Research Article

Conductivity-Type Sensor Based on CNT-WO₃ Composite for NO₂ 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-H₂ atmosphere (6 kPa). The CNTs with entangled shape formed the network structure with contacting each other. In the CNTs-WO₃ composite, WO₃ grains with disk shape (50–200 nm) were independently trapped. The CNTs-WO₃ composite sensor showed the fairly good sensor response ($R_a/R_g = 3.8$ at 200°C). The sensor response was greatly improved with CNTs-WO₃ composite, comparing with that of CNT sensor ($R_a/R_g = 1.05$). This phenomenon can be explained by formation of p-n junction, between CNT(p) and WO₃(n), and thus improvement of NO₂ adsorption. The sensor response was decreased with increasing the WO₃ amount in CNTs-WO₃ composite, suggesting the electronic conduction due to WO₃ 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 NO₂ and O₂ molecules would yield considerable larger adsorption energies than H₂O, NH₃, CH₄, CO₂, and so on [7, 8]. However, it has been reported that sensor response (R_a/R_g), 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 NO₂ [9–13]. It is important to enhance the sensor response to NO₂ for future application of CNTs gas sensor. It was well known that WO₃ is an excellent sensing material for NO_x detection [14]. The conductive-type sensors using WO₃ have enhanced their sensor response to NO₂ by adopting thin film structure [15–17] and by doping foreign oxides [18, 19]. Recently, we have developed the high sensitivity NO₂ sensor by employing disk shape WO₃ particles and Au interdigitated microelectrode [20, 21]. These WO₃ sensors can detect dilute NO₂ less than 1 ppm with high sensitivity. Interestingly, the modification of CNT with WO₃ nanoparticles would be

nanocomposite with p-n junction and might give us new concept for effect of interaction between CNT and WO₃ on NO₂ detection.

In this paper, we modified the surface of CNT with the WO₃ grains with 300 nm in diameter and 50 nm in thickness to improve sensor response to NO₂, and discuss the interaction between CNT and WO₃ when varied the additional amount of WO₃ 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 μm, gap size of 5 μm, and thickness of 0.3 μm was formed on SiO₂ substrate by photolithography (lift off), as shown in Figure 1. Second, growth catalyst for CNTs, Ni was deposited on Au electrode with 5 μm gap, in which 0.05 wt% Ni(CH₃COO)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).

FIGURE 1: Schematic diagram of Au electrode with the gap of 5 μm and line width of 20 μm on SiO_2 substrate fabricated by means of photolithography (lift off).

The WO_3 powder was prepared from $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ by wet process. Aqueous solution of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ was neutralized by dilute nitric acid solution. The precipitate obtained (H_2WO_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_2WO_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 ($S = R_a/R_g$) was defined as a ratio of resistance in air (R_a) to that in NO_2 -containing atmosphere (R_g).

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 com-

FIGURE 2: (a) SEM image of CNT directly grown on Au microgap; (b) magnified view of (a) indicates the entangled CNTs contacting each other.

posite 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 (R_a/R_g) of CNT-0.1 wt% WO_3 microsensor was as high as 3.8, while the CNT microsensor showed almost no response ($R_a/R_g = 1.05$).

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% WO_3 composite microsensor; (b) CNT-1 wt% WO_3 composite microsensor; and (c) 7 wt% WO_3 composite microsensor.

FIGURE 4: Response transients of CNT and CNT- WO_3 microsensors to 5 ppm NO_2 at 200°C.

FIGURE 5: The sensor resistance and the sensor response of CNTs- WO_3 composite microsensors as function of amount of WO_3 .

thus high sensor response to NO_2 of CNT- WO_3 composite sensor. When higher than 1 wt%, the conduction pass was formed via WO_3 grains to decrease the sensor resistance. At more than 1 wt% WO_3 , the WO_3 grains begin to contact with each other to dominant n -type conduction pass due to WO_3 . It is well known that WO_3 is excellent sensing material for NO_2 detection. Although the WO_3 sensor shows the response of resistance-increase, the CNT- WO_3 (7 wt%) composite sensor exhibited no response to 5 ppm NO_2 ($R_a/R_g = 1$). It is considered that the sensor response (R_a/R_g) would be decreased to less than unity (resistance increase) at higher amount of WO_3 . Finally, the reproducibility of

sensor response to 5 ppm NO_2 was examined at 200°C for 0.1 and 1 wt% WO_3 -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)- WO_3 composite showed the fairly good sensor response (R_a/R_g) to dilute NO_2 , 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 NO_2 adsorption on the surface of CNT.

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