Effect of IDE Spacing on the Performance of ErGO Chemiresistive Humidity Sensor.

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***Abstract*— This research demonstrates the effect of the use of different Aurum (Au) interdigitated electrode (IDE) spacing on the performance of electrochemically reduced graphene oxide (ERGO) humidity sensor via electrodeposition method. Electrochemically deposition (ECD) is regarded as a green route approach where it does not require capping reagents or surfactant agents in the graphene oxide (GO) reduction process as well as a simple and economical synthesis procedure. In this experiment, four Au with different spacing used were 5um, 10um, 100um and 200um. The synthesis procedure was set up with cyclic voltammetry window parameter at sweep potential range 0.05V (start) to 0.05V (stop), vertex potential between the range -0.4V (upper) and -1.1 (lower), scan rate 5mV/s and 10 cycles in the aqueous solution graphene oxide (GO) for each sample at the 40°C water bath temperature. The fabricated samples with reduced graphene oxide (RGO) deposited on the surface of IDE were characterized on its humidity performance based on the results obtained in the current measurement (I-t) on the different relative humidity (RH) 40%RH-90%RH at 0.2V potential applied based on sensitivity, response time and recovery time. Moreover, the electrochemical properties ERGO was investigated via electrochemical impedance spectroscopy (EIS) with FRA measurement set up at applied voltage 0.2V for each fabricated sample. As a finding, 5um electrode spacing produce a great humidity performance with higher sensitivity, higher response time as well as higher recovery time. Whereas, the electrochemical impedance spectroscopy measurement showed the shorten the spacing the greater the ionic conductivity at electrode-electrolyte interface due to their low charge transfer resistance.**

Keyword: Humidity sensor; Electrochemical reduced graphene oxide (ERGO), Reduced graphene oxide (RGO), Graphene oxide (GO), Interdigitated electrode (IDE), Electro Impedance Spectroscopy (EIS)

I. INTRODUCTION

Humidity sensors plays an important role in life as well as many areas of application ranging from humidity control to various types of industrial processing, agricultural humidity monitoring, medicine, weather forecasting, internal humidity sensing, controlling machines, chemical and automated industrial processes as well as many more, research related has persisted for two decades to date. Simply, the humidity sensors indicate humidity by converting the number of water molecules in the environment into a measurable signal. Thus, moisture measurement is essentially as it affects the quality of the product produced as well as health. The parameters are defined in numerous ways and the measurement units are dependent on the technique employed namely 'Relative Humidity (RH)', 'Parts Per Million (PPM)', and 'Absolute Humidity (AB)'. The humidity sensors can be classified into wide ranging categories, such as resistive type, impedance type, capacitive type, quartz crystal microbalance type, surface acoustic wave and optic fiber type which depends on the suitability of its application [1]. Additionally, the parameters that need to be emphasized for a sensor is its performance capability in sensitivity, response time, stability, accuracy, repeatability, linearity and potential applied [2]. Thus, many materials sensitive to water vapor molecules that presence in the air has been explored as sensing materials in humidity sensors, including ceramics, semiconductors, conducting polymers, semiconducting polymers, 2D and 3D materials, black phosphorus and carbon materials for instance carbon nanotubes and graphene. Among them, graphene and its derivatives show great potential in various application fields due to their remarkable properties. Graphene is a unique material,

978-1-6654-1232-2/21/$31.00 ©2021 IEEE

bonded with a planar membrane of carbon atoms in honeycomb lattice arrangement-like two-dimensional (2D) crystal structure consist of sp^2-carbon atom. It is a single layer of graphite, which exhibits semi -metallic characteristics with zero band gap [3], in contrast to the behavior of graphite metals. The great structure of atomic arrangement has resulted in excellent electronic structure as well as remarkable physical and chemical properties, Furthermore, with promising potential to detect moisture due to large surface area, high electron mobility at room temperature, and low electrical noise due to the quality of the crystal lattice and high electrical conductivity along with good mechanical strength which leading graphene materials in various applications including electrodes, batteries, biosensor, high energy capacitors, electrocatalysis, chemical sensor and optoelectronics [4].However, the aforementioned properties are possessed only by pristine graphene which differs from graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO). Although, it has tremendous features and can be employed in various fields but some insurmountable defects, such as zero band gap and low dipersibility may cause the limitations in medium and large-scale production as well as real world applications. Thus, various methods for functionalizing graphene have been studied to enhance their real applicability such as thermal reduction, chemical reduction, photocatalytic reduction, and electrochemical reduction [5]. The most prominent method for graphene synthesis is based on the exfoliation of graphite. This exfoliation process introduces many oxygenic functional groups, such as epoxides, hydroxyl and carboxyl, may defect induce on the graphene structure specifically in basal plane and edges. This event, expand the graphite separation layer and produce the graphene oxide (GO) that's able to dispersible in the water, which is known as hydrophilic [6]. The derivation of graphene-to-GO via exfoliation method made up the GO become an electrical insulator. Nevertheless, the properties of GO and RGO can further chemically modified to improve their properties and functionality. Therefore, numerous established treatments have been extensively explored to grow high quality graphene with superior properties seems to be like pristine. The process can be obtained through electrochemical reduction, chemical reduction, thermal reduction, and laser induced reduction. [7] The restoration process is necessary to make the graphene derivates more conductive for more extensive applications.

Generally, after reduction, the atomic arrangement of graphene oxide is altered to conductive RGO, its conductivity is more sensitive towards water molecules due to defects induced by abundant hydrophilic oxygenic functional groups, which have a potential to be applied as a material for humidity sensor. Since 2004, the most common approach to synthesis graphene is via thermal reduction although the process can produce the ultra-high specific surface area like pure graphene, but the process requires very high temperature to synthesis GO into its derivatives. Due to this factor, it can cause material destruction due to high internal pressure. Moreover, chemical reduction with the solution-phased approach or known as a Hummer's method is used to overcome the issues, however, the process requires to use the strong acidic and oxidants agents such as potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrazine and various types of reducing agents to obtain a single layer of graphene oxide, which results in release a toxicity gas into the environment [8]. Although, this approach can produce GO/RGO at very high scale and low-cost production in massive applications, but it has some shortages instances environmental pollution, long oxidation process and resultants a bunch of defects thus it rarely used nowadays [9]. As an alternative, the electrochemically deposition is renowned as a simple, clean, fast, cost-effective, and green-route approach to substitute the toxicity conventional Hummer's method. It produces a thin metal film by action an electric current on a conductive material/electrode immersed in aqueous solution containing of the metal to be deposited. The high quality of RGO with a structure similar to pristine graphene was produced since the reduction process efficiently reduce the oxygen functional groups in the graphene oxide (GO) [10,11].

Henceforth, the intent of this research work, is to investigate the performance of the electrochemically reduced graphene oxide (ERGO) onto different Aurum electrode spacing used were 5um, 10um,100um and 200um via electrochemical deposition (ECD) approach. In this experimental work, four samples were used and immersed into aqueous GO solution. The cyclic voltammetry (CV) window parameters were set up at potential sweep from 0.05V (start) to 0.05V (stop), vertex potential ranging from -0.4V (upper) to -1.1V (lower), scan rate 5mV/s and 10 cycles deposition at 40°C water bath temperature. The ERGO fabricated samples were characterized based on humidity performance results obtained from voltage-current measurements at the different relative humidity range 40%RH-90%RH at 0.2V potential applied. The results were analyzed based on sensor sensitivity, response time and recovery time. While electrochemical impedance spectroscopy (EIS) was performed by setting FRA measurements on a frequency of 1MHz at 0.2V applied voltage. The results were analyzed based on the resistance and impedance extracted from the Nyquist plot and "Simplified Randell Cell"

II. METHODOLOGY

A. Fabrication of reduced graphene oxide (RGO)

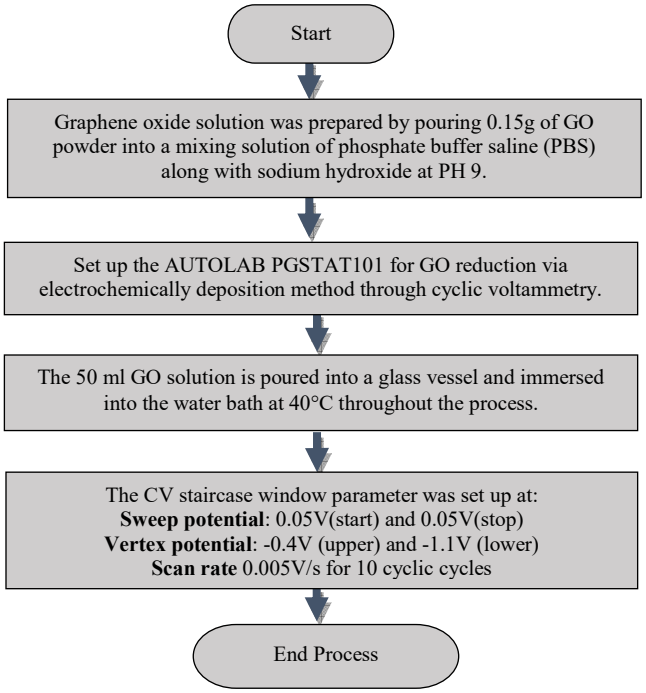

Fig 1: The process flow of electrochemical deposition (ECD) method via cyclic voltammetry.

Fig 1 shows the process flow of electrochemical deposition via cyclic voltammetry. Throughout, GO synthesis process, the electric current causes the graphene oxide receives an electron to form an insoluble electrochemical reduced graphene oxide (RGO) adhere directly as a coated thin film onto the electrode surface. This process was repeated for each sample used were 5um,10um,100um as well as 200um.

B. Electrical and Electrochemical Characterization

The humidity performance of fabricated samples was characterized through the voltage-current measurement, the chamber (ESPEC SH261) and sensor measurement (Keithley 2400) were used to execute the process. Through the results obtained, the performance was assessed based on their sensitivity, response time and recovery time. Whereas electrochemical characterization was conducted by Metrohm Autolab PGSTAT101 and NOVA 2.1. software. The electro impedance spectroscopy (EIS) measurement was set up at frequency 1Mhz with 0.2V potential applied. From the fitting evaluation, the internal resistances and impedance were generated via the "Simplified Randle's Cell" which comprises the significant parameters from EIS measurement such as solution resistance (Rs), charge transfer resistance (Rp) and constant phase element (CPE).

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III. RESULTS AND DISCUSSION

A. Humidity sensing performance

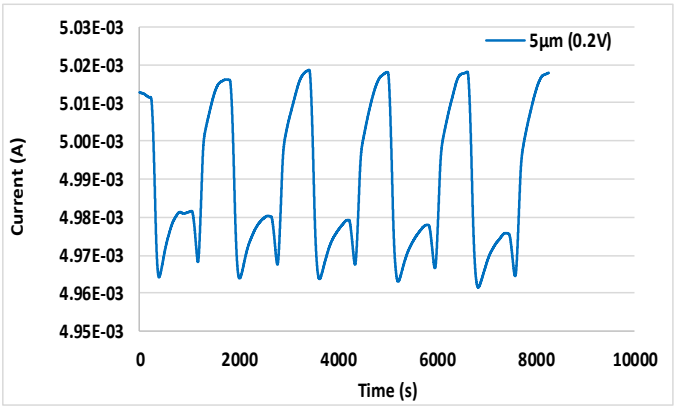
Humidity measurements can be determined through the water vapor content present in the environment. The fabricated sample of ERGO adsorbed the oxygen from the moisture around it. The sensing experiments were carried out by exposing the sample to the relative humidity (RH) in the ranges of 40%RH to 90%RH at 0.2V applied potential with the interval time of 800 seconds for each cycle. In humidity sensing mechanism is related to a water adsorption and desorption process, the oxygen adsorbed onto the surface of fabricated sample and free electron was trapped at the low humidity level which can be expressed by the following equation:

$$O + e^- = O_2^- \text{ .....[1]}$$

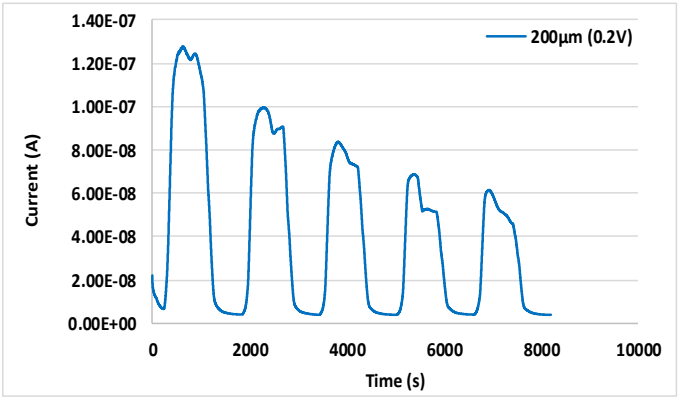
Thus, when the electrode sample was exposed to the humid environment then the dipole of water electricity allows an electron to be trapped in the conduction band. The water molecule releases the free electrons and remain on the sample surface when it begins to separate due to the O_{2-} present, which this phenomenon can be expressed by equation:

$$2H_2O + O_2^- = 2H_2O_2 + e\text{- .....[2]}$$

The sample continue to adsorb the water molecules till formed the hydrogen bonds. This process reduces the carrier concentration and create an electron thinning layer on the sample surface. While the second layer of water molecule decomposed into H_3O^+ and OH^- cause by electrostatic field that produce by the main layer. When these ions become the primary carriers, therefore it will increase the electrical conductivity of the humidity sensor.



(a)



(b)

Fig 2: The I-t measurement for humidity response on different Au IDE spacing (a) 5um and (b) 200um via ECD

TABLE 1: The parameters for humidity sensing at 0.2V potential applied

IDE substate spacing	*Sensitivity*	*Response time, tr (s)*	*Recovery time (s)*
5µm	100.6	150	200
10µm	10	200	250
100µm	2.03	220	300
200µm	1.68	250	350

Fig 2 and Table 1 showed the I-t curve measurement and significant parameters towards humidity response respectively. The performance of sensor was evaluated based on their sensitivity, response time, recovery time as well as repeatability. The results obtained shows the sensitivity of samples towards humidity were 5um>10um>100um>200um at 100.6>10>2.03>1.68 respectively. From the result obtained, it reported that the highest sensitivity is at 5um sample, which is indicates a better response towards humidity. This high sensitivity is ascribed from the large coverage area of RGO on the substate made the interaction with the H_2O molecular is easily. The imperfection structure was formed due the hydrophilic oxygenic functional group was initiate into bonded sp^3 carbon atoms which causes the atomic structure bonding layer was expanded. Due to the large separation of layer made a water molecule simply absorbed, as well as produce the great medium for electron conductivity on the surface area. Besides that, the response time and recovery

time samples were observed. The response time indicated how well the system maintain a fast transition in the input signal from the lower threshold to upper threshold toward humidity response while the recovery time vice versa. The response time of the samples can be obtained using the equation $t_r=t_{90}-t_{10}$ and recovery time $t_r=t_{10}-t_{90}$. The results showed, the fastest response is falling at 5um>10um>100um>200um as well as recovery time is falling at 5um>10um>100um>200um which depicted the smaller spacing results in shortest transition time in the input signal due to their small internal resistance built in between electrode spacing. Moreover, the electrode distance at 5um showed a similar repetition pattern throughout the humidity test compared to 200um, which there was a drift sensor occurred due to the degraded humidity performance as a sensor.

B. Electrochemical performance

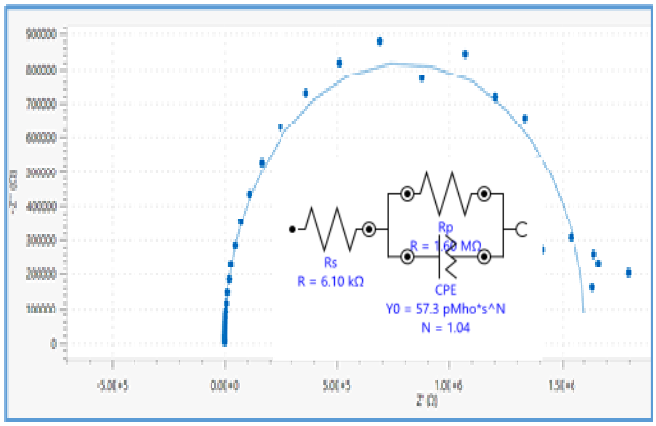


Fig 3: A Nyquist plot for ERGO at 200um Au IDE spacing. The graph represents Z'(Ω) vs Z''(Ω) at applied potential 0.2V

Fig 3 depicted the Nyquist plot for RGO on 200um spacing at potential applied 0.2V along with frequency 1MHz. The results were analyzed by measuring the resistance of charge transfer (Rp), that is extracted from Nyquist plot and the equivalent circuit models. The semicircular diameter represent the estimation of charge transfer resistance (Rp) on the electron mobility between electrode-electrolyte interface. Thus, the linear correlation between size diameter of semicircular and charge transfer resistance (Rp) shows that as the value of Rp increases, then the diameter of the semicircular increases. From the tabulated Table 2, shows that the value of Rp is extensively higher at the 200um compared to the 5um and 10um distance. This indicates that only a small number of electrons can penetrate through the electrode-electrolyte interface which is reflects the weak ionic conductivity as well as electrical conductivity. Moreover, the 5um and 10um, shows extremely low Rp value at 2.2468Ω and 1.8925Ω respectively result in greater ionic conductivity.

TABLE 2: The significant parameters for EIS measurement at 0.2V applied potential.

IDE Substrate Spacing	*Solution resistance (Rs)*	*Charge Transfer resistance (Rp)*	*Constant Phase Element (CPE)*	X^2
5µm	38.128 Ω	2.2468 Ω	9.375×10^{-5}	0.00046
10µm	81.048 Ω	1.8925 Ω	5.8435×10^{-8}	0.00096
200µm	-276.24 Ω	1.6038M Ω	4.6899×10^{-11}	0.16645

IV. CONCLUSION

As a conclusion, the ERGO was successfully deposited on the different spacing of electrode used were 5um, 10um, 100um and 200um via electrochemically deposition method. The effect of spacing electrode towards performance as humidity sensor was investigated through voltage-current measurement and electrochemical impedance spectroscopy (EIS). The approach was simple, low at production cost and environmentally friendly which substitute the highly toxicity Hummer's method. Moreover, the result was carried out explicated that the 5um produce the great humidity performance based on higher sensitivity, higher response time toward transition time in the input signal as well as excellent in recovery time. The results in agreement with the electrochemical properties measurement where, it revealed that with shorten distance spacing 5um and 10um gives a remarkable result in their ionic conductivity and electrical conductivity at electrode-electrolyte interface due to low charge transfer resistance.

ACKNOWLEDGEMENT

The research work is funded by the UiTM Special Research Grant 2021.

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