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Fast-speed, high-sensitivity polyimide humidity sensors with superhydrophilic carbon nanotube network electrodes

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ABSTRACT

We present a highly fast capacitive humidity sensor based on superhydrophilic carbon nanotube network electrodes prepared by using spray deposition of multiwalled carbon nanotubes (MWCNT). Spray-deposited MWCNT films form a well-entangled and interconnected porous network with nano-scale open pores. These properties are highly desirable for fast-speed capacitive humidity sensors. In addition, the effect of plasma functionalization (pf) of the MWCNT surface on sensor response was evaluated. The pf-MWCNT electrode sensor exhibited a much faster response time (about 1.5 s) and a higher sensitivity (0.647 pF/%RH) to humidity, compared to untreated MWCNT and porous Cr electrodes. The large improvement in performance was explained by the percolated pore network, which is more accessible to water molecules; the superhydrophilic surface of the MWCNTs favorable to more adsorption of water vapor; and capillary condensation, which can amplify the capacitance response to relative humidity.

1. Introduction

Carbon nanotube (CNT) networks, made of randomly distributed CNTs, are a unique class of materials generating strong interest and research efforts among scientists to develop CNT-based devices for many potential applications, including nano electronics [1], gas and biosensors [2–4], field emission devices [5], and actuators [6]. Carbon nanotubes have received considerable attention as chemical gas sensors because of their outstanding properties such as high surface-to-volume ratio, excellent chemical stability, and dramatic change in electronic properties in response to a target gas at room temperature [3,7]. They have shown high sensitivity towards such gases as NH_3 [8,9] NO_2 [10], H_2 [11], CH_4 [12], CO [13], SO_2 [14], H_2S [15], and O_2 [16]. Carbon nanotube films also exhibit sensitivity to water vapor. Recently, several groups have developed CNT humidity sensors based on different sensing mechanisms; resistance change of CNTs [17,18], CNT FETs [19], CNT/polymer nanocomposite [20–22], CNT-based capacitor [23], and CNT-coated quartz-crystal microbalance (QCM) [24,25]. Some of the potential drawbacks of using CNTs as humidity sensing materials are the lack of specificity to different gaseous analytes and a very slow response time. A challenge faced by all CNT-based humidity and gas sensors is analyte selectivity because, in most cases, CNT-based chemical sensors have been shown to be sensitive to a wide range of gas molecules at room temperature [3,7,26]. The limitation of selectivity is caused by the non-selective character of the adsorption process. Another problem is that most gas and humidity sensors based on CNTs show a slow response (a few minutes) and recovery time (several hours). A fast response time is required for real-time sensing.

These shortcomings can be, at least in part, circumvented by using CNT networks as a top electrode in capacitive-type humidity sensors. Since the CNT films have low electrical resistivity, high surface area, percolated pore structure, and excellent physical and chemical stability, they have been investigated extensively as electrodes for supercapacitors, fuel cells, and lithium ion batteries [27–29]. The suggested benefit of CNT electrodes is their interconnected mesoporous structure that may be more accessible to mobile ions. The hybridization of the low resistivity and high porosity properties of CNTs also has the potential to yield interconnected microscopic pore networks that can be more accessible to water molecules. Thus, an open porous CNT network can be utilized, in a similar fashion as the previously described electrodes, as an effective electrode for high-speed humidity sensors.

In this article, we evaluate the application of superhydrophilic carbon nanotube network electrodes for fast-speed, high-sensitivity capacitive humidity sensors. While tangled CNT networks show promise as stable electrode materials, characteristically hydrophobic properties have limited their practicality. Wetting of the CNT surface are of crucial importance to obtain good adsorption of water vapor and subsequent fast diffusion into humidity sensing film. The wettability of CNT may be controlled

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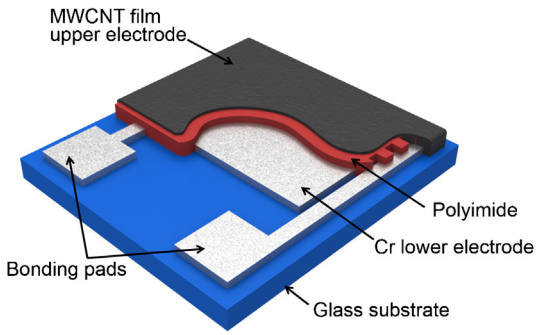

Fig. 1. A schematic illustration of PI capacitive humidity sensor device with MWCNT film upper electrode.

by several chemical and physical treatments for their functionalization. As known, the hydrophilicity of materials can be enhanced by introducing strong polar groups to the surface, increasing the roughness or a combination of the two [30]. The specific methods include exposure to strong acids [31], ultraviolet radiation [32], and plasma [33]. The oxygen plasma treatment is known as an effective method to simultaneously introduce hydrophilic functional groups, such as —OH and —COOH and roughness to the CNT. CNT films have been reported to turn hydrophilic after proper plasma treatment [34,35]. This feature together with open porous structures suggests that plasma-functionalized MWCNT networks are suitable electrode materials for high-speed, high-sensitivity humidity sensing. The optimized pf-MWCNT film electrodes demonstrate significantly enhanced response time and sensitivity for capacitive humidity sensors. The mechanism behind the super-enhanced performance characteristics of the pf-MWCNT electrode is investigated with respect to several factors resulting from the highly porous film morphology and hydrophilic functional groups linked to the MWCNTs.

2. Experiments

The typical layout of a PI capacitive humidity sensor with an MWCNT electrode is illustrated in Fig. 1. The sensor consists of a parallel plate capacitor with two conductive electrodes. An upper electrode of the MWCNT film is patterned on top of the moisture-sensitive PI film. A Cr lower electrode layer is located between the PI sensing film and the glass substrate.

The sensor device was fabricated on a 4-in.-thick glass wafer. First, a 2000-Å Cr layer was blanket-deposited by e-beam evaporation on the entire wafer surface and then patterned by optical lithography to form the lower electrode and the contact pad for the upper electrode. Next, a polyamic acid solution of the Poly(pyromellitimide-1,4-diphenyl ether) (PDMA-ODA) (PI-2545, purchased commercially from HD Microsystem, Japan) was spin-coated on the patterned Cr lower electrode and soft-baked at 110 °C for 10 min. The soft-baked polyamic acid film was patterned using a positive photoresist, followed by a two-step ramp curing process to complete the conversion of the precursor to PI. The first cure was carried out at 250 °C for 30 min in N_2 atmosphere, and then the temperature was increased up to 350 °C. The final cure was carried out at 350 °C for 1 h. The process described above is almost the same as that of a conventional PI sensor.

High-purity MWCNTs (99%) were produced by the catalytic reaction of C_2H_4 over an $Fe/Mo/Al_2O_3$ catalyst in a manner described previously [36]. In brief, the catalyst was calcined at 923 K in O_2 for 2 h, followed by mechanical grinding for several hours. It was then placed in a quartz boat and inserted into the center of a reactor. C_2H_4, Ar, and H_2 were introduced then into the quartz tube at flow rates of 300, 500, and 500 sccm, respectively.

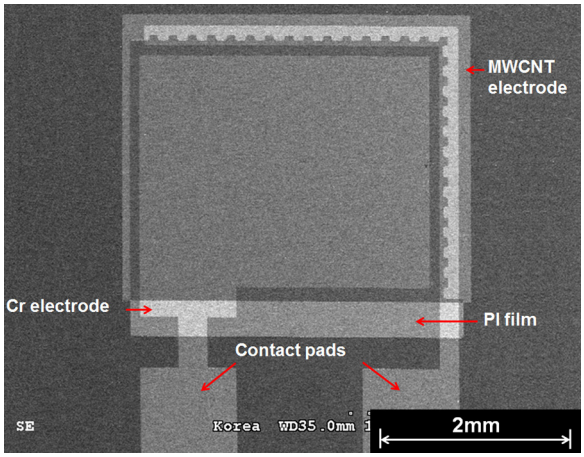

Fig. 2. SEM image of microfabricated capacitive humidity sensor with MWCNT film electrode.

The flow rates and reaction temperature (923 K) were maintained for 100 min before the furnace was cooled to room temperature in Ar atmosphere. The MWCNTs were purified by treatment with 3 N nitric acid. To prepare the solutions for the spray-coated films, 3 mg MWCNT diluted with 150 ml DichloroBenzene was tip-sonicated for 20 min to obtain a homogeneous solution, and then isolated and dispersed MWCNTs were then separated from the aggregated MWCNTs and insoluble material by ultracentrifugation (20,000 × *g*, 20 min, 4 °C).

MWCNT films were spray-deposited all over the substrate using the MWCNT solution. The film thickness was controlled by holding the spray conditions constant and varying the spray application rate. An atomic force microscopy (AFM) system was used to record the topography of the region around the vertical step and to measure the MWCNT film thickness. Several lateral AFM scans across the steps were taken and an average of the scanned thicknesses was calculated to obtain the final film thickness. The MWCNT thickness derived from AFM line profiles was about 71 nm at 1 ml/cm^2 (spray application rate).

The MWCNT upper electrode was finally plasma-treated in O_2 gas. The typical treatment parameters were 30 sccm O_2 flow rate, 25 °C substrate temperature, 20 RF power, and 20 s treatment time. The scanning electron microscopy (SEM) picture of the microfabricated sensor device is shown in Fig. 2. The device size is 3.3 mm × 4.4 mm with an active area of 0.625 mm^2.

3. Results and discussion

3.1. Spray-deposited MWCNT films

Fig. 3 shows SEM micrographs of spray-deposited MWCNT film electrodes of 71 nm thickness. For comparison, a porous Cr electrode was included. The MWCNTs formed well-entangled and interconnected porous structures, with the more uniform networks and open microscopic pores than the porous Cr film, which contained slit pores, indicating that MWCNT films are much more effective in forming microscopic pores in the sensor electrode than metal films. Because of this unique architecture, several properties which were unobtainable with metal electrodes were realized: a pore structure determined by the open space between the entangled MWCNTs, high accessible surface area, and controllable electrode density.

A pore size distribution analysis of the MWCNT films by SEM image analysis [37,38] revealed that the nanotube electrodes were essentially free of micropores. Pores were measured between 5 and 280 nm width, giving an apparent mean pore diameter of