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Preparation of ZnO Thin Films by Spin Coating Technique for LPG Detection

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Abstract

In the present study, zinc oxide (ZnO) thin films were successfully synthesized using the spin coating technique, a simple and cost-effective method suitable for producing uniform and adherent films. The primary objective of this work was to investigate the gas sensing properties of the prepared ZnO thin films, with particular emphasis on their response to liquefied petroleum gas (LPG). The gas sensing characteristics were evaluated using a static gas sensing system. Among the various target gases tested including ethanol, methanol, compressed natural gas (CNG), and ammonia the ZnO thin films exhibited the highest sensitivity towards LPG. A maximum sensitivity of 85.59% was recorded at an optimal operating temperature of 100 °C for an LPG concentration of 1000 ppm, demonstrating the film's excellent gas sensing performance at relatively low temperatures. The films showed high selectivity towards LPG over other interfering gases, indicating their potential utility in practical applications where gas discrimination is essential. In addition to high sensitivity and selectivity, the ZnO films displayed fast dynamic response characteristics, with a response time of 23 seconds and a recovery time of 55 seconds. These results suggest that ZnO thin films prepared via spin coating are promising candidates for efficient and reliable LPG gas sensor devices.

Keywords: Zinc Oxide, Spin Coating, Sensitivity, Thin Films, Recovery Time

1. Introduction:

Thin films are extremely fine layers of material, typically ranging from a few nanometers to several micrometers in thickness, deposited onto a substrate surface [1]. These films play a crucial role in modern science and technology due to their unique physical, chemical, optical, and electrical properties, which differ significantly from their bulk counterparts. In material science and sensor technology, thin films are widely used for their high surface-to-volume ratio, which enhances surface-related phenomena such as gas adsorption and reaction kinetics making them highly suitable for gas sensing applications [1, 2]. The structural uniformity and controlled thickness of thin films allow for precise tailoring of properties, including conductivity, porosity, and crystallinity, which are critical for sensor performance. Thin film deposition methods, such as spin coating, dip coating, sol-gel processing, sputtering, and chemical vapor deposition, offer flexibility in material design and integration onto various substrates [3, 4]. In gas sensors, thin films serve as the active sensing layer, where gas molecules interact with the surface, inducing changes in resistance or conductivity. These changes are then

measured and analyzed to detect and quantify the presence of specific gases. Due to their rapid response, low power consumption, and compatibility with miniaturized electronic devices, thin films are indispensable in the development of advanced sensing technologies, optoelectronic devices, photovoltaic cells, and protective coatings [3-5].

Metal oxide semiconductor (MOS) thin films are a vital class of materials extensively used in gas sensing, optoelectronics, and electronic devices due to their excellent physicochemical properties, environmental stability, and ease of fabrication [6, 7]. These films are composed of semiconducting metal oxides such as ZnO, SnO_2, TiO_2, WO_3, and In_2O_3, which exhibit a wide band gap and a high surface reactivity. When deposited as thin films typically in the nanometer to micrometer range their high surface area-to-volume ratio significantly enhances gas adsorption, making them highly responsive to chemical changes in their environment [7]. The working principle of MOS thin film gas sensors is based on the modulation of electrical conductivity caused by the interaction between the surface-adsorbed oxygen species and target gas molecules. Upon exposure to a reducing or oxidizing gas, the charge carrier concentration within the film changes, resulting in a measurable resistance change. This property makes MOS thin films highly sensitive to a variety of gases such as LPG, CO, NH_3, H_2, and volatile organic compounds [7, 8]. The sensitivity, selectivity, and response-recovery behavior of these films can be finely tuned by modifying their thickness, morphology, crystallinity, and dopant concentration. Fabrication methods such as sol-gel spin coating, sputtering, chemical vapor deposition, and pulsed laser deposition allow for precise control over film characteristics. MOS based thin films are indispensable in the development of low-cost, compact, and highly efficient gas sensing devices for environmental monitoring, industrial safety, and smart sensing applications [8, 9].

Zinc oxide (ZnO) nanoparticles have garnered significant attention due to their unique physicochemical properties, such as a wide bandgap (~3.37 eV), high exciton binding energy, and excellent chemical and thermal stability [10]. Synthesis of ZnO nanoparticles can be achieved through various methods, including sol-gel, hydrothermal, co-precipitation, and green synthesis techniques, each offering control over particle size, morphology, and crystallinity. These nanoparticles find diverse applications across fields such as gas sensing, photocatalysis, UV-blocking in sunscreens, antibacterial agents, piezoelectric devices, and optoelectronic components like LEDs and solar cells. Particularly in gas sensing, ZnO's high surface-to-volume ratio and reactive surface sites make it highly responsive to gases like LPG, NO_2, H_2S, and ethanol [10, 11]. In terms of recent advancements, researchers are focusing on doping ZnO with metals (e.g., Cu, Fe) or coupling it with other semiconductors (e.g., SnO_2, TiO_2, graphene) to enhance sensitivity, selectivity, and room-temperature operation [12]. The novel synthesis routes involving green chemistry and nano-structuring (nanorods, nanosheets, hierarchical architectures) are being explored to optimize surface activity and charge transport. These developments continue to broaden ZnO's applicability in next-generation sensor technologies, biomedical systems, and energy-efficient devices [12, 13].

The sol-gel spin coating technique is a widely used method for the fabrication of thin films, particularly for metal oxide semiconductors, due to its simplicity, low cost, and excellent control over film composition and thickness. The process begins with the sol-gel method, in which a stable colloidal solution or "sol" is prepared by dissolving metal precursors—such as metal alkoxides or metal salts in a solvent, usually accompanied by stabilizing agents or chelating compounds [15, 16]. Through hydrolysis and condensation reactions, the sol gradually evolves into a gel-like network. This sol is then deposited onto a substrate using the spin coating technique, where a few drops of the sol are dispensed onto the

center of a cleaned substrate which is then rapidly rotated at high speeds (typically between 1000–5000 rpm). The centrifugal force spreads the sol uniformly across the surface, forming a thin liquid film. As the substrate continues to spin, excess liquid is expelled, and solvent evaporation leads to film solidification [16]. The thickness and uniformity of the resulting film depend on parameters such as sol viscosity, spin speed, and spin duration. After deposition, the coated substrate is usually subjected to thermal treatment (drying and annealing) to remove organic residues and to convert the amorphous gel into a crystalline metal oxide phase. This combination of sol-gel chemistry and spin coating allows for precise control over film composition, microstructure, and functional properties, making it ideal for applications in gas sensors, optical coatings, photovoltaics, and microelectronics [16, 17].

In this research work, zinc oxide thin films were successfully fabricated using the spin coating technique, a reliable and cost-effective method that enables uniform film deposition with controlled thickness. The primary objective of the study was to evaluate the gas sensing performance of the ZnO thin films, with a specific focus on detecting liquefied petroleum gas.

2. Experimental work

All AR grade chemical were used in the present research work. The zinc oxide (ZnO) thin films were synthesized using a sol-gel based spin coating technique, employing zinc nitrate hexahydrate as the zinc precursor, ethanol as the solvent, and citric acid as the complexing and stabilizing agent. Initially, a 0.1 N of zinc nitrate was dissolved in 100 ml ethanol under constant magnetic stirring to ensure complete dissolution and uniformity. Citric acid was then gradually added to the solution in a molar ratio for chelating the zinc ions, leading to the formation of a clear and stable sol. The mixture was stirred continuously for 3 hours at room temperature to promote hydrolysis and polycondensation reactions, forming a homogeneous sol suitable for spin coating. The resulting sol was then deposited onto thoroughly cleaned glass substrates using a spin coater. A few drops of the sol were placed at the center of the substrate, which was then spun at a 3000rpm for 50seconds to achieve a uniform thin layer. After that the drying steps performed at around 80 °C under IR lamp to remove solvent residues. Then the coated films were annealing at a 400 °C temperature for 2 hours to enhance crystallinity. This process resulted in uniform, adherent, and porous ZnO thin films suitable for gas sensing applications [17-19].

3. Result and discussion

The gas sensing characteristics of the prepared ZnO thin films were evaluated using a static gas sensing system, as illustrated in Fig. 1 [20]. This setup is specifically designed to study the response of films to different target gases under controlled conditions. The core part of the system is the gas chamber, where the sensor is placed and exposed to the desired gas concentration. The sensor element, which consists of the ZnO thin film coated on a suitable substrate, is mounted on a heater assembly to achieve the required operating temperature. The heater is powered by a 230 V AC supply and is placed beneath the sensor to uniformly heat it. The thermocouple is in contact with the sensor or very close to it, and it continuously monitors the sensor's temperature, which is displayed on a temperature indicator. An insulator is used to isolate the sensor electrically and thermally from the base plate, ensuring accurate measurements without heat losses or electrical interference. The gas inject unit, connected to a syringe, introduces a known concentration of the target gas into the chamber. As the gas interacts with the ZnO thin film sensor, the resistance of the sensor changes is measured as a gas response [20, 21].

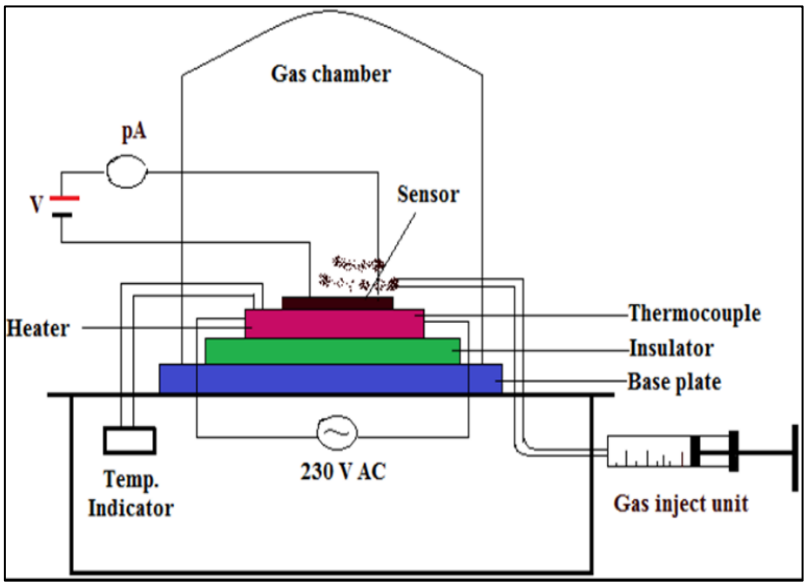

Fig. 1. Schematic diagram of static gas sensing system

The gas sensing behavior of pure ZnO thin films toward various gases, including LPG, CNG, ethanol, methanol, and ammonia, is illustrated in Fig. 2. Fig. 2 shows among all the tested gases, ZnO exhibits significantly higher sensitivity to LPG, with a pronounced peak of 85.59% observed at 100 °C. This clearly indicates that 100 °C is the optimal operating temperature for LPG sensing using ZnO thin films. At this temperature, ZnO demonstrates excellent selectivity to LPG compared to other interfering gases such as CNG (maximum ~17%), ethanol, methanol, and ammonia, all of which show relatively low sensitivities below 12%. The high selectivity and sensitivity can be attributed to the favorable interaction between LPG molecules and the surface-active sites of ZnO at this specific temperature [21, 22].

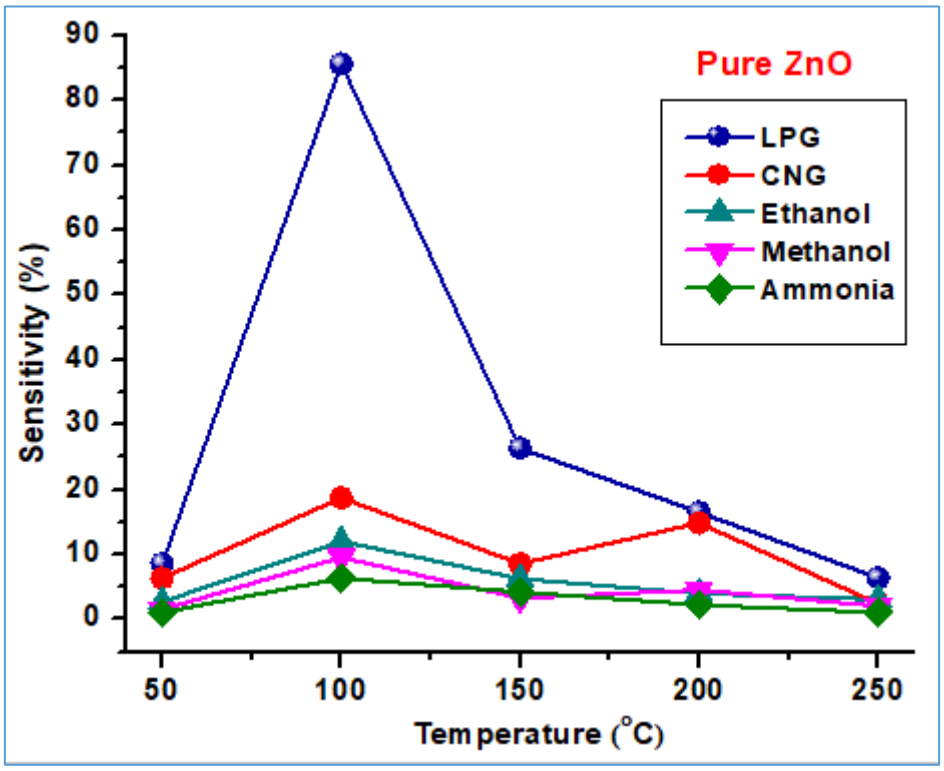

Fig. 2. Sensitivity versus operating temperature plot of ZnO thin films

The underlying gas sensing mechanism of ZnO towards LPG involves a typical chemiresistive response based on surface adsorption and redox reactions. ZnO is an n-type metal oxide semiconductor, and its gas sensing relies on the modulation of electrical resistance due to gas-surface interactions. In ambient air, oxygen molecules adsorb onto the ZnO surface and extract electrons from the conduction band, forming negatively charged oxygen species (O_2^-, O^-, or O^{2-}) depending on temperature. This creates a surface depletion layer, resulting in increased resistance [22, 23]. LPG is a reducing gas when it is introduced into the system, it reacts with the adsorbed oxygen species on the ZnO surface as follows–

$$C_nH_{2n+2}\ (LPG) + O^-\ (ads) \rightarrow CO_2 + H_2O + e^-$$

This reaction releases electrons back into the conduction band of ZnO, thereby reducing the thickness of the depletion layer and decreasing the film's resistance. The degree of resistance change is proportional to the gas concentration and is recorded as the sensor's response or sensitivity [23, 24]. The sharp peak at 100 °C suggests that this temperature offers optimal surface reactivity and electron mobility, enhancing gas adsorption and reaction kinetics.

Selectivity is a crucial parameter in gas sensing, representing the sensor's ability to preferentially respond to a specific gas in the presence of other interfering gases. Fig. 3 illustrates the selectivity performance of pure ZnO thin films when exposed to different target gases, namely LPG, CNG, ethanol, methanol, and ammonia. The bar chart clearly shows that ZnO thin films exhibit remarkably high selectivity toward LPG**,** with a selectivity value approaching 100%**,** which is significantly greater than that for other gases. The selectivity values for CNG, ethanol, methanol, and ammonia are considerably lower, indicating minimal cross-sensitivity. CNG shows moderate selectivity (~20%), while ethanol and methanol exhibit even lower values (~10–12%). Ammonia shows the least selectivity, below 10%, confirming that the ZnO sensor is least responsive to NH_3 under the tested conditions. The superior selectivity toward LPG can be attributed to the optimized surface reactivity of ZnO at the operating temperature (100 °C), which promotes stronger interaction and redox reactions specifically with LPG molecules. These reactions enhance electron exchange and lead to a more significant change in sensor resistance compared to other gases. Furthermore, the molecular size, bonding nature, and chemical reactivity of LPG may align more favorably with the active sites on the ZnO surface, enhancing its preferential detection [24, 25].

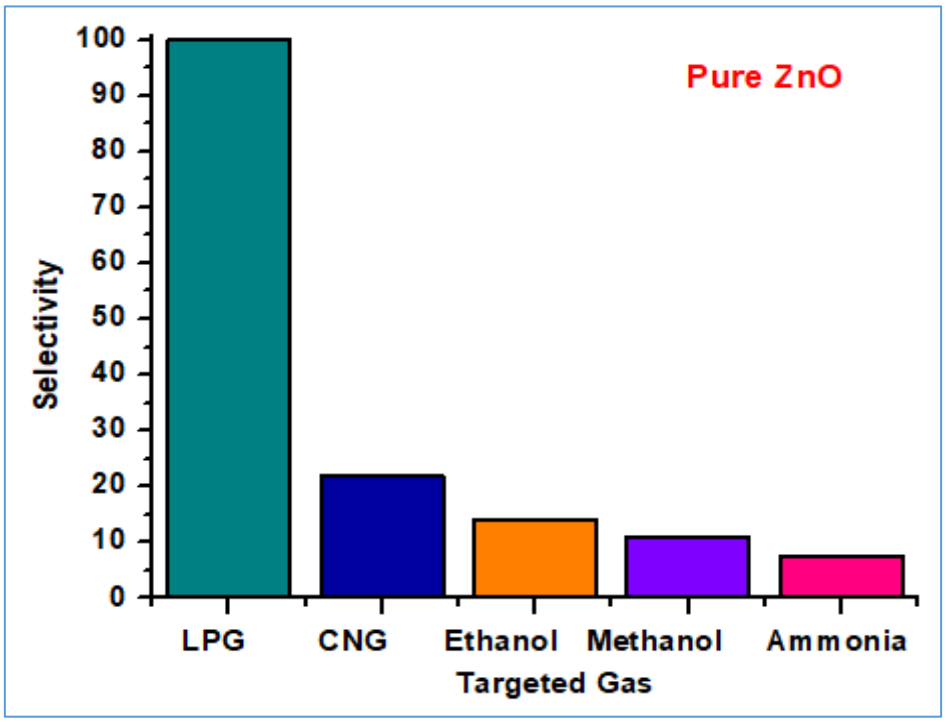

Fig. 3. Selectivity plot of ZnO thin films

Fig. 4 presents the variation in sensitivity of pure ZnO thin films with respect to different concentrations of LPG gas, ranging from 200 ppm to 1000 ppm.

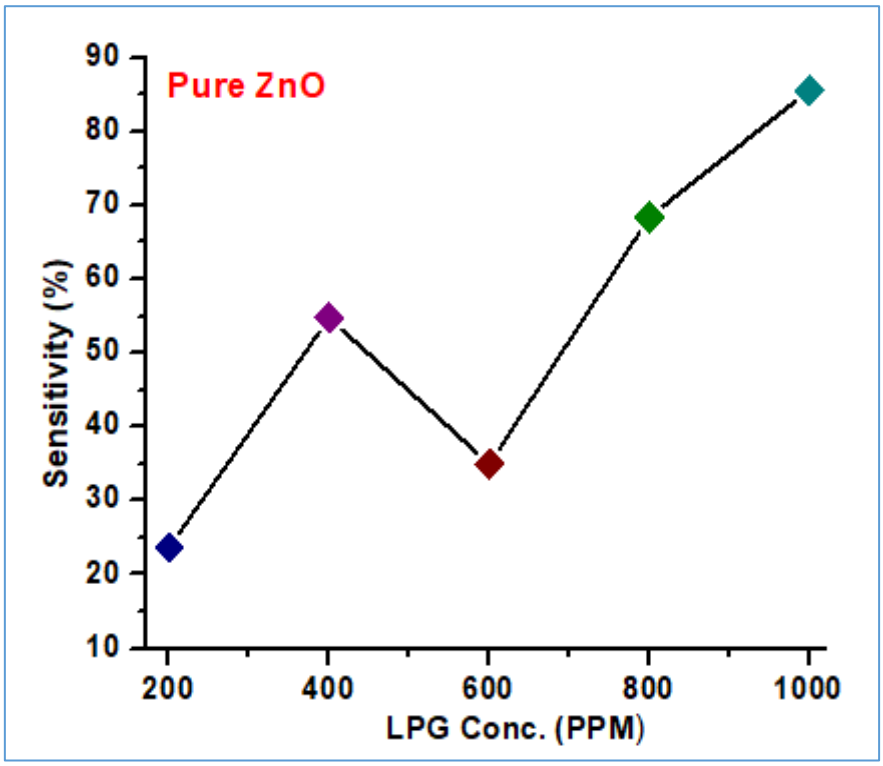

Fig. 4. Sensitivity versus LPG gas concentration (ppm) plot of ZnO thin films

Fig. 4 shown the sensitivity of the ZnO sensor increases with increasing LPG concentration, indicating that the film is highly responsive to the amount of target gas in the environment. The trend demonstrates a non-linear but overall rising response curve. At 200 ppm of LPG, the sensitivity is approximately 23%, indicating the sensor's capability to detect even low concentrations of the gas. As

the concentration is increased to 400 ppm, the sensitivity sharply increases to around 55%, suggesting an enhanced interaction between the gas molecules and the active sites of the ZnO surface [22, 25]. Interestingly, a slight dip in sensitivity is observed at 600 ppm (approximately 35%), which could be attributed to temporary saturation of adsorption sites or minor fluctuations in experimental conditions. However, beyond this concentration, the sensitivity rises again reaching approximately 68% at 800 ppm and achieving a maximum value of around 85.59% at 1000 ppm. This behavior confirms that ZnO thin films exhibit a concentration-dependent gas sensing performance, where more LPG molecules interacting with the surface lead to more pronounced changes in electrical resistance [29]. The increasing trend validates that ZnO has a high number of active surface sites and effective electron transfer capability, which contribute to its high sensitivity toward LPG [25, 26].

Fig. 5 illustrates the dynamic gas sensing behavior of ZnO thin films when exposed to and then removed from LPG gas, highlighting both the response time (ON time) and recovery time (OFF time) of the sensor.

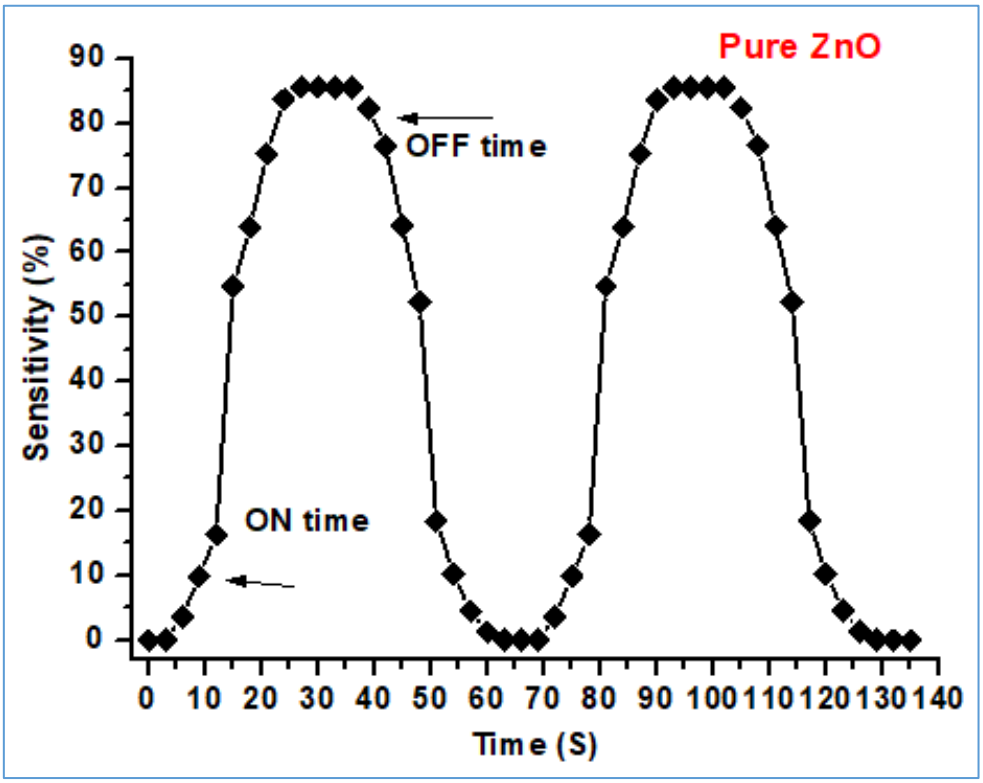

Fig. 5. Response and recovery time plot of ZnO thin films to LPG

The graph plots sensitivity (%) on the y-axis versus time (s) on the x-axis. Two cycles of gas exposure and removal are depicted, showing the repeatability and stability of the sensor's behavior. During the ON time, LPG gas is introduced into the chamber, leading to a rapid increase in sensitivity [21, 27]. The sensor's response begins near 10% and quickly rises to a maximum sensitivity of approximately 85.59%, indicating a response time of 23 s. This sharp increase is attributed to the interaction between LPG molecules and the ZnO surface, which alters the resistance of the material due to changes in charge carrier concentration. Following this, in the OFF time, the gas is evacuated or replaced with clean air, and the sensor begins to recover to its baseline state [27, 28]. The sensitivity gradually drops from its peak back toward 10%, and this transition occurs, which defines the recovery time of 55 s. This period reflects the time required for the desorption of gas molecules and re-adsorption of atmospheric oxygen on the ZnO surface [29, 30].

Conclusions

The ZnO thin films synthesized via the spin coating technique exhibit excellent sensitivity, selectivity, and stability toward LPG gas. The films demonstrated a maximum sensitivity of 85.59% at an optimum operating temperature of 100 °C and 1000 ppm LPG concentration, significantly outperforming other tested gases such as ethanol, methanol, CNG, and ammonia. The selectivity plot confirmed that ZnO thin films are highly selective to LPG, with minimal cross-sensitivity to other gases. The sensitivity increased with rising LPG concentration, indicating strong concentration-dependent behavior. The response and recovery analysis showed fast dynamics, with a response time of 23 seconds and recovery time of 55 seconds, highlighting the films' quick and reversible interaction with LPG molecules. These findings suggest that ZnO thin films are promising candidates for the development of efficient, selective, and fast-responding LPG gas sensors for practical applications.

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