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Bias-heating recovery of MWCNT gas sensor

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Abstract

A sensor was made using Au/Cr electrodes on a glass substrate and a thin carbon multiwall nanotube film printed between them. A biasheating method was used completely to desorb gas molecules and restore its initial conductance. The temperature of the thin carbon nanotube film varied depending on the magnitude of the voltage used, and this relationship was investigated. After being used to detect NO_2 , the sensor returned to its initial conductance. This method enables complete recovery without additional processing steps, such as the fabrication of heat structure and ambient heating.

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1. Introduction

Since the report on the use of carbon nanotubes (CNTs) as a gas sensor [1,2], they have been investigated as materials of chemical sensor because they can detect small concentrations of molecules with a high sensitivity under ambient conditions (the large surface area of CNT provides a very large gas absorptive capacity) and the CNT sensor has a fast response [3–6]. However, the CNT sensor does not perfectly return to its initial conductance at room temperature [7–10]. Its reversibility is achieved through slow recovery under ambient condition at room temperature or through heating of the sensor to a sufficiently high temperature. Therefore, to decrease the recovery time of CNT sensor, the additional process or structure is necessary [10].

Also, we have reported previously about recovery by using ambient heating and a fabricated microheater [11-13]. In case of using microheater, the recovery time was reduced within several minutes, but the microheater had complicated the fabrication

process. The sensor is essential to simple fabrication process and fast recovery time in a commercial product. In the previously published reports, the temperature variation has a significant influence on the electrical properties of CNT [14].

In this work, we fabricated the chemical sensor employing multiwall CNTs (MWCNTs) as an active sensing element by using screen-print method and the sensor returned to the initial conductance employing a bias voltage. And, this relationship between the sensor temperature and variation of bias voltage was investigated.

2. Experimental

A sensor schematic is shown in Fig. 1. The sensor consisted of a soda-lime glass substrate (with a size of 8×5 mm with 1 mm thick), a thin MWCNT film, a pair of metal (Au/Cr) electrodes, and temperature sensor (thermocouple, K-type). MWCNTs were 95% pure of ~10–15 nm in diameter and synthesized using thermal chemical vapor deposition [15]. The paste was made of an MWCNT (5 wt.%), a glass frit, a solvent, and an organic binder by 3-roll milling process. The sensitive

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Fig. 1. Schematic of the carbon nanotube sensor structure (a) and the fabrication process by a screen-printing method (b).

area of 3×3 mm was fabricated by a screen printer. The printed paste was dried at 100 °C for 1 h in air and then burned at 400 °C for 30 min in a furnace. The samples were fired under a combinational atmosphere of N₂ and then naturally cooled to room temperature.

The MWCNT sensor was loaded into a vacuum system to 10^{-3} Torr and then exposed to a NO₂ concentration of 50 ppm. The sensor output was measured using a Keithley 2400 sourcemeasure meter and LabVIEW software. The input voltage was fixed at 1 V, and the recovery voltage was biased using a HP power source (HP E3611A). The sensor was connected in parallel between Keithley 2400 and power source. When the sensor was saturated with NO₂, Keithley 2400 was turned off, and at the same time, power source was turned on by the recovery switch. In addition, when the temperature reached a target value, power source was turned off, and Keithley 2400 was turned on.

3. Results and discussion

In case of CNT chemical sensor fabricated by screen-print method, the sensitive MWCNT films were covered with the organic materials. Fig. 2 shows a typical high-resolution scanning electron microscopy (HR-SEM) images of the MWCNT films of the burnout before (Fig. 2a and b) and after (Fig. 2c and d). The organic materials disturbed the adsorption between target gas and MWCNT surface. Accordingly, to remove the organics, the thin sensitive MWCNT films were thermally treated and then were more protruded from the substrate surface [16]. Therefore, thermal treatment plays an important role in the removal of organic materials such as binders, which improves the sensitivity of gas sensor.

Fig. 3 shows the temperature variation depending on a bias voltage in vacuum of 10^{-3} Torr. The temperature of A curve was kept constant (~50 °C) at a bias voltage of 10 V for 15 min. In this result, MWCNT film was operated as a heating element with a bias voltage. In addition, when the power of bias voltage was turned off, the temperature rapidly returned to room temperature. From A to E, it is shown that the temperature variation was dependent on the bias voltage. And, the bias voltage was increased with a step of 5 V in the range of 0–25 V. Here, temperature change was proportional to the bias voltages, and appeared very stable. Temperatures of B, C, D, and E curves were ~49 °C, ~66 °C, ~80 °C, and ~103 °C, respectively. The thermal generation resulted in dc heating of the nanotube under high-bias current flow in the contact resistances between CNT–CNT and CNT–Electrode [17]. The currents of B, C, and D curves for bias voltage were approximately



Fig. 2. HR-SEM images of MWCNT films before (a, b) and after (c, d) burnout. (a) and (b) show the residual organic material with only dry treatment, and (c) and (d) don't show the residual material owing to thermal treatment.

20 mA, and that of E curve was 30 mA. In this result, the temperature variation ratios of B, C, and D curves for bias voltage were decreased step by step, but that of E curve for bias voltage was increased owing to the increased current. The increased current in E curve was due to high voltage and high rising temperature [14]. And, the temperature variation was also dependent on the possible high electrical current. Through this result, we knew that thin MWCNT films in the sensor could be used as a heater. Accordingly, the sensor did not need additional heating structures and the recovery time could be controlled by a bias voltage.

In general, NO_2 molecules are weakly binded to the nanotube, and the tube-molecule interaction can be identified as physisorption [18]. The sensor has a limitation in the return to its initial conductance through degassing in a vacuum. Accordingly, the thermal energy was needed to desorb gas molecules from MWCNT surface.

Fig. 4 shows the sensitivity and recovery responses of the sensor to NO2 and that the sensor returned to its initial conductance depending on the time. In a vacuum state, the sensor conductance was refreshed using a CNT-bias-heating method. This process removed the residual gas from the MWCNT surface to obtain its initial conductance (Fig. 4a). NO2 was injected into the chamber. When the sensor was saturated, the injection was stopped (Fig. 4b). Then, the MWCNT film was heated by bias voltage with parallel vacuum pumping. All of the bias voltages are 10 V at a bias current of ~20 mA. The heating operation by a bias voltage was continuously performed as follows: for 2 min (Fig. 4c and d), 5 min (Fig. 4e and f). In c curve, the sensor did not perfectly return to the initial conductance because of a low bias voltage and a short-time recovery. The experiment of heat treatment was repeated. Generally, heating value is described by Joule's law as follows: $Q=0.24P\Delta t$, where P is electric power [voltage (V)×current (I)], and Δt is the time interval. Accordingly, the heating values in c and d curves were 5.76 cal. In addition, the heating values in e and f curves were 14.4 cal. It is known that recovery degree was increased if the time became longer. NO₂ was injected into the chamber again (Fig. 4g). The conductance variation ratio, the sensitivity of the sensor (S) is defined as Gg/G0, where G_0 is the initial conductance of the sensor and G_g is the conductance of nanotube films when exposed to NO2. The sensitivity was approximately 22.7%.

And the recovery was maintained for 10 min with the same bias voltage (Fig. 4h). Then, heating value in h curve was 28.8 cal. This result shows that recovery time was decreased when the degassing

- Temperature for bias

A and B: 10V

C:15V

D : 20V

E:25V

120

110

100

90

80

70



Fig. 3. Temperature variation depends on a bias voltage. The room temperature was achieved with the bias voltage of 0 V. A, B, C, D, and E were achieved at voltages of 10, 10, 15, 20, and 25 V, respectively.



Fig. 4. The sensor conductance was measured from (a) to (f) by several heating with one injection of NO2 as follows: (a) initial condition, (b) injected NO2, (c, d) heating for 2 min under saturation condition, (e, f) continuously again heating for 5 min, (g) injected NO2 again in vacuum, and (h) heating for 10 min under saturation condition (Inset box: Real image of an MWCNT gas sensor).

energy was provided all at once, more than the divided heating. Finally, it was known that gas desorption is affected by heating value which is controlled by time and bias voltage. Therefore, we could be known that the recovery time was more decreased at a high bias voltage.

4. Conclusions

In summary, the MWCNT sensor was realized through the simple structure by repeating sensing and recovery. We knew that the MWCNT sensor could possibly return to initial conductance through a bias voltage without heat structures, such as heater and heating oven. Therefore, it is confirmed that the sensor could be fabricated without complex process.

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References

- [1] J. Kong, et al., Science 287 (2000) 622-625.
- [2] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 287 (2000) 1801 - 1804
- [3] E.S. Snow, F.K. Perkins, E.J. Houser, S.C. Badescu, T.L. Reinecke, Science 307 (2005) 1942-1945.
- [4] A. Modi, N. Koratkar, E. Lass, B. Wei, P.M. Ajayan, Nature 424 (2003) 171 - 174.
- B. Philip, J.K. Abraham, A. Chandrasekhar, V.K. Varadan, Smart Mater. [5] Struct. 12 (2003) 935-939.
- A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377-379.
- L. Valentini, C. Cantalini, I. Armentano, J.M. Kenny, L. Lozzi, S. Santucci, Diam. Relat. Mater. 13 (2004) 1301-1305.
- L. Valentini, I. Armentano, J.M. Kenny, C. Cantalini, L. Lozzi, S. Santucci, Appl. Phys. Lett. 82 (2003) 961-963.
- [9] L. Valentini, C. Cantalini, I. Armentano, J.M. Kenny, L. Lozzi, S. Santucci, J. Vac. Sci. Technol., B 21 (2003) 1996-2000.

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- [10] J. Li, Y.J. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, Nano Lett. 3 (2003) 929–933.
- [11] W.S. Cho, S.I. Moon, K.K. Paek, Y.H. Lee, J.H. Park, B.K. Ju, Sens.
 [15] C. Actuators, B, Chem. 119 (2006) 180–185.
 [16] H.
- [12] Y.D. Lee, et al., Chem. Phys. Lett. 433 (2006) 105-109.
- [13] Y.T. Jang, S.I. Moon, J.H. Ahn, Y.H. Lee, B.K. Ju, Sens. Actuators, B, Chem. 99 (2004) 118–122.
- [14] G.U. Sumanasekera, C.K.W. Adu, S. Fang, P.C. Eklund, Phys. Rev. Lett. 85 (2000) 1096–1099.
- [15] C.J. Lee, J. Park, Carbon 39 (2001) 1891–1896.
- [16] H.J. Lee, et al., Carbon 44 (2006) 2625–2630.
- [17] E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai, Nano Lett. 6 (2006) 96–100.
- [18] J. Zhao, A. Buldum, J. Han, J.P. Lu, Nanotechnology 13 (2002) 195-200.