JOURNAL OF SCIENCE AND TECHNOLOGY
ISSN: 2229-8460 e-ISSN: 2600-7924

JST

Vol. 16 No. 1 (2024) 1-9
https://publisher.uthm.edu.my/ojs/index.php/jst

Conductivity and Chemiresistive H_2S Gas Sensitivity of Graphene (75 wt%)/ Cu (25 wt%) Composite Thin Film

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DOI: https://doi.org/10.30880/jst.2024.16.01.001

Article Info

Received: 8 February 2024
Accepted: 23 May 2024
Available online: 23 June 2024

Keywords

Sensor, conductivity, annealing temperature, gas chamber, spectra

Abstract

This paper studies the conductivity and chemiresistive H_2S gas sensitivity of graphene (75wt%)-Cu(25wt%) composite thin film, using self-made chamber and common laboratory apparatus. The method adopted involves mixture of 2 drops of ethanol with the synthesized composite and prepared on a glass substrate by tape casting method. Two small copper metal sheets were used as electrodes for clipping of crocodile which were also connected to digital meter for resistance readings and its changes. The X-ray Diffraction (XRD) shows that annealing temperature reduced the crystallite sizes. The Fourier Transform Infrared Radiation (FTIR) spectra show the functional groups present to be transition metal carbonyls or aromatic combination bands, terminal alkyne (monosubstituted), isothiocyanate and that between 2300 and 2400 cm^{-1} indicates N=C=S functional group and evidence of CO_2 interaction with external surface of the material or intercalating in the interlayer of the host material Also, increase in the conductivity was observed due to decrease in resistivity. The response/sensitivity peak of the sensor to hydrogen sulfide was seen to rise proportionally as temperature rose with percentage 3.97% for as grown, annealed at 200°C is at 12.98% while the annealed at 400°C is at 27.34%.

1. Introduction

The population growth which has led to more industrial births has resulted in hazardous environmental pollution [1] such as air, land, and water pollution. These forms of pollution have necessitated the desire for efficient sensors in the observation of our environment [2]-[5]. Hydrogen sulphiide (H_2S) is a gas known to be colourless, acidic, flammable, and hazardous to lives and as also, corrodes metal equipments [3],[6]. It is a waste product of many industrial processes and would cause paralysis when it is above 250 parts per million (ppm) in air. Thus, the need to develop a sensor capable of detecting its presence in the atmosphere is important. Many researchers have developed metal oxide semiconductors (MoS) and their composite sensors with 2-D materials such as SnO_2, WO_3, SnO_2-WO_3, WO_3/CuO, MoS_2/TiO_2 among others, which are all aimed at monitoring a particular gas [7]. Composite-based sensors have the merit of selectivity of a particular gas over MoS counterparts and temperature can be tuned for more suitability [8].

Graphene is a 2-D material with various applications such as gas sensor, ethanol, and hemoglobin detectors. Synthesis method, annealing conditions, cooling rate and dispersibility are some of the factors that determine the electrical conductivity of graphene and the composites [9]. The electrical property of an insulator and a

semiconductor can be tuned with conductive fillers for conductivity features. On the other hand, annealing temperature was observed to vary directly with the electrical conductivity and the graphene concentration [10]. Chemiresistive gas sensors are essential in detecting harmful gases exposure to the surroundings which may be from commercial waste and could endanger lives [6],[11]. Chemiresistive sensors are regarded to have shortcomings in stability and percentage accuracy in relation to sensitivity [12]. The elements figuring out the sensitivity of sensors are the species of the material and gas to be detected whether it is oxidizing or reducing, size and form, and the content ratio. Chemiresistive gas sensors can either be an n-type or a p-type gas sensor [2],[13] and are dependent on annealing temperature. Annealed graphene composite between 100°C-250°C is p-type because holes become the major charge carrier [10].

Nanomaterials of graphene extraction [14]-[16] were discovered to be of outstanding potential for purposeful technology of materials such as gas sensor due to optimized surface area from their nano size, charge presence and transfer, and smooth fabrication [17]-[19]. Stacking in graphene materials is a huge setback and affects the performance of graphene or graphene-based gas sensors to which solving this stacking issue will greatly improve the gas sensitivity [20]. Graphene nanoparticles are considered as present and future potentials of nanomaterials applications [21]-[24]. Graphene and its oxide have been proven to be of excellent sensitivity towards diverse gases [25]-[28] but, the resistance value is never constant when exposed to target gas [29]. In this paper, we study the conductivity and chemiresistive H_2S gas sensitivity of graphene (75wt%)/Cu(25wt%) composite thin film.

2. Materials and Methodology

2.1 Materials

Graphene oxide produced by Adnano technologies was obtained from India; pure copper nitrate of Kemel Corporation in China and pure glucose from Surechem in England, were bought additionally from a store in Nigeria. The synthesis was done using ratio 1:3 of copper nitrate ($Cu(NO_3)_2$) and graphene oxide (GO) respectively.

2.2 Synthesis

Samples measured were blended in distilled water, in a 25 ml beaker at room temperature, and the catalyst (99% natural glucose) was added as 10 wt% of the samples. The entire combination was subjected to boiling at 100˚C for 90 minutes. The composite was washed with distilled water two times to ensure purified content and filtered with filter paper. The filtrate was saved for twenty-four hours and portions had been subjected to annealing in an oven at 200˚C and 400˚C respectively for 12 hours.

2.3 Fabrication of Sensor

A small quantity of each composition sample was mixed with 2 drops of ethanol and mixed, prepared by tape casting method on the glass substrate. The mixture was spread in the space and allowed the evaporation of the ethanol for some minutes. Two copper metal sheets were used as electrodes on which the crocodile clips were clipped and resistance readings in Ohms. The readings were taken at every 30 second interval from the time of unlocking the knob to when the readings become stable by fluctuating within a range before removal from gas and then exposed to air.

2.4 Gas Synthesis (H_2S)

The formula below was used to determine the mass of hydrogen sulphide (H_2S).

Determining the space in the chamber, we use

$$Number\ of\ moles\ of\ air\ (n) = \frac{P(atm)\times V(L)}{0.082057\left(\frac{L\times atm}{K\times mol}\right)\times T(K)} \quad (1)$$

To find the mass of air in 1 liter chamber where molar mass of air ≈ 28.97 g/mol.

$$Mass\ of\ air\ (g) = n(mol) \times molar\ mass\ of\ air\ \left(\frac{g}{mol}\right) \quad (2)$$

Next is to solve for the mass of ZnS that will produce the H_2S gas ppm value.

$$100\ ppm = \frac{X\ (\mu g)of\ H_2S}{mass\ of\ air} \quad (3)$$

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X(μg) is the mass of H_2S corresponding to mass of ZnS in the equation below in terms of mole ratio:

$$ZnS_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(s)} + H_2S_{(g)} \quad (4)$$

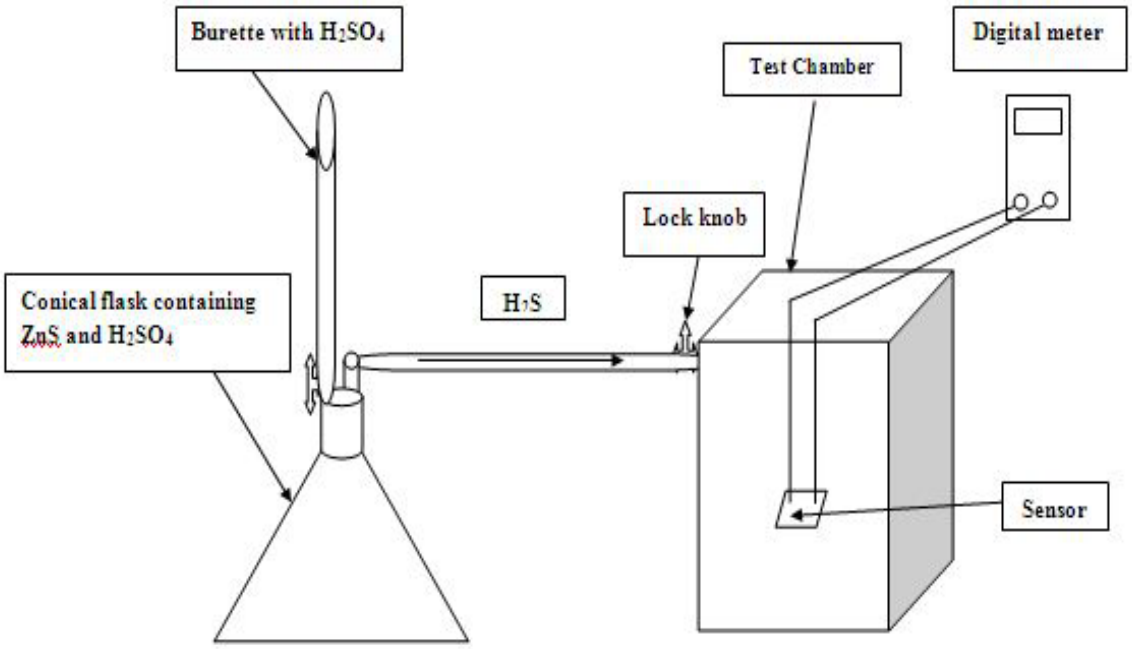


Fig. 1 *Experimental set-up of G-Cu thin film sensor*

3. Results and Discussion

The X-ray diffractogram peaks in Fig. 2 are at 26.63° and 44° and the crystallites sizes are estimated around 4.63 nm and 3.58 nm for G-Cu. It is a multi-walled carbon nanotube (MWCNTs) and it is similar to an atom of graphite. For annealed at 400˚C, at 26.6°, the crystallite size is 3.00 nm and 44° is 3.21 nm. The broad base is an indication of amorphous presence and the sharp peak shows crystallite constituent and may be visible for each as-grown and the annealed at 400˚C [30]. The result in Fig. 3 shows the structural and morphology of the composite to be rutile with reduced layers of graphene at the temperature of 400˚C.

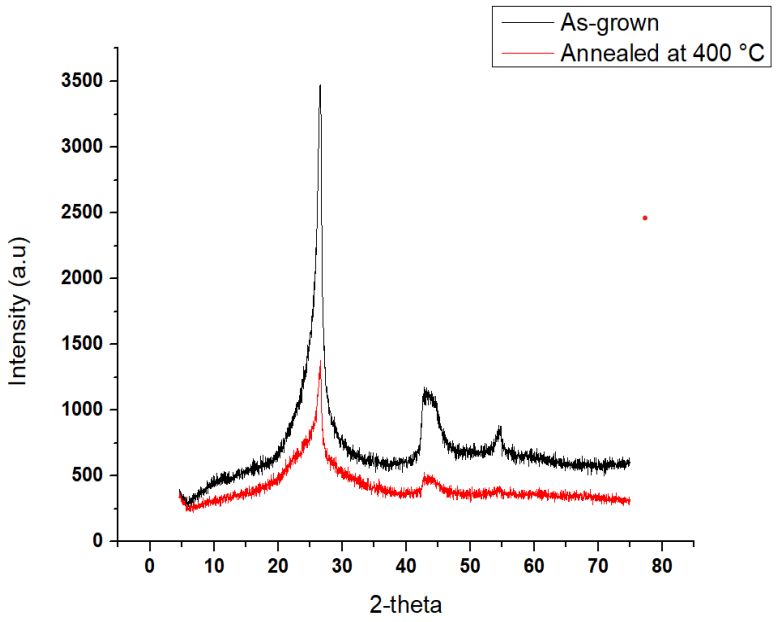


Fig. 2 *Diffractogram of as-grown and annealed at 400˚C*

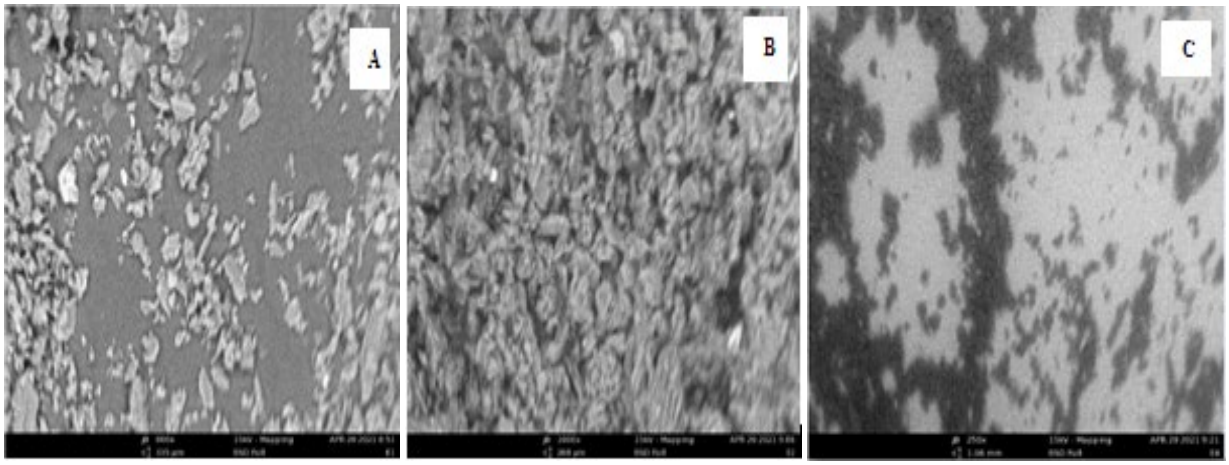
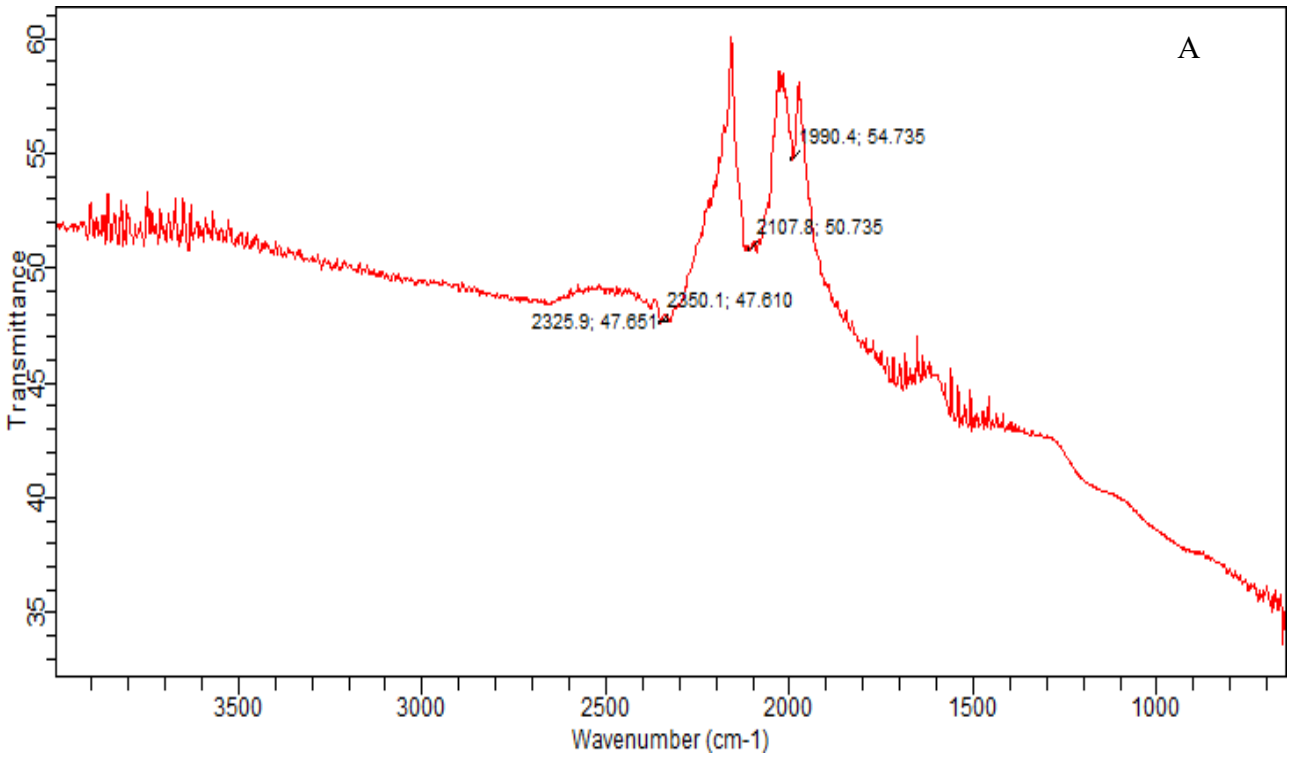


Fig. 3 *SEM micrograph (A) as-grown (B) annealed at 200°C (C) annealed at 400°C*

Adopting Cameron (2011) [31] Fourier Transform Infrared (FTIR) spectra analysis, Fig. 4(A) infrared radiation (IR) peaks are: 1990.4 cm^{-1} which could be transition metal carbonyls or aromatic combination bands;



2107.8 cm^{-1} which could be attributed to terminal alkyne (monosubstituted), while 2325.9 and 2350.1 cm^{-1} indicate isothiocyanate (N=C=S) presence [32]. The Fig. 4(B) IR peaks are: 1996.0 cm^{-1} which could be transition metal carbonyls or aromatic combination bands; 2085.4 cm^{-1} could be attributed to terminal alkyne (monosubstituted), 2109.7 and 2325.9 cm^{-1} reflects isothiocyanate (−NCS) presence [32]. The Fig. 4(C) IR peaks are: 1996.0 cm^{-1} which could be transition metal carbonyls or aromatic combination bands; 2083.6 cm^{-1} could be attributed to terminal alkyne (monosubstituted), 2111.5, 2348.2 and 2379.9 cm^{-1} indicate isothiocyanate presence.

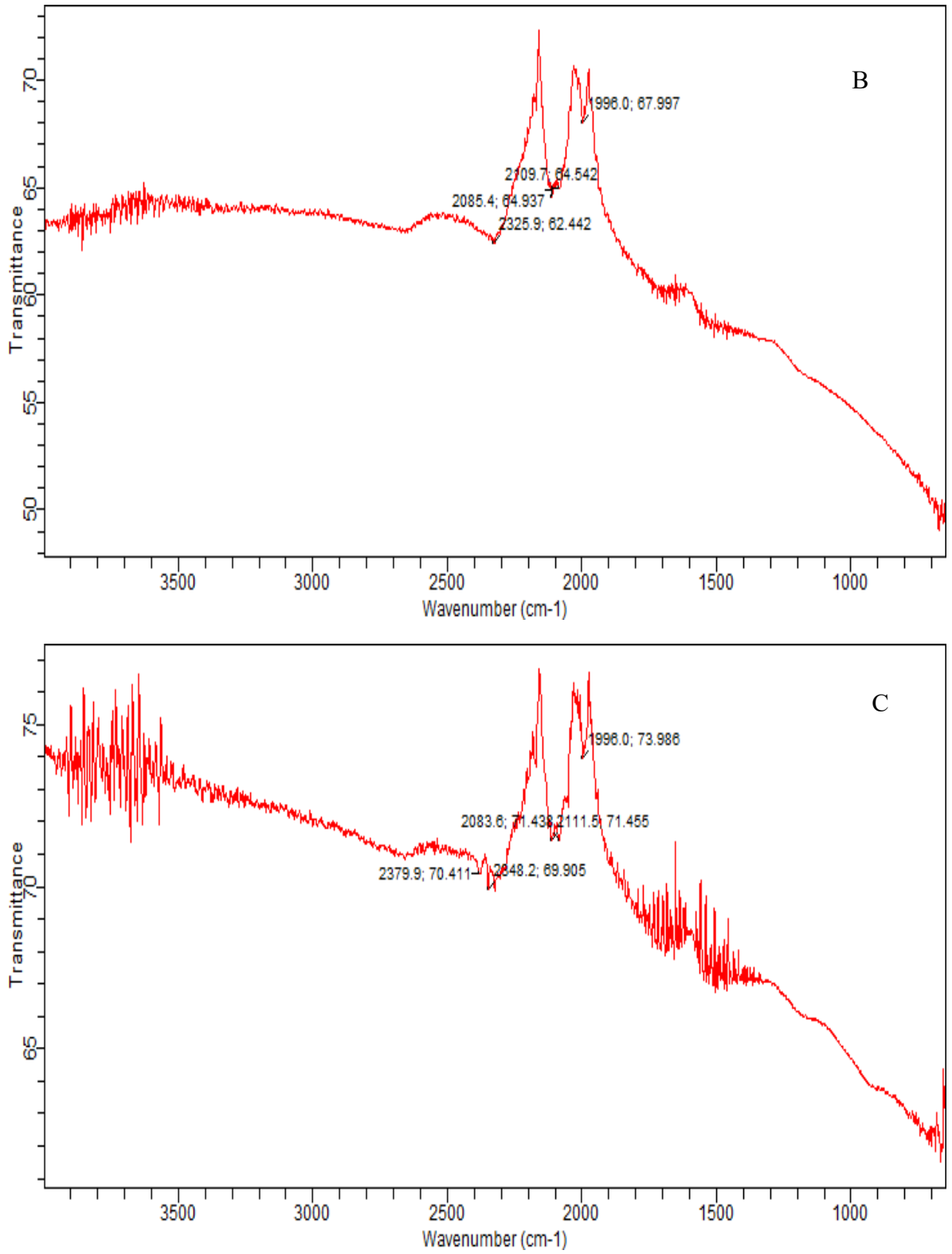


Fig. 4 *FTIR Spectra of G-Cu (a) as-grown (b) 200°C (c) 400°C*

In Table 1, the conductivity increases with annealing temperature and according to Rahman *et al.,* (2019) [33], the conductivity of the composite annealed at 400°C, is in the category of useful materials for thermal interface and electromagnetic shielding. The as-grown composite and that annealed at 200°C are conducting films and elastic electrodes. Table 1 shows that the conductivity increases with annealing temperature as the resistivity decreases. If the annealing temperature is increased further, the conductivity will also increase but, the atmosphere must be inert for temperature of 600°C and above, to prevent decomposition of the composite.

Table 1 *Electrical property at different annealing temperature of G-Cu composite*

Weight of copper (%)	Temperature (°C)	Average Sheet resistance R_s (Ω/sq)	Resistivity ρ (Ω-m)	Conductivity $(\sigma = 1/\rho)$ (S/m)
25	As-grown	29000.00	868.5360	0.0012
25	200	23066.00	693.1240	0.0014
25	400	61.21	1.8364	0.5445

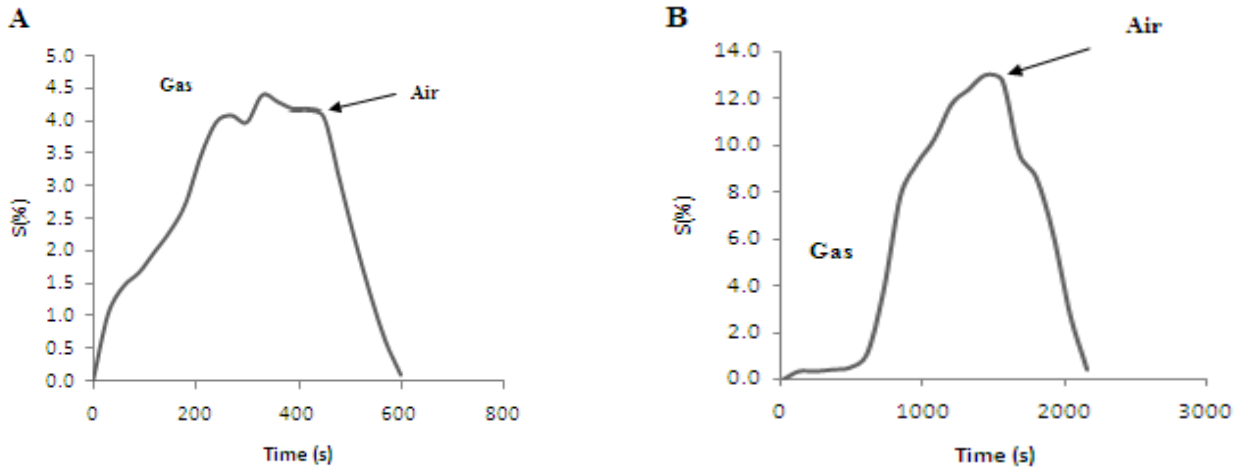
The graphs (Fig. 5) show as grown with sensitivity peak at 3.97% with response time of 190 s and recovery time of 100 s; the annealed at 200°C attains 12.98% peak with response time of 600 s and recovery time of 480 s, while the annealed at 400°C attained 27.34% with response time of 75 s and recovery time of 80 s. The annealed at 400°C shows the fastest response with highest sensitivity in a short duration. The sensors fabricated are sensitive to hydrogen sulfide and were able to recover more than 80% rate especially that of annealed at 400°C, when repeated within a short time as shown in Fig. 5(D). The increase in the resistance value of a sensor when exposed to a reducing agent depicts that it is a p-type chemiresistive gas sensor. The high sensitivity/response of G-Cu composite is due to its highly reduced size and good electrical contact network of the G-Cu film with the copper electrodes [20]. The effect of Hydrogen sulphide (H_2S) on the sensor also increases the resistances by forming a corroded thin film of either Cu_2S, CuS or/and CuS_2 which decouple graphene from copper and become almost free standing with a neutral charge under controlled experimental condition [34] depending on the volume of H_2S and copper presence for adsorption in the composite.

The quantity of copper in the composite is a factor in the sensitivity rate and peak of the fabricated sensor. Also, increase in the annealing temperature increases the defect, surface area and pores of the composite for interaction.

The resistance response *R(%)* or sensitivity *S(%)* was determined using equation 5;

$$R(\%) = \frac{\Delta R}{R_0} \times 100 = \frac{R_{H_2S} - R_0}{R_0} \times 100 \quad (5)$$

Where R_0 is the resistance before exposure to gas and R_{H2S} is the resistance after contact with H_2S gas.



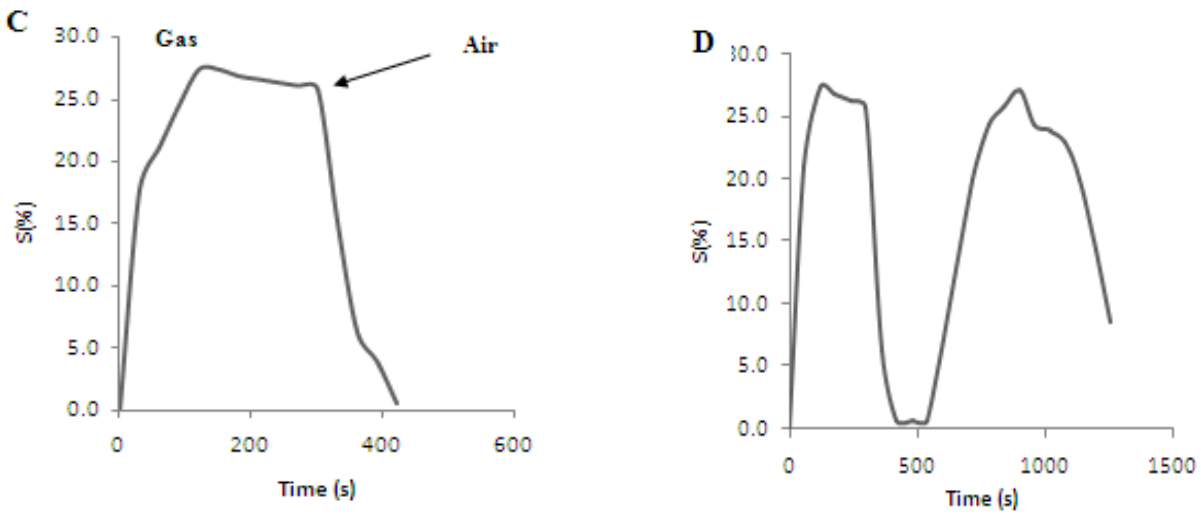


Fig. 5 *Response against time of 25 wt% of copper in G-Cu for 100 ppm (a) As-grown; (b) Annealed at 200°C; (c) Annealed at 400°C; (d) Repeated test of annealed at 400°C after each exposure to air*

4. Conclusion

The composite was successfully synthesized with quality crystallite size as revealed by the XRD. The graphene diffraction peak was identified at 26.6° and the G-Cu merger peak at 44°. The functional groups are similar and show the presence of transition metal carbonyl or aromatic combi, terminal alkyne and isothiocyanate (N=C=S). The sensors are conductive, and the conductivity increases with an increase in annealing temperature which determines their suitability. Further increase in the annealing temperature will aid increase in the conductivity of the composite due to increase surface area and pores. The composite sensors show good sensitivity which is dependent on the annealing temperature that factors grain size and tuned the suitability, as well as the specie of the gas that was sensed. The sensors are p-type, and the response/sensitivity is best with annealed temperature of 400°C due to reduced grain size, increased surface area and pores. Future work with annealing to temperature from 600°C should be done in an inert atmosphere to prevent decomposition of the composites.

Acknowledgements

We acknowledged the support given by the laboratory staff of Physics Department, University of Abuja.

Conflict of Interest

The authors declare that there is no conflict of interest.

Author Contribution

Study conception and design: *Francis O. Omoniyi, Aderemi B. Alabi, Olayinka A. Babalola;* ***literature review:*** *Francis O. Omoniyi;* ***data collection****: Francis O. Omoniyi;* ***analysis and interpretation of data:*** *All authors;* ***draft manuscript:*** *Francis O. Omoniyi;* ***revision of manuscript:*** *Francis O. Omoniyi.*

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