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A Study on Gas Sensor Based on Carbon Nanotubes on Anodized Aluminum Oxide

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A new type of CNTs based ammonia gas sensor was investigated. The array of carbon nanotubes was synthesized into the pore of anodized aluminum oxide (AAO) by thermal chemical vapor deposition method without metal catalyst. The anodized aluminum oxide was synthesized on the p–type Si(100) substrates by two step anodization process. After removing the carbon top layer, a thin Ag electrode was deposited on the surface of sample to get the opened end of the CNTs for gas sensor. The electrical and gas sensing properties of carbon nanotubes based sensor were characterized by I-V test after metal deposition on the top of carbon nanotubes. The device shows high sensitivity for detecting the NH_3 gas at room temperature.

Keywords: carbon nanotubes; CVD; electrical properties; gas sensor

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1. INTRODUCTION

The study of gas sensor is of current interest for varied applications [1–4]. The traditional gas sensor devices are based on the electrical conductance changes in semiconducting oxide materials e.g., TiO_2, SnO_2, ZnO [5–7]. However, metal oxide based gas sensors operate at higher temperatures rendering its practical application difficult. Among all surface reacting materials carbon nanotubes (CNTs) with special geometry and amazing structural features, are potential candidates for gas sensor material [9–13]. Recently, CNTs based gas sensor for the detection of hydrogen [14,15], nitrogen dioxide-NO_2 [16], carbon dioxide [17], nitrogen and ammonia have been reported. However, CNT based gas sensor have some drawbacks in terms of its lower structural quality, impurities of metal catalyst used during its synthesis and poor adhesion between the CNTs and the substrate. These shortcomings are attributed to the procedure used for the synthesis of CNTs where these are grown in the pores of AAO with the help of a metal catalyst. Also, CNTs usually come out of the pores of the AAO and grow to uneven lengths with metal contamination, thereby rendering them not suitable for practical use.

In order to prevent the growth of CNTs outside the pores of AAO and to eliminate the problem of metal contamination, the present work describes the synthesis of CNTs grown on AAO/p-type Si (100) by thermal CVD at high temperature without using a metal catalyst. As synthesized CNTs showed open-ended hexagonal array of uniform pore size and length and were successfully incorporated in the design of an electrode for its application as ammonia gas sensor. The prepared sensor was tested for current versus apply voltage (I-V) characteristic in N_2 and NH_3 flow at room temperature. The NH_3 absorption mechanism on CNTs was investigated by resistance measurement under various NH_3 filling pressure (15 m–400 m Torr).

2. EXPERIMENTAL

The fabrication process of new type gas sensor is described in Figure 1. Firstly we synthesized the AAO template on the p-type Si(100) substrate (Fig. 1a). Secondly, the CNTs were grown on the AAO by thermal CVD method (Fig. 1b). And then the carbon on the top surface of the sample was removed by oxygen plasma (Fig. 1c). Lastly, the Ag electrode was deposited on the surface the sample for sensor measurement.

The AAO template on p-type Si substrate was synthesized by two-step anodization process. A 2 μm thick layer of aluminum with purity

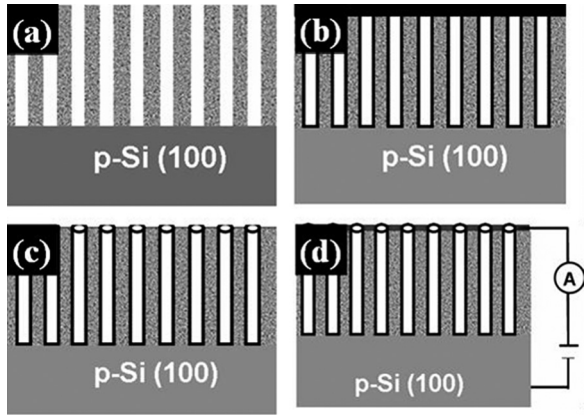

FIGURE 1 The schematic of sensor fabrication, (a) synthesized the AAO/Si, (b) grown CNTs by thermal CVD method, (c) remove the carbon on the surface of sample, and (d) deposited the opened-Ag electrode.

of 4 N was deposited on Si (100) wafer by radio-frequency sputtering method using a 4 inch aluminum target. Anodization process was done in a 0.3 M oxalic acid solution maintained at 10°C. The first anodization was carried out by applying a constant voltage of 45 V between cathode and anode for 700 s. The second anodization was carried out for 25 min in the same conditions used for the first anodization to obtain a regular array of channels. The pores of the AAO channel were then widened by dipping in 0.1 M phosphoric acid for 35 min to get the AAO template with the length of 1.4 μm and the pore of 65 nm in diameter.

CNTs were synthesized via thermal chemical vapor deposition (CVD) method without using a metal catalyst. In this work, the high temperature thermal CVD method was used for growing MWNTs(Multi wall nanotubes) on the pore of the AAO template. The tube furnace was vacuumed to 10^{-3} torr by using a rotary pump and the temperature was raised to 1200°C at a rate of 15°C/min. At this temperature, a mixture gas of C_2H_2 (90 sccm) and NH_3 (10 sccm) was introduced in the furnace for 30 minutes to generate the CNTs on the pores of AAO.

The morphology and quality of synthesized CNTs were characterized by scanning electron microscope (HITACHI-4700), high-resolution transmission electron microscopy (HRTEM).

This carbon layer prevents the gas absorption on the CNTs therefore the sensitivity of gas sensor is low. In order to open the mouth of CNTs, the oxygen plasma PECVD was used to remove the carbon

on the top surface. The oxygen plasma was carried out for 20 min with radio frequency (r.f.) power of for 100 W at pressure of 5×10^{-2} Torr. Then the Ag electrode was deposited on the surface of sample by DC sputtering method. In order to get the Ag electrode, which is not covering the mouth of CNTs (see Fig. 2c), the sample was tilted an angle of 30°. The spurted pressure is 5×10^{-3} Torr, the current is 40 mA and deposited time is 2 min. We can get the Ag opened-electrode with thickness of 40 nm (see Fig. 2d).

The gas sensing properties were measured in a high vacuum chamber. Two types of measured experiment were carried out. Firstly the chamber was vacuumed out to get the pressure of 10^{-5} Torr then the N_2 was filled in the chamber and the I-V was carried out. The NH_3 gas detection was studied by switching the ambient from N_2 to NH_3 (1000 ppm). Secondly, the electrical resistance variations of sensor upon exposure to NH_3 filling and pumping were studied to investigate the mechanic absorption of NH_3 gas on CNTs. The electrical properties and gas sensing property of our devices were characterized

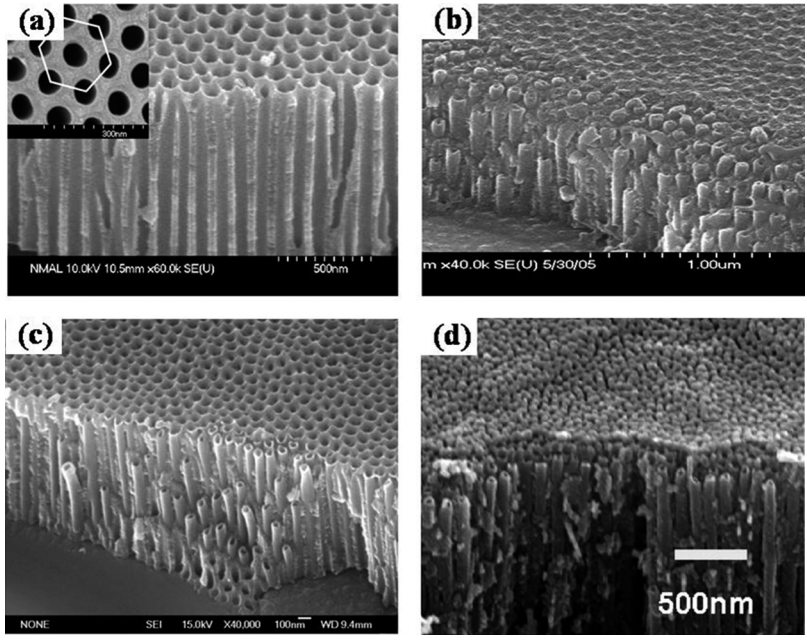

FIGURE 2 SEM images of AAO/Si template (a), the grown MWNTs in AAO after removing the carbon top layer (b), the schematic of gas sensor (c) and the gas sensor with open pore CNTs (d).

by using the programmable electrometer (Keithley 2400). All the experiments were conducted at room temperature.

3. RESULTS AND DISCUSSION

The surface and cross section morphology of the AAO template and as synthesized CNTs were studied by scanning electron microscope (SEM). Figure 2a is the SEM images of the AAO before growth the carbon nanotubes. The nanopores of uniform size exhibit a perfect two dimensional arrays with a hexagonal structure (Fig. 2a. inset). The diameter and inter-pore distances are about 65 nm and 105 nm, respectively. The cross section image shows straight pore channel with the parallel arrangement. The channel length is about 1.4 μm. The AAO membrane is in good adhesion to the substrate.

The morphology of synthesized CNTs after removing the carbon top layer by oxygen plasma is presented in Figure 2b and 2c, respectively. The CNTs were formed inside of the AAO and no growth outside the pores of AAO was detected (Fig. 2b). This is contrary to the CNTs grown on AAO using a metal catalyst where CNTs usually grow outside the pores of AAO rendering it difficult material to design an electrode and other devices due to their different length. Under the present experimental conditions for the synthesis of CNTs, it is opened that the AAO itself serves as a catalyst during cracking of carbon feedstock enabling the synthesis of graphite layer on the surface of the alumina. During the oxygen plasma for carbon layer on the top of AAO, the reactive oxygen ions interact with the top layer of carbon that burn out to open the mouth of CNTs. The SEM image of sensor with Ag electrode is shown in Figure 2d. The Ag electrode with thickness of 40 nm was deposited on the surface of the and not covering the mouth of CNTs. This makes it easier for the gases to fill in the pore of CNTs during gas sensor measurement. This increases the sensitivity of designed sensor.

The electrical property of sensor was studied by the I-V measurement in high vacuum chamber of 10^{-5} Torr. The sensor shows rectifying behavior with the turn-on voltage of 0.5 V, which is in good agreement with the reported of multiwalled CNTs [18,19]. The ammonium gas detection was studied by switching the ambient from 30 sccm N_2 to 30 sccm NH_3 (1000 ppm) flown. Figure 3a shows the current reduction when exposing the NH_3. The sensitivity S of new type sensor depend on the applied voltages was also calculated in detecting the NH_3 gas. The sensitivity S is defined as $S = 100\% \times (I_1 - I_o)/I_o$ where I_o is the current in the presence of N_2 and I_1 is the current after exposing NH_3 gas. The sensitivity increases with increasing the

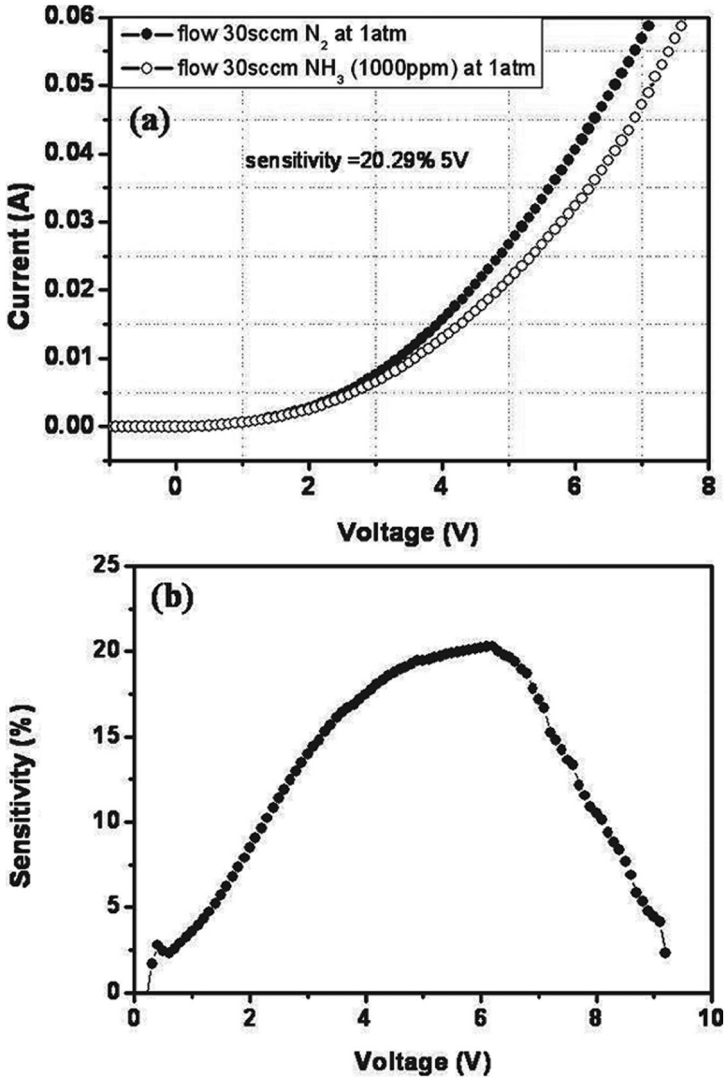

FIGURE 3 The I-V curves of sensor with N_2 flow and NH_3 flows (a), the sensitivity depends on the applied voltage (b).

applied voltages in the range from 0.5 to 6 V, then decreases with increasing the applied voltages (Fig. 3b).

In order to understand the absorption mechanism of NH_3 on the MWNTs, the dependence of sensor electrical resistance on the NH_3 (1000 ppm) filling pressure was carried out in a high vacuum chamber

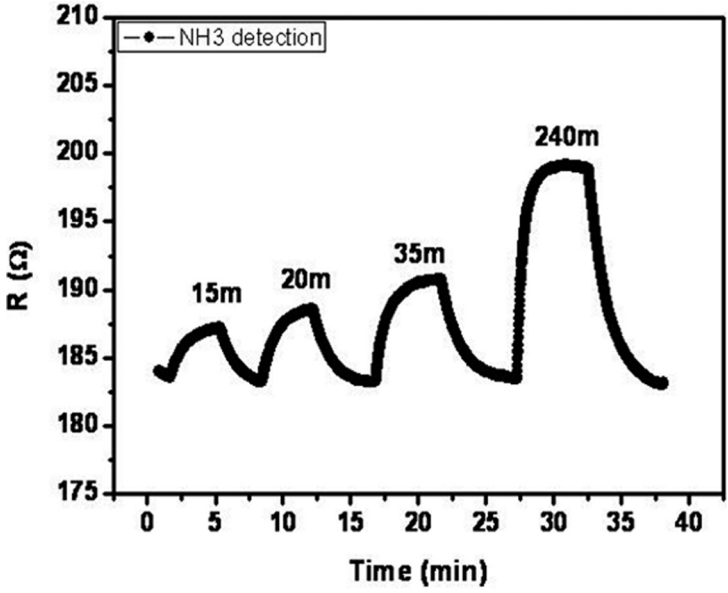

FIGURE 4 The resistance of sensor under various NH_3 filling pressure.

of 10^{-5} Torr. Figure 4 shows the resistance changes of sensor upon exposure to NH_3 filling and pumping condition. When filling the NH_3 in the chamber, the NH_3 molecule bonded with the carbon atom on the surface of CNTs and changes the Fermi level of CNTs. As a result, the resistance along the CNTs increases. After pumping, the NH_3 molecules left the CNTs surface and the resistance decrease to its initial value. The absorption amount of NH_3 on CNTs depends on the concentration of NH_3 and gas-binding sites on CNTs. Increasing the NH_3 pressure, the absorption amount of NH_3 increase therefore it increases the resistance of CNTs. When the pressure reaches to about 240 mTorr, the resistance gets saturated values.

4. CONCLUSIONS

High ordered CNTs with good quality was prepared on the AAO/p-type Si substrate by thermal CVD without using metal catalyst. The CNTs grown inside the pore of AAO crested good condition for designing the electrode. A new type of NH_3 gas sensor was explored. The sensitivity of sensor was increased because of the electrode with opened end CNTs.

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