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A hydrogen gas sensor using single-walled carbon nanotube Langmuir–Blodgett films decorated with palladium nanoparticles

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ABSTRACT

We report the fabrication of a fast response hydrogen gas sensor based on palladium decorated single-walled carbon nanotube (Pd-SWNT) Langmuir–Blodgett (LB) film. To construct the sensor device, a monolayer of aligned SWNT film is deposited on an Au inter-digital transducer (IDT) by the LB technique at a surface pressure of 25 mN/m, followed by the electrochemical reductive deposition of palladium nanoparticles on the SWNT LB films. The Pd-SWNT sensor showed a detection ability of 0.025–2.5% (v/v) of hydrogen in nitrogen (N_2) atmosphere at room temperature and demonstrated a reversible detection process and very fast response time. We analyzed the effect of the palladium acetate concentration used for synthesis of the Pd nanoparticles on the conductance change of the Pd-SWNT sensor. A palladium acetate concentration of 10 μM yielded the highest response of hydrogen detection whereas higher concentrations led to a change of the electron transport property of the films from semiconducting to metallic and consequently decreased the performance of the sensor. The study demonstrates that the Pd-SWNT sensor can easily be extended to detect other gaseous molecules.

1. Introduction

In recent years, single-walled carbon nanotube (SWNT)-based gas sensors have been receiving much attention for their applications in real-time monitoring of various gaseous molecules involved in environmental pollution, chemical processes, biowarfare and so on [1]. Unlike classical metal oxide semiconductor (MOS) gas sensors with operating temperature above 200 °C, the SWNT-based gas sensors have shown the capability to operate at room temperature [2]. It is well known that adsorption of electron donating or withdrawing molecules on the SWNT surface can cause partial charge transfer between the two entities. The resulting change in electrical resistance of the SWNT is measured as sensor signal. However, the weakly adsorbed molecules, such as methane, carbon monoxide and hydrogen, are not detected very well by the SWNT-based gas sensors. Therefore, appropriate chemical modification of the nanotubes with addition of transition metal nanoparticles or conducting polymers that can improve detection sensitivity of the SWNT-based gas sensors is needed [3].

Hydrogen is a technologically important gas used across many industries, and examples include its use as a reactant gas in semiconductor processes and petroleum transformation. In addition, hydrogen has been recognized as an energy storage medium that has the potential to overcome problems associated with traditional fuel sources. There is common need in both existing and developing hydrogen applications to detect and quantify the amount of hydrogen present. Not only is effective hydrogen monitoring important for safety reasons, as hydrogen is odorless, colorless, and highly combustible with a lower explosion limit (LEL) of 4% in air, but also required for process control of hydrogen-based energy systems [4].

The SWNT-based hydrogen sensors have been studied for more than a decade since Kong et al. first proposed use of the SWNT in gas sensors [2]. Sensitive hydrogen gas sensors operating at room temperature can be obtained via functionalization of the SWNT with palladium (Pd), which has excellent hydrogen adsorption ability [5]. Due to its stability at room temperature and in atmosphere; palladium does not react with other gaseous molecules. Palladium deposited single-walled carbon nanotube (Pd-SWNT) sensor is an ideal combination of two materials properties since it utilizes hydrogen adsorption ability of palladium as well as semiconductor properties of the SWNT substrates [6]. Sagoya et al. demonstrated

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fabrication of carbon nanotube-based hydrogen sensors by air-brushing Pd-functionalized SWNTs on alumina. They showed that the chemically Pd-functionalized SWNT sensors provided more sensitive and stable responses than Pd-sputtered SWNT sensors [7]. Sippel-Oakley et al. fabricated carbon nanotube network film by filtration method followed by subsequent coating with Pd nanoparticles by ion sputtering or thermal evaporation. The device marked a sensitivity to detect H_2 to the levels of ~10 ppm at room temperature, and the recovery time was found to be less than 30 s when exposed to the air [8]. The hydrogen detection using Pd-decorated multilayer graphene nanoribbon network based sensor also has been reported recently [9].

Most recently, Mubeen S. et al. showed the fabrication of the hydrogen nanosensor by electrodeposition of Pd nanoparticles (Pd-NPs) on SWNT network film, and optimized the electrodeposition conditions such as electrodeposition charge and potential to improve sensing performance [10]. The response time for their sensor was about 18 min for hydrogen concentrations up to 300 ppm and 7 min for 3000 ppm. Lee et al. reported significant electrical conductance modulation upon exposure to extremely low concentrations (10 ppm) of hydrogen gas (H_2) in air using Pd NPs-dendrimer-SWNTs sensors after heat treatment, owing to the reduced length of the dendrimers [11]. Rumiche et al. reported that the hydrogen sensing responsivity of the double wall carbon nanotube (DWNT) network-palladium nanoparticle nanostructure was affected by the thickness of the Pd layer. Nanoparticle layers of 1 nm did not show reliable sensor response toward hydrogen, while layers of 3 and 6 nm showed a comparable and reversible increase in resistance upon exposure to hydrogen. However the 3 nm Pd coating thickness could detect the lowest hydrogen concentrations at 0.05%, response time was longer [12].

Although the previous studies revealed the capability of the SWNT-Pd nanoparticle hybrid system based device as hydrogen sensor, to the best of our knowledge, there are no reports on the detection of the hydrogen gas using palladium decorated highly aligned and uniform SWNT film. The use of aligned carbon nanotubes provides additional advantages for a maximized access of the nanotube surface and an efficient device construction. In addition, the decoration of Pd nanoparticles on the nanotube surface at right density and uniformity would help to maximize the sensitivity. Therefore, uniform SWNT film fabrication and homogeneous deposition of palladium nanoparticles on the SWNT surface are important factors that determine hydrogen detection sensitivity of the Pd-SWNT based sensor.

The most of all basic platforms, the uniformity of SWNT film is a crucial point to make reproducibility of electro signal for the sensor. There are several methods available for the preparation of SWNT films, such as filtration, spray, electro-spinning, self-assembled monolayer (SAM), and the Langmuir–Blodgett (LB) technique. Most of these preparation processes would require a fabrication method capable of producing uniform organization of SWNT with well-defined and controllable SWNT density for reproducibility of sensor property. Among these fabrication methods, the LB technique holds more advantages since it allows fabrication of uniform SWNT film with controllable surface coverage and aligned orientation of SWNTs on sensing surface [13–15]. Also, the directional alignment of nanotubes in electronic devices and sensors has shown to enhance its performance as opposed to that for SWNT networks. For effective functionalization of the SWNT surface with the palladium nanoparticles, various deposition processes have been proposed, which include simple chemical vapor deposition (CVD), sputtering, and electrochemical reductive deposition [16]. Herein, we focus on the use of the electrochemical reductive deposition of the palladium nanoparticles on the SWNT LB films since they can be grown easily and selectively on the SWNT surface by controlling the input potential and reaction time.

In this contribution, we report a facile fabrication of the Pd-SWNT sensor by first preparing the hierarchically aligned SWNT film on inter-digital transducer using the LB technique, and then depositing the palladium nanoparticles selectively on the SWNT through the electrochemical method. We investigated resistance changes of the Pd-SWNT sensor upon exposure to 0.025–2.5% (v/v) of hydrogen in N_2 atmosphere and analyzed resistance changes according to the palladium contents on the SWNT surface. In order to enhance the performance of device, optimization of electrodeposition was by controlling the concentration of Pd acetate solution and the deposition time.

2. Experimental

2.1. Reagents

All reagents were received and used without further purification. The SWNT (synthesized by arc-discharge, 60–70% purity) was purchased from Iljin Nanotech (Korea). Palladium acetate (reagent grade) and all solvents (HPLC grade) were purchased from Sigma–Aldrich (USA), and deionized (DI) water was purified to the resistivity of at least 18.2 MΩ cm through a Millipore water purification system (USA).

2.2. Preparation of the SWNT LB films on silicon sensor chip

To enhance dispersibility of the SWNT in various solvents, such as methanol, acetone, water, and chloroform, the SWNTs were subjected to chemical oxidation and purification process [17]. The SWNT dispersion in chloroform for LB film fabrication was prepared according to the process described in our previous reports [13,14].

The SWNT LB film was transferred onto a 10 mm × 80 mm sensor chip which was patterned with Au IDT electrode (electrode pitch and width of 20 μm) on SiO_2 coated silicon substrate (Si/SiO_2 substrate, SiO_2 thickness = 300 nm) with at a surface pressure of 25 mN/m. The sensor chip obtained was placed in an oven at 120 °C for 1 h under nitrogen atmosphere to remove water.

2.3. Decoration of the palladium nanoparticles on the SWNT surface

The palladium nanoparticles were grown on the surface of the SWNT LB films by using the cyclic voltammetry instrument (MF-9063, Bioanalytical Systems, USA) with 1–100 μM palladium acetate dissolved in DI water, at a voltage of −800 mV and charge of 0.01 C at ambient conditions. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively. The SWNT film and the deposited palladium nanoparticles were investigated in 1 μm × 1 μm sections by energy dispersive spectroscopy (EDS; Genesis 2000, EDAX, USA) and field emission scanning electron microscopy (FE-SEM; LEO Supra 55, Carl Zeiss SMT, Germany).

2.4. Detection of hydrogen with the Pd-SWNT sensors

After treatment under UV irradiation at 120 °C for 10 min to remove adsorbed water and oxygen from the sensor surface, the Pd-SWNT sensors were placed in a temperature and moisture controlled nitrogen filled chamber (batch type, 4 L) to evaluate the hydrogen detection performance of the prepared sensors. The sensor signal was allowed to stabilize, and 0.025–2.5% of hydrogen (v/v) in a N_2 atmosphere was injected at an interval of 5 min. The variation in electrical resistance was measured as the sensor signal. We used a nitrogen filled chamber for the detection of H_2 gas because the moisture and the constituent gases of air present in the atmospheric condition may affect the response time of the