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NO₂ Sensing Properties of Ag-Doped ZnO Thin Film Synthesized via Chemical bath Deposition Method

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ABSTRACT: Ag-doped ZnO thin film was synthesized on glass substrate using chemical bath deposition (CBD) method at room temperature. Gas sensing performance of this film was evaluated towards toxic gas like nitrogen dioxide (NO₂). Ag doped ZnO film showed maximum sensing response 2.7 to NO₂ gas at operating temperature 200°C. It is observed that the maximum sensitivity was increased from 1.57 for 5 ppm to 3.68 for 50 ppm gas respectively. The response time initially decreases from 135 seconds at 5 ppm to 115 seconds at 10 ppm but increases with further gas concentration. Recovery time steadily rises with gas concentration, from 68 seconds at 5 ppm to 257 seconds at 50 ppm. The Structural and morphological properties were analysed using XRD and SEM spectroscopy respectively.

KEYWORDS: Ag doped ZnO, Gas sensor, NO₂ gas, Chemical Bath Deposition Method.

I. INTRODUCTION

Nitrogen dioxide (NO₂) is a prominent air pollutant with significant impacts on human health and the environment. It is mainly produced during the combustion of fossil fuels such as coal, oil and natural gas, as well as through vehicle exhaust emissions. Major industrial contributors include pulp mills and power plants [1]. The permissible exposure limits for NO₂ are 5 ppm for short-term exposure (10 minutes) and 3 ppm for long-term exposure (8 hours) [2]. NO₂ significantly contributes to ozone formation, amplifying its harmful effects on both health and the environment. To address the adverse impacts of elevated nitrogen oxide levels, it is essential to implement strict emission controls and establish continuous monitoring systems in both ambient air and industrial settings. To meet this need, a variety of gas sensors have been developed, many of which are commercially available. These sensors detect gases and convert them into measurable signals, playing a significant role in various industries and applications. Gas sensors are essential for ensuring safety, monitoring air quality, and managing industrial processes. By detecting hazardous gases, these sensors help prevent accidents and safeguard human health.

Among the various types of gas sensors, chemiresistive gas sensors are the simplest types of solid-state gas sensors, primarily due to their simple detection method. They operate by measuring the change in electrical resistance when exposed to different gases. These sensors are based on metal oxide semiconductors. The sensitivity of surface conductivity in metal oxide semiconductors enables their extensive application in gas sensing [3,4]. The working principle of these gas sensors involves the interaction between the gas and the metal oxide semiconductor, which alters the electrical resistance of the sensor material [5-7]. Among the various metal oxide semiconductors Zinc Oxide (ZnO) is a II-IV semiconductor material that has been the subject of research interest since the 1930's due to its exceptional physical and chemical properties. At low temperatures, ZnO exhibits a direct and broad band gap of 3.44 eV, decreasing to 3.37 eV at room temperature. These properties make it ideal for various optoelectronic applications [8-12]. Additionally, the incorporation of metal dopants into zinc oxide (ZnO) significantly alters its properties [13-15]. ZnO also exhibits a variety of diverse nanostructures, including nanowires, nanotubes, nanoribbons, nanorings. These unique and versatile nanostructures make ZnO a highly attractive and promising material for advanced and future applications [16, 17]. Among a various metal dopants Silver (Ag) is considered a promising dopant for ZnO due to its unique properties, such as non-toxicity and excellent electrical and thermal conductivities. These attributes significantly enhance the optical and electrical characteristics of ZnO, making it an attractive material for advanced applications. Ag doped ZnO synthesized by various methods such as electrodeposition, spray pyrolysis, pulse deposition methods etc

[18-20]. We have employed chemical bath deposition method to synthesize Ag doped ZnO due to its cost-effectiveness and suitability for large-scale industrial applications and ability of doping [21].

II. MATERIALS AND METHODS

Ag doped ZnO thin film of an average thickness 3-4 μm is deposited on glass substrate using the chemical bath deposition method at room temperature as described in our earlier research work [22]. The process involved preparing a precursor solution by dissolving an appropriate amounts of Zinc Nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] and Silver Nitrate [AgNO_3] (analytical grade, SDFCL) in double-distilled water. The deposited film was then annealed at 500°C for two hours. The prepared film was characterized for structural and morphological properties. X-ray diffraction pattern was recorded by using an X-ray diffractometer (Miniflex-II) and morphology was studied by using scanning electron microscope SEM (ZIESS). Further this film was used to investigate its gas sensing properties towards Nitrogen dioxide (NO_2) gas using our Static Gas Sensing Measurement System [23].

III. EXPERIMENTAL RESULTS

(i) X-ray Diffraction Characterization (XRD)

The X-ray diffraction (XRD) spectrum of Ag-doped ZnO is shown in Fig.1. The peak positions in XRD patterns confirm a hexagonal wurtzite phase, consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36-14519. The prominent diffraction peaks correspond (100), (002), (101), (102), (110) and (103) planes. No additional phases associated with silver or silver oxides were observed. The average crystallite size 'D' was calculated from X-ray spectra using the following Scherrer's formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where,

D = crystallites size (nm)

K = 0.9 (Scherrer's constant)

λ = 0.15405 nm (wavelength of X-ray sources)

β = Full width of the diffraction line measured at half of its maximum intensity (FWHM) in radians.

θ = Peak position (radians)

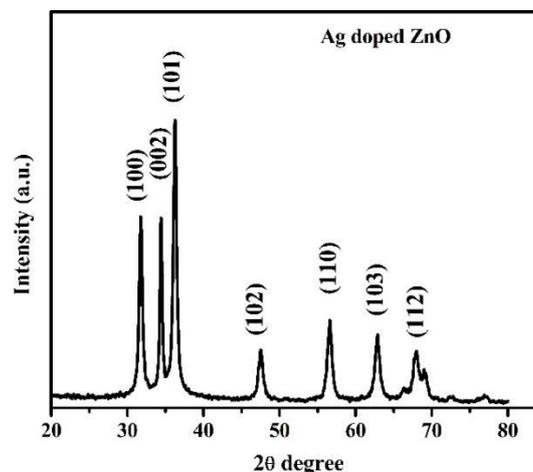


Figure 1: XRD pattern of Ag-doped ZnO Thin Film

The average crystallite size for Ag doped ZnO was calculated as 15.88 nm.

(ii) Scanning Electron Microscopy

The surface morphology of Ag doped ZnO film is shown in figure 2. The SEM images clearly shows that the average size of the crystallites in the range of about 100-300 nm uniformly distributed over the substrate.

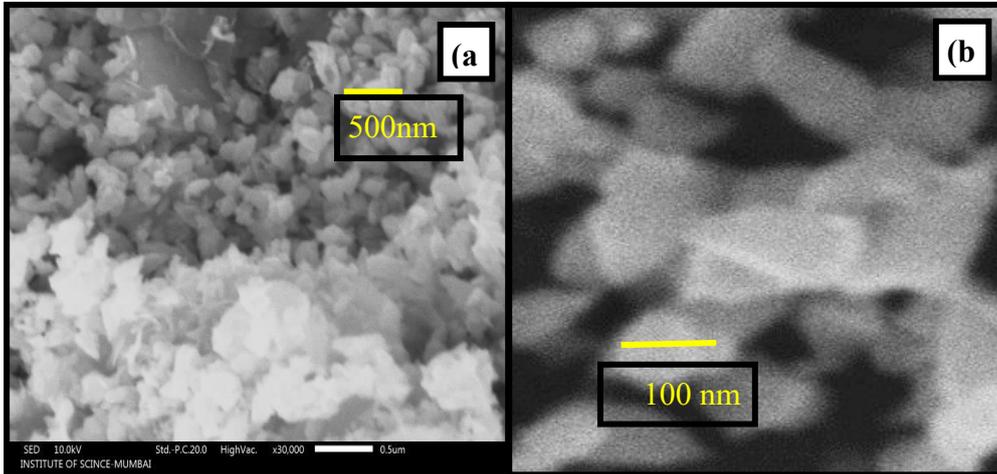


Figure 2: SEM image of (a) Ag doped ZnO (b) its magnified image

(iii) Gas sensing performance of Ag-ZnO films towards NO₂ gas

The maximum sensitivity of Ag-doped ZnO towards 25 ppm of NO₂ gas was determined at various operating temperatures including 100°C, 150°C, 200°C, 250°C, 300°C, and 350°C as shown in Figure 3. The results indicate that the sensitivity of Ag increased with increase in temperature. It reached to a maximum value of 2.7 at 200°C, beyond this temperature sensitivity gradually reduces to 1.2 at higher temperatures. The temperature 200°C was considered as the optimal operating temperature for Ag-doped ZnO. Then NO₂ gas concentration was varied at this temperature, and the corresponding gas response was recorded and shown in Figure 3 (a,b,c,d). It shows the gas response of Ag doped ZnO observed for 5ppm, 10ppm, 25ppm and 50ppm gas concentration respectively. All curves showed the typical characteristic response curves towards oxidising gas with complete recovery. The sensitivity seems to be increased with the gas concentration.

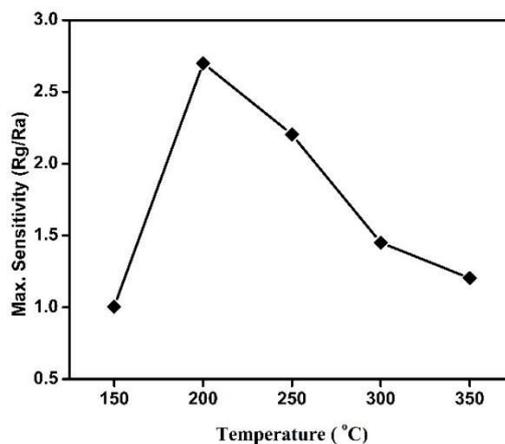


Figure 3: The plot of Maximum Sensitivity of Ag-doped ZnO versus Temperature (°C)

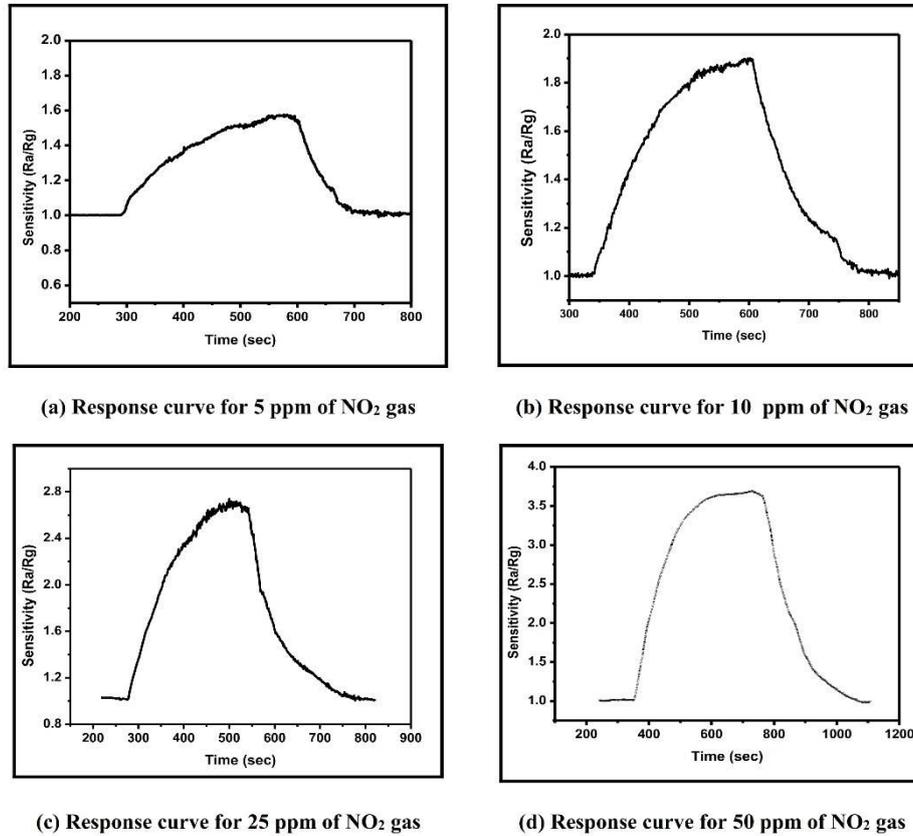


Figure 4: Response curves for (a) 5 ppm (b) 10 ppm (c) 25 ppm and (d) 50 ppm of NO₂ gas concentration.

Figure 5 shows the plot of maximum sensitivity versus gas concentration. It is seen that the sensor has linearly increasing response towards NO₂ gas with increasing gas concentration and it does not saturate upto 50 ppm test gas concentration. The sensitivity increases from 1.57 for 5 ppm to 3.68 for 50 ppm gas concentration respectively.

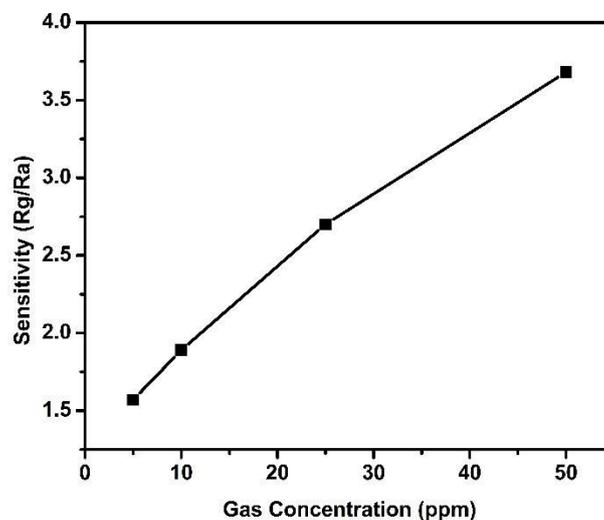


Figure 5: Sensitivity of Ag doped ZnO versus NO₂ gas concentration

Figure 6 shows the response time and recovery time of Ag-doped ZnO versus NO₂ gas concentration.

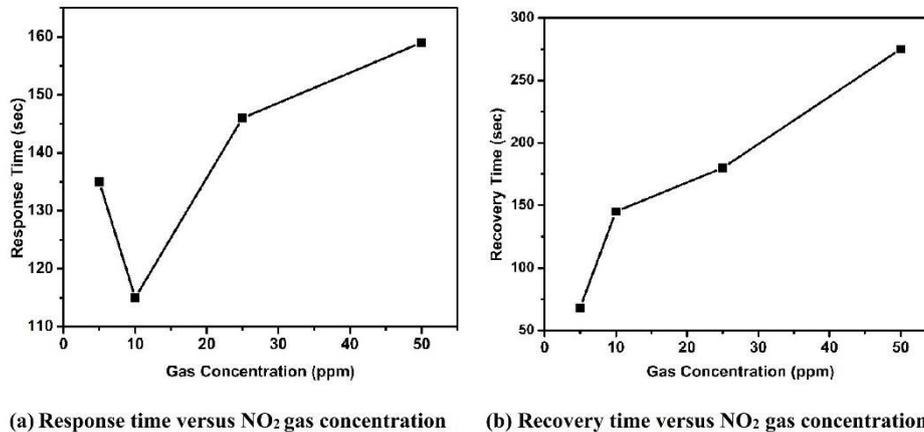
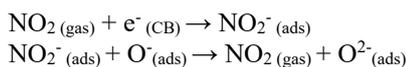


Figure 6 : Response time and Recovery time versus NO₂ gas concentration of Ag doped ZnO

The response time initially decreases from 135 seconds at 5 ppm to 115 seconds at 10 ppm but then increases with higher gas concentrations, reaching 146 seconds at 25 ppm and 159 seconds at 50 ppm, suggesting a trend towards saturation. While the recovery time increases consistently with gas concentration, rising from 68 seconds at 5 ppm to 145 seconds at 10 ppm, and further to 180 and 257 seconds at 25 and 50 ppm, respectively.

To understand the response of Ag-doped ZnO films towards NO₂ gases, it is important to consider the adsorption of oxygen molecules from the air onto the sensor surface. These oxygen molecules primarily chemisorb in ionic forms such as O₂⁻, O⁻, and O²⁻. The specific type of chemisorbed oxygen species is highly temperature-dependent [24]. When Ag-doped ZnO exposed to an oxidizing gas such as NO₂, the interaction can be attributed to a specific reaction [25].



The adsorbed NO₂ gas on the surface of the ZnO sensing surface undergoes reduction through the transfer of electrons from the conduction band of ZnO. This reduction process leads to an increase in the resistance of ZnO.

The gas sensing response of a sensor is directly influenced by the number of adsorption sites available on its surface, which, in turn, depends on the concentration of the target gas. As the gas concentration increases, more adsorption sites are occupied, leading to a corresponding rise in the sensor's response. As shown in Figure 5, the sensing response increases linearly with gas concentration, indicating that unoccupied adsorption sites remain available, and the sensor has not yet reached saturation. At 200°C temperature the sensor showed considerably good response. This investigation indicated that when Ag is doped into ZnO, it acts as a catalyst that facilitates the adsorption and reaction of gas molecules on the ZnO surface at lower temperatures. This catalytic effect lowers the energy barrier for gas reactions, enabling the sensor to operate effectively. Also, Ag doping enhances the charge transfer between the gas molecules and the ZnO surface. This improved charge transfer promotes faster and more efficient gas sensing even at lower temperatures.

IV. CONCLUSION

A uniform and crystalline Ag-doped ZnO film was synthesized on a glass substrate using the chemical bath deposition method at room temperature. XRD analysis confirmed a hexagonal wurtzite structure with an average crystallite size of 15.88 nm, with no separate peaks attributed to silver doping. SEM images revealed uniformly distributed Silver-doped ZnO crystallites, averaging 100–300 nm in size. The Ag-doped ZnO film demonstrated maximum sensing response 2.7 to NO₂ gas at 200°C, with sensitivity 1.57 for 5 ppm and 3.68 for 50 ppm. Ag-doped ZnO shown the response time 135

seconds for 5 ppm and 115 seconds for 10 ppm, while the recovery time steadily increased from 68 seconds at 5 ppm to 257 seconds at 50 ppm. From the sensor response study, it is concluded that Ag-ZnO sensor shown noticeable good gas sensing performance towards NO₂ at 200°C. Thus, Ag-doped ZnO synthesized using chemical bath deposition method is a promising gas sensing material for detecting toxic NO₂ gas.

REFERENCES

1. L.Sloss, A.Hjalmarsson, H. Soud, L.Campbell, D. K. Stone, G. Shareef, T. Emmel, et al. , 'Nitrogen oxides control technology fact book,' Noyes Data Corporation, Park Ridge, NJ, USA, 1992, pp. 8–14.
2. P. Rai , S. Raj, K. Ko, K. Park, Y. Yu., 'Synthesis of flower-like ZnO microstructures for gas sensor,' Sensors and Actuators B, vol. 178, pp. 107-112, 2013.
3. D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, W. C. Harsch, Solid State Commun., vol. 105, p. 399, 1998.
4. K. Maeda, M. Sato, I. Niikura, T. Fukuda, Semicond. Sci. Technol., vol. 20, p. S49, 2005.
5. A. Mandelis , C. Christofides, 'Physics, Chemistry and Technology of Solid State Gas Sensor Devices,' Wiley, 1993.
6. P. T. Moseley ,B. C. Tofield, 'Solid State Gas Sensors,' Adam Hilger Bristol and Philadelphia, 1987.
7. C. A. Papadopoulos, D. S. Vlachos, J. N. Avaritsiotis, 'Comparative study of various metal oxide based gas sensor architectures,' Sensors and Actuators B, vol. 32, pp. 61-69, 1996.
8. D. G. Thomas, 'The exciton spectrum of zinc oxide,' Journal of Physics and Chemistry of Solids, vol. 15, nos. 1–2, pp. 86-96, 1960.
9. A. Mang, K. Reimann, St. Rübenacke, 'Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure,' Solid State Communications, vol. 94, no. 4, pp. 251-254, 1995.
10. Y. Chen, D. M. Bagnall, H.-J. Koh, K.-T. Park, K. Hiraga, Z.-Q. Zhu, T. Yao, 'J. Appl. Phys.,' vol. 84, p. 3912, 1998.
11. D. C. Reynolds, D. C. Look, B. Jogai, 'Optically pumped ultraviolet lasing from ZnO,' Solid State Communications, vol. 99, no. 12, pp. 873-875, 1996
12. D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, T. Goto, Appl. Phys. Lett., vol. 70, p. 2230, 1997.
13. J. Pearton, D. P. Norton, M. P. Ivill, A. F. Hebard, J. M. Zavada, W. M. Chen, I. A. Buyanova, 'ZnO doped with transition metal ions,' IEEE Transactions on electron Devices, vol. 54, no. 5, pp. 1040-1048, 2007.
14. I. A. Buyanova, W. M. Chen, M. P. Ivill, R. Pate, D. P. Norton, S. J. Pearton, J. W. Dong, A. Osinsky, B. Hertog, A. M. Dabiran, P. P. Chow, 'Optical characterization of ZnMnO-based dilute magnetic semiconductor structures,' Journal of Vacuum Science & Technology B, vol. 24, pp. 259-262, 2006.
15. C. L. Hsu, S. J. Chang, 'Doped ZnO 1D Nanostructures: Synthesis, Properties, and Photodetector Application,' Small, vol. 10, no. 22, pp. 4562–4567, Nov. 2014.
16. A. B. Durrisc Y. H. Leung, "Optical properties of ZnO nanostructures," Small, vol. 2, pp. 944-961, 2006.
17. A. K. Radzimska and T. Jeisonwski, 'Zinc oxide- from synthesis to application, A review,' Materials, vol. 7, pp. 2833-2881, 2014.
18. N. L. Tarwal, A. V. Rajgure, J. Y. Patil, M. S. Khandekar, S. S. Suryavanshi, P. S. Patil, M. G. Gang, J. H. Kim, J. H. Jang, "A selective ethanol gas sensor based on spray-derived Ag–ZnO thin films," J. Mater Sci, vol. 48, no. 20, pp.7274–7282, 2013.
19. C. Hong, Q. Zhou, Z. Lu, A. Umar, R. Kumar, Z. Wei, X. Wu, Lingna Xu, S. H. Kim, 'Ag-doped ZnOnanoellipsoids based highly sensitive gas sensor,' Mater. Express, vol. 7, no. 5, pp. 3817–3823, 2017.
20. O. Lupan, V. Cretu, V. Postica, M. Ahmadi, B. R. Cuenya, L. Chow, I. Tiginyanu, B. Viana, T. Pauporté, R. Adelung, 'Silver-doped zinc oxide single nanowire multifunctional nanosensor with a significant enhancement in response,' Sensors and Actuators B, vol. 223, pp. 893–903, 2016
21. B.R. Sankpal, S.D.Saratale, C.D Lokhande., A.Ennaoui ., 'Sol. Energy Mater. Solar Cells,' vol. 83, p. 447, 2004.
22. S.S.Dange, S.N.Dange, P.S.More ' Cost effective ZnO Thin Film using Chemical Bath Deposition for NO₂ gas sensing ' Int. Journal of Innovative Research and in Science, Eng. and Tech. Vol 13, Issue11, 19204- 19209, 2024.
23. S.S.Dange and S.N.Dange 'Development of Low Cost Static Gas Sensing Measurement System' Int. Journal of Innovative Research and in Science, Eng. and Tech. Vol 13, Issue12, 20704-20709, Nov 2024.
24. M. Takata, D. Tsubone, H. Yanagida, 'Dependence of electrical conductivity of ZnO on degree of sintering,' Journal of the American Ceramic Society, vol. 59, no. 1-2, pp. 4–8, 1976.
25. Y. Li, X. Zhao, W. Fan, 'Structural, electronic, and optical properties of Ag-doped ZnO nanowires: first principles study,' Journal of Physical Chemistry C, vol. 115, 3552–3557, 2011.



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