DEVELOPMENT OF GRAPHENE OXIDE BASED HUMIDITY SENSORS

Thesis submitted to the Indian Institute of Technology, Kharagpur for award of the degree

of

Doctor of Philosophy

by

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Under the guidance of

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Dedicated to

my beloved parents and family members

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ABSTRACT

Humidity measurement ascertains the amount of water molecules available in the atmosphere and it is denoted mostly as relative humidity (RH). Humidity sensing and monitoring are quite important for today's advanced manufacturing as well as environmental monitoring. It finds extensive applications in semiconductor industry, pharmaceutical, agriculture, food processing, textile and biotechnology sectors. The types of techniques available for humidity measurement are capacitive, resistive, surface acoustic wave (SAW), quartz crystal microbalance (QCM), and mass spectrometry. Most of the commercially available humidity sensors are based on capacitive technique. However, such sensors suffer from instability for prolonged use and hysteresis due to the polymer dielectric layer. This apart, its fabrication is not cost-effective. In this respect, resistive humidity sensor is attractive because of its simple structure and easy to integrate with silicon technology.

A successful attempt has been made to develop chemically synthesized graphene oxide (GO) based resistive type low-cost humidity sensor. Afterwards, GO was functionalized in order to enhance humidity response. It was observed that metal oxide functionalized GO cannot give good response whereas Nafion[®] ionomer functionalized GO enhanced humidity response immensely. The sensing materials were characterized using optical microscope, scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), energy dispersive analysis of X-rays (EDAX) and fourier transform infrared (FTIR) spectroscopy. The sensor devices were fabricated by drop-casting of sensing materials on patterned gold electrodes on Si/SiO₂ substrate. Humidity sensing devices were exposed to six different relative humidity (RH %) and the response of humidity sensors were found to be excellent due to large proton conduction of GO and Nafion. The sensing mechanism is based on large proton conductivity (in presence of humidity) provided by GO, which follows Grotthuss mechanism. Apart from these, a FET based humidity sensor was also developed utilizing Nafion functionalized GO as its channel material. The humidity measurement was performed in custom-made humidity sensing setup coupled with semiconductor parameter analyzer (SPA) via test fixture. The developed humidity sensors showed ultrafast response and recovery (within few secs) with extremely good repeatability and stability. The GO/Nafion based resistive humidity sensor gave response as high as ~ 18000 times (88% RH). I believe realization of such humidity sensor will help in development of good performance low cost resistive humidity sensor.

Key words: *Humidity, sensor, graphene oxide, proton conduction, Nafion, SnO*₂*, resistive, FET.*

LIST OF SYMBOLS AND ABBREVIATIONS

AFM	Atomic Force Microscopy
Al	Aluminium
a.u	Absolute Unit
CNT	Carbon nanotube
DI	Deionized water
EDS	Energy Dispersive Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
GO	Graphene Oxide
h	Hours
HRTEM	High Resolution Transmission Electron Microscopy
IC	Integrated Circuit
IU	International Unit
Kg	Kilogram
L	Litre
m	Metre
mg	Milligram
min	Minute
mL	Milliliter
mg	Milligram
μm	Micrometer
nm	Nanometer
rpm	Revolutions Per Minute

RGO	Reduced Graphene Oxide
RH	Relative Humidity
SAED	Selected Area Electron Diffraction
Si	Silicon
SiO ₂	Silicon Dioxide
SnO ₂	Stannic Oxide
SEM	Scanning Electron Microscopy
SPA	Semiconductor Parametric Analyzer
SWCNT	Single-walled Carbon Nanotube
TEM	Transmission electron microscopy
UV	Ultra Violet
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
°C	Degree Celsius
%	Percentage

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Curriculum Vitae

Chapter 1

Introduction

1.1 Introduction

This chapter discusses about the various parameters related with humidity sensor and its applications in different industries. Apart from this, it describes about the measurement techniques used in humidity sensing. Lastly, market situation of humidity sensors have been explored in brief.

1.2 Background

Detection of different physical and chemical parameters (like pressure, air flow, chemicals, temperature and humidity) is often necessary for various industrial operations. A sensor is a transducer which detects such parameters and generates corresponding output mostly in the form of an electrical signal [1]. On the other hand, an actuator is a transducer which takes electrical or other form of energy and subsequently converts them into different forms of motion. Such transductions of both these transducers can be resistive [2], or capacitive [3] or inductive [4] or other kinds.

Humidity sensor is a type of sensor, which when comes in contact with water vapour interacts with them. This interaction initiates changes in certain properties of the sensing material. Thus, by measuring the changes in that property of the material, the concentrations of the water vapour can be detected [5].

The efficiency of a humidity sensor can be evaluated by following parameters:

Response:

The response of humidity sensor is denoted as the relative deviation in device current owing upon exposure to the moisture. The response of the humidity sensor is calculated as:

Response =
$$\frac{I_{RH} - I_{air}}{I_{air}} \approx \frac{I_{RH}}{I_{air}}$$
 as $I_{RH} >> I_{air}$

where, I_{RH} -current through the device in presence of humidity and I_{air} -current through the device in presence of compressed air.

Sensitivity:

Sensitivity of humidity sensor is the amount of change in output current in response to a change in relative humidity. The sensitivity of the humidity sensor is evaluated as:

$$S = \frac{\Delta I}{\Delta RH\%}$$

where, ΔI is device current variation and $\Delta RH\%$ depicts corresponding change in relative humidity.

Response time:

The response time of a humidity sensor is defined as the time taken to reach 90% of the full response

Recovery time:

Recovery time of a humidity sensor is defined as the time taken to reach 90% of the baseline value.

Selectivity:

The selectivity of a humidity sensor is the ability of a humidity sensor to detect and measure only water vapour presence in a gaseous mixture. Apart from the above parameters, long term stability (often poor stability of humidity sensitive polymer can be an issue), power consumption (sometimes heat treatment is required to desorb the adsorbed water vapour, this requires power), linearity (non-linear response needs complex circuitry or algorithm to linearise the sensor output) and cost (sensor cost can be reduced by using low cost substrate and sensor material, also sensor realization with interface circuit on the same silicon die can reduce the cost drastically) are also key aspects for a good humidity sensor.

1.3 Humidity sensor applications

Humidity sensing and control are quite important for today's advanced manufacturing as well as environmental monitoring. Controlling of humidity is indispensable particularly for semiconductor industry. For production of extremely advanced electronic system in semiconductor foundry especially in wafer processing, moisture contents are continually observed. In health care, humidity sensors are utilized in sterilizers, incubators and pharmaceutical processing. In biotechnology sectors, measurement of moisture control is substantially important for synthesis and preservation of biological products [6]. In agriculture, humidity sensors are employed for humidity monitoring of greenhouses and soil moisture sensing. In food processing and preservation, detection of the moisture content is indispensable [7]. Besides, in the textile manufacturing humidity takes part a crucial role as the fibers prone to adhere with one another in presence of humidity [8]. Above all humidity sensors play a significant role in detecting amount of moisture of surrounding atmosphere for human comfort [9].Various types of humidity sensing instruments have been developed based on different working principles and diverse hygroscopic sensing materials [10-14]. Based on the units of measurement, humidity sensors are divided in two main classes: Relative Humidity (RH) and Absolute Humidity sensors (hygrometers). In the majority of humidity measurement applications relative humidity measurements are more preferable than absolute humidity ones [15].

1.4 Humidity measurement

Humidity measurement ascertains the quantity of water molecules available in a gaseous medium. In hygrometry relative humidity (RH) is defined as:

$$RH = \frac{p_w}{p_s} \times 100\%$$

Where p_w is the partial pressure of water vapour present in a gas and p_s is the saturation vapour pressure of the gas at a given temperature. Relative humidity depends on temperature, and hence most of the commercially available humidity sensor contains in-built temperature sensor. RH calculation is done in percentage. But the range of humidity required to be detected for all the mentioned applications are different. So, there have been continuous efforts on developing highly sensitive humidity sensors that perform over wide range of humidity and temperature with ultrafast response and recovery time. Apart from these, good reproducibility, stability over days and resistance against chemical contaminants are also required criteria for a humidity sensor.

1.5 Market Survey

Humidity sensor is gaining considerable marketplace due to its extensive application in different industries. According to MarketsandMarkets [16], an organization involved in market survey for sensors, humidity sensor market at automotive sector was approximately \$1,084.38 Million in 2013 and is predicted to grow at\$2,129.68 Million, at a CAGR of 11.05% between 2014 and 2020. Although there are different types of humidity sensors, generally commercially available humidity sensors are mostly capacitive. In market technology, platform used for humidity sensors are CMOS, MEMS, TFPT and packaging types are SMT and Pin type.

1.6 Motivation

Considerable number of humidity sensors have been developed employing various transduction techniques. Among them mostly capacitive humidity sensor is commercially available. But its fabrication cost is high due to its intricate multilayered structure. This apart, it sometimes shows long term instability and hysteresis problem due to agglomeration of water molecules on its dielectric polymer layer. On the other hand, resistive humidity sensor offers simpler structure, cost-effective fabrication and also it is easy to integrate with CMOS platform. Several nanomaterials (e.g. metal oxides [17]), polymers [18] and their composites have been reported in literature as humidity sensing layers. Metal oxides sometimes require heat treatment to desorb water molecule. Long term stability with polymers is always an issue. Recently there are reports of using carbon like nanomaterial (e.g. CNTs [19], RGO [20], and graphene [21]) as humidity sensing layer. Although, such materials do not show good response towards humidity. In this respect, GO can be a good humidity

sensing material because it usually contains lot of defects, functional groups and also it helps in large proton conductivity in presence of humidity.

1.7Objective of the thesis

- a. Design and development of graphene oxide (GO) based resistive type humidity sensor.
- b. Development of functionalized GO based resistive humidity sensor to enhance response.
- c. Development of a Field Effect Transistor (FET) based humidity sensor.

1.8 Thesis Layout

The present thesis contains six chapters. Chapter 1 covers the introduction of the present work. Chapter 2 demonstrates the significant literature survey of the research work focused on humidity sensing material at room temperature and also discusses with different transduction technique employed in development of humidity sensors. Chapter 3 explores the performance of graphene oxide (GO) as humidity sensor. It includes the brief synthesis and characterization of graphene oxide and fabrication of resistive type humidity sensor. Chapter 4 investigates humidity response of functionalized GO. It has two sections. In section I GO was functionalized with SnO₂ in order to get larger response than GO based humidity sensor. In section II GO was functionalized with Nafion so as to attain enhanced humidity response. Chapter 5 discusses development of back gate field effect transistor (FET) based humidity sensor employing GO/Nafion composite as its channel material. Chapter 6 presents conclusion of the current work. This chapter also point out the chief findings and novelty of the present work. Moreover, the chapter also explains the future scope of present study.
1.9 Contribution Made by the Scholar

Graphene oxide based resistive type humidity sensor has been developed successfully. It has shown high humidity response. Afterwards, GO was functionalized with SnO₂ and Nafion successively in order to get higher response. SnO₂ functionalized GO based humidity sensor was unable to enhance response whereas Nafion functionalized GO based humidity sensor exhibited ultrahigh response. After achievement of considerable response in GO/Nafion composite based resistive type humidity sensor, field effect transistor (FET) based humidity sensor has been developed utilizing GO/Nafion composite as its channel material. Notable sensitivity was attained from FET based sensor towards humidity.

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Chapter 2

Literature Review

2.1 Introduction

This chapter discloses the elaborate review of literature of the various kinds of nanomaterial based humidity sensors and their transduction techniques. Also it discusses evolution of electrical humidity sensor in brief. In literature reports of different transduction techniques and usage of numerous nanomaterials, polymeric materials are found. Response, repeatability, stability, response and recovery time are essential parameters of a humidity sensors. It is difficult to develop a single sensing material which will meet all the above objectives. For that reason, composites of humidity sensing materials are usually employed so as to obtain high response towards moisture. Moreover, choice of suitable transduction technique also matters. Comprehensive arguments over scholarly articles related to different attributes of humidity sensors are discussed in this chapter.

2.2 Evolution of Humidity Sensor

One of the most ancient type humidity sensors is LiCl humidity sensor. In 1938 it was developed by Dunmore and it was named as Dunmore-type humidity sensor [1]. This LiCl electrolyte based humidity sensor found to be pioneer for long days in humidity sensing field [2]. LiCl based humidity sensor is the first electrical humidity sensing device. The working principle is based on alteration of the ionic conductivity of lithium chloride solution upon water vapour absorption. Humidity sensors made of polymer film have also been invented long ago [3]. Polymer based sensors were favoured over LiCl based sensors as they are relatively inexpensive and compatible with integrated circuit (IC) technology. The polymer based relative humidity sensors can be divided into ionic and electronic conduction types [4].

2.3 Transduction Techniques

2.3.1 Capacitive

Most of the commercially available humidity sensors are based on capacitive technique [5-7]. The distinctive architecture of capacitive relative humidity sensors resembles a sandwich having electrodes on either side [8]. Afterwards, humidity sensitive polymer is deposited as dielectric between the two electrodes. Permittivity of dielectric made of polymer material modifies upon moisture adsorption [9]. Following this principle, the deviation in humidity level is sensed by determining the shift of the dielectric capacitance. Adsorbed water can increase the relative permittivity and the capacitance. Actually adsorption of moisture intensifies the polarization and enlarges the relative permittivity of polymer dielectric. However, this type of sensors also has drawbacks due to the polymer dielectric. The major problem arises from this polymer dielectric layer is instability and hysteresis in case of prolonged usage [10]. As polymer material prone to degrade over time, so long term stability is hard to achieve. Hysteresis actually arises from agglomeration of adsorbed water molecules inside the polymer dielectric layer. Moreover, the dielectric material for capacitive type humidity sensors ought to be polar yet non ionic so that it does not dissolve in aqueous environment [11]. Market price of capacitive type sensing devices is normally more than resistive type sensing devices owing to their significant manufacturing expenditure. Nevertheless, capacitive relative humidity sensors are more lucrative than resistive type sensors because of considerable linearity in humidity response. However, hydrophobic cross-linked polymeric materials are preferred to be used as dielectric of capacitive moisture sensors so as to avoid generation of clusters of absorbed water [12]. Fig. 1.1 shows device geometry of capacitive type sensing device.



Figure 1.1: Schematic illustration of the device geometry of capacitive humidity senor.

$$C = \frac{A\varepsilon_0 \varepsilon_r(\% RH)}{d}$$

Where

C = total capacitance;

d = thickness of the polymer dielectric layer;

 $\varepsilon_r(\% RH)$ = relative permittivity of the polymer layer

Relative permittivity changes with relative humidity and capacitance alters accordingly. This apart, the capacitance and sensitivity are also affected by reduction in dielectric layer thickness.

A. Oprea *et al.* [13] developed capacitive type moisture sensing devices on adjustable RFID. It showed achievements of sufficient sensing attributes like adequate sensitivity and faster response time. The response and recovery time were within few minutes. This planar humidity sensor is attracting for its low power consumption.

The most notable report of capacitive type humidity sensor was made by H. Bi *et al.* [14]. They developed a graphene oxide (GO) based ultrahigh responsive humidity sensor operated at room temperature. Drop-casted GO was treated as insulated moisture sensitive substance. This capacitive humidity sensor showed sensitivity of up to 37800 due to large proton conductivity. Its response and recovery time was 10.5 s and 41 s. This highly sensitive sensor is appropriate where fast response and recovery is not indented. Moreover, the sensor exhibited comparatively small hysteresis and considerable reproducibility.

2.3.2 Resistive

Resistive humidity sensor gains advantage owing to its cost-effective fabrication, easy to integrate with CMOS platform and easy and efficient operation. Resistive humidity sensors usually hold metal electrodes fabricated on a wafer by conventional photolithography technique. The resistive type sensing device actually estimates the deviation of the relative humidity and interprets it in term of an alteration in electrical resistance or current. The modification of resistivity due to presence of moisture usually obeys an inverse exponential relation [15]. The resistive humidity sensing devices are classified into ionic and electronic conduction types. The electronic and ionic conductive devices evaluate the humidity level by measuring the modifications of conductivity of the sensing layers at various relative humidity [16]. Fig. 1.2 shows schematic illustration of the device geometry of resistive type humidity senor.



Figure 1.2: Schematic illustration of the device geometry of a resistive type humidity sensor.

2.3.3 Surface Acoustic Wave (SAW)

These sensors intrinsically transform tiny radio frequency pulses into acoustic waves. Afterwards, these acoustic waves are revamped by SAW sensor and then convert back to the radio frequency pulses without any outer power source. There is no junction potential in SAW type sensor. This apart, SAW devices are extremely robust, steadfast and are fabricated using fine layer of lithography technique. SAW type humidity sensors have comb like IDT structure patterned on piezoelectric substrate. They serve the purpose of input and output transducers. SAW devices are popular even today because of their straightforward architecture which in turn helps to achieve large scale manufacturing with high yield [17]. Fig. 1.3 exhibits schematic illustration of the device geometry of SAW type humidity sensor.



Figure 1.3: Schematic illustration of the device geometry of SAW type humidity senor.

2.3.4 Quartz Crystal Microbalance (QCM)

QCM humidity sensor, an acutely sensitive mass sensor is constructed following the microbalance concept. It can assess changes of mass even in nanoscale order. It observes the deviation of mass by estimating the change of its resonant frequency. QCM sensors are fundamentally piezoelectric based instrument where metal electrodes are deposited on either side of the quartz crystal plate. A quartz crystal attached with Peltier module can quantify humidity changes. QCM humidity sensors are highly precise owing to its frequency measurement technique. It is feasible to ameliorate this type of mass sensor by decreasing the thickness of the quartz crystal plate. The sensitivity of the QCM humidity sensing devices is mostly determined by moisture sensitive coating element. It should have capability to adsorb the water molecules effectively. QCM humidity sensors can measure very low humidity and it also has a broad measuring range [18]. Fig. 1.4 shows schematic illustration of the fundamental component of QCM type humidity senor.



Figure 1.4: Schematic illustration of the fundamental component of QCM type humidity senor.

2.3.5 Mass Spectrometry

Mechanical resonators are extensively employed as inertial balances to identify minute amount of adsorbed mass by monitoring changes of oscillation frequency. However, with the progress in microelectronics fabrication technology and material synthesis nanomechanical resonators have been developed. In mass spectrometry humidity sensor, nanoelectromechanical resonators act as precision mass detector. Here resonant frequency alters upon minute amount of moisture adsorption. Normally relation between deviation in resonant frequency and changes in mass is determined by the architecture of the resonator and the position of the adsorbed element. The most important fact is that the sample under test does not need to be ionized [19]. For this reason it finds an appropriate application in biotechnology sectors as the biomolecules very often prone to be damaged when subjected to ionization. Fig. 1.5 shows schematic illustration of the fundamental component of mass spectrometry type humidity senor.



Figure 1.5: Schematic illustration of the fundamental component of mass spectrometry type senor.

2.3.6 Optical

The optical waveguide is equivalent to interior reflection spectroscopy. It works on the principle where light transmits via a channel by reflection inside the channel. The transmitted light tends to be affected by moisture adsorbed to the reflecting plane of the optical wave guide. The influence of vapour molecules is dependent to the angle and wavelength of the input light wave. Apart from this, refractive indexes of the core and cladding layer of optical waveguide also play an important role. If the refractive indexes of the cladding layer are modified upon water uptake then a phase shift is occurred at the output light wave that can easily be detected by the detector [20]. Fig. 1.6 displays schematic illustration of the fundamental principle of optical humidity senor.



Figure 1.6: Schematic illustration of the fundamental principle of optical humidity senor.

2.3.7 Field Effect Transistor (FET)

The back gate FET type device usually is fabricated by drop casting humidity sensitive material over metal electrodes patterned by conventional photolithography on Si/SiO_2 substrate. Patterned electrodes, conducting silicon, drop-casted material and SiO_2 are generally served the purpose of source, drain, back gate, channel and dielectric of FET. The drain characteristics and transfer characteristics of FET type sensors generally are explored in various level of humidity and sensitivity is calculated from drain current

shift due to humidity level shift. The sensitivity of the FET type sensor was evaluated as:

$$S = \frac{\Delta I}{\Delta R H \%}$$
[21]

The advantage of FET type humidity sensor is that its sensitivity can directly be adjusted using applied drain bias voltage. Sung Pil Lee *et al.* [22] successfully demonstrated a FET type humidity sensor. The FET device was developed using traditional microelectronics technology. The insulator was layers of $TiO_2/Si_3N_4/SiO_2$. The device was operated in enhancement mode and exhibited significant drain current increment with rise in relative humidity. The humidity sensitivity of the sensor was 3.2 μ A/%RH. Fig. 1.7 shows schematic illustration of the device geometry of FET type humidity senor.



Figure 1.7: Schematic illustration of the device geometry of FET type humidity senor.

Although in literature there are different types transduction techniques of for development of humidity sensors still resistive humidity sensor gains advantage over all type of humidity sensors owing to its cost-effective fabrication, easy to integrate with CMOS platform and easy and efficient operation.

2.4 Traditional Metal Oxide Sensor

Conventional humidity sensors based on bulk metal oxide (TiO₂, ZnO, SnO₂) required external micro heater in order to provide activation energy and desorption of water molecules during recovery operation. Heaters were generally fabricated at the bottom of substrate and humidity sensing material was coated on top of IDT electrodes [23]. Fig. 1.8 demonstrates schematic illustration of the device geometry of conventional bulk metal oxide based humidity senor.



Figure 1.8: Schematic illustration of the device geometry of conventional bulk metal oxide based humidity senor.

2.5 Nanomaterials in Humidity Sensing

The preferable criteria of a humidity sensing device are large and faster response, repeatability, stability, cost effectiveness and long lifetime. Till now, no such material has been reported to fulfil the entire requirement at a time. Moreover, there are some materials whose instantaneous performance is quite good but they lack in chemical and thermal stability. But it is obvious that nanomaterials are far better than that of their bulk counterpart due to their high surface to volume ratio [24]. In recent years there have been several reports of nanomaterial based resistive humidity sensors. Metal oxide nano particles (like TiO₂, ZnO, Al₂O₃, SnO₂), polymers nanocomposite and carbon nanotubes are promising humidity sensing nanomaterials because of their high surface to volume ratio. Metal oxides nanoparticles offer better performances with respect to organic polymer materials owing to their improved chemical, mechanical and thermal stability [25].

2.5.1 TiO₂

In TiO₂ humidity sensing is generally understood by the adsorbed vapour molecules in porous framework and thereby forming proton conduction. Despite having semiconducting properties, as humidity sensor TiO₂ shows humidity sensing property because of its surface protonic conduction mechanism. Basically TiO₂ nanoparticle is chosen as humidity sensing material because of its larger water adsorption capability [26, 27]. Pi-Guey Su *et al.* [27] proposed a TiO₂ nanoparticle based resistive humidity sensor working at room temperature. Its response and recovery time are 40 s and 20 s respectively. They deposited composite humidity sensing layer on an Al substrate. They also showed long-term stability, linearity, smaller temperature influence in their work.

2.5.2 ZnO

ZnO is a flexible semiconducting material being implemented in various sectors of modern technology. It mostly finds applications as chemical sensors owing to its unique chemical features. Humidity sensors of large sensitivity, stability and quicker response have been developed utilizing ZnO nanowire as humidity sensing nanoparticle. In case of resistive type ZnO based humidity sensor generally resistance of ZnO layer reduces with rise in humidity. On the other hand, for capacitive type moisture sensors permittivity modifies by water molecules adsorption of ZnO nanoparticles acting as dielectric medium. In fact, vapour molecules adsorption take places through chemisorption and physisorption. Chemisorption generally arises by dissociation whereas physisorption is guided by hydrogen bonding [28]. Y. Zhang et al. [29] developed a ZnO nanomaterial based resistive humidity sensor. This sensor displayed considerable moisture sensitivity with substantial stability and fast response. It showed a sensitivity factor of 5442 times at 12% RH and its response and recovery time were 3 s and 20 s respectively. They coated zinc oxide nanorod and nanowire on comb type Pt electrodes fabricated over Si/SiO₂ substrate.

2.5.3 Al₂O₃

 Al_2O_3 is also considered most suitable humidity sensing metal oxide nanoparticle in terms of its independency of sensitivity over a wide range of temperature. Apart from this, its nanoporous structure makes it sensitive to even extremely small humidity. Al_2O_3 is a promising nanomaterial to detect low level of moisture content as a consequence of electron tunnelling among the trapped immobile water molecules into its nanoporous structure [30].

2.5.4 SnO₂

Development of humidity sensors nearly at ambient temperature was possible due to emergence of SnO_2 nanoparticle. SnO_2 is basically a semiconducting material having large bandgap. Water molecules are adsorbed on the metal oxide plane in hydroxyl format [31]. Unlike TiO₂, here sensing mechanism is based on electronic conduction. Qin Kuang *et al.* [32] demonstrated a SnO_2 nanowire based resistive humidity sensor due to high surface to volume ratio and special physical and chemical properties resulting from the reduced sizes of SnO_2 nanowire. This new type of SnO_2 nano wire based sensor showed large and quick response towards humidity in ambient environment. Besides, it has exhibited significant repeatability. It provided a normalized response of 1200 at 85% RH that was quite large with respect to previously mentioned humidity sensors but its response and recovery times were substantially high. Its response time was 120s-170s where as recovery time was 20s-60s. The sensing mechanism is based on displacement of already adsorbed oxygen molecules on the surface of the SnO_2 nanowire by moisture adsorption.

2.5.5 Carbon Nano Tube (CNT)

Problem associated in many cases with the bulk metal oxide based humidity sensors are the requirement of external heating for their operation as bulk metal oxides sense humidity usually above room temperature and also their response is poor. Although metal oxide in nanoparticle form sense humidity even at room temperature. Like nanoparticle of metal oxide, CNT also sense humidity at room temperature [33]. The conductivity of CNT is modified upon minute change of surrounding environment. It has also been noticed that at room temperature, carbon nanotube based devices exhibit larger sensitivity than organic (polymeric) humidity sensing devices. At room temperature organo-functionalized CNT offers much more humidity sensitivity than the pristine CNT [34]. But this type of organo-functionalized composite suffers from long term stability [35]. Fig. 1.9 exhibits schematic illustration of the hollow structure of single-walled carbon nanotube and its functionalizing agents.



Figure 1.9: Schematic illustrations of the hollow structure of single-walled carbon nanotube and its functionalizing agents.

A. Paul *et al.* [21] demonstrated deoxyribonucleic acid functionalized (DFC) carbon nanotube based zero gate biased FET type room temperature operated humidity sensor with response and recovery time within few seconds. The sensor is operated on the mechanism of change of channel resistance of the DFC network with rise in humidity. The humidity sensor showed sensitivity of 0.57 (nA/RH%) at 88% RH.

Resistive humidity sensors were developed on cellulose paper by J-W Han *et al.* [33]. Carboxylic acid functionalized single walled carbon nanotubes were employed as humidity sensing element. The humidity sensor was cost-effective and environment friendly.

2.5.6 Graphene

Recently there have been some reports on graphene based humidity sensors owing to their 2-D (two dimensional) structure, where most of the atoms are surface atoms and hence they interact with any environmental perturbations [36, 37]. The chemical nature begins to be like bulk graphite as soon as the number of layers becomes more than 10 and this agglomerated graphene layers hardly sense humidity [38]. Nowadays a considerable number of methods have been reported regarding synthesis of single or few layer graphene. But their quality varies from one another in scalability issue. However, pure graphene is less sensitive to analytes due to the absence of functional groups and defect sites. Graphene is also suitable for making of composite materials [39, 40]. Fig. 1.10 presents two dimensional honeycomb structure of graphene nanosheet.



Figure 1.10: Two dimensional honeycomb structure of graphene nanosheet.

However, A. Ghosh *et al.* showed a graphene based resistive humidity sensor capable of working at room temperature [41]. Although its sensitivity was low and response and recovery time were very large still their work attracted attention of researchers towards sensing attributes of graphene. Its sensitivity was 76 times at 84% RH whereas response time was 3 to 5 min and recovery time was few hours.

2.5.7 Graphene Oxide (GO)

Alternatively graphene oxide (GO), a graphene precursor, offers significant benefits as a humidity sensing material [42]. GO is also a 2-D honeycomb structure of sp² and sp³-bonded hybridized carbon atoms [43]. It consists of large no of reactive oxygen functional groups like -OH, -COOH and epoxy [44-46]. These functional moieties are attached at the basal planes and edges of hexagonal C-chains [47]. The presences of polar oxygenated functional groups in GO make it electrically insulating and highly hydrophilic [48]. In ambient environment GO is almost an insulator, hence shows very large resistance. Thus instead of GO, researchers have also been trying reduced GO (also known as RGO) as a resistive humidity sensor [49, 50]. Though RGO usually shows finite resistance, but the amount of functional groups present is usually less compared to GO [51-53]. Thus the existence of larger amount of functional groups, especially sp^3 hybridized carbon atoms strengthen the hydrophilic attribute of GO, and also owing to ionic conduction it exhibits excellent proton conductivity in presence of humidity [54-56]. Hence, the coupling of GO with water molecules can be utilized in humidity sensing application [14, 57-58]. Fig. 1.11 shows graphene oxide nanosheet with hydrophilic functional groups. Yao Yao et al. [44] developed a graphene oxide based humidity sensor recognizing possibilities of GO as a promising humidity sensing material. The impedance type room temperature operated sensor

exhibited sensitivity of 1100 at 98% RH. They studied the impact of moisture adsorption on the electrical attributes of GO layer with the help of impedance spectroscopy and also described the sensing mechanism sufficiently. Comb-like electrodes were realized using conventional photolithography technique on a silicon substrate. S. Borini *et al.* [57] reported development of GO based ultrafast humidity sensor. It displayed very fast response and recovery time of 30 ms. They studied the effect of water molecules on the electrical properties of GO films.



Figure 1.11: Graphene oxide nanosheet with functional groups.

2.6 Humidity Sensitive Polymer

Numerous electrically conductive polymeric materials like polypyrrole, polyimide, polyamide, polyaniline and PMMA exhibited great potentiality in humidity sensing [59-65]. Polymer based substances are generally modulated chemically to form cross-linked polymer and moisture sensing devices are usually developed utilizing this

modified materials [66, 67]. While developing moisture sensor, the hydrophilic polymeric materials are actually modified so that they cannot dissolve in aqueous medium during adsorption process and establishing ionic conduction [68, 69].

P. J. Schubert *et al.* [11] successfully developed a polymide based capacitive humidity sensor worked at room temperature. In this moisture sensor, the dispersal of vapour molecules across the polyimide is utilized to trace the modification in relative permittivity of a capacitive device. The sensor showed stability with negligible hysteresis. The response and recovery time were 6 s and 30 sec. In this capacitive architecture, polymide was used as dielectric and metal was used as top and bottom electrode. The bottom electrode was basically a metal film coated over a silicon dice. It was fully silicon Integrated Circuit (IC) compatible device. Apart from this, sensing mechanism was also described.

M. Matsuguchi *et al.* [69] developed crosslinked polyimide and fluorinated polyimide-based capacitive type humidity sensors. Crosslinked polyimide and crosslinked fluorinated polyimide were used as the dielectric of capacitive type devices. The dielectric layers acted as moisture sensing element as relative permittivity changes with humidity. These polymer based sensors exhibited stable behaviour over long days. This apart, the stability of these sensors was assessed by exposing the humidity sensing material to different test environment. The crosslinked polyimide sensor was chemical-resistant and the crosslinked fluorinated polyimide sensor showed quite stable performance even in coarse weather. The sandwich type capacitive architecture used platinum bottom electrode and gold top electrode.

P.M. Harrey *et al.* [9] demonstrated polymide and polyethersulphone based capacitive humidity sensor. It was developed applying the lithographic printing technology.

Simple parallel plate capacitive architecture was adopted taking polyimide and polyethersulphone as moisture sensing dielectric. The dielectric layers adsorb moisture and dielectric constant changes with humidity. The humidity sensors were operated in the range of 10–90% RH. Polyimide based device displayed significantly large modification in capacitance with respect to polyethersulphone device. The capacitance change (pF) and sensitivity (pF/%RH) of the sensors was found to vary in reverse order with the thickness of the dielectric. Nevertheless, polyethersulphone sensor exhibited faster response than that of its polyimide counterpart.

M Dokmeci *et al.* [8] fabricated extremely sensitive polyimide based moisture sensing devices for observing relative humidity inside the hermetic glass soldered micro packages. Highest sensitivity of 3.4 pF/%RH was achieved for 300 Å thick polymide film. The sensor was designed to show excellent stability as the calibration is not possible after being locked into the micro package. This sensor also exhibited good linearity. The device shows very negligible hysteresis. It is comprised of thin film of polyimide inserted in between two metal electrodes to develop a humidity sensing capacitor. A SiO₂ passivation layer is deposited at the bottom of lower electrode to diminish parasitic effect. The upper electrode is basically interdigitated to render water vapour inside the polyimide layer. Fig. 1.12 displays schematic illustration of the cross-linked polymer.



Figure 1.12: Schematic illustration of the cross-linked polymer

2.7 Nafion Ionomer

Nafion[®], a sulfonated fluropolymer, is being extensively utilized in proton-exchange membrane fuel cells (PEMFCs) owing to its ultrahigh proton conductivity especially in hydrated condition. It is also attracting considerable attention in humidity sensing applications [70-74]. Actually the existence of ions in polymers influences a broad range of attributes. Nafion was introduced first by the E. I. DuPont Company. In Nafion proton conduction actually occurs by the generation of protons (H⁺) and hydrated protons like H_3O^+ (hydronium ion), $H_5O_2^+$ (zundel ion) and $H_9O_4^+$ (eigen ion) which evolve from the dissociation of the sulfonic acid functional group of Nafion [75-80]. Fig. 1.13 shows chemical formula of Nafion ionomer whereas Fig. 1.14 indicates fluorinated side chain of Nafion polymer.



Chemical Formula

Figure 1.13: Chemical formula of Nafion ionomer



Fluorinated Side Chains

Figure 1.14: Flurinated side chain of Nafion polymer

2.8 Nanocomposite

A nanocomposite is a multiphase solid material to which nanomaterials have been incorporated to ameliorate a specific attributes of the substance. It was noticed that composites of nanomaterials are advantageous over their elemental counterpart. Nanocomposite substances have appeared as appropriate substitute to conquer the shortcoming of bulk material. These nanocomposites generally provide significantly larger sensitivity. A large number of nanocomposites like CNT/Nafion, ZnO/TiO₂, TiO₂/SnO₂, GO/polypyrrole were utilized on the development of humidity sensor [81-87]. Fig. 1.15 shows development of a nanocomposite based humidity sensor. Hui-Wen Chen *et al.* [81] reported nano sized CNT/Nafion composite based quartz crystal microbalance (QCM) type room temperature operated humidity sensor for estimation of very small amount of moisture content in air. Its sensitivity was 4.86 (Hz/ppm_v). It showed response and recovery time within 5 s. Sensing film was deposited on the gold electrode of QCM. CNT/Nafion sensing material, drop-casted on the gold electrode of the Quartz Crystal Microbalance exhibited wonderful response with nice stability and linearity.



Figure 1.15: Development of a nanocomposite based humidity sensor

Wang-De Lin *et al.* [87] developed Graphene/Polypyrrole based room temperature operated impedance type humidity sensor. It offered response and recovery time within few seconds with a significant sensitivity. Its sensitivity was 138 at 90% RH and it exhibited response and recovery time of 15 s and 20 s respectively. The humidity hysteresis was low at all relative humidity (RH) (<0.16%). The humidity sensitive layer was coated on an aluminium substrate and interdigitated type electrodes were used to fabricate humidity sensing device. Moisture sensing mechanism was also explained elaborately.

2.9 Sensing Mechanism

2.9.1 Grotthuss Mechanism

Sensing mechanism of GO and Nafion are mostly based on ionic conduction [88]. The functional groups present in GO and Nafion play a vital role in humidity sensing. The hydrophilic functional groups of GO create protons (H^+) when it adsorbs water molecules. The proton conductivity of Nafion occurs due to dissociation of sulfonic acid group (-SO₃H). The conjugate hydrophilic and hydrophobic structure of Nafion is also play a crucial role in development of stable humidity sensor. Literally the proton transport depends on the Grotthuss mechanism [89]. In case of Grotthuss mechanism proton jumps via water molecules through formation and disappearance of hydrated ions (H_3O^+ , $H_5O_2^+$ etc). Although this ionic conduction process has been introduced long ago still its actual atomistic process needs considerable amount of clarification. Fig. 1.16 exhibits Grotthuss mechanism of proton hopping.



Figure 1.16: Grotthuss mechanism of proton hopping

M. R. Karim *et al.* [54] pioneered in the proton conductivity calculation of GO nanosheet and they demonstrated how graphene oxide, a so-called electrically non conducting material can display considerable ion conduction in presence of moisture. The proton conductivity was estimated by a quasi-four-probe technique utilizing an impedance analyzer. For development of sensor device, interdigitated gold electrodes were patterned over substrate and water dispersible GO was drop-casted onto it. They explined proton conduction mechanism of hydrated GO in details. This discovery drawn considerable amount of attention of researhers working in the field of fuelcell and sensor.

M. Koinuma *et al.* [55] also investigated on proton conduction of graphene oxide nanosheets in presence of humidity. Proton conduction mechanism was explored elaborately. The conduction basically based on the Grotthuss mechanism, in which protons, created by the interaction of hydrophilic functional groups with water vapors hop between water molecules.

2.9.2 Vehicle Mechanism

There is also an alternate proton transport method that is mostly applied in bulk water. This highly water adsorption induced proton conduction process is called vehicle mechanism where proton moves through the water molecules. Actually in bulk water when amount of protons becomes surplus then these excess protons start propagating in conjugation with solvent molecules. Vehicular mechanism generally occurs at higher level of humidity and in case of a highly proton conductive materials like Nafion. The total ion transport is strongly affected by the vehicle movement rate. In Grotthuss like conduction process protons are propagated via the generation and deletion of hydrogen bonds so as to establish proton hopping. Unlike vehicle mechanism, Grotthuss mechanism does not require any vehicle [90].

2.10 Comparative Performance

The modern nanomaterial based humidity sensors are unable to provide an overall performance which is an essential characteristic of an ideal humidity sensor. In Table 1.1 comparative performances of various nanomaterials based humidity sensors have been summarized.

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Previous Works	Sensor Type	Materials Used	Temperature	Response	Response & Recovery Time
Y. Zhang <i>et al.</i> (2005) [29]	Resistive	Metal Oxide (ZnO)	room temperature	5442 (12% RH)	3 s 30 s
Pi-Guey Su <i>et al.</i> (2007) [27]	Resistive	Metal Oxide (TiO ₂)	room temperature (25 °C)	not given	40 s 20 s
Qin Kuang <i>et al.</i> (2007) [32]	Resistive	Metal Oxide (SnO ₂)	room temperature (30 °C)	1200 (85% RH)	120-170 s 20-60 s
A. Ghosh <i>et al.</i> (2009) [41]	Resistive	Graphene	room temperature (25 °C)	76 (84% RH)	3 to 5 min few hours
Wang-De Lin <i>et al.</i> (2013) [87]	Impedance	Graphene/ Polypyrrole	room temperature	138 (90% RH)	15 s 20 s
A. Paul <i>et al.</i> (2013) [21]	FET	CNT/DFC	room temperature	0.57 (nA/RH%) (88% RH)	4 s 8 s
Hui-Wen Chen et al. (2005) [81]	QCM	CNT/Nafion	room temperature (23°C)	4.86 Hz/ppm _v	less than 5 s
Yao Yao <i>et al.</i> (2012) [44]	Impedance	Graphene Oxide	room temperature (25 °C)	1100 (98% RH)	not given
H. Bi <i>et al.</i> (2013) [14]	Capacitive	Graphene Oxide	room temperature (25 °C)	37800 (95% RH)	10.5 s 41 s
S. Borini <i>et al.</i> (2013) [57]	Impedance	Graphene Oxide	room temperature (25 ∘C)	0.25-0.75 (Normalized Response) (80% RH)	30 ms 30 ms

Table 1.1: Comparative Performance of Recently Developed Humidity Sensors

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Chapter 3

GrapheneOxide Based Resistive Humidity Sensor

3.1 Introduction

In this chapter, synthesis of graphene oxide (GO) and its usage in humidity sensing has been described. GO has been derived from fine graphite powder. The humidity sensing laver was characterized rigorously using different nanomaterial characterization techniques. Atomic force microscopy (AFM), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used for this purpose. In order to develop humidity sensing device GO was drop-casted on lithographically patterned gold electrodes on Si/SiO₂ substrate. The humidity sensor exhibited significant response. It showed response of 1200 at 88% RH. It also showed ultrafast response and recovery time. Its response and recovery time were within few seconds (5 s and 6 s). This apart, it offered considerable stability and repeatability. The function of oxygenated hydrophilic functional moieties attached with GO has also been investigated experimentally by fabricating the humidity sensing devices by thermally reducing GO for different time span. Besides these, sensing mechanism has also been clarified thoroughly.

3.2 Material Synthesis

GO was produced utilizing modified Hummers and Offeman method [1-7]. Graphite fine powder was purchased from Loba Chemie, India. The typical reaction includes chemical exfoliation of graphite fine powder using NaNO₃, KMnO₄ and H₂SO₄ [8-11]. At first, oxidation of graphite was done by reacting graphite with concentrated H₂SO₄, NaNO₃, and KMnO₄. H₂O₂ (30%) was also used in this process. The whole synthesis needs almost 120 min for completion. The major process equipment involves in GO synthesis are ice bath, stirrer, high-speed centrifuge and ultrasonicator.

3.3 Material Characterization

3.3.1 SEM

Surface morphology of GO was identified utilizing Carl Zeiss Auriga Compact scanning electron microscopy. SEM image of Fig. 3.1 discloses that GO contains of randomly align, thin, crumpled flakes adjoined with one another.



Figure 3.1:SEM image of synthesized graphene oxide nanosheets

3.3.2 TEM

Transmission electron microscopy (FEI TECNAI G2) was utilized to investigate the structural information. The wrinkled GO flakes are noticed in Fig. 3.2 (a). The selected area electron diffraction (SAED) pattern of GO in Fig. 3.2 (b) is displaying six shining dots aligned in hexagonal order. It actually depicts six carbon atoms of

graphene. Besides these shining dots, few concentric rings were observed. It represents the existence of functional moieties adjoined to the carbon atoms [12].



Figure 3.2:(a) TEM image of graphene oxide flakes (b) SAED pattern of graphene oxide flakes.

3.3.3 AFM

Graphene oxide nanosheets were characterized using tapping mode AFM (Agilent Technologies) so as to confirm the exfoliation of graphene oxide from graphite fine powder. GO was spin coated on silicon substrate. The thickness of the nanosheets was appeared to change in between 2-2.5 nm as exhibited in Fig. 3.3. In this way it was confirmed that graphene oxide nanosheets were bilayared [13-15].



Figure 3.3: AFM image of GO flakes spin coated over Si/SiO_2 substrate with thickness profile

3.3.4 Raman Spectroscopy

Raman spectroscopy is extensively applicable method to characterize few attributes of graphene like defected structures [16, 17]. The G band is associated with the in-plane vibration of sp2-bonded carbon atoms. On the other hand, the D band is related to the vibrations of carbon atoms with sp3 electronic configuration of defected graphene [18, 19]. The D peak, situated at 1350 cm⁻¹ owing to first-order zone boundary phonons, is available only in defected graphene structure [20]. Thus in Fig. 3.4 presence of D band indicates that used graphene has defective sites which are particularly essential for sensing applications.



Figure 3.4: Raman spetra of graphene oxide

3.3.5 XPS

X-ray photoelectron spectroscopy was employed to confirm reduction of graphene oxide using PHI 5000 Versa Probe II. After synthesis of GO by the modified Hummers technique, the characteristic peaks of GO appeared as C-C (284.6 eV), C-O (286.3 eV) and C=O (289.5 eV) in C1s spectrum as exhibited in Fig. 3.5 (a). XPS characterization shown in Fig. 3.5 (b) and Fig. 3.5 (c) are displaying significant elimination of C-O and C=O functional moieties after 60 minute and 180 minute of heat treatment at 160°C. It is explicitly noticed that hydrophilic oxygenated functional moieties are decreased as it is reduced thermally. This apart, C/O ratios have also been evaluated for GO and RGOs. C/O ratios were found to be 2.02, 3.44 and 4 for GO, RGO 60 min and RGO 180 min. It is observed distinctly that C/O ratio rises with thermal reduction owing to continuous removal of hydrophilic oxygenated functional moieties from GO flakes. These hydrophilic functional moieties take part crucial role in proton transport of GO flakes in humid environment.



(a)



Figure 3.5: XPS Characterization (a). High-resolution XPS C1s spectra of GO (b)High-resolution XPS C1s spectra of RGO after 60 min reduction. (c) High-resolution XPS C1s spectra of RGO after 180 min reduction.

3.4 Sensor Fabrication

Silicon wafer of two inch diameter was taken for batch fabrication of humidity sensing devices. At first, wafer was purified by piranha solution ($H_2O_2:H_2SO_4::1:1$). Afterwards, native oxide was removed with 1% buffered hydrofluoric (BHF) acid. Tempress thermal oxidation system was employed to develop 300 nm SiO₂ on the Si wafer. Gold electrodes of thickness 150 nm were then defined on Si/SiO₂ substrate employing conventional photolithography process. GO or RGO was drop-casted in between the gold electrodes and then dried at room temperature. The schematic of the device fabrication process steps have been demonstrated in Fig. 3.6 and Fig. 3.7 displays schematic of resistive type sensor device. Fig. 3.8 is showing fabricated device.



Figure 3.6: Fabrication process steps of resistive type humidity sensor.



Figure 3.7:Schematic of resistive type humidity sensing device with dimensions



Figure 3.8:Various part of humidity sensing device

Fig. 3.9 is showing Carl Zesiss optical microscopic image of drop-casted GO in between gold electrodes. Inset is showing device and drop-cast dimensions. Gap between gold electrode was 100 μ m and diameter of drop-casted GO was 200 μ m approximately. The details device dimensions are shown at Fig. 3.9. However, this optical microscopic image gives an idea of size and shape of electrode and dropcasted film. After drop-casting, GO was not dried using heat treatment in order to avoid any thermal reduction. Device was kept in ambient environment for 1.5-2 hours after drop-casting.



Figure 3.9: Carl Zesiss optical microscopic image of drop-casted GO in between gold electrodes

Mask was design using AutoCAD 2010 and verified using CleWin software before fabrication. Spin coating was done using positive photoresist (HPR504). Mask aligner and UV exposure were used for proper pattern transfer at photolithography process. HPRD 429 and acetone were used as developer and photoresist remover. DI water was used to rinseto remove excess acetone. Fig. 3.10 exhibits shape and dimension of mask prepared by AutoCAD 2010 software.Fig. 3.11 demonstrates optical microscopy image of fabricated emulsion mask on glass plate. Afterwards, patterned gold electrodes were fabricated on Si/SiO₂ substrate using the mask. Fig. 3.12 shows Dektak surface profilometric image of fabricated gold electrodes whereas Fig. 3.13exhibits Dektak surface profilometric thickness measurement of gold electrodes. Thickness was found to be 147 nm approximately.



Figure 3.10: Shape and dimension of mask



Figure 3.11: Fabricated emulsion mask on glass plate and its optical microscopy image



Figure 3.12:Dektak surface profilometric image of gold electrodes



Figure 3.13:Dektak surface profilometric thickness measurement

3.5 Device Fabrication Instruments

Fig. 3.15 shows digital image of device fabrication instruments. Tempress System was used as oxidation furnace as shown in Fig. 3.14 (a) and Figure 3.14 (b) exhibits Hind High Vacuum metallization chamber for metal deposition by thermal evaporation.



Figure 3.14: Digital images of device fabrication instruments. (a) Tempress oxidation furnace (b) Hind high vacuum metallization chamber.

3.6 Device Characterization Equipment

Fig. 3.16 is displaying device test and measurement instruments. Fig. 3.15 (a) shows semiconductorparameter analyzer of Agilent technologies whereas Fig. 3.15 (b) exhibits a vacuum probe station.



Figure 3.15: Device test and measurement instruments. (a) Agilent technologies semiconductor parametric analyzer (b) Vacuum probe station.

3.7 Humidity Test Setup

The humidity measurement was performed in custom-made humidity sensing setup which comprised of a stainless steel sealed chamber where the samples were placed for carrying out the humidity sensing measurements. The setup was coupled with Agilent 4155C semiconductor parameter analyzer (SPA) via Agilent 16088-60046 test fixture. Fig. 3.16 shows schematic diagram of experimental setup for measurement of the humidity. Compressed dry air was allowed to enter into humidity test chamber directly to maintain baseline humidity and compressed dry air was passed through water bubbler in order to provide humid air. Humidity level of humid air was controlled by flow controller. In order to release the extra air an exhaust was placed at the humidity test chamber. The humidity test chamber was purged with flow of dry compressed air as and when required.



Figure 3.16: Schematic diagram of experimental setup for measurement of humidity

The digital image of the humidity test setup is shown in Fig. 3.17. Fig. 3.18 shows detailed description of humidity measurement setup.



Figure 3.17: Digital image of humidity measurement setup.

Inside the air tight chamber, apart from humidity sensing device there was also a reference humidity sensor. In Fig. 3.18 it is noticed clearly. The exhaust for letting extra air to pass outside the sealed chamber is also seen. Compressed air (25% RH) comes from dry air compressor and humid air (40%-88% RH) was created by passing this dry air through a water bubbler. There are a dry air control valve and dry air pressure indicator to achieve the base line humidity (25% RH). There are a humid air control valve and humid air pressure indicator to adjust the humidity inside the sealed chamber. There is also a display to indicate humidity and temperature. All the required components of humidity test chamber are clearly visible in Fig. 3.18.



Figure 3.18: Elaborate description of humidity measurement setup.

Fig. 3.19 indicates the probed device inside the stainless steel sealed chamber. The optical microscopic image of electrodes and drop-casted GO with dimension are displayed in inset of Fig. 3.19.



Figure 3.19: Humidity sensing resistive device inside humidity test chamber.

3.8 Humidity Measurement

Measurements of the humidity were performed in ambient condition. The device was fixed inside the humidity chamber and a voltage of 2 V was applied across the electrodes. The devices were primarily purged with compressed dry air for 30 minutes to obtain a steady baseline current. The relative humidity (RH) inside the test chamber was maintained constant at 25% while purging the sample with compressed air. This was the baseline test condition for the samples. Once the baseline current of the sensors got stabilized, they were exposed to different % RH. Humid air for 10 minutes followed by 10 minutes of dry air was passed through device. Fig. 3.20 is displaying biasing arrangement for resistive type humidity sensor schematically.



Figure 3.20: Biasing arrangements for resistive type humidity sensor

3.9 Humidity Sensing Result

V-I characteristics of probed GO based device was observed in lab ambience so as to ascertain establishment of proper electrical connectivity. Fig. 3.21 shows V-I characteristics of probed GO based device with negligible hysteresis.



Figure 3.21: VI Characteristics of probed device with hysteresis

The GO based humidity sensor was exposed to six different values of RH (40%-88%). It was noticed that current through the GO based humidity sensor rises when it comes into contact of humid air. The response of the GO based humidity sensor was evaluated as:

Response =
$$\frac{I_{RH} - I_{air}}{I_{air}} \approx \frac{I_{RH}}{I_{air}}$$
 as $I_{RH} >> I_{air}$

where, I_{RH} is current through the humidity sensing device in humid environment and I_{air} is current through the sensor in dry environment.

The response obtained from the humidity sensing device was found to be large. The humidity sensor exhibited a response of ~180 times at 40% RH, whereas nearly 1200 times at 88% RH. This response is much larger in comparison to the responses published in recent past from graphene based moisture sensors [21-23]. Fig. 3.22 displays response of GO based humidity sensor towards six relative humidity (40% RH–88% RH).

A humidity sensor is characterized by various parameters. Response, response time, recovery time, repeatability and stability are mostly desired parameters. The response of the sensor found to be very high. The response time (denoted as the time required to achieve 90% of the highest response) and recovery time (denoted as the time required to achieve 90% of the baseline value) of the humidity sensor were quite fast as exhibited in Fig. 3.23 and Fig. 3.24 respectively. Response time altered in between ~2 seconds (40% RH) and ~5 seconds (88% RH) whereas recovery time changed in

between 2 seconds (40% RH) and 6 seconds (88% RH). Recovery operation did not require any heat treatment. Figure 3.25 and Fig. 3.26 exhibit how response and recovery time vary with humidity. These results are much higher than the published values in recent past [21, 23, 24-26].



Figure 3.22: Response of GO based sensor towards various relative humidity (40% RH-88%RH)



Figure 3.23: Response time of GO based humidity sensor



Figure 3.24: Recovery time of GO based humidity sensor



Figure 3.25: Response time variation with humidity of GO based sensor



Figure 3.26: Recovery time variation with humidity of GO based sensor

Humidity sensitivity of GO flakes is based on proton conduction which depends on level of hydration of GO flakes and quantity of oxygenated functional moieties attached with it. Proton is generated when water vapours are in contact with functional moieties of GO. Although ample functional moieties are present at GO nanosheets, still at low humidity very less quantity of protons are created owing to lack of vapour molecules. But at elevated level of humidity all the functional moieties come into contact with water vapours and thus create protons in full extent [27]. In order to obtain saturated current due to excessive proton creation at elevated humidity level larger time is needed than that of low level of humidity. As a result response time appears to be greater for elevated level of humidity. Same things occur in reverse order for recovery time when a completely hydrated GO flake is dried and come back to its primary stage [28-30]. As at higher humidity level nearly all the oxygenated functional moieties adsorb vapours, naturally GO flakes require larger time to recover to its primary condition.

This apart, linearity is also an important parameter for a humidity sensor. The response of humidity sensor is said to be linear if the difference in response at two % RH is proportional to the difference in % RH. Such response appears as a straight line in the calibration curve. Linear fitted response vs. relative humidity is displayed in Fig. 3.27.



Figure 3.27: Linear fitted response vs. relative humidity.

Apart from response, stability, quick response and recovery time, repeatability are also important parameters of a good humidity sensor. The GO based humidity sensor was exposed to 50% RH for five cycles continually and the response of GO based sensor showed excellent repeatability as exhibited in Fig. 3.28. In this process compressed dry air (25% RH) and humid air (50% RH) were passed at the interval of 10 minute.



Figure 3.28: Repeatability test of GO based sensor with 50% relative humidity.

GO plays a crucial part in moisture sensing owing to the presence of the hydrophilic oxygenated functional moieties. This theory was proved experimentally by testing humidity response of RGO where functional moieties are gradually eliminated through heat treatment. GO was thermally reduced for four different time span (30, 60, 120 and 180 min) and the humidity sensing behaviour of each of the devices were noticed so as to establish this fact experimentally. The comparative response of these RGO based humidity sensors along with the GO based humidity sensor towards 88% RH is displayed in Fig. 3.29.



Figure: 3.29: Comparative responses of GO and thermally reduced GO based humidity sensors (30–180 min) against 88% RH.

3.10 Variation of Humidity Response over Film Thickness

The proton conductivity σ can be evaluated by using the following relationship:

$$\sigma = l/(R \times d \times w)$$

Where, l is the distance between the electrodes, R is resistance, d and w are the thickness and width of the film, respectively [31, 32]. The analytical equation reveals this fact how proton conductivity is determined by thickness of drop-casted film, width of the film and gap between the electrodes [33]. However, to ensure the requirement of this widely used equation, some humidity response experiments have been performed using single, twice and thrice drop-casted GO film. It was noticed that humidity response of GO sheet was decreasing at larger film thickness. Width of
the film and distance between electrodes were unchanged during this time. This simple investigation discloses validation of the analytical equation referred previously. Fig. 3.30 exhibits thickness of the drop-casted film and humidity response of respective drop-casted GO film towards 88% RH. Grpaphene Oxide was drop-casted on Si/SiO₂ wafer to prepare sample of different thickness. After drying the film in ambient air film thickness was measured using Veeco Dektak profilometer. It was found that thickness was 512.93 nm for single drop-casting while it was 744.35 nm for twice drop-casting. Thickness was 1396.92 for thrice drop-casting. Fig. 3.31 to Fig. 3.33 demonstrate the Dektak thickness profilometric images of GO films.



Figure 3.30: Dependency of humidity response over thickness of drop-casted GO film



Figure 3.31: Dektak surface profilometer image of the onetime drop-casted GO film.



Figure 3.32: Dektak surface profilometer image of the twice drop-casted GO film



Figure 3.33: Dektak surface profilometer image of the thrice drop-casted GO film

3.11 Response Stability

One of the crucial fact in developing a humidity sensor is its reproducibly of response on different humidity sensing devices. Humidity response experiments were conducted taking three separate GO based humidity sensor devices so as to ensure response stability. Fig. 3.34 displays the comparative response plot of three similar GO based humidity sensor. It has been noticed that all the humidity sensors are offering nearly same response of approximately 1200.



Figure 3.34: Repeatability and variation of response from device to device.

3.12 Device Stability

Nanomaterials based humidity sensing devices are affected from response instability with the time. However, current work is showing quite high stability. The stability of GO based humidity sensor has been investigated month long. The sensor showed almost same response even test was carried out after more than a month (in between the tests the sensor was kept in ordinary lab ambience) Fig. 3.35 displays stability of GO based humidity sensor with time towards 88% RH.



Figure 3.35: Stability of GO based humidity sensing device over time

3.13 Summarized Results and Comparison of GO Based Humidity Sensor

Till now developed humidity sensors are unable to show an overall progress which has been significantly reduced in current work [34]. In Table 3.1 results are summarized of present work along with a comparative progress of GO based recently developed humidity sensors. Although capacitive GO based sensor have shown much higher response towards humidity still its response and recovery time are larger with respect to the current work [25]. Besides this, an ultrafast GO based impedance type humidity sensing device was developed [35], but this work did not mention any stability and reproducibility of its sensor performance.

Previous Works	Sensor Type	Materials Used	Response	Response / Recovery Time
Yao Yao <i>et</i> <i>al.</i> (2012) [22]	Impedance	Graphene Oxide	1100 times	not given
H. Bi <i>et al.</i> (2013) [24]	Capacitive	Graphene Oxide	37800	10.5 s 41 s
S. Borini <i>et</i> <i>al.</i> (2013) [35]	Impedance	Graphene Oxide	0.25-0.75 (Normalized Response)	30 ms 30 ms
S. Ghosh <i>et</i> <i>al.</i> (2015) [34]	Resistive	Graphene Oxide	1200 times	5 s 6 s

Table 3.1: Comparative Performance of GO Based Humidity Sensors

3.14 Sensitivity of other Carbon Material

Humidity sensing experiments have been executed taking graphite and carbon nanotube as sensing element also. It was observed that graphite was not sensing humidity at all in any concentration of aqueous solution (10 mg graphite fine powder purchased from Loba Chemie, India has been ultrasonicated initially with 2 ml of DI water and subsequently thinner solutions have been made). Fig. 3.36 is showing humidity response of graphite fine powder at relative humidity of 25% RH and 88% RH. Actually C atoms at graphite powder are not exposed to environment whereas in case of two dimensional GO nanosheets C atoms are almost exposed to surrounding environment [9]. So, graphite does not sense.



Figure 3.36: Humidity response of graphite fine powder

On the other hand, single-walled carbon nanotube was showing small sensitivity towards moisture offering a response of nearly 120 that was comparable with highly reduced GO. Carbon nanotube was purchased from Reinste Nano Ventures Private Limited, India. Unlike graphite powder, CNT is nanomaterial. They can be imagined as the outcome of folding graphite layers into carbon cylinders and may be produced of a single-wall or multi-wall layer of graphene. The unique electrical properties of single-wall carbon nanotubes (SWCNTs) have created a tremendous research platform on nanoelectronic devices and nanosensors. The conductivity of the semiconducting carbon nanotubes (CNTs) alters when water molecules are adsorbed on the walls. This adsorption gives rise to change in local electrostatic environment. But sensing performance of GO is better than pristine CNT as GO gathers lots of hydrophilic functional groups during its synthesis from graphite powder. Fig. 3.37 is showing humidity response of single walled carbon nanotube at relative humidity of 25% RH and 88% RH



Figure 3.37: Humidity response of Carbon Nanotube

3.15 Study of Electrode Effect on Response

It was found that the device dimension will not affect response of GO humidity sensor. Current through device obviously will be changed depending on the device dimensions (especially gap between electrodes, electrode width) but as normalized current (I_{RH}/I_{air}) are considered as sensor response, so ultimately the changes will cancel out each other keeping a constant sensitivity irrespective of device dimension. Fig. 3.38 is showing few of the fabricated electrodes of various dimensions.



Figure 3.38: Dektak surface profilometric images of fabricated electrodes on Si/SiO₂

3.16 Sensing Mechanism

The humidity sensing of hygroscopic nanomaterial towards humidity is function of the adsorption of water vapours. Actually the proton jumps in between adjacent water molecules. This mechanism is called Grotthuss mechanism [36, 37]. In case of sufficient water adsorption by the hygroscopic material, adsorbed water becomes bulk water and then proton conduction is mostly governed by vehicular mechanism where extra protons are attached with water molecules and propagate through the water molecules. Although this sensing mechanism has been thoroughly studied, there is still an obscurity about this mechanism [38, 39].

GO is an electrical insulator owing to its hydrophilic oxygenated functional moieties. They hinder the usual conjugation of graphene and make it an electrical insulator. But due to proton conduction at high level of humidity, reverse trend was noticed, as it showed excellent proton conduction in humid environment. Actually transport properties of graphene oxide are entirely different in presence of high relative humidity. The significant interaction of water molecules with hydrophilic functional groups of GO generates proton (H⁺). Now the protons hop between adjacent water molecules. The mobility of the proton is exceptionally large. In this way, protonconductivity is established following Grotthuss chain reaction [36]. At low relative humidity, water molecules are bound with the hydrophilic functional moieties of the GO sheets via double hydrogen bonding and they cannot proceed freely due to the limitation of double hydrogen bonding and for this cause GO sheets show high electrical resistance. Now at higher level of humidity, more water molecules are adsorbed by GO flakes resulting single hydrogen bond between GO and water molecules. Now the adjacent protons can easily move through water molecules [37]. In most of the cases proton (H⁺) conjugates with water molecules and form hydronium ion (H₃O⁺) [40-42].

On the other hand, in dry environment RGO has lower electrical resistivity than GO due to elimination of hydrophilic oxygenated functional moieties. But in presence of humidity the opposite phenomenon is observed [39]. The robust conjugation of water molecules with functional groups of GO actually generates protons and thus proton conduction is prevailed across GO nanosheets. But as GO is reduced thermally, the functional moieties start eliminating thereby lowering the proton conduction [43]. The sensing mechanism is schematically described in Fig. 3.39. The importance of functional groups was examined in the current work using an experimental investigation (Fig. 3.29). Thus performance of GO is better than that of RGO. Fig. 3.39 exhibits honeycomb graphene oxide lattice with oxygenated functional groups. It also indicates how proton (H^+) are created and further hydrated to form hydronium ion (H_3O^+).



Figure 3.39: Honeycomb graphene oxide lattice with oxygenated functional groups, water molecules along with created proton (H^+) and hydrated proton

3.16.1 Grotthuss Mechanism

In Grotthuss chain reaction mechanism, movement of H^+ is very fast exhibiting ultra high proton conductivity through hydrated graphene sheets [39, 43]. But segregated protons (H^+) are hardly available in aqueous medium. In bulk water, almost all protons are attached with H₂O molecules to form H₃O⁺ (hydronium ions). Some of the hydronium ions are further hydrated and constitute zundel ($H_5O_2^+$) and eigen ($H_9O_4^+$) cations. Amount of higher order cations depend on the degree of hydration. However, these cations eventually becomes H⁺ leaving water molecules they captured. Fig. 3.40 (a) displays the proton (H⁺) hopping through water molecules whereas Fig. 3.40 (b) shows how hydrated protons are formed [43, 44].



Figure 3.40: (a) Proton hopping mechanism (Grotthuss chain reaction) through water molecules (b) Hydrated proton formation

In spite of the widespread familiarity of the word 'Grotthuss' it is obvious that bulk liquid medium is most unlikely to provide a neat Grotthuss type proton transport [40]. Although proton jumping between adjoining hydrophilic sites may occur recurrently still it may not provide proper proton conduction due to absence of net charge transport. Fig. 3.41 displays schematic illustration of water mediated short distance proton transport.



water mediated short distance proton transport

Figure 3.41: Schematic illustration of water mediated short distance proton transport

3.16.2 Vehicular Mechanism

On the contrary, the hydrogen-bonded system is highly compact and restrains vehicular type charge transfer across the solvent. In case of excessive water adsorption vehicular mechanism dominates where the proton propagates through solvent. Actually proton disperses jointly with a vehicle like water molecules and forms hydrated proton $(H_3O^+, H_5O_2^+, \text{ and } H_9O_4^+)$. Later on the vehicle is released from the hydrated proton and thereby letting the charge transfer of protons through water molecules. The gross proton conduction is firmly determined by the vehicle transmission rate [45]. In the Grotthuss mechanism, protons are transported via the generation and destruction of hydrogen bonds in order to form proton jumping and so Grotthuss-type mechanism does not require a vehicle. Fig. 3.42 is showing schematic illustrations of Grotthuss and Vehicular type proton conduction.



Vehicle type transport

Figure 3.42: Schematic illustrations of Grotthuss and Vehicular type proton conduction.

3.16.3 Prediction of proton conduction

Proton conductivity of GO can be predicted using experimental and theoretical approaches.

Experimentally proton conductivity (σ) can be evaluated simply utilizing GO as conductive material in between two electrodes fabricated on non-conducting wafer. However, conductivity varies with resistance that is depended on humidity level whereas in theoretical method proton conductivity is predicted using intrinsic parameters of GO.

3.16.4 Experimental Conductivity Measurement of GO

Experimentally proton conductivity σ can be evaluated by using the following relationship:

$$\sigma = l / (R \times d \times w)$$

Where, l is the distance between the electrodes, R is resistance, d and w are the thickness and width of the films, respectively [31].

This analytical equation represents dependency of proton conduction on drop-casted film thickness, width and gap between the electrodes. Several humidity response tests have been carried out here using single, twice and thrice drop-casted GO flakes in order to show the requirement of the analytical equation. It was noticed that humidity response of GO film was decreasing for thicker film. Width of the film and electrodes gap was unchanged during this time. This experiment discloses validation of the frequently utilized analytical equation shown earlier. Fig. 3.31 has shown drop-cast thickness of single drop-casted GO film. Fig. 3.43 is displaying the distance between the electrodes l and width of the drop casted film w. R is found from voltage current relationship across the drop casted film at 88% RH.



Fig. 3.43: Dimension of drop-casted film and distance between two electrodes

$$l = 100 \mu m$$

$$R = \frac{2V}{41.412nA} = 48.3Mohm(at 88\% RH)$$

$$d = 512.93nm$$

$$w = 200 \mu m$$

$$\sigma = l/(R \times d \times w) = \frac{100 \,\mu m}{(48.3 Mohm \times 512.93 nm \times 200 \,\mu m)} = 0.02 \,S \,/\,m$$

3.16.5 Theoratical Conductivity Prediction of GO

Protons generate from dissociation of acid groups into water. They are divided into two groups: protons situated near to the channels surfaces that take part in the surface diffusion mechanism and those which are in the pore bulk region of the channel and other that take part in the Grotthuss mechanisms. A simple equation for the prediction of proton conductivity of GO membranes was derived by Choi et al [46]. The equation predicts the overall proton conductivity, σ_{H^+} and it is based on the various proton transport mechanisms within a proton conductive membrane.

$$\sigma_{H^{+}} = \xi_{i} \tau \left[\frac{F^{2}}{RT} \left(D_{H^{+}}^{\sum} C_{H^{+}}^{\sum} + D_{H^{+}}^{G} C_{H^{+}} + D_{H^{+}}^{E} C_{H^{+}} \right) \right]$$

where F is the Faraday constant, R is the molar gas constant, T is temperature (K) and $D_{H^+}^{\Sigma}$, $D_{H^+}^{G}$ and D_{H}^{E} are diffusion coefficients of protons for the surface, Grotthuss mechanisms, and enmasse diffusion mechanisms respectively. Also $C_{H^+}^{\Sigma}$ is concentration of protons participating in surface diffusion while C_{H^+} is concentration of protons participating in Grotthuss diffusion. ξ_i and τ represent porosity of membrane and the tortuosity factor, respectively [46,47].

3.16.6 Surface diffusion transport

In the nanocomposite membranes, surface diffusion coefficient is dependant not only on the type of surface acid groups of the host membrane and nanoparticle, but on their concentration as well.

$$D_{H^+}^{\sum} = \frac{1}{4} \left[\frac{\left(\frac{K_B T}{h}\right)(1+q)}{\left(\frac{1}{l_{\sum,M}^2}\right) \exp\left(\frac{\Delta G_M^{e,0}}{K_B T}\right) + \left(\frac{q}{l_{\sum,p}^2}\right) \exp\left(\frac{\Delta G_p^{e,0}}{K_B T}\right)} \right]$$

where q, K_B and h are moles of acid sites of nanoparticle/moles of acid groups of membrane, Boltzmann constant and Planck constant, respectively. $l_{\sum,M}$ and $l_{\sum,p}$ are jump length of the surface proton for acid groups of membrane and nanoparticles,

respectively. $\Delta G_{\sum,M}^{e,0}$ and $\Delta G_{\sum,p}^{e,0}$ are effective Gibbs free energy of activation of surface diffusion around the acid groups of the membrane and the nanoparticles, respectively.

3.16.7 Grotthuss Proton Transport

$$D_{H^{+}}^{G} = \frac{l_{G}^{2} \mu_{w}(Z_{H^{+}} q_{e^{-}})}{192\pi^{2} \eta(\xi_{r} \xi_{0}) R^{3} \delta^{2}} / \left[\ln \left\{ \frac{\tan(\theta_{I}/2)}{\tan(\theta_{F}/2)} \right\} \right]$$

where l_G , μ_w , Z_{H^+} , θ_I , θ_F , η , R and δ are jump length of proton in the Grotthuss

mechanism, the dipole moment of water, the charge number of a proton, the initial and the final angle of rotating water molecule, water viscosity, the hydrodynamic radius of the water molecules and distance between protons in the hydronium ion and proton accepting water molecules, respectively.

3.16.8 Conductivity Calculation of GO

At 88% RH humidity adsorbed water molecules becomes like bulk liquid and conduction process occurs by Grotthuss mechanism and total conductivity (σ_{H^+}) comprised of only Grotthuss transport.

$$\sigma_{H^{+}} = \xi_{i} \tau \left[\frac{F^{2}}{RT} \left(D_{H^{+}}^{\sum} C_{H^{+}}^{\sum} + D_{H^{+}}^{G} C_{H^{+}} + D_{H^{+}}^{E} \right) \right] = \xi_{i} \tau \left[\frac{F^{2}}{RT} \left(D_{H^{+}}^{G} C_{H^{+}} \right) \right]$$

It is calculated as $D_{H^+}^G \approx 7 \times 10^{-5} \, cm^2/s$ at room temperature [46, 47]

$$R = 8.314 J mol^{-1} K^{-1}$$

$$F = 96485 C mol^{-1}$$

$$T = 300 K$$

$$D_{H^{+}}^{G} \approx 7 \times 10^{-5} cm^{2} / s$$

$$C_{H^{+}} = 11.018 \times 10^{6} mol / m^{2}$$

$$\xi_{i} = 0.63$$

$$\tau = 1.36$$

So, $\sigma_{\mu^+} = 0.0186 S / m$

3.16.9 Specific Conclusion of the Conductivity Calculation

Proton conductivity of GO can be predicted using theoretical approaches where proton conductivity is calculated using intrinsic parameters of GO. On the other hand, proton conductivity can be evaluated experimentally simply by utilizing GO as conductive material in between two electrodes fabricated on non-conducting wafer. To validate the experimental work, proton conductivity of GO is also calculated by using theoretical approaches. Theoretical value of proton conductivity has found to be 0.0186S/m whereas experimentally it is 0.02S/m. So, deviation of experimental value from theoretical value is 7.53 %.

3.17 Summary

Chemically synthesized graphene oxide based humidity sensing device was fabricated on Si/SiO₂ substrate. The sensor exhibited significant response in the range between 40% and 88% RH. The response of GO based resistive type humidity sensor varied from ~180 times (40% RH) to ~1200 times (88% RH). The sensor is also quite fast. Response and recovery time are found to be within few seconds. This apart, substantial reproducibility and stability have been shown by GO based resistive type humidity sensor.

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Chapter 4

Functionalized GO Based Resistive Type Humidity Sensor

4. Introduction

Though GO based resistive sensor showed excellent performance in presence of humidity, however in this work effort was made to improve the sensor performance even further by functionalizing GO with metal oxides and polymer. In this respect, tin oxide nanoparticle was used with GO; because literature showed tin oxide can give good sensitivity in presence of humidity. Also, as polymer Nafion was chosen because from literature it was seen that Nafion was used extensively in fuel cell particularly because of its high proton conducting behaviour.

Section I: SnO₂ Functionalized GO Based Humidity Sensor

4.1 Introduction

 SnO_2 nanoparticle was mixed with GO systematically and humidity response was measured in each case. It was found that addition of SnO_2 nanoparticle in GO did not improve the performance of the sensor, in fact the response was lower compared to GO based humidity sensor.

4.2 Material Preparations

GO was synthesized using modified Hummers and Offeman method as discussed in earlier chapter. Graphite fine powder purchased from Loba Chemie, India was chemically exfoliated using NaNO₃, KMnO₄ and H₂SO₄. The synthesized GO was purified afterwards. On the other hand stannous chloride hydrate [SnCl₂·2H₂O] was purchased from Sisco Research Laboratories (SRL), India, in order to synthesize SnO₂ nanoparticle hydrothermally [1]. DI water was used in the experimentation as solvent (MilliQ, resistivity 18.2 M Ω at room temperature). The mixture of water dispersible GO and SnO_2 were then ultrasonicated to achieve SnO_2 functionalized (non covalent bond) GO. Fig. 4.1 shows GO/SnO_2 composites with different proportion.



Figure 4.1: GO/SnO₂ composite with different proportions.

4.3 Material Characterization

4.3.1 Optical Microscopy

Fig. 4.2 exhibits optical microscopic image of GO/SnO_2 composite. It indicates intermingling of GO and SnO_2 as composite. However, details of composite formation can be ensured at SEM and EDAX characterization.



Figure 4.2: Optical microscopic image of GO/SnO₂ composite

4.3.2 SEM

Surface morphology of GO, SnO₂ and their composite were characterized using Jeol SEM. SEM image displayed in Fig. 4.3 (a) discloses that synthesized GO consists of randomly aligned, thin, folded nanosheets adjoined with one another whereas Fig. 4.3 (b) and Fig. 4.3 (c) exhibit SEM images of SnO₂ and GO/ SnO₂ composite respectively.





(b)



Figure 4.3: (a) SEM Image of GO (b) SEM Image of SnO_2 (c) SEM Image of GO/SnO_2 nanocomposite

4.3.3 EDAX

EDAX is an extensively used method to identify the chemical constituents of a sample. This technique detects the X-rays created as the outcome of the electron beam interactions with the material. X-ray data is processed to acquire the percentage of each measured substance present in the sample particles. SEM-EDAX is very often employed to achieve morphological information of the material surface and recognition of chemical constituents. Fig. 4.4 shows EDS spectra of (a) GO (b) SnO₂ and (c) GO/SnO₂. In section (b) and (c) of Fig. 4.4 existence of tin, oxygen and carbon are clearly noticed with their atomic percentage. Fig. 4.4 (c) also shows decrease of tin and carbon contents when SnO₂ is mixed with GO.



Element	Weight%	Atomic%
СК	53.81	60.81
ОК	46.19	39.19
Totals	100.00	

(a)



Element	Weight%	Atomic%
ОК	40.16	83.27
Sn L	59.84	16.73
Totals	100.00	



(c)

Figure 4.4: (a) EDS spectra of (a) GO (b) SnO₂ (c) GO/SnO₂ nanocomposite

The EDAX of composite shows considerable decrease in C and increase in O atomic %, thereby signifying the presence of GO in the composite. Also, the existence of Sn (lesser % than in pure SnO₂) proved the presence of SnO₂ as GO does not contain Sn.

4.3.4 AFM

Here category of GO is same as GO used at chapter 3. So, AFM image with thickness of the GO flakes can be found in Fig. 3.3 of chapter 3.

4.4 Sensor Fabrication

Gold electrode was fabricated on Si/SiO_2 surface following the process described in chapter 3. Synthesized SnO_2 and GO/SnO_2 composites were drop-casted in between the gold electrodes using Tarsons T100 Accupipet and then dried in ambient conditions. Fig. 4.5 displays the fabricated devices of SnO_2 and GO/SnO_2 .



Figure 4.5: Fabricated humidity sensing devices

4.5 Humidity Measurement

The humidity measurement was performed in custom-made humidity sensing setup which comprised of an air tight stainless steel chamber. The details of humidity measurement of resistive type humidity sensor can be found in chapter 3.

4.6 Humidity Sensing Results

V-I characteristics of probed GO/SnO_2 based device was observed (in ambient condition) in order to ascertain establishment of electrical connectivity. Fig. 4.6 shows V-I characteristics with almost no hysteresis.



Figure 4.6: V-I Characteristics of GO/SnO₂ humidity sensing device

During the humidity measurement, the baseline humidity was fixed at 25% RH. SnO_2 , GO and GO/SnO₂ composite based sensors were kept inside the humidity test chamber and the humidity level was varied from 40% RH to 88% RH. It was noticed that current through the sensors rise when exposed to humidity. The response of the sensors was evaluated as:

Response =
$$\frac{I_{RH} - I_{air}}{I_{air}} \approx \frac{I_{RH}}{I_{air}}$$
 as $I_{RH} >> I_{air}$

where, I_{RH} -current through the sensor in high relative humidity and I_{air} -current through the sensor in dry air. Humidity sensing devices were made with different

proportion of GO and SnO₂. It was noticed that a controlled addition of SnO₂ with GO give maximum normalized response. First of all, humidity response of SnO₂ was measured. Humidity response of SnO₂ was found to be very less with respect to GO. SnO₂ nanoparticle then was mixed with GO in different proportion and humidity response was measured in each case. It was found that addition of SnO₂ nanoparticle in GO made response diminished. Fig. 4.7 exhibits a comparative responses of devices made of different composition of GO and SnO₂ exposed at 88% RH. However, addition of 1 mg SnO₂ with 3 ml GO gave a considerable response as shown in Fig. 4.7. The response got was around 1050. The sensing performance improves with increase in GO proportion. Still, its response was lower than GO based humidity sensor. Table 4.1 shows compositions of hybrid materials subjected to humidity response measurement.

	-
Material	Compositions
1,14,01141	compositions
SnO.	1 mg in 1 ml DI water
51102	I mg m I m DI water
SnO_2 -GO (1)	SnO_2 -GO (SnO_2 :1 mg + GO: 1 ml)
SnO_2 -GO (2)	SnO_2 -GO (SnO_2 :1 mg + GO: 2 ml)
SnO_2 -GO (3)	SnO_2 -GO (SnO_2 ·1 mg + GO·3 ml)

Table 4.1 Material Preparation of SnO₂-GO nanocomposites



Figure 4.7: Humidity responses of SnO₂/GO nanocomposites

4.7 Sensing mechanism

The conduction process of GO/SnO₂ is considered to be simultaneously electronic and ionic. In contrast to GO, there are no hydrophilic functional groups in SnO₂. It is generally believed that water molecules are adsorbed in surface of SnO₂. Nanoparicle of the SnO₂ is much more sensitive towards water vapours due to its high surface to volume ratio. The sensing mechanism is determined mostly on the charge transfer processes [2]. Tin oxide is inherently n-type material and water usually acts as donor molecule. The presence of water reduces the resistance of tin oxide because of more no of electrons available from water. However, in presence of GO proton transport takes place, and tin oxide does not support this proton conduction. So, this might be the reason of overall degradation of sensor performance where one is supporting electron conduction whereas the other is supporting proton conduction. In fact, proton conduction of composite might diminish because of conjugation of electron with proton (H⁺) and thereby neutralizing the charges.
4.8 Summary

GO was functionalized with SnO_2 in order to get larger response than GO based humidity sensor. SnO_2 nanoparticle was mixed with GO in different proportion and humidity response was measured in each case. It was found that addition of SnO_2 nanoparticle in GO made response smaller. It was also observed that amount of GO determine the magnitude of response and SnO_2 has very negligible contribution.

Section II: Nafion Functionalized GO Based Resistive Humidity Sensor

4.9 Introduction

As SnO₂ functionalized GO did not show any enhancement in response, alternative material was tried to enhance the response. It was noticed that Nafion polymer shows extensive proton conduction in hydrated environment, particularly in low relative humidity. It has been observed that GO based humidity sensor does not offer adequate sensitivity in low humidity [3, 4]. In order to address this drawback of pure GO based humidity sensor an attempt has been made to add Nafion systematically with GO. Nafion is a widely investigated ionomer because of its high proton conductivity. Nafion owing to its ultrahigh proton conductivity in hydrated condition has been extensively utilized in proton-exchange membrane fuel cells (PEMFCs) applications. GO/Nafion composite was characterized using SEM/EDAX, XRD and FTIR. The sensor was fabricated by drop casting GO/Nafion composite over gold electrodes patterned by photolithography on Si/SiO₂ substrate. The sensor exhibited excellent sensitivity towards humidity (18000 times at 88% RH) with response and recovery time within few seconds when GO and Nafion were mixed at 1:3 proportion. Proton conduction mechanism due to presence of hydrophilic functional groups in GO and Nafion have also been investigated in details here.

4.10 Material Preparation

GO was synthesized using modified Hummers and Offeman method. It was dispersible in aqueous medium. Graphite fine powder purchased from Loba Chemie, India was chemically exfoliated using NaNO₃, KMnO₄ and H₂SO₄. The synthesized GO was cleaned afterwards. 5 wt.% Nafion[®] in lower aliphatic alcohol and water was

bought from Sigma Aldrich, USA (274704-25ML). It is basically Nafion[®] perfluorinated resin solution containing 15-20% water. After that, GO and Nafion were mixed in different proportion to obtain GO/Nafion solution. Fig. 4.8 shows a digital image of synthesized GO and purchased Nafion along with their chemical formula. Fig. 4.8 also displays a composition of GO and Nafion. DI water was used in this experimentation as solvent (MilliQ, resistivity 18.2 MQ at room temperature).



Figure 4.8: Synthesized GO, Nafion and GO/Nafion composite (1:3)

Fig. 4.9 displays how aqueous solution of GO was mixed with Nnafion systematically. It was possible to mix water dispersible GO with Nafion polymer as it also contains 15-20% water.



Figure 4.9: Graphene Oxide / Nafion composite with different proportions

Fig. 4.10 shows process flow of Nafion functionalization of GO using a flow chart. It describes how GO is functionalized with Nafion step by step. At first, GO was synthesized usung modified Hammers method and it was mixed with Nafion systematically. Now, considering one ratio of mixing, they were ultrasonicated for half an hour to form good composite of GO and Nafion. But mixing them and ultrasonication always do not ensure proper composite formation or functionalization. For that reason composie was characterized using SEM, EDAX, XRD and FTIR. If one of the characterization fails to prove the proper composite formation then whole process was to start again from mixing of the GO and Nafion. Otherwise, composite is ready for further use.



Process flow of the Nafion functionalization

Figure 4.10: Description of the process flow of the Nafion functionalization

4.11 Material Characterizations

4.11.1 SEM

Surface morphology of GO and GO/Nafion nanocomposites were characterized using Carl Zeiss SEM. SEM image displayed in Fig. 4.11 (a) disclose that synthesized GO consists of randomly aligned, thin, folded nanosheets adjoined with one another whereas Fig. 4.11 (b) and Fig. 4.11 (c) exhibit SEM images of Nafion and GO/Nafion composite (1:3) respectively. SEM images explicitly disclose formation of GO/Nafion composites.



(a)



(b)



(c)

Figure 4.11: SEM images of (a) Graphene Oxide (b) Nafion (c) GO/Nafion composite(1:3)

4.11.2 EDAX

EDAX is an extensively used method to identify the chemical constituents of a sample. This technique detects the X-rays created as the outcome of the electron beam interactions with the material. Fig. 4.12 shows EDS spectra of (a) GO (b) Nafion and (c) GO/Nafion (1:3). In section (b) and (c) of Figure 4.12 existence of fluorine and sulphur are clearly noticed with their atomic percentage. Fig. 4.12 (c) also shows decrease of fluorine and sulphur contents and increase of carbon and oxygen when Nafion is mixed with GO.

\$ 0				Spectrum	2
0 1 Full Scale 552	2 cts Cursor: 0.00	3 4)0	4 5	6 7 ke	e٧
Element	Weight%	Atomic%			
ск ок	48.70 51.30	55.84 44.16			
Totals	100.00				

(a)



Element	Weight%	Atomic%
СК	23.49	32.64
ОК	15.45	16.11
FK	54.42	47.79
SК	6.64	3.46
Totals	100.00	

(b)



Element	Weight%	Atomic%
ск	36.25	46.23
ок	21.67	20.75
FK	39.31	31.70
S K	2.76	1.32
Totals	100.00	

(c)

Figure 4.12: EDS spectra of (a) GO (b) Nafion (c) GO/Nafion (1:3)

The EDAX of composite shows considerable increase in C and O atomic %, thereby signifying the presence of GO in the composite. Also, the existence of F and S (lesser % than in pure nafion) proved the presence of Nafion as GO does not contain F and S.

4.11.3 TEM

GO utilized in GO/Nafion composite was prepared by modified Hummers and Offeman method as described in Chapter 3. Details of TEM characterization with SAED pattern have been exhibited Fig. 3.2 of chapter 3.

4.11.4 AFM

Thickness of the GO flakes was found to be in between 2 to 2.5 nm. It has been shown in Fig. 3.3 of chapter 3.

4.11.5 XRD

X-ray Diffraction is an analytical technique that uses an inherent attributes of the xray beam, its wavelength and the laws of physics that evaluate how that beam interacts with matter for materials characterizations. Primarily the technique has been applied to well-ordered crystalline structures to identify crystal structures, determining phase composition, measurement of stress, orientation. Apart from this, XRD also includes the characterization of noncrystalline materials. X-ray diffraction analysis (XRD) of drop-casted samples was performed on PANalytical's X-ray diffractometer (X'Pert difractometer 3040/60) with monochromatic CuK α radiation. Data were recorded from 05° to 80°. The XRD spectra in Fig. 4.13 (a) reveal the oxidation of graphite powder wherefrom graphene oxide was synthesised [5]. Fig. 4.13 (b) indicates a major peak related to the carbonated structure of Nafion nearly at 2θ =18° [6]. Fig. 4.13 (c) shows peak for GO/Nafion (1:3) composite. The peaks are mostly originated from carbonated groups those are almost equally present in GO and Nafion.







(b)



Figure 4.13: XRD pattern of (a) GO (b) Nafion and (c) GO/Nafion (1:3)

4.11.6 FTIR

Fourier transform infrared spectroscopy is ideal for the recognition of both organic and inorganic materials. Aggregates of atoms (or functional moieties) are all coupled with characteristic infrared absorptions. Thus, infrared spectrometry is useful for the identification of functional moieties present within a material. The FTIR characterization was also carried out for sensing layers (as shown in Fig. 4.14). The FTIR spectra of GO shows an absorption peak at around 850 cm⁻¹ [7]. The FTIR spectra of Nafion shows absorption peaks at different wavenumbers which corresponds to different bonds as has been described in the literature [8]. The FTIR of GO/Nafion composite shows coexisting peaks of both GO and Nafion and hence ensure proper composite formation. FTIR spectra of the graphene oxide, Nafion and composite were recorded on a Agilent Technologies Cary 630 spectrometer. Fig. 4.14 shows FTIR spectra of (a) GO (b) Nafion and (c) GO/Nafion (1:3).



Wavenumber (cm⁻¹)



129



Figure 4.14: FTIR spectra of (a) GO (b) Nafion and (c) GO/Nafion (1:3)

4.12 Sensor Fabrication

Gold electrode was fabricated on Si/SiO_2 surface following the process described in chapter 3. Synthesized GO/Nafion was drop-casted in between the gold electrodes using Tarsons T100 Accupipet and then dried in ambient conditions. Fig. 4.15 displays the schematic of the device with dimension and scale. Fabrication process steps of this type of resistive device have already been shown in Fig. 3.6 of chapter 3.



Figure 4.15: Schematic diagram and dimensions of sensor device

Fig. 4.16 further demonstrates description of GO/Nafion based humidity sensing resistive type device in details.



Figure 4.16: GO/Nafion based humidity sensor

4.13 Humidity Measurement

The humidity measurement was performed in custom-made humidity sensing setup which comprised of an air tight stainless steel chamber. The details of humidity measurement of resistive type humidity sensor can be found in chapter 3.

4.14 Humidity Sensing Results

That (1:3) is not weight ratio, it is volume ratio of GO and Nafion. Actually mixture was prepared taking GO and Nafion solution using Tarsons's Accupipet T100 (Variable volume micro pipette: 10-100 μ l.). Here, volume was adjusted to100 μ l. Now GO/Nafion composite with different proportions were prepared. However, V-I characteristics of probed GO/Nafion resistive device was observed (in ambient environment) in order to ascertain establishment of proper electrical connectivity. Fig. 4.17 shows V-I characteristics of probed GO/Nafion based device with small hysteresis.



Figure 4.17: VI Characteristics of probed device with hysteresis

During the humidity measurement, the baseline humidity was fixed at 25% RH. The GO based sensor was kept inside the humidity test chamber and humidity level was varied from 40% RH to 88% RH. It was noticed that current through the GO sensor rise when exposed to humidity. The response of the GO sensor was evaluated as:

Response =
$$\frac{I_{RH} - I_{air}}{I_{air}} \approx \frac{I_{RH}}{I_{air}}$$
 as $I_{RH} >> I_{air}$

where, I_{RH} -current through the sensor in high relative humidity and I_{air} -current through the sensor in dry air.

Humidity sensing devices were made with different proportion of GO and Nafion mixture and humidity response was observed for each composition. It was noticed that a controlled addition of Nafion with GO give maximum normalized response. This is due to optimization between on humidity current and off humidity current of a particular device. However, when GO and Nafion were mixed in 1:3 ratio an ultrahigh response was found. A response of ~1400 times against 40% RH and around 18000 times against 88% RH were offered by the humidity sensing device. This response is substantially higher in contrast to the values published in recent past [9-11]. Fig. 4.18 exhibits a comparative responses of devices made of different composition of GO and Nafion exposed at 88% RH. Fig. 4.19 shows humidity response of best composition (GO:Nafion :: 1:3) at different humidity levels (40% RH-88%RH). The quality of a sensor is evaluated by various criteria like response, response time, recovery time, repeatability. This sensor found to be highly responsive. Like response, response time and recovery time are other important criteria of an ideal humidity sensor. The

response time (which is described as the time required to gain 90% of the maximum response) and recovery time (which is described as the time required to gain 90% of the baseline value) of the sensing device were also significantly rapid as demonstrated in Fig. 4.20 and Fig. 4.21 successively. Response time is 4 seconds while recovery time has been found as 5.5 seconds at room temperature without applying any heat treatment. It was observed that response and recovery time varied with humidity level. Fig. 4.22 and Fig. 4.23 display the variation of response and recovery time with humidity. The reason has already been explained in details at previous chapter. However, the large response along with these response and recovery time is better than the published results in literature in recent past [12-14].



Figure 4.18: Comparative responses of GO, Nafion and GO/Nafion composite of different proportions towards 88% RH.



Figure 4.19: Response of GO/Nafion (1:3) based humidity sensor to six different % RH (40%-88%)



Figure 4.20: Response time of GO/Nafion (1:3) based sensor



Figure 4.21: Recovery time of GO/Nafion (1:3) based sensor



Figure 4.22: Response time variation with humidity of GO/Nafion based sensor



Figure 4.23: Recovery time variation with humidity of GO/Nafion (1:3) based sensor

Sensor's repeatability or reproducibility towards a particular relative humidity level is also an useful parameter. The reproducibility of the GO/Nafion based sensor was tested by exposing to 50% RH for five cycles repeatedly and the response of the humidity sensor was found to be distinctly repeatable as can be observed in Fig. 4.24. Compressed dry air was purged for 10 minute in between two successive exposing to 50% RH for 10 minute.



Figure 4.24: Repeatability test of GO/Nafion (1:3) based sensor with 50% humidity

4.15 Sensing Mechanism

Nafion is an extensively studied ionomer because of its high proton conductivity in presence of high relative humidity. It is a perfluorosulfonic polymer. Fig. 4.25 shows the chemical structure of Nafion.



Figure 4.25: Chemical structure of Nafion

It unites the hydrophobicity of the perfluorinated polymer structure with the hydrophilicity of the end sulfonic acid function (-SO₃H). This property of Nafion creates a natural hydrophilic and hydrophobic nano separation. Ultimately, an immobile micro structure is established which absorbs and desorbs water molecules [15].

The salient feature of such micro structures is that their hydrophobic part provides superior mechanical stability even in highly humid environments, while the hydrated hydrophilic zones produce extremely large proton conduction. Actually the polymer material behaves as a chemically inactive highly permeable spongy material for the water of hydration, which actually exhibits significantly small interaction with the polymer except for the first three water molecules per sulfonic acid group needed for its initial hydration [16]. The better transport phenomenon of Nafion is, therefore, mostly an outcome of a superior hydrophilic / hydrophobic segregation, which happens automatically during the synthesis and hydration of the ionomer [17]. The

amount of sulfonation, which intensifies the hygroscopicity, also diminishes the morphological stability in the highly humid environment. There are few dissociated protons those stay near to the anion surface sites and take part in surface diffusion, whereas others with an elevated level of hydration engage in bulk diffusion following Grotthuss mechanisms [18]. In case of Nafion proton conduction actually occurs by the propagation of hydrated protons like H_3O^+ (hydronium ion), $H_5O_2^+$ (zundel ion) and $H_9O_4^+$ (eigen ion) which evolve from the utter dissociation of the sulfonic acid functional group. This is based on the postulate that sulfonic acid groups are adequately powerful acids so that ion pairs $SO_3^-H_3O^+$, $SO_3^-H_5O_2^+$ or $SO_3^-H_9O_4^+$ are formed. Fig. 4.26 shows generation and association of hydrated protons with sulfonic acid functional group [19, 20].



Figure 4.26: Generation and association of hydrated protons with sulfonic acid functional group

The proton conduction in Nafion is firmly determined by its nanostructure and degree of hydration. At low humidity, very few acid sites are dissociated and the interaction among water molecules through hydrogen bonding is small. In this condition, Nafion shows negligible conductivity due to very less amount of proton hopping limited within the surface area [21-23]. When water content is low, very few acid sites are dissociated and the interaction among water molecules through hydrogen bonding is poor. As a result, rate of proton transfer becomes very low. Proton hopping is limited basically to the surface region showing very low conductivity. Still proton conduction is much higher in case of Nafion in low humidity than that of GO. At high humidity level, however, the behavior of water in Nafion becomes like bulk water [24]. Therefore, two distinct water atmospheres become prominent in Nafion. As for an example, water molecules inside the central area of the pore is treated as "bulk water". Mobility of proton is very rapid in this region. On the contrary, water molecules close to the pore surface across the array of sulfonic groups is considered as "surface water" and the proton movement via the surface is significantly meager than that of bulk water. Thus proton conductivity of Nafion is consequence of weighted average of the surface and bulk conductivities [25]. Fig. 4.27 shows dissociation of sulfonic acid of Nafion in water and formation of hydrated protons those in turn take part in Grotthuss mechanism.



Figure 4.27: Dissociation of sulfonic acid of Nafion in water and formation of hydrated protons those in turn take part in Grotthuss mechanism.

4.16 Summary

Chemically synthesized graphene oxide and Nafion composite based humidity sensor was fabricated on Si/SiO₂ substrate. The sensor demonstrated exceptional humidity response in presence of moisture in the range between 40% and 88% RH. This happens due to the enormous proton conductivity of GO/Nafion nanosheets in hydrated conditions. This ultrahigh sensitive sensor also offers fast response and recovery time. Apart from this, GO/Nafion based humidity sensor has also shown excellent reproducibility.

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Chapter 5

Graphene Oxide/Nafion Based FET Humidity Sensor

5.1 Introduction

FET type sensors have some advantages over resistive or capacitive humidity sensors [1]. In FET architecture sensitivity can be adjusted using applied bias in the gate terminal [2, 3]. In this work, Graphene Oxide/Nafion composite based humidity sensing field effect transistor (FET) has been developed. GO and Nafion were intermingled systematically in order to maintain significant response even in low humidity. GO was synthesized using modified Hummers and Offeman method and Nafion was purchased from Sigma Aldrich, USA. A conducting silicon back gate FET has been fabricated using traditional microelectronics technology. GO/Nafion was drop-casted on patterned aluminium electrodes on Si/SiO2 substrate. It was used as channel material of FET. Patterned electrodes, conducting silicon, drop-casted material and SiO₂ served the purpose of source and drain, back gate, channel and dielectric of FET [4-6]. GO was characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). GO/Nafion composite was characterized using scanning electron microscopy (SEM), high resolution X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). GO/Nafion based sensor was exposed to six different relative humidity (RH %). The sensitivity of FET type sensor was appeared to be very high due to large proton (H⁺) conduction of GO and Nafion. The drain characteristics and transfer characteristics of GO and GO/Nafion based FET type sensors have been explored in various levels of humidity. However, the sensor displayed excellent sensitivity. Apart from this, the onset of proton conduction owing to interaction of hydrophilic functional moieties of GO and Nafion with water molecules have also been explained rigorously.

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5.2 Material Preparation

Material preparation is same as described in GO/Nafion based resistive type humidity sensor that has been described at section II of chapter 4. As GO/Nafion (1:3) found to be best sample, so FET based humidity sensor has been designed using that composition.

5.3 Material Characterization

AFM, TEM characterizations of GO can be found at Chapter 3 whereas SEM/EDAX, XRD and FTIR characterizations of GO/Nafion (1:3) can be found at section II of Chapter 4.

5.4 Sensor Fabrication

Two inch silicon wafer was cleaned at first using piranha solution ($H_2O_2:H_2SO_4:$ 1:1). After that, native oxide was removed using 1% buffered hydrofluoric (BHF) acid. SiO₂ layer of thickness 300 nm was developed on the silicon using thermal oxidation system made by Tempress System. Afterwards, a 150 nm thin aluminium layer was deposited on Si/SiO₂ substrate by thermal evaporation system. Aluminium electrodes were then fabricated on Si/SiO₂ substrate using photolithography process. Thereafter a small portion of SiO₂ layer was etched to unveil conducting silicon to be used as gate terminal of back gate FET. HPR 504 and HPRD 429 were used as photoresist and developer. This apart, buffered HF was employed as SiO₂ etchant. Aluminium was etched using aluminium etchant.

Synthesized GO and GO/Nafion (1:3) were drop-casted in between the aluminium electrodes using Tarsons T100 Accupipet and then dried at ambient conditions. Fig.

5.1 demonstrates details fabrication steps of FET type humidity sensor and Fig. 5.2 displays the schematic of the complete back gate FET device with dimension and scale. Fig. 5.3 shows actual fabricated back gate FET in details.



Figure 5.1: Fabrication steps of FET type humidity sensor



Figure 5.2: Schematic diagram and dimensions of back gate FET sensor device



Figure 5.3: Digital image of fabricated back gate FET device

5.5 Humidity Measurement

The humidity measurement was performed in custom-made humidity sensing setup which comprised of an air tight stainless steel chamber. The humidity sensor, placed inside shield chamber, was coupled with Agilent 4155C semiconductor parameter analyzer (SPA) via Agilent 16088-60046 test fixture. The humidity measurements were performed at room temperature. The device was fixed inside the humidity chamber. At first a dc sweep of 0V to 5V was applied in between the source and drain electrode keeping gate terminal constant at 2V. Next a dc sweep from -2V to 2V was given at gate terminal keeping drain bias at 2V. In this way drain characteristics and transfer characteristics were observed successively. The devices were primarily purged with compressed dry air for 30 minutes to obtain a steady baseline current. After a while, they were exposed to different relative humidity levels followed by 15 minute of dry air flow. Compressed dry air was allowed to enter into humidity test chamber through water bubbler in order to provide humid air. Humidity level of humid air was controlled by flow controller valve. In order to outlet the extra air an exhaust was placed at the humidity test chamber. In chapter 3 details of humidity test chamber can be found. Fig. 5.4 is showing biasing arrangements for FET type humidity sensor and Fig. 5.5 is showing probed humidity sensing device inside humidity test chamber.



Figure 5.4: Biasing arrangements for FET type humidity sensor



Figure 5.5: Humidity sensing FET type device inside humidity test chamber.
5.6 Humidity Sensing Results

GO/Nafion 1:3 is not weight ratio, it is volume ratio. It has been described at section II of Chapter 4.

5.6.1 GO based FET characteristics at ambient condition

First of all, GO based FET device was characterized in ambient environment in order to ensure proper FET action of the fabricated device. Fig. 5.6 shows drain current variation of GO based FET at ambient environment upon zero gate bias condition.



Figure 5.6: Drain current variation of GO based FET at zero gate bias in lab ambience

Afterwards, transfer characteristics of GO based FET were studied at ambient condition. Fig. 5.7 exhibits transfer characteristics of GO based FET at ambient condition. Lastly, in order to establish FET action firmly drain characteristics was

investigated at ambient condition. Fig. 5.8 displays the drain characteristics of GO based FET in ambient condition.



Figure 5.7: Transfer characteristics of GO based FET (at ambient condition)



Figure 5.8: Drain characteristics of GO based FET (at ambient condition)

5.6.2 GO based FET characteristics at variable humidity

Thereafter, the drain characteristics of GO based FET humidity sensor was explored to six different %RH (40%–88%) taking drain to source voltage (V_{DS}) in the range of 0-5 V and gate bias (V_{GS}) with 2 Volt. Fig. 5.9 shows how drain characteristics modifies with humidity.



Figure 5.9: Drain characteristics of GO based FET (at variable humidity)

The transfer characteristics of GO based FET humidity sensor was studied to six different %RH (40%–88%) taking gate to source voltage (V_{GS}) in the range of -2 to 2 V and drain bias (V_{DS}) with 2 Volt. Fig. 5.10 demonstrates how transfer characteristics modulate with humidity.



Figure 5.10: Transfer characteristics of GO based FET (at variable humidity)

Fig. 5.11 displays how transconductance modulates with relative humidity for a GO based humidity sensor.



Fig. 5.11 Variation of transconductance with relative humidity

5.6.3 GO/Nafion (1:3) composite based FET Characteristics at variable humidity

It was observed experimentally that only controlled addition of Nafion with GO can give maximum normalized current (I_{RH}/I_{air}). This is due to trade-off between on humidity current and off humidity current for a particular resistive type device. However, it was found that when GO and Nafion were blended in 1:3 ratio an ultrahigh normalized current was found. Fig. 4.17 shows comparative response of GO, Nafion and GO/Nafion composite of various proportions towards 88% RH.

During the humidity measurement, the baseline humidity was fixed at 25 % RH. The GO/Nafion (1:3) based FET humidity sensor was placed inside the humidity test chamber and humidity level was altered from 25% RH to 88% RH. It was observed that current through the GO sensor increased when exposed to humidity. Thereafter, the drain characteristics of GO/Nafion (1:3) based FET humidity sensor was explored to six different %RH (25%–88%) taking drain to source voltage (V_{DS}) in the range of 0-5 V and gate bias (V_{GS}) with 2 Volt. Fig. 5.12 shows how drain characteristics modifies with humidity.

The transfer characteristics GO/Nafion (1:3) based FET humidity sensor was studied to different %RH (25%-88%) taking gate to source voltage (V_{GS}) in the range of -2 to 2 V and drain bias (V_{DS}) with 2 Volt. Fig. 5.13 demonstrates how transfer characteristics modulate with humidity.

Fig. 5.14 displays how transconductance modulates with relative humidity for a GO/Nafion based humidity sensor. Fig. 15 shows how normalized current (I_{RH}/I_{air}) modulate with relative humidity.



Figure 5.12: Drain characteristics of GO/Nafion (1:3) based FET sensor to seven different % RH (25%-88%)



Figure 5.13: Transfer characteristics of GO/Nafion (1:3) based FET sensor to different % RH (25%-88%)



Fig. 5.14 Variation of transconductance with relative humidity



Fig. 5.15 Variation of normalized current (I_{RH}/I_{air}) with relative humidity Table 5.1 describes how sensitivity of GO based FET changes with % RH and applied bias voltages. Fig. 5.16 and Fig. 5.17 display dependency of sensitivity on relative humidity and bias voltage for GO based FET. Table 5.2 describes how sensitivity of GO/Nafion based FET changes with % RH. Fig. 5.18 and Fig. 5.19 demonstrate dependency of sensitivity on relative humidity and bias voltage for GO/Nafion (1:3) composite based FET. It is observed that sensitivity of GO/Nafion (1:3) composite based FET humidity sensor is far better than only GO based FET humidity sensor. In Fig. 5.16 to Fig. 5.19 it is noticed how resolution of sensitivity can be adjusted using applied gate bias voltage.

5.6.4 Sensitivity Calculation

The sensitivity of the FET type sensor was evaluated as:

$$S = \frac{\Delta I}{\Lambda RH\%}$$
^[7]

Table 5.1 Sensitivity of GO Based FET Humidity Sensor

Humidity	40%	50%	60%	70%	80%	88%
Sensitivity (V _{GS} =0V,V _{DS} =2V) (analogous to resistive sensor)	0.012	0.014	0.017	0.032	0.036	0.039
Sensitivity (V _{GS} =2V V _{DS} =2V)	0.277	0.381	0.395	0.716	0.796	0.814
Sensitivity (V _{GS} =2V,V _{DS} =5V)	1.498	1.748	3.245	5.391	5.429	5.867



Figure 5.16: Dependency of sensitivity of GO based FET on humidity.



Figure 5.17: Dependency of sensitivity of GO based FET on humidity.

Table 5.2 Sensitivity of GO/	Nafion (1:3) Based FET	Humidity Sensor
------------------------------	------------------------	-----------------

Humidity	40%	50%	60%	70%	80%	88%
Sensitivity	0.221	0.243	0.366	0.592	0.636	0.861
$(V_{GS}=0V, V_{DS}=2V)$						
(analogous to						
resistive sensor)						
Sensitivity	0.545	0.552	0.783	0.843	0.923	1.822
$(V_{GS}=2V V_{DS}=2V)$						
Sensitivity	75.858	78.453	93.285	96.489	106.651	132.343
$(V_{GS}=2V, V_{DS}=5V)$						



Figure 5.18: Dependency of sensitivity of GO/Nafion (1:3) based FET on humidity.



Figure 5.19: Dependency of sensitivity of GO/Nafion (1:3) based FET on humidity.

5.6.5 Comparative Performance of FET Humidity Sensors

In literature, among the developed FET type humidity sensors three works are worth mentioning including the current work. Their comparative analysis are mentioned at Table 5.3.

				•	
Authors	Materials Used	Response	Response &	Advantages	Disadvantages
			Recoverv		
			Time		
S. P. Lee <i>et</i> <i>al.</i> (1996)	TiO ₂	3.2 μA/%RH.	not mentioned	Response is larger than current work	No information about its response and recovery time Complex structure not cost effective
A. Paul <i>et</i> <i>al.</i> (2013)	CNT/DFC	0.57 (nA/RH%) (88% RH)	4 s 8 s	Simple structure Response time is faster than current work	Response is quite smaller and recovery time is larger than current work Zero gate bias FET Unstable
					composite
Current Work	GO/Nafion	132.343 nA/RH%	not calculated	Simple structure Low cost	Response is smaller than work of S.P Lee <i>et al</i> .
				Response is larger than work of A. Paul <i>et al</i> .	Response & Recovery time is not calculated

Table 5.3: Comparative Performance of FET type Humidity Sensors

5.7 Sensing Mechanism

FET based humidity sensor has been made using same composite as has been employed at resistive humidity sensor of chapter 4 (section II). In this section, sensing mechanism has been explained elaborately. Chemically synthesized graphene oxide and graphene oxide /Nafion based FET type humidity sensor were developed on Si/SiO_2 substrate using conventional microelectronics technology. GO/Nafion (1:3) composite based FET humidity sensor also showed considerable sensitivity towards humidity compared to resistive humidity sensor. Sensitivity was 132.343 nA/RH% at 88% RH taking V_{GS} and V_{DS} as 2V and 5V respectively.

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Chapter 6

Conclusions and Future Scope

6.1 Conclusion

Humidity sensing is crucial for various industrial applications (e.g. wafer processing, food processing, textile etc) and environmental monitoring (e.g. human comfort in smart building). A wide variety of humidity sensors have been developed over the years depending on transduction technique and materials used. Among them capacitive sensor is mostly available in the market. Major problem of capacitive humidity sensor is lack in long-term stability and hysteresis due to its polymer dielectric. It is also not cost effective because of its complex structure. On the other hand, resistive humidity sensor gains advantage owing to its simple structure and easy compatibility with CMOS platform. To date, different metal oxides (e.g. ZnO, SnO₂, TiO₂) have been employed for development of resistive humidity sensors, but they usually need micro heater for recovery operation. In this respect, carbon based nanomaterials like CNT, graphene are advantageous because usually they don't need application of heat. But they need to be functionalized to sense humidity and they too suffer from long term stability due to functionalization (if polymer is used for functionalization).

In this work, GO and functionalized GO based resistive and FET type humidity sensors have been developed. Here GO was synthesized using Hummers and Offemen method. It was characterized using FESEM, TEM, AFM, XPS and Raman spectroscopy. GO based sensor has found to give considerable sensitivity along with fast response and recovery (within few seconds). It has also exhibited excellent stability and reproducibility. The response of GO based resistive type humidity sensor varied from ~180 times (40% RH) to ~1200 times (88% RH) (six different humidity levels were used), which can be considered much superior compared to the resistive

humidity sensor results already published in the literature. Afterwards, GO was functionalized in order to enhance the response even further. It was initially functionalized with SnO₂ (as metal oxides show humidity sensing property). But GO/SnO₂ composite did not show any enhancement in sensitivity compared to the GO based sensor. On the contrary, when GO was functionalized with Nation polymer, it showed exceptionally good sensitivity towards humidity. The response got from GO/Nafion sensing layer was around 18000 times (against 88% RH). This is the response from the optimised GO/Nafion composite (1:3). The nano composite was made by controlled addition of Nafion with chemically synthesis GO.

Resistive humidity sensors were fabricated using conventional photolithography technique. At first, silicon dioxide was grown on silicon wafer and then gold electrodes were fabricated by thermal evaporation. Later, GO or functionalized GO were drop-casted on the electrodes to fabricate the devices.

Humidity measurement was carried out in a customarily made humidity test chamber. Device was probed inside the stainless steel air-tight chamber applying fixed bias voltage of 2V across electrodes. In FET type, test was carried out by applying gate and drain bias. It was observed that sensitivity can be adjusted using gate and drain bias. Here optimised GO/Nafion sensing layer (1:3) was used to develop the FET based sensor. FET humidity sensor also showed considerable sensitivity towards humidity. Sensitivity was 132.343 nA/RH% at 88% RH taking V_{GS} and V_{DS} as 2V and 5V respectively. Apart from these, the humidity sensors have also shown excellent reproducibility and stability.

The large response achieved from GO and GO/Nafion sensing layer were because of excellent proton conductivity in the adsorbed water layer. The large sensitivity is also

because of inherent defects and presence of different functional groups in GO sensing layer. The addition of Nafion improves the performance even further because Nafion helps to promote proton conductivity. I believe the work carried out on GO and GO/Nafion based resistive and FET type devices will help in developing future generation resistive and FET type humidity sensors.

6.2 Future Scope of the Work

The future scope of the work will be developing such sensors on the CMOS platform and its interface electronics. Thus one will be able to achieve a single chip solution of humidity sensor and circuit on the same silicon die. This will be low power, compact and low cost. The other work might be to develop a rigorous sensing mechanism model of GO/Nafion sensor's proton conductivity in presence of humidity.

Appendix A

Working principle of different characterization techniques

XPS

XPS is utilized to study the surface chemistry of both conducting and insulating materials. It supplies the required information from the top 10 nm of a sample with a spatial resolution between 3 to several hundred micron. As a surface is exposed with X-rays in vacuum and it conveys its energy to a core-level electron, electron is scattered from its primary condition with a kinetic energy determined by the incident X-ray and binding energy of the atomic orbital from which it is derived. The energy and intensity of the released photoelectrons are investigated to recognize and find out the concentrations of the elements available. These photoelectrons emit from a depth of less than 10 nm and so, the information acquired also comes from a depth of less than 10 nm.

FTIR

FTIR depends on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption relates particularly to the bonds exist in the molecule. The frequency ranges are estimated as wave numbers typically over the range 4000 – 600 cm⁻¹. The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is similar to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies the existence of various chemical bonds and functional moieties exist in the sample. FTIR is particularly useful for recognition of organic molecular and compounds owing to the range of functional moieties, side chains and

cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range.

XRD

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to generate monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample creates constructive interference with diffracted ray when conditions obeys Bragg's Law ($n\lambda = 2d \sin \theta$). This law connects the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then identified, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be obtained due to the random dispersion of the powdered sample. Conversion of the diffraction peaks to dspacings permits detection of the mineral because each mineral has a set of unique dspacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based on generation of X-rays in an Xray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

SEM

A scanning electron microscope (SEM) scans a focused electron beam over a surface to generate an image. The electrons in the beam communicate with the sample, producing various signals that can be used to attain information about the surface topography and composition. The electron microscope was constructed when the wavelength became the limiting factor in light microscopes. Electrons have much shorter wavelengths, allowing better resolution.

Scanning electron microscopy (SEM) is a technique for high-resolution imaging of surfaces. The SEM uses electrons for imaging, much as a light microscope uses visible light. The advantages of SEM over light microscopy include much higher magnification (>100,000X) and greater depth of field up to 100 times that of light microscopy. Qualitative and quantitative chemical analysis information is also attained utilizing an energy dispersive x-ray spectrometer (EDS) with the SEM. The SEM creates a beam of incident electrons in an electron column above the material chamber. The electrons are generated by a thermal emission source, such as a heated tungsten filament, or by a field emission cathode. The energy of the incident electrons can be as low as 100 eV or as high as 30 keV depending on the evaluation objectives. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of the column direct and position the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging. The beam can also be focused at a single point or scanned along a line for x-ray analysis. The beam can be focused to a final probe diameter as small as about 10 Å.

AFM

The atomic force microscope (AFM) is one kind of scanning probe microscopes (SPM). SPMs are developed to estimate local properties, such as height, friction,

magnetism, with a probe. To acquire an image, the SPM raster-scans the probe over a small area of the sample, measuring the local property simultaneously.

AFMs operate by measuring force between a probe and the sample. Normally, the probe is a sharp tip, which is a 3-6 um tall pyramid with 15-40nm end radius. Though the lateral resolution of AFM is low (~30nm) due to the convolution, the vertical resolution can be up to 0.1nm.

To acquire the image resolution, AFMs can generally detect the vertical and lateral deflections of the cantilever by using the optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photo-detector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever.

Piezo-ceramics position the tip with high resolution. Piezoelectric ceramics are a class of materials that expand or contract when in the presence of a voltage gradient. Piezoceramics make it possible to generate three-dimensional positioning devices of randomly high precision.

In contact mode, AFMs utilize feedback to regulate the force on the sample. The AFM not only estimates the force on the sample but also controls it, allowing acquisition of images at very low forces. The feedback loop comprises of the tube scanner that controls the height of the tip; the cantilever and optical lever, which identifies the local height of the sample; and a feedback circuit that strive to keep the cantilever deflection constant by adjusting the voltage applied to the scanner. A well-constructed feedback loop is mandatory to microscope operation.

The transmission electron microscope (TEM) uses on many of the same optical principles as the light microscope. The TEM has the adjoied advantage of larger resolution. This augmented resolution allows us to study ultrastucture of organelles, viruses and macromolecules. Specially made materials samples may also be viewed in the TEM. The light microscope and TEM are commonly employed in conjunction with each other to complement a research project.

Since electrons are very small and easily deflected by hydrocarbons or gas molecules, it is necessary to use the electron beam in a vacuum environment. A series of pumps are used to accomplish an adequate vacuum for this purpose. Rotary Pumps are the first in the series. They are also called the "roughing pumps" as they are used to initially lower the pressure within the column through which the electron must travel to 10-3 mm of Hg range. Diffusion Pumps may achieve larger vacuums (in the 10-5 mm Hg range) but must be backed by the rotary pump. The diffusion pump also maintains pressure. In addition a Turbo, Ion, or Cryo Pumps backed by the preceding pumps may be utilized when an even larger vacuum is necessary.

EDAX

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a chemical microanalysis method utilized in conjunction with scanning electron microscopy (SEM). The EDS technique detects x-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as 1 μ m or less can be processed.

When the sample is bombarded by the SEM's electron beam, electrons are emitted from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an x-ray is ejected to balance the energy difference between the two electrons' states. The x-ray energy is characteristic of the element from which it was ejected.

The EDS x-ray detector measures the relative abundance of emitted x-rays versus their energy. The detector is typically a lithium-drifted silicon, solid-state device. When an incident x-ray strikes the detector, it generates a charge pulse that is proportional to the energy of the x-ray. The charge pulse is converted to a voltage pulse (which becomes proportional to the x-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The energy, as determined from the voltage measurement, for each incident x-ray is sent to a computer for display and further data evaluation. The spectrum of x-ray energy versus counts is evaluated to evaluate the elemental composition of the sampled volume.

Raman Spectroscopy

Raman spectroscopy, a molecular spectroscopy which is noticed as inelastically scattered light, permits for the interrogation and identification of vibrational (phonon) states of molecules. As a result, Raman spectroscopy gives an invaluable analytical tool for molecular finger printing as well as monitoring changes in molecular bond structure (e.g. state changes and stresses & strains).

In comparison to other vibrational spectroscopy methods, such as FT-IR and NIR, Raman has different important advantages. These advantages stem from the fact that the Raman effect manifests itself in the light scattered off of a sample as opposed to the light absorbed by a sample. As a result, Raman spectroscopy requires little to no sample preparation and is insensitive to aqueous absorption bands. This property of Raman facilitates the measurement of solids, liquids, and gases not only directly, but also through transparent containers such as glass, quartz, and plastic.

Similar to FT-IR, Raman spectroscopy is highly selective, which allows it to identify and differentiate molecules and chemical species that are very similar. Figure R-1 shows an example of five similar molecules – Acetone, Ethanol, Dimethyl Sulfoxide, Ethyl Acetate, and Tolune. Although each chemical has a similar molecular structure, their Raman spectra are clearly differentiable, even to the untrained eye. Using Raman spectral libraries, it is easy to see how easily Raman spectra can be used for material identification and verification.

Appendix B

List of Publications from the PhD Work

- 1. Sourav Ghosh, Ruma Ghosh, Prasanta Guha, and Tarun Bhattacharyya. "Humidity Sensor Based on High Proton Conductivity of Graphene Oxide." IEEE Transaction on Nanotechnology, vol. 14, no. 5, pp. 931-937, 2015.
- Sourav Ghosh, Ruma Ghosh, Prasanta Guha, and Tarun Bhattacharyya. "Enhanced Proton Conductivity of Graphene Oxide/Nafion Composite Material in Humidity Sensing Application" IEEE Transaction on Nanotechnology (Accepted on 12th June 2016) IEEE Xplore DOI: 10.1109/TNANO.2016.2580739

Appendix C

National/International Conferences

 Sourav Ghosh, Prasanta Kumar Guha and Tarun Kanti Bhattacharyya "Effect of Temperature and Electrode width on Reduced Graphene Oxide based FET Performance", Nano India 2015, 29 & 30th January 2015, Nano Mission, Dept. of Science & Technology, New Delhi, SASTRA University, Thanjavur, Tamil Nadu, India.

CURRICULUM VITAE

Address: Sourav Ghosh C/O:Prankrishna Ghosh Vill+P.O: Gurap Dist: Hooghly Pin code: 712303 Mobile: 9432976270 Email: <u>sourav.ghosh@ece.iitkgp.ernet.in</u> <u>sourav.ghosh.vlsi@gmail.com</u>

Career Objective:

To utilize my technical skills towards a challenging carrier in a growth oriented leading edge organization where professionalism is respected and which will provide opportunities for continuous growth and advancement.

Teaching Experience: 5 years

Designation	Dept.	Institute	From	То
Part time lecture	ETC	Ramakrishna Mission	July	December
		Shilpapitha , Belgharia, India	2006	2006
Lecturer	ECE	Saroj Mohan Institute of Technology	January	July
		(Degree Engineering Division)	2007	2007
		Guptipara , Hooghly		
Lecturer	ICE	Calcutta Institute of Engineering &	August	June
		Management, Kolkata	2007	2011

Educational Background: PhD

Degree	Institute	Department	Date of	Broad Area of	Title of Thesis
			Joining	Research	
				Silicon and Carbon	Development of
PhD	IIT	E & ECE	18.07.2011	Based	Graphene Oxide
	Kharagpur			Nanostructure and	Based Humidity
				Devices	Sensors

Publication

Sourav Ghosh, Ruma Ghosh, Prasanta Guha, and Tarun Bhattacharyya. "Humidity Sensor Based on High Proton Conductivity of Graphene Oxide." IEEE Transaction on Nanotechnology, vol. 14, no. 5, pp. 931-937, 2015.

Sourav Ghosh, Ruma Ghosh, Prasanta Guha, and Tarun Bhattacharyya. "Enhanced Proton Conductivity of Graphene Oxide/Nafion Composite Material in Humidity Sensing Application" IEEE Transaction on Nanotechnology (Accepted on 12th June 2016) IEEE Xplore DOI: 10.1109/TNANO.2016.2580739

Conference

Sourav Ghosh, Prasanta Kumar Guha and Tarun Kanti Bhattacharyya "Effect of Temperature and Electrode width on Reduced Graphene Oxide based FET Performance", Nano India 2015, 29 & 30th January 2015, Nano Mission, Dept. of Science & Technology, New Delhi, SASTRA University, Thanjavur, Tamil Nadu, India.

Degree	University	Course Name	Year of	C.G.P.A
			Passing	
M.Tech	Jadavpur	VLSI Design &	2010	8.33
	University	Microelectronics		
		Microelectronics		
		Technology		
1^{st}	2^{nd}	3 rd	4 th	Project Grade
Semester	Semester	Semester	Semester	
Grade	Grade	Grade	Grade	
8.76	8.07	7.63	7.18	10

Degree	Institute Name	Course Name	University	C.G.P.A	Year
B.Tech	B.P.Poddar	Electronics	West Bengal	7.78	2001
	Institute of	&	University of		to
	Management &	Communicati	Technology		2005
	Technology	on			
		Engineering			

Name of the Examination	Year	Board / University	Percentage
Higher Secondary Examination.	2001	West Bengal Council of Higher Secondary Exam.	75.2%
Madhymik Pariksha (Secondary Exam.)	1998	West Bengal Board of Secondary Exam.	82.5%

Technical Skills:

- Microelectronics Fabrication Technology, Nanoelectronics, Nanosensors, chemical sensors.
- Microprocessor, FPGA/VHDL, Microcontroller (PIC/8051/ARM).
- Silvaco TCAD, Cadence EDA, PSPICE (Orcad), TSPICE, C, MATLAB,
- > Analog and Digital VLSI, Analog and Digital Circuits.
- AutoCAD, ChemDraw, Avogadro, Origin.

Personal details:	Date of Birth	:	25th December 1982
	Father's name	:	Mr. Prankrishna Ghosh
	Nationality	:	Indian
	Sex	:	Male

I certify that all the above information is true to the best of my knowledge and belief

Date: 20.06.16

Sourav Ghosh