Diamond & Related Materials 60 (2015) 42–49

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Room temperature gas sensors based on carboxyl and thiol functionalized carbon nanotubes buckypapers

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ARTICLE INFO

Article history:
Received 22 June 2015
Received in revised form 25 September 2015
Accepted 10 October 2015
Available online 22 October 2015

Keywords:
Carbon nanotubes
Scanning electron microscopy
Carbon monoxide
Methane
Gas sensors

ABSTRACT

In this paper, we report the carbon monoxide (CO) and methane (CH_4) gas detection using carboxyl (COOH) and thiol (SH) functionalized carbon nanotubes buckypapers as active material. We observed that the chemical reactivity of nanotubes had shown to improve considerably by functionalizing the sidewalls with specific functional groups at room temperature. Buckypapers were formed by using "4,4′ diaminobenzophenone" in functionalized carbon nanotubes via chemical route. A comparative study is presented for different types of buckypapers by varying the concentration of cross-linker ratio to nanotubes. The maximum sensitivity observed for 20 ppm CO was 4.78% and for 400 ppm CH_4 was 2.08% on thiolated CNTs buckypapers. It was also observed that the carboxylic functionalized buckypapers showed decrease in resistance and thiolated buckypapers showed increase in resistance upon exposure to CO gas while carboxylic and thiolated buckypapers showed increase in resistance upon exposure to CH_4 gas. Further investigations showed that by increasing the cross-linker concentration to CNTs, thiolated buckypapers exhibited more sensitive to reactive gases.

1. Introduction

Chemical sensors are important for environmental monitoring, military and in biomedicine. High selective and high sensitive chemical sensors are required for leakage and hazardous gas detection. Scientists are looking for the nanotechnology based chemical sensors to provide high sensitive and low power consumption for chemical analysis in military, space and terrestrial applications [1–5]. Carbon nanotubes (CNTs) and their buckypapers have been known as exceptionally promising material for applications in nanoscience like composite materials [6–8], field emitters [9,10] battery electrode materials [11], infrared sensors [12] and gas sensors. One dimensional quantum nature and large surface to volume ratio of CNTs makes their intrinsic properties highly sensitive to small external perturbations [12–14]. However, pristine carbon nanotubes are chemically inactive and prevent the formation of chemical bonds with surrounding molecules due to strong sp^2 bonding in hexagonal network. Chemical reactivity of carbon nanotubes can be improved by functionalizing the sidewalls with functional groups. Sidewall of nanotubes can be modified with carboxylic functional group for base molecules, amine group for acidic molecules and aromatic group (thiol) for large organic molecules. Base molecule produces smaller defects while aromatic group creates higher defects for gas molecules adsorption. Subsequently defects sites in nanotubes sidewall significantly increase the molecule adsorption [15]. Sidewall defects for grafting of functional groups can be created by employing either wet chemistry or plasma techniques [16]. The chemical treatment causes hole doping in CNTs and introduces defects on the nanotube surface leading to produce impurity states at the Fermi level [17]. Consequently, reactive gases in the surrounding environment bond to the nanotubes, the adsorbed molecules may act as dopants, shifting the Fermi level of the nanotube, or may change the band structure of the nanotube due to the local orbital hybridizations for bond formation, possibly influencing the electronic properties in nanotubes network. Thus CNTs based gas sensing employs the change in electrical resistance due to adsorption of reactive gases as the output signal. The sensor response is the characteristics to the p-type conductivity in CNTs and charge transfer is found to be the sensing mechanism at room temperature.

Since adsorbed molecules may act as dopants and shifts the Fermi energy of the nanotube [18]. So the interaction of gas molecules with carbon nanotubes either chemisorb or physisorb at the CNT sidewalls leading to change the transport properties of nanotubes. As sp^2 hybridized carbon network is very stable so bond breaking is rare and only local sp^3 hybridization is possible onto sidewalls. These local sp^3 hybridized sites are enhanced by curvature in smaller diameter nanotubes and contributes to greater molecular adsorption [19].

Depending upon the nanotubes and type of interacted gas molecules, the CNTs conductance can be increased or decreased by either transferring of electrons to or withdrawing from nanotubes thus giving

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http://dx.doi.org/10.1016/j.diamond.2015.10.010
0925-9635/

nanotubes more charge carriers or holes. The interaction between functionalized CNTs and gas molecule can be denoted as:

$$Fun.CNT + Gas.Mol \rightarrow CNT^{\Delta e}\ Gas.Mol^{\Delta h} \text{ or } CNT^{\Delta h}\ Gas.Mol^{\Delta e.}$$

Where, "Δ" is a number indicating the amount of charge transferred (electrons or holes) during the interactions between nanotubes and reactive gas molecule.

Thus sensing mechanism can be attributed to charge transfer or electronic interactions between CNTs and adsorbed molecules. Therefore molecular adsorption on CNTs has great impact on transport properties. In Fig. 1(a) it is shown that with the interaction of reducing gas with functionalized nanotubes leads to withdrawing of electrons from CNT. This increased the hole carriers in semiconducting CNTs and results in Fermi level shifting down or closer to valance band. Furthermore, interaction of oxidizing gas with adsorption sites on CNTs leads to donating of electrons to semiconducting CNT. This increased the electron carriers in CNTs and leads the Fermi level shifts up closer to conduction band of CNT (Fig. 1(b)). Solid lines in Fig. 1 shows the Fermi level positions before the adsorption of gas molecules on CNT surface whereas dashed lines shows the Fermi level positions after the adsorption of gas molecules on CNT surface.

Up till now, much work has been done on CNTs based gas sensor. To improve the sensitivity and selectivity, CNTs either single walled or multiwalled were successively used for the detection of gases such as O_2, NO_2, CO, NH_3, H_2, Br_2, I_2, CH_4, by using CNT-FET, functionalized or by decorating nanoparticles [20–27]. Still there is need to improve the performance of device. Ki-Young Dong et al. reported the fast response and recovery time of 10 ppm of CO gas at 150 °C using carboxylic acid single walled carbon nanotubes [28]. Yang Zhang et al. reported the 100 ppm CO gas detection using SnO_2 nanoparticles on single walled carbon nanotubes. The sensitivity of the device was 0.27 and response time was 2 s at room temperature [29].

The detection of CH_4 with CNT based sensors has not been fabricated as much as CO, H_2 and NH_3, but a few research has been made. For example, Lu et al. reported the fabrication of CH_4 sensor based on Pd-decorated single walled nanotubes network having detection limit of 6–100 ppm and Enid Contes-de Jesus et al., reported the Pt nanoparticles decorated SWCNTs showed 1.7% relative resistance response for methane detection up to 250 ppm at room temperature [30,31]. Further research is required to explore the interactions between gas and chemically treated CNTs and to enhance the sensitivity, reproducibility and repeatability of device at room temperature.

In this paper, we have studied the CO and CH_4 gas sensors based on variety of carboxyl and thiol functionalized MWCNTs buckypapers at room temperature. The buckypapers were fabricated by varying chemical cross-linker reagent in CNTs. Change in resistance of functionalized CNTs buckypapers under these gases is investigated. The comparison in gas sensor response for CO and CH_4 is studied. Moreover, the response time is also calculated.

2. Experimental

2.1. Chemicals

2-mercaptoethanol ($HSCH_2CH_2OH$) 99% pure "4,4′ diaminobenzophenone" ($C_{13}H_{12}N_2O$), nitric acid (HNO_3), hydrogen per oxide (H_2O_2), dimethylformamide (DMF) 99% pure, and all organic solvents were purchased from Sigma Aldrich and were used as received without further purification.

2.2. Fabrication and sensor setup

The acidic treatment requires a long processing time and extensive ultrasonic treatment for direct attachment of functional moieties to the sidewalls of MWCNTs. Consequently, sidewalls of MWCNTs were carboxyl functionalized (CNT-COOH) using 5 M HNO_3 and 35% H_2O_2 for 5 h at 100 °C and thiol functionalized (CNT-SH) using 2-mercaptoethanol after sonication for 3 h at room temperature. Cross-linker reagent "4,4′ diaminobenzophenone" (DABP) was used to connect the sidewalls or tube-end to body of functionalized nanotubes for buckypaper formation. The buckypapers were designated as CNT-CBPs for carboxylated and CNT-TBPs for thiolated nanotubes respectively. Three types of buckypaper were formed by changing the CNTs to cross-linker ratio as 1:5, 1:7, and 1:9 by weight.

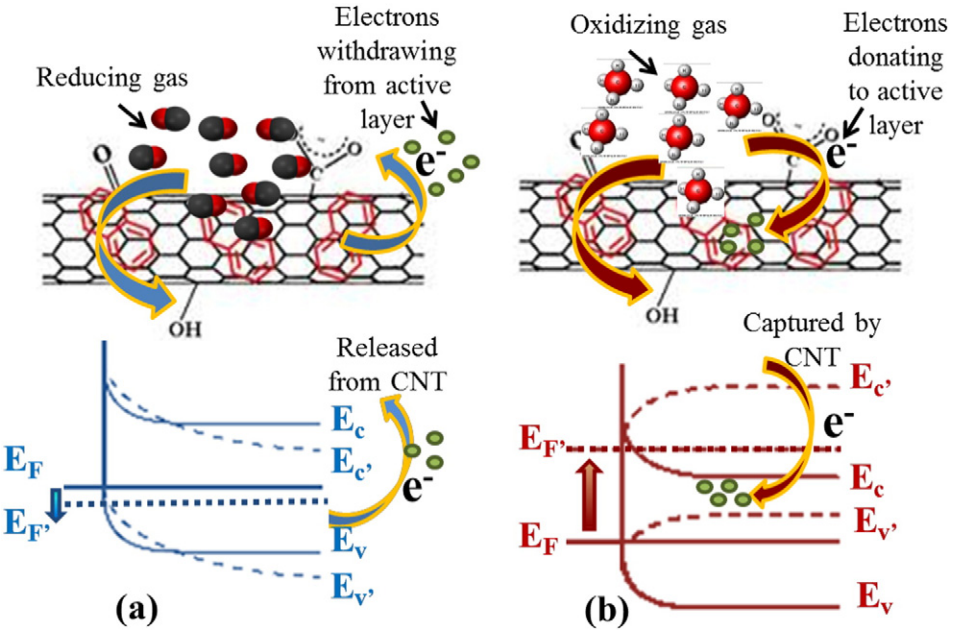

Fig. 1. Schematic of mechanisms comes across in CNT chemical sensors. (a,b) Band diagrams and corresponding interaction of gas molecules with CNT, solid lines in band diagrams show before adsorption of molecules and dashed lines show after adsorption of molecules.