Alcohol Vapor Sensors Using Multiple Spray-Coated SWCNTs

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ABSTRACT

We suggest a gas sensor using single-walled carbon nanotubes (SWCNTs) thin film for alcohol vapor detection. The SWCNTs thin film were deposited by cost-effective and scalable spray method on flexible PES (polyethersulfone) polymer substrates. From the fabricated sensors, conductivity response properties were measured and discussed. Although alcohol sensors are currently studied for the use of various purposes such as bio-sensing and detection of VOCs (volatile organic compounds), they have been most widely commercially used as a meter for breath alcohol measurement which is applicable to checking whether car drivers are drinking-driving or not. Our sensors showed good sensitivity and linearity in conductance response.

Keywords: alcohol sensors, spray, SWCNTs, conductance

1 INTRODUCTION

The main requirements of a good sensor are high sensitivity, fast response, low cost, high mass production and high reliability. Sensors continue to make significant impact in everyday life with application spreading from biomedical to automotive industry. This has led to intensive research activities across the world in developing new sensing materials and technologies. Currently, the discovery of carbon nanotubes has generated outstanding interest among researchers to develop carbon nanotube(CNT)-based sensors for many applications[1]. Their peculiar properties, especially high surface area and atomic structure, make carbon nanotubes promising candidates for nanoscale sensing materials. Nanotube sensors offer potential and significant advantages over traditional sensor materials (mainly semiconducting metal oxides) in terms of sensitivity, operation at room temperature, small sizes for device miniaturization, massive sensor arrays, and it has been experimentally demonstrated that the electrical conductance of carbon nanotubes can be modulated upon exposure of gaseous molecules of CO_2, NO_2 and NH_3, etc.[2-3]

Currently alcohol sensors using CNTs have been developed for the use of various purposes such as bio-sensing [4] and detection of VOCs (volatile organic compounds)[5]. Among them, alcohol vapor sensors have been most widely commercially used as a meter for breath alcohol measurement which is applicable to checking whether car drivers are drinking-driving or not, and also they are expected as alcohol detecting devices attached to a dashboard for traffic safety. In general, alcohol gas sensors for breath alcohol measurement should be able to measure samples at low concentrations of the order of a few hundred parts per million. To do this, several types of alcohol vapor sensors have been developed, that is, fuel-cell, semiconductor and infrared absorption. But there are a few drawbacks in the present alcohol gas sensors, so we suggest a new type of SWCNTs-based alcohol gas sensors showing potential and significant advantages in terms of sensitivity, operation at room temperature and small sizes for device miniaturization.

2 EXPERIMENTAL

2.1 Device Fabrication

The gas sensors studied in our experiment were comprised of bundles of single-walled carbon nanotubes (SWCNTs). Although dispersion and distribution of CNTs in aqueous media are proved to be challenging, some organic solvents cause less coagulation of the carbon nanotubes and thus permit greater extent of dispersion. In this work, we used SWCNTs solution dispersed in ethanol solvent with epoxy resin, and SWCNTs thin films were formed by multiple spray-coating with the SWCNTs solution where the SWCNTs were modified and functionalized by carboxyl groups during acid treatment for high solubility and gas selectivity. Many current sensors using CNTs follow this approach because of easiness in sensor fabrication.

To fabricate the gas sensors at first, 100 mg of unpurified HiPco SWCNTs (CNI, 35% metal catalyst) was used. In general bundle of CNTs is purified and dispersed by acid treatment with sonication. The unpurified SWCNTs were dispersed in 50 ml of 30 vol% nitric acid and subsequently sonicated for 1 hour in a water bath sonicator, and then the sonicated suspensions were refluxed at boiling condition for 1 hour. The suspensions were filtered through filter paper (Fisher Scientific, No. 1), 40mg of the SWCNT suspensions were added with 40mg of epoxy resin into 100ml of ethanol to complete final SWCNTs solution, and then were bath sonicated for 6 hours to be dispersed clearly.

Next, Al metallization was carried out on the surface of the SWCNTs thin films with a shadow mask to form two electrodes, and then wire bonding with silver paste was followed. Figure 1 indicates a diagram of our alcohol vapor sensors.

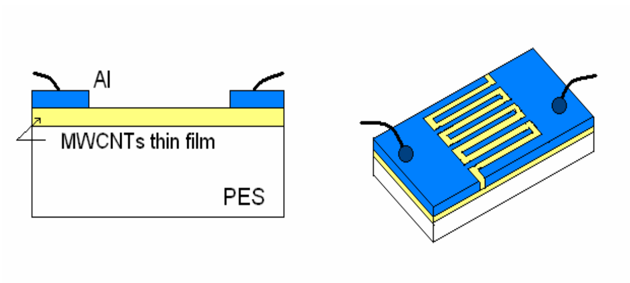

Figure 1: A diagram of our alcohol vapor sensors

2.2 Measurements

Electrical measurements for the sensors were carried out with a semiconductor device analyzer and a HP-4280A in a chamber. We used industrial ethanol diluted in water instead of drinkable alcohol. To adjust the experiment to normal breath alcohol measurement, we injected ethanol molecules vaporized from different vol% ethanol solutions at 36°C, close to the temperature of human body, into the surface of the sensors with N_2 carrier gas. The sensors were first flushed with clean nitrogen gas before exposure to vapors, and were measured 30 seconds after exposure to gases. Figure 2 shows a set of equipment for testing alcohol gas sensors. Current-voltage (I-V) measurement was carried out with a dc power meter to observe the current under a bias to Al electrodes from -5 to 5 V, and electrical conductance and capacitance characteristics were examined.

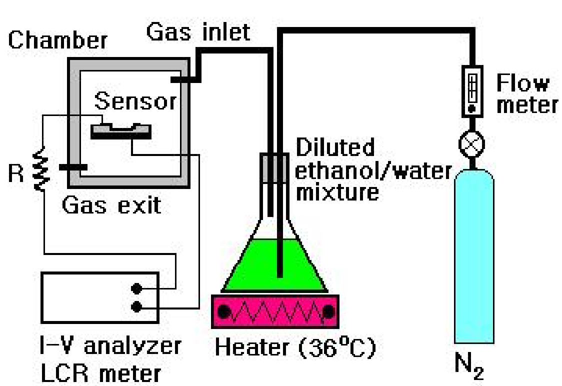

Figure 2: A set of equipment for testing alcohol gas sensors

3 RESULTS AND DISCUSSION

We used PES (polyethersulfone) polymer instead of typical silicon or glass as substrate in this experiment. Since PES polymer has excellent characteristics in flexibility, thermal stability (Tg: 225°C) and surface roughness, it is expected as substrate applicable for flexible sensors. Figure 3 shows an image of multiple spray-coated SWCNTs thin film on a flexible PES substrate

Figure 3: multiple spray-coated SWCNTs thin film on a flexible PES substrate

As the electrical properties of SWCNTs are a critical function of their atomic structure, any gas adsorption can induce great changes in conductance. The promotion or mediation of charge transfer in CNTs thin film by adsorption of electroactive molecules is a main mechanism in most CNT-based chemical sensors application. When gas molecules are adsorbed and then transfer charges on SWCNTs, the molecules may be operated as an electron-acceptor such as NO_2 and O_2, or an electron donor such as NH_3 and H_2O[6]. If an electron-acceptor type of gas molecules is adsorbed at the surface of SWCNTs, the SWCNTs thin films will show p-type semiconducting property of increasing conductance while showing decreasing conductance against an electron-donor type of gas molecules. Figure 4 (a), (b) and (c) show variations of conductance (G) for the three different sensors. Before exposure to alcohol vapor, the conductance was about 3, 15 and 50[μS], respectively, from the 20, 40 and 60 times-coated sensors at room temperature. When the sensors were exposed to alcohol molecules vaporized from 0 to 0.3 vol% ethanol solutions, the conductance of all sensors was increased considerably while the capacitance was nearly invariable. The average value of $\Delta G/Go$ per 0.1 vol% alcohol concentration (where Go indicates the value of conductance at 0.0vol% and ΔG, the variation of conductance) was about 4.0%, while the capacitance is little changed. The invariance of capacitance is due to low face-to-face area between the electrodes in structure.

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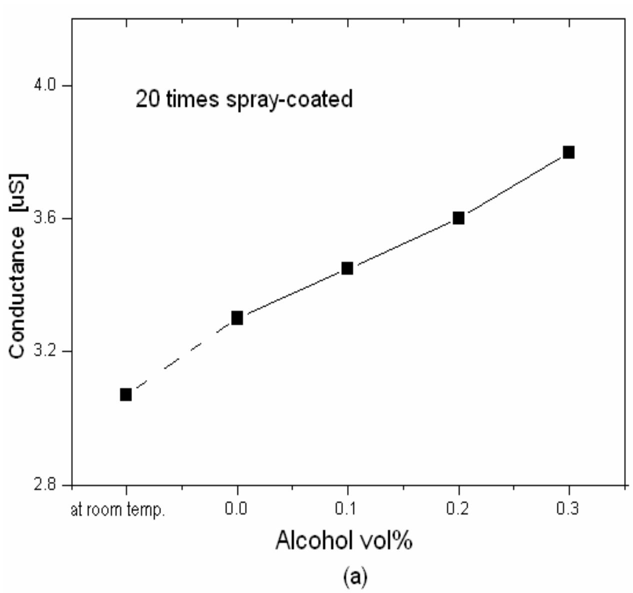
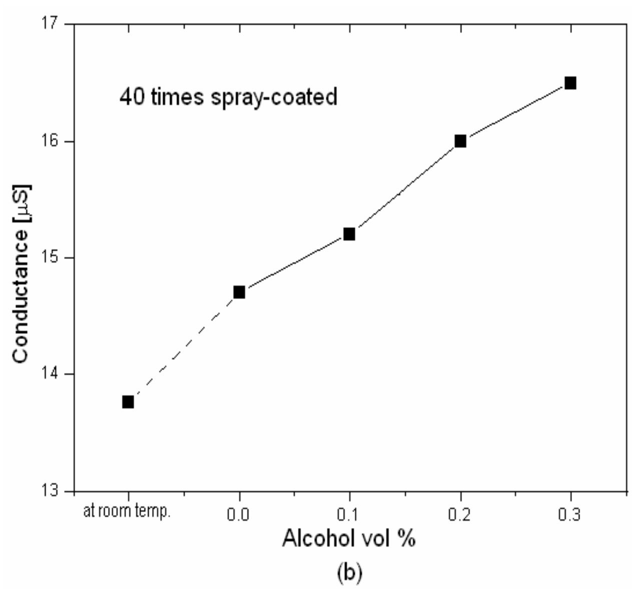
In result, the increase of conductance seems to be related to the charge transfer due to the electron-acceptor characteristic of alcohol molecules and physical adsorption of these molecules in the tube wall when the SWCNTs functionalized by carboxyl groups are exposed to alcohol molecules. Nearly linear relationship between the change in conductance and alcohol concentration was observed and considerable change in electrical conductivity was found in response to alcohol gas adsorption at room temperature.





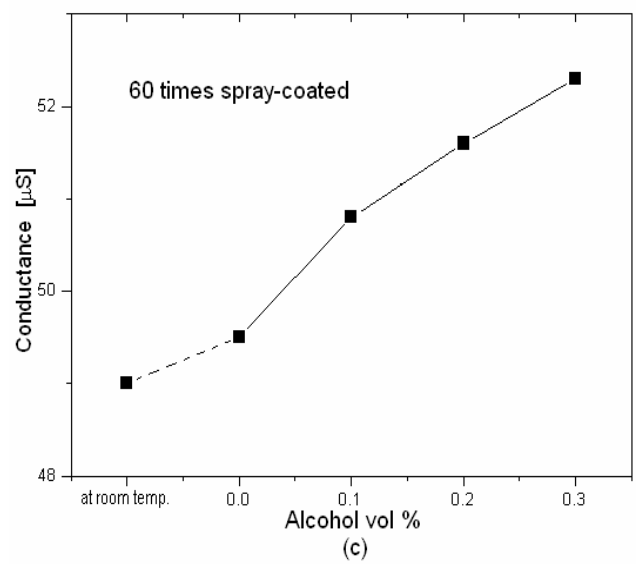


Figure 4: The dependence of conductance on different vol% alcohol solutions for the three different sensors

4 CONCLUSIONS

With the advent of nanotechnology, research is underway to create miniaturized sensors. Miniaturized sensors can lead to reduced weight, lower power consumption and low cost. Carbon nanotubes have been known as one of the most proper materials for miniaturized sensors due to their unique electronic, mechanic, thermal and chemical properties.

The aim of this paper is to present alcohol gas-sensing results for single-walled carbon nanotubes (SWCNTs) thin film prepared by multiple spray-coating on PES (polyethersulfone) substrate. CNTs thin films can be formed simply with the dispersed CNTs solution by screen printing, spray coating, spin coating, imprinting or ink-jet printing onto various substrates and subject to solvent evaporation. In this work, SWCNTs thin films were formed by multiple spray-coating. The multiple spray-coating procedure is very reliable on relatively large area (maximum 20x20cm2), leading to cost reduction and it provides easiness in controlling thickness and conductivity of SWCNTs thin film.

In conclusion, it is expected that our sensors are superior to present alcohol sensors in respects of simple process, low power consumption and good flexibility as well as working at room temperature without heating. Besides, they showed good sensitivity and linearity in conductance response.

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