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Ethanol Gas Sensors Composed of Carbon Nanotubes with Adsorbed Gold Nanoparticles

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Ethanol gas sensors were produced using vertically aligned carbon nanotubes (CNTs) synthesized by thermal chemical vapor deposition from ethylene at 700°C. Scanning electron microscopy showed that the average length and average diameter of the CNTs were about 4.52 μm and 45 nm, respectively. Carbon nanotube ethanol gas sensors with and without adsorbed Au particles of 5nm diameter were fabricated. With an 800 ppm ethanol vapor concentration at room temperature, the sensitivity of a carbon nanotube ethanol gas sensor was increased from 1.67% to 3.28% by the adsorption of Au particles.

Keywords: carbon nanotubes, gas sensor, Au nanoparticles, ethanol, CVD

1. INTRODUCTION

Gas sensors which can be used in many factories and hospitals are important to environmental monitoring. In order to avoid the toxic gas leaking and endangering the human body, it is necessary to do the detection and examination on different gases. Due to the development of nanostructural materials [1], nanoparticles [2], nanobelts and nanowires [3], it has been concluded that the smaller material size and high specific surface area would improve the sensitivity and response times of gas sensors. In recent years, carbon nanotube [4-6] gas sensors [7-12] have been widely studied. Carbon nanotubes with excellent chemical sensing properties for large-scale integration into advanced sensor systems are considered as ideal molecular nanowires for gas adsorption. The individual carbon nanotubes can be either metallic or semiconducting depending on their chirality and diameter, thus they electrically behave as a metal or semiconductor [13].

Chemical sensors based on nanowires of semiconducting CNTs have been used for detecting pollutant and toxic gases like CO, ethanol and isopropyl alcohol, etc [14-16]. CNTs were suitable for gas detection because of their larger effective surface area, with many sites available to adsorb gas molecules, and their hollow geometry that may be helpful to enhance the sensitivity and reduce the operating temperature [17]. The sensing mechanism of the gas sensors is mainly based on the p-type CNT semiconducting property. Generally, their electrical conductance is modified by the electron transfer between CNTs and oxidizing or reducing gas molecules adsorbed on their surface. If p-type semiconducting CNTs adsorb oxidizing molecules, the electric resistance of the CNTs decreases with the increase of the adsorbed gas molecules [18]. In terms of the CNTs gas sensors, capable of being operated at room temperature, prove themselves the most promising candidate for the applications of gas sensors are the main goal that many researchers want to achieve.

Ethanol, also called ethyl alcohol, pure alcohol, grain alcohol, or drinking alcohol, is a volatile, flammable, colorless liquid. Prolonged heavy consumption of alcohol can cause significant permanent damage to the brain and other organs. Thus, it is important to develop a high performance gas sensor that could be used in ethanol gas detection.

In this study, we report the growth of CNTs on Si substrate and the adsorption of Au on nanotube surfaces. Sensing properties of the CNTs with and without Au adsoprtion to ethanol vapor were also discussed.

2. EXPERIMENT

Prior to the growth of CNTs, Si (100) substrate was cleaned by immersing it in boiled acetone and isopropyl alcohol for 10 min, respectively. The chemically cleaned substrate was then rinsed in deionized water and dried with nitrogen flow. We then thermally oxidized the substrate to form a 50-nm-thick SiO_2 layer to act as a catalyst diffusion barrier followed by sputtering a 10-nm-thick Fe layer [19]. Subsequently, the Si substrates were loaded on the aluminum hydroxide boat and put inside the horizontal tube furnace. Nitrogen (N_2) gas was then introduced into reaction tube at a flow rate of 100 sccm with 6.5 Torr for 20 min without the introduction of C_2H_2. The pretreated process was maintained at 600°C [20]. Reaching the 700 °C growth temperature, N_2 was switched off and C_2H_2 reactant was switched on at a flow rate of 30 sccm with 3.5 Torr for 10 min. Then, C_2H_2 reactant was switched off and the reactor was slowly cooled down to room temperature in N_2 ambient. To adsorb Au, similar mechanism of Au adsorption on CNTs surface has been reported by Penza et al [13]. We used electron beam evaporate of a controlled loading of noble metal (Au) naonpartical with an equivalent nominal thickness of ~5 nm over the entire CNTs. Surface morphology of the sample was then characterized by a Hitachi S-4700I field-emission scanning electron microscope operated at 15 keV. A Philips TECNAI 20 high resolution transmission electron microscopy (HRTEM) operated at 200kV and a VG Scientific ESCA LAB 250 were also used to characterize element and bonding electron of the CNTs.

For the fabrication of CNTs gas sensor device, Ag metal deposited by electron beam evaporator was used to serve as the two contact electrodes. Figure 1 shows the schematic diagram of the fabricated CNTs gas sensor device.

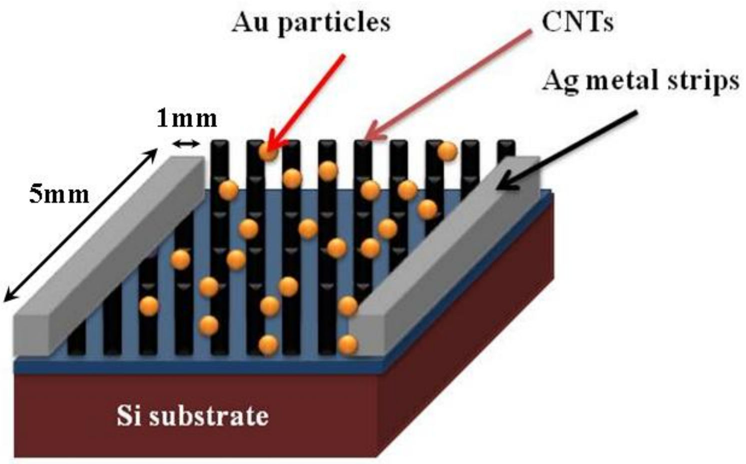

Figure 1. Schematic diagram of the fabricated carbon nanotubes gas sensing device.

We designed the metal mask with a metal contact width of 1 mm wide, length of 5 mm and detection area of 25 mm^2. Further, ethanol sensing experiments were carried out by a high vacuum I-V measurement system by a Keithley 237 semiconductor parameter analyzer. The resistance of various CNTs was measured under a series of ethanol filling and pumping cycles, with the filling pressure from 50 mTorr to 800 mTorr.

3. RESULTS AND DISCUSSION

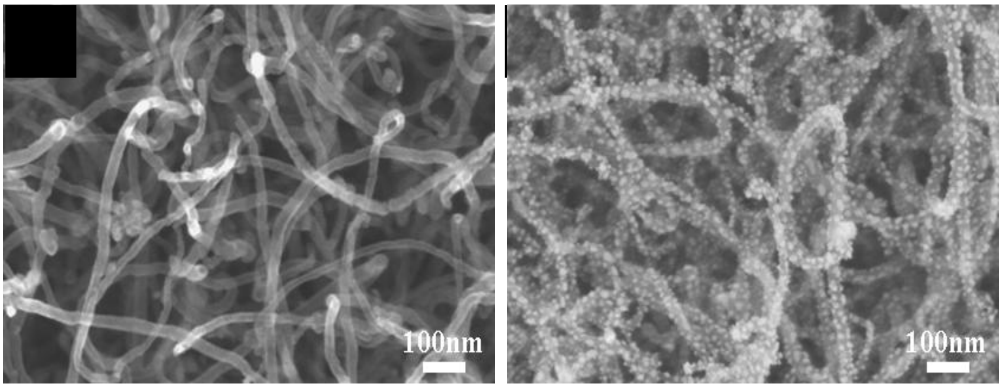

Figure 2. (a) Top-view FESEM image of the CNTs grown onto SiO_2 Si substrate (b) with Au adsorption.

Figures 2(a) and 2(b) show top view FESEM images of the CNTs without and with Au adsorption, respectively. Fe particles as catalyst, it can be seen that high density CNTs were successfully grown on oxidized Si substrates by CVD [21]. From figure 2(a), it was found that the average diameter of the CNTs were about 45nm. Figure 2(b) clearly shows that some of the Au nanoparticles that were coated on the CNT sidewalls were isolated, while some connected with each other, increasing their size to 5 nm.

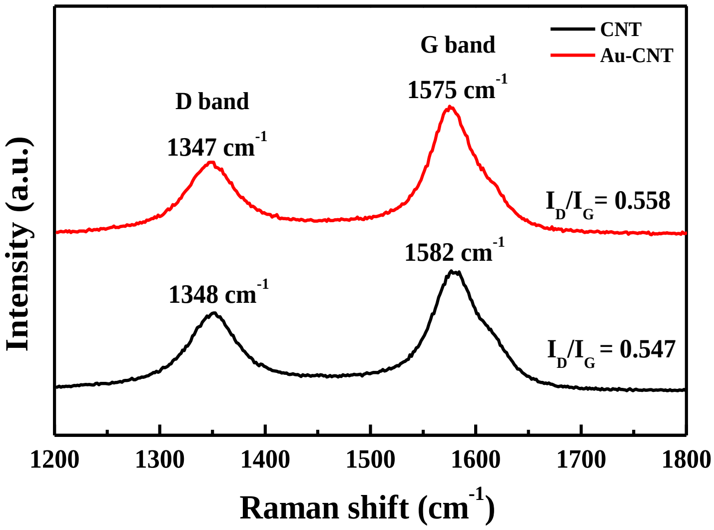

Figure 3. Raman spectrum of the CNTs and Au-coated measured at room temperature.

Figure 3 shows the Raman spectra of pure CNTs and Au-coated CNTs measured by 514 nm Nd:YAG laser line. Both the typical disorder-induced D band (~1350 cm^{-1}) and E_{2g} G band (~1580 cm^{-1}) for multi-walled CNTs mode were revealed [22]. The Gaussian components fitting gave the peak values and the ratio I_D/I_G, which would be an graphitization index for CNTs. Smaller I_D/I_G ratio indicated high graphitic crystallinity of CNTs. Without Au, the I_D/I_G ratio was 0.547. Coating with Au nanoparticles increased this ratio 0.558, because the Au nanoparticles caused disorder in the carbon wall.

Very recently, Chang et al. [23] reported the fabrication of ZnO nanowire CO gas sensors with Au adsorption and high-sensitivity. By measuring the changes in impedance under different ethanol concentrations, we successfully improved the response speed of the CNT gas sensor. The fabricated sensors also show good stability. Since as-grown CNTs were p-type and ethanol were categorized as reducing species, the resistance CNTs would increase when exposing to ethanol ambient [13, 24]. Sensitivity (S) was defined as the ratio $S=[(R_{gas}-R_o)/R_o]\times100$, where R_{gas} represented the gas adsorbed saturated resistance of CNTs in gas ambient during the filling half-cycle and R_o represented the resistance in pumping half-cycle [25]. M. Penza et al. reported the fabrication of CNT networked films gas sensors with Au nanoclusters adsorption [13]. The larger sensitivities observed from the CNTs with Au nanoclusters should be attributed to the enhanced interaction with ethanol gas on CNTs surfaces by Au nanoclusters.

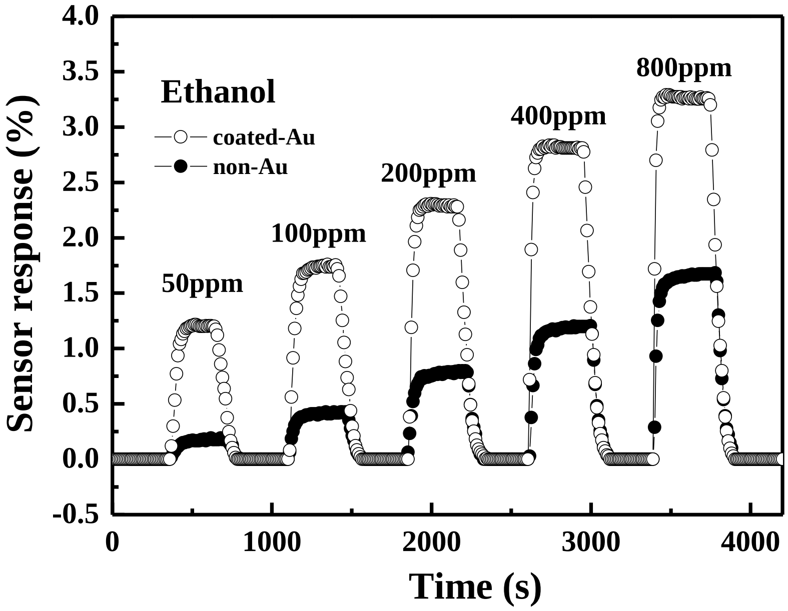

Figure 4. CNT gas sensors measured at various ethanol concentrations.

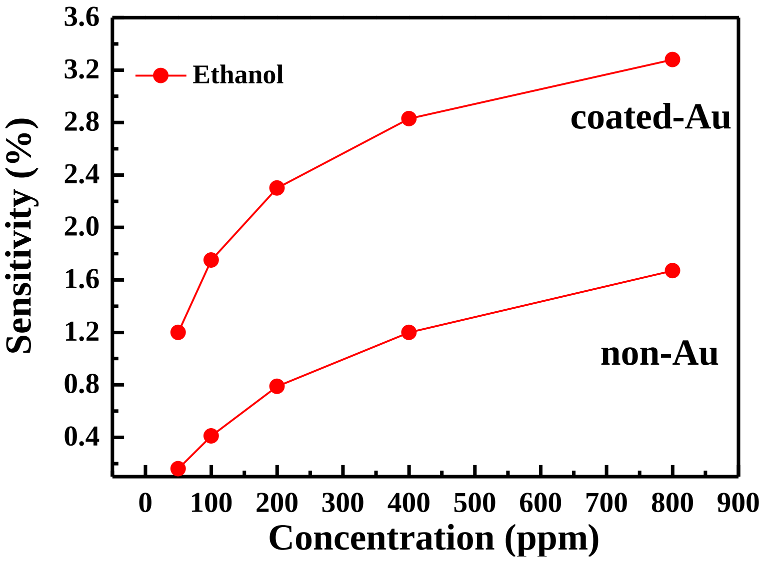

Figure 5. Sensitivities of the CNTs sensors without and with Au adsorption measured at various ethanol concentrations.

Figure 4 shows sensor response variations of the CNTs with non-Au and coated Au exposure under ethanol filling and pumping cycles, with the filling pressure from 50 mTorr to 800 mTorr. These measurements were performed by injecting various amounts of ethanol vapor gas into the sealed chamber following by pumping at fixed voltage 5V. Figure 4 shows the sensor response of the CNTs with Au as a function filling pressure ethanol gas. It was found that measured sensitivities were around 1.2%, 1.75%, 2.3%, 2.83% and 3.28% when concentration of the injected ethanol gas was 50, 100, 200, 400 and 800 ppm, respectively. The increase of sensitivity (S) seemed to be associated with the graphitization of CNTs. The five potential types of site for adsorption on CNTs are the parts of their external surfaces that are decorated with metal nanoparticles, internal (endohedral) sites, interstitial channels, external groove sites, or external surfaces [26, 27]. It can be seen that the coated Au particles improve the gas sensitivity of the CNTs sensors via catalytic effects. In other words, sensor response increased with the increase of vapor gas concentration. It was also found that the sensor sensitivity responded rapidly as we injected vapor gas into the chamber and pumped it away. Figure 5 plots the sensitivities of the sensors that were coated without and with Au nanoparticles to different ethonal vapors and concentrations, based on Fig. 4. The sensor that was coated with Au nanoparticles exhibited higher sensitivity than non-coated one. Besides, it was found that the sensitivities for both devices increased with injected ethanol gas concentration increased. The sensitivities have no obvious saturation at large vapor concentration, indicating the samples are very ideal for practice use.

4. CONCLUSION

In summary, we reported the growth of high-density CNTs on oxidized Si substrate, adsorption of Au nano-particles on nanotube surfaces and the fabrication of CNTs-based ethanol gas sensors. It was found that we could significantly enhance the device sensitivities by Au adsorption. With Au adsorption, it was also found that we could achieve a large 3.28% sensitivity at room temperature when concentration of the injected ethanol gas was 800 ppm. Furthermore, it was also found that the response speed and stability of the fabricated sensor were both good.

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