SYNTHESIS AND CHARACTERIZATION OF MACRO-POROUS Gd₂O₃-ZnO NANOCOMPOSITE SENSOR FOR NO₂ GAS DETECTION

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ABSTRACT

A simple solution combustion technique was used to manufacture Gd₂O₃-ZnO nanocomposite successfully. The presence of different peaks in sample XRD patterns confirms the formation of a Gd₂O₃-ZnO nanocomposite. According to the Debye-Scherrer formula, the typical crystallite size ranges from 26 to 34 nm. Microstrain and dislocation density both rose from Z1 to Z4, according to thorough microanalysis. A well-organized spongy network with pore sizes ranging from 50 nm to 800 nm was produced, according to the FE-SEM and TEM research. EDS analysis was used to determine the quantitative analyses of the materials. The optical study shows the bandgap of the Z1 to Z4 thin film was varied between the range of 3.20 to 3.25 eV. The sensing nature of Gd₂O₃-ZnO nanocomposite was thoroughly examined for NO₂ at various temperatures and concentrations. Enhanced sensitivity of 24.79% is observed for 60 ppm of NO₂ at 200°C for sample Z2. Also, the quick response of 27sec was noted.

Keywords: Combustion Method, XRD, Microstrain Analysis, FE-SEM, TEM, EDS, Gas Sensing, etc.

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INTRODUCTION

Numerous hazardous gases such as CO, NO_x, CH₄, etc emit into the environment due to rapid industrialization and some domestic reasons. Among them, NO_x class of gases is more hazardous as far as a human health concern. NO₂ emissions are primarily exhausted gas from boilers and automobiles. It is highly annoying and corrosive to the lung tissue and, after inhalation, riskier.¹ Henceforth, the Development of sensors that detect NO₂ at very low concentration and enhance sensitivity becomes key importance in concern with biological and environmental issues. On account of this much research, groups focused on developing a new variety of materials that gives better results in terms of sensitivity towards NO₂ gas.²⁻⁵ However, ZnO-based sensors synthesized by different routes are extensively applied as NO₂ sensing elements.⁶⁻⁷ Gd₂O₃ has another promising agent in sensing devices owing to their exceptional physical and physicochemical properties. It exhibits n-type conductivity with a large bandgap. But it has seldom been used as a gas sensor to date.

Another unique approach for enhancing sensing performance is synthesizing composite metal oxide sensors since the morphologies can be customized by modifying the atomic ratio of an individual element. Sensing properties of binary oxides TiO₂-WO₃⁸, ZnO-CuO⁹, CdO-ZnO¹⁰ have been reported. Composite oxides can be synthesized by employing different techniques such as electrospinning¹¹, sol-gel¹², hydrothermal¹³, CBD¹⁴, etc. Combustion synthesis is a simple and convenient way of producing a wide variety of nanomaterials, catalysts, etc. Also, the synthesis of different nanostructures with homogenous

microstructure is possible comparatively at a lower temperature with other methods such as solid-state synthesis or nitrate method.¹⁵

By keeping in this mind, our present work emphasizes the preparation of Gd₂O₃-ZnO composite by solution combustion method. The potential impact of variation of Gd₂O₃ and ZnO in composition on structural, topographical, and optical properties of Gd₂O₃-ZnO nanocomposites was studied by XRD, FE-SEM, EDS etc. analysis. Similarly, the Gd₂O₃-ZnO gas sensing characteristic was investigated for NO₂ gas. In the study regarding sensitivity, the effect of concentration is studied.

EXPERIMENTAL

Material and Methods

Gadolinium Nitrate [Gd(NO₃)₃.6H₂O], Zinc Nitrate [Zn(NO₃)₂.6 H₂O], urea [CH₄N₂O] and glycine [C₂H₅NO₂] were used in the experiment and all chemicals are of AR grade (Alfa Aesar chemicals). The synthesis of Gd₂O₃-ZnO nanoparticles was successfully synthesized by using the Solution Combustion Method.

General Procedure

Nitrates of Gadolinium and Zinc were used as a precursor and that of urea and glycine was used as a fuel for the preparation of Gd₂O₃-ZnO. Urea holds an excessive heat of combustion. It is an organic fuel that offers a platform for redox reactions during combustion. Nitrates of Gd and Zn, urea and glycine were taken in proper stoichiometric quantities and a homogenous solution was made. This solution was maintained on a hot plate and evaporated at around 80°C to create a thick gel, which was then heated to 170 degrees Celsius to 180 degrees Celsius for auto combustion. After a minor explosion, this gel was transformed into nanocrystalline Gd₂O₃-ZnO powder. Continuous heating resulted in the formation of fine black nanocrystalline Gd₂O₃-ZnO. This powder was sintered at a temperature of 700°C. The synthesized samples were coded as Z1, Z2, Z3, and Z4 for (Gd₂O₃)_{1-x}-(ZnO)_x where X = 0.2, 0.4, 0.6 and 0.8 respectively. The screen printing technique is further used to deposit the obtained Gd₂O₃-ZnO powder onto the glass substrate. Finally, the characterization of the synthesized Gd₂O₃-ZnO sample was carried out with different characterization techniques.

Detection Method

To study the structural and morphological aspects of obtained Gd₂O₃-ZnO samples includes X-Ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and ultraviolet (UV)-visible spectroscopy.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

To get the identification of phases and structural evidence of the Gd₂O₃-ZnO samples, XRD was recorded. Figure-1 gives the recorded XRD patterns for all samples with different compositions with diffraction angles ranging (2θ) from 25° to 70°. The recorded XRD pattern exhibit peaks (222), (400) and (431) planes related to the cubic Gd₂O₃ phase¹⁶⁻¹⁷ [coded as "%" (JCPDS no. 65-3181)]. Moreover, distinct peaks (101), (002), (102), and (110) were also seen with less intensity related to ZnO phase (coded as "#" (JCPDS no. 5-664). The intensity of peaks corresponding to the ZnO phase is observed to be increased from Z1 to Z4. But, no remarkable change in the intensity of the Gd₂O₃ phase is observed.

Microstructural Analysis

Table-1 shows the microstructural study of Gd₂O₃-ZnO films deposited with various compositions (from Z1 to Z4). The change of crystallite size with microstrain produced for all variations is shown in Fig.-2(a). The crystallite size falls steadily from Z1 to Z4 and reaches a minimum of 26.75 nm, as seen in Fig. 2(a). The microstrain, on the other hand, continues to rise. This pattern might be explained by the fact that when crystallite size decreases from Z1 to Z4, flaws in the lattice grow, increasing the value of the microstrain. Furthermore, as seen in Fig.-2(b), the dislocation density rises from Z1 to Z4 as well. Stresses might build upon the various layers from Z1 to Z4, causing more dislocation lines to be sliced per unit area.

Fig.-1: XRD Patterns of Gd_2O_3 -ZnO (Z1 to Z4) Sample

Fig.-2: Plot of Avg. Crystallite Size and (a) Microstrain (b) Dislocation Density for Different Samples

Table-1: Microstructural Parameter of Gd_2O_3 -ZnO (Z1 to Z4) Sample

S. No.	Sample Name	Avg. Crystallite Size (nm)	Dislocation Density $\times 10^{14}$ (lines/cm ²)	Microstrain(ϵ) $\times 10^{-3}$
1	Z1	33.35	0.935	4.21
2	Z2	32.88	1.03	4.36
3	Z3	28.69	1.311	4.95
4	Z4	27	1.425	5.19

Scanning Electron Microscopy and Transmission Electron Microscopy

It is evident from Fig.-3 (a-d) that synthesized samples of Gd_2O_3 -ZnO nanocomposites show a well-arranged spongy network with 50 nm to 800 nm range of pore size. Interestingly, sample Z2 shows the Development of interconnected wired-porous morphology whose edge thickness is in the range of 300-400nm. Such morphology may act as conducting channels for the transportation of electrons across it and contribute to conductivity. Thus, such morphologies find useful in sensing applications.

Furthermore, to deep study of the wire-like Gd_2O_3 -ZnO nanocomposite, the detailed TEM micrographs were further carried out for sample Z2 and presented in Fig.-4 (a to c) and Fig.-4(d) shows the SAED pattern for sample Z2. It is evident from Fig.-4 that nanocomposite exhibits an interconnected wire-like network with all the grains are connected to form continuous wire-like morphology. The selected area electron diffraction (SAED) given in Fig.-4(d) confirms the good crystallinity of the obtained Gd_2O_3 -ZnO nanocomposite (Z2). The particle size of the Z2 sample nanoparticles is in good agreement with XRD results.

Energy Dispersive X-Ray Analysis

The Fig.-5 shows EDS spectra of samples Z1 to Z4 and the inset table shows the corresponding weight percentage and atomic percentage of Gd, Zn, and O present in the sample. It is obvious from Fig.-5 that the atomic percentage of Gd decreases from Z1 to Z4. The findings obtained are in good accordance with the stoichiometric proportion of the elements we had held during the experiment. Also, all the samples are rich in oxygen.

Fig.-3: Scanning Electron Micrographs of (a1-a3) Z1, (b1-b3) Z2, (c1-c3) Z3, (d1-d3) Z4

Fig.-4: Transmission Electron Micrographs of Sample Z2

Optical Absorbance Studies

The optical properties of the films were investigated from a variety of optical absorbances with Wavelength (200 – 800 nm). The plots of absorbance and transmittance of the films vs. Wavelength (nm) are shown in Fig.-6.

The intercept of the absorbance (αt) and transmittance curves to the plot on the x-axis provides approximate bandgap energy of the material. Two separate band edges are clearly seen in the absorption spectra, which can be related to the formation of separate phases of ZnO and Gd₂O₃. The bandgap of the thin film varied between the range of 3.20 to 3.25 eV. A slight redshift is observed in-band energy as the percentage of

Gd₂O₃ decreases. The calculated bandgap for Gd₂O₃-ZnO nanocomposite is comparable to the value between 3.62 to 3.98 eV obtained by C. A. Lopez-Lazcano *et al.*¹⁸ using a sputtering method.

Fig.-5 Energy Dispersive Spectroscopy (EDS) of Gd₂O₃-ZnO Samples (Z1 to Z4)

Fig.-6: Graph of Optical Study of Gd₂O₃-ZnO Samples (Z1 to Z4) (INSET shows Tauc's Plot of respective Sample)

Gas Sensing Studies

To determine the gas sensing characteristics for the synthesized Gd₂O₃-ZnO nanocomposite sensor domestic static gas sensor was used as discussed by potdar.et.al¹⁰. For estimation of sensing characteristic of Gd₂O₃-ZnO composite, primarily, the temperature at which sensitivity is maximum is estimated since the temperature is most impacting parameter on sensors performance¹⁹. Figure-7 shows the typical linear variation of gas sensitivity of Gd₂O₃-ZnO nanocomposite (Z1 to Z4) at various operating temperatures at an interval of 25°C at 60ppm of NO₂. It is recognized from Fig.-7 that sensitivity initially increases and after a particular operating temperature, all of the samples begin to decline. At 200°C, sample Z2 demonstrates the highest sensitivity of 24.79%. Figure- 8 shows a transient sensitivity curve for samples Z1 to Z4 at 200°C and 60ppm of NO₂. It is clear from Fig.-8 that sample Z2 is most responsive as compared

with other variants. Moreover, sample Z4 also shows comparable results. It's possible that the increased sensitivity is related to morphological change and a synergistic impact of two oxides.

In addition, for sample Z2, the influence of concentration on sensing performance was calculated and shown in Fig. 9(a). It displays good improvement with concentration, which might be attributed to the fact that concentration results in greater surface covering. The feature of response and recovery is also important in determining sensing performance. Figure-9(b) shows the variation of response and recovery time for sample Z2 at various concentrations of NO_2 gas. The quick response of 27 sec is shown by Sample Z2 towards 60 ppm of NO_2 gas. The Fig.-9(b) (INSET) shows scattered variation of samples Z1 to Z4 at 200°C and 60 ppm of NO_2 . It is pointed out that sample Z4 is more responsive with a response time of 16 sec and recovery of 52 sec. The rapid response may be attributed to the less time taken for the diffusion of the NO_2 gas through voids between porous wires like a network. The response time shortens as the pressure increases due to the formation of porous wires like structures with a large surface area.

Fig.-7: Plot of Sensitivity Vs. Operating Temperature for Z1 to Z4 for 60 ppm of NO_2

Fig.-8: Transient Gas Sensitivity of Samples Z1 to Z4 at 200°C for 60 ppm of NO_2

Sensing Mechanism

The mechanism of sensing of $\text{Gd}_2\text{O}_3\text{-ZnO}$ sensor for the detection of NO_2 gas can be described by the fact of the exchange of electrons between the sensor and the oxygen present in the environment. As the nanocomposite sensor $\text{Gd}_2\text{O}_3\text{-ZnO}$ is exposed to the environment, surrounding oxygen adsorbs the electron from the surface of the sensors and produces O_2^- , O^{2-} and O^- oxygen ions²⁰. Due to this, a thin depletion layer induces at the surface and resulting in the lowering of the resistance of the sensor in the air. Now, after being exposed to NO_2 gas, due to its higher oxidizing nature in comparison with O_2 , it absorbs electrons from the surface of the $\text{Gd}_2\text{O}_3\text{-ZnO}$ film and growth in the depletion layer resulted and subsequently, the resistance of the sensor increases as shown in Fig.-10.

The absorption of NO_2 gas by the surface of the sensor is highly sensitive to nanostructure size, morphology and nature. The effects of size and the incorporation of defects may provide more functional sites for charge transport.

Fig.-9: (a) Transient concentration curve of sample Z2 at 200°C at various ppm of NO₂; (b) Response characteristic of sample Z2 at 200°C (INSET- Response time for samples Z1 to Z4 at 200°C for 60 ppm of NO₂)

Fig.-10: Schematic of the Depletion Layer of Gd₂O₃-ZnO in Air and NO₂ Atmosphere

Moreover, the reaction of NO₂ gas molecules with O²⁻ ions are given by:²¹

The difference in resistance of nanocomposite material is highly efficient may be due to a presence of two or more nanoparticles that may inhibit agglomeration of the individual materials up to a certain level, resulting in a greater functionalized area for adsorption and reaction to occurs²². Additionally, due to the collective chemical interaction between the Gd₂O₃ and ZnO atoms on the surface, the rich defect chemistry may result in more active sites for sensor reaction²³. However, the enhanced sensitivity for Z2 might be due to interconnected wires like network (as evident from SEM and TEM analysis), which offers more active adsorption sites.

CONCLUSION

The $\text{Gd}_2\text{O}_3\text{-ZnO}$ nanocomposite with different stoichiometric compositions has been successfully synthesized by the combustion method. The XRD confirms the formation of the $\text{Gd}_2\text{O}_3\text{-ZnO}$ nanocomposite. Moreover, microstructural analysis shows that dislocation density and microstrain were increased from Z1 to Z4. The FE-SEM and TEM study illustrates that, interconnected wired-porous morphology over the substrate. The elemental confirmation is done by EDS findings. The optical study shows the bandgap of Z1 to Z4 thin film was varying between the range of 3.20 to 3.25 eV. The gas sensing nature of $\text{Gd}_2\text{O}_3\text{-ZnO}$ nanocomposite was systematically studied for NO_2 at various temperatures and concentrations. The maximum sensitivity of 24.79% is noted for 60 ppm of NO_2 at a temperature of 200°C for sample Z2. Also, quick response of 27sec was recorded. Thus, the present approach of synthesis of $\text{Gd}_2\text{O}_3\text{-ZnO}$ nanocomposite may deliver a convenient track for the preparation of a competent electrode in high-performance gas sensing devices.

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