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"A COMPREHENSIVE REVIEW ON ZnO THICK FILM GAS SENSORS: FROM SYNTHESIS TO SENSING"

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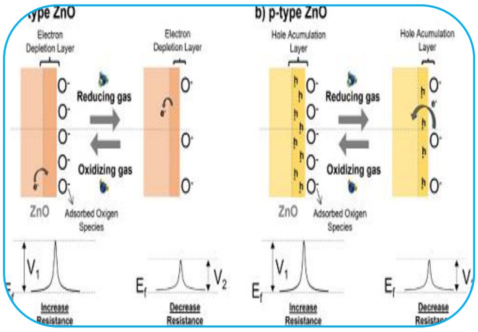
ABSTRACT

Zinc oxide (ZnO) is gaining attention for gas sensing due to its wide band gap, fast electron mobility, and strong chemical stability, making it suitable for industrial, healthcare, and environmental applications. This review focuses on ZnO thick film-based gas sensors, discussing their sensing mechanisms, synthesis methods, and characterization techniques. Common fabrication methods—sol-gel, screen printing, spray pyrolysis, and hydrothermal synthesis—offer distinct advantages in film shape, porosity, and crystallinity, influencing sensor performance. These techniques have shown success in detecting reducing gases and volatile organic compounds. Key characterization tools such as FTIR, UV-Vis spectroscopy, SEM, and XRD help link material properties to sensing behavior. The sensing mechanism relies on changes in ZnO's electrical resistance due to interactions with target gases and surface oxygen species. Factors like grain size, film thickness, surface area, and operating temperature affect sensitivity, selectivity, and response time. Future research aims to enhance low-temperature operation, selectivity, and long-term stability.



KEYWORDS: *X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR, and UV-Vis spectroscopy etc.*

INTRODUCTION:

The rapid industrialization and urbanization of modern society have heightened the need for efficient, reliable, and cost-effective gas sensing technologies. Gas sensors play a critical role in environmental monitoring, industrial safety, automotive systems, and medical diagnostics. Among the various sensing materials investigated, zinc oxide (ZnO), a wide band gap (3.37 eV) n-type semiconductor with high exciton binding energy (60 meV), has emerged as a promising candidate due to its excellent chemical stability, high electron mobility, and strong sensitivity to a variety of gases.

ZnO can be fabricated into various nanostructured and microstructured forms, including nanorods, nanowires, and thick films, each offering unique advantages for gas detection. Among these, thick film sensors are particularly attractive for practical applications owing to their mechanical robustness, ease of fabrication, and compatibility with commercial sensor platforms. The performance of ZnO thick film gas sensors, however, is highly dependent on the synthesis route, morphology, microstructure, and the method of film deposition. By systematically analyzing the relationship between synthesis parameters, film characteristics, and sensing behavior, this review provides valuable insights into the design of high-performance ZnO thick film gas sensors and outlines future directions for research and development in this field.

LITERATURE REIVIEW:-

In recent years, extensive research has been conducted on zinc oxide (ZnO) due to its remarkable potential in gas sensing applications. The gas sensing mechanism of ZnO primarily relies on changes in electrical resistance caused by the adsorption and desorption of gas molecules on the surface, making its surface morphology and crystalline quality crucial for sensor performance.

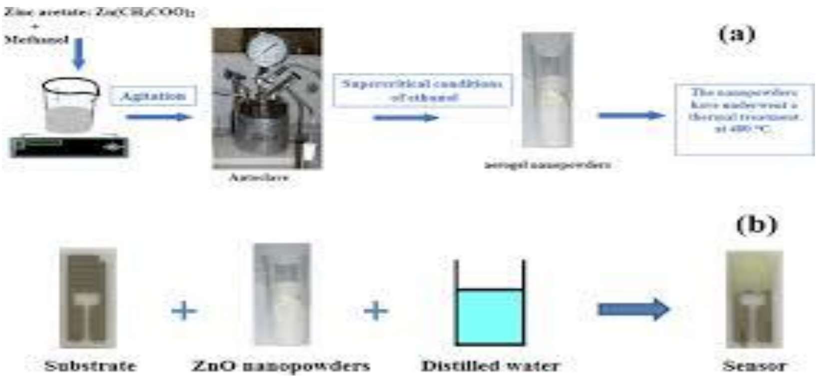
Several studies have explored different synthesis techniques to optimize ZnO thick film properties. For example, **screen printing** has gained popularity for its simplicity and suitability for mass production, as demonstrated by Sharma et al. (2018), who showed that screen-printed ZnO thick films exhibited good sensitivity to ethanol and acetone vapors. **Sol-gel methods**, as discussed by Kim et al. (2019), offer better control over stoichiometry and homogeneity, leading to films with high porosity and enhanced gas response.

The **spray pyrolysis technique** is another widely used method, known for its versatility and ability to produce uniform films over large areas. Studies by Singh and Bhatnagar (2020) reported high sensitivity and fast response times for ZnO thick films synthesized via spray pyrolysis, especially when detecting volatile organic compounds (VOCs). Similarly, **hydrothermal synthesis** has been explored for creating hierarchical and nanostructured ZnO films, which provide a large active surface area and improved gas sensitivity, as observed in the work of Zhang et al. (2021).Characterization techniques such as **X-ray diffraction (XRD)**, **scanning electron microscopy (SEM)**, and **Fourier-transform infrared spectroscopy (FTIR)** are routinely employed to analyze the structural and morphological features of ZnO films. These tools are crucial in correlating material properties with gas sensing performance. For instance, porous structures with high surface roughness, as revealed by SEM analysis, are often associated with enhanced sensitivity due to increased gas adsorption sites.

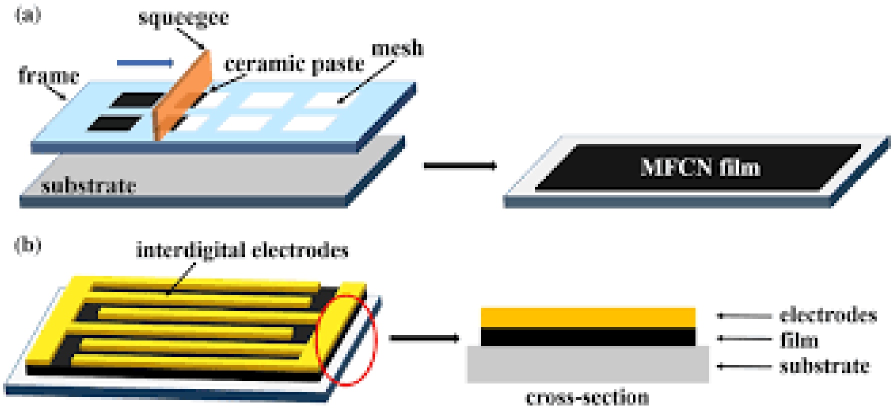
Synthesis Techniques of ZnO Thick Films:

The performance of ZnO thick film gas sensors is closely linked to the synthesis method, which determines the structural, morphological, and surface properties of the material. Various techniques have been developed to produce ZnO thick films with tailored characteristics for specific sensing applications. The most common methods include sol-gel processing, screen printing, spray pyrolysis, and hydrothermal synthesis.

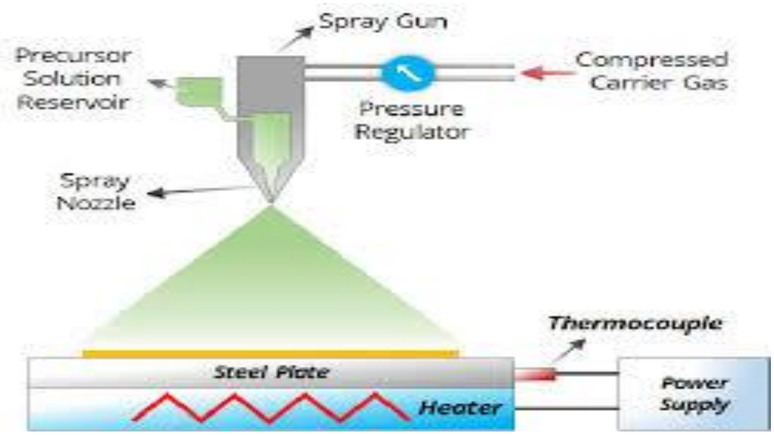
1. Sol-Gel Method: The sol-gel technique is widely used due to its simplicity, low processing temperature, and ability to control chemical composition at the molecular level. In this method, a zinc precursor such as zinc acetate or zinc nitrate is dissolved in a solvent, typically ethanol or water, followed by the addition of a stabilizer or catalyst. The resulting sol is aged and then deposited on a substrate via spin coating or dip coating. Upon drying and annealing, a thick ZnO film is formed. Sol-gel-derived films are generally uniform, porous, and suitable for detecting gases like ethanol and hydrogen due to their high surface area.



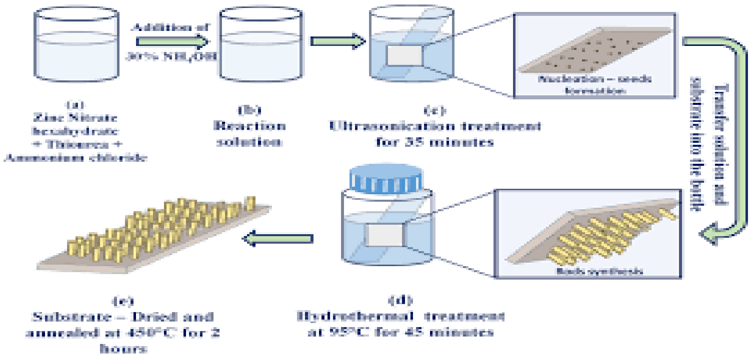
2. Screen Printing: Screen printing is a cost-effective, scalable method ideal for commercial sensor fabrication. It involves printing a ZnO paste—composed of ZnO powder, a binder, and a solvent—onto an alumina or glass substrate using a patterned mesh screen. The printed film is then dried and sintered at high temperatures (typically 400–600°C). This technique offers precise control over film thickness and allows for large-area deposition. The resulting films are often polycrystalline with interconnected grains, which provide effective pathways for gas diffusion and electron transport.



3. Spray Pyrolysis: Spray pyrolysis is a versatile technique where a solution containing a zinc salt is atomized and sprayed onto a heated substrate. The thermal energy causes rapid evaporation of the solvent and decomposition of the precursor, resulting in film formation. Parameters like spray rate, substrate temperature, and solution concentration greatly influence film morphology. This method allows for the production of uniform films with moderate porosity and is especially suitable for preparing ZnO films for NO_2 and CO detection.

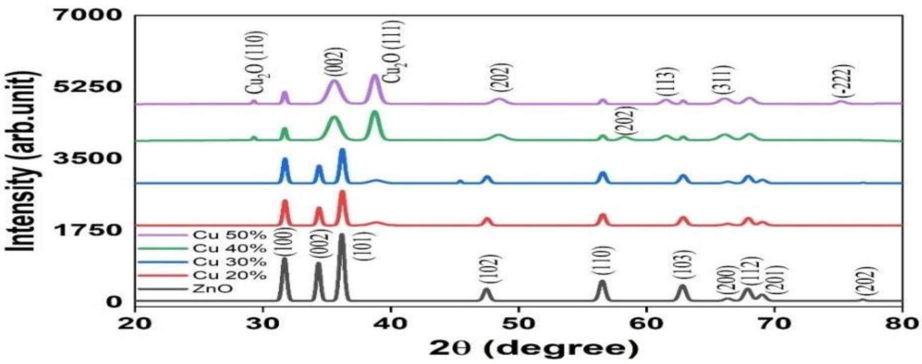


4. Hydrothermal Synthesis: The hydrothermal method is used to grow ZnO nanostructures directly on substrates under controlled temperature and pressure in an aqueous solution. Typically, zinc nitrate and hexamethylenetetramine (HMTA) are used as precursors. This process produces vertically aligned nanorods or nanowires embedded in a thick film matrix. These nanostructures enhance gas sensing by increasing the surface-to-volume ratio and improving gas accessibility. Hydrothermal growth is favored for applications requiring high sensitivity and fast response times.



Characterization Techniques: Understanding the structural, morphological, and electrical properties of ZnO thick films is essential for optimizing their performance in gas sensing applications. A variety of characterization techniques are employed to analyze these films, each providing specific insights into different aspects of the material.

1. X-ray Diffraction (XRD): XRD is used to determine the crystalline structure, phase purity, and grain size of ZnO films. The presence of sharp and well-defined peaks in the diffraction pattern indicates high crystallinity. The most prominent peak for ZnO is typically observed at $2\theta \approx 36.25°$, corresponding to the (101) plane of the hexagonal wurtzite structure. Scherrer's formula is often applied to estimate the crystallite size, which influences electron mobility and sensor response.



2. Scanning Electron Microscopy (SEM): SEM provides detailed images of the film's surface morphology, including grain size, porosity, and the distribution of particles or nanostructures. Porous and rough surfaces are desirable for gas sensing, as they offer more active sites for gas adsorption. Cross-sectional SEM imaging can also be used to measure the film thickness, which typically ranges from a few micrometers to tens of micrometers in thick films.

3. Fourier Transform Infrared Spectroscopy (FTIR): FTIR analysis is used to detect functional groups and residual organic species in the film, particularly important for films synthesized by chemical routes like sol-gel. It can confirm the presence of Zn–O bonds and any surface adsorbates that may influence sensing behavior.

4. UV–Visible Spectroscopy: This technique is used to study the optical properties of ZnO films, especially the band gap energy. A typical ZnO film exhibits a sharp absorption edge near 375 nm, corresponding to a band gap of ~3.3 eV. Any shift in the absorption edge can indicate quantum confinement or the presence of defects, both of which affect gas sensitivity.

5. Electrical and Gas Sensing Measurements: Gas sensing behavior is evaluated by exposing the ZnO thick film sensor to target gases under controlled conditions and measuring the change in electrical resistance. Parameters such as sensitivity, response and recovery time, operating temperature, and selectivity are recorded. These tests help correlate material characteristics with sensor performance.

Gas Sensing Mechanism and Performance

The gas sensing mechanism of ZnO thick films is primarily governed by surface reactions between adsorbed gas molecules and the charge carriers in the semiconductor. Being an n-type metal oxide, ZnO's conductivity is highly sensitive to changes in surface chemistry, especially in the presence of oxidizing or reducing gases.

1. Basic Sensing Mechanism

At elevated operating temperatures (typically between 200°C and 400°C), oxygen molecules from the air are adsorbed onto the surface of the ZnO film. These oxygen molecules capture free electrons from the conduction band and form chemisorbed oxygen species (O_2^-, O^-, or O^{2-}), creating a depletion layer near the surface:

O2(gas)+e−→O2−(ads)\text{O}_2(gas) + e^- \rightarrow \text{O}_2^-(ads)O2(gas)+e−→O2−(ads)

This process increases the resistance of the film. When a reducing gas (e.g., ethanol, CO, H_2, or NH_3) comes into contact with the surface, it reacts with the adsorbed oxygen ions, releasing the trapped electrons back into the conduction band and thereby decreasing the resistance:

R-H+O−→R+H2O+e−\text{R-H} + \text{O}^- \rightarrow \text{R} + \text{H}_2\text{O} + e^-R-H+O−→R+H2O+e−

In contrast, oxidizing gases such as NO_2 tend to extract electrons directly from the ZnO surface, further increasing the resistance.

2. Factors Affecting Performance

- **Surface Area and Porosity:** Higher surface area and porosity enhance gas adsorption, leading to improved sensitivity.
- **Grain Size:** Smaller grain sizes increase the number of grain boundaries, which act as active sites for gas interaction.
- **Operating Temperature:** Each gas has an optimal sensing temperature where the response is maximized. ZnO typically operates best in the range of 250–350°C.
- **Film Thickness:** An optimal film thickness ensures efficient gas diffusion while maintaining good electrical connectivity.
- **Doping and Surface Modification:** Incorporating dopants (e.g., Al, Sn, or noble metals like Pt and Pd) can tailor the electrical properties and enhance selectivity and sensitivity.

3. Performance Parameters

- **Sensitivity (S):** Ratio of the change in resistance upon gas exposure to the baseline resistance.
- **Response Time:** Time taken to reach 90% of the total change after gas exposure.
- **Recovery Time:** Time to return to 90% of the original resistance after gas removal.
- **Selectivity:** Ability to distinguish between different gases.
- **Stability and Repeatability:** Consistent performance over multiple cycles and extended operation.

ZnO thick film sensors have shown promising results in detecting gases like ethanol, acetone, methane, hydrogen, and ammonia, with good sensitivity and relatively fast response/recovery times. However, challenges remain in improving selectivity, reducing operating temperatures, and ensuring long-term stability in varying environmental conditions.

CONCLUSION AND FUTURE OUTLOOK:

Zinc oxide (ZnO) thick film gas sensors are promising due to their good semiconducting properties, chemical stability, and easy production. They are used to detect harmful gases in industries, healthcare, and the environment. Many methods like sol-gel, screen printing, spray pyrolysis, and hydrothermal techniques are used to make these films, helping improve their shape, structure, and ability to detect gases. Tools like XRD, SEM, FTIR, and UV-Vis help scientists understand how the material's structure affects its sensing ability.

However, there are still some challenges. ZnO sensors often need high temperatures to work, don't always detect specific gases well, and can be affected by humidity. Also, making the sensors consistently can be difficult. To solve these issues, researchers are trying surface modifications, adding metals, and combining ZnO with other materials or nanostructures.In the future, sensors that work at room temperature, use UV light, or connect with smart technologies like IoT and machine learning could make gas sensing faster, smarter, and more accurate.

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