FORM 2

THE PATENTS ACT, 1970

(39 of 1970)

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COMPLETE SPECIFICATION

(See Section 10 and Rule 13)

Very sensitive humidity sensor based on conducting polymer nano-composite

Amity University Uttar Pradesh, Sector-125, NOIDA, India

ABSTRACT

Very sensitive humidity sensor based on conducting polymer nano-composite

The present invention provides a humidity sensor device and a method of manufacturing the same are provided. The humidity sensor includes a substrate having a film of polymer nano-composite. The nano-composite film consists of activated carbon nanotube/ conducting polymer in ratio of 0.94 - 15mg/ml. A pair of electrodes is used to take the connections from both the sensing materials. The resistance of nano-composite element follows the reverse trend in comparison to pure conducting polymer film with increasing humidity. The chemically activated single walled carbon nanotubes and polymer nano-composite films can increase the sensitivity of the humidity sensor. High sensitivity of the polymer nanocomposite is achieved for activated SWCNT of 3.75 mg/polymer solution.

Dr. B. L. Arya
Registrar
AMITY UNIVERSITY
UTTAR PRADESH

CLAIMS:

1. An highly sensitive humidity sensor to detect moisture at low level comprises of a combination of a conducting polymer and chemically activated single walled carbon tubes based nano-composite that can improve the sensitivity in wide humidity range (20%-80%) .

2. The humidity sensor as claimed in claim 1, wherein the sensor consists of a thin film of conducting polymer poly (3, 4-ethylene dioxythiophene)-poly (styrene sulphonate) (PEDOT: PSS) and single walled carbon nanotubes (SWCNT) nanocomposite on glass substrate.

3. The humidity sensor as claimed in claim 1, wherein the nano-composite film consists of chemically activated carbon nanotube (0.94 to 15 mg/ml) and conducting polymer PEDOT:PSS.

4. The humidity sensor as claimed in claim 1, wherein the best sensitivity of humidity sensor is obtained with CT-CNT concentration of 3.75 mg/ml in the polymer nanocomposite.

5. The humidity sensor as claimed in claim 1, wherein the resistance of the chemically treated SWCNT (CT-CNT) decreases with the increase in CT-CNT from 0.94 to 15 mg/ml in the polymer nanocomposite.

6. A method to prepare the highly sensitive humidity sensor of claim 1, comprising the steps of:

a. dispersing low conducting grade polymer in water and single walled carbon nanotubes (SWCNT) used is purchased from Aldrich Co. USA.

b. functionalizing the SWCNTs chemically using acid treatment carried out by adding acid mixture of sulphuric acid and nitric acid in volume ratio of 3:1 and stirred for 2 hours on 110 ^{o}C on hot plate,

d. diluting the mixture to 400 ml and the SWNTs are collected by membrane filtration and washed by deionised water to remove the residual acids.

e. chemically treated different concentrations of SWCNTs (0.94 to 15 mg/ml) each individually mixed in 1ml of polymer PEDOT:PSS.

f. dispersing again the SWCNT in the polymer solution by stirring for 2 hours and coated on 1 inch X 1 inch glass substrates by drop casting technique;

g. dry the coated films in vacuum oven at 150 °C for one hour.

7. The method to prepare the highly sensitive humidity sensor as claimed in claim 1, wherein to functionalize the CNTs the acid treatment is carried out by adding 80 ml of acid mixture of sulphuric acid (98wt %) and nitric acid (69wt %) in volume ratio of 3:1 and stirred for 2 hours at 110 °C on a hot plate.

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Dr. B. L. Arya
Registrar
AMITY UNIVERSITY
UTTAR PRADESH

FIELD OF INVENTION:

The present invention in general relates to humidity sensor. More particularly it relates to nanocomposite based humidity sensor which is excellent in moisture-sensitiveness and workability and can be manufactured with ease and at a low cost.

DESCRIPTION OF THE RELATED ART:

Humidity relates to the amount of water vapor that exists in the air. One measure of humidity is relative humidity which is the amount of water vapor in a sample of air as compared to the maximum amount of water vapor the air can hold at any specific temperature. Relative humidity may be defined as the ratio of the partial pressure of water vapor in a gaseous mixture of air and water vapor to the saturated vapor pressure of water at a given temperature.

The highly sensitive humidity sensor is based on carbon nanotube and poly(dimethyldiallylammonium chloride) composite films reported by Litao Liu et al *(IEEE Sensors Journal, 9, No. 10, 1308, 2009).* The composite film is deposited between inter-digitated electrodes on a Si/SiO2 substrate through layer-by-layer self-assembly technique. The resistance stability of the composite film is effectively improved through thermal annealing and I-V characteristic of the film exhibits a very good linear behavior. The resistance increases exponentially with relative humidity from 20% to 98%, and a much higher sensitivity in comparison with pure carbon nanotube networks is achieved. With temperature increased, the water vapor density versus RH shifts upwards, while the resistance is reduced downwards. The resistance is dependent on temperatures with a negative coefficient. The composite films with multi-walled carbon nanotubes show an adjacent sensitivity as compared to the single-walled carbon nanotube composite films. The experimental results show that the humidity sensors have a fast response and a short recovery time, and their response is reversible. A simple model is proposed to explain the change of composite film resistance with humidity. The carbon nanotubes junctions may play a more important role in the overall resistance change for water molecule absorption.(*Litao Liu, Dept. of Precision Instrum. & Mechanology, Tsinghua Univ., Beijing, China,2009)*

Patent No. CN101078705 relates to a resistance film humidity sensor with the combination of polymer and graft carbon black and the fabricating method. Glass

ceramic is used as the substrate and on it there are multiple pairs of inter-digital golden electrodes. Combination humidity film obtained by graft carbon black of poly 4-vinypyridine with cross-linking quaternary amination is coated on surfaces of glass ceramic and inter-digital golden electrodes. The invention is provided with a simple preparing process and is of low cost. It is suitable for mass production.

Patent No. JP2011080833 relates to a humidity detection sensor with superior temperature characteristics, even having a protective layer. The humidity detection sensor includes a substrate, a sensor provided on the substrate, sandwiching a humidity-sensitive polymer film of which dielectric constant changes with humidity by a pair of electrodes, and having a humidity-sensitive area where the humidity-sensitive polymer film is partially exposed to the outside; and a protective layer formed on at least the exposed electrode of the pair of electrodes.

Patent No. CN101545883 (A) relates to a nuclear shell structure micro-nano material humidity sensor and a preparation method thereof. The preparation method comprises preparation of a metallic nano particle solution and a polymer solution, surface treatment of the silicon chip, and coating and encapsulation. The selectivity on materials which are sensitive to the target quantity of the sensor is wide, and raw materials are easy to obtain. Compared with the prior art, the invention has the advantages of a simple method, convenient operation, low production cost, pollution-free environment, great improvement of the electrical properties of the sensor, high integrity and small volume

Patent No. US2010/0134948 relates to a humidity sensor and a fabricating method thereof. The humidity sensor includes a substrate, an anodic aluminum oxide layer formed on the substrate and having a plurality of holes, and electrodes formed on the anodic aluminum oxide layer in order to improve sensitivity and accuracy of the humidity sensor. Further, the fabricating method of a humidity sensor includes preparing an aluminum substrate, forming an anodic aluminum oxide layer by oxidizing the aluminum substrate and forming electrodes on the anodic aluminum oxide layer.

Patent No. US 6806722 relates to a polymer-type humidity sensor for use in a microwave oven and which has a polymer structure which includes a rubber and a predetermined amount of carbon and a pair of electric terminals connected to the polymer structure. The polymer-type humidity sensor of this invention has a rapid response time, durability, excellent adherence to terminals, low hysteresis, and exhibits stability to exposures of high temperatures and high relative humidity.

The paper entitled "Carbon-film-based humidity sensor containing sodium or potassium Recovery effect" by Jerzy P. Lukaszewicz et al. talks about the recovery effect of some modified carbon films applied as a humidity-sensitive resistor. The carbon films were prepared using mixtures of furfuryl alcohol and NaOH (or KOH) solution. The films have been tested as humidity-sensitive resistors. The process of humidity sensitivity development (caused by oxidation of carbon surface) is reversible, i.e., the sensitivity disappears upon HCl and/or heat treatment but recovers after a sufficiently long storage in air. (*P. Lukaszewicz, Sensors and Actuators B: Chemical , Volume 60, Issues 2–3, Pages 184–190,1999)*

A humidity sensor typically contains a moisture sensitivity film such as; (1) moisture-liable film containing a conducting material, (2) moisture absorbing film containing electrolyte or (3) polymer electrolyte film.

Major disadvantages in the known humidity sensors is that humidity measuring range is narrow, while second type of films is not suitable for long term use at high humidity environment because the electrolyte contained therein can be diluted and lost due to excessive moisture adsorption. The third types of the films have the problem of being damaged at high temperature and so the humidity detection may be influenced.

Hence the present invention provides efficient, durable and a sensitive humidity sensor based on a combination of a conducting polymer nano-composite as humidity sensing film that can detect moisture in the range 20% to 80% relative humidity.

OBJECTS OF THE INVENTION:

The principal objective of the present invention is to provide a humidity sensor element which comprises a substrate using a conducting polymer nano-composite as humidity sensing film with high sensitivity in wide humidity range (20% - 80%).

Another object of the present invention is to provide the humidity sensor which combines the effect of both polymer and single walled carbon nanotubes which can increase the sensitivity of the humidity sensor.

Another object of the present invention is to provide a nanocomposite based humidity sensor that has rapid response time, is cost effective and is highly sensitive and more durable.

Another object of the present invention is to provide a method and system for making an inexpensive nanocomposite based humidity sensor for the detection and quantification of moisture at low level.

Still another object of the present invention is to provide a humidity sensor that has long-term storage stability.

SUMMARY OF THE INVENTION:

The present invention provides a humidity sensor element, device and a method for manufacturing thereof. The humidity sensor includes a substrate having a film of a polymer nano-composite. The said polymer film is conducting p or n-type and its nano-composite film consisting of chemically activated carbon nanotube/ conducting polymer.

In a preferred embodiment of the present invention, the sensor consists of a thin film of polymer nanocomposite of conducting polymer poly (3, 4-ethylene dioxythiophene)-pol (styrene sulphonate) (PEDOT:PSS) and chemically activated single walled carbon nanotubes (SWCNT).

In another embodiment of the present invention, a pair of electrodes is used to take the connections from the sensing nanocomposite top layer.

In still another embodiment of the present invention, the resistance of nano-composite element follows the reverse trend in comparison to pure conducting polymer film with increasing humidity.

In yet another embodiment of the present invention, the combining effect of both polymer and chemically activated single walled carbon nanotubes can increase the sensitivity of the humidity sensor.

In still another embodiment of the present invention, polymer nanocomposite film is highly sensitive in detecting infinitesimal amount of moisture.

It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered for limiting of its scope, for the invention may admit to other equally effective embodiments.

Fig. 1 illustrates the schematic diagram of humidity sensor.

Fig. 2 illustrates the humidity response of Prestine PEDOT: PSS.

Fig. 3 illustrate the humidity response of PEDOT: PSS + CT-CNT 0.94 mg /ml nanocomposite.

Fig. 4 illustrate the humidity response of PEDOT:PSS + CT-CNT 1.87 mg/ml nanocomposite.

Fig. 5 illustrate the humidity response of PEDOT:PSS + CT-CNT 3.75 mg/ml nanocomposite

Fig. 6 illustrates the humidity response of PEDOT: PSS + CT-CNT 7.5 mg/ml nanocomposite.

Fig. 7 illustrates the humidity response of PEDOT: PSS + CT-CNT 15 mg/ml nanocomposite.

Fig. 8 illustrate the sensitivity of polymer nanocomposite films with different concentrations of CT-CNT (0.94, 1.87, 3.75, 7.5 and 15 mg/ml)

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

Accordingly, the present invention relates to a humidity sensor element, device and a method for manufacturing thereof. The humidity sensor includes a substrate

having a polymer nano-composite. The said polymer film is conducting p or n-type and its nano-composite film consisting of activated carbon nanotube/ conducting polymer. A pair of electrodes is used to take the connections from both the sensing materials. The resistance of nano-composite element follows the reverse trend in comparison to pure conducting polymer film with increasing humidity. The combining effect of both polymer and chemically activated films can increase the sensitivity of the humidity sensor. The polymer nanocomposite film is highly sensitive in detecting infinitesimal amount of moisture.

Research based on conducting polymers has gained much attention in the last decade due to the potential advantage of low cost, light weight and vacuum free fabrication for various ultra thin and flexible optoelectronic devices, photovoltaic applications and sensors [*R. H. Friend, Pure Appl. Chem., 73, (3) 425 (2001); D. T. McQuade, A.E. Pullen, and T.M. Swager, Chem. Rev., 100, 2537 (2000); K. M. Coakley and M. D. McGehee, Chem. Mater., 16 (23), 4533 (2004)]*. Among them poly (3, 4-ethylene dioxythiophene)-poly (styrene sulphonate) (PEDOT:PSS) is the most commonly used conducting polymer. The polymer PEDOT:PSS which is environmentally stable exhibits good conductivity and fairly high degree of visible light transmittance. The conjugated polymer poly (3,4-ethylenedioxythiophene) (PEDOT) has a low band gap, high charge mobility and good thermal stability. PEDOT was initially found to be an insoluble polymer but when doped with a water dispersible polyelectrolyte poly(4-styrenesulphonate (PSS) during polymerization, the polymeric blend PEDOT:PSS exhibits good film forming properties.

Our sensor consists of a thin film of conducting polymer poly (3, 4-ethylene dioxythiophene)-poly (styrene sulphonate) (PEDOT: PSS) and chemically activated single walled carbon nanotubes (SWCNT) nanocomposite. The polymer used is of low conductivity grade and the resistance of the conducting polymer decreases with humidity. They have found that on increasing the concentration of SWCNT in the polymer nanocomposite the resistance decreases which can easily be measured using a simple multimeter. Very small changes in humidity can easily be detected with the corresponding change in resistance of the polymer and chemically activated SWCNT nanocomposite.

The invention is described in detail with reference to the examples given below. The examples are provided just to illustrate the invention and therefore, should not be construed to limit the scope of the invention.

Example 1:

The low conducting grade polymer poly (3, 4-ethylene dioxythiophene)-poly (styrene sulphonate) (PEDOT: PSS) dispersed in water and single walled carbon nanotubes (SWCNT) used were purchased from Aldrich Co. USA. SWCNTs were chemically functionalized so as to open the COOH bonds. To functionalize CNTs acid treatment was carried out by adding 80 ml of acid mixture of sulphuric acid (98wt %) and nitric acid (69wt %) in volume ratio of 3:1 and stirred for 2 hours on 110 ^{o}C on hot plate. The mixture was then diluted to 400 ml and the SWNTs were collected by membrane filtration and washed by deionised water to remove the residual acids. Different concentrations of chemically treated SWCNTs (0.45 to 15 % by weight) were each individually mixed in 1ml of polymer PEDOT:PSS. SWCNT were dispersed in the polymer solution by stirring for 2 hours and coated on 1 inch X 1 inch glass substrates by drop casting technique on previously cleaned glass substrates (Fig.1).

The coated films were then dried in a vacuum oven at 150 ^{o}C for one hour. The thickness of the film was in the range of 100 – 140 nm. Two point contacts of silver were made on the top surface for electrodes from which electrical wires are taken out for resistance measurements. The separation between the electrode contacts is 6mm. An indigenously developed humidity controlled chamber was used for studying the humidity response of the sensor. Electrical measurements were carried out using Kiethley electrometer (model no. 6514).

Example 2:

Fig. 2 shows the humidity response of pristine polymer film. Resistance was in the M ohms range at low relative humidity and was found to decrease with increase in humidity. The humidity response of chemically treated SWCNT polymer nanocomposites is shown in Fig. 3 to Fig. 7 for various concentrations of SWCNTs. It can be seen that the resistance of the chemically treated SWCNT (CT-CNT) polymer nanocomposite decreases with the increase in CT-CNT

concentration from 0.94 to 15 mg/ml in the polymer nanocomposite. Fig. 3 to Fig. 7 show the nanocomposite response to humidity at 0.94, 1.87, 3.75, 7.5 and 15 mg CT-CNT/ml in the polymer nanocomposite respectively. From figures 3 to 7 it can be seen that the resistance increases with humidity for various concentrations of the CT-CNT. Sensitivity of these films were also determined by the relation

$$\text{Sensitivity} = (R_{RH} - R_{(\text{dry air})}) * 100 / R_{(\text{dry air})}$$

Where R_{RH} = resistance at any relative humidity; $R_{(\text{dry air})}$ is the resistance of the dry air (here we have taken at 20 % humidity). Fig. 7 shows the sensitivity curves of the various devices prepared. It can be seen from Fig. 8 that the sensitivity increases with increase in concentration of CT-CNT from 0.94 to 3.75 mg/ml in the polymer solution but it starts decreasing on further increase in CT-CNT concentration. At 7.5 mg/ml and 15 mg/ml CT - CNT concentration in the polymer polymer solution sensitivity of the nanocomposite drops down. Maximum sensitivity is obtained in the case of 3.75 mg/ml CT-CNT concentration in the polymer nanocomposite film for humidity measurements (Table 1). Therefore the best sensitive humidity sensor polymer nanocomposite should contain 3.75 mg/ml CT-CNT. The sensitivity curve is found to be linear in the humidity range from 20 to 80 %. The sensor film on glass substrate shows repeatable results and stability.

Table 1

S. No.	Weight of CT-CNT in 1 ml polymer solution (mg)	Sensitivity (%)		
		At 40% RH	At 60% RH	At 80 % RH
1	0.94	5	25	55
2	1.87	7	30	-
3	3.75	10	32	-

It is easy to fabricate this sensor which shows fast response to small changes in increase in humidity and also shows very little hysteresis in the reverse cycle that is on decreasing the humidity from higher values to lower values.

From our studies we have found that the best sensitivity is obtained with CT-CNT concentration of 3.75 mg/ml in the polymer nanocomposite. Below this concentration of CT- CNT the resistance curves becomes non-linear around 60 % relative humidity as shown in Fig. 8 for 1.87 and 0.94 mg/ml CT-CNT conentrations. Above 3.75 mg/ml CT-CNT concentration the overall sensitivity of the polymer nanocomposite is found to be lower.

Numerous modifications and adaptations of the system of the present invention will be apparent to those skilled in the art, and thus it is intended by the appended claims to cover all such modifications and adaptations which fall within the true spirit and scope of this invention.

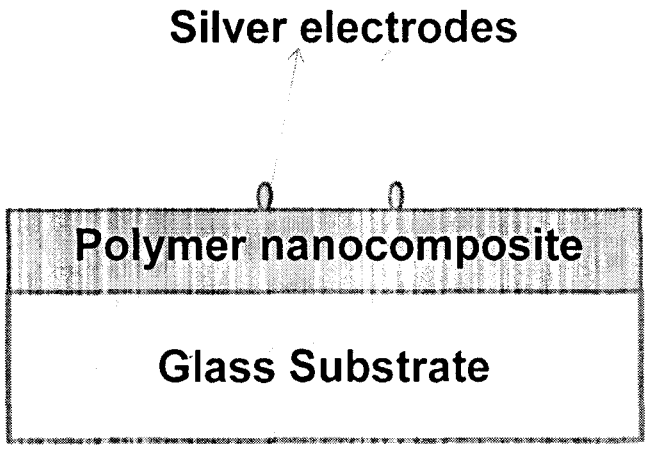

Fig. 1

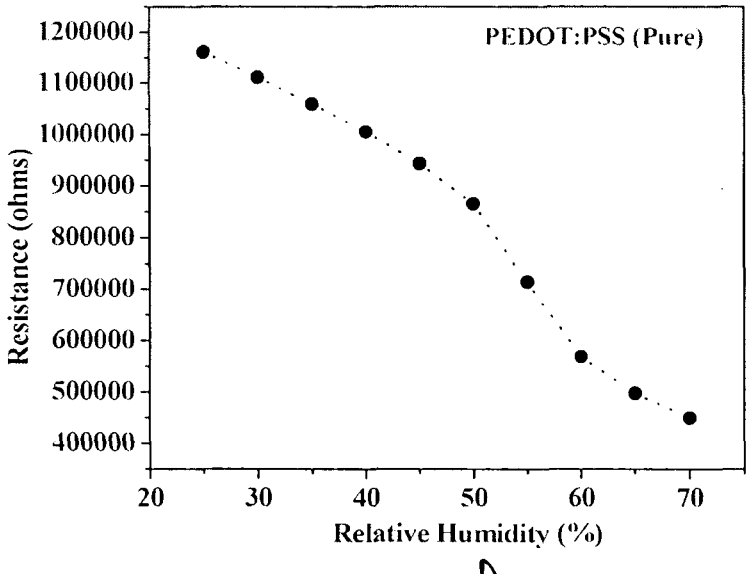

Fig. 2

Dr. B. L. Arya
Registrar
AMITY UNIVERSITY
UTTAR PRADESH

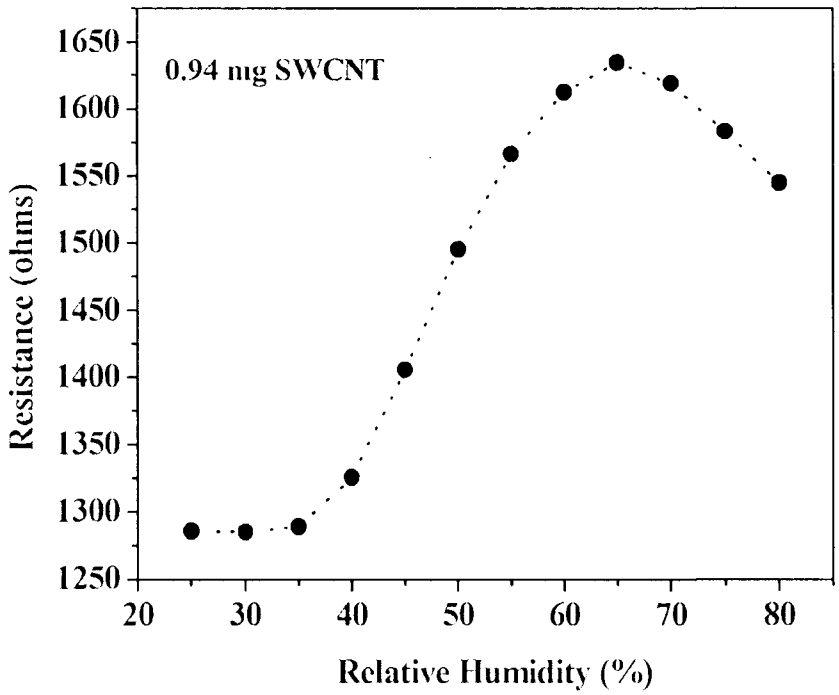

Fig. 3

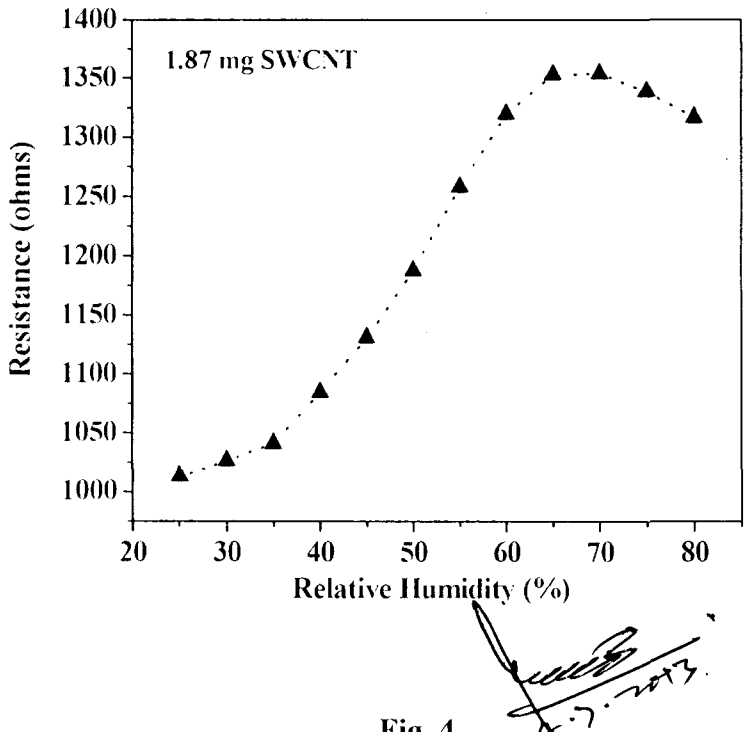

Fig. 4

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Registrar
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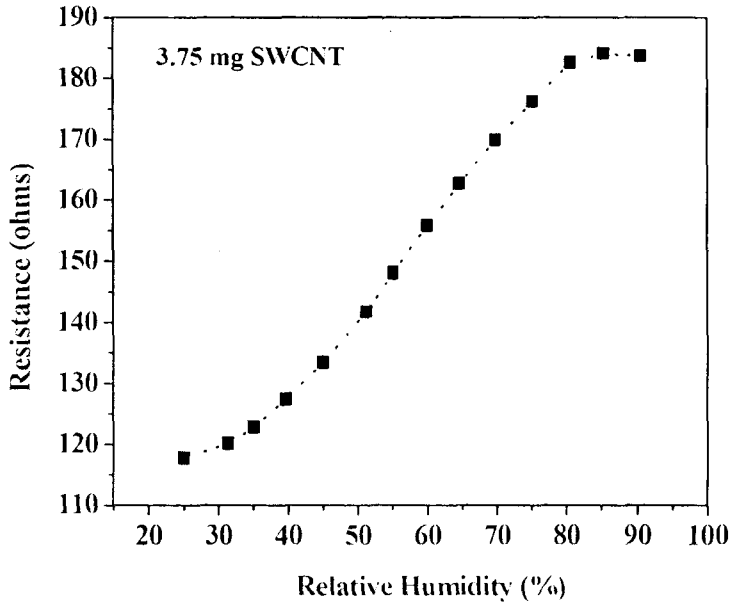

Fig. 5

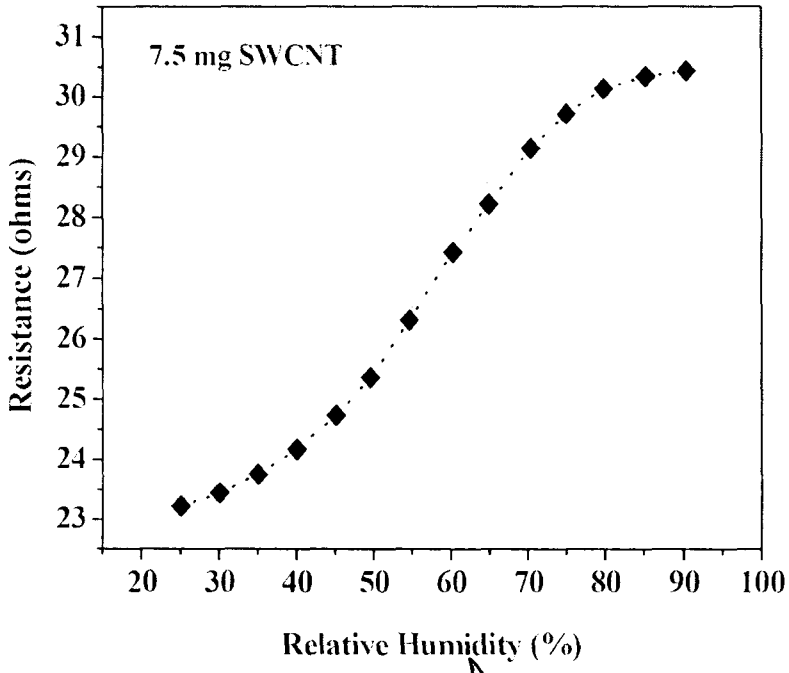

Fig. 6

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Registrar
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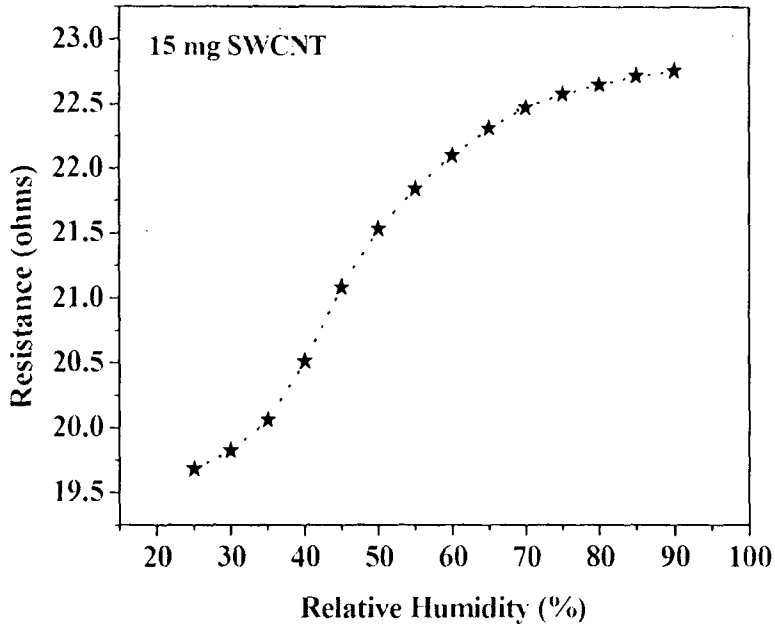

Fig. 7

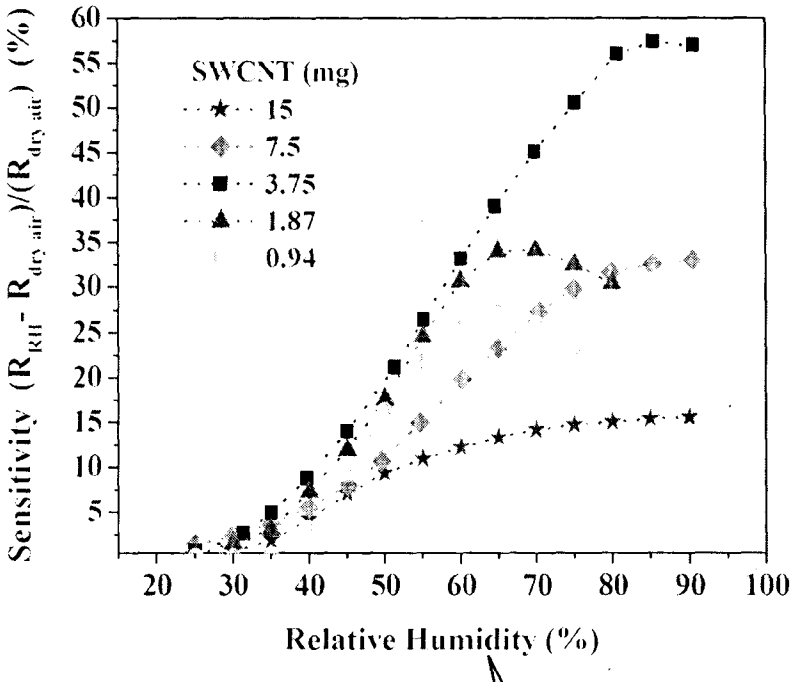

Fig. 8

Dr. B. L. Arya
Registrar
AMITY UNIVERSITY
UTTAR PRADESH