Development of Graphene Oxide Thick Film Sensors via Screen Printing Technique for NO_2 Gas Monitoring

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Abstract:
Graphene oxide (GO) thick film gas sensors were successfully fabricated on glass substrates using a simple, economical and scalable screen-printing technique. The prepared films were evaluated for their gas sensing performance using a static gas sensing system toward different test gases including nitrogen dioxide (NO_2), acetone, methanol, ethanol and LPG over an operating temperature range of 40–120 °C. The sensing characteristics revealed that the GO thick films exhibit a strong dependence on operating temperature and type of gas analyte. Among the tested gases, the sensor demonstrated excellent selectivity toward NO_2 gas, showing the maximum sensitivity of 58.62 % at an optimum operating temperature of 100 °C. The response of the sensor toward other gases such as acetone, methanol, ethanol, and LPG at the same temperature was comparatively lower, with values of 26.54 %, 13.27 %, 16.32 % and 12.44 % respectively, indicating good selectivity for NO_2 detection. The sensor exhibited a fast response time of 14 s and recovery time of 53 s toward NO_2 gas at the optimum temperature. The enhanced sensing performance of the GO thick film can be attributed to the large specific surface area, presence of oxygen-containing functional groups, and effective adsorption–desorption processes on the graphene oxide surface. These results demonstrate that screen-printed GO thick films are promising candidates for low-temperature, fast and selective NO_2 gas sensing applications, particularly for environmental monitoring and air quality control.

Keywords: Graphene oxide; Screen printing technique; Thick film sensor; NO_2 gas sensing; Gas sensitivity; Environmental monitoring.

1. INTRODUCTION

Air pollution has become a serious environmental and public health issue due to rapid industrialization, urbanization, and increasing vehicular emissions. Among the various toxic gases present in the atmosphere, nitrogen dioxide (NO_2) is considered one of the most hazardous pollutants because of its strong oxidizing nature and harmful effects on human health and the environment [1]. Exposure to NO_2 even at low concentrations can cause respiratory diseases, lung irritation, and contribute to the formation of photochemical smog and acid rain. Therefore, the development of reliable, sensitive, and low-cost gas sensors for the detection and monitoring of NO_2 is of great importance for environmental safety and industrial process control [1, 2]. Semiconducting metal oxide gas sensors have been widely investigated for the detection of toxic gases due to their simple structure, high sensitivity, and low fabrication cost. However, many conventional metal oxide sensors require high operating temperatures, which increases power consumption and limits their practical applications [2, 3].

In recent years, carbon-based nanomaterials such as graphene and its derivatives have attracted considerable attention for gas sensing applications because of their excellent electrical conductivity, large surface area, and high adsorption capacity for gas molecules. Among these materials, graphene oxide has emerged as a promising sensing material due to the presence of abundant oxygen-containing functional groups such as hydroxyl, epoxy, and carboxyl groups, which enhance the adsorption of gas molecules and improve sensing performance [3, 4]. Graphene oxide possesses several advantageous physicochemical properties including high surface-to-volume ratio, tunable electronic structure, and good chemical stability, making it highly suitable for gas sensing applications [5]. The interaction between gas molecules and the functional groups present on GO sheets leads to significant changes in electrical resistance, which can be utilized for gas detection. In addition, GO-based sensors can operate at relatively lower temperatures compared to conventional metal oxide sensors, thereby reducing energy consumption and improving sensor efficiency [5, 6]. Various fabrication techniques such as drop casting, spin coating, chemical vapor deposition, and screen printing have been employed for the preparation of sensing films. Among these techniques, the screen printing technique is widely preferred for the fabrication of thick film gas sensors because it is simple, cost-effective, reproducible, and suitable for large-scale production [6, 7]. Screen printing allows uniform deposition of sensing materials on substrates and provides good adhesion and mechanical stability of the sensing layer. Thick film sensors prepared by this method generally exhibit enhanced gas sensing characteristics due to their porous microstructure, which facilitates efficient gas diffusion and adsorption on the sensing surface [7-9].

In the present work, graphene oxide thick films were fabricated on glass substrates using the screen printing technique and investigated for their gas sensing performance toward different gases including NO_2, acetone, methanol, ethanol and LPG. The influence of operating temperature on gas sensitivity was studied in the temperature range of 40–120 °C. The prepared GO thick film sensor exhibited high sensitivity and selectivity toward NO_2 gas at an optimum operating temperature, demonstrating its potential application in environmental monitoring and toxic gas detection systems.

2. EXPERIMENTAL WORK

2.1 Development of GO thick films

Graphene oxide thick films were prepared on glass substrates using the screen printing technique as shown in Figure 1.

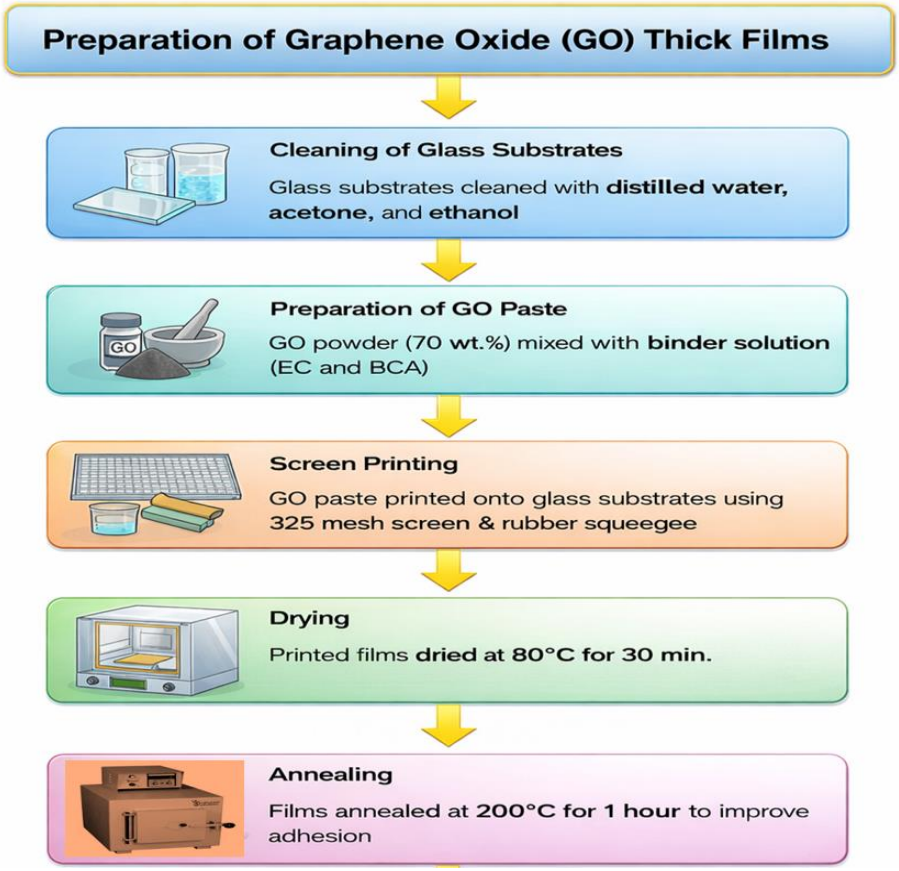

Figure 1. Steps of preparation of GO thick films

Initially, the glass substrates were cleaned with distilled water and acetone to remove impurities and then dried. A thixotropic paste was prepared by mixing 70 wt.% graphene oxide powder with 30 wt.% organic–inorganic binder solution consisting of ethyl cellulose (EC) and butyl carbitol acetate (BCA) to obtain a uniform viscous paste [10, 11]. The mixture was ground thoroughly in an agate mortar to achieve a homogeneous paste suitable for printing. The prepared paste was deposited onto the cleaned glass substrates using a 325 mesh stainless steel screen and a rubber squeegee. After printing, the films were dried at 80 °C for 30 minutes under IR lamp to remove solvents and then annealed at 200 °C for 1 hour to improve adhesion and stability of the sensing layer [11-13]. Then further used for gas sensing study.

2.2 Gas sensing characterization:

Figure 2 illustrates the schematic representation of the static gas sensing system used to evaluate the sensing performance of the graphene oxide thick film sensor.

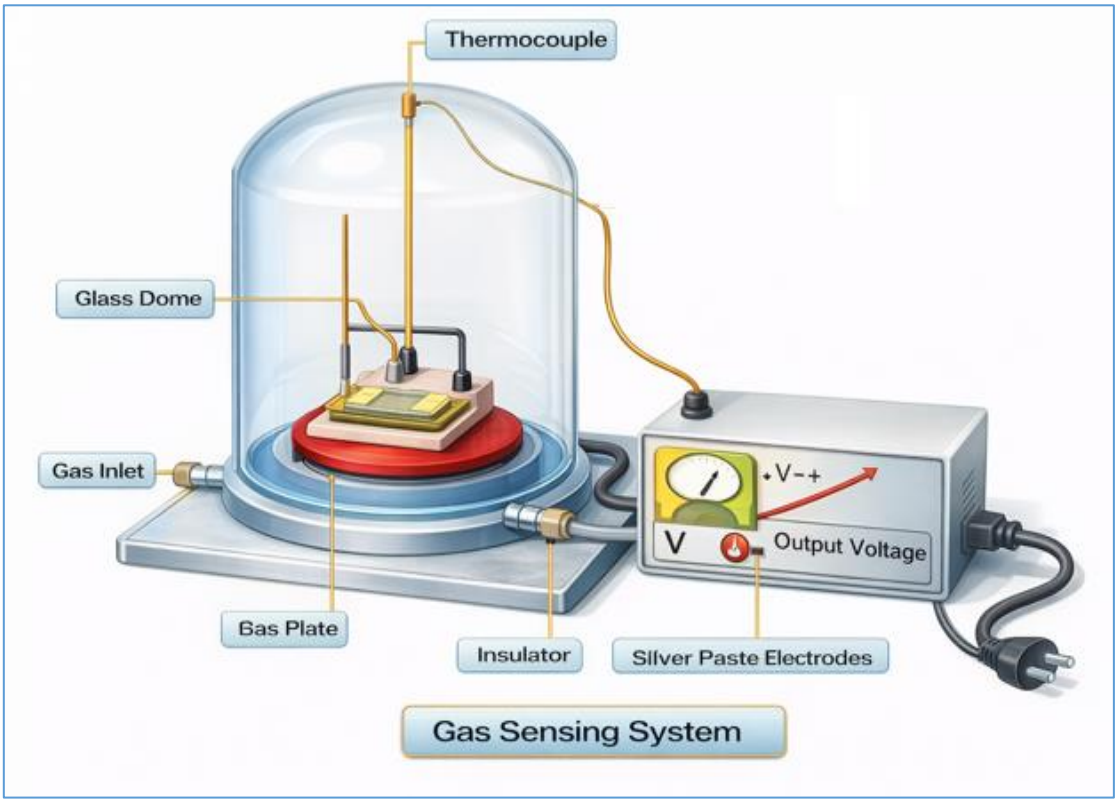

Figure 2. Schematic diagram of gas sensing system

The sensing setup mainly consists of a gas inlet, glass dome (gas chamber), sensor element, heater, thermocouple, insulator, base plate, electrical circuit and gas outlet. The GO thick film sensor with silver paste electrodes is mounted on an insulating substrate and placed on a heater inside the gas sensing chamber. The heater is supplied with AC power of 230 V, which helps in maintaining the required operating temperature of the sensor. The operating temperature during the sensing study was varied in the range of 40 °C to 120 °C, and the optimum sensing response was obtained at 100 °C. A thermocouple is inserted inside the chamber near the sensor surface to measure and monitor the exact temperature of the sensing element. The entire sensing assembly is covered by a glass dome, which acts as the gas chamber and ensures controlled exposure of the sensor to the target gas [13, 15]. The test gas is introduced into the chamber through the gas inlet, while the excess gas is released through the gas outlet to maintain proper gas flow inside the chamber. The electrical circuit consists of a load resistor (RL) connected in series with the sensor. A constant input voltage (Vin) is applied across the circuit, and the output voltage (Vout) is measured across the load resistor. When the sensing material interacts with the target gas molecules, the electrical resistance of the GO thick film changes, which results in a variation in the output voltage. These resistance changes are recorded and used to calculate the gas sensitivity [14, 17]. During the gas sensing measurements, the GO thick film sensor was exposed to different gases such as NO_2, acetone, methanol, ethanol and LPG. Among these gases. This gas sensing setup provides a controlled environment for studying the sensing behavior, selectivity and stability of thick film gas sensors [16, 18].

3. RESULT AND DISCUSSION

3.1 Gas response study

Gas response is defined as the relative change in the electrical resistance of the sensing material when it is exposed to a target gas compared to its resistance in air. For oxidizing gases such as NO_2, the gas response is generally expressed as shown in Eq. 1 [19, 20].

$$\text{Gas response (\%)} = Rg - Ra / Ra \times 100 \qquad \text{(Eq. 1)}$$

Where,
Ra is the electrical resistance of the sensor in air and Rg is the electrical resistance in the presence of the target gas.

Figure 3 shows the variation of gas response of graphene oxide thick films toward different gases such as NO_2, acetone, methanol, ethanol, and LPG at operating temperatures ranging from 40 °C to 120 °C. It is observed that the gas response strongly depends on the operating temperature of the sensor. At 40 °C, the GO thick film shows relatively low responses for all gases, where the responses are 9.86 % for NO_2, 2.35 % for acetone, 4.58 % for methanol, 6.11 % for ethanol and 2.35 % for LPG [19, 20]. As the operating temperature increases to 60 °C, the response toward acetone increases significantly to 28.45 %, while the responses for NO_2, methanol, ethanol and LPG are 16.53 %, 8.75 %, 3.62 %, and 6.18 % respectively.

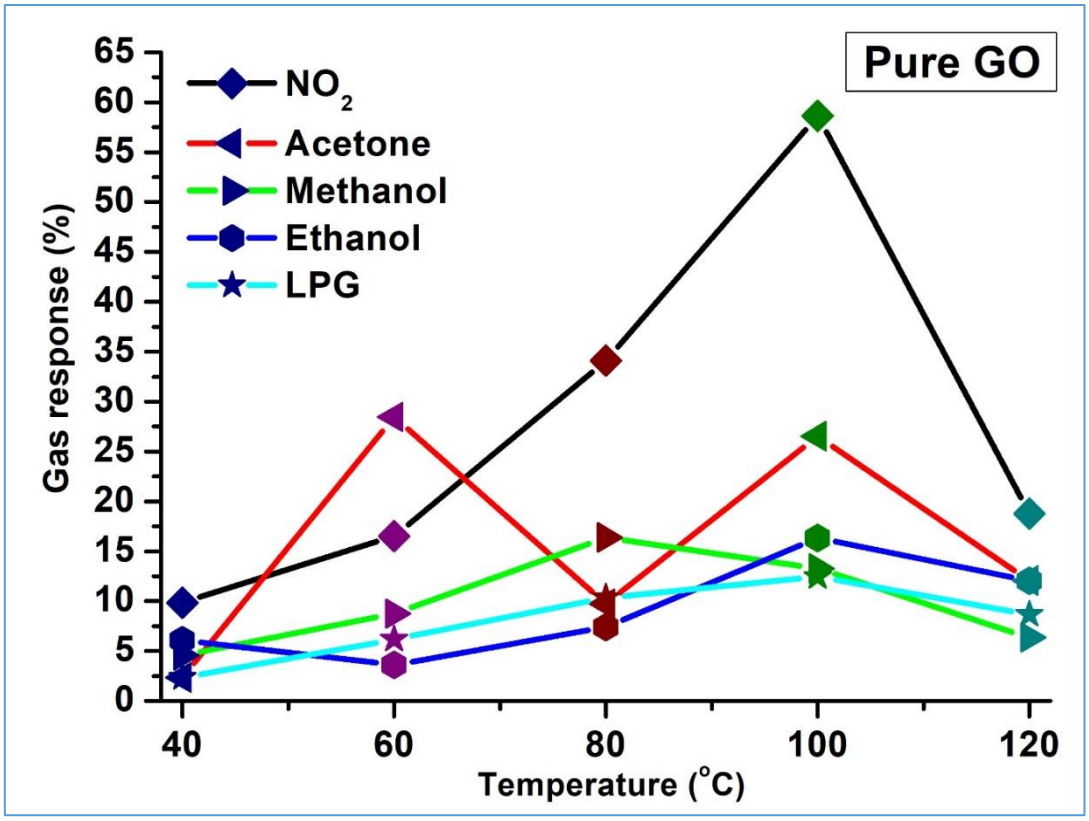

Figure 3. Gas response versus operating temperature plot of GO thick films

The increase in gas response with temperature up to 100 °C is attributed to the enhanced adsorption and reaction of gas molecules on the GO surface, which facilitates efficient charge transfer between the gas molecules and the sensing layer. Beyond this temperature, the decrease in response is mainly due to the faster desorption of gas molecules from the sensing surface. These results indicate that 100 °C is the optimum operating temperature for GO thick films for effective NO_2 gas detection [20, 22].

3.2 Selectivity

Figure 4 shows the selectivity behavior of graphene oxide thick films towards different gases such as NO_2, acetone, methanol, ethanol and LPG. Selectivity is an important parameter that indicates the ability of a gas sensor to preferentially detect a particular target gas in the presence of other interfering gases. The selectivity histogram clearly demonstrates that the GO thick film sensor exhibits the highest response towards NO_2 gas compared with other tested gases. The selectivity value for NO_2 is 100 % is considered as the reference maximum response of the sensor [21, 22].

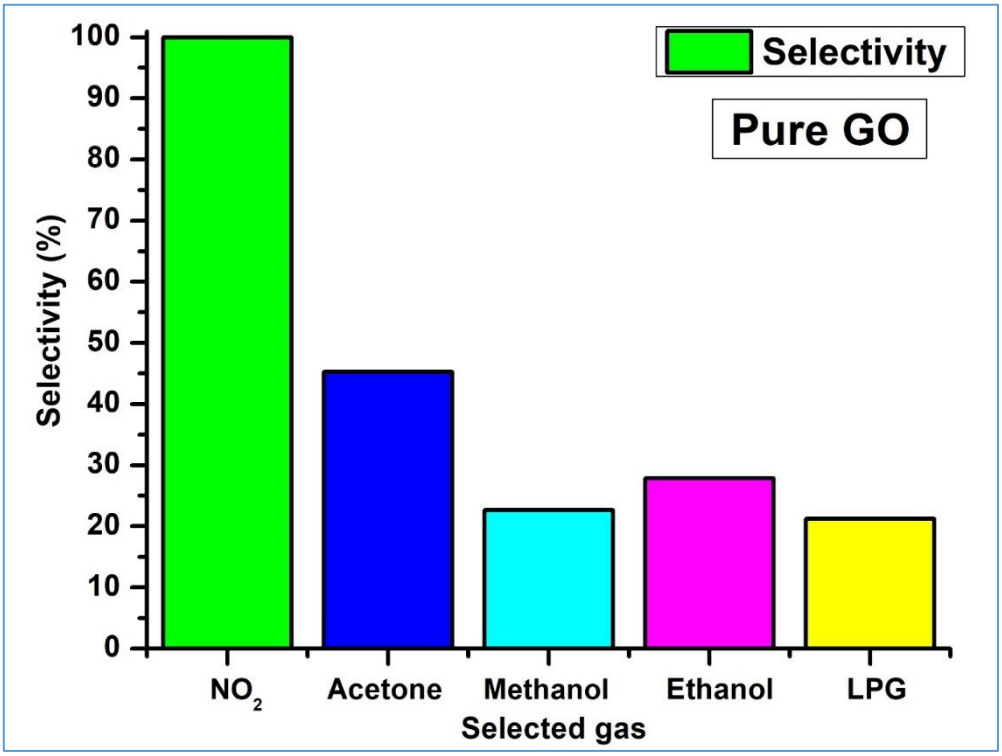

Figure 4. Selectivity histogram of GO thick films

In comparison the selectivity values for other gases are significantly lower where acetone shows 45.27 % methanol shows 22.64 % ethanol shows 27.84 % and LPG shows 21.22 %. This large difference in response indicates that the GO thick film sensor possesses strong selectivity towards NO_2 gas. The enhanced selectivity could be attributed to the strong interaction between NO_2 molecules and the oxygen functional groups present on the graphene oxide surface which promotes effective charge transfer and adsorption of NO_2 molecules [18-20]. Therefore, the results confirm that the GO thick film sensor is highly selective for NO_2 detection compared with other interfering gases which makes it suitable for environmental monitoring and toxic gas detection applications.

3.3 PPM variation

Figure 5 shows the variation of gas response of graphene oxide thick films with respect to different NO_2 gas concentrations measured at the optimum operating temperature of 100 °C. The sensing performance was evaluated at various gas concentrations ranging from 100 ppm to 1200 ppm. It is clearly observed that the gas response of the GO thick film sensor increases with the increase in NO_2 gas concentration up to a certain level. At 100 ppm the sensor exhibits a gas response of about 23.5 %. When the concentration increases to 300 ppm the gas response increases to around 32.4 % indicating enhanced interaction between NO_2 molecules and the sensing surface [16, 19].

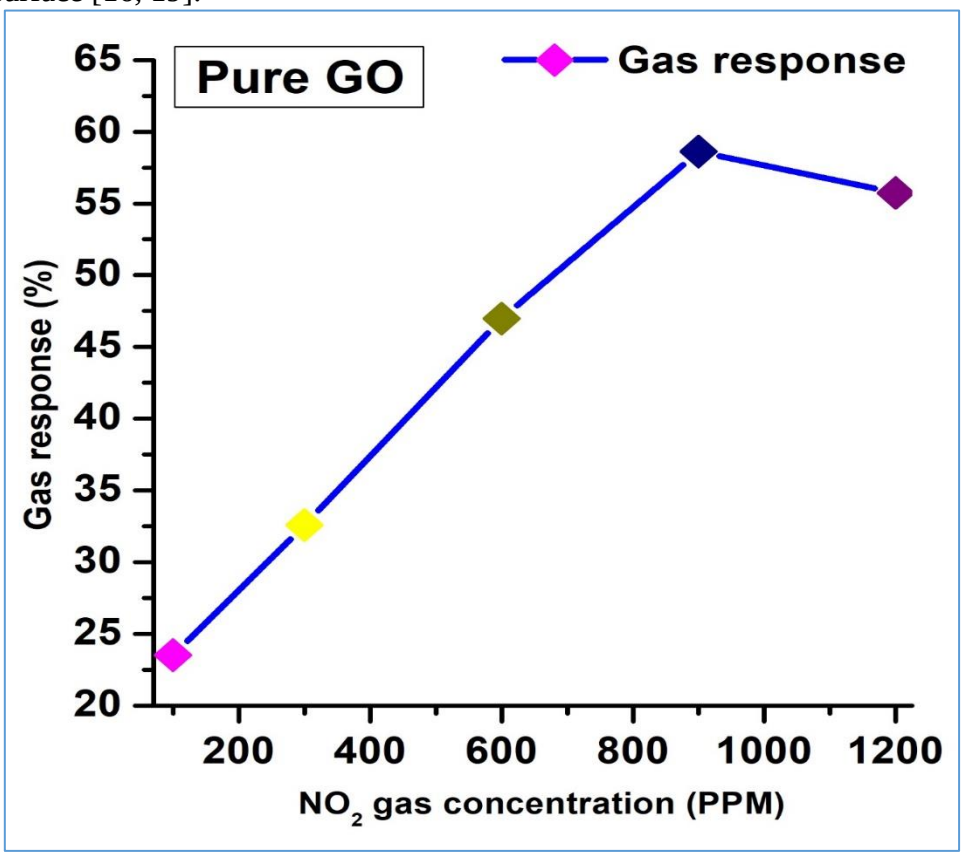

Figure 5. Gas response versus NO_2 gas concentration plot of GO thick films at 100^oC

Further increase in NO_2 concentration to 600 ppm results in a higher gas response of about 46.9 % due to the increased adsorption of gas molecules on the GO surface. The maximum response is observed at 900 ppm where the sensor shows a gas response of approximately 58.6 % which corresponds to the optimum sensing performance of the GO thick film sensor. However when the gas concentration further increases to 1200 ppm the response slightly decreases to around 55.8 % which may be attributed to partial saturation of the active adsorption sites on the sensing surface [14, 18]. The increase in gas response with increasing NO_2 concentration is due to the greater number of gas molecules interacting with the oxygen functional groups present on the graphene oxide surface which enhances charge transfer and resistance change in the sensing layer. These results indicate that the GO thick film sensor exhibits strong sensitivity and a good response towards different concentrations of NO_2 gas.

3.4 Response and recovery time

Figure 6 shows the dynamic gas sensing behavior of graphene oxide thick films in terms of gas response versus time for NO_2 gas at the optimum operating temperature of 100 °C. The plot clearly illustrates the response time (ON time) and recovery time (OFF time) characteristics of the sensor [16]. When the GO thick film sensor is exposed to NO_2 gas the gas molecules interact with the sensing surface which results in a rapid increase in gas response. Initially the response starts from nearly 0 % and gradually increases reaching the maximum value of about 58.6 % within approximately 14 seconds. This duration required for the sensor to reach 90 % of its maximum response after exposure to the target gas is known as the response time.

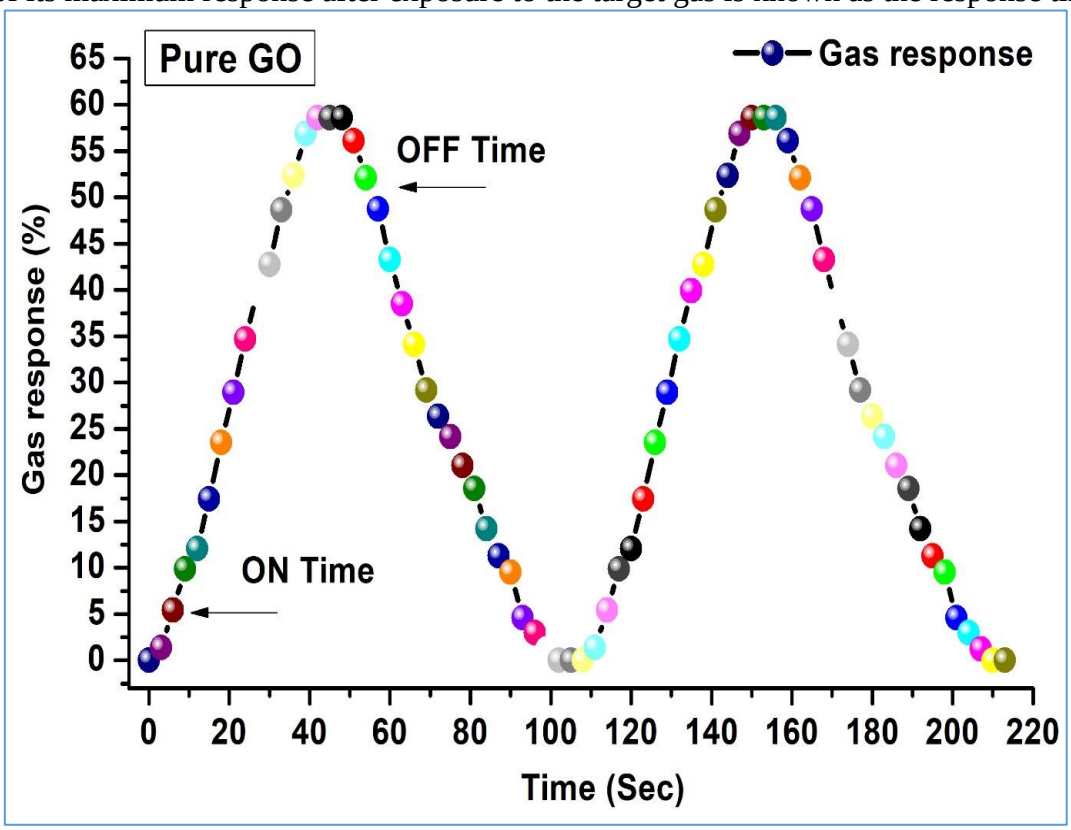

Figure 6. Gas response versus time plot of GO thick films

After the gas supply is stopped and the chamber is exposed to fresh air the adsorbed NO_2 molecules start desorbing from the surface of the GO thick film. As a result the gas response gradually decreases and returns close to its original baseline value. The time required for the sensor to recover 90 % of its initial resistance is known as the recovery time. In the present study the GO thick film sensor shows a recovery time of approximately 53 seconds. The cyclic rise and fall of the response curve indicates good repeatability and stability of the GO thick film sensor [18, 19]. The relatively fast response and recovery behavior can be attributed to the large surface area of graphene oxide and the presence of oxygen containing functional groups which facilitate efficient adsorption and desorption of NO_2 molecules on the sensing surface [20, 21].

3.5 Reproducibility

Reproducibility is an important parameter of a gas sensor that indicates its ability to produce nearly identical sensing responses when the measurement is repeated under the same operating conditions over a period of time. It reflects the stability reliability and consistency of the sensing material [21, 22]. A sensor with good reproducibility shows only small variations in gas response during repeated sensing cycles.

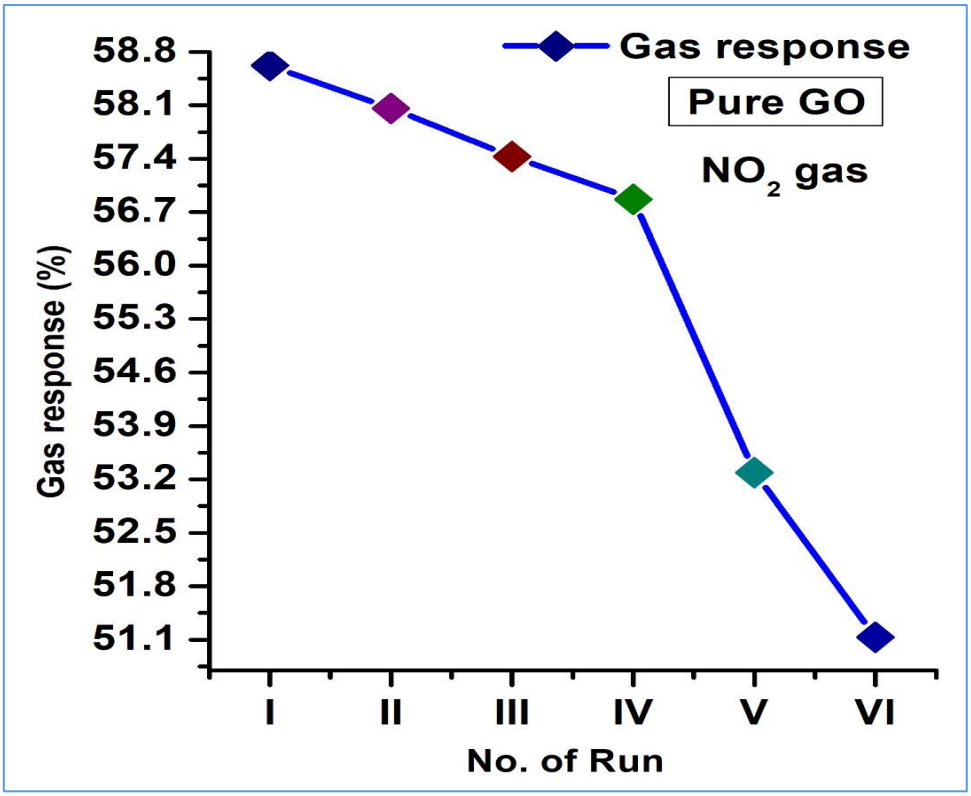

Figure 7. Gas response versus run plot of GO thick films

Figure 7 illustrates the reproducibility behavior of graphene oxide thick films towards NO_2 gas at the optimum operating temperature of 100 °C. The sensing performance was evaluated for six consecutive runs where each run represents an interval of 7 days. From the results it is observed that the GO thick film sensor maintains a high gas response during repeated measurements [23, 24]. During the first run (I) the sensor exhibits a gas response of 58.62 %. In the second run (II) the response slightly decreases to 58.06 % while the third run (III) shows a response of 57.43 %. Further measurements indicate responses of 56.87 % in the fourth run (IV) and 53.29 % in the fifth run (V). In the sixth run (VI) the sensor still exhibits a considerable response of 51.13 %. Although a gradual decrease in gas response is observed over several runs the sensor maintains relatively high sensitivity towards NO_2 gas even after 42 days of operation [25, 26]. This slight reduction in response may occur due to partial occupation of active sensing sites or minor surface contamination on the GO surface [27]. The results confirm that the GO thick film sensor demonstrates good reproducibility and long term stability which is essential for reliable gas sensing applications.

CONCLUSIONS

Graphene oxide thick films were successfully fabricated on glass substrates using a simple and cost effective screen printing technique. The prepared thick films were systematically investigated for their gas sensing performance using a static gas sensing system towards different gases such as NO_2 acetone methanol ethanol and LPG. The sensing studies revealed that the GO thick film sensor exhibits strong dependence on operating temperature and type of gas. The maximum gas response of 58.62 % towards NO_2 gas was observed at the optimum operating temperature of 100 °C which indicates high sensitivity and selectivity of the sensor towards NO_2 gas compared with other tested gases. The sensor also demonstrated fast response time of 14 seconds and recovery time of 53 seconds showing rapid adsorption and desorption of gas molecules on the GO surface. In addition the sensor showed good selectivity high reproducibility and stable sensing performance even after repeated measurements over several weeks. The enhanced sensing characteristics can be attributed to the large surface area and the presence of oxygen containing functional groups in graphene oxide which promote effective interaction with NO_2 molecules. Therefore the results confirm that the screen printed GO thick films are promising sensing materials for efficient detection of NO_2 gas in environmental monitoring and air quality control applications.

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