Conductivity-Type Sensor Based on CNT-WO\textsubscript{3} Composite for NO\textsubscript{2} Detection

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The CNTs with 20–50 nm in diameter were directly grown on Au microgap electrode by means of thermal CVD at 700°C for 60 minutes under EtOH-Ar-H\textsubscript{2} atmosphere (6 kPa). The CNTs with entangled shape formed the network structure with contacting each other. In the CNTs-WO\textsubscript{3} composite, WO\textsubscript{3} grains with disk shape (50–200 nm) were independently trapped. The CNTs-WO\textsubscript{3} composite sensor showed the fairly good sensor response (Ra/Rg = 3.8 at 200°C). The sensor response was greatly improved with CNTs-WO\textsubscript{3} composite, comparing with that of CNT sensor (Ra/Rg = 1.05). This phenomenon can be explained by formation of p-n junction, between CNT(p) and WO\textsubscript{3}(n), and thus improvement of NO\textsubscript{2} adsorption. The sensor response was decreased with increasing the WO\textsubscript{3} amount in CNTs-WO\textsubscript{3} composite, suggesting the electronic conduction due to WO\textsubscript{3} connection.

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1. INTRODUCTION

Conductivity-type gas sensors based on carbon nanotubes (CNTs) have received considerable attention because of their intrinsic properties such as high-surface area, size, hollow geometry, and chemical inertness [1–6]. To elucidate the effects of gas adsorption on the electrical properties of CNTs for gas sensing, it has been estimated that NO\textsubscript{2} and O\textsubscript{2} molecules would yield considerable larger adsorption energies than H\textsubscript{2}O, NH\textsubscript{3}, CH\textsubscript{4}, CO\textsubscript{2}, and so on [7, 8]. However, it has been reported that sensor response (Ra/Rg), which is used for resistance decrease of sensing materials by adsorption of gas molecule, was as low as 1.2, or 1.3 to 5 ppm NO\textsubscript{2} [9–13]. It is important to enhance the sensor response to NO\textsubscript{2} for future application of CNTs gas sensor. It was well known that WO\textsubscript{3} is an excellent sensing material for NO\textsubscript{2} detection [14]. The conductive-type sensors using WO\textsubscript{3} have enhanced their sensor response to NO\textsubscript{2} by adopting thin film structure [15–17] and by doping foreign oxides [18, 19]. Recently, we have developed the high sensitivity NO\textsubscript{2} sensor by employing disk shape WO\textsubscript{3} particles and Au interdigitated microelectrode [20, 21]. These WO\textsubscript{3} sensors can detect dilute NO\textsubscript{2} less than 1 ppm with high sensitivity. Interestingly, the modification of CNT with WO\textsubscript{3} nanoparticles would be nanocomposite with p-n junction and might give us new concept for effect of interaction between CNT and WO\textsubscript{3} on NO\textsubscript{2} detection.

In this paper, we modified the surface of CNT with the WO\textsubscript{3} grains with 300 nm in diameter and 50 nm in thickness to improve sensor response to NO\textsubscript{2}, and discuss the interaction between CNT and WO\textsubscript{3} when varied the additional amount of WO\textsubscript{3} to CNT.

2. EXPERIMENTAL

At first, the microgap electrodes with various gap sizes were fabricated by means of MEMS techniques [16]. The Au line with width of 20 \( \mu \)m, gap size of 5 \( \mu \)m, and thickness of 0.3 \( \mu \)m was formed on SiO\textsubscript{2} substrate by photolithography (lift off), as shown in Figure 1. Second, growth catalyst for CNTs, Ni was deposited on Au electrode with 5 \( \mu \)m gap, in which 0.05 wt% Ni(CH\textsubscript{3}COO)\textsubscript{2} aqueous solution was dropped by using microinjector, and dried at room temperature for 30 minutes. The Ni-deposited substrate was subsequently set on the electric furnace, and CNTs were grown on the microgap at 700°C for 60 minutes from the nickel growth catalyst under gas mixture of ethanol, argon, and hydrogen (33/53/14 vol% = 6 kPa).
The WO$_3$ powder was prepared from (NH$_4$)$_{10}$W$_{12}$O$_{41}$·5H$_2$O by wet process. Aqueous solution of (NH$_4$)$_{10}$W$_{12}$O$_{41}$·5H$_2$O was neutralized by dilute nitric acid solution. The precipitate obtained (H$_2$WO$_4$) was thoroughly washed with deionized water, dried, and dispersed into deionized water to be a suspension. The microdrop of suspension ranged from 0.1 to 7 wt%H$_2$WO$_4$ was directly dropped on the surface of CNTs grown between Au electrodes with microgap (5 μm) by using microinjection, dried, and calcined at 400°C for 3 hours under inert gas of argon to prevent oxidation of CNTs. The microstructure of the WO$_3$ trapped on CNTs microsensor was measured by high-resolution FE-SEM (S-4800, Hitachi Ltd.), TEM (JEM-2010, Jeol Ltd.), and Raman spectroscopy (NRS-2100, JASCO Co. Ltd.).

The CNTs-WO$_3$ composite microsensor was set into a flow apparatus equipped with electric furnace and the sensing properties to dilute NO$_2$ (5 ppm) were measured at room temperature to 200°C. The sensor response (S = Ra/Rg) was defined as a ratio of resistance in air (Ra) to that in NO$_2$-containing atmosphere (Rg).

3. RESULTS AND DISCUSSION

The CNTs with 20–50 nm in diameter were grown at 700°C for 60 minutes under gas mixture of ethanol, argon, and H$_2$ (6 kPa) have entangled shape, as shown in Figures 2(a), 2(b). The microstructural analysis by means of Raman and TEM techniques indicated that the ratio of G- to D-band was mostly closed to 1 and they had multiwalled carbon layers. The entangled CNTs formed the network structure with contacting each other (Figure 2(b)).

The SEM images of CNT-WO$_3$ composites with various WO$_3$ amounts are shown in Figure 3. In the CNT-WO$_3$ composite with 0.1 wt% WO$_3$, WO$_3$ grains were independently trapped and CNTs were clearly observed (Figure 3(a)). The grain size of WO$_3$ trapped on CNTs was ranging from 50 to 200 nm and the grains were almost disk-like or platelet. With increasing WO$_3$ amount (Figures 3(b), 3(c)), WO$_3$ grains were increased and CNTs could not be visible, suggesting the formation of WO$_3$ connection.

Figure 4 shows the response transients of CNT and CNT-WO$_3$ microsensors to 5 ppm NO$_2$ at 200°C. The resistances of both CNT and CNT-WO$_3$ microsensors were decreased upon exposure to NO$_2$, suggesting that the conduction occurs through p-type CNT in both CNT and CNT-WO$_3$ microsensors. The sensor response (Ra/Rg) of CNT-0.1 wt% WO$_3$ microsensor was as high as 3.8, while the CNT microsensor showed almost no response (Ra/Rg = 1.05).

Figure 5 depicts the sensor resistance and the sensor response of CNTs-WO$_3$ composite microsensors as a function of amount of WO$_3$. The resistance was steeply increased at 0.1 wt% WO$_3$ addition. After the maximum at 0.1 wt%, the resistance was gradually decreased with increasing WO$_3$ amount. This behaviour can be explained by the formation of p-n junction at 0.1 wt% and the WO$_3$ connection higher than 1 wt%. The similar behaviour was observed for the sensor response, which had the maximum at 0.1 wt%. At 0.1 wt%, the p-n junction was formed between CNT and WO$_3$ grains to generate the large depletion layer within CNT, inducing the large resistance of CNTs-WO$_3$ composite sensor. The highly depleted surface state of CNT resulted in the increasing amount of NO$_2$ adsorption on CNT and
Figure 3: SEM images of (a) CNT-0.1 wt% WO3 composite microsensor; (b) CNT-1 wt% WO3 composite microsensor; and (c) 7 wt% WO3 composite microsensor.

Figure 4: Response transients of CNT and CNT-WO3 microsensors to 5 ppm NO2 at 200°C.

Figure 5: The sensor resistance and the sensor response of CNTs-WO3 composite microsensors as function of amount of WO3.

thus high sensor response to NO2 of CNT-WO3 composite sensor. When higher than 1 wt%, the conduction pass was formed via WO3 grains to decrease the sensor resistance. At more than 1 wt% WO3, the WO3 grains begin to contact with each other to dominant n-type conduction pass due to WO3. It is well known that WO3 is excellent sensing material for NO2 detection. Although the WO3 sensor shows the response of resistance-increase, the CNT-WO3 (7 wt%) composite sensor exhibited no response to 5 ppm NO2 (Ra/Rg = 1). It is considered that the sensor response (Ra/Rg) would be decreased to less than unity (resistance increase) at higher amount of WO3. Finally, the reproducibility of sensor response to 5 ppm NO2 was examined at 200°C for 0.1 and 1 wt% WO3-CNT composites. As the result, the sensor response of both composites was, respectively, 3.6 and 1.4, which was closed to the plotted data of Figure 5.

4. CONCLUSION

Conductivity-type gas sensor based on carbon nanotubes (CNTs)-WO3 composite showed the fairly good sensor response (Ra/Rg) to dilute NO2, comparing that the sensor fabricated from only CNT exhibited almost no response. The large depletion layer due to p-n junction was formed on CNT, inducing the enhancement of NO2 adsorption on the surface of CNT.

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