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One-Pot Synthesis of ZnO Nanorods for LPG Sensing Applications

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In the present work, the authors have successfully deposited uniformly upright standing ZnO nanorods on glass substrates by using simple one-pot chemical bath deposition method. XRD reveals the polycrystalline nature of ZnO thin films. SEM micrograph depicts the well resolved standing growth of ZnO nanorods on glass substrate with an average diameter of 200–300 nm. The optical measurements show that the band gap is 3.3 eV. The detail investigation of LPG sensing study demonstrates the lower operating temperature 190°C with gas response of 105%, with fast response/recovery times 80/70 s, respectively. In addition, the LPG gas uptake capacity remained sensible up to 10 000 ppm.

1. Introduction

Metal oxide nanostructures have gained great attention among researchers for nano-device applications.[1] In sensor application, it is well-known that an anticipated gas sensor must to possess a combination of enhanced sensitivity, excellent selectivity, rapid response-recovery times, long-term stability, and low working temperature. These factors are mostly reliant on surface area to volume ratio, micro porosity, and nanostructures of sensing layer.[2] Conferring to these factors, one-dimensional (1D) nanostructures are sensible and highly favorable to enhance the performance of a gas sensor.[3] These 1D nanostructures have an extraordinarily high surface area and high density of active sites on the surface, which will grant more gas reaction with a sensing material.[4] Metal oxide in nanorod (NR) structures is area of interest due to its special characteristics and potential to be used in many electronic devices. The thin and vertical NR structure has shown less agglomeration due to its larger dimensions. Thus, more test gas is adsorbed and diffused quickly on the sensor surface, leads to contribute to the enhancement of the sensing performance.[5] Among these, 1D ZnO nanostructures, such as nanorods, nanowires, nanobelts, and nanotubes have attracted a great research interest because of their scientific and technological applications.[6] ZnO is an n-type semiconductor (e.g., 3.37 eV) with a large exciton binding energy of 60 meV at room temperature. Moreover, it has good characteristics namely, chemical sensitivity to different adsorbed gases, and amenability to doping, high chemical stability, nontoxicity, low cost, easy fabrication of various nanostructures with a variety of methods.[7,8] In different gases, LPG is one of the extensively used gases in day-to-day activities. There is a need to detect the leakage in its early stages before explosion and perform active suppression. In order to accomplish this, researcher paid more attention for the development of LPG sensor with low operating temperature.[9]

Recently, Nkosi et al. successfully synthesized ZnO NR and flower like structures and implemented for LPG sensing at the operating temperature 200°C with gas response of 80%.[10] Gonugade et al. reported maximum gas response of 20% upon exposure of 5200 ppm LPG concentration at 673 K for ZnO thin films.[11] Dhingra et al. demonstrates the LPG sensing using ZnO worm like structures showed the 19% gas response at an operating temperature 200°C.[12] Gurav et al. synthesized vertically aligned ZnO NRs it shows gas response of 49% at 573 K upon exposure to 5200 ppm of LPG.[13] Shinde et al. reported Pd-sensitized ZnO nanobeads showed 63% LPG response at 275 °C.[14] Moreover, some other reports demonstrated the evolution of ZnO morphologies towards LPG sensing at comparatively high operating temperature above 200°C.[15–19] Therefore, our present investigation is aimed to develop a LPG sensor competent to quick and high gas response with low operating temperature based on ZnO NR synthesized using one-pot chemical bath deposition method. The synthesized ZnO NR is characterized for their structural, optical, and morphological analysis and further employed for detailed investigation of operating temperature, response/recovery time, and uptake capacity for LPG sensing applications.

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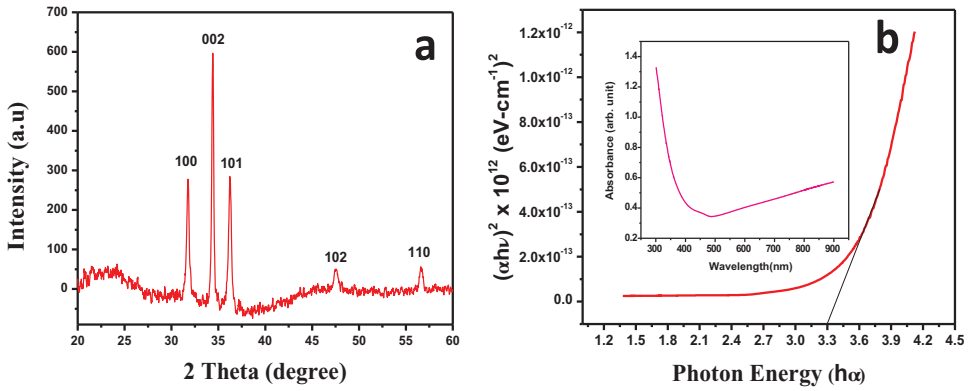

Figure 1. **a)** The X-ray diffraction pattern of ZnO NR. **b)** UV-Visible Spectra of Tauc's plot and absorption spectra (inset) for ZnO NR.

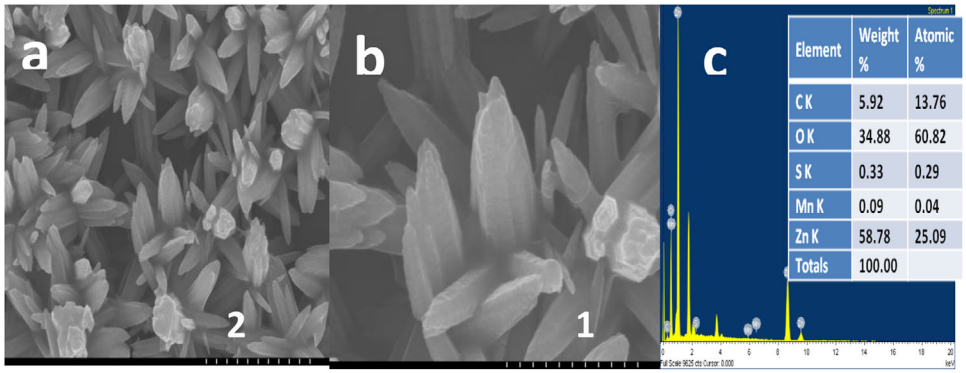

Figure 2. **a-b)** The SEM Images of ZnO NR at two magnifications. **c)** EDAX spectra.

2. Results and Discussion

2.1. X-ray, SEM, and UV Analysis

The XRD diffractogram (Figure 1a) revealed that the ZnO films were polycrystalline nature with a wurtzite type structure. Peak positions indexed to (100), (002), (101), (102), and (110) observed at 2θ values such as 31.98°, 34.67°, 36.48°, 47.71°, 56.79°, respectively. All reflections were found common in ZnO thin film, which supports the formation of wurtzite structure of ZnO films under the preparative conditions [JCPDS data card 36-1451]. As shown, the strongest reflection observed along the (002) direction indicates that the ZnO rod arrays are preferentially well-oriented in the direction of the *c*-axis.[5]

The optical study performed to evaluate the optical properties of the ZnO NR as shown in Figure 1b. The optical band gap (Eg) of the films can be described by the Tauc relationship: An extrapolation of the linear relation between $(\alpha h\nu)^2$ and photon energy ($h\nu$). The direct band gap values were determined from the intercept of $(\alpha h\nu)^2$ versus ($h\nu$) curve. The band gap obtained using the variation showed the value 3.3 eV, which was in good agreement with the reported value of ZnO.[9] Figure 2a and b shows the SEM images of two magnifications, which depicts the uniformly upright standing well-aligned nanopencil rods in flower-like morphology with micro porous structure having diameters 200–300 nm. The elemental composition was also confirmed by EDAX analysis as shown in Figure 2c. The estimated amounts of atomic weight percentage of Zn and O in deposited thin film were close to 58.78% and 34.88%, suggesting that obtained ZnO film is rich in Zn content.[13]

2.2. Temperature Optimization, Response-recovery Time, and Uptake Capacity

Figure 3a shows the variation of the gas response (%) as a function of temperature for ZnO NR at 1000 ppm of fixed LPG gas concentration. The gas response (%) was increased rapidly and reached to a maximum value at 190°C with gas response of 105%. Furthermore, with increase in temperature the gas response decreases sharply and hence, the 190°C was accounted as an optimum operating temperature and used in our further studies. It is worthwhile to note here that the reported value of operating temperature for ZnO NR was certainly lower and gas response is higher than other ZnO thin films previously reported for LPG gas sensors.[10–19] The response and recovery time were defined as the time taken for the sensor to attain 90% of maximum change in resistance upon gas exposure and the time taken by the sensor to get back 90% to its original resistance value, respectively. Figure 3b represents the typical variation in gas response (%) with respect to time in response to 1000 ppm of LPG gas for the ZnO NR held at 190°C. It shows increasing trend with increase in time

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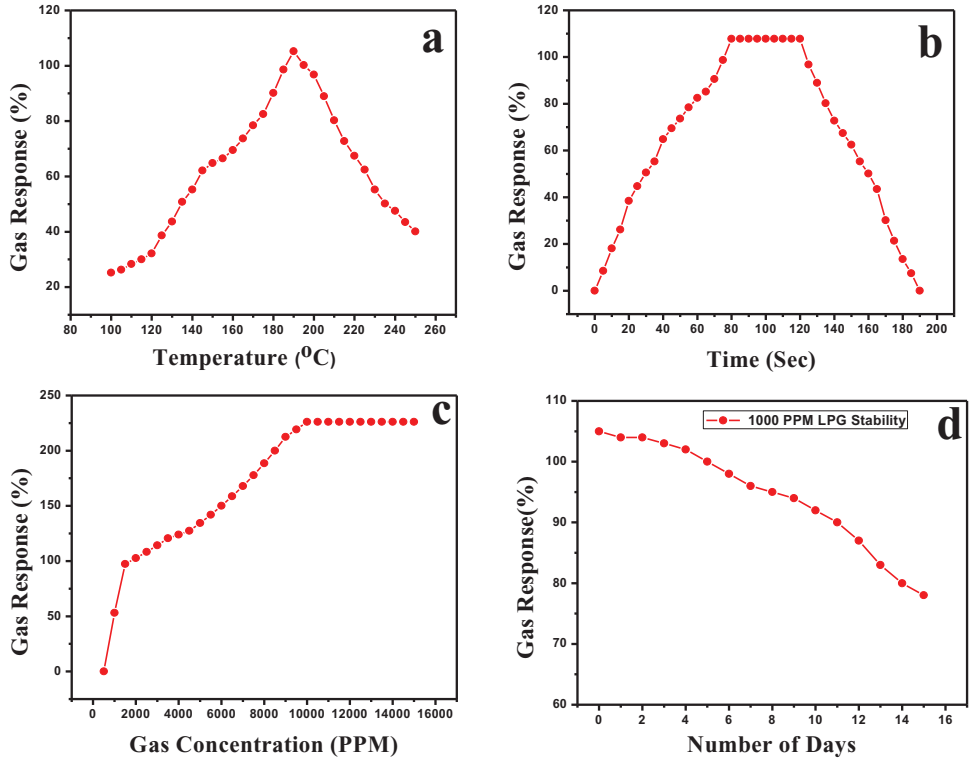

Figure 3. **a)** The variation of Gas response (%) with respect to operating temperature at 1000 ppm of LPG gas concentration. **b)** Response and Recovery plot at 190°C operating temperature. **c)** Variation of Gas response (%) with respect to LPG gas concentration. **d)** Long-term stability curve of ZnO NR for 100 ppm of LPG gas concentration.

after exposure of the ZnO NR to the gas atmosphere, remains constant on further increase in time and then suddenly gets distorted when the sensor was exposed to air atmosphere. From Figure 3b, it was clearly seen that the response and recovery time are 80 and 70 s, respectively. Figure 3c shows the variation in gas response (%) in the range from 500 to 15 000 ppm LPG gas concentration. It shows mainly three regions; first, sharp initial rise in gas response (high response region), second, nearly linear intermediate region and third, region in which the sensor completely saturates (saturation region). For ZnO NR, the active region or gas uptake capacity is up to 10 000 ppm, as further increase in the gas concentration does not show significant response. It may be due to the mono/multi-layer adsorption of gas molecules on the surface that could cover the whole surface of the film. The excess gas molecules cannot reach surface active sites of the sensor, hence the gas response at higher concentration not expected to increase further. Therefore, from this observation, it can conclude that the ZnO NR having gas uptake capacity of 10 000 ppm for LPG gas.

In addition, stability of the gas sensor is very important aspect to assess the long-term gas sensing performance. Therefore, we have studied the stability curve of ZnO NR for LPG as shown in Figure 3d. It was observed that the gas response of ZnO NR remains nearly stable up to 15 days, which conclude its steady gas response even after its long-term exposure. Moreover, the possible reaction kinetics for LPG sensing mechanism on ZnO NR surface is understood as follows. Prior to exposure of LPG, air oxygen gets adsorbed on the sensor surface and captures electrons from the conduction band of the sensor material and forms several oxides such as peroxides and superoxide ions. This depends on the operating temperature as explained by the following reactions.[1,13]

$$O_2{-}_{(ads)} + e{-} \rightarrow 2O{-}_{(ads)} (100^{\circ}C - 300^{\circ}C) \quad (1)$$

After saturation of the chemisorbed oxygen, the surface resistance of sensor martial stabilizes at operating temperature. The electrical property or resistance of the sensing film changes, when redox reaction between the target gas and adsorbed oxygen ions takes place. Wherein, LPG interacts with surface O_2 molecules and gets converted to CO_2 and H_2O vapors.[9] The reaction of oxygen species with LPG at an operating temperature of 190°C is understood as follows.

$$C_nH_{2n+2} + 2O{-}_{(ads)} \rightarrow C_nH_{2n} : O + H_2O + e{-} \quad (2)$$

$$C_nH_{2n} : O + O{-}_{(ads)} \rightarrow CO_2 + H_2O + e{-} \quad (3)$$

Where, C_nH_{2n+2} represent the CH_4, C_3H_8 and C_4H_{10} and $C_nH_{2n:O}$ represent partially oxidized intermediates on the ZnO NR surface. This reaction gives product CO_2, H_2O and releases electrons back to the conduction band of sensing material; hence the resistance of the sensing material decreases with the exposure of LPG.[10]

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3. Conclusion

In summary, this work demonstrates the synthesis of uniformly upright standing flower like morphology of ZnO NR using one pot chemical bath deposition method. Structural, optical, and morphological analyses were confirmed using XRD, UV, and SEM. The systematic study of LPG sensing has demonstrated 105% gas responses with as low as 190°C operating temperature. The fast response and recovery time of 80 and 70 s, respectively, proves its feasibility to be employed as gas sensor. The maximum gas uptake capacity (saturation region) is noted to be up to 10 000 ppm. In summary, the as-grown ZnO NR would be an excellent candidate for developing LPG gas sensors.

4. Experimental Section

Materials: Zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_2O$), Hexamethylenetetramine (HMT, $C_6H_{12}N_4$), Ammonia (NH_4OH), and Acetic acid (CH_3COOH) were purchased from Sigma Aldrich, USA. Micro slide glasses were obtained from BLUE STAR, India.

Synthesis and Preparation of thin film: ZnO NR arrays were grown by chemical bath deposition method from 0.01 M zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_2O$) and 0.01 M hexamethylenetetramine (HMT, $C_6H_{12}N_4$) on glass slides. Glass slides were cleaned by detergent and then completely rinsed in acetone and deionized water, respectively and dried in air. The pH of starting solutions was adjusted to 10 using ammonia (NH_4OH) and acetic acid (CH_3COOH). ZnO NR growth was carried out at 90°C for 2 h. The prepared film was washed with distilled water and ethanol and finally dried at 90°C for 12 h and annealed at 300°C in air for 2 h.

Characterizations: The structural, surface, optical characterization was carried out using XRD, SEM, and UV analysis. XRD pattern was recorded with a Bruker AXS Germany (Model D8 Advanced) having CuKα ($\lambda = 1.54$ Å) incident radiation. The surface morphology and elemental analysis was visualized by means of Scanning Electron Microscope (Hitachi S-4800) with EDAX. UV–Visible absorption spectra were obtained by a Shimadzu UV-3600 spectrophotometer. The electrical and gas sensing characteristics were monitored using a home built static gas sensing system reported in our earlier work.[20] The sensor matrix in the form of thin film was typically 1 cm x 1.5 cm in dimension, which was placed on the heating plate in the test chamber where it was preheated at the required temperature using a temperature controller to remove the humidity effect. The two-probe dc measurement technique was used to measure the electrical resistance of film in air atmosphere and in the presence of test gas. Silver paste contacts were applied at the edges of the film separated by 1 cm, as top electrodes whose ohmic nature was tested within ± 10 V. The desired gas concentration inside the system was achieved by injecting a known volume of the LPG gas. Measurement of the voltage across the reference resistance was followed by measurement of sensor resistance in air and gas (LPG) atmosphere as a function of temperature. The change in resistance of the sensor, due to the presence of LPG gas, was noted in Gas response (%), calculated using classical relation,

$$Gas\ response\ (\%) = \left[R_g - R_a\right]/R_a * 100 = (R/R_a * 100) \quad (4)$$

where R_g and R_a are the resistances measured in gas and air, respectively.

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Conflict of Interest

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chemical bath deposition, gas sensors, LPG, ZnO nanorods

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[1] R. Ahmad, S. M. Majhi, X. Zhang, T. M. Swager, K. N. Salama, *Adv. Colloid Interface Sci.* **2019**, *270*, 1.
[2] V. L. Patil, S. A. Vanalakar, N. L. Tarwal, A. P. Patil, T. D. Dongale, J. H. Kim, P. S. Patil, *Sens. Actuators A* **2019**, *299*, 111611.
[3] V. L. Patil, S. A. Vanalakar, S. S. Shendage, S. P. Patil, A. S. Kamble, N. L. Tarwal, K. K. Sharma, J. H. Kim, P. S. Patil, *Inorganic and Nano-Metal Chemistry* **2019**, *49*, 191.
[4] S. S. Shendage, V. L. Patil, S. A. Vanalakar, S. P. Patil, J. L. Bhosale, J. H. Kim, P. S. Patil, *Z. Phys. Chem.* **2020**, *234*, 1819.
[5] V. L. Patil, S. A. Vanalakar, A. S. Kamble, S. S. Shendage, J. H. Kim, P. S. Patil, *RSC Adv.* **2016**, *6*, 90916.
[6] V. L. Patil, S. A. Vanalakar*, S. A. Vhanalakar, A. S. Kamble, T. D. Dongale, D. N. Kurhe, P. P. Kamble, S. P. Patil, S. S. Shendage, P. S. Patil, J. H. Kim, *Z. Phys. Chem.* **2019**, *233*, 1183.
[7] A. B. Yadav, P. V. L. Parvathi, S. R. Thabassum, *Appl. Phys. A* **2019**, *125*, 446.
[8] A. B. Yadav, P. V. L. Parvathib, R. T. Shaik, *Thin Solid Films* **2019**, *685*, 343.
[9] K. Aishwarya, R. Nirmala, R. Navamathavan, *Sensors International* **2021**, *2*, 100091.
[10] S. S. Nkosi, I. Kortidis, D. E. Motaung, R. E. Kroon, N. Leshabane, J. Tshilongo, O. M. Ndwandwe, *Mater. Chem. Phys.* **2020**, *242*, 122452.
[11] M. D. Gonugade, S. B. Powar, B. S. Salokhe, C. D. Lokhande, J. H. Kim, K. V. Gurav, *Materials Today: Proceedings* **2021**, *43*, 2668.
[12] M. Dhingra, N. K. Singh, S. Shrivastava, P. S. Kumar, S. Annapoorni, *Sens. Actuators A: Phys.* **2013**, *190*, 168.
[13] K. V. Gurav, M. G. Gang, S. W. Shin, U. M. Patil, P. R. Deshmukh, G. L. Agawane, M. P. Suryawanshi, S. M. Pawar, P. S. Patil, C. D. Lokhande, J. H. Kim, *Sens. Actuators, B* **2014**, *190*, 439.
[14] V. R. Shinde, T. P. Gujar, C. D. Lokhande, *Sens. Actuators, B 123*, **2007**, 701.
[15] S. Mondal, S. Bhattacharya, P. Mitra, *Adv. Mat.Sci.Eng.* **2013**, *382380*, 1.
[16] D. B. S. Sarkar, *Sens. Actuators B* **2013**, *176*, 374.
[17] A. Sivapunniyam, N. Wiromrat, M. T. Z. Myint, J. Dutta, *Sens. Actuators, B.* **2011**, *157*, 232.
[18] L. A. Patil, A. R. Bari, M. D. Shinde, V. Deo, *Sens. Actuators, B* **2010**, *149*, 79.
[19] A. Ghosh, R. Sharma, A. Ghule, V. S. Taur, R. A. Joshi, D. J. Desale, Y. G. Gudage, K. M. Jadhav, S. H. Han, *Sens. Actuators, B* **2010**, *146*, 69.
[20] R. U. Mene, M. P. Mahabole, R. Sharma, R. S. Khairnar, *Vacuum* **2011**, *86*, 66.

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