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Highly dispersed platinum sputtered multiwall carbon nanotubes based hydrogen gas sensor at room temperature

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ABSTRACT

We present here, a simple approach for the detection of 0.05% concentration of hydrogen (H_2) gas at room temperature conditions using pristine and functionalized multiwall carbon nanotubes (MWCNTs). To enhance the sensitivity of the MWCNTs, platinum (Pt) nanoparticles have been sputtered on the surface of the nanotubes which helps in dissociation H_2 molecules to H atoms. The structural and morphological studies of Pt deposited nanotubes were investigated by X-ray diffraction (XRD) spectra and scanning electron microscopy (SEM). The concentration of the deposited Pt nanoparticles on the nanotubes was determined by energy dispersion spectroscopy (EDS). Also, in the present study, Sievert's law is found to be applicable for the H_2 gas concentrations (0.05–1%) at room temperature condition. In addition, the influence of bombardment of energetic particles on the surface of nanotubes and its role in the uniform deposition of Pt nanoparticles on the surface of tubes were also discussed.

1. Introduction

The interaction of carbon nanotubes (CNTs) with the environmental gases has been attracting the attention of many worldwide researchers in the last decade [1–3]. Among all gases, hydrogen (H_2) is odorless, colorless, toxic and tasteless gas and cannot be detected by human senses [4]. Also, H_2 gas contains explosive properties therefore, it is necessary to detect this gas for petroleum industry to automotive applications. Moreover, to generate the H_2 energy revolution, it is essential to make sure the secure utilization of H_2 sources. In almost every area, sensors are widely used to detect the low concentration of H_2 gas [5].

The research on CNTs and gas sensing applications attracted a great deal of attention because of their physical, electrical and mechanical properties [6]. Their large surface to volume ratio, hollow geometry and size also make them probable contender for use as vigorous sensing material in gas sensor [7,8]. In addition, the electrical properties of CNTs are modified upon exposure to different gases such as NO_2, H_2S, CO, NH_3 and H_2 [9]. This change is due to the adsorption/desorption of gas molecules, which alter the charge carrier (hole or electron) concentrations in the nanotubes. This phenomenon inspires the necessary condition for the application of CNTs to chemiresistive gas sensors [10,11]. The pristine CNTs based gas sensor has many limitations such as shortage of specificity to diverse gases and low sensitivity towards analyte that contain no affinity to CNTs. This limitation can be resolved with acid treatment, nanoparticles (metal/metal oxide) and polymer composites. These processes will change the electrical behavior of CNTs, which improves the selectivity and response to different gases [12]. In addition, metal decorated CNTs show well physico-chemical properties, like large reactivity with gas molecules, excellent charge transfer ability and superb adsorption/desorption capacity [13–15]. Moreover, these nanoparticles give a continuous pathway for moving carriers, between the tubes, where sensitivity is enhanced by the existence of both the nanoparticles surface and the charge transfers between the nanotubes and nanoparticles induced by gas adsorption/desorption [16,17]. However, agglomeration of these attached nanoparticles on the tubes surface produce poor sensitivity of the gas sensors. Also, it is well known, H_2 diffuses more rapidly in the metals as compared the other solute [18]. For instance, Kaniyoor et al. [17] have reported hybrid carbon nanostructures consisting of Pt coated graphene nanoplatelets dispersed on MWCNTs for the detection of 5% H_2 gas in air. They found that, nafion solubilized hybrid structures show good response with large recovery and response time. Kumar et al. [19] have reported the Pt based chemiresistive sensor for the detection of 4% H_2 gas in air atmosphere at room temperature. They found that Pt functionalized MWCNTs are good H_2 sensor but it possesses response and recovery time of the order of minutes [19]. On the other hand, Tromico et al. [20] fabricated the Pt/TiO_2/MWCNTs hybrid H_2 gas sensor above room temperature (50–200 °C). They showed that catalytic action

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of Pt metal is responsible for the H_2 adsorption. Most recently, Randeniya et al. [21] have reported the detection of 20 ppm to 2% H_2 gas in the nitrogen atmosphere using MWCNTs yarns. They deposited the layers of Pd and Pt on the yarns to enhance the sensitivity for H_2 gas. However, in present work we have reported the detection of low concentration (0.05–1%) of H_2 gas with less recovery time and complete resistance recovery in N_2 atmosphere as compared to other reported sensors [17–21].

The objective of the present work is to synthesize the nanostructures using sputtering technique showing enhanced structural, electrical and sensing properties of nanotubes without significantly damaging their structure. The fabricated gas sensors show excellent resistance recovery, low recovery time, good repeatability, baseline stability in N_2 atmosphere and verification of Sievert's law for the detection of H_2 (0.05–1% by volume) gas at room temperature. Here, we have used only $100 \times 120\ \mu m^2$ area of fabricated interdigitated electrodes (IDEs) to measure the electrical and sensing response. The Pt deposited nanotubes exhibit better sensitivity and good electrical response as compared to our previous work [22], in which we have investigated H_2 gas sensor of pristine and functionalized nanotubes at the room temperature conditions.

2. Experimental

2.1. Sample preparation

The pristine MWCNTs (P-MWCNTs) were purchased from Global Nanotech, (Mumbai, India) with a purity level >95%. These tubes were synthesized by chemical vapor deposition (CVD) method. Here, to improve the sensitivity of the H_2 gas sensor functionalized MWCNTs (F-MWCNTs) were used. The details of functionalization process were reported in our previous work [22].

2.2. Samples characterization techniques

The XRD spectra of prepared thin film samples were recorded on PANalytical X'Pert Pro diffractometer, utilizing Cu Kα- X-ray with the wavelength 1.54 Å. The morphology of the samples was analyzed by scanning electron microscope (SEM) using Raith 150 Two. The energy dispersion spectroscopy (EDS) of samples was recorded using FE-SEM (Model: JSM-7600F). Current–voltage (I–V) characteristics of the all samples were obtained using a Keithley 4200 source meter using the two-probe configuration.

2.3. Sensor fabrication and metal deposition

To fabricate IDEs with finger width 10 μm, finger length 100 μm and a gap between the two fingers being 5 μm, a mask was designed in Kelvin software. A thin layer (120 nm) of SiO_2 was grown on p-type Si wafer by dry oxidation. Then, by photolithography technique (double side aligner-EVG 620), a designed mask prepared via laser writer (LW405) was transferred on the oxidized Si wafer. By using thermal evaporator, a thin layer of chromium-gold (Cr = 20 nm, Au = 80 nm) was deposited on developed IDEs. Afterwards, the wet etching technique was used to remove unwanted Cr–Au layer to get the desired IDEs. The fabricated IDEs was used for the electrical and sensing measurements. A network of the P-MWCNTs and F-MWCNTs was drop casted on the fabricated IDEs. The thin film of Pt was sputtered on these networks via metal sputtering system (Nordiko). An ultra high vacuum with base pressure 1.3×10^{-5} bar was maintained in the chamber for metal sputtering. After that, deposition was done in the argon atmosphere at pressure 2.7×10^{-3} bar with the power of 20 W. Finally, both the prepared samples were annealed in argon atmosphere at 550 °C using rapid thermal processing (RTP) system. The rate of rising temperature was kept as 70 °C/s and average cooling rate as 16.2 °C/s. These Pt deposited P-MWCNTs and F-MWCNTs were notated as P-MWCNTs/Pt and F-MWCNTs/Pt. All aforesaid steps are shown in Fig. 1.

2.4. Experimental set up of sensing

Sensor testing was done with customized system (Fig. 2), composed of Teflon test chamber. In this process, N_2 (nitrogen 99.9% and 0.1% oxygen) gas was used as carrier gas. The sensor response was recorded using Keithley 2000 multimeter with GPIB computer interface. Mass flow controllers (MFCs) were attached to the inlets to the chamber (Fig. 2) to control the flow rates of N_2 and H_2 gases. The sensitivity of the sensor was calculated according to formula:

$$Sensitivity(\%) = 100\left[\frac{(R_H - R_N)}{R_N}\right]\%$$

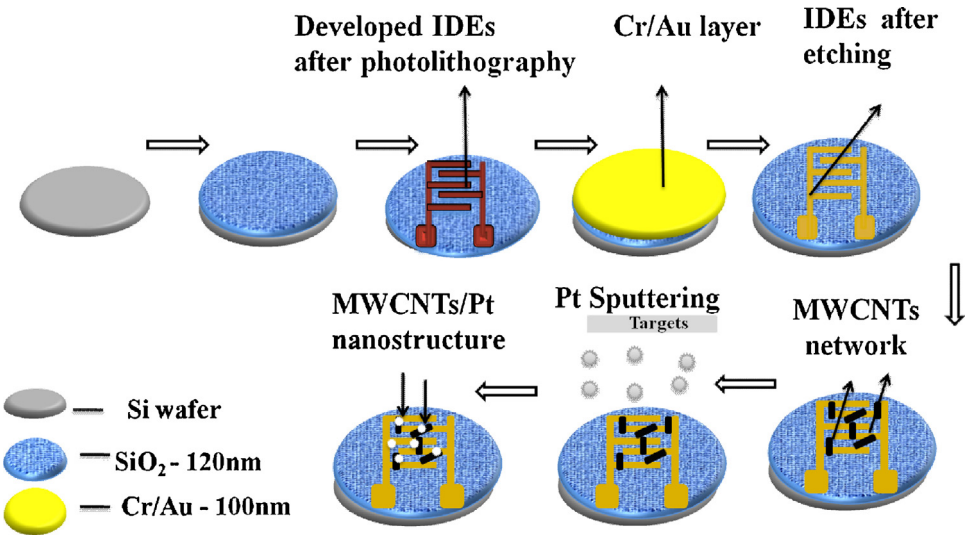

Fig. 1. Schematic diagram of Pt deposited sensor.