Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.1006-1007

G-8-4

Development of an Ultrasensitive Gas Sensor Based on Single-Walled Carbon Nanotubes

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1. Introduction

Gas sensing technology plays an important role in monitoring environmental pollution. To date, however, for monitoring gas pollutants, such as NO_2, conventional gas sensors such as metal oxide thin-film sensors have serious limitations due to their poor sensitivity and slow response. To satisfy the environmental standard requirement, since the pioneering work by Kong *et al.* [1], efforts have been devoted to creating gas sensors with a sensitivity on the ppb order using single-walled carbon nanotubes (SWNT) [2,3]. However, its fabrication complexity makes it difficult to produce in large-scale production. Therefore, a novel sensing technique with a simple architecture for ultrasensitive gas detection has been stringently required.

In this study, we demonstrated an ultrasensitive gas sensor fabricated by growing an SWNT thin film directly on a conventional sensor substrate. NO_2 and Cl_2 were detected down to the ppb level under room-temperature operation with a fast response. Using an electrical breakdown technique, gas response sensitivity was improved by an order of magnitude. The relationship between gas concentration and sensor response was derived based on the Langmuir adsorption isotherm.

2. Experimental

SWNT thin-film sensor was fabricated by growing an SWNT thin film onto a conventional gas sensor platform, which consists of an interdigitated Pt measuring electrode (a gap size of 50 mm), an Al_2O_3 insulator layer and a Pt heater. The growth procedure has been described elsewhere [4]. Figure 1 shows a schematic of the SWNT thin-film sensor. The high-yield of netlike SWNTs with an approximately uniform diameter was grown on the Al_2O_3 layer and there was a good contact between the Al_2O_3 layer and the Pt electrodes [5].

Regarding gas sensing characterization, the SWNT sensor device was mounted in a sealed chamber (20 *l*). After the chamber was filled under atmospheric pressure with the air filtered by activated carbon, NO_2 and Cl_2 gases at

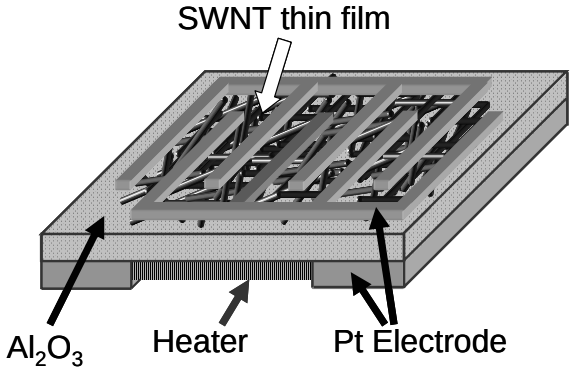

Fig. 1 Schematic view of SWNT thin-film gas sensor.

standard concentrations were diluted in the air. The resistance of the sensor was measured during a gas test at a constant input voltage of 100 mV. Heating of the sensor to 340ºC and cooling were repeated at intervals of 180 s. The sensor response, *S*, was defined as the ratio of the sensor conductance after gas exposure to that before gas exposure; G_{gas}/G_0.

3. Results and Discussion

Figure 2 shows sensor responses of an as-grown SWNT thin-film sensor. Four cycles were successively obtained, corresponding to four different NO_2 gas concentrations. The conductance of the SWNT sensor increased upon gas introduction while turning off the heater at point ① and decreased immediately when the heater was turned on at point ②. When the heater was turned off at point ③, the conductance reverted to an initial conductance due to desorption of the adsorbates, indicating that the sensor was reactivated and ready for the subsequent gas exposure. The higher the gas concentration introduced, the more enhanced the conductance modulation. The same result was obtained for Cl_2 detection. This result implies that surpassing the conventional gas sensor, the SWNT thin film acts as an ultrasensitive gas detector with an excellent sensitivity down to 50 ppb for NO_2 and Cl_2 even though an as-grown

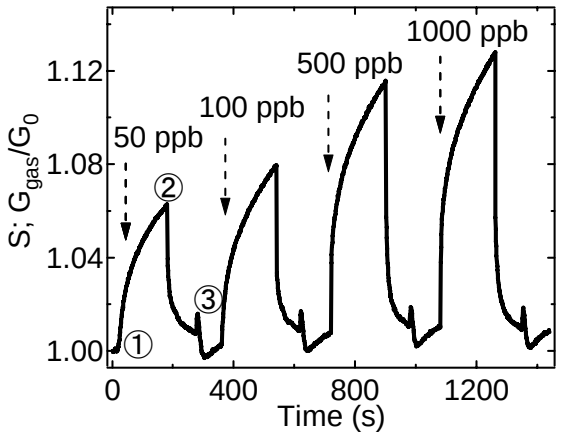

Fig 2. Sensor responses of SWNT thin film to NO_2 at different concentrations.

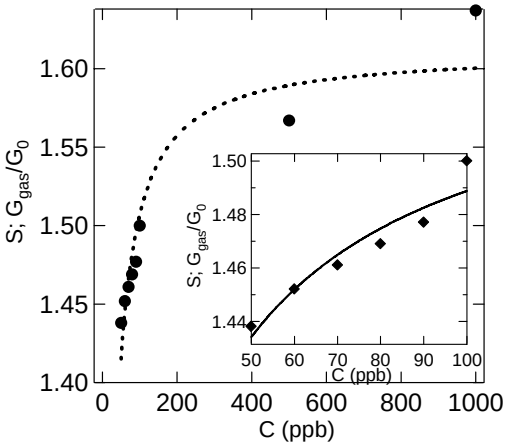

Fig 3. Sensor response in the low-concentration range with a fitting curve plotte using eq. (1).

SWNT film, a mixture of both metallic (m-) and semiconducting (s-) SWNTs, was used as the sensor head. In gas detection, p-type s-SWNTs contributed to the conductance change due to charge transfer between the SWNTs and the adsorbed molecules [1].

To enhance the semiconducting properties of the as-grown sample, the method of electrical breakdown was used. The SWNT sensor was found to be more sensitive than the as-grown SWNT for both NO_2 and Cl_2 detections, in which the conductance change improved by one order of magnitude at maximum. The enhancement of sensor sensitivity can be attributed to a decrease in the number of m−SWNTs by the breakdown method.

To explore the quantitative correlation between sensor response and gas concentration, NO_2 gas sensing was systematically conducted in the equilibrium state as shown in Fig. 3. The experimental curve is rather linear at low concentrations but tends to saturate at a concentration higher than 100 ppb. This result reveals that the SWNT thin-film sensor affords quantitative detection of NO_2 in a low-concentration range rather than that in a high-concentration range.

Next, we focused on gas detection in the range of 50−100 ppb (the inset of Fig. 4). The feature of gas adsorption in our sensing system can be described based on the Langmuir isotherm; $\theta = K{\cdot}C/(1+K{\cdot}C)$, where θ is the fractional monolayer coverage of adsorbate molecules, K the equilibrium constant and C the gas concentration. Because θ is assumed to be proportional to the sensor response, that is, $\theta = S/S_{max}$, where S_{max} is the maximum response of the sensor at saturation coverage, the gas concentration can be given by

$$C = \frac{S}{K \cdot (S_{\max} - S)} \qquad (1)$$

From the best fitting curve using eq. (1), K and S_{max} were estimated to be 0.23 $(ppb)^{-1}$ and 1.56, respectively. Thus, providing the K and S_{max} of the SWNT sensor, the gas concentration can be easily measured from the conductance change. Since the minimum sensor response is close to 1; $S_{min} = G_{gas}/G_0 = \sim 1$, the detection limit can be derived as $C = 1/(K{\cdot}(S_{max} - 1))$, which predicts that the detection limit for NO_2 is approximately 8 ppb. This implies that the sensor sensitivity can be improved by increasing its initial resistance, which was proved using SWNT sensors treated by the electrical breakdown process.

4. Conclusions

Our SWNT thin-film sensors responded selectively to NO_2 and Cl_2. The systematic study on sensing property disclosed a high sensitivity in the ultralow concentration range of 50–100 ppb and the detection limits of ~ 8 ppb for NO_2. The SWNT sensors exhibited a rapid response (order of seconds) at room temperature. By exploiting heating for gas molecule desorption, a quick sensor recovery was achieved with a high reproducibility. The SWNT thin-film sensors proposed here, owing to their excellent sensitivity, fast response and simplicity in large-scale production, will serve as a novel ultrasensitve detector and replace commercially available existing gas sensors in the foreseeable future.

Acknowledgements

This work was partly supported by the Handai Frontier Research Center, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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