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Fabrication of nanostructured ZnO thin film sensor for NO_2 monitoring

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Abstract

Nanocrystalline zinc oxide (ZnO) thin films were deposited onto glass substrates by a spin coating method. These films were characterized for their structural and morphological properties by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The ZnO films are oriented along (1 0 1) plane with the hexagonal crystal structure. These films were utilized in NO_2 sensors. The dependence of the NO_2 response on the operating temperature, NO_2 concentration was investigated. The ZnO film showed selectivity for NO_2 over H_2S compared to NH_3 ($S_{NO_2}/S_{H_2S} = 3.32$ and $S_{NO_2}/S_{NH_3} = 5.32$). The maximum gas response of 37.2% was achieved with 78% stability for ZnO films upon exposure of 100 ppm NO_2 at operating temperature 200 °C.
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Keywords: ZnO thin films; XRD; AFM; HRTEM; SEM; NO_2 sensor

1. Introduction

Increased concerns with the toxic effects of chemicals in the environment lead to novel sensors development for continuously monitoring of pollutions at various points in industrial and recycling processes, at agricultural and urban sites. Nitrogen dioxide, NO_2, is one of the most harmful gases emitted from combustion of the exhaust of automobiles engines, home heaters, furnaces, plants, etc. Therefore the development of portable fast-response sensors that are robust, small sized, long lifetime, quick in response and with sufficient sensitivity for the detection of nitrogen dioxide in low concentrations, such as few ppm, in the ambient is necessary and demanded also in order to prevent irreversible changes in the global atmosphere.

For this reason efforts made nowadays by scientific research community in leading laboratories all over the world have been focused on the development and investigation of novel NO_2 sensitive materials suited for solid-state gas sensors, consequently, their performances have to be improved dramatically by adopting preparation conditions and by controlling post-deposition processing.

Extensive research done during the past decade has revealed many novel optical, electrical and mechanical properties of semiconductor nanoparticles [1]. These include size quantization effect, photocatalytic properties, and photoelectro chemical effects.

ZnO is one of the few ceramic oxides that shows quantum confinement effects in the experimentally accessible size and is a wide band gap semiconductor (3.37 eV) that displays interesting luminescent properties, which include the recent demonstration of ultraviolet lasing from nanowires [2,3]. These properties have stimulated the search for new synthetic methodologies for well-controlled ZnO nanostructures. Several reports on high temperature physical [4,5] or chemical [6–10] synthesis have been published. Semiconducting oxides such as SnO_2, TiO_2, Fe_2O_3 and ZnO have extensively been used for detecting reducing gases such as CO, CH_4, NH_3 and alcohol [11,12]. But ZnO is very sparsely used for detecting most harmful and high toxic gas NO_2.

In order to have precise and reliable detection of gas there is an urgent need for development of NO_2 gas sensor. Nanocrystalline semiconducting oxides are very important as a sensor material since size reduction and gas diffusion control are the main factors enhancing gas-sensing properties. For gas sensors it is necessary to have a porous microstructure with small particle size yielding large ratio of surface area to bulk [13].

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To the best of our knowledge, the sol gel spin coated ZnO thin films have not been used for NO_2 detection.

In the present study, we adopted spin coating technique which provides one step stable ZnO films, which were further utilized for investigating NO_2 sensing properties. The ZnO films were deposited onto a glass substrate and films were annealed at 700 °C to eliminate hydroxide inclusion, the effect of operating temperature, gas concentration and surface morphology on the NO_2 sensing properties has been studied.

2. Experimental details

Nanostructured ZnO thin film sensor was developed on glass substrate using sol-gel spin coating method [14]. X-ray powder diffraction (XRD) pattern of the fabricated film was measured for the phase identification and estimation of the average crystallite size using Philips PW-3710 model. High resolution transmission electron microscopy (HRTEM) was obtained in order to investigate the morphology of Zinc Oxide thin films using Hitachi Model H-800 TEM. The size and morphology of the thin films were then observed on SEM Model: JEOL JSM 6360 operating at 20 kV. The thickness of the film was measured by using Dektak profilometer and found in the range of 100–140 nm.

The NO_2 sensing properties of ZnO films were studied in the home-fabricated gas sensor unit shown in Fig. 1.

In order to measure the gas response, the resistance of the films was measured in air ambient and in gas atmosphere. For resistance measurement, two silver electrodes, separated by 1 mm, were deposited on ZnO film and silver wires were attached using silver paint. The resistance was measured using 6- digit Keithley 6514 Electrometer data acquisition system. For monitoring the response of the films to various gases, the films were mounted in 250 cm^3 airtight container and the known gas (NO_2, NH_3, H_2S, C_2H_5OH and CH_3OH) of particular concentration was injected through a syringe. All the gas sensitivity measurements were carried out at 200 °C operating temperature. Fig. 2 shows photograph of experimental setup for gas sensor measurement.

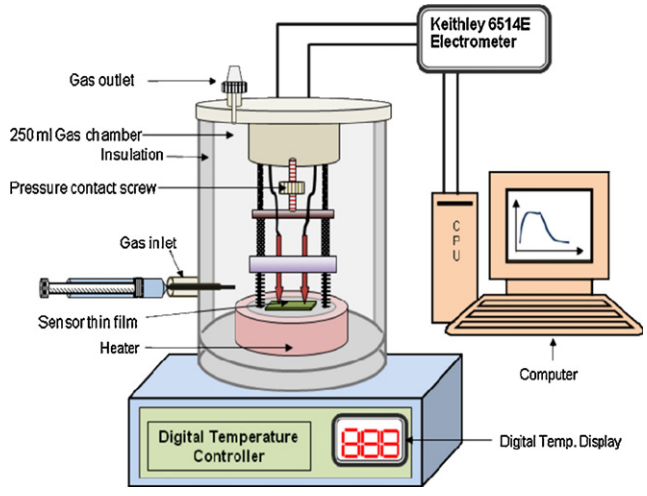

Fig. 1. Schematic view of high temperature gas sensor unit.

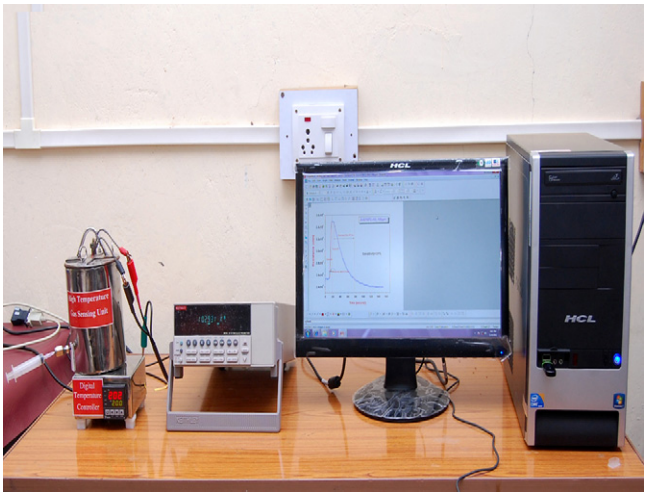

Fig. 2. Photograph of experimental setup for gas sensor measurement.

The electrical resistance of ZnO film in air (R_a) and in the presence of NO_2 (R_g) was measured to evaluate the gas response, S, defined as follows:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100$$

3. Results and discussions

3.1. Structural analysis

Fig. 3 shows X-ray diffraction patterns of ZnO thin films deposited on glass substrates by spin-coating technique at different annealing temperatures of 400, 500, 600, and 700 °C. The X-ray spectra show well-defined diffraction peaks showing

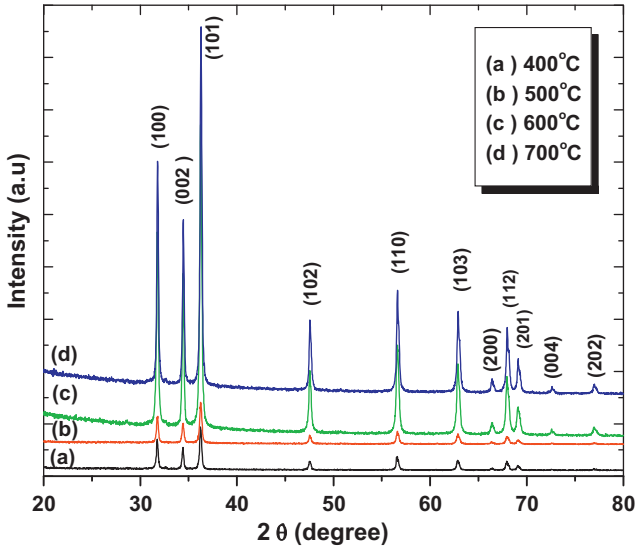

Fig. 3. X-ray diffraction patterns of ZnO films annealed at different temperatures.

good crystallinity. The crystallites are randomly oriented and the *d*-values calculated for the diffraction peaks are in good agreement with those given in JCPD data card (79.0208) for ZnO [14–17]. This means that ZnO has been crystallized in a hexagonal wurtzite form. The lattice constants calculated from the present data for (1 0 1) phase (strong reflection) are $a = 3.265$ Å and $c = 5.214$ Å, respectively.

The average particle sizes of ZnO thin films were calculated using the full width at half maximum (FWHM) of (1 0 1) peak from the Scherer's method the value of the crystallite sizes varies between 61.82 and 73.48 nm when ZnO film annealed between 400 and 700 °C.

It was observed that crystallite size increased with increasing annealing temperature, which can be understood by considering the merging process induced from thermal annealing [14–17].

3.2. Surface morphological studies

The two-dimensional high magnification surface morphologies of ZnO thin films annealed at 400–700 °C were carried out using SEM images are shown in Fig. 4(a–d). From the micrographs, it is seen that the film consists of nanocrystalline grains with uniform coverage of the substrate surface with randomly oriented morphology and the crystallite size is increased from 40–52 nm as annealing temperature increases from 400 to 700 °C. The crystallite size calculated from SEM analysis is quite in good agreement with that of crystallite size calculated from XRD analysis.

3.3. Compositional and micro structural analysis

The energy-dispersive X-ray (EDX) spectrometry shown in Fig. 5 clearly shows Zn and O elements in the products with an approximate molar ratio of 1:1 (the Cu and S signal is attributed to the copper meshes for TEM).

AFM (non contact mode) was used to record the topography of the ZnO thin film annealed at 700 °C. The surface morphologies of the ZnO nanoparticles exhibit notable features. The surface roughness of the film over a 3 μm × 3 μm mm area was measured by AFM (Fig. 6).

The surface roughness mean square (RMS) of the film is 25 nm, which demonstrates that the surface morphology of ZnO film annealed at 700 °C is smooth. Fig. 7 shows High resolution TEM image of ZnO thin film annealed at 700 °C. It clearly shows that a grain of about 40–60 nm in size is really aggregate of many small crystallites of around 10–20 nm.

From structural, microstructural and morphological studies it is observed that ZnO thin films annealed at 700 °C ($t = \sim 140$ nm) provides the desired hexagonal wurtzite crystal structure and nanocrystalline ZnO particles. These studies have revealed that the ZnO thin films annealed at 700 °C may provide improved gas sensing properties and therefore the present paper aims at the gas sensing properties of nanostructured ZnO thin films annealed at 700 °C.

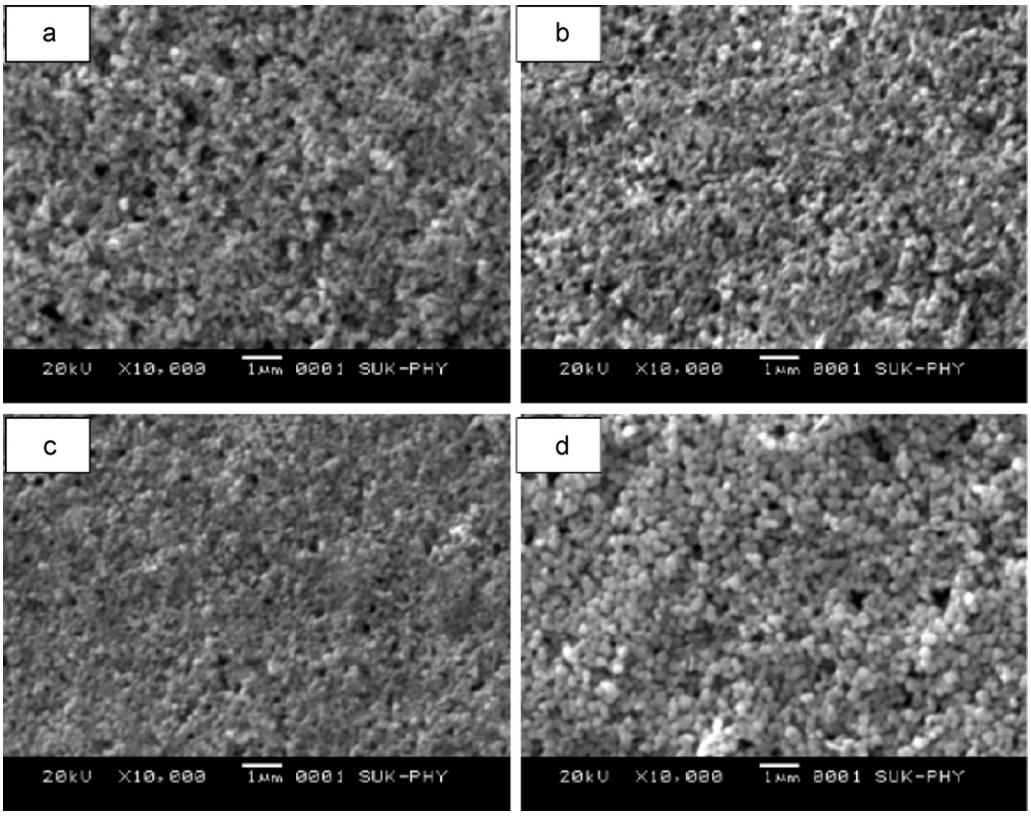

Fig. 4. SEM images of ZnO thin films anneled at (a) 400 °C, (b) 500 °C, (c) 600 °C and (d) 700 °C.

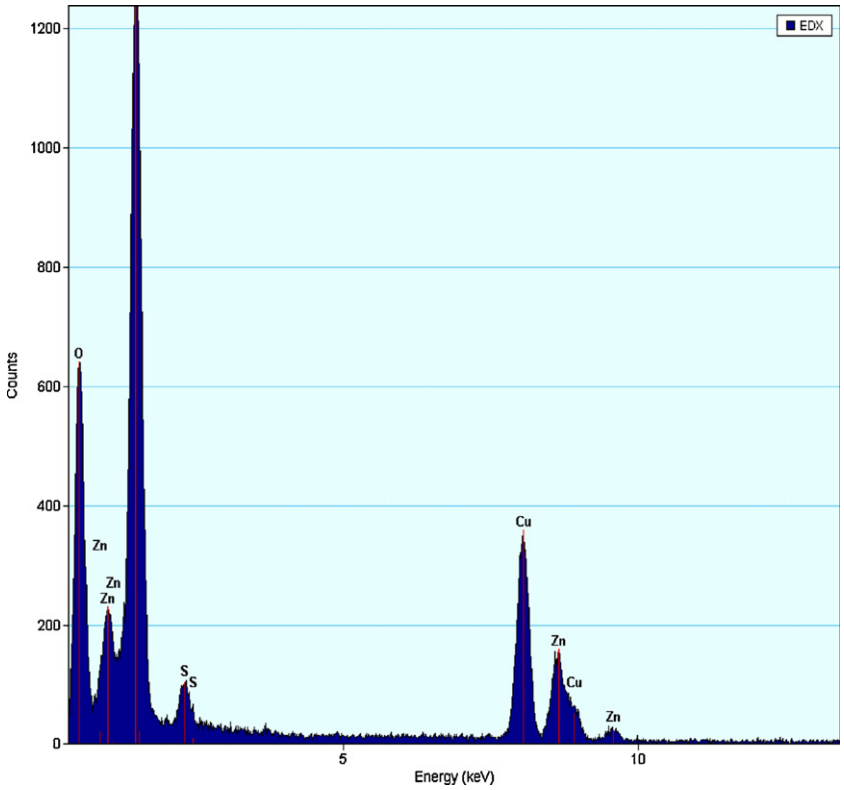

Fig. 5. EDAX spectra of ZnO thin film annealed at 700 °C.

3.4. Gas sensing studies

3.4.1. Stabilization of sensor resistance

The stabilization of the ZnO film resistance in ambient air prior to exposure of gas is important, because it ensures stable zero level for gas sensing applications. Since the SEM image of ZnO film annealed at 700 °C showed the spherical clusters of order of 1 μm size, consisting of fine nanoparticles with porous space in between, it was decided to study the NO_2 sensing properties of ZnO film (annealed at 700 °C) at the beginning. Fig. 8 shows the typical initial stabilization curve of resistance of ZnO film at 200 °C from nonequilibrium to equilibrium. Initially, when the temperature of 200 °C was attained, the resistance was decreased rapidly within few seconds and then raised and exhibited a stable value. This can be attributed to the generation of electrons due to thermal excitations. However, some of these electrons from the conduction band of ZnO are extracted by oxygen adsorbed on the surface of the

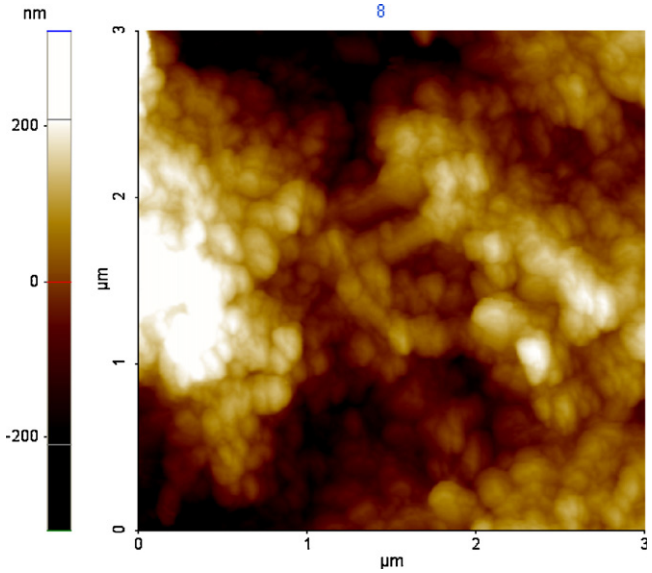

Fig. 6. AFM images (planer view) of ZnO thin films annealed at 700 °C.

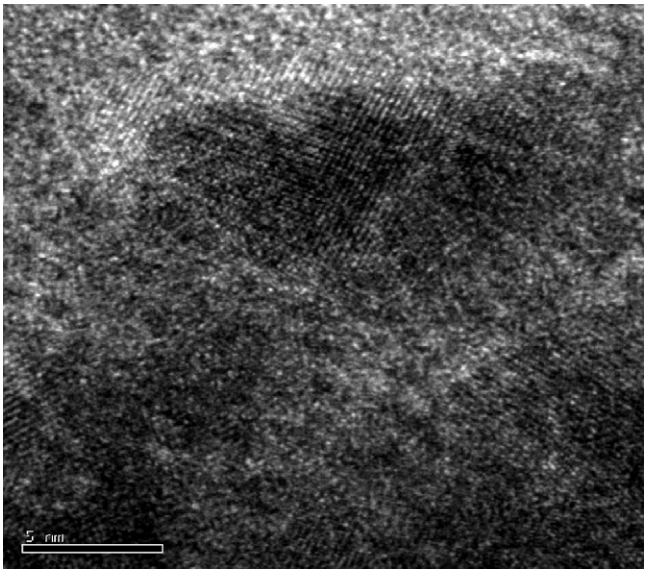

Fig. 7. HRTEM of ZnO thin film annealed at 700 °C.

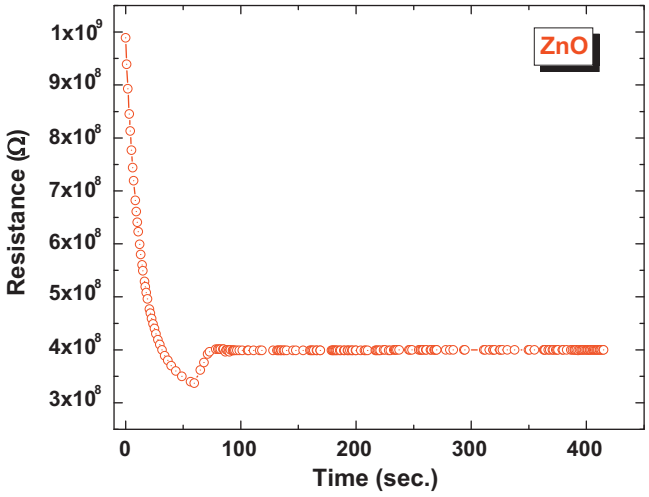

Fig. 8. Resistance stabilization curve with time for ZnO film at 200 °C.

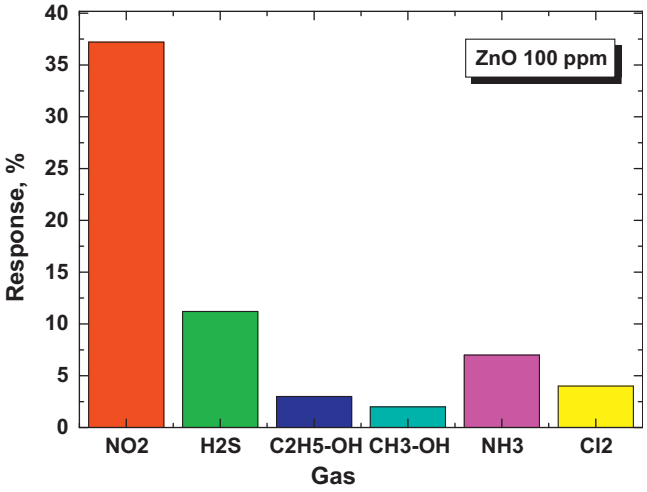

Fig. 9. Gas responses of ZnO sensor film to 100 ppm of NO_2, H_2S, NH_3, CH_3–OH, C_2H_5–OH and Cl_2.

semiconductor, hence increasing the resistance of the semiconductor. The oxygen adsorbed undergoes the following reaction [18]:

$$O_2(\text{gas}) \leftrightarrow O_2(\text{ads}) \quad (1)$$

$$O_2(\text{ads}) + e^- \leftrightarrow O_2(\text{ads}) \quad (2)$$

$$O_2{}^-(\text{ads}) + e^- \leftrightarrow 2O^-(\text{ads}) \quad (3)$$

Thus, the equilibration of the chemisorption process results in stabilization of surface resistance. Any process that disturbs this equilibrium gives rise to changes in the conductance of the semiconductors [19]. The conductance change is correlated with the concentration of gases in an ambient air.

3.4.2. Selectivity of ZnO thin film sensor

The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity. The selectivity of a sensor in relation to a definite gas is closely associated with its operating temperature. Here, the selectivity measured in terms of selectivity coefficient/factor of a target gas to another gas is defined as $K = S_A/S_B$, where S_A and S_B are the responses of a sensor to a target gas A and an interference gas B, respectively.

3.4.3. Temperature dependent gas detection

Fig. 9 shows the histogram of gas response of different gases at a fixed concentration of 100 ppm. The histogram revealed that the ZnO sensor offered maximum response to NH_3 (7%), H_2S (11.2%), Cl_2 (4%), CH_3OH, (2%) C_2H_5OH (3%) and NO_2 (37.2%) at 200 °C.

The ZnO film showed more selectivity for NO_2 over H_2S compared to NH_3 ($S_{NO_2}/S_{H_2S} = 3.32$, $S_{NO_2}/S_{NH_3} = 5.32$) at an operating temperature 200 °C. It is revealed that NO_2 is the more selective against NH_3 and poor selective against H_2S. Therefore, further dependence of NO_2 response on operating temperature and NO_2 concentration of ZnO film was studied.

3.4.4. Sensitivity of ZnO film

3.4.4.1. Effect of operating temperature and NO_2 concentration. Before exposing to NO_2 gas, the ZnO film was allowed to be stable for electrical resistance for 30 min and the stabilized resistance was taken as R_a. Initially, the gas response to 100 ppm of NO_2 was measured as a function of operating temperature for ZnO film and is shown in Fig. 10. The sensor response reached maximum at 200 °C (gas response = 37.2%) and then decreased. It is well known that at low temperature, the response is restricted by the speed of chemical reaction, and at high temperature, by the speed of diffusion of gas molecules. At some intermediate temperature, the speeds of the two processes become equal, and at that temperature, the sensor response reaches to its maximum [20].

As evident, the sensitivity increases with the temperature and reaches a maximum value in correspondence of $T = 200$ °C. If the temperature increases again, the sensitivity

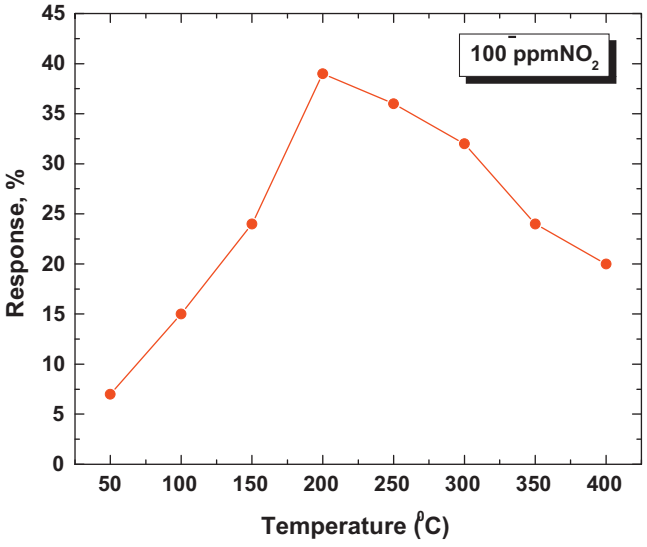

Fig. 10. Response of ZnO films to 100 ppm of NO_2 gas as a function of operating temperature.

decreases. This behavior can be explained in analogy with the mechanism of gas adsorption and desorption.

3.4.4.2. Gas sensing mechanism. There are two types of semiconductors: p-type and n-type. The majority carriers in n-type semiconductors are electrons. The electron injected into the conduction band recombine with some electrons and this process results in increasing the number of charge carriers, which leads to decreasing the resistance (opposite of p type) [21]. This happens in our study. However, electrical conductance of n-type semiconductors increases (or decreases) when reducing (or oxidizing) gases are adsorbed on their surfaces (opposite for p-type semiconductors) [22]. In all cases the sensors exhibited an increase in resistance upon exposure to the gases vapours, this suggested that the metal–oxide layers were behaving as expected for n-type semiconductors in response to an oxidizing gas. In an n-type semiconducting oxide, adsorbed oxygen behaves as a surface acceptor state, trapping holes from the valence band and hence increasing the electron concentration.

For zinc oxide thin films-based sensor elements obtained by sol–gel spin coating method, the sensitivity (electrical resistivity) change in the NO_2 ambient can be caused by the change in the surface composition of the oxide layer at the chemisorption of gas molecules. The mechanism of nitrogen dioxide detection of tested sensors at the 200 °C operating temperature can be explained by the chemisorption and removal of the surface chemisorbed species.

The desorption of NO_2^-(ad) is limiting at the decomposition of the NO_2 at the zinc oxide, which is determined by the extensive recovery time after the expose of the sensor to highly toxic NO_2 gas and depend on the sensors operating temperature as can be concluded from Fig. 10. At a higher operating temperature (~200 °C) the increase in sensitivity for samples can be explained by reversible oxidizing interaction of NO_2 molecules with sufficient thermal energy with the predominant surface adsorbed oxygen species

$$O^-_2 \rightarrow 2O^- + e^- \quad (4)$$

Physisorbed nitrogen dioxide molecules form new surface acceptor levels deeper than surface oxygen ions. Therefore, bound electron is transferred from O_2^- ion to physisorbed NO_2 molecule

$$NO_2 + e^- \rightarrow NO_2^-(ad) \quad (5)$$

and form NO_2^- species and increased band bending at the zinc oxide surface [23,24]. Thus, can be explained the resistivity increase when sensor is placed in test atmosphere. According to performed investigations the NO_2 gas adsorption is principally a function of surface properties and requires a further research.

Once the operating temperature is fixed, the sensor response is studied at different NO_2 concentrations. Fig. 11 shows the response of ZnO film as a function of NO_2 concentration. The response increased from 9% to 37.2%, as the NO_2 concentration increased from 10 to 100 ppm. The gas response showed saturation at NO_2 concentration more than 100 ppm due to increased surface reaction [25,26].

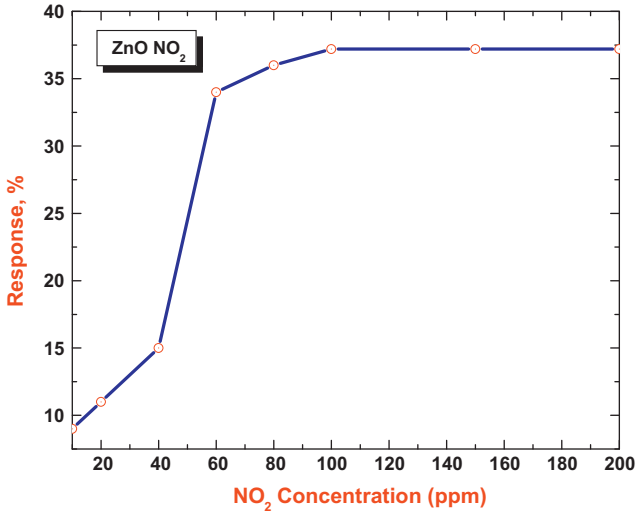

Fig. 11. Variation of NO_2 response of ZnO film with different concentrations of NO_2 at operating temperature at 200 °C.

3.4.5. Dynamic response transients of ZnO thin film

The dynamic variation of gas response with time for NO_2 (20–100 ppm) is shown in Fig. 12. The figure revealed that the initially the response of sensor film increase from 9% to 37.2% with increasing the concentration of NO_2 at 100 ppm, The ZnO film showed the maximum response of 37.2%. Such a higher value of response is believed to be due to the sensitivity of the metal oxide semiconductor sensors mainly determined by the interactions between the target gas and the surface of the sensor. So, it is obvious that for the materials of greater surface area, the interactions between the adsorbed gases and the sensor surface are significant. The ZnO granular morphology provided a high surface area to interact NO_2 molecules resulting in increased response.

3.4.6. Response and recovery times of ZnO films

The response/recovery time is an important parameter used for characterizing a sensor.

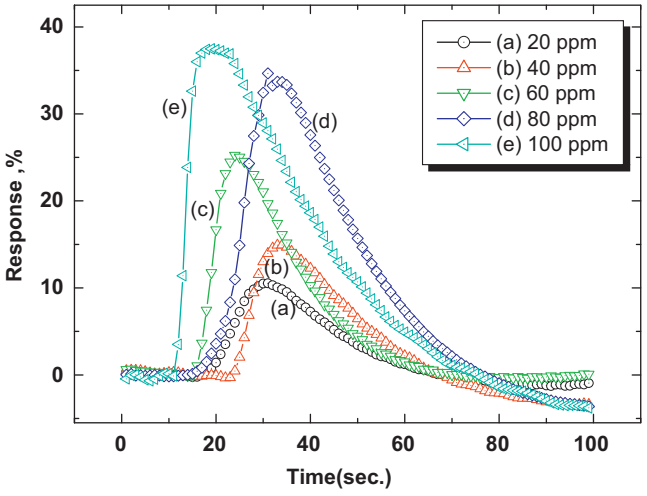

Fig. 12. The dynamic response of ZnO films for 20–100 ppm NO_2 in at the optimum working temperature.

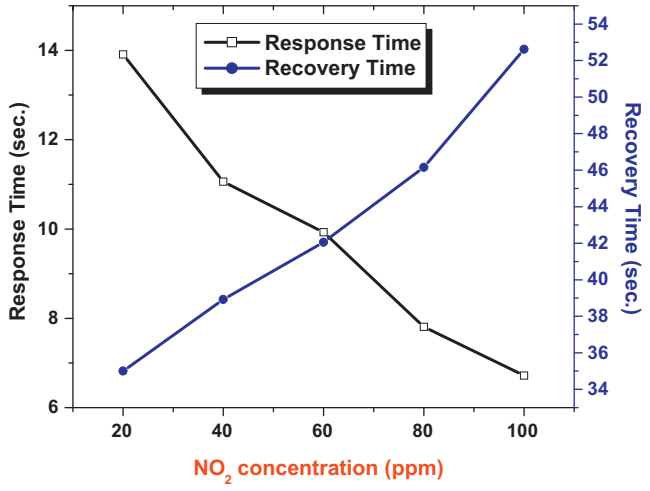

Fig. 13. Variation of response and recovery time of ZnO sensor with NO_2 concentration (20–100 ppm).

The response time is defined as the time taken by the sensor to attain 90% of the maximum increase in resistance on exposure of target gas and recovery time as the time to get back 90% of the maximum resistance when exposed to clean air. The variation of response and recovery times with different concentration of NO_2 at temperature 200 °C is represented in Fig. 13. It is observed that the response time and recovery time varies inversely with respect to concentration of NO_2. The response time decreases from 13.91 s to 6.72 s while recovery time increases from 35 to 52.62 s with increasing NO_2 concentration from 20 to 100 ppm. The decrease in response time may be due to large availability of vacant sites on thin films for gas adsorption as evident from SEM image; and increasing recovery time may be due to gas reaction species which left behind after gas interaction resulting in decrease in desorption rate.

3.4.7. Stability of ZnO Sensor

In order to check the stability of ZnO sensor, the change in resistance is studied at 200 °C temperature upon exposure of fixed concentration (100 ppm) of NO_2 for 45 days at an interval of 5 days, after the first measurement and the results of gas response are shown in Fig. 14. Initially, ZnO sensor showed relatively high response, however it dropped from 37.2% to 29% and stable response obtained after 25 days (78% stability). This is because in the initial stage ZnO sensor may undergo interface modification during operation and then reaches to steady state indicating the stability of the ZnO sensor operating at 200 °C temperature.

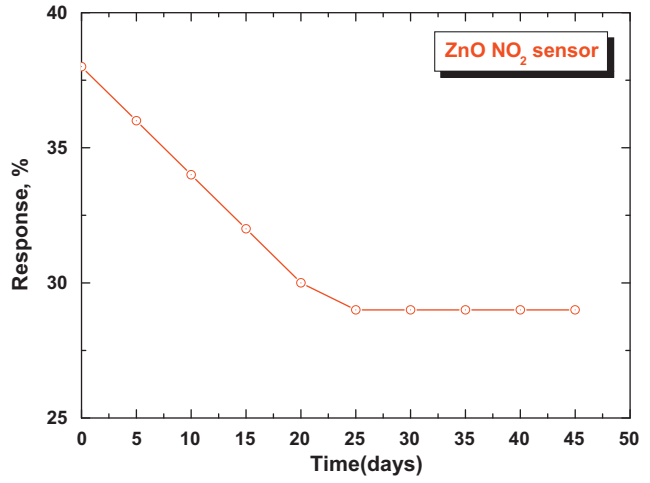

Fig. 14. The sensing stability studies for ZnO thin film at an operating temperature of 200 °C.

4. Conclusions

Nanostructured zinc oxide films were prepared by low-cost sol gel spin coating technique exhibit hexagonal wurtzite structure. Microstructural analysis revealed uniform, smooth surface morphology with an average size of ~50 nm.

The gas sensing studies were carried out at low concentrations of NO_2, i.e. from 10 to 100 ppm. The selectivity study showed that films were most selective to NO_2 against H_2S, NH_3. The maximum gas response of 37.2% was achieved with 78% stability for ZnO films upon exposure of 100 ppm NO_2 at operating temperature 200 °C.

The stability study indicates that ZnO is potential material to be used as an effective NO_2 sensor.

Acknowledgments

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