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Conducting polymer coated single-walled carbon nanotube gas sensors for the detection of volatile organic compounds



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ABSTRACT

The current work involves fabrication, characterization and subsequent evaluation of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) coated single walled carbon nanotubes (SWNTs) sensors for detecting analytes of interest in industrial manufacturing. By varying the conducting polymer's synthesis conditions in terms of charge controlled electropolymerization of the monomer EDOT in presence of the dopant PSS, the sensing performance of the PEDOT:PSS functionalized SWNT sensors was systematically optimized. Electrical characterization in terms of change in resistance, cyclic voltammetry and field-effect transistor measurements was performed to confirm the presence of PEDOT:PSS coating on SWNTs. The optimized sensors exhibited sensing properties over a wide dynamic range of concentrations towards saturated vapors of volatile organic compounds (VOCs) such as methanol, ethanol and methyl ethyl ketone (MEK) at room temperature. The limit of detection of this sensor was found to be 1.3%, 5.95% and 3% for saturated vapors of methanol, ethanol and methyl ethyl ketone (MEK) respectively. In terms of performance, when compared with bare SWNTs, these hybrid sensors exhibited better sensitivity. The underlying mechanism of sensing was also investigated by using them in chemFET mode of sensor configuration.

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1. Introduction

Carbon nanotubes (CNTs) are being put into a variety of electronic applications such as room temperature field effect transistors [1], [2], interconnect [3] and actuators [4]. Very high electrical and thermal conductivities, extraordinary mechanical strength together with their ultrasmall size and low power consumption make them perfect candidates for being used as an electronic material [5]. Sensors constitute a field in which CNTs are being increasingly used as active material for sensing gases and vapors [6,7]. Their high surface area which consists of all surface atoms gives them the property of exhibiting high sensitivity and rapid response times towards any change in their chemical environment. The earliest attempts at using carbon nanotubes as gas sensors were made by Kong et al. in 2000 where they demonstrated bare carbon nanotubes to respond to gases like ammonia and NO₂ at room temperature [8]. Since then studies have shown that carbon nanotubes can be used to sense a large number of other gases and volatile organic

compounds [7,9–11]. However, gases which have low absorption capacity on carbon are difficult to be detected using single walled carbon nanotubes (SWNTs) [8]. To overcome this difficulty several techniques have been incorporated which involve modifying the surface of SWNTs using materials like conducting polymers [12,13], metals [14–17] and metal oxides [18]. Conducting polymers and their derivatives have been long used as chemical sensors. However their wide application is limited due to their inability to be used in a broad pH range [19]. Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) is widely used in chemical sensors owing to its properties of being electrochemically active, environmentally stable and maintaining its activity over a wide pH range. The use of PSS as the counter ion renders enhanced conductivity and facilitates easier processibility [20]. Reports have been made governing the use of PEDOT nanowires and thin films towards sensing gases and alcohols [21–24].

In this work, surface functionalization of SWNTs with PEDOT:PSS using electropolymerization is reported and subsequent evaluation of the real time response of these SWNT coated PEDOT:PSS hybrid chemFET sensors towards sensing three volatile organic compounds namely methanol, ethanol and methyl ethyl ketone is performed. Electropolymerization offers a great deal of flexibility in terms of controlling the thickness of the conducting polymer film on the

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surface of the SWNTs by altering parameters like charge, electrolyte composition and potential [15]. SWNTs act as the charge conduit material along with PEDOT:PSS as the sensing element which bring about an increase in the overall sensitivity of the sensors towards detection of VOCs.

2. Experimental

2.1. Sensor design and fabrication

Microfabricated gold electrodes were fabricated on highly doped p-type silicon substrate using the cleanroom facilities available at the University of California, Riverside. Briefly, a 300 nm SiO₂ thick film was deposited on a (100) oriented highly doped p-type Si substrate by thermal CVD deposition to insulate the substrate. It was followed by defining the drain and source electrode areas by photolithography using the positive photoresist 5214. The thickness of the chromium adhesion layer was maintained at 20 nm and that of gold above it was 180 nm. The width and gap of the electrodes were fixed at 200 μm and 3 μm, respectively.

2.2. SWNTs solubilization and alignment

Carboxylated-SWNTs (SWNT-COOH 80–90% purity) procured commercially from Carbon Solution, Inc., Riverside, CA, were dispersed (1 μg/mL) in dimethyl formamide obtained commercially from Sigma Aldrich, MO. Though carbon nanotubes are known to have poor solubility in most solvents, the amide group of dimethyl formamide (DMF) can attach to the surface of the nanotubes making it a suitable solvent for obtaining uniformly suspended SWNTs in DMF [8]. The suspension of SWNTs in DMF solution was prepared in steps which involved first sonicating the dispersed carboxylated SWNTs followed by centrifugation at a speed of 10,000 rpm to remove soluble fraction and aggregates.

The suspended SWNTs were aligned in the 3 μm spaced micro-fabricated gold electrodes by AC dielectrophoresis (DEP) [21]. The procedure involved addition of a 0.1 μL drop of SWNTs suspended in DMF and subsequent application of an AC voltage of 3 V peak to peak amplitude at a frequency of 4 MHz across the electrodes. The aligned SWNTs were then annealed at 300 °C for 1 h in an atmosphere of 5% hydrogen and 95% nitrogen gas to improve the contact between the electrodes and the SWNTs and to remove DMF residues accumulated during the process of SWNTs alignment.

2.3. Electropolymerization

Electrochemical functionalization of SWNTs with PEDOT:PSS was conducted at ambient temperature with a three electrode configuration where the aligned SWNTs network with the gold electrodes, a Pt wire, and chlorinated silver wire (Ag/AgCl wire) were used as working, counter, and reference electrodes, respectively. A 0.1 μL drop of 5 mM solution of the electrolyte EDOT (monomer) and 5 mM PSS (dopant) in water was placed on top of the SWNT networks followed by potentiostatic electropolymerization at 0.9 V vs. Ag/AgCl wire reference. The electrodes were placed in contact with the electrolyte to constitute an electrochemical cell. Charge controlled electropolymerization was performed at three different charges namely 1, 2.5 and 5 μC. After the functionalization, the sensors were washed gently with deionized water followed by blow drying lightly with nitrogen gas.

2.4. Device characterization and sensing

The SWNT devices were characterized before and after electropolymerization by a scanning electron microscope (SEM). SEM

images were obtained using a Zeiss Leo SUPRA 55 with beam energy of 20 kV. Sensors were characterized in terms of their current–voltage (I – V) response measured using a potentiostat (Model 1202A, CH Instruments, Inc., TX, USA) before and after electropolymerization. The voltage was swept from -1 V to $+1$ V and the current was recorded. The device resistance was measured as the slope of I – V near zero voltage in the linear range of ± 100 mV. Transport measurements were performed using a dual channel Keithley source meter (Keithley-Model 2636A, CA) wherein the gold electrodes acted as the source and drain while polysilicon behaved as the back gate. A drain to source bias of -1 V was applied while the gate voltage was swept in the range of ± 20 V at a scan rate of 0.1 V/s. Source–drain current (I_{SD}) as a function of the gate voltage (V_{GS}) was measured. Cyclic voltammetry was conducted in an aqueous solution of 0.1 M NaCl at a scan rate of 50 mV/s using a potentiostat (Model 1202A, CH Instruments, Inc., TX, USA).

2.5. Gas sensing setup

The 16 electrodes pair chip consisting of 16 individual addressable sensor devices, each electropolymerized with PEDOT:PSS were wirebonded and packaged to a 40 pin ceramic inline package, which was then mounted on to the breadboard of the sensing system setup. The sensors were connected in series with a load resistance of equal resistance value and were subject to a fixed voltage of 1 V DC. Real time measurements were carried out using a custom made sensing setup that was controlled by LabView program.

A 3.6 cm³ air tight sealed glass chamber with gas inlet and outlet ports for gas flow-through was positioned over the sensor chip. Saturated vapors of the VOCs were produced by bubbling dry air through the bubbler column containing the VOC. The carrier gas in this setup was dry air. Various concentrations of the vapors were introduced to the gas chamber by regulated flow of the vapors with the help of mass flow controllers purchased from the Alicat Scientific Incorporated, Tucson, AZ. Prior to all the sensing experiments, the sensors were first exposed to dry air (purity: 99.998%) to attain a steady baseline resistance. The sensors were then exposed to different concentrations of the saturated vapors of the VOC mixed in dry air for 15 min with an interval of 20 min recovery in air between two successive vapor exposures. This constituted one complete cycle. This cycle was repeated for n number of times based on the range of concentrations being sensed. For real time gas sensing, the sensors thus fabricated were operated as chemiresistive sensors wherein the change in resistance upon exposure to an analyte formed the basis for measuring the sensitivity of the sensor. All sensors with an initial resistance in the range of 3–9 kΩ were used for sensing for better reliability and consistency in gas sensing results.

3. Results and discussions

Several techniques have been used over the past few years for fabricating carbon nanotube based semiconducting devices. They involved manipulating CNTs onto pre-patterned electrodes by an atomic force microscope [25], random dispersion of suspended carbon nanotubes onto pre-patterned electrodes, [26] and lithographically patterning catalyst [27] as CNT nucleation sites on electrode and drop casting to obtain CNT network between the electrodes. However these techniques yielded low throughput and their complexity and limited controllability rendered them unsuitable for applications which require high density sensor arrays that can be mass producible. The DEP technique eliminates such issues by offering a simple, cost-effective and controllable

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