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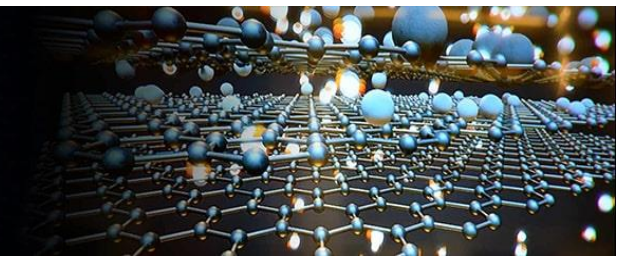

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Development of zinc oxide based ethylene glycol sensor

Malikarjun Wakade and Megha Mahabole

Abstract
This study presents the design and evaluation of a low-temperature ethylene glycol (EG) sensor utilizing zinc oxide (ZnO) as the sensing material. The sensor aims to operate efficiently at reduced temperature, enhancing its versatility for various environmental conditions. Thick film of procured ZnO is developed on glass substrate using screen printing technique. The material is characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis-Differential Thermal Analysis (TG-DTA), and Uv-visible (UV) spectroscopy. The properties of the ZnO sensor are thoroughly investigated for ethylene glycol. And various gas sensing parameters are determined. The sensor detects EG at 155 °C with fast response and recovery time (120 sec.), lower saturation limit (2ppm to 100ppm). It demonstrating long-term stability. This study contributes to the development of new EG sensor and highlights ZnO as a promising material for sensitive and reliable EG detection.

Keywords: Zinc oxide, EG sensor, thick films and screen printing techniques

1. Introduction
Pollution is one of common issues faced all over the world. Specifically, air pollution is the major type of pollution. The presence of pollutants or toxins or compounds in the air that can cause damage to the living beings and the environment can be referred to as environmental air pollution. Air pollution can be created by either natural processes or human actions. Existence of various toxic gases namely carbon monoxide, carbon dioxide, nitrous oxide, sulphur dioxide, volatile organic compounds in excess may be responsible for respiratory issues, health & environmental impacts, cardiovascular effects, environmental damage and climate change [1]. Therefore, the monitoring and detection of hazardous gases is essential for safeguarding human health which may be helpful in preventing environmental degradation, ensuring compliance with regulations, and responding effectively to emergencies.
Ethylene glycol (EG), one of the main air pollutants, is a commonly used chemical in various industrial applications. Ethylene glycol is a key component in many automotive antifreeze and coolant formulations. It is used as a deicing agent for aircraft and as a heat transfer fluid in industrial processes. It is a common ingredient in the production of polyester fibers and films. It is recycled in some household products, such as de-icing solutions and also used in some fire suppression systems. Though it has several uses, it is considered hazardous in certain contexts [2-4]. Ethylene glycol metabolizes in the body to toxic compounds that can damage the kidney and nervous system. There is a risk of accidental ingestion, especially if the coolant leaks or spills. Accidental spills or releases can contaminate soil and water which may pose a threat to the environment. Ethylene glycol is also harmful to aquatic life. Exposure to EG vapor or skin contact can cause irritation. Prolonged exposure during manufacturing processes may lead to adverse health effects [5]. Due to various adverse effects of proper handling, storage, and disposal procedures, it is essential to minimize the hazards associated with ethylene glycol. Hence, the detection of EG is must to minimize the impact of hazardous ethylene glycol on both human health and the environment.
According to literature survey very few EG sensor have been developed by the researchers so far. Peng Fei Cao and colleagues have shown the effectiveness of a hydrothermally synthesized Bi_2WO_6 nanomaterial for detect ethylene glycol at an ideal working temperature of 270 °C [6]. Ting Han and group have developed an electrospun $SmFeO_3$ nanomaterial for detection of EG with an ideal working temperature of 240 °C [7]. Miao Miao Liu *et al*. effectively identified ethylene glycol using $SmFeO_3$ microspheres [8].

Somayeh Saadat Niavo *et al*. have developed mesoporous Zn_2SnO_4, which was successful in detecting ethylene glycol vapour [9]. Paiva *et al*. were able to identify ethylene glycol using an electrochemical sensor based on a modified glassy carbon electrode with reduced graphene oxide and Ni-Au nanoparticles [10]. A high-performance ethylene glycol sensor was developed by Jin Sha Wei and associates using fibrous $ErFeO_3$, via electrostatic spinning process [11]. Ultra-sensitive Bi_2WO_6 nanostructures that resemble dandelions were studied by Peng Fei Cao and colleagues for sensing ethylene glycol [12]. $ZnFe_2O_4$ hollow spheres have shown to enhanced gas sensing capabilities notably in terms of ethylene glycol sensitivity and long-term stability [13]. C Su and associates have synthesized CuO-NiO nanotubes for detection of EG [14]. According to research by Wenjin Wan, 2D SnO_2 sheets could detect EG vapours at 3.4 V [15]. This revels that variety of materials are employed for detection of EG Still there is a scope to develop EG sensor. The scarcity of literature for the use of ZnO as ethylene glycol sensor has prompted us to study in this field. Therefore, the efforts have been made to devolve ZnO based EG sensor.

Zinc oxide (ZnO) is one of the most widely used n type semiconducting metal oxide materials due to its excellent optical and electrical properties, high chemical stability and ecofriendly nature. Zno is a representive of II - VI group compound with wide band gap of 3.37 eV. ZnO has attracted much attention as a gas sensor because of its chemical sensitivity towords various gases, high chemical stability, suitability to doping, non-toxicity, low cost and oxygen vacancy based conducting mechanism. ZnO can be easily synthesized and deposited onto various substrates using various methods. ZnO has alredy been used to detect an array of gases like carbon monoxide (CO), nitrogen dioxide (NO_2), methane (CH_4), hydrogen (H_2), and volatile organic compounds (VOCs). In-depth research on feather-like ZnO nanopowder, produced hydrothermally, was carried out by Somayeh Saadat Niavol, wherein good selectivity to EG was observed [16]. ZnO/rGO nanosheets, developed by Jijun Ding works a very sensitive ethylene glycol gas sensor that can be operated at 220 °C [17]. $ZnO/ZnCO_2O_4$ hybrid ethylene glycol sensors were studied by Miao Liu *et al*. in an effort to overcome $ZnCO_2O_4$ sensors' poor response at low working temperatures (160 °C) [18]. As per literature survey, almost all ZnO based sensors developed to detect EG, work at high temperatures (in the range of 160 to 220 °C) moreover ZnO material is employed generally in thin film form to detect EG. However, EG detection by screen printed ZnO thick film has not been reported so far. Hence, efforts have been made to develop ZnO thick film sensor for detection of EG. Similarly the effect of temperature, gas concentration, exposure time and durability have been investigated and various gas sensing parameter also been optimized in the present study.

2. Experimental

In this work, ZnO and ethylene glycol are used as the main precursors. They are used without further purification for this experimental study and are procured from Sigma Aldrich and S.D. Fine Chemical Limited respectively. The procured ZnO powder is characterized by various analytical methods namely XRD, FTIR, TG-DTA and SEM to have details about structural, functional, thermal, and morphological, characterization of ZnO. Optical properties of ZnO are studied in film form with the help of UV-Visible photo spectrometer. Thick films of ZnO are developed via screen printing technique. Initially thixotropic paste is prepared by homogenous mixing of ZnO (functional material) and binders (glass frit, ethyl cellulose and BCA) by maintain the inorganic to organic ratio as 70:30. The films (1X2 cm^{-1}) are deposited on a pre-cleaned glass substrate by forcing the paste to pass through porous screen. The films are first dried under IR lamp for 20 min for removal of temporary binders and finely annealed in air at 550 °C for 2 hrs using programmable furnace for the proper adhesion of material on the glass substrate. These films ware used as sensors for further study [19].

3. Gas sensing performance of developed thick films

The gas sensing performance of ZnO thick film sensor is studied using static gas characterization system developed in our lab. Briefly, the sensor is kept on a substrate the sensor is heated with the help of heater from room temperature to 200 °C to have stable base. Sensor resistance is measured in air at an interval of 5 °C temperature. Later on a 2 ppm of EG is injected into the test chamber through a gas inlet valve by using the syringe to have an EG + air mixture. This is followed by the measurement of resistance with respect to change in temperature. The sensing characteristics of the ZnO thick film sensor is determined by measuring the change in electrical resistance of the sensor film in air (R_a) and in EG–air mixture (R_g). The sensitivity to ethylene glycol is calculated using the following equation [19, 20]:

$$Gas\ response\ S(\%) = \frac{R_g - R_a}{R_a} \times 100 \quad (1)$$

Where R_a is the resistance of sensor in air and R_g the resistance of sensor after (EG + air) exposure. The change in sensitivity of the film is plotted as a function of temperature and operating temperature is determined corresponding to a maximum sensitivity. The maximum EG uptake capacity of the sensor film is determined by exposing the film to variable EG concentrations (ppm) and simultaneously measuring the change in sensitivity as a function of variable EG concentration (ppm). The time taken by the sensor to respond to a fixed EG concentration (response time) and to regain its original state upon exposure to air (recovery time) are determined by exposing ZnO thick film to air and fixed concentration of (EG + air) mixture alternately. Stability of the sensor is determine by measuring sensitivity after every 5 days up to one month.

4. Results and Discussion

4.1 X-ray Diffraction

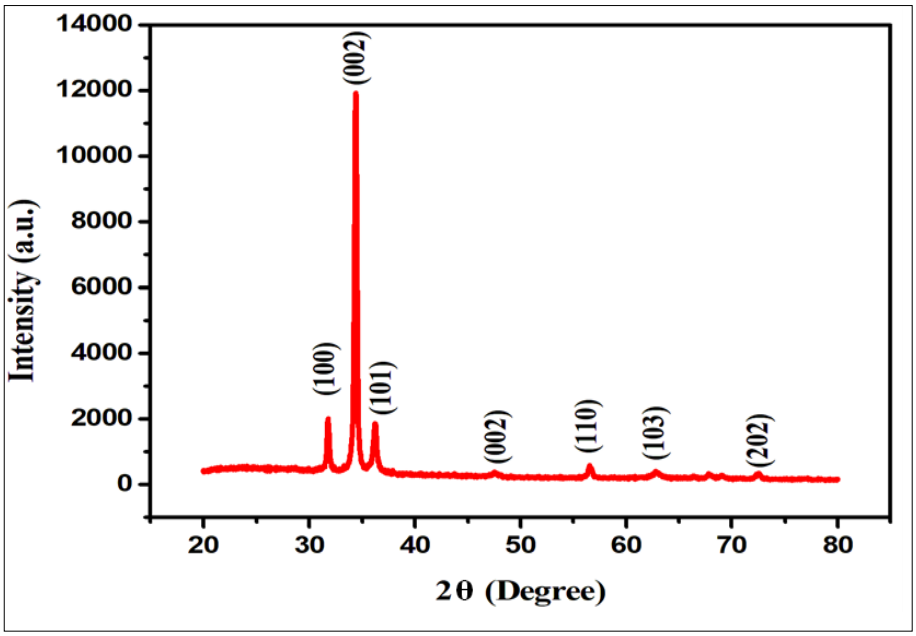

Fig 1: X-ray diffraction pattern revealing highly crystalline structure of ZnO

Figure1 shows the X-ray diffraction pattern of ZnO nanoparticles in the 2θ range of 20°-80°, X-ray diffraction patterns confirm the hexagonal phase with a wurtzite structure, showcasing peaks corresponding to (100), (002), (101), (002), (110), (103), and (202) planes [20]. The grain size is calculated for highest intensity diffraction peak appearing at around 2 θ value of 34° the grain size, calculated using Scherrer's formula, is found to be 61 nm. It show the growth of along (002) plane.

4.2 Fourier Transform Infrared Spectroscopy

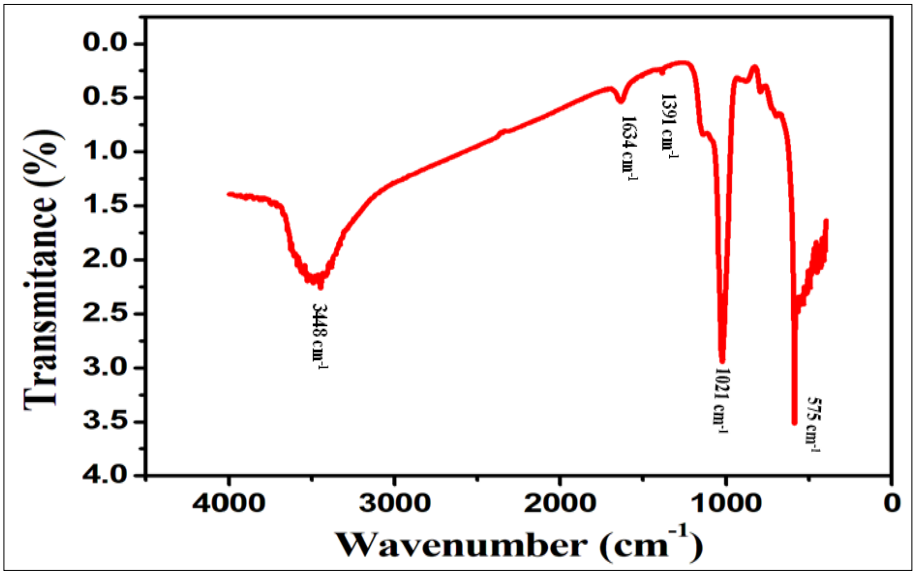

Fig 2: FTIR Spectra of ZnO showing the presence of corresponding functional groups

Figure 2 indicates the FTIR spectrum of ZnO in the range of 400-4000 cm^{-1}: it reveals the presence significant bands at 575 cm^{-1} (Zn-O bonds), 1021 cm^{-1}, 1391 cm^{-1} & 2356 cm^{-1} which can be assigned to starching Zn-O. The peaks at 1634 cm^{-1} and 3448 cm^{-1} are due to O-H stretching vibrations.

4.3 Thermogravimetric Analysis

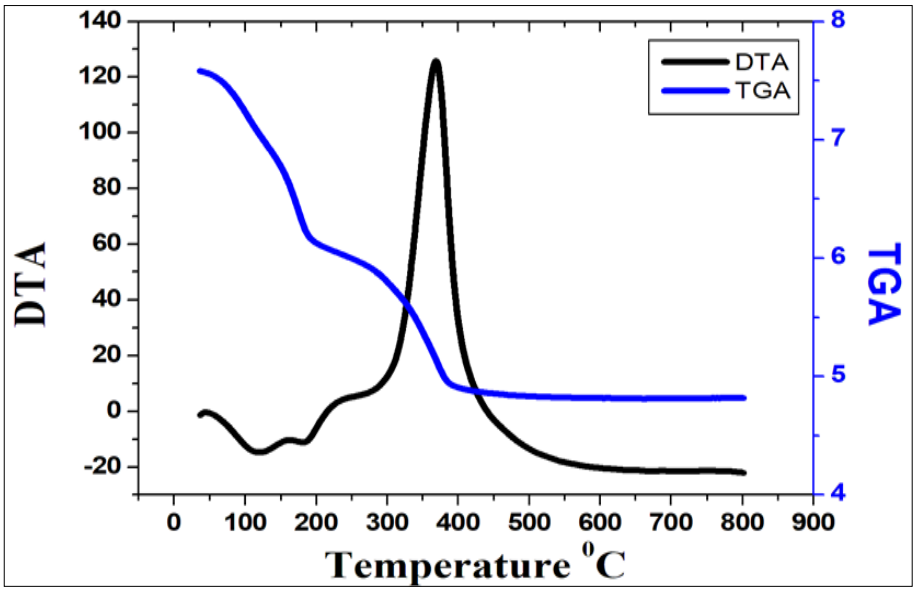

Fig 3: TG-DTA plot showing thermal behaviour of ZnO nanoparticles

Thermal behavior of ZnO is presented in figure 3 two stage weight loss is observed for ZnO. Significant weight loss observed in a temperature range RT to 150 °C (1st stage) can be assigned to removal of moisture. Second stage weight loss is observed in a temperature range of 200 °C to near about 400 °C. This result is well supported by the occurrence of exothermic peak at around 350 °C to 400 °C.

4.4 Scanning Electron Microscopy

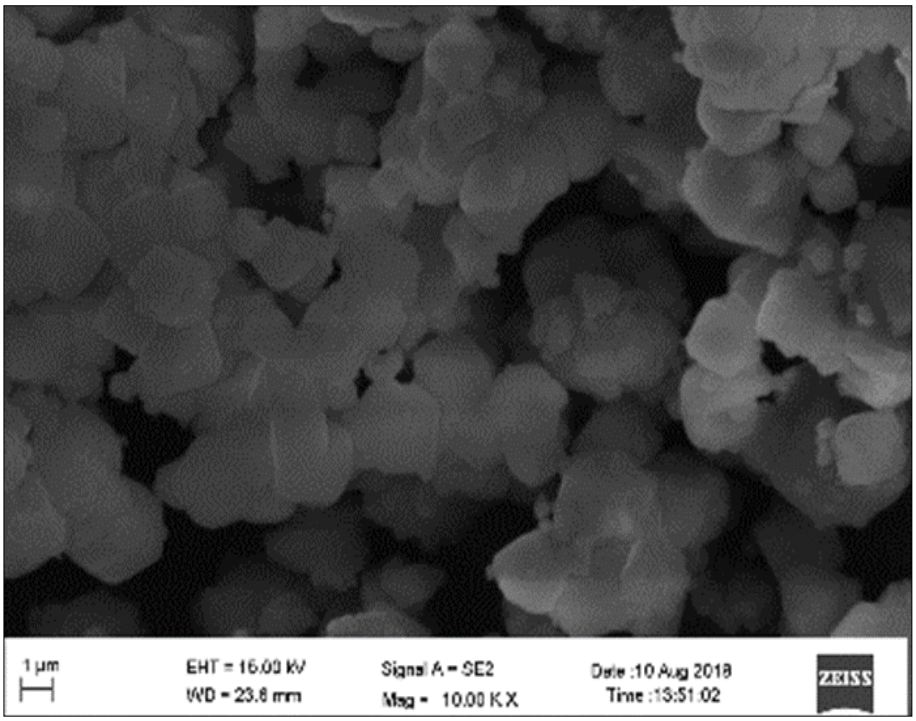

Fig 4: Scanning Electron Micrograph depicting surface morphology of ZnO nanoparticles

The SEM image of ZnO shows the particle of cubical shape particles of variable sizes. Agglomeration of particles can also be seen from figure 4.

4.5 UV-Vis Spectroscopy

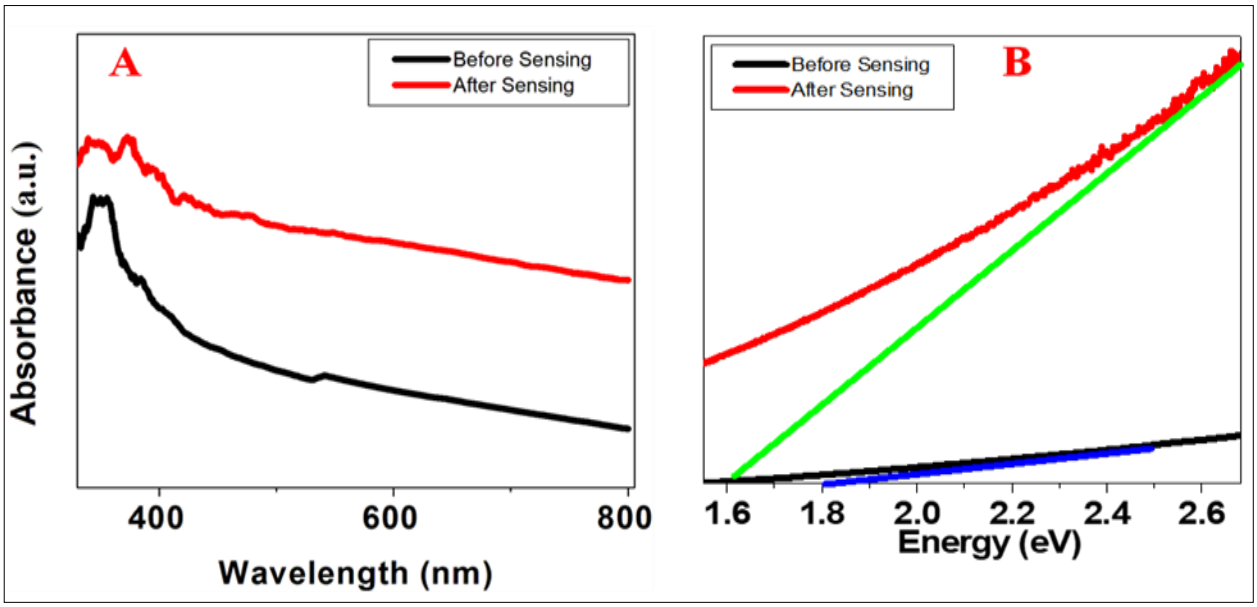

Fig 5: UV-Visible absorbance spectra; (A) ZnO nanoparticles before and after adsorption of EG molecules, (B) corresponding Tauc plot.

Variation in optical absorbance as a function of wavelength is shown in figure 5A. The corresponding Tacu plots are presented in figure 5B and are employed for band gap determination. Plot of wavelength vs absorbance showing the optical properties of ZnO screen printed thick film before and after exposure to EG. UV-visible absorption spectroscopy indicates a strong absorption band at 352 nm which can be attributed to surface-bound ZnO particles. The band gap decreases after adsorption of EG form 1.8 eV to 1.6 eV. This may be due to the formation of dopant energy level.

5. Gas Sensing Performance

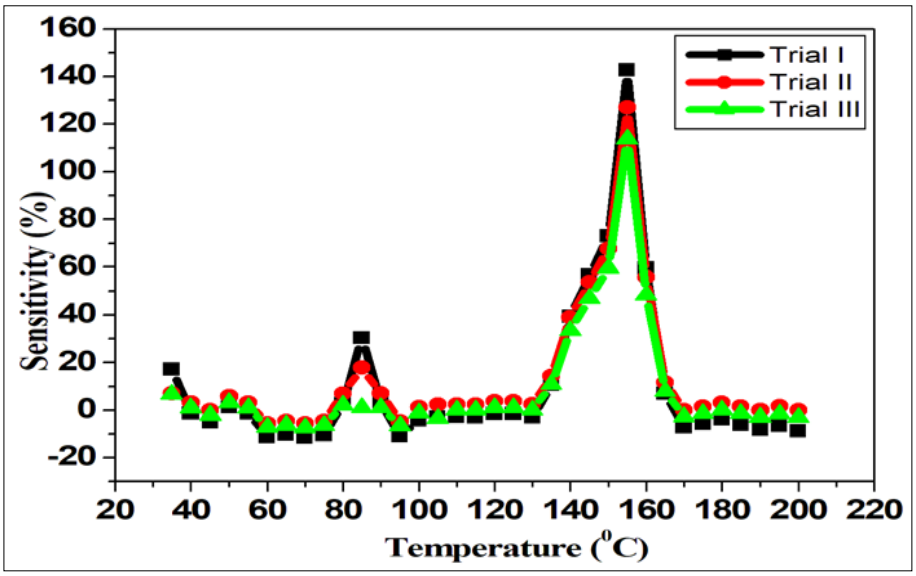

Fig 6: Variation in response to EG with temperature

Figure 6 depicts the variation of the sensitivity as a function of temperature in Ethylene glycol atmosphere. The gas response initially remains very low at lower temperatures and increases with increase in temperature and becomes maximum at particular temperature. With further increase in temperature, it goes on decreasing. The maximum gas response shows a maximum corresponds to operating temperature of the sensor film. For ZnO thick film, the gas response is found to be 140% at an operating temperature 155 °C [10-21].

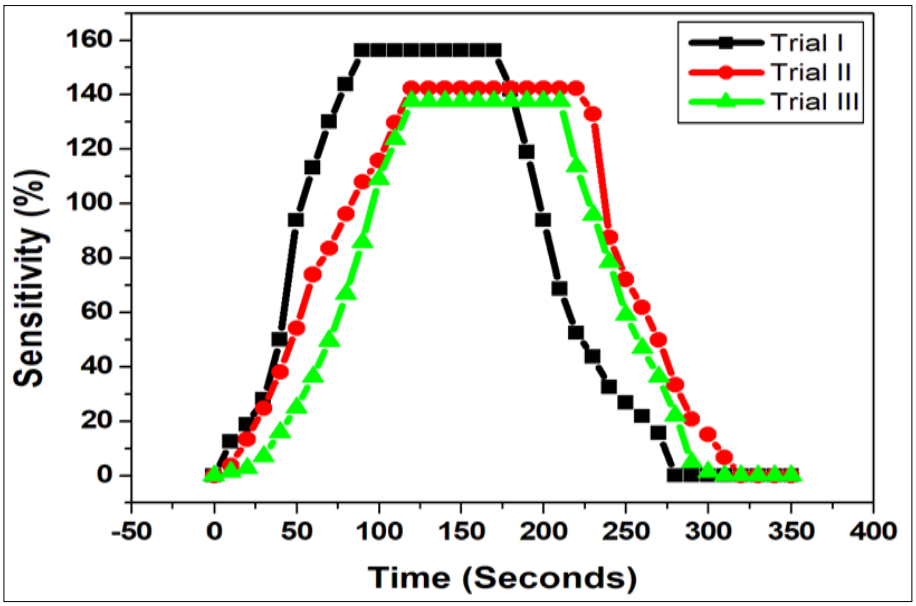

Fig 7: Change in response to EG as a function of time

Figure 7 represents the variation in sensitivity factor with time in response to 2 ppm ethylene glycol for the ZnO thick film held at 155 °C. When the sensor is exposed to EG atmosphere, sensitivity factor is found to be increasing with time which later on remains constant with further increase in time. Upon exposure to air, again sensitivity factor is reduce. It can be concluded that the average response time of ZnO thick film to ethylene glycol is 120 sec, and the average time needed to reach original base value is 120 sec when exposed to air atmosphere. This value found to be lower than that reported in literature [17, 18].

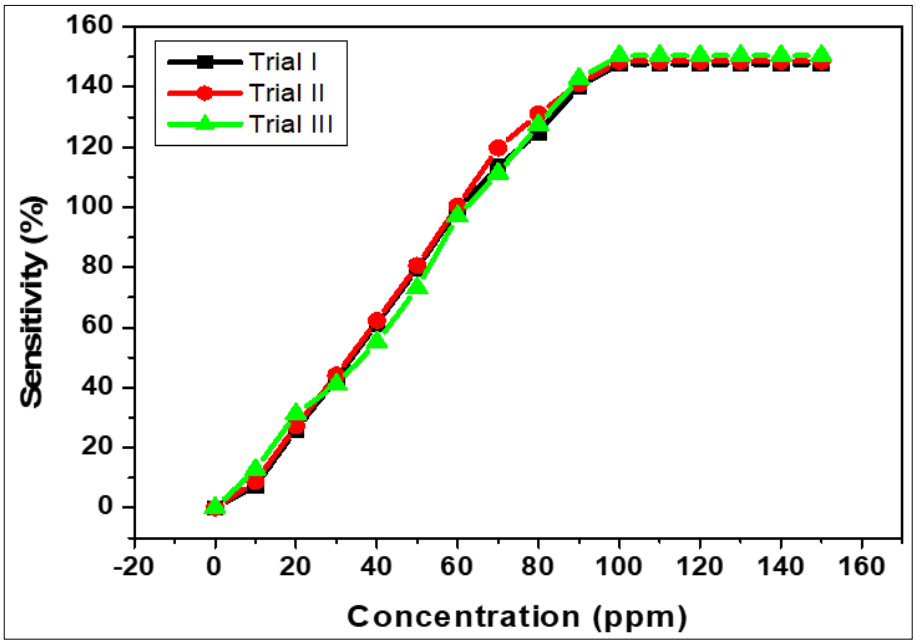

Fig 8: Change in response as a function of EG concentrations

Figure 8 shows the gas response as a function of EG concentration ranging 2 to 100 ppm. It is observed that response increases linearly with EG concentration from 2 ppm to 100 ppm. For further increase in EG concentration response saturates.

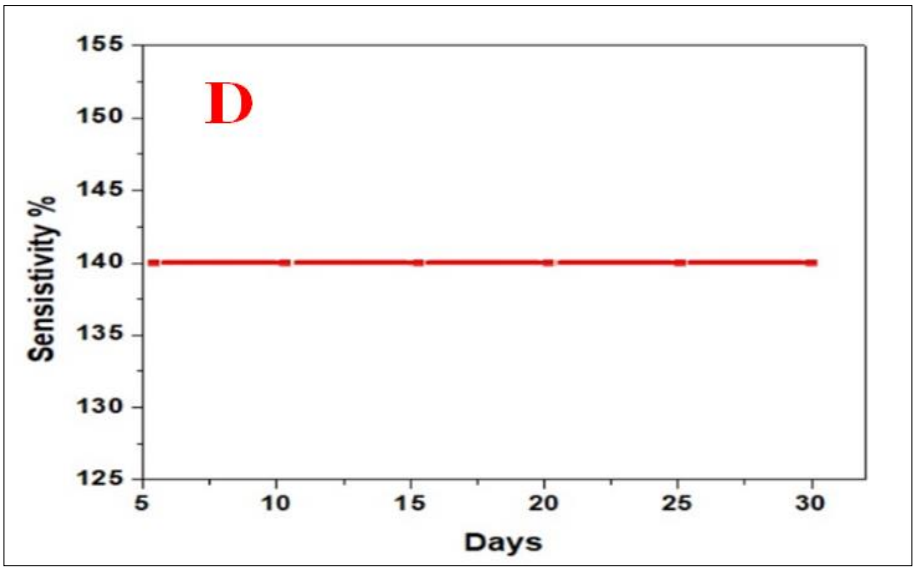

Fig 9: A plot of sensitivity with time duration revealing stability of ZnO sensors.

The stability of the EG sensor is examined by repeating the readings after every five days for a fixed 2ppm ethylene glycol concentration. Thus, the reproducibility of the manufactured sensors is verified by exposing the sensor films to set EG concentrations while maintaining the same environmental conditions. It can be concluded that there is negligible variation in sensitivity with duration indicating the long term durability of the sensor.

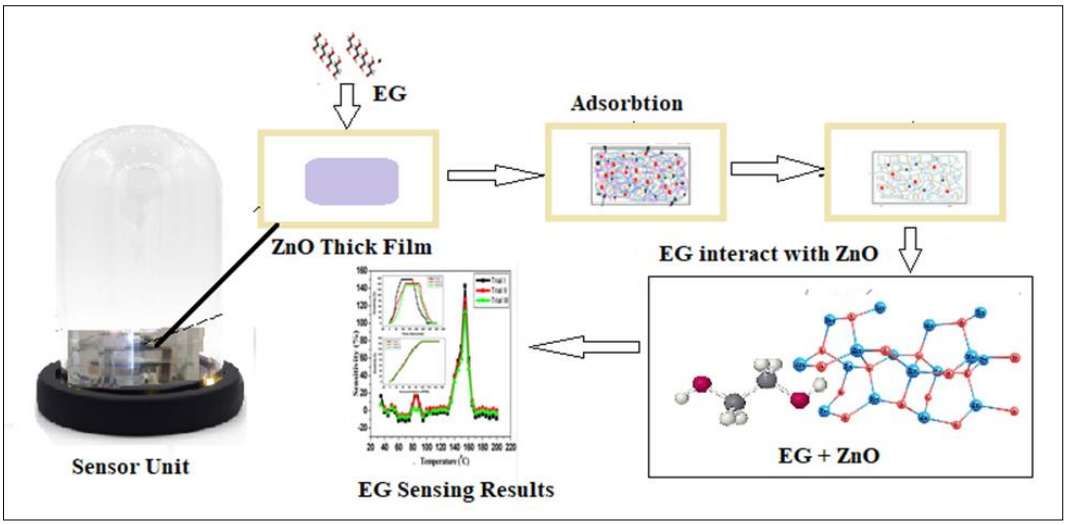

Fig 10: A schematic picture demonstrating potential mechanism of adsorbed ethylene glycol molecules interacting with the ZnO surface.

Figure 10 shows the schematic representation of interaction of ethylene glycol with ZnO. Gas sensing is surface phenomenon where in gas are adsorbed in case of ZnO the oxygen molecule from air adsorb on the ZnO surface and changes oxygen in to oxygen ions. Thus, electron transport between adsorb oxygen and ZnO surface takes place. As a result, electron depleted layer is formed within the surface and Fermi level decreases. Therefore electrical conductivity changes. When EG molecule adsorb on the sensor surface they interact with oxygen ions and get oxidized. Adsorption can involve the attachment of EG molecules to surface imperfections, oxygen vacancies, or other areas of interaction on the ZnO surface. This results in decreasing thickness of depletion layer and decreasing electrical resistance. Thus, the response of sensor towards EG changes. The maximum sensitivity at a particular temperature indicates the availability of large number of active sites on the surface at that temperature (155 °C) in comparison to that at other temperatures. The change in sensitivity with gas concentration is found to be low initially indicating availability of few active sites. The response changes linearly in low concentration region. For further increase in concentration the response remains almost constant. This may be due to the occupancy of all active sites thick film surface.

6. Conclusion

In conclusion, this study successfully developed thick film ZnO sensor for detection of ethylene glycol (EG). The operating temperature of ZnO thick film sensors is low (155 °C) The gas sensing performance showcased excellent sensitivity (140%), response & recovery time (120 sec.), concentration range (2ppm to 100ppm), and stability.

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8. References

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