Effect of Graphene Derivatives and its Concentration for Soil Moisture Sensing Properties

by

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MASTER OF TECHNOLOGY
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Declaration

I hereby declare that

i) the thesis comprises of my original work towards the degree of Master of Technology in Information and Communication Technology at Dhirubhai Ambani Institute of Information and Communication Technology and has not been submitted elsewhere for a degree,

ii) due acknowledgment has been made in the text to all the reference material used.

N. Panchal.

Nikul Panchal

Certificate

This is to certify that the thesis work entitled Effect of Graphene Derivatives and its Concentration for Soil Moisture Sensing Properties has been carried out by Nikul Panchal for the degree of Master of Technology in Information and Communication Technology at *Dhirubhai Ambani Institute of Information and Communication Technology* under my/our supervision.

P. Vinay 05 July 2022

Vinay S Palaparthy
Thesis Supervisor

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Contents

Abstract

In this thesis work, we devised a different concentration and morphology of graphene oxide-based susceptible capacitive sensor. This sensor is designed as an inter digitated electrodes (IDE) and drop cast of chemically synthesized graphene oxide as the sensing platform. The IDE has fabricated by the MEMS fabrication technique. Response of the sensor changes from 1745% to 6275% for the soil moisture change from 1% to 23%. The noticed response time is 280 to 300 seconds to measure soil moisture. During in situ soil moisture measurement salt concentration is one factor that affects response and for that, we notice that output varies by 6%.

List of Principal Symbols and Acronyms

GO	Graphene Oxide
GQD	Graphene Quantum Dot
rGO	Reduced Graphene Oxide
XPS	X-ray photoelectron spectroscopy

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CHAPTER 1
Introduction

Monitoring the soil moisture at in situ application would bring out the best health of the plants. Continuous monitoring will result in high quality of croup. For centuries, farmers have used various coverings to physically protect crops from weather inconsistencies. The technology used to cover crops has evolved, but the motivation remains the same: weather changes are risky for high-value vegetable crops. Freezes, droughts, floods, and other weather events all-cause yield dips and production inconsistencies. So just as I insure my apartment against fire, farmers invest in technologies that minimize crop loss.

Maintaining the soil moisture at an optimal level between wilting point and field capacity. Measurement for soil moisture can be carried out in both laboratory and field conditions. At laboratory conditions, the standard gravimetric method uses to dry soil for 24 hours at 105°C. This method is often referred to measure soil moisture due to the accuracy of detection. During in situ application soil is charged with different salt concentrations and it will mandate that the soil moisture sensor should be independent of salt concentration. This soil moisture sensor has a change in capacitance of 6%.

Researchers have reported a study on graphene oxide with a fixed concentration. They took a particular concentration of GO and give a study on it but here we have done work on different concentrations and figured out the best sensitive concentration. Then after we fixed the concentration of GO we took different morphology of the fixed concentration of GO and figure out the best morphology for the optimum concentration.

Graphene is a two-dimensional nanomaterial, the most widely studied nanomaterial is graphene because it has the top electrical and sensing properties. GO has an oxygen functional group which increases the hydrophilic properties of GO. The oxygen functional intensifies the sensitivity of water molecules present in the soil.

CHAPTER 2

Literature Review

The designed a robust graphene oxide (GO) based capacitive sensor which is highly sensitive to soil moisture. For 0.1mg/ml the sensor response changes by 340% and 370% over soil moisture changes from 1% to 55% for red and black soil, respectively. GO sensor array shows a fast response time of 100–120 seconds for the soil moisture measurements. For in situ soil moisture measurements, the diurnal temperature and salt concentration.The sensor response changes by 340% and 370% over soil moisture changes from 1% to 55% for red and black soil, respectively. GO sensor array shows a fast response time of 100–120 seconds for the soil moisture measurements. For in situ soil moisture measurements, the diurnal temperature and salt concentration[5].The sensor is based on graphene quantum dots (GQDs) with 0.5mg/ml concentration and is highly sensitive. . The conductance of IDE structure with GQDs changes from 0.06×10^{-6} / Ohm to 0.68×10^{-6} / Ohm in white clay as the gravimetric moisture content changes from 4% to 45%. For bentonite soil, the conductance of the sensor changes from 0.06×10^{-6} / Ohm to 0.48×10^{-6} / Ohm across the gravimetric moisture range of 11% to 90%[2]. The sensor probe having dimensions $22 \times 4 \times 0.5\ cm^3$, embedded with a series of five microsensors (scalable according to the need), is developed using a graphene oxide (GO) sensor array with 0.2mg/ml.It has been observed that, for black soil, all of the microsensors displayed response in the range of 500%550% when the soil water content is varied from 3.2 to 55.5%. The graphene oxide-based array probe sensor (GO-APS) shows fast response and recovery time of 140 and 20 s, respectively, for 10% soil moisture samples. The soil moisture profile has been monitored up to a scale of 20 cm depth using the fabricated design. In-depth soil moisture profiling shows a maximum deviation of ±2.4% compared with a standard oven-drying method. The lump formation effect in soil mass showed a maximum deviation of ±4% for the GO-APS array[7].A series of materials such as Graphite oxide (GO), Molybdenum disulfide (MoS2), Vanadium oxide (V2O5), and Molybdenum oxide (MoO3) are tested in realizing a receptor layer that can efficiently sense soil moisture. The corresponding increase in the sensitivities for MoO3, GO, MoS2, and V2O5 are 13%, 11%, 30%, and 9% respectively, for a variety of temperature up to 45 °C. A temperature variation of 25 °C to 50 °C showed a minimal increase in the sensitivity response for all the devices. We further demonstrated a record sensitivity of 540 % with MoS2 in black soil and the corresponding response time was 65 s. Finally, the recovery time for the MoS2 sensor is 27 s, which is quite fast[8]. Graphene quantum dots (GQDs) with concentration of 1mg/ml the quantum dot variety of graphene represent a new group of quantum dots with exciting properties. Herein we report the electrochemical synthesis of GQDs with size ranging from 3 to 5 nm in diameter from graphene oxide (GO) at room temperature with LiClO4 in propylene carbonate as the electrolyte. when soil water content varies from 0% to 32%, then sensor resistance changes by 99% and 97% for the red soil (silt loam) and black soil (clayey), respectively. We found that sensor response time was around 180 s for the both silt loam and clayey soils[3]. Soil moisture and temperature are important variables in controlling the exchange of water and heat energy between the land surface and the atmosphere through evaporation and plant transportation. As a result, soil temperature and moisture play a significant role in the development of weather patterns and the production of precipitation and irrigation. Current techniques for detecting soil moisture and temperature such as gamma attenuation, soil heat flux, and GPR are mostly surface measurements and these surface measurements cannot provide profound temperature and moisture profile. The sensor is based on a shear stress principal, which the microsensor chip combines a proprietary polymer sensing element and Wheat stone Bridge piezoresistor circuit to deliver two DC output voltages that are linearly proportional to moisture and temperature[1]. A moisture microsensor based on poly(3,4-ethylenedioxythiophene–poly(styrene-sulfonate) (PEDOT–PSS) conductive polymer is developed and presented in this paper. The change in electrical characteristics of the PEDOT–PSS polymer film is used to determine its sensitivity and working mechanism when exposed to different levels of moisture content. The output characteristics, the change in electrical sheet resistance of the PEDOT–PSS film versus the percentage change in relative humidity (%RH), show that the conductivity of the film decreases when it is exposed to increasing levels of moisture content[4]. The surface functionalisation is confirmed by FTIR, SEM and contact angle measurements. The sensor exhibited a maximum response of 28mV towards 93% RH with sensitivity of 64 μV/0.1% RH. Sensitivity value of 43.6, 275 and 78.6μV/0.1% change in the moisture content for bentonite soil, white clay and sand, respectively, are achieved[6].

CHAPTER 3

Experimental Section

3.1 Synthesis of graphene oxide (GO)

The modified hummers method has been used to synthesize graphene oxide from graphene powder. For 0.1mg/ml concentration we took 1grams of graphite with H_2SO_4 of 62 grams and also $NaNO_3$ of 0.76 grams. Afterward, this mixture is stirred in an ice bath at 500-600 rpm. Then remove the solution from the ice bath and add 0.5 grams of $KMnO_4$ to the solution. Then cool the solution for 5 hours and then stirred the solution for 5 days at 300 RPM. Afterward gradually added 100ml of H_2SO_4 in an aqueous solution for about 1 hour. Then stirred the solution for 2 hours. Afterward, 3 grams of H_2O_2 is added to the solution and stirred for 2 hours. Then the solution was used to purify 15 times with centrifugation at 5000 rpm for 5 min and by adding a mixed aqueous solution of H_2SO_4 and H_2O_2 in the solution for removing the oxidant ion. Steps for cleaning are performed copiously with deionized water. At the end highly dispersed aqueous brown-colored solution of GO is obtained.

3.2 Fabrication and Packaging of Micro-sensor

Fabrication of Inter-digitated electrodes (IDE) done using microelectronics fabrication process. First of all p-type silicon wafer for 100 orientation and 250 μm thickness has been cleaned with RCA clean wet bench. Then after as shown in figure 3.1(i) with a thermal oxidation furnace of 2 inches, a layer of 1 μm grown on a silicon wafer. Then a layer of positive photo-resist (PPR) S1813 is spin-coated with lithography process on the Si wafer at 3000 rpm using PPR spin coating and after it a pre-bake at 90°C as shown in figure 3.1(ii). A mask is made with a dimension of around 1500 μm x 2400 μm to pattern the PPR with IDE. For PPR to take the structure of IDE, it is exposed to UV light using Karl Suss MJB-3 mask aligner and then post-baked for 2 min at 90°C. Then after IDE pattern is developed by

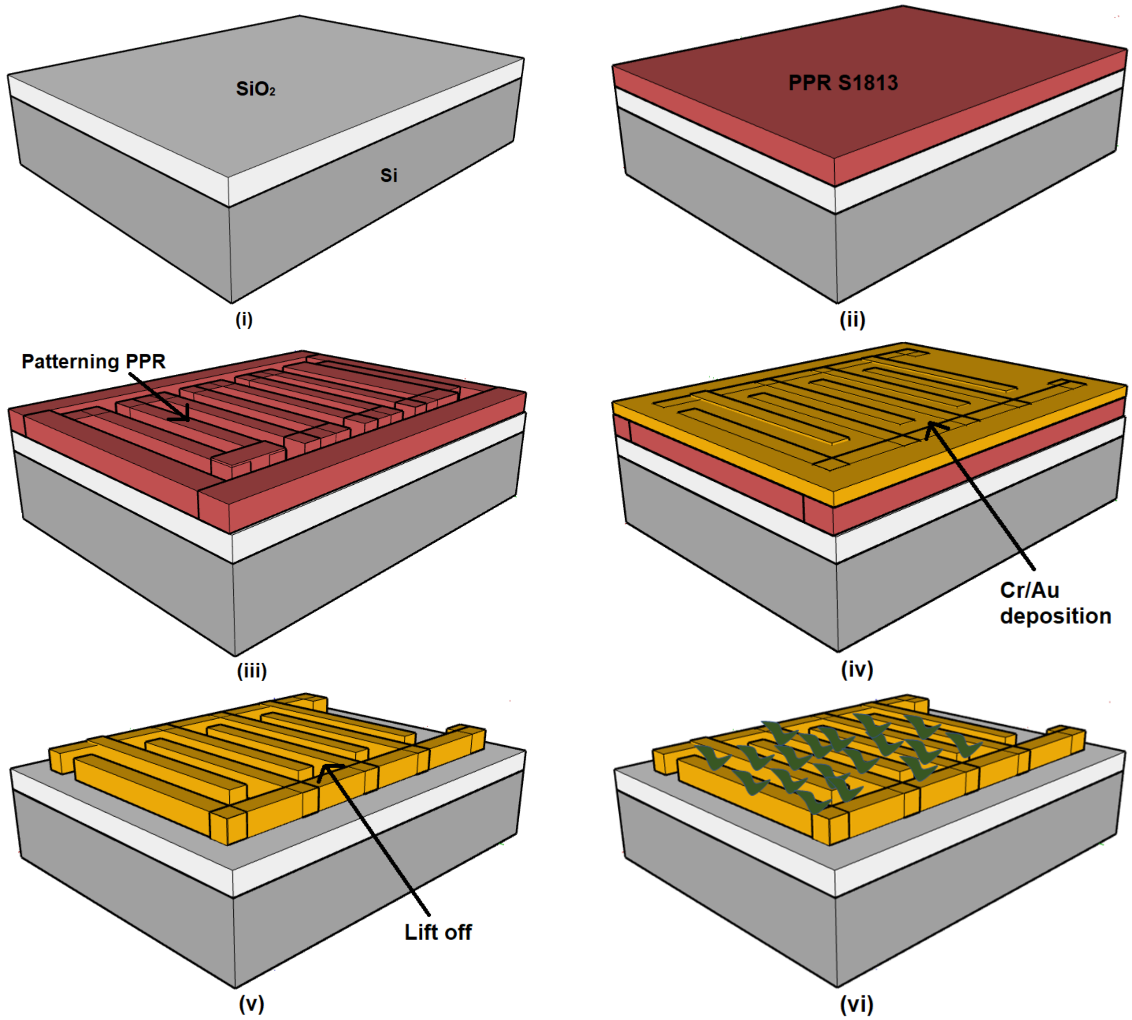


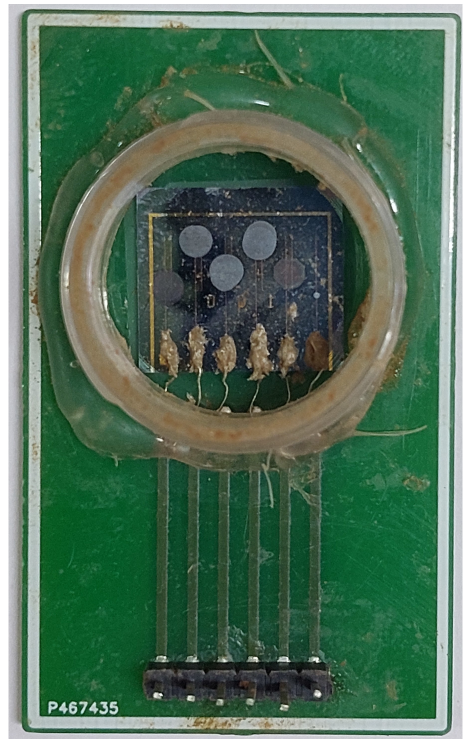
Figure 3.1: Inter digitated electrode structure fabrication process

dipping the Si wafer in MF319 solution for 30 seconds as shown in figure 3.1(iii).

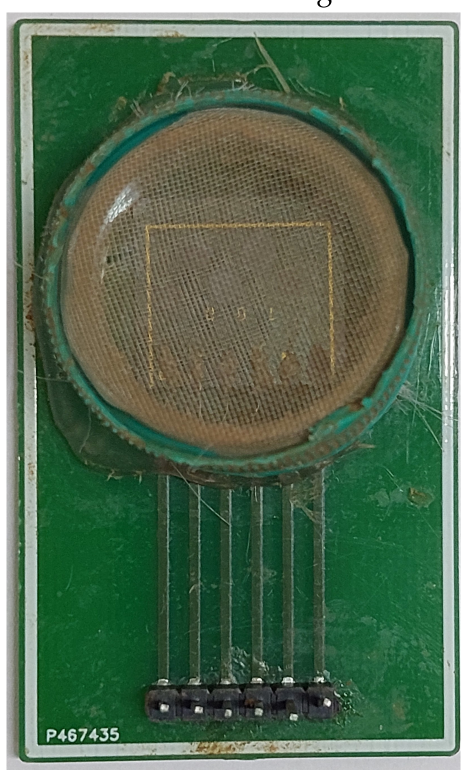
Further using DI water Si wafer is rinsed and dried using N_2 gas. Then after using Au thermal evaporation Cr/Au is deposited on SiO_2 as shown in figure 3.1(iv). Further Cr/Au present on PPR and also PPR is removed by lift-off as shown in figure 3.1(v) then clean the Si wafer ultrasonically for 1-2 min. Fallowing by wafer is cleaned with IPA and then rinsed with distilled water. Then after 20 μL of GO sheets water collided suspensions dispersed in water for 0.1 mg/mL is drop cast between IDE as shown in figure 3.1(vi) and air-dried for 3-4 hours before any electrical measurements.

Now the Si wafer is placed on PCB and pulled out a wire from the Si wafer to PCB using epoxy as shown in figure 3.2(i). On another side, buck strips are shoulder to bring out connections. To cover the Si wafer a plastic cover is placed and on the topside, a net is used to stop soil to come in contact with the Si wafer as shown in figure 3.2(ii) and figure 3.2(iii).

(a) Si wafer placed on PCB and pull out a wire from Si wafer to PCB



(b) Cover Si wafer with plastic covering



(c) Cover top part of Si wafer with net

Figure 3.2: Packaging of Si wafer on PCB

3.3 Preparation of soil sample

The preparation of soil samples plays a vital role in error-less measurement. Collect the soil sample from the agriculture field and then over dried the sample for 24 hours at 105°C. This process removes the water contained in a soil sample. Then in over dried soil sample add water to achieve desired water content and keep for maturing for 48 hours. Afterward to know the soil moisture of the prepared soil sample by standard gravimetric method, which gives gravimetric water content.

3.4 Experimental setup

First of all these experiments are performed at laboratory conditions with a temperature of 25°C and humidity of 50% RH. Take GO sensor packaged in place cover and raped by the net as shown in figure 3.3(i) and a mold takes a soil sample with know moisture as prepared as shown in figure 3.3(ii). Then deploy the sensor in the soil sample and wait for 3 min to achieve the perfect time to start reading. Then connect the LCR meter(HIOKI IM 3536) to the electrodes of the sensor as shown in figure 3.3(iii) and the value of capacitance is seen on the LCR meter display as shown in figure 3.3(iv).

(a) GO sensor

(b) Soil sample in mold mad GO sensor deploy in a soil sample

(c) Connection of Go sensor with LCR meter

(d) Sensor deploy in soil sample connected with LCR meter

Figure 3.3: Experimental setup

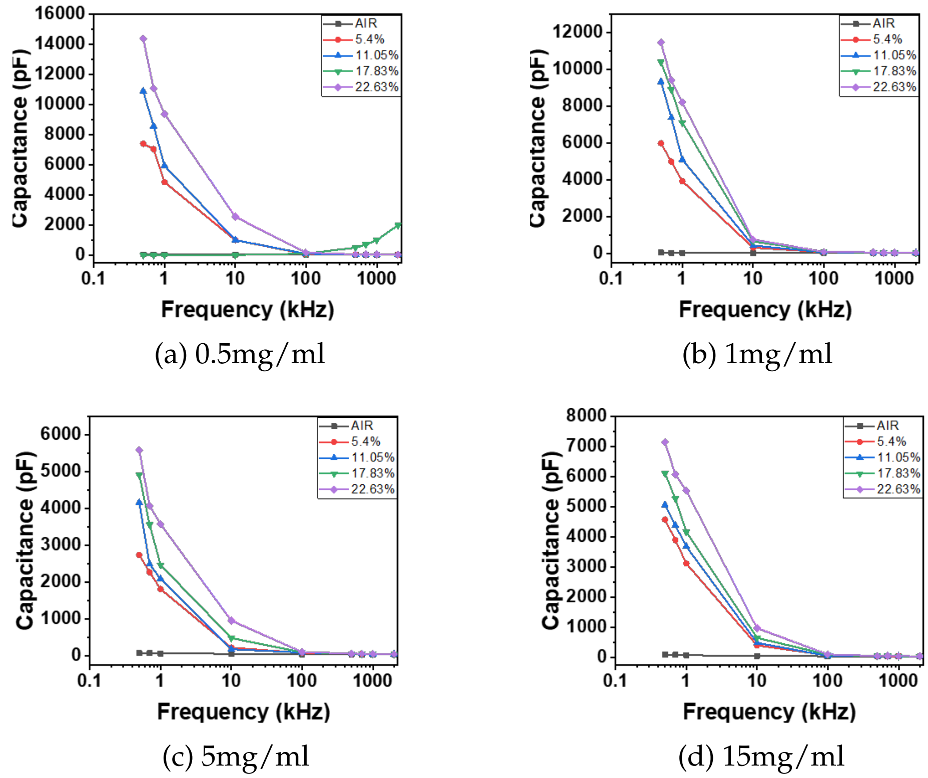
CHAPTER 4

Results and Discussions

4.1 Go sensor response to different soil moisture for different frequency for different concentration

Now measurements are taken with to sensor for different soil moisture at different frequency. As shown in figure 4.1a, 0.5 mg/ml of concentration is taken, the frequency is swapped from 500Hz to 2MHz, as the frequency increase there is decrease in capacitance at lower frequency and at higher frequency capacitance is very low. The same scenario is shown in 1mg/ml, 5mg/ml and 15mg/ml as shown in figure 4.1b, 4.1c and 4.1d respectively. And as we increase the soil moisture there in increase in capacitance, let focus on 1kHz frequency of 5mg/ml concentration as the moisture increase from air fallow by 5.4%, 11.05%, 17.83% and 22.63% there in increase in capacitance gradually.

It is observed that at lower frequencies capacitance is higher and at a higher frequency than 10kHz capacitance is lower. This is happen because at the lower frequency the electric field direction changes slower which affect the space charge polarization of absorbed water molecule. And when the frequency has increased the change in direction of electric field direction changes rapidly and the polarization of absorbed water molecule cannot catch up at this higher frequency hence the dielectric constant is small and independent of RH.



(a) 0.5mg/ml (b) 1mg/ml

(c) 5mg/ml (d) 15mg/ml

Figure 4.1: Frequency response of GO at different concentration

4.2 Go sensor response to different concentrations for different frequency

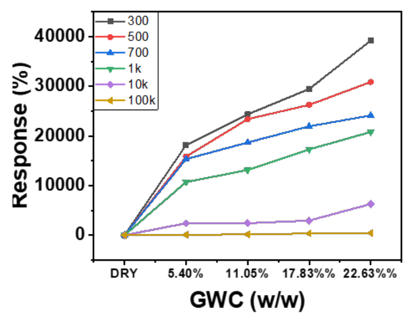
As shown in figure 4.2a the change in capacitance if shown concerning dry soil sample. As the soil moisture increases the change in capacitance also increases. This scenario is take place for all 0.5mg/ml, 1mg/ml, 5mg/ml and 15mg/ml concentration. And also for particular soil moisture as the frequency increase the change in capacitance decreases.

4.3 Go sensor hysteresis study for different concentration

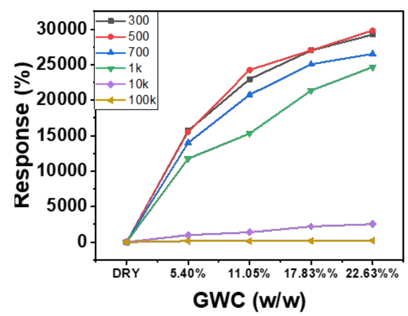
To calculate the error in sensor hysteresis performed, the first capacitance of the sensor takes in air and gradually deploys in a soil sample with increasing soil moisture this process is known as absorption, and then after gradually deploying the sensor in soil moisture in decreasing manner, this process is known as desorption. Hysteresis curve of 0.5mg/ml, 1mg/ml, 5mg/ml and 15mg/ml is shown in figure 4.3a, 4.3b, 4.3c and 4.3d respectively. This graph shows that the maximum error that occurs in the GO sensor is about ±2.5%.

4.4 Go sensor response time for different concentration

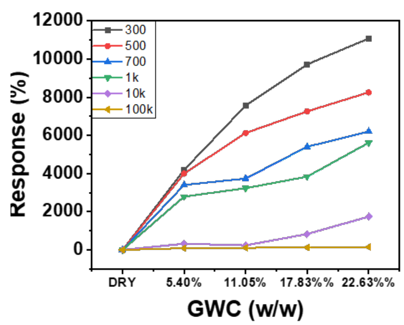
Response time shows how fast is the sensor is and response time of GO is shown in figure 4.4a, 4.4b,4.4c and 4.4d for 0.5mg/ml, 1mg/ml, 5mg/ml and 15mg/ml respectively. The response time of each concentration is 300 seconds.



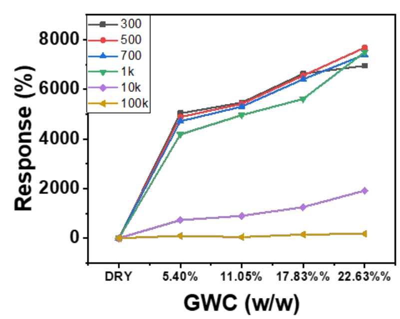
(a) 0.5mg/ml



(b) 1mg/ml

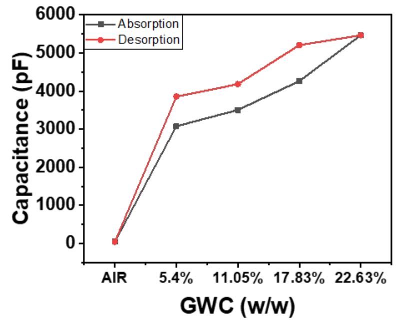


(c) 5mg/ml

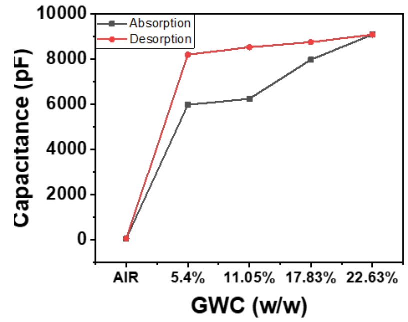


(d) 15mg/ml

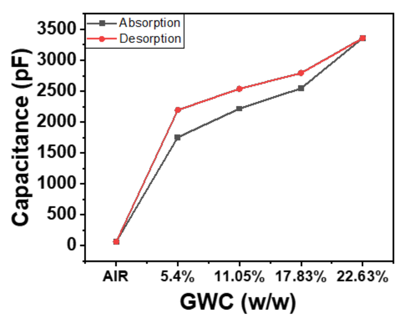
Figure 4.2: Response of GO at different concentration



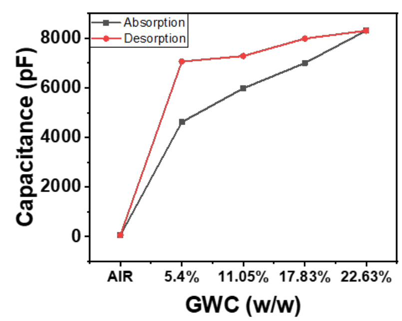
(a) 0.5mg/ml



(b) 1mg/ml

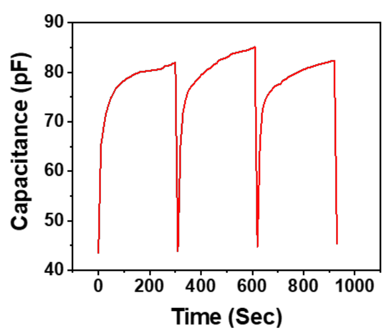


(c) 5mg/ml

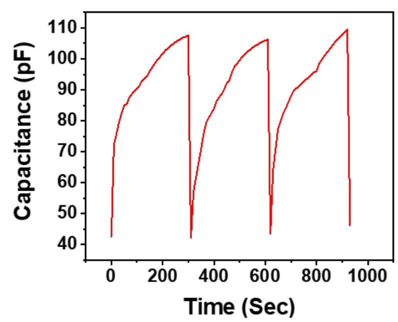


(d) 15mg/ml

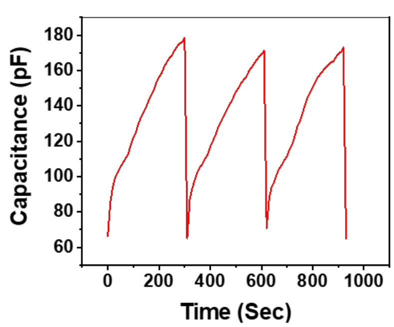
Figure 4.3: Hysteresis study of GO at different concentration



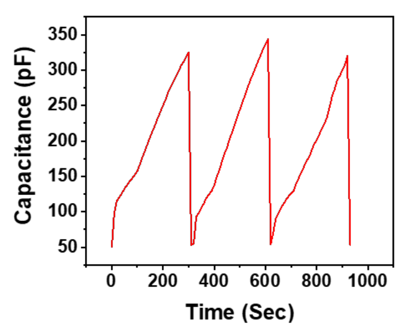
(a) 0.5mg/ml



(b) 1mg/ml



(c) 5mg/ml

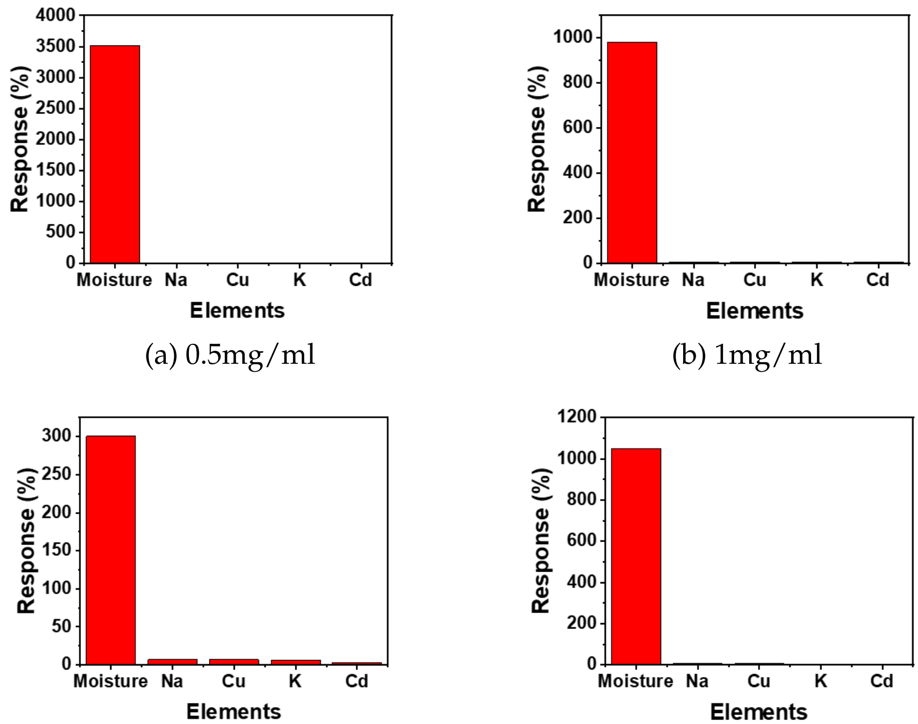


(d) 15mg/ml

Figure 4.4: Response time of GO at different concentration

4.5 Go sensor selectivity for different concentration

At in situ application soil contains some salt so sensor should be more sensitive to moisture present in soil rather then any salt. As shown in figure 4.5a, 4.5b, 4.5c and 4.5d for 0.5mg/ml, 1mg/ml, 5mg/ml and 15mg/ml respectively, this graphs show that GO sensor is most sensitivity to H_2O rather then Sodium Chloride, Potassium Chloride, Cupric Chloride and Cranium Chloride.



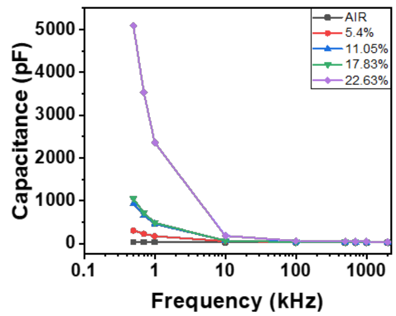
(a) 0.5mg/ml (b) 1mg/ml

(c) 5mg/ml (d) 15mg/ml

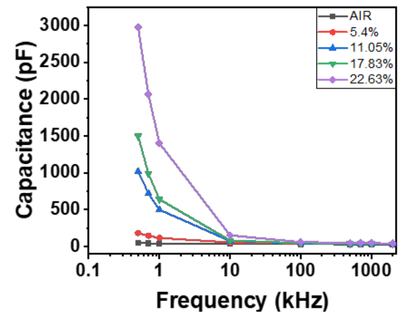
Figure 4.5: Selectivity of GO at different concentration

4.6 Go sensor response to different soil moisture for different frequency for different morphology

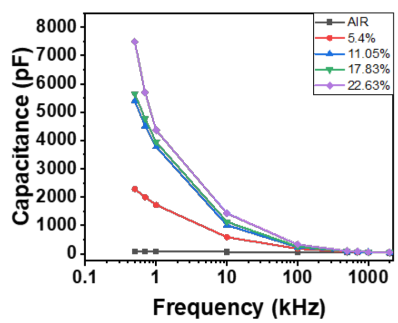
As the frequency response give study about capacitance of sensor with respect to different frequency, as shown in figure 4.6a, 4.6b, 4.6c, 4.6d and 4.6e at lower frequency the capacitance of GO sensor is high and as the frequency increase the capacitance of sensor decrease.



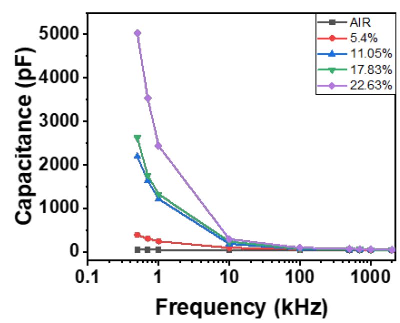
(a) GO



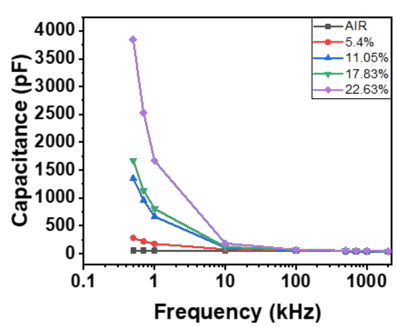
(b) rGO



(c) GO Polymer



(d) GQD



(e) carbon Nano graphite

Figure 4.6: Frequency response of GO at different morphology

4.7 Go sensor response to different morphology for different frequency

To identify that sensor is how much sensitive to change in soil moisture, as shown in figure 4.7a, 4.7b, 4.7c, 4.7d and 4.7e the as the soil moisture increase the change in capacitance also increase for different frequency. And for any particular soil moisture as the frequency increase the response of GO sensor decrease.

4.8 Go sensor hysteresis study for different morphology

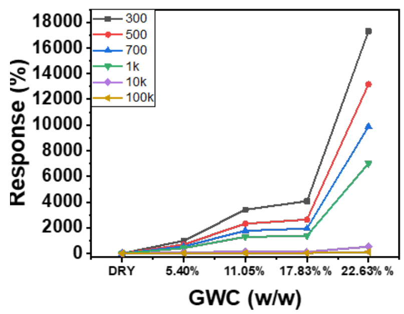
The study of hysteresis shows the error in soil moisture concerning capacitance. As shown in figure 4.8a, 4.8b, 4.8c, 4.8d and 4.8e first the GO sensor is place in air then deploy in soil moisture in increasing manner and this process is known as adsorption and then gradually decrease the soil moisture and a hysteresis type curve is plotted which shows the error in soil moisture.

4.9 Go sensor response time for different morphology

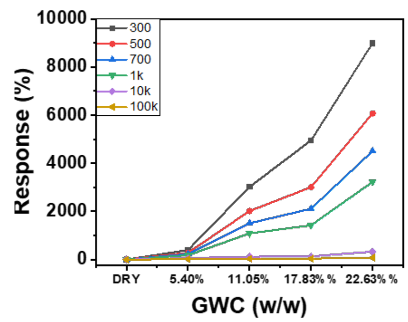
GO sensor should have good response time and for this response time study is more important and as shown in figure 4.9a, 4.9b, 4.9c, 4.9d and 4.9e the response time of GO, rGO, GO Polymer, GQD and Carbon Nano graphite respectively, which gives that the response time is of200 seconds.

4.10 Go sensor selectivity for different morphology

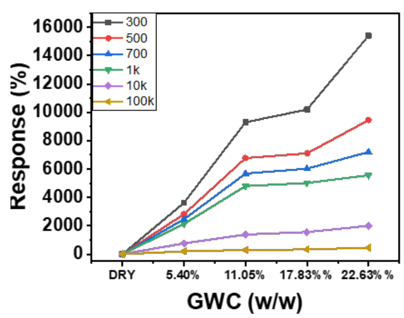
Every agriculture soil have some amount of salt present in it like Sodium Chloride, Potassium Chloride, Cupric Chloride and Cranium Chloride so GO sensor should be less sensitive to such salt, So selectivity study is perform and as shown in figure 4.10a, 4.10b, 4.10c, 4.10d and 4.10e the Go sensor for GO, rGO, GO Polymer, GQD and Carbon Nano graphite are much more selective to moisture compare to salt.



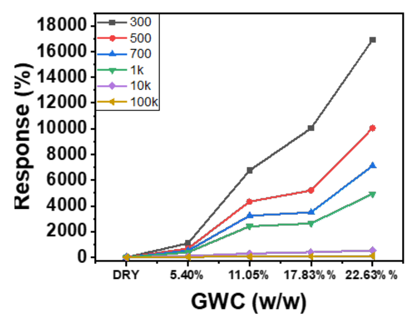
(a) GO



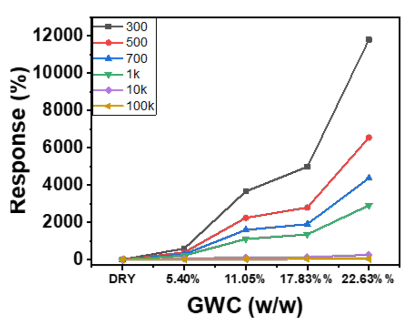
(b) rGO



(c) GO Polymer

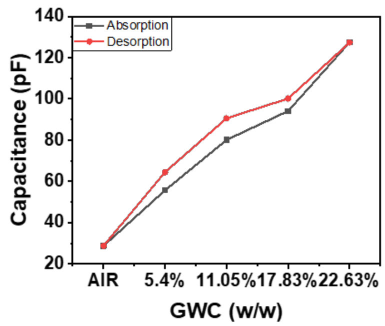


(d) GQD

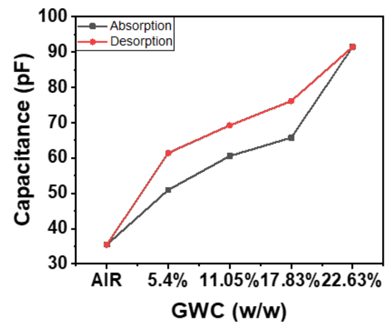


(e) carbon Nano graphite

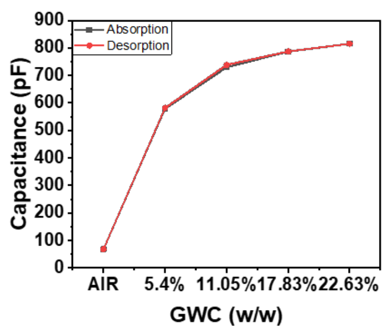
Figure 4.7: Response of GO at different morphology



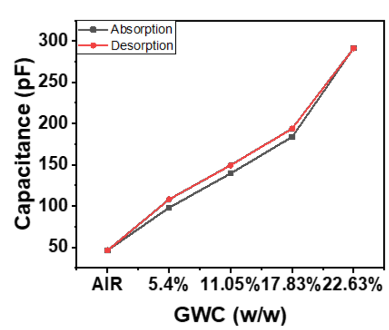
(a) GO



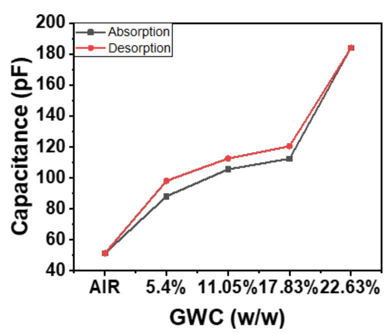
(b) rGO



(c) GO Polymer

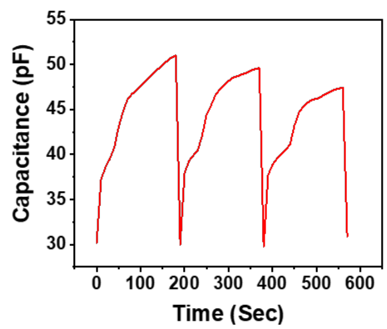


(d) GQD

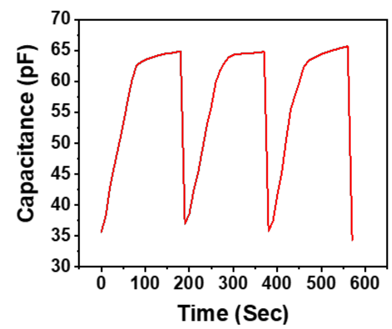


(e) carbon Nano graphite

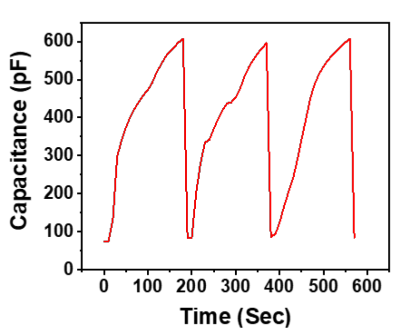
Figure 4.8: Hysteresis study of GO at different morphology



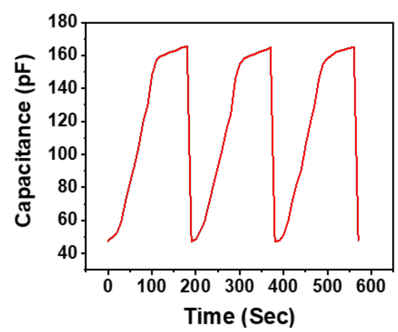
(a) GO



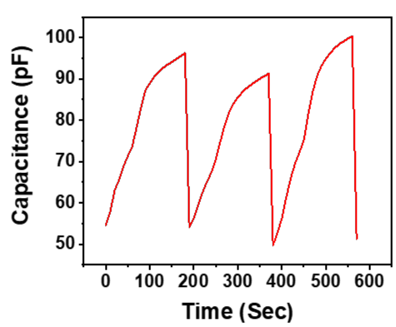
(b) rGO



(c) GO Polymer

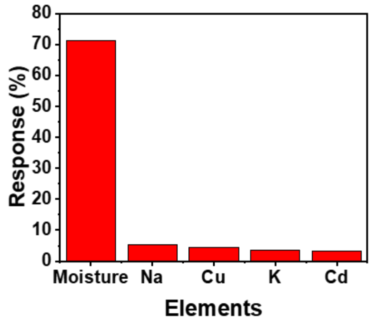


(d) GQD

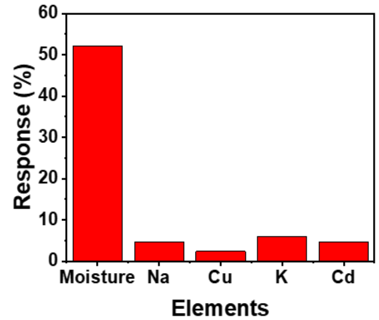


(e) carbon Nano graphite

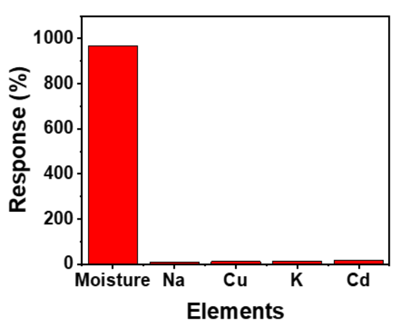
Figure 4.9: Response time of GO at different morphology



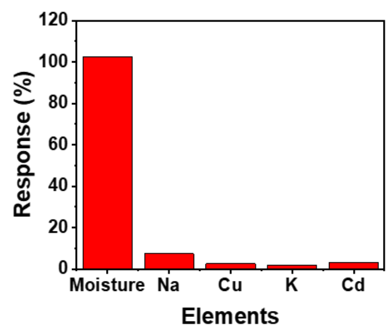
(a) GO



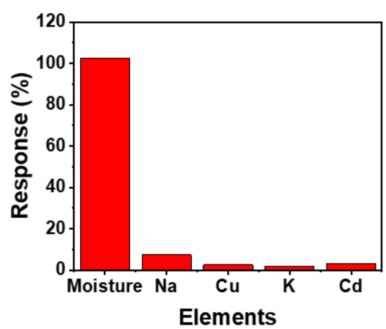
(b) rGO



(c) GO Polymer



(d) GQD



(e) carbon Nano graphite

Figure 4.10: Selectivity of GO at different morphology

4.11 Go sensor sensing mechanism

GO have such an atomic structure that it consists of three functional groups and there are epoxy, carboxyl, and hydroxyl[5]. As shown in figure 4.11 the physisorbed layer binds through double hydrogen bonding with the oxygen functional group present on the surface of GO. Through XPS analysis oxygen function groups present in GO had conformed. As the moisture in the soil increases more physisorbed layers create and absorb more water molecules. And as the physisorbed layer increase the upper physisorbed layer bond with the lower physisorbed layer with single hydrogen bonding. For a higher physisorption regime, the water molecule is free to move which seems to those in the bulk liquid. And as an increase in moisture of soil, there is a liquid like a bearing is observed in physisorbed layers. When an electric field is applied then a higher physisorbed regime can be ionized to hydronium ion (H_3O^+) that acts as the charge carrier. The absorbed water on the GO surface will increase the dielectric constant, result increase in the capacitance of the fabricated sensor. Relatively at higher humidity or moisture level, the polarization strength increase results in an increase in dielectric constant.

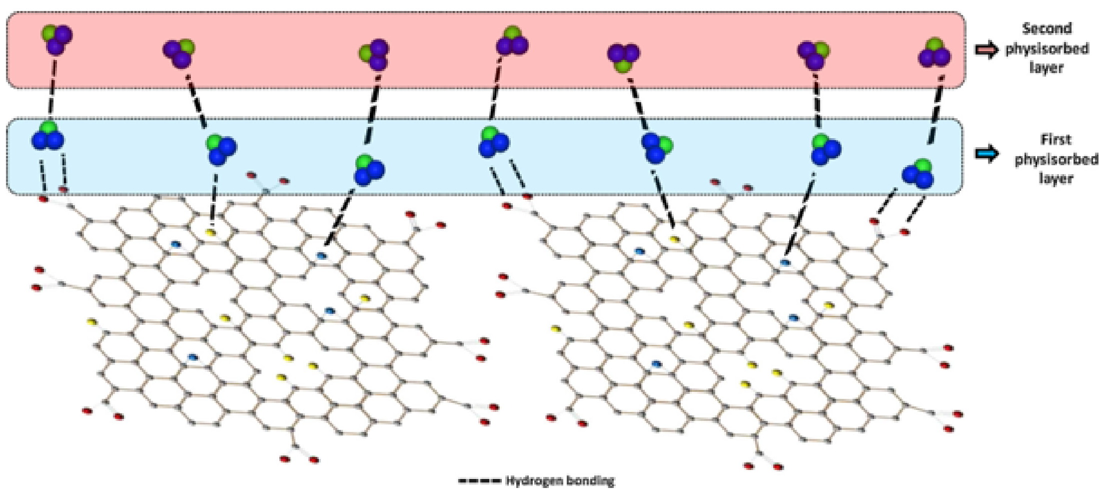


Figure 4.11: Bonding of GO with a water molecule[5]

CHAPTER 5

Conclusions

In summary, we develop a GO micro sensor with different concentrations of 0.5mg/ml, 1mg/ml, 5mg/ml, and 15mg/ml and study its response to soil moisture concentration from 1% to 23% and know that from all sleeted concentration 5mg/ml is the most sensitive concentration and its response is 2794% to 5616% for different soil moisture. The response time of the GO sensor is of 300 seconds and has an error of $\pm$2.5%. The GO sensor is most selective to moisture present in soil rather than salt present in the soil. Then the morphology study is carried out on 5mg/ml of concentration with five different morphology as GO, rGO, GO Polymer, GQD, and Carbon Nano-graphite. and the most sensitive morphology among them is GO Polymer which has a response of 2135% to 7201% and the error is almost negligible. The response time is of 200 seconds and the sensor is most selective to moisture present in soil rather than salt present in the soil. Thus this study brings out 5mg/ml as the best concentration of GO and GO Polymer as the best morphology.

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