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Cost-Effective ZnO Thin Film using Chemical Bath Deposition Method for NO₂ Gas Sensing

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ABSTRACT: A ZnO thin film with was synthesized using the low-cost chemical bath deposition (CBD) method at room temperature. Structural, morphological, and optical properties were analyzed using XRD, SEM with E-DAX and UV-Vis spectroscopy, respectively. ZnO films showed maximum sensing response to toxic NO₂ gas at operating temperature 250°C. It is seen that the increase in the sensitivity is linear with the gas concentration. The sensitivity increases from 1.87 to 4.9 for change in gas concentration from 5 ppm to 50 ppm and does not seem to saturate. The response time of the sensor ranged between 30 and 75 seconds, while the recovery time varied from 100 to 150 seconds. This finding evident that the potential of the prepared ZnO film for detecting and monitoring toxic NO₂ gas at low concentrations.

KEYWORDS: ZnO, Gas sensor, Chemical bath deposition method, NO₂ gas

I. INTRODUCTION

The rapid growth of the economy, industrialization, and population has resulted in harmful gas emissions from vehicles, agriculture, and industry. These emissions adversely affect air quality and human health. Therefore, monitoring these pollutants is essential for protecting both the environment and public health. Nitrogen dioxide (NO₂) is a major air pollutant with harmful effects on human health and the environment. NO₂ primarily produced through fossil fuel combustion and industrial activities, such as power generation and vehicle emissions. The threshold limit values for short-term and long-term exposure to NO₂ are 5 ppm for 10 minutes and 3 ppm for 8 hours, respectively [1]. This underscores the urgent need for effective monitoring of toxic and potentially harmful gases. Among various gas sensor technologies, metal oxide semiconductor (MOS) gas sensors are widely used due to their excellent sensor response, short response time, rapid recovery, high selectivity, accuracy, and cost-effectiveness. Zinc Oxide (ZnO) is a II-IV semiconductor material which exhibits a direct and broad band gap of 3.37 eV at room temperature It's exceptional physical and chemical properties makes it ideal for various optoelectronic, phosphor applications and gas sensors [2-5]. Additionally, ZnO is non-toxic, abundant, easy to synthesize, cost-effective, making it a versatile and attractive semiconductor material [6,7].

Among various synthesis methods of ZnO such as chemical vapour deposition method (CVD) , rf reactive sputtering ,electrochemical deposition method etc [8-11], we opted the chemical bath deposition method in the present research work for the production of ZnO films due to its cost-effectiveness and suitability for large-scale industrial applications.

II. MATERIALS AND METHODS

ZnO thin films was synthesized using the chemical bath deposition method, as described in our earlier work [12]. The process utilized only two analytical-grade chemicals: zinc nitrate (Zn(NO₃)₂·6H₂O) and 25% ammonia solution (NH₄OH, sp.gr. 0.91) from SDFCL, both used without further purification. Glass slides used as substrates, cleaned with acetone and distilled water prior to use. To prepare the bath solution, an appropriate weight of zinc nitrate was dissolved in double-distilled water using a magnetic stirrer. The cleaned glass substrate was immersed in the bath solution. The uniform and well covered ZnO film is obtained as shown figure 1 (a). The prepared film was characterized for structural, morphological and optical properties. X-ray diffraction pattern was recorded by using an

X-ray diffractometer (Xpert Pro MPD), Morphology of the prepared ZnO nanoparticles was studied by using FESEM (ZEISS) and absorption spectra of the films was recorded using a UV-vis spectrophotometer (SHIMADZU UV-1800). The prepared ZnO film was used to study its gas sensing properties towards NO₂ gas using static gas sensing measurement setup. The films were mounted on a heating probe, inserted into a gas chamber, and heated for 15 minutes to stabilize their resistance. The known volume of a test gas injected into the test chamber using calibrated air tight syringe and needle. The operating temperature was varied between 100-350°C, with gas concentrations ranging from 5 to 100 ppm.

III. EXPERIMENTAL RESULTS

(i) X-ray diffraction characterization (XRD)

The XRD pattern of ZnO thin film is shown given in Fig. 1(c). The peak positions of XRD pattern reveal a hexagonal wurtzite structure and in good agreement with the data of Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36-14519. The intense diffraction peaks of ZnO films corresponds to (100), (002), (101), (102), (110), (103) and (112) planes.

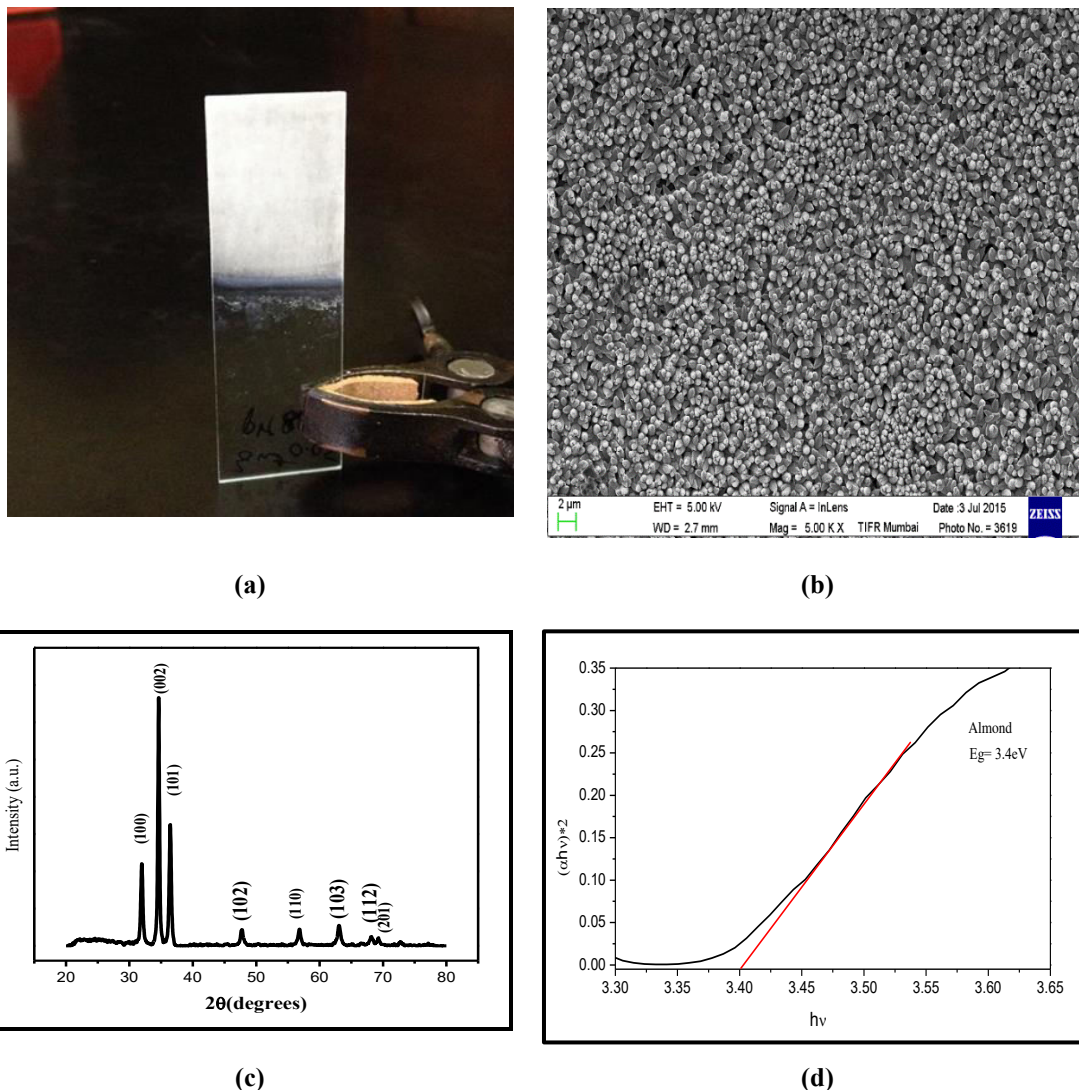


Figure 1: (a) Actual photograph of ZnO thin film (b) SEM image of ZnO (c) XRD pattern of ZnO and (d) The graph of $(\alpha hv)^2$ versus $h\nu$ of ZnO (Tauc Plot) [12]

The crystallite size was determined individually for each plane based on the Full Width at Half Maximum (FWHM) of the corresponding X-ray diffraction peaks. The average crystallite size was then obtained by calculating the mean of the crystallite sizes from all planes. The estimation of the average crystallite size D was performed using the X-ray diffraction spectra and calculated using Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ ----- (I)}$$

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)

The average crystallite size of ZnO is 20.33 nm.

The lattice constants 'a' and 'c' were determined using the following equations,

$$a = \sqrt{\frac{1}{3} \frac{\lambda}{\sin\theta}}$$

$$c = \frac{\lambda}{\sin\theta}$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

The values of lattice parameters were found to be, $a = 3.229 \text{ \AA}$ and $c = 5.176 \text{ \AA}$ with orientation of the grains along (100), (002), (101), (102), (110) and (103) planes.

(ii) Scanning Electron Microscopy (SEM)

Fig 1(b) shows almond like surface morphology of ZnO thin film. It can be observed that the microcrystals are evenly distributed. The microcrystals exhibit a distinct surface morphology resembling the structure of an almond and their growth direction is predominantly perpendicular to the glass substrate. These microcrystals have similar dimensions, with an approximate length of 1.5 μm , diameter of 0.5 μm , and a tip measuring 100 nm.

(iii) UV-Vis Spectroscopy- Optical absorption studies

The UV absorption measurements were carried out at room temperature. The absorption spectrum of pure ZnO thin film observed in the wavelength range 200 nm to 800 nm.

The energy band gap of ZnO were calculated by using Tauc's relations,

$$\alpha = \left(\frac{k}{h\nu}\right) (h\nu - E_g)^\beta$$

$$(\alpha h\nu)^2 = C(h\nu - E_g)$$

Where, α is the absorption coefficient, $\beta=1/2$ for direct band gap semiconductors and $k = \alpha \lambda / 4 \Pi$ is the extinction coefficient, h is Planck's constant and $h\nu$ is the incident photon energy [13] The energy band gap value of ZnO was determined by plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$, as shown in Fig. 1(d). The band gap energy was obtained by extrapolating the linear region of the plot to intersect the energy axis ($h\nu$). From this, the energy band gap of the ZnO film was calculated to be 3.4 eV.

(iv) Gas Sensing studies of ZnO film towards NO₂

ZnO film was exposed to NO₂ to study its gas sensing properties. The optimal operating temperature was obtained by measuring the sensor response at the operating temperatures 100 °C, 150 °C, 200 °C, 250 °C and 300 °C. The Fig. 2 (a) showed the graph of maximum sensitivity versus operating temperature. It is seen that the maximum sensitivity increased with temperature, showing maximum response (3.14) at 250 °C and further decreased for 300 °C.

Since maximum response was obtained at 250 °C, the effect of variation in gas concentration on the sensor was studied at this temperature considering it as optimal temperature. The gas concentration variation of the sensor was studied by varying the gas concentration from 5 to 50 ppm of NO₂. The graph of maximum sensitivity versus gas concentration is shown in fig.2(b). It is seen that the sensitivity increases from 1.87 to 4.9 for change in gas concentration from 5 ppm to 50 ppm and does not seem to saturate. The increase in the sensitivity is linear with the gas concentration.

The relation of the response and recovery time of zinc oxide (ZnO) with concentration of nitrogen dioxide (NO₂) are shown in fig 2 (c) and 2(d). It can be observed that as the gas concentration increases from 5 ppm to 25 ppm, the response time of ZnO sensor increases rapidly from 35 to 121. However, beyond 25 ppm, the increase in response time slows down when the gas concentration reaches 50 ppm. Figure 2(d), illustrates the relation of the recovery time with varying NO₂ concentrations. Initially, as the gas concentration increases from 5 ppm to 10 ppm, the recovery time decreases from 99 to 60. However, when the gas concentration is further increased from 10 ppm to 50 ppm, the recovery time exhibits an upward trend, rising from 60 to 140.

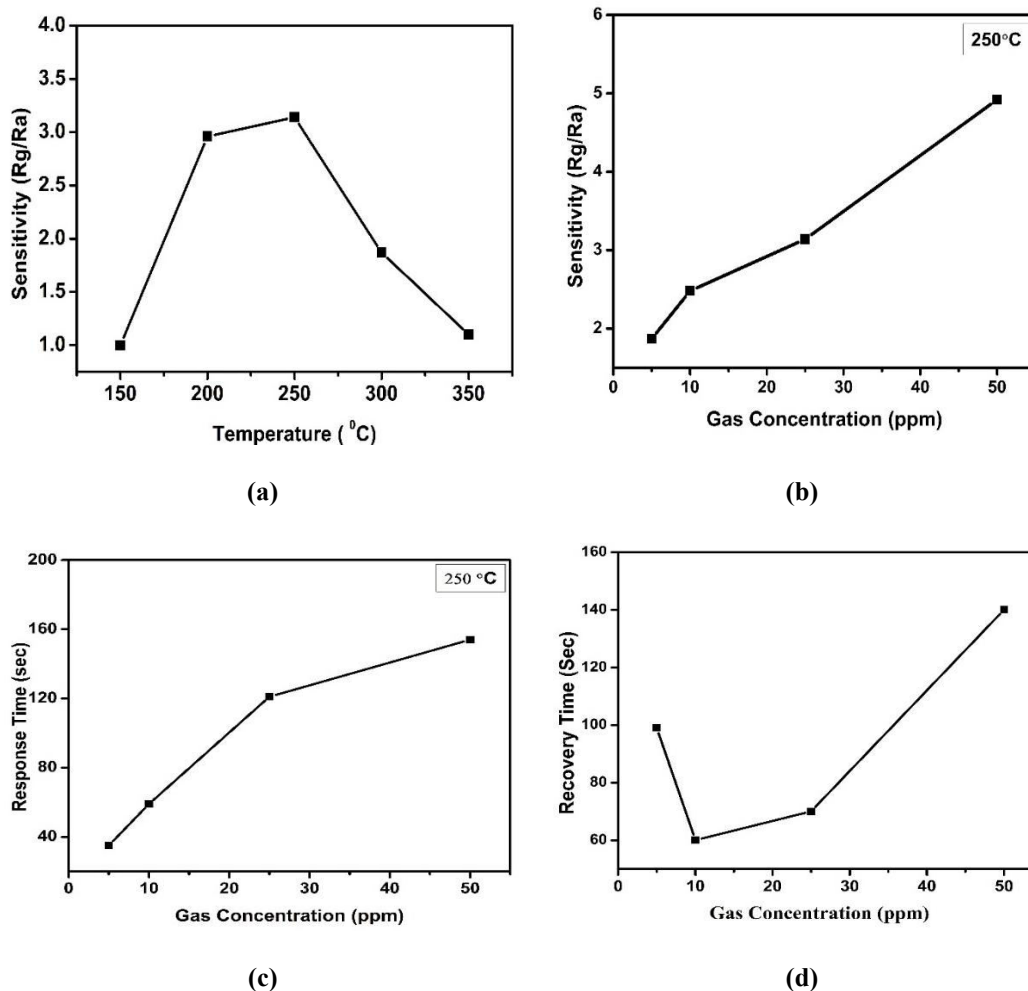


Fig 2: (a) Sensitivity of ZnO versus Temperature (b) Sensitivity of ZnO versus NO₂ gas concentration at 250°C (c) Response time of ZnO versus NO₂ gas concentration at 250°C. (d) Recovery time of ZnO versus NO₂ gas concentration at 250°C

Fig.3 (a,b,c,d) shows the response curves for 5ppm, 10ppm, 25ppm and 50 ppm gas concentrations of NO₂ respectively. It is seen that as the gas concentration increased the sensitivity was also increased. ZnO film has shown good response towards 5ppm of NO₂ gas concentration with response time 35 sec. All the response curves shown characteristic curves

with complete recovery. Initially the response was increased rapidly then it tend towards saturation. The corresponding response and recovery time is calculated and plotted in figure 2 (c) and figure 2(d) respectively.

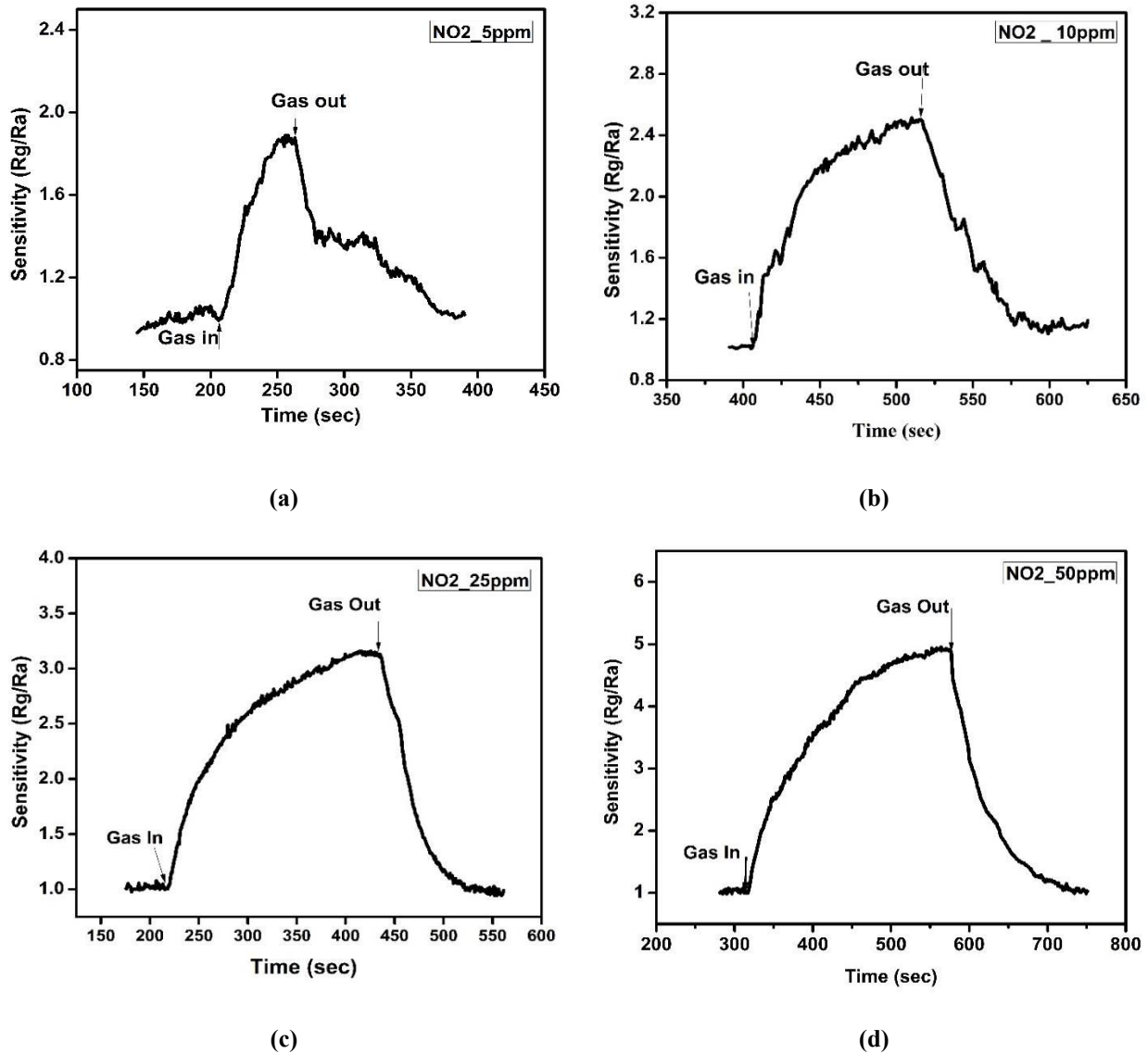
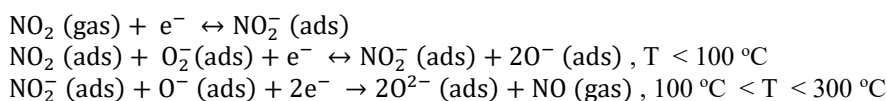


Fig. 3 Sensitivity of ZnO versus Time ($^{\circ}$ C) towards (a) 5 ppm (b) 10 ppm (c) 25 ppm (d) 50 ppm of NO₂.

(v) NO₂ Sensing Mechanism

In an atmospheric environment, oxygen molecules act as electron acceptors and chemically adsorb onto the surface of the ZnO material. As a result, they trap electrons from the ZnO conduction band, causing ionization of the oxygen molecules on the material's surface and forming oxygen ions. This process creates an electron-depleted space charge layer on the ZnO surface and leads to a decrease in electron density, resulting in the formation of a potential barrier. This barrier, in turn, reduces the electron conduction of ZnO and increases its resistance [14,15]. When ZnO is exposed to NO₂. The reactions that can take place on surface of ZnO on NO₂ adsorption are given below.



No sensing response was observed up to 150°C, as the reaction with NO₂ was limited by insufficient thermal energy for electron interaction with adsorbed oxygen. As the temperature rises, thermal energy overcomes the potential barrier, increasing electron concentration and sensitivity. Maximum sensitivity occurs at the optimum temperature, where adsorbed oxygen ions effectively react with NO₂.

IV. CONCLUSION

ZnO thin film was deposited on glass substrates at room temperature using the chemical bath deposition method. SEM revealed distinct almond-shaped microcrystals (~1.5 μm length, ~0.5 μm diameter, ~100 nm tip). XRD pattern indicated a pure ZnO phase with a hexagonal wurtzite structure and lattice constants 'a' = 3.229 Å and 'c' = 5.176 Å. The band gap energy is obtained as 3.4 eV. ZnO film showed sensitivity increased linearly with NO₂ gas concentration, rising from 1.87 at 5 ppm to 4.9 at 50 ppm, without saturation. The sensor exhibited a response time of 30–75 seconds and a recovery time of 100–150 seconds, demonstrating its potential for detecting and monitoring low concentrations of toxic NO₂ gas

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