Hydrothermally grown 1D ZnO nanostructures for rapid detection of NO₂ gas

P. R. Godse¹ · A. T. Mane^{1,2} · Y. H. Navale¹ · S. T. Navale¹ · R. N. Mulik³ · V. B. Patil¹

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Abstract

The present paper reports novel approach of surfactant and template free aqueous hydrothermal growth of 1D ZnO nanostructures, which facilitates the generation of large scale, low cost, and moderate working temperature films with controlled morphology for NO₂ gas sensor application. Gas sensing properties of 1D ZnO nanostructures were studied at various temperatures for different reducing and oxidizing gases. As-fabricated by 1D ZnO nanostructures showed the highest sensor response of 11,791% with rapid response time of 9 s and recovery time of 220 s towards 100 ppm NO₂. Moreover, for 5 ppm NO₂ concentration, sensor showed a significant response of 70% with an response time of 16 s and recovery time of 200 s. The sensor shows good continuous performance in terms of response, response time, and recovery time, indicating that the sensor is highly reproducible and stable as well. This study successfully employed 1D ZnO nanostructures based NO₂ sensing within the higher (100 ppm) and lower exposure limit (5 ppm) of NO₂ gas.

Keywords ZnO · Hydrothermal method · Nanorod · Nanotube · NO₂ · Gas sensor

1 Introduction

The World Health Organization (WHO) has accredited that the air pollution is a main environmental health problem affecting everyone in developed and developing countries alike. Advancements in sensing pollutant gases, therefore is a key area of research. The improved living standards of human beings and the increase in world population have gained tremendous industrial development. Number of polluting gases like NO₂, NH₃, CO, and CO₂ are released into the surroundings due to various industrial processes. Our eco-systems polluted by introducing these poisonous gases into the environment due to the industrial growth. Out of the poisonous gases, nitrogen dioxide (NO₂) is one common atmospheric pollutant [1]. NO₂ emissions occurred due to various industrial processes, electricity generation, combustion of fossil fuel, on-road vehicles,

waste disposal, and fires [2]. Emission of NO₂ causing harsh problems on human beings, like respiratory problems, pulmonary edema and even death to human beings along with plants and animals, both terrestrial and aquatic [3]. Thus, require a good quality sensor for detection of NO₂. Due to features like good sensitivity to the ambient conditions metal oxides based sensing materials have been extensively studied in sensing applications. Metal-oxides (MOs) like ZnO [4], TiO₂ [5], SnO₂ [6], WO₃ [7], and In₂O₃ [8] have been largely explored as sensing materials from the several years, due to their high selectivity and sensitivity to the particular gases and their preparation with least condition. In recent time, one-dimensional (1D) metal oxide nanostructures, such as, nanotubes, nanorods, nanofibers and nanowires have been intensively researched for their prospective application in gas sensors [9]. Among the 1D nanostructure predominantly nanorods are most suited

✉ V. B. Patil, drvbpatil@gmail.com | ¹Functional Materials Research Laboratory, School of Physical Sciences, Solapur University, Solapur, Maharashtra 413255, India. ²Maharshi Parshuram College of Engineering, Velneshwar, Ratnagiri, Maharashtra, India. ³D.B.F. Dayanand College of Arts and Science, Solapur, Maharashtra, India.

to this application because of their high electron mobility along with the growth direction, high crystallinity and high surface-to-volume ratio. Moreover, the good thermal and chemical stability under different operating conditions of nanorods could ensure the high-performance sensing behavior [10, 11]. Out of various types of MOs, ZnO is an important MOs material with comprehensive applications in optical devices, electronics and sensors. It is generally known that at room temperature its large exaction binding energy is of 60 meV and high electron mobility, wide band gap of 3.37 eV and excellent chemical and thermal stability. In nanocrystalline ZnO films, the overall electron mobility increases by a factor of 50, using one dimensional (1D) rod-like ZnO crystals rather than spherical crystals [12]. Therefore, one dimensional (1D) ZnO nanostructure sensors have been largely used to detect gases like H_2 , C_2H_5OH , NH_3 and NO_2 [13–15].

In the past, ZnO nanostructures have been fabricated by using solution-phase technique and various gas-phase technique [16]. The solution-phase technique have lower operating temperatures, simplicity and low cost, but in solution-phase processes, micelles, polymers, and organic surfactants are often introduced to act as deciding agents and promote oriented crystal growth. As a result, the residual organic or complexing agents can become impurities that complicate the experimental procedure, increasing the cost and ultimately reducing the industrial potential. On the other hand in gas-phase synthesis techniques involve strict experimental conditions like high temperature, vacuum techniques, and the presence of a catalyst, and sometimes poisonous gases. This involves either high-energy consumption or a relatively high cost for gas-phase based approaches. Therefore to overcome these problems low-energy-consuming, safe, low cost and more eco-friendly solution-phase routes to preparing metal oxides like ZnO nanostructures with defined size and morphology are of interest. For producing inorganic nanomaterials hydrothermal synthesis reactions have gained interest as a quicker, safer, low cost, versatile synthetic, large-scale and more controllable technique. Hydrothermal is one of the method not only helps in developing mono-dispersed homogeneous nanoparticles but also acts as one of the most efficient method for developing various 1D nanostructures [17–19]. In this regard, recently B. Shouli et al. developed one-dimensional (1D) ZnO nanorods using a (CTAB)-assisted hydrothermal process at 90 °C for that they got high response and selectivity to NO_2 , highest response reached to 206 for 40 ppm of NO_2 [20]. M. Sinha et al. developed ZnO nanowire arrays by hydrothermal process for ultra-fast and reversible gas sensing with about 93% response for 200 ppm CO and 98% response for 100 ppm of H_2 as well as an ultra-fast recovery of 1–2 ms for CO with high repeatability [21]. Wang et al. detected hydrogen

gas at 200 °C and found 4.2% response at 500 ppm of response with greater than 20 s recovery time [22]. Rout et al. employed ZnO nanorods (diameters 30–40 nm), nanowires (diameters 20–30 nm), and nanotubes (diameters 60–100 nm) for sensing H_2 gas and obtained a sensitivity of as-prepared nanowires of about 43 for towards 1000 ppm of at 150 °C, with the response and recovery times of 54 s and 5 s respectively [23]. Motaung et al. have grown ZnO nanoparticles and columnar structures using the aerosol spray pyrolysis technique at 20 min and 30 min deposition time and used for room temperature methane and hydrogen gas sensing [24]. Mhlongo et al. grown by aerosol spray pyrolysis technique on Corning glass substrates using an aqueous solution of 0.1 M zinc acetate dihydrate at 350 °C for different growth times. The gas sensing was carried out under UV irradiation and the subsequent exposure to O_2 and NO_2 at room temperature [25]. Motaung et al. reported induced ferromagnetic and gas sensing properties in ZnO-nanostructures by altering defect concentration of oxygen and zinc vacancies [26]. Jagadale et al. carried out preparation at various molar concentrations, characterization of 1D ZnO nanorods and studied their gas sensing properties for various gas concentrations [27]. Kortidis et al. prepared ZnO nanostructures at various pH and reaction times and showed maximum response and sensitivity of approximately 450 and 14.04 ppm⁻¹ at an optimum operating temperature of 75 °C [28]. Agarwal et al. obtained response to ethanol at ppm level and nitrogen dioxide at ppb level of the ZnO nanostructures at different operating temperatures i.e., 150 °C, 200 °C, and 250 °C [29]. Nkosi et al. got highest response of 80 towards 5000 ppm LPG exposure at 200 °C of ZnO hierarchical nanostructures prepared by chemical hydrothermal method [30].

In this paper, we report a one-step simple, cost effective, surfactant free and template-less hydrothermal technique for developing sensing material of ZnO nanostructures. These 1D ZnO nanorods have shown ultrafast sensitivity (11,791%), response time (9 s) and recovery time (220 s) for 100 ppm concentration NO_2 and for 5 ppm NO_2 concentration the significant response of 36% with average response time of 16 s and recovery time of 200 s. In addition ZnO sensor shows fairly consistent performance after every cycle in terms of response, response time and recovery time indicate sensor is highly reproducible. In addition stability varies from 76 to 93% depending upon temperature. All these sensor parameters lead the prepared ZnO sensor towards ideal gas sensor. The growth mechanism, morphology, gas sensing properties and gas sensing mechanism at different temperature of the grown ZnO sensors were consistently studied in this paper. The developed ZnO nanostructure showed essential and efficient gas sensing properties within lower and higher exposure

limit of NO_2 . To the best of our knowledge and belief, there are no reports of high response of 11,791% towards to NO_2 gas at 100 ppm along with excellent reproducibility and stability. Thus, prepared 1D ZnO sensor gratify eventual goal of manufacture functional nanomaterials for realistic and practical applications in terms of low cost and large scale material synthesis which fulfill the magnificent challenges of nanotechnology.

2 Experimental section

2.1 Chemicals

For the deposition, pure zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (AR grade, Thomas Baker) was used as a source material. Ammonia (NH_3) solution (AR grade, sd-fine), used to maintain pH of the solution, and hydrogen peroxide (H_2O_2) (LR grade, Thomas Baker) used as chemical reagent, were used for material synthesis.

2.2 Synthesis of ZnO nanostructures

Initially, 3.56 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 ml distilled water and stirred using magnetic stirrer with 150 rpm at room temperature until a clear solution is obtained, then NH_3 solution was poured drop-wise into the stirred solution to adjust the solution pH = 12. Thereafter, 2–3 ml of H_2O_2 was added in the solution and reaction mixture was continuously stirred for 1 h. Then the reaction mixture was transferred into 100 ml Teflon-lined stainless steel autoclaves. Glass substrates ($10 \times 10 \text{ mm}^2$) were cleaned and spin dried before being loaded in the Teflon-lined stainless steel autoclave. The hydrothermal reaction was carried out at 150 °C, 160 °C, and 170 °C for 3, 6, and 12 h duration to understand the effect of temperature at various deposition times on ZnO films. The obtained films were further utilized to study gas sensing performance for various reducing and oxidizing gases. Finally, by varying

deposition temperature and time, the best condition for preparing nanostructure thin films was optimized. Figure 1 shows the formation of ZnO nanostructures schematically.

2.3 Characterization

The yields gained at diverse stages of preparation were taken out for efficient characterization to recognize the growth of ZnO thin films using special analytical techniques. The prepared samples were characterized by X-ray powder diffractometer Rigaku, Ultima IV, $\text{Cu K}_\alpha/40 \text{ kV}/40 \text{ mA}$, $\lambda = 1.5406 \text{ \AA}$ in 2θ range of 20° to 80°. The morphology of prepared sample was observed by a field emission scanning electron microscope MIRA3 TESCAN, USA, operated at 15 kV. The crystallinity of ZnO nanorods were observed by a transmission electron microscope (TEM) Philips CM 200 with an accelerating voltage of 20–200 kV and a resolution of 2.4 Å. X-ray photoelectron spectroscopy (XPS) was performed by VG Multilab 2000, Thermo Scientific, UK.

2.4 Gas sensing measurements

Custom designed gas sensor unit was used to analysis the gas sensing properties of hydrothermally grown 1D ZnO films. This gas sensor unit is made up of an airtight stainless steel chamber having a volume capacity of 250 ml with a provision of a gas inlet–outlet and a flat heating plate with a digital temperature controller, fitted out with computer-interfaced Keithley-6514 Electrometer as shown in Fig. 2a, b. Using this system, the changes in electrical resistance with respect to the variation in the NO_2 gas concentrations (from 5 to 100 ppm) were investigated at an optimized temperature 200 °C. The gas canisters of nitrogen dioxide (NO_2), ammonia (NH_3), ethanol ($\text{C}_2\text{H}_5\text{OH}$), liquefied petroleum gases (LPG), and methanol (CH_3OH) have been procured from Space cryo gases Pvt. Ltd. Mumbai and used for the sensing study.

Fig. 1 Schematic of formation of 1D ZnO nanostructures

Fig. 2 **a** Photograph of gas sensing measurement setup and **b** schematic diagram of the gas sensing chamber

A known amount of desired gas from standard canister of 1000 ppm concentration was injected into the air tight test chamber (volume 250 cc) by a syringe. For resistance measurements, two silver electrodes (1 mm wide and 10 mm apart) are deposited onto the sensing material for contacts. To measure the response of sensing material, resistance of film was measured in presence of fresh air and gas atmosphere simultaneously. The resistance was measured using a computer-controlled Keithley 6514 system electrometer. The resultant response of hydrothermally grown ZnO films was expressed according to following equation

$$\text{Response (\%)} = \frac{|R_a - R_g|}{R_a} \times 100 \quad (1)$$

where R_a is the resistance of sensor material in presence of fresh air and R_g is the resistance of sensor material in presence of target gas.

3 Results and discussions

3.1 Structural analysis

The X-ray diffraction (XRD) pattern acquaints crystallinity and phase information for the prepared sample. As a result, initially, the hydrothermally grown 1D ZnO samples deposited at different temperatures and time were characterized by XRD for their structural information and presented in Fig. 3. The diffraction pattern of ZnO samples processed at 150 °C, 160 °C, and 170 °C for 3, 6, and 12 h is shown in Fig. 3a–c. The observed diffraction peaks are indexed and represents the theoretical powder diffraction ZnO pattern

from the JCPDS-ICDD card #36-1451 (wurtzite hexagonal structure with $a = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$). All peaks found for the samples could be assigned to this reference card and, furthermore, no noticeable diffraction peaks arising from other phases, suggesting the formation of impurity free ZnO. Prominent and well-defined XRD peaks indicate the sample prepared under various temperatures and deposition times are well crystallized. Also it is observed that, as temperature and deposition time increases the crystallinity of sample increases. When comparing the XRD patterns, a significant over-expression of the crystal growth along (002) was obvious for the samples synthesized at 150 °C and 170 °C but not at 160 °C; a similar behavior was observed elsewhere [31–34].

The calculation of the average crystallite size of the ZnO samples, were carried out by Scherer relation ($D = 0.9\lambda / \beta \cos \theta$). In addition, another structural factor of ZnO nanostructures like stacking fault value (SF), micro-strain (ϵ) and dislocation density (δ) were obtained by the using following relations;

$$\text{SF} = \frac{2\pi^2}{45(3 \tan \theta)^{\frac{1}{2}}} \beta \quad (2)$$

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

XRD parameters and thickness (measured by thickness Profilometer, XP Stylus Profiler) obtained for ZnO samples at various temperatures and time is shown in Table 1. The XRD observations confirmed that there is no significant

Fig. 3 X-ray diffraction pattern of ZnO at processing temperature of **a** 150 °C (3 h), **b** 160 °C (6 h) and **c** 170 °C (12 h)

Table 1 Comparison of XRD parameters and thickness obtained for 1D ZnO nanorods at various temperature and time

Sample	Synthesis duration (hr)	Average crystallite size (nm)	Dislocation density (δ)	Stacking fault (SF)	Micro-strain (ϵ)	Thickness (μm)
ZnO (150 °C)	3	44.54	0.000504081	0.158050185	0.0778	8.55
	6	48.62	0.000979624	0.148102904	0.0713	10.03
	12	47.16	0.000855469	0.152691258	0.0735	1.29
ZnO (160 °C)	3	45.08	0.000492078	0.159726208	0.0769	8.86
	6	47.04	0.000979624	0.153057412	0.0737	13.55
	12	44.14	0.000513954	0.159621647	0.0786	9.38
ZnO (170 °C)	3	42.88	0.000543863	0.164196057	0.0808	9.30
	6	48.45	0.000426003	0.148609655	0.0715	6.53
	12	47.44	0.000444336	0.151764868	0.0731	7.04

change in the lattice parameters with change in temperature from 150 to 170 °C. Also, there are no additional peaks, indicated in JCPDS-ICDD card #36-1451, confirming formation of pure ZnO and, thus, the reliability of present synthesis method. In general, the XRD peak intensities of ZnO samples of 3 h are lower when compared to those of 6 h and 12 h, which indicates an increase of crystallinity with increasing synthesis time. The diffraction peaks turned sharper and stronger when the duration is increased, which indicates the purity of the resultant nanostructure as well as a growth of the crystals over time.

3.2 Morphological analysis

The morphology of deposited materials play a vital role in gas sensing applications and to understand the morphology of ZnO material FESEM analysis were carried out. The morphology of ZnO films processed at different reaction times (3 h, 6 h, and 12 h) and temperatures (150 °C, 160 °C and 170 °C) is shown in Fig. 4, demonstrating the top view of FESEM images of the vertically well aligned 1D ZnO nanorods with a hexagonal structure and uniformly distributed on the glass substrate. From morphological analysis it is observed that the surface porosity increases with increase in reaction time and deposition temperature. The 1D ZnO nanorods synthesized at lower temperature (i.e. 150 °C) and reaction time (i.e. 3 h) were found to have compact alignment of nanorods (Fig. 4a), while

at higher temperature (i.e. 170 °C) and reaction time (i.e. 12 h) aligned nanorods are converted to aligned nanotubes (Fig. 4i), thus the exposed area of the sensing layer remarkably enhanced due to conversion from nanorod to nanotubes, hence, sensing material shows superior gas response at 170 °C temperature and 12 h reaction time (discussed later). In general, the initial cross-section of the materials is the smallest for 150 °C (Fig. 4a). Figure 5 shows a TEM and SAED patterns of ZnO nanorods synthesized at 150 °C (a and b), 160 °C (c and d), 170 °C (e and f) for 3, 6, and 12 h respectively. TEM analysis shows that the diameter of a nanorod is about 252 nm at 150 °C, 141 nm at 160 °C, and 76 nm at 170 °C. This clearly indicates that with increase in temperature the diameter of nanorod decreases, which provides more surface area to volume ratio and plays a vital role in enhancing gas response of sensing material. The diameter of the single-crystalline nanorod is proportional to the diameter of the (002) grains. This is ascribed to the epitaxial growth of the nanorods from the columnar grains of the seed layer. The SAED pattern of synthesized 1D ZnO nanorods exhibited clear diffraction rings, which corresponds to the (1 0 0), (0 0 2), and (1 0 1) planes of hexagonal phase of ZnO. These peaks are the dominant diffraction peaks in the XRD pattern as well, which indicated that the 1D ZnO nanorods were well crystallized at the time of hydrothermal synthesis.

The surface area of as-synthesized 1D ZnO samples (150 °C (12 h), 160 °C (12 h) and 170 °C (12 h)) were carried

Fig. 4 FESEM top view of aligned 1D ZnO nanorods prepared using the hydrothermal method at **a–c** 150 °C, **d–f** 160 °C and **g–i** 170 °C

Fig. 5 TEM and SAED patterns of 1D ZnO nanorods processed at **a**, **b** 150 °C, **c**, **d** 160 °C, and **e**, **f** 170 °C

out though BET technique. The obtained surface areas are, 16.29, 7.56, and 13.22 m²/g for 1D ZnO prepared at 150 °C (12 h), 160 °C (12 h) and 170 °C (12 h) respectively. Observed pore volume for 1D ZnO prepared at 150 °C (12 h), 160 °C (12 h) and 170 °C (12 h) are 0.045, 0.015 and 0.021 cc/g respectively. The higher specific surface area obtained for 1D ZnO sample prepared at 150 °C (12 h).

3.3 Composition analysis

X-ray photoelectron spectroscopy (XPS) is the most powerful and sensitive technique available for investigating the compositional analysis of material surfaces. The surface elemental compositions and chemical states of the pure ZnO nanorods were analyzed with XPS, and the results are displayed in Fig. 6. The typical XPS survey spectra obtained for ZnO nanorods is shown in Fig. 6a, which reveals the presence of C-1s, O-1s, and Zn-2p. The C-1s spectra (Fig. 6b) of the ZnO samples show a major

peak at 285 eV, attributed to the presence of adventitious carbon on the surface of the samples, e.g. due to traces of carbon being abstracted from the Teflon lining of the autoclaves. Figure 6c shows the O 1 s spectra of the ZnO samples, showing a peak, which can be de-convoluted into three peaks at binding energies of 530.1 eV, 531.8 eV, and 533.8 eV, caused by the oxygen binding states of ZnO, C-OH, and H₂O. The Zn-2p spectra (Fig. 6d) of the ZnO samples show doublets de-convoluted at 1021 eV and 1044 eV, corresponding to the Zn-2p_{3/2} and Zn-2p_{5/2} lines, respectively. The binding energy difference of 23 eV between Zn-2p_{3/2} and Zn-2p_{5/2} lines suggests the Zn is in the +2 oxidation state, supporting to the formation of ZnO [35].

3.4 Gas sensing properties

3.4.1 Selectivity

The surface states and adsorption/desorption process of the sensing material plays a vital role in establishing the gas sensing properties. The working temperature of a sensor is mainly responsible for influencing the surface states as well as adsorption/desorption process of the sensing layer. Thus, to obtain a best possible selective gas, sensors exposed to various test gases were carried out (NO₂, SO₂, propane, Cl₂ and CO). Figure 7 demonstrates the selectivity of ZnO sensor prepared at various synthesis temperature and deposition time at 100 ppm exposure of test gases. Thus one can conclude that, prepared ZnO sensor is highly selective for NO₂ gas than for all gases tested.

In gas sensing clarification, the operating temperature is a decisive factor because it influences the adsorption/desorption route on top surface of the sensor, which is contribution task in the gas sensing application. The corresponding response as a function of operating temperature up on exposure of 100 ppm NO₂ gas is shown in Fig. 8a–c [preparation temp. @ (a) 150 °C, (b) 160 °C and (c) 170 °C]. On the top surface of ZnO sensors, forms O⁻, O²⁻ and O₂⁻ species caused by adsorption oxygen from air atmosphere in the range of 100–300 °C temperature. At an operating temperature of 200 °C ZnO sensors attain extreme response towards NO₂ gas. At slighter temperature (i.e. < 200 °C), the sensor response constrained through the tempo of chemical reaction, while at temperature higher than 200 °C the sensor response is controlled through beat of diffusion of gas molecules, however; at conciliator temperature (i.e. @200 °C) the strike of these two reactions outfit equivalent [36] and at that meticulous temperature, sensors afford its crest response to gas.

Fig. 6 **a** Survey spectrum, **b** C-1 s, **c** O-1 s, and **d** Zn-2p XPS core level spectrums of 1D ZnO nanorods

Fig. 7 Selectivity of 1D ZnO sensor prepared at various temperature and deposition time at 100 ppm exposure of target gases

3.4.2 Transient gas response study

The plot of transient response versus time of the 1D ZnO nanorods sensor upon exposure to 5–100 ppm NO_2 concentrations is shown in Fig. 9, 10 and 11 for the 150 °C, 160 °C and 170 °C preparation temperature. It is obvious that the response increases with increasing NO_2 -concentration. In addition, 1D ZnO nanorods sensor at 150 °C and deposition time of 12 h shows highest response on exposure of 100 ppm of NO_2 gas. The adsorption/desorption process of gas molecules by sensing layer plays a vital role in this case. The low concentration means a lower surface coverage of NO_2 gas molecules, resulting in lower surface reactions hence low gas response. Whereas a higher response at high concentration is due to the higher surface coverage of NO_2 gas molecules as a result in increases the surface reactions and enhances the response. Furthermore, 1D ZnO nanorods sensor can easily

Fig. 8 Operating temperature dependent study of 1D ZnO NRs sensor prepared at various temperature and deposition time at 100 ppm exposure of target gases

detect as low as 5 ppm NO_2 with reasonable response of 70%. Response curves for 1D ZnO nanorod sensors on exposure of 1 ppm NO_2 gas for 150 °C (12 h), 160 °C (12 h) and 170 °C (12 h) are shown in Fig. 12. Calibration curves for 1D ZnO nanorod sensors for (a) 150 °C, (b) 160 °C, and (c) 170 °C (12 h) are shown in Fig. 13.

The response time is a time necessary for resistance of a sensor material to changes from 10 to 90% of closing value when the interaction of gas molecules with concentration, and hand recovery time is a time taken by sensor to reach from 90 to 10% of its giving out value behind exposing the sensor to air ambience. A minute response/recovery time, suggested as a superior sensor. Table 2 shows the comparative study of gas sensing parameters of 1D ZnO sensor. From table it is seen that, as concentration of NO_2 increases from 5 to 100 ppm the response goes on increasing while response time decreases and recovery time increases. The decrease in response time of ZnO sensor film is attributed with increasing NO_2 concentration might be due to the large openness of vacant sites as evident from morphology.

On the other hand, increase in recovery time is due to the fact that rate of desorption becomes slow due to large concentration of gas. Thus rate of desorption becomes slow and sensor requires fair time to come into its original state. This might also be the reason for increase in response of sensor. The change in resistance as a function of time on exposure of 100 ppm NO_2 of the various 1D ZnO nanorods sensors as shown in Fig. 14.

3.4.3 Sensing mechanism

The proposed schematic gas sensing mechanism in terms of change in depletion layer width of ZnO nanorods with the NO_2 gas is described in Fig. 15. It is well-known that, the gas sensing properties of metal oxide based gas sensors based on diffusion of gas inside crystal lattice, surface states as well as adsorption/desorption process. In this case, sensing mechanism is described in terms of adsorption and desorption of gas species on the surface of sensor. This is a chemiresistive gas sensing mechanism followed by ZnO sensor. Before exposure of NO_2 , oxygen in air gets adsorbed

Fig. 9 Transient response versus time plot of the 1D ZnO nanorods sensor upon exposure to 5–100 ppm NO_2 concentrations at prepared temp. of 150 °C at deposition time of **a** 3 h, **b** 6 h, and **c** 12 h

on the sensor surface and withdrawn electrons from the conduction band of the sensor material [37]. The $\text{O}_{2(\text{ads})}^-$ acts as an electron trap, which limit the further movement of conduction band electrons and resistance of sensor get stabilized, that can be explained by the following reactions:

The sensor changes its resistance or electrical properties only when any chemical oxidation or reduction process happens on sensor surface [37]. When NO_2 gas is exposed on ZnO nanorods, NO_2 adsorb directly on the surface of ZnO nanorods. NO_2 gas is oxidizing in nature, i.e. it withdraws electron from ZnO nanorods; therefore, the concentration of electrons on the surface of ZnO nanorods decreases, which leads to increase in the resistance of sensor. The process of the reaction can be described as follows:

In addition, following reaction is happened between $\text{NO}_{2(\text{ads})}^-$ and O_{ads}^-

and the reaction continued:

These cycles of reactions result in the further decreased concentration of electrons on the surface of ZnO, which led to the increase in resistivity of the material. This increase in resistance is ascribed to an increase in the width of depletion layer as shown in Fig. 15. This change in resistivity can be used for the detection of NO_2 .

3.4.4 Reproducibility and stability

In order to use sensors for commercially purpose it should show reproducible and stable performance

Fig. 10 Transient response versus time plot of the 1D ZnO nanorods sensor upon exposure to 5–100 ppm NO₂ concentrations at prepared temp. of 160 °C at the deposition time of **a** 3 h, **b** 6 h, and **c** 12 h

over the period of time. To check reproducible performance, the sensor was exposed in NO₂ for four cycles and the results are shown in Fig. 16a–c. From figure it is observed that ZnO sensor shows fairly consistent performance after every cycle in terms of excellent response, less response time and fair recovery time. The less response time of sensor shows the easy adsorption of gas molecules while fair recovery time indicates effortless desorption by ZnO sensor. The stability of ZnO sensor was consistently measured for 25 days with time interval of 5 days at fixed concentration of 100 ppm NO₂ and the corresponding results are depicted in Fig. 16d. The sensor shows selectivity of 76%, 84%, and 93% for 150 °C, 160 °C, and 170 °C, respectively. Generally, sensor

exhibits a maximum response and depending on nature of material response goes on decreasing as number of days increases. This decrease in response is due to the aging induced effect [38]. The ideal sensor shows no variation in response value as number of days increased. Herein, all sensors shows similar kind of behavior but the sensor prepared at 170 °C shows less variation in the response as number of days progresses as shown in Fig. 16d. Thus one can conclude that ZnO sensor operates at 170 °C can be identified as stable sensor and used commercially for detection of NO₂ gas in 5 to 100 ppm concentration. This suggests minute differences in surface morphology and, specifically, that the 170 °C series

Fig. 11 Transient response versus time plot of the 1D ZnO nanorods sensor upon exposure to 5–100 ppm NO_2 concentrations at prepared temp. of 170 °C at the deposition time of **a** 3 h, **b** 6 h, and **c** 12 h

has better packed crystals, which are more resistant to withstanding surface corrosion occurring over time.

4 Conclusions

ZnO nanostructures were fabricated by hydrothermal method at 150 °C, 160 °C and 170 °C for 3, 6, and 12 h using $\text{Zn}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$. The size and shape of the ZnO

nanostructures could be tuned by varying the temperature and time of reaction in hydrothermal synthesis. The advancement in temperature and time changes morphology from aligned nanorods to nanotubes, which result in enhancing the gas sensing parameters of ZnO sensor. Also with increasing temperature, the diameter of nanorod decreases from 250 to 76 nm, which provides more surface area to volume ratio and applicable for gas sensing. On the other hand, NO_2 sensing

Fig.12 Response curves for 1D ZnO nanorod sensors on exposure of 1 ppm NO_2 gas for **a** 150 °C (12 h), **b** 160 °C (12 h) and **c** 170 °C (12 h)

Fig.13 Calibration curves for 1D ZnO nanorods Sensors **a** 150 °C, **b** 160 °C, and **c** 170 °C

Table 2 Comparative study of gas sensing parameters of as-fabricated 1D ZnO nanorods sensor (150 °C, 160 °C and 170 °C, for 12 hr) towards 5 to 100 ppm exposure of NO₂ gas

Sample	NO ₂ Concentration (ppm)	150 °C			160 °C			170 °C		
		Re (%)	Res Time (s)	Rec Time (s)	Re (%)	Res Time (s)	Rec Time (s)	Re (%)	Res Time (s)	Rec Time (s)
ZnO	5	70	16	200	190	72	480	68	60	790
	10	74	13	210	281	28	440	158	58	850
	20	402	12	225	728	25	530	329	56	890
	40	919	11	300	940	25	570	744	54	950
	60	1722	10	320	1337	22	574	866	54	1100
	80	4963	10	650	1713	21	650	2356	41	1130
	100	11,791	9	220	3673	20	835	10,069	34	560

Re = Response, Res/Rec time = Response/Recovery time

Fig. 14 Change in resistance 1D ZnO nanorods Sensors **a–c** 150 °C (3, 6, and 12 h), **e–f** 160 °C (3, 6, and 12 h), and **g–i** 170 °C. (3, 6, and 12 h), respectively

Fig. 15 The proposed schematic gas sensing mechanism, in terms of change in depletion layer width, of 1D ZnO nanorods in air and in presence of NO_2 gas

Fig. 16 **a–c** Reproducibility and **d** stability study of as-fabricated 1D ZnO nanorods sensor

properties of hydrothermally grown ZnO nanostructures were investigated depending on the temperature and time of reaction towards various oxidizing and reducing gases. It was observed that the highest sensor response for 150 °C processed films, which is 11,791% with rapid response time of 9 s and recovery time of 220 s for 100 ppm NO₂ concentration. The lowest response (36%), response time (16 s) and recovery time (200 s) were obtained for 150 °C processed films for 5 ppm NO₂ concentration.

The eventual goal of such a study is to manufacture functional nanomaterials for realistic and practical applications in terms of low cost and large scale material synthesis which fulfill the magnificent challenges of nanotechnology.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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