ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

# Preparation, characterization of 1D ZnO nanorods and their gas sensing properties

Supriya B. Jagadale[a,b], Vithoba L. Patil[b], Sharadrao A. Vanalakar[c], Pramod S. Patil[b,*], Harish P. Deshmukh[a,*]

[a] Department of Physics, Bharati Vidyapeeth University, Yashwantrao Mohite College, Pune 411038, Maharashtra, India
[b] Thin Films Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, Maharashtra, India
[c] Department of Physics, Karmaveer Hire Arts, Commerce Science and Education College, Gargoti 416009, India

ARTICLE INFO

*Keywords:*
1D ZnO nanorods
Hydrothermal method
Gas sensor

ABSTRACT

The 1D ZnO nanorods (NR's) were grown with Zinc (Zn) ion precursor concentration variation on seed layer glass substrate by the low temperature hydrothermal method and utilized for nitrogen dioxide ($NO_2$) gas sensing application. Zn ion precursor concentration varied as 0.02, 0.03, 0.04, 0.05 and 0.06 M and thin films were characterized for structural, morphological, optical, electrical, surface defect study and gas sensing properties. All the film showed dominant orientation along the (002) direction, the intensity of the peak vary with the length of the nanorods. SEM cross images confirmed that nanorods had vertical alignment perpendicular to the plane of the substrate surface. The PL intensity of oxygen vacancy related defects for prepared samples was found to be linearly proportional to gas sensing phenomena. This result in good agreement with the theoretical postulation that, oxygen vacancies plays the important role for adsorption sites to $NO_2$ molecule. The gas sensing performance was studied as a function of operating temperature, Zn ion precursor concentration variation, and gas concentration. The maximum gas response is 113.32–100 ppm $NO_2$ gas at 150 °C for 0.05 M sample out of all prepared samples. Additionally, ZnO thin film sensor has potential to detect $NO_2$ as low as 5 ppm.

## 1. Introduction

In the 21st century, environmental pollution is the major problem, to overcome this problem some of the researchers have been developing semiconductor devices including a gas sensor, air quality control etc. There are a number of toxic gasses present which are responsible for pollution, but out of these gases, $NO_2$ plays major role in the atmospheric reaction that produces ground-level ozone. According to the recent survey, human exposure to a low concentration of $NO_2$ (about 3 ppm) can cause irritation of the throat and respiratory system, while increasing concentration can cause more severe respiratory diseases, lung function, and even death [1]. Therefore, a number of gas monitoring devices has been developed to detect $NO_2$ gas, including metal oxide semiconductors, conducting polymer composite, and metal oxide polymer composite. Out of which metal oxide semiconductor gas sensors have attracted significant attention due to their long time stability, compact size and their simple sensing principle [2,3] which assist their miniaturization and integration into electronic circuits. Gas sensors based on metal oxide functions according to the response of their electrical conductivity with exposure to gasses. Numerous physically and chemically stable metal oxides (such as ZnO, $TiO_2$, $SnO_2$, $WO_3$, $Fe_2O_3$, etc.) have been developed to utilize for gas sensing application, solar cell, water splitting etc. Among them zinc oxide (ZnO), with low cost environmentally benign components, have been widely studied because of its good physical and chemical properties like long time stability, resistant to corrosion, thermal conductivity etc. [4–8].

Recently, amongst a variety of possible ZnO nanostructures, one-dimensional (1D) nanorods have been attracted researchers attention for its use in gas sensing application, it has proven to be highly sensing material because of large surface to volume ratio, slower electrons destroy rate and a variety of surface morphologies. A number of physical synthesis methods for producing these 1D ZnO nanorods, such as chemical vapor deposition, thermal evaporation, microwave irradiation and magnetron sputtering have been investigated in the last few years. While it has the advantage of producing high purity crystalline products in a single step, although these gas phase methods have a need of generally high temperature, costly equipment, tedious methodology and inflexible experimental conditions, which may limit to their potential applications. Recently, solution based approaches have been extensively deployed owing to their unique advantage of elastic

* Corresponding authors.
*E-mail addresses:* psp_phy@unishivaji.ac.in (P.S. Patil), hp_deshmukh52@yahoo.com (H.P. Deshmukh).

https://doi.org/10.1016/j.ceramint.2017.11.116
Received 4 August 2017; Received in revised form 15 November 2017; Accepted 16 November 2017

conditions cost and simple equipment [9–12]. Out of them, the hydrothermal method is one of the most promising and eco-friendly methods to synthesize oriented and aligned nanorods at low temperature [13,14]. ZnO is one of the well-established gas sensing material, which has been extensively studied for the detection of inflammable and toxic gasses. $NO_2$ gas is one of the main/primary air pollutants with serious adverse effect on health and environment. It is of great importance and interest to develop gas sensing materials with high response [15]. To study $NO_2$ gas sensing properties there are various synthesis routes for ZnO nanostructures have been reported by different researchers groups. Quantum-sized ZnO nanoparticles were synthesized using a mild sol-gel process by Bai et al. [16], the reported $NO_2$ gas response 280–40 ppm at 290 °C operating temperature. Nanopetal structured ZnO was prepared by using chemical precipitation method reported by Sonker et al. [17], the fabricated nanopetals ZnO sensor gives high response 119 to $NO_2$ for 20 ppm concentration at room temperature. Direct growth of hierarchical ZnO nanostructure on chip patterned electrodes using evaporation method gives $NO_2$ gas response 32 for 20 ppm was reported by Pan et al. [18]. Also Chen et al. [19] have used a microemulsion based solvothermal method to synthesize hierarchical flower-like and 1D tube like ZnO. The gas response was measured to different gasses they observed the maximum gas response for tube like ZnO gas sensor was more than 350 at 190 °C to $NO_2$. Using Successive Ionic Layer Adsorption and Reaction (SILAR) method Shaikh et al. [20] have produced spherical nanogranular ZnO gas sensor and reported gas response 31.10–100 ppm $NO_2$ gas at 175 °C operating temperature. Wang et al. [21] used the mechanoelectrospining-assisted continuous hydrothermal route for the fabrication of ZnO nanorods based gas sensor it shows the response to 1–5 ppm of $NO_2$ gas between 200 and 225 °C operating temperature. Jiao et al. [22] have grown ZnO nanorods on-chip with a two-step low-temperature (85 °C) hydrothermal method. Tests with $NO_2$, hydrogen, ethanol, and ammonia showed that the gas sensor had a very high sensitivity of 6.1, to $NO_2$ for 10 ppm concentration at 450 °C.

In present study, we report the ZnO nanorods thin film based $NO_2$ gas sensing properties. ZnO NR's were prepared with the zinc precursor concentration variation using easy, inexpensive, low temperature and simple hydrothermal method. In this report ammonia was used as hydroxide ion agent because with ammonia we can vary pH of solution over a wide range, (which is otherwise restricted in case of Hexamethylenetetramine (HMTA)) and therefore we can modify the growth rate of ZnO NR's [23,24]. Song et al. have studied in the case of ammonia based growth of ZnO NR's arrays with the effect of pH variation and it was found that the ZnO NR's with high aspect ratio can be obtained at the pH of nearly 11 [25]. While the ZnO nanorods give discrete advantages including high surface to volume ratio and chemical stability [26]. In the present study, we depict the hydrothermally grown 1D ZnO NR's at different Zn ion precursor concentration used as $NO_2$ gas sensor. The structural, surface morphological, electrical and optical properties of the prepared ZnO NR's were studied using X-ray diffraction (XRD), Scanning electron microscopy (SEM), two probe resistivity method and the room temperature photoluminescence (PL) spectroscopy. The prepared ZnO NR's gas sensor shows a highly sensitive reversible and fast response to $NO_2$ at relatively low gas concentration and low operating temperature.

## 2. Experimental procedure

Zinc Nitrate ($Zn(NO_3)\cdot 6H_2O$) and ammonia solution with AR grade were purchased from Thomas Baker (99.5% pure) and used without further purification. The glass micro slides were used as a substrate which was cleaned with laboratory detergent and heated in 100 ml double distilled water. Chromic acid treatment for 15 min followed by rinsing with double distilled water and finally treated with ultrasonic waves for 15 min. These cleaned substrates were used to make seed layer. ZnO seed layer is needed to initialize the uniform growth of oriented nanorods. The seed solution was prepared in absolute ethanol with 0.06 M zinc acetate and 0.06 M diethanolamine. The cleaned glass substrates were dip coated for the 20 s in a seed solution, and then dried 24 h at room temperature. The dried films were annealed at 400 °C for 10 min in air to yield a seed layer of ZnO. The growth of nanorods based on dip coated seed layered ZnO thin films were performed using simple and cost effective hydrothermal method. In the experimental procedure seeded substrates were placed vertically in 50 ml aqueous solution of zinc nitrate with concentration ranging from 0.02 to 0.06 M and ammonia solution was added to adjust pH of solution ~ 11. The solution with vertically immersed seed substrate was placed in the autoclave at controlled growth temperature 80 °C. Furthermore substrates were removed after 8 h and were rinsed with deionized water and dried at room temperature. The ZnO nanorod (NR's) synthesized at different Zn ion precursor concentrations such as 0.02, 0.03, 0.04, 0.05 and 0.06 denoted as $Z_1$, $Z_2$, $Z_3$, $Z_4$, and $Z_5$, respectively.

As per literature there are different methods like microemulsion [27], oxygen assisted thermal evaporation [28], vapor phase transport method [29] etc. has been used for synthesis of ZnO nanorods for gas sensing application. Comparatively in our case simple and cost effective, low temperature, ammonia solution based route was employed to synthesize well-aligned ZnO nanorods and it showed better gas response.

## 3. Characterization of ZnO thin films

The structural and morphological characterizations were studied by Bruker D2 phase diffractometer with CuKα-1 radiations of wavelength 1.5406 Å and Scanning Electron Microscope (Model JEOL-JSM-6360, Japan) respectively. The optical characterizations were carried out by UV–vis spectrophotometer (UV–vis 1800 spectrophotometer, Shimadzu, Japan) and the room temperature photoluminescence study of films was carried out by using a JASCO F. P. -750 Model (Japan) spectrophotometer with excitation energy of 325 nm using 1000 W Xenon lamp. The electrical resistivity measurements were taken as a function of temperature in the range 328–528 K by two probe method. A gas sensor system was used to measure the gas sensitivity of ZnO NR's thin film which consists of an air tight stainless steel test chamber. Gas sensing performance was evaluated by measuring changes in resistivity. 1 × 2 cm large dimension film was placed at sample holder, which was inserted into the test chamber which is already reported in our earlier paper [8]. The thin film area was kept constant for all samples during gas sensing measurement. Change in electrical resistance of thin films was measured after injection of a known amount of gas inside the test chamber. Change in electrical resistance after and before injection of target gas was measured. The gas response is calculated using formula in Eq. (1)

$$S = R_g/R_a \tag{1}$$

where, $R_g$ is the resistance of sensor material in presence of target gas and $R_a$ is the resistance of Sensor material in presence of atmospheric air.

## 4. Structural properties

Fig. 1 shows the X-ray diffraction (XRD) spectra of ZnO NR's thin films deposited on glass substrate at different Zinc ion precursor concentrations. The XRD result shows highly dominant orientation along the c-axis direction (i.e. perpendicular to the plane of the substrate) of the hexagonal wurtzite structured ZnO NR's well matched with powder diffraction file number 00-036-1451 which is reported earlier [30]. It is observed that from Fig. 1 all ZnO NR's samples shows (002) and less intense (004) diffraction peak at 34.4° and 72.8° respectively, indicates highly crystalline nature of the nanorod arrays, grown along the (00l) direction. ZnO NR's orientation is determined by the nucleation and growth of the first few layers of zinc and oxygen atoms, in our case c-