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Gas sensing properties of printed multiwalled carbon nanotubes using the field emission effect

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Abstract

Gas sensors for NO_2 detection were fabricated using printed multiwalled carbon nanotubes (MWCNTs) before and after electric field surface treatment. Printed MWCNTs showed an increase of sensitivity upon exposure to NO_2 and field emission due to vertical alignment and protrusion of CNTs from surface layer after electric field surface treatment. Electron field emission plays a role recovery when exposed to gas molecules in CNT. A Fast recovery time of the printed MWCNT gas sensor was obtained by ohmic heat with a partial field emission effect at room temperature.

1. Introduction

Carbon nanotubes (CNTs) have attracted great interest due to their unique electronic properties and nanometer size. Because of these unique properties, they are great potential candidates in many important applications such as nanoscale electronic devices, chemical sensors and field emitters. The effect of gas adsorption on the electrical resistance of a CNT has received great attraction because of fast response, good sensitivity of chemical environment gases and low operating temperature [1–3]. Theoretical studies have confirmed the remarkable change in electronic properties of CNT due to the detection of gas molecules [4,5]. Most molecules are known to be an electron-acceptor such as NO_2 and O_2 or an electron donor such as NH_3 and H_2O displaying relatively small charge transfer between adsorbed molecules weakly on the CNT wall. Multiwalled carbon nanotube (MWCNT) thin films show p-type semiconducting property of decreasing resistance upon exposure of NO_2 gas [6–8]. CNT sensors require thermal-heat to desorb the chemisorbed molecules from the surface. The sensor exhibits variation of the electrical resistance of CNT films in the adsorption–desorption cycles and reproducible recovery in the operating temperature range of 25–250 °C [6–9]. Especially, for field emitters, CNTs have a small diameter and a great aspect ratio as well as high chemical stability and excellent mechanical strength.

Here, we demonstrate a simple screen-printed MWCNT sensor that combines the MWCNT field emission and CNT-based system for the detection of gas molecules. In particular, we focus on the field emission of vertically aligned MWCNTs by electric field surface treatment and the characteristics of the sensor when exposed to NO_2.

2. Experimental

Fig. 1a shows a schematic of the testing equipment setup that was used to examine the gas sensor. A computer was used to control the volt-amperometric for

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electrical resistance measurement and the current–voltage for field emission measurement via GPIB interfaces. The electric resistance of the printed CNT was measured by using the Keithley 2400 series multimeter (V_1) and the field emission current was measured by using a high voltage source (V_2) to remove the adsorbed gas molecules from CNT. The gas concentration of NO_2 mixture was 100 ppm, and N_2 was used to purge gas. The printed CNT sensor structure is illustrated in detail in Fig. 1b. We printed CNTs paste mixed with MWNTs, terpineol, ethylcellulose, and glass frits onto electrode coated glass as the gas sensing element and emitters (cathode plate). After drying at 150 °C for 1 h in air, the organic binder was removed by annealing at 380 °C in N_2 ambient. The printed MWCNT sensor was connected by the cathode electrode to a metal wire with diameter of 50 μm to measure the electrical parameter. In addition, the anode plate was used to ITO coated soda-lime glass. Two glass plates were assembled by a distance of 450 μm. When the cathode plate applied high voltage, field emission current was obtained. The morphology of the printed MWCNT was observed by scanning electron microscopy (SEM, Hitachi S-4300). During the experiment, printed MWCNT gas sensor was placed in a sealed chamber through vacuum at a pressure of 1×10^{-3} Torr. The gas was introduced at a pressure of 5×10^{-3} Torr in the vacuum system. The sensor resistance was measured at 1 V throughout the whole process and all the measurements were carried out at room temperature.

3. Results and discussions

The surface treatment of printed MWNT performed to vertical alignment as well as protrusion of CNTs from surface to increase of field emission current and to improve the sensitivity of gas sensor. The MWCNTs in the printed cathode layers have very poor field emission characteristics because of insufficient MWCNTs protrusion from the surface or due to random distribution. Therefore, special surface treatment methods are indispensable such as adhesive tape, focused ion beam, plasma exposure or laser irradiation for attaining high emission current site density [10–13]. We have suggested that the printed CNT emitters as gas sensing element could be protruded to the field direction by applying biasing higher than the commonly applied voltage to activate field emission without the application of other surface treatments [10–13] and have provided a new surface treatment technique to improve the field emission characteristics without the detachment of MWCNTs by a critical bias field process. Fig. 2 shows the surface treatment process by a critical electric field. In order to improve the field emission, printed MWCNTs were setup up for surface treatment by electric field, as shown in Fig. 2a. Printed MWCNT layers were tested in a diode configuration under the vacuum of 1×10^{-6} Torr, with the anode and cathode spaced 450 μm apart. The surface treatment by critical electric field using direct current (DC) voltage was directly performed on one of the specimens. Fig. 2b shows emission current–voltage (I–V) curve measured after the surface

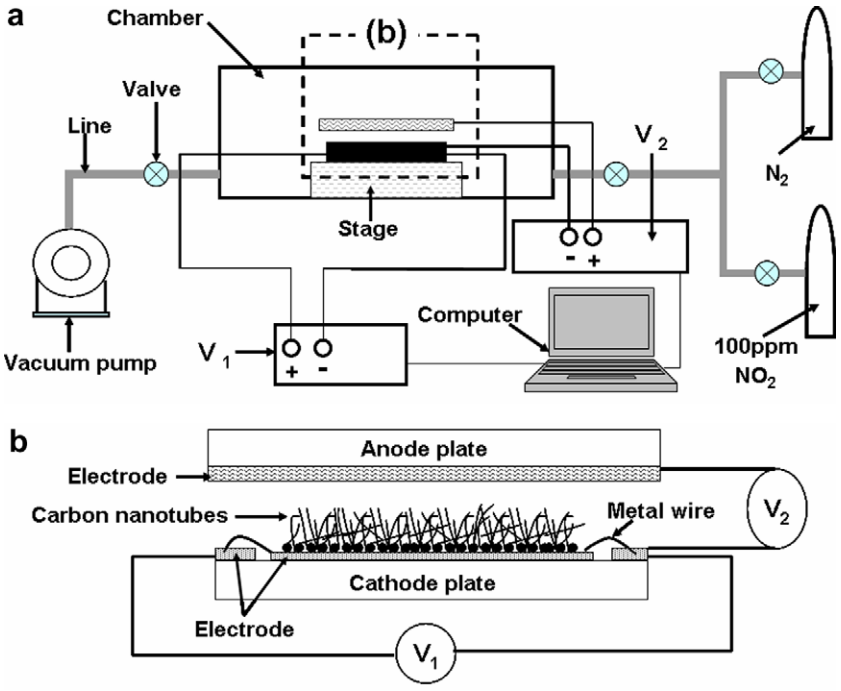

Fig. 1. (a) Schematic of experimental setup for testing the gas sensor and (b) the printed MWNT sensor placed inside the vacuum chamber. A computer was used to control the measurement of electrical resistance and field emission via GPIB interface. V_1 and V_2 are the voltage sources as a function of gas detection and removal of the adsorbed gas molecules by field emission, respectively.

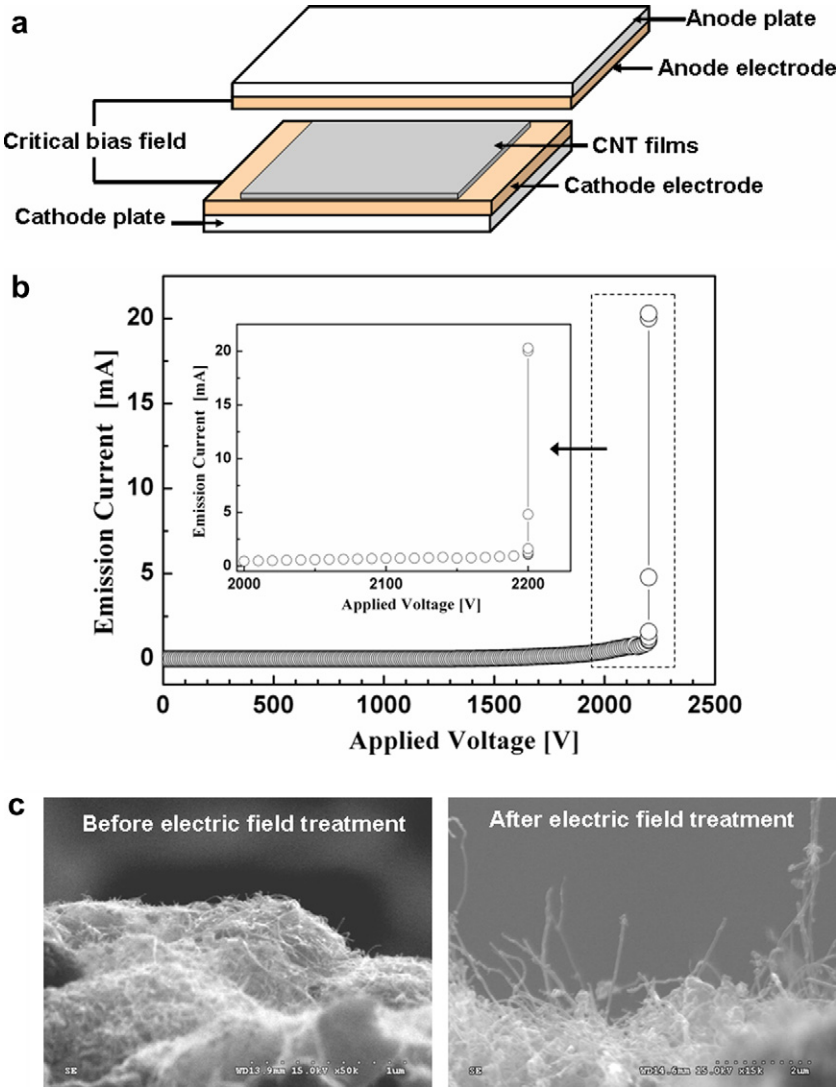

Fig. 2. The surface treatment process shows an activation of field emission by a critical electric field. (a) Schematic diagram of the surface treatment method and (b) the *I–V* curve of the surface treatment procedure by only a critical bias field. (c) Cross sectional SEM images of the printed MWNT before and after surface treatment.

treatment procedure and the *I–V* curve for voltage ranging from 2000 V to 2200 V in the inset of figure. At applied voltages of 2000 V (4.44 V μm^{-1}) and 2200 V (4.89 V μm^{-1}), emission currents were 0.45 mA and 1 mA, respectively. When maintaining the 2200 V for a few seconds, emission current increases drastically from 1 mA to 20 mA. After the surface treatment process was completed, the field emission properties were obtained, such as the low turn-on voltage and the stability. The remarkable difference in emission current induced by the critical bias field of 4.89 V μm^{-1} is clearly shown in the figure. The influence of applied critical field effect on the printed MWCNTs was investigated by using SEM. A cross-sectional SEM view of the MWCNT tips, as shown in Fig. 2c, indicates that the surface morphologies are quite different before and after critical field treatment. Before application of the critical bias for surface treatment, the structure changed only slightly. During surface treatment, the morphology of the MWNTs are predominantly protruded with respect to the cathode palate, although electric field was removed from the nanotubes, which were deformed in the direction of the electric field. Therefore, the surface treatment of electric field induced rise to vertical alignment and protruded MWCNT tips from matrix materials, significantly influenced the field emission characteristics as well as change of electric resistance.

Fig. 3 shows the plots of field emission current versus the applied voltage tips and the sensitivity S versus time of the printed MWCNT as a function of surface treatment. The gas sensitivity S is defined as: $S = (R - R_0)/R_0$, where R_0 is the resistance in vacuum (10^{-3} Torr) and R is the resistance in NO_2 exposure and the sensitivity is the resistance change ratio. Fig. 3a shows *I–V* curves before and after electric field treatment. Before the surface treatment, the turn-on voltage was about 1290 V (2.87 V μm^{-1}). On the other hand, the turn-on voltage became as low as 920 V (2.04 V μm^{-1}) with electric field treatment. The emission current increased from 0.04 mA to 8.36 mA at an

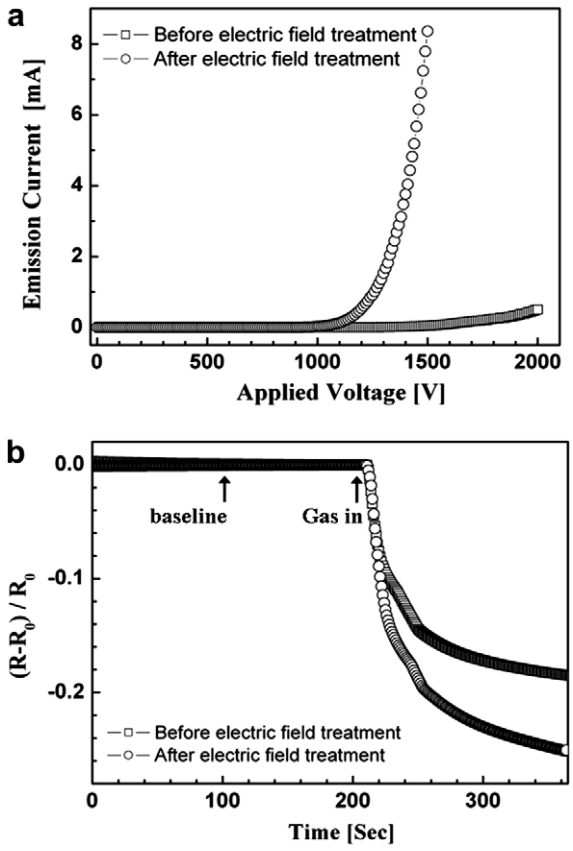

Fig. 3. (a) I–V characteristics and (b) sensitivity changes of the printed MWNT after exposure to 100 ppm NO_2 gas with and without a critical bias field treatment.

applied voltage of 1500 V (3.33 V μm^{-1}), before and after activation of surface treatment. As a result, the average emission current was about 200 times higher than the current of the untreated sample, which indicates that the activated field emission site area increased. Fig. 3b shows the sensitivity response of the printed MWCNT exposed to 100 ppm NO_2 gas versus time before and after application of the critical bias field for surface treatment. The baseline is sensitive in vacuum. The sensitivity improved by a change in the morphological surface and both samples showed a decrease in electrical resistance in NO_2 gas. The improvement of sensitivity caused the protrusion of MWCNTs by electric field surface treatment, as shown in Fig. 2c. This difference could be explained absorption area increase of the nanotubes exposed to the gas because of surface morphological change of printed MWCNTs by the surface treatment. The small resistance change is due to the presence of semiconducting MWCNTs dispersed among the predominant metallic MWCNTs. The sensitivity of the response to gas molecules seems to be related to the charge transfer due to the electron-acceptor characteristic of NO_2 molecules and physical absorption of these molecules in the tube wall [1,2,4]. Also, the inner tubes in single-walled carbon nanotube (SWCNT) ropes are blocked from interacting with NO_2 because the molecules are not expected to intercalate into SWCNT ropes [1].

Fig. 4 shows that the printed MWCNT sensor gives the dynamic response and shows the recovery behavior of electric resistance by field emission at 10^{-3} Torr at room temperature as a function of NO_2 gas exposure time. The sensor is tested sensing cycles by repetition of sensing and recovery (adsorption and desorption). When the gas was exposed to printed MWCNT within about 4 min, the electrical resistance decreased rapidly, and when the gas supply was turned off, the resistance increased sharply in Fig. 4a. The recovery process was carried out at applied voltage (V_2) of 1700 V between the cathode and anode plate as shown in Fig. 1b, which displayed the plot of the emission current versus time, as in Fig. 4b. There is strong difference in emission current values at 1700 V in Figs. 3a and 4b. The emission current is higher in Fig. 3a than in Fig. 4b, since less remaining gas molecules exist under high vacuum (10^{-6} Torr) than low vacuum level (10^{-3} Torr) in the chamber. The recovery time was accelerated to a few minutes by applied voltage (V_2) which may enhance desorption of adsorbed gas molecules. We expected increase in emission current during recovery process, but emission current decreased as shown in Fig 4b. It is caused by the remaining O_2 in the chamber due to use of 100 ppm NO_2 gas in the air and low vacuum level (10^{-3} Torr) [14,15]. After exposure

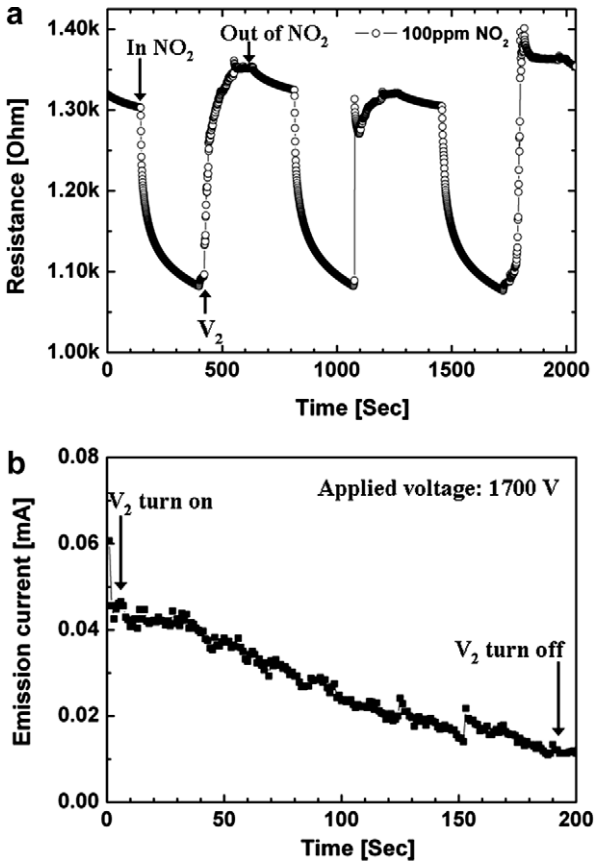

Fig. 4. (a) The change of the resistance of printed MWNT vs. time show cycles of a sequence of 100 ppm NO_2 exposure (adsorption) and with applied voltage (V_2) for sensor recovery (evacuation) at room temperature. (b) Emission current vs. time curve obtained at applied voltage 1700 V for sensor recovery.

to 200 ppm NO_2, the resistance of SWCNT exhibited a recovery time of ~12 h, and heating the exposed sample led to recovery in ~1 h [1]. Also the resistance of a MWCNT-film had an observed recovery by thermal treatment in ~10 min [8]. It could be explained that the recovery characteristics mainly govern ohmic heat by contact resistance and partially have an effect on field emission.

4. Conclusions

In summary, a combined electric response to 100 ppm NO_2 molecule exposure and the recovery of printed MWCNT by field emission effect were studied. We have demonstrated that the printed MWCNTs were vertically aligned and also that MWCNTs protruded from the surface only by the critical bias field without application of other surface treatments. The sensitivity of MWCNTs to NO_2 and field emission of printed MWCNTs can be improved by surface treatment. The recovery time of the printed MWCNT could be shortened by ohmic heat with a partial field emission effect.

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