of NH_3 gas was controlled. In our experiments, the device was first stabilized in dry air environment, followed by exposure to NH_3 gas with a concentration of 500 ppm. Different electrical measurements were performed by selecting the temperature of the films in the range of 25-280 °C.

Results and Disscusion

The clear solution of HNO_3 became a dark yellow color 20 minutes after adding the carbon nanotubes and did not lose its integrity even after 24 h. After treatment with the solution of HNO_3 and $LiNO_3$, most of the carbon nanotubes were opened [13]. Chemical treatment with HNO_3 solution revealed a process of opening of carbon nanotubes from which it was concluded that the chemical reactivity is highest at the end of the caps. When the single-wall carbon nanotubes are immersed in the HNO_3 solution for a longer period of time, the bundles become disordered and partially exfoliated. With the presence of $LiNO_3$, the Li-containing compound will be absorbed on the surface of the carbon nanotubes. According to Tsang and Chen [3], the nanotubes will be filled with $LiNO_3$. At the temperature, the reaction will occur as follows:

$$2\ LiNO_3 \rightarrow 2\ LiNO_2 + O_2 \quad (1)$$

The elemental analysis results of AAS shows that the Li concentration has decreased from 7777 ppm to 4093 ppm. This lithium loss equals approximately 1.3 weight percentage of the lithium dopant in the carbon nanotubes. There is no obvious difference in the XRD patterns of the raw carbon nanotubes. The XRD pattern of the raw carbon nanotubes and carbon nanotubes doped with lithium is shown in Fig. 3. The (002) reflection observed at about a diffraction angle $2\theta = 25.67$ corresponds to a spacing $d = 3.4$ A°. The band around 42.3 corresponds to the carbon layers in a turbostatic arrangement[14]. A little shift can be observed at d = 3.4 from $2\theta = 25.67$ ° to $2\theta = 26.1$ °.

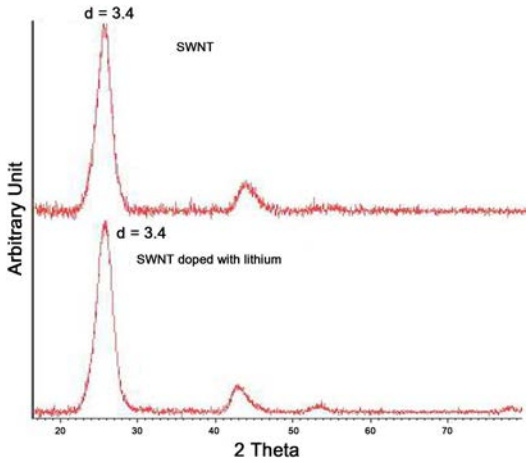

Fig. 3. XRD diffraction of SWCNT and SWCNT doped with lithium.

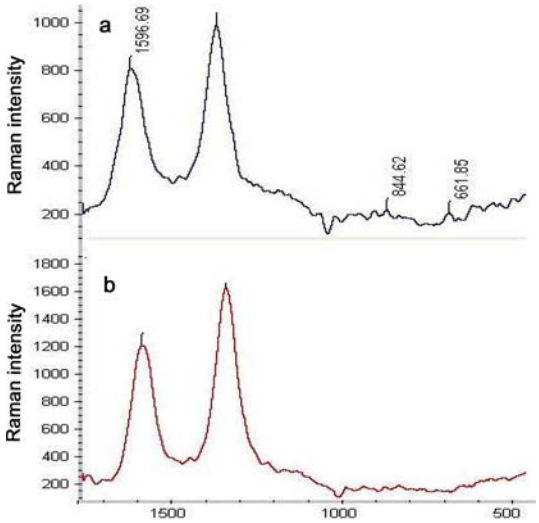

Fig. 4. (a) Raman spectra of SWCNTs. (b) Raman spectra of SWCNTs doped with lithium.

So we think that the raw carbon nanotubes have been doped with lithium. This result corresponds to the work done by Yang et al. [13].

Fig. 4 displays the Raman spectra in the 500-1800 cm^{-1} region for SWCNTs and SWCNTs doped with lithium. The two main features in the Raman spectra are the D and G peaks at approximately 1330 cm^{-1} and 1600 cm^{-1}, respectively [16-18]. The G band corresponds to the symmetric vibrational mode in graphite-like materials, while the appearance of the strong D line can be explained as: (a) the turbostratic structure of carbon sheets in tubes; and (b) a high density of the twisted tubes. Thus, the enhancement of the D lines at 1330 cm^{-1} accounts for the large amount of crystalline domains on the nanometre scale. In particular, the effect of previous experimental and theoretical studies has shown that doping SWCNTs with either electron donors or acceptors or electrochemically caused evident shifts in particular characteristic vibrational modes. Specifically, removing a charge from a SWCNT (i.e. p-doping or oxidizing) resulted in an upshift in the G band peak and adding charge (i.e. n-doping or reducing) to a SWCNT resulted in a downshift [8, 17-19]. The downshift observed upon n-doping is due to the additional electron density that is placed in the anti-bonding conduction bands of the SWCNT. The average C-C bond strength is weakened, resulting in a downshift or softening of the vibrational frequency.

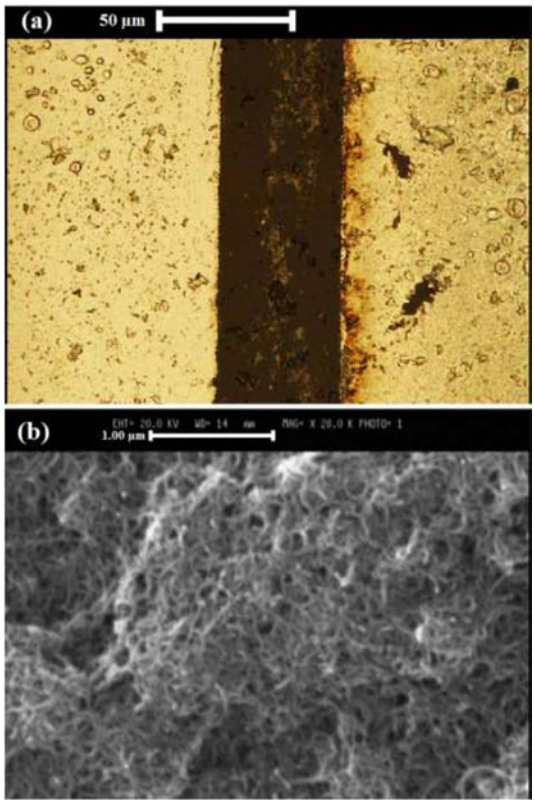

Fig. 5. (a) microscopic image of the same device (b) SEM image of a SWCNT-lithium doped film deposited between interdigitated electrodes.

Based on this consideration, if the SWCNTs were to lose charge from lithium ions, an upshift in the G band was expected. Fig. 4 shows the measured Raman spectra of the laser with $\lambda = 532$ nm before and after doping lithium. An upshift of 4 cm^{-1} is observed in the G band. Fig. 5 (a) shows a microscopic image of a SWCNT-lithium doped film deposited between interdigitated electrodes. Fig. 5 (b) is the SEM image of the same SWCNT-lithium doped deposited between electrodes. An appropriate voltage should be imposed otherwise no deposition can occur [7, 20] or the electrodes will be deformed.

Fig. 6 plots a typical response curve at an environmental temperature of 25 °C to 500 ppm ammonia gas of a SWCNT/1.3 %Li sensor. In this investigation, at $V = +12$ V, the current decreases exponentially within the first 20 s after NH_3 introduction at room temperature of 25 °C. It can be concluded that the resistance increases upon exposure to NH_3 gas and it returns to the original value upon exposure to air. Since NH_3 is an electron donating gas [9, 17, 21, 22], the increase of the

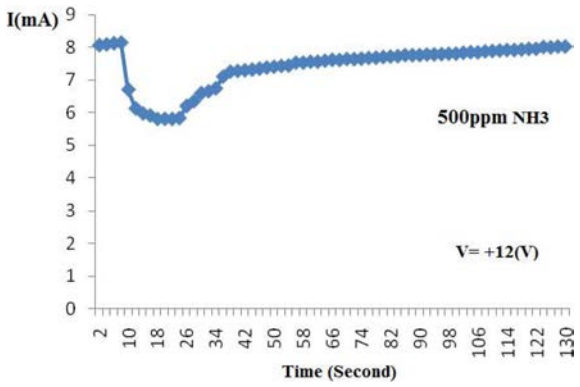

Fig. 6. Response curve of SWCNT/1.3% Li sensor to 500 ppm ammonia gas at environmental temperature.

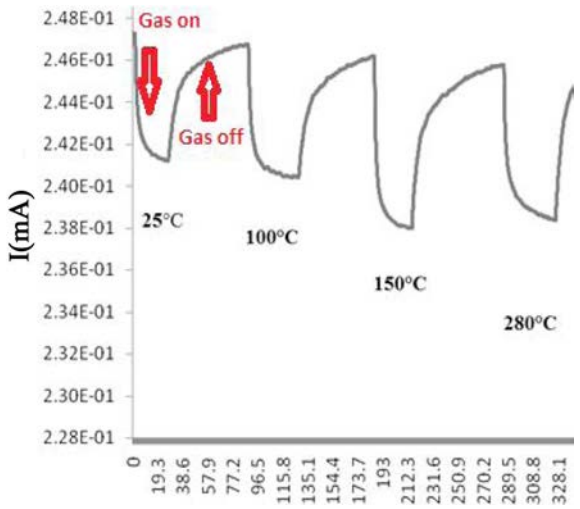

Fig. 7. Sensor response curves of a SWCNT/1.3% Li sensor at different temperatures 25, 100, 150 and 280 °C.

sensor resistance can be hypothesized that the sensing layer behaves as a p-type semiconductor. This sensor has a small regeneration at room temperature. It is concluded that heat treatment at 200 °C for 30 minutes is the best condition for completing the regeneration process. Because without this treatment, the gas molecules are not desorbed completely. So the sensor is not sensitive enough for the next sensing process and its response will have a lot of noises.

The electric response as a function of temperature for the sensor of single wall carbon nanotubes with 1.3% lithium dopant under 500 ppm ammonia gas is shown in Fig. 7. A dependency of the ammonia sensing with temperature has been detected. The response (I_g-I_o) increased as the temperature was raised from 25 to 280 °C. The sensor recovered rapidly when the ammonia gas was removed from the testing atmosphere in each cycle, indicating that the gas sensor has a good response in different temperatures in each cycle.

Sensitivity is dependant to the temperature and increases with temperature as the interaction at the interface between the gas and solid is enhanced. However, the thermal desorption of the target gas

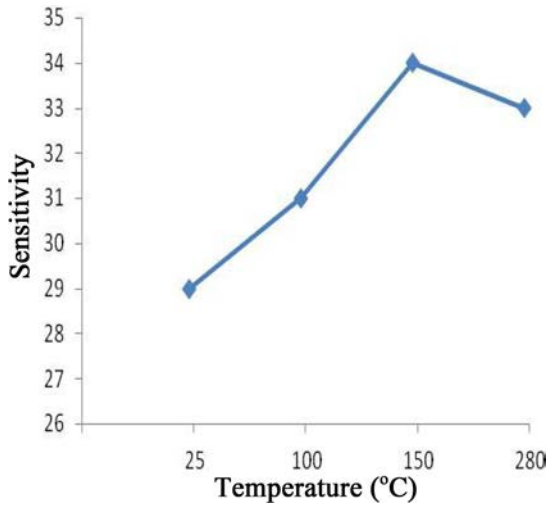

Fig. 8. Sensor response curves of a SWCNT/1.3% Li sensor at different temperatures 25, 100, 150 and 280 °C.

molecules from the sensitive surface at higher temperatures becomes more significant and hinders the solid-gas interaction [22]. Hence it is important to find the maximum sensitivity temperature for the sample. In Fig. 8, the results of sensitivity measurements at different temperatures are presented. Sensitivity (S) has been defined as the current change divided by the current value in a dry air environment:

$$S = \frac{|I_g - I_0|}{I_0} \times 100 \quad (2)$$

Sensitivity increases at higher temperatures but the change is small. The electrical conductivity of carbon nanotubes increases as the temperature rises. A temperature increase effects the electrical conductivity more than sensitivity. The sensitivity decreases at a temperature higher than 150 °C. These results are probably due to the higher desorption process than adsorption process rate at temperatures above 150 °C. In addition, carbon nanotubes with lithium dopant transform from semi electrical conductors to electrical conductors as the temperature rises, thus less carbon nanotubes contribute to the gas sensing. The highest sensitivity achieved is 34%. It was concluded that the maximum sensitivity of the sensor occurred in the temperature range of 140-170 °C. Therefore the optimum temperature is considered to be 150 °C.

Conclusion

We demonstrated a sensor based on single wall carbon nanotubes (SWCNTs) dispersed in a DMF solution for detecting NH_3 gas molecules at room temperature. DMF was chosen to untangle the SWCNT bundles because the amide groups can easily attach to the surface of SWCNTs providing a uniformly suspended solution. Without heat treatment, they cannot detect NH_3 molecules effectively. The optimal heating

time was 5 h. The NH_3 sensing of our sensor can be understood by intra- and inter-tube electron modulation in terms of charge-transfer mechanisms. Sensitivity, response and regeneration times of this sensor can also be improved in higher temperatures. The goal of this work was to assess the possibility of carbon nanotubes doped with lithium as an innovative gas sensor for environmental applications. Moreover, this is a promising step towards the development of miniaturized devices with extensive analytical capabilities.

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