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Study of humidity sensors based on nanostructured carbon films produced by physical vapor deposition

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ABSTRACT

In this study, carbon nanosheets and nanohoneycombs were synthesized on Si (1 0 0) substrates using a hot filament physical vapor deposition technique under methane ambient and vacuum, respectively. The four-point Au electrodes are then sputtered on the surface of the nanostructured carbon (n-C) films to form prototypical humidity sensors.

The sensing properties of prototypical sensors at different temperature, humidity, direct current (DC), and alternative current (AC) voltage were characterized. Linear sensing response of sensors to relative humidity ranging from 11% to 95% is observed at room temperature. Experimental data indicate that the carbon nanosheets based sensors exhibit an excellent reversible behavior and long-term stability. It also has higher response than that of the humidity sensor with carbon nanohoneycombs materials.

1. Introduction

Humidity sensors are widely used in industry and agriculture such as air conditioning systems, food quality monitoring, meteorology and medical equipment. Commercial sensors are mostly based on metal oxides [1,2], porous silicon [3–6] and polymers [7,8]. In these materials the adsorption of water vapor drastically changes the electrical properties, such as resistivity and capacity, of the device. Recently, carbon films have attracted great attention for their potential applications in the humidity sensors because of their large sensing area and high chemical inertness [9–11].

Various structures of electrodes have been proposed for the sensor systems. Traditionally, the humidity signals obtained using a sensor with two-electrode techniques are affected by polarization effect. This is because of the migration of some electrons from the metal probe into the conductive samples. As a result, positive charges in the samples migrate towards the metallic probe, creating a cation layer between the metallic probe and the samples. For nanostructured carbon (n-C) based humidity sensor, the polarization effect frequently occurs under direct current (DC) circuit due to the existence of physisorption of water when relative humidity (RH) is high enough [12,13]. Polarization effect could be caused by the migration of the H^+ ions into the metallic probe because H^+ ions appear in the physisorbed absorbed water [14–16]. To avoid or reduce this effect, four-point probes are commonly used [17,18]. The voltage is measured on the inner electrodes without polarization effects because no current flows in the measuring circuit.

In this work we have demonstrated simple, fast response, and high sensitive resistive-type n-C based humidity sensors. The films are produced by a hot filament physical vapor deposition (HFPVD) method on Si (1 0 0) substrates with a SiO_2 buffer layer. The newly designed humidity sensors consist of n-C sensing elements combined with four-point electrodes. The sensing properties are characterized, and humidity sensing mechanism is discussed. What's more, comparisons of sensing properties of the sensors in the DC and alternative current (AC) circuits are also presented.

2. Experiment details

2.1. Preparations and characterization of the carbon nanomaterials

n-C films were synthesized on Si (1 0 0) substrates with an area of 10 mm × 10 mm using a HFPVD technique in methane ambient (57.5 Pa) and vacuum, respectively. The easily-get graphite stick (0.7 mm diameter, 15 mm length) was used as a precursor to provide carbon source and filament, to replace the tungsten filament in the system described elsewhere in our previous publications [19,20]. No catalyst was used. After placing Si substrates, the chamber was pumped down to 2.67×10^{-3} Pa, following feeding Ar gas up to ambient pressure, it was then pumped down to 2.67×10^{-3} Pa again. Repeated this process 3 times to keep oxygen

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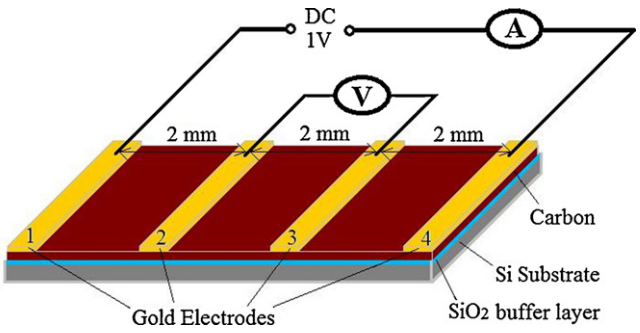

Fig. 1. Schematic illustration of four-point electrodes measurement of resistance between electrodes 2 and 3.

out and obtain a good vacuum. A DC power supply HY3020E with an electric current of 18 A was used to heat the graphite stick to a temperature up to 2000 °C to promote gas phase activation. The substrates were placed on a holder under the hot graphite stick. No an extra heater was used to heat the substrates. The deposition duration for each sample was 30 min.

The morphologies and chemical contents of n-C were characterized by Field Emission Scanning Electron Microscope (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDS). Micro Raman scattering was performed using a Jobin-Yvon T64000 Triple-mate system with the radiation of 514.5 nm from a coherent argon ion laser and a liquid nitrogen cooled charge coupled device was used to collect and process the scattered data.

2.2. Preparation of sensor electrodes

After deposition of the n-C sensing materials, a four-point configuration of Au electrodes marked as 1–4 were sputtered onto the surface of as-deposited n-C sensing materials using properly desired mask. Each electrode was controlled in the thickness of 30 nm, width of 1 mm, length of 1 cm that is separated (center-to-center) by 2 mm. The illustration of the sensor is schematically shown in Fig. 1. Current is supplied via the outer electrodes 1 and 4. The voltage is measured across the inner electrodes 2 and 3. The contact for the Au electrodes with silver wires was made by silver paste.

2.3. Measurement of sensing properties

Fig. 2 depicts a schematic diagram of the facility aiming at the charactering resistive-type humidity sensors. It consists of a stainless steel chamber with a volume of 1 L, pipelines and valves to transfer and control gases RH inside the test chamber, a dryer device to dry the sensors, an electrical circuit (marked as A) connected a DC (or AC) power supply with outer electrodes to offer current and a meter to measure the current flows in the circuit, and another electrical circuit (marked as B) to measure the voltage drop. The desired level of humidity was regulated by mixing different percentages of humid air and dry air, and the humidity was measured by a standard hydrothermal meter. The humidity response of the sensors was probed by monitoring the variation of the resistance of the sensors (the part between electrodes 2 and 3) in different RH environments, which was estimated based on the measurement of the electrical signals of the two testing circuits, according to the Ohm's law: $R = V/I$, where the R, V and I are the resistance, voltage drop and the current flow of the n-C based sensors, respectively. Unless otherwise stated, the whole system was maintained at room temperature around 25 °C during measurements with a homogeneous pressure distribution inside the chamber.

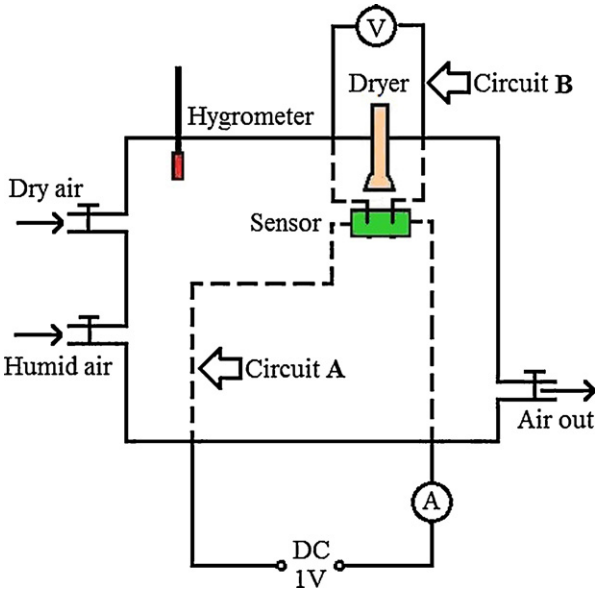

Fig. 2. A schematic diagram of device assembly.

3. Results and discussions

3.1. Characterizations of the carbon nanostructure

Fig. 3 shows the FESEM images of n-C films grown under methane (57.5 Pa) and in vacuum, respectively. The presence of nanoparticles on the surfaces of carbon nanosheets can be observed in the sample grown under methane, as shown in Fig. 3(a). The average size of the particles is about 80 nm. These nanoparticles can be regarded as the sites that enhance the adsorption of water vapor molecules. For the sample grown in vacuum, vertically and well-organized nanohoneycomb structures are obtained. The thickness of the two samples is 550 and 210 nm, respectively.

Table 1 lists the EDS data of the obtained n-C films. Besides the C element and Si (from substrate and SiO_2 buffer layer), O elements (from SiO_2 buffer layer and adsorbed by sample surface), a small quantity of Sn and Fe are also emerged. This may be due to the contamination of chamber or impurity of carbon source. The existence of the metallic elements Sn and Fe makes the synthesized samples to be p-type semiconductors, which is in accordance with previous reports [21,22].

Fig. 4 shows the Raman spectra of the carbon nanosheets and nanohoneycombs, respectively. Characteristic graphite peaks are identified in the Raman spectra between 1000 and 2800 cm^{-1}. The one at around 1350 cm^{-1}, which is called D peak, has been attributed to dislocation defects in the graphite [23]. It is associated with disorder-allowed zone edge modes of graphite that became Raman active due to the lack of long-range order in amorphous carbon based materials [24]. The G peak at around 1596 cm^{-1}

Table 1
EDS data of the two samples.

Element	Nanosheets (atomic%)	Nanohoneycombs (atomic%)
C K	53.08	38.09
O K	7.94	9.25
Si K	38.73	52.46
Fe K	0.09	0.07
Sn L	0.16	0.13