Chemical synthesis of zinc oxide nanorods for enhanced hydrogen gas sensing*

Musarrat Jabeen[a)†], Muhammad Azhar Iqbal[a)], R Vasant Kumar[b)], Mansoor Ahmed[a)], and Muhammad Tayyeb Javed[c)]

[a)] *Department of Physics, University of the Punjab Lahore, Pakistan*
[b)] *Department of Material Science and Metallurgy, University of Cambridge, England*
[c)] *Department of Chemical Engineering, Pakistan Institute of Engineering and Applied Sciences, Nilore, Islamabad, Pakistan*

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Zinc oxide (ZnO) nanorods are prepared using equimolar solution of zinc nitrate ($(Zn(NO_3)_2$) and hexamethylenetetramine ($C_6H_{12}N_4$) by the hydrothermal technique at 80 °C for 12 h. Epitaxial growth is explored by X-ray diffraction (XRD) patterns, revealing that the ZnO nanorods have a hexagonal (wurtzite) structure. Absorption spectra of ZnO are measured by UV–visible spectrometer. The surface morphology is investigated by field emission scanning electron microscopy (FESEM). The synthesized ZnO nanorods are used for detecting the 150 °C hydrogen gas with a concentration over 1000 ppm. The obtained results show a reversible response. The influence of operating temperature on hydrogen gas detecting characteristic of ZnO nanorods is also investigated.

Keywords: zinc oxide, hydrothermal synthesis, nanorods, hydrogen gas sensor

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1. Introduction

Semiconductor metal oxide has received great attention due to its low cost, small size, and exceptional properties compared with nano structures based on silicon.[1–6] Zinc oxide (ZnO) is an n-type semiconductor that is thermally stable and has structurally and chemically interesting applications. Researchers are greatly interested in ZnO compound because of its unique and outstanding properties.[7–9] It is an appealing semiconductor for scientists, which belongs to the II-VI family and has numerous vital applications due to its direct bandgap (3.37 eV) and high value of exciting binding energy about 60 meV.[10] The optical and electronic properties of ZnO are exceptional; with these properties, ZnO has great possibility to be greatly used in high technology applications in optoelectronics, nano electronics, UV sensors, solar cells, devices of surface acoustic waves, light emitting diodes, piezoelectric transducers, and detectors sensitive to combustible and toxic gases.[11,12]

The interesting properties in excellent cohesive energy value 1.89 eV, high value of optical gain (300 cm^{-1}), and radiation hardness make ZnO an auspicious semiconducting material for sensor and optoelectronic applications. One-dimensional nanostructure of ZnO has been synthesized by a variety of techniques such as electrochemical deposition (ECD), metal organic chemical vapor deposition (MOCVD),[13] and sol–gel hydrothermal methods.[14] Among these techniques, the sol–gel hydrothermal method is considered to be a cost-effective, simple, and low temperature growth technique to synthesize high quality nanorods. In sol–gel hydrothermal technique, there are a number of parameters that should be taken into account in order to attain good-quality one-dimensional ZnO nanorods, for example, precursor solution concentration, annealing temperature, deposition temperature, and time. The hydrothermal technique is an environmentally friendly process to synthesize ZnO nanorods randomly and along the *c* axis.[15] Zinc nitrate ($(Zn(NO_3)_2$) and hexamethylenetetramine ($C_6H_{12}N_4$) precursors with equimolar concentrations have been used to synthesize ZnO nanorods at a temperature less than 100 °C.[16] $C_6H_{12}N_{14}$ acts as a nonpolar chelating agent for most preferably being attached to nonpolar facets of ZnO and allowing random growth in the different directions.[17]

Hydrogen (H_2) is an odorless, invisible, and flammable gas, so it is essential to detect hydrogen effluent.[18] Moreover, it is necessary to design a unique sensor for H_2 to be used in cars which require its storage and consumption in fuel cells.[19] Hydrogen gas sensors are subjected to many restrictions such as high cost and power consumption, instability, slow response and recovery time, etc.[20] It is necessary to design a H_2 sensor that possesses superior gas detecting properties like fast recovery and response time, high sensitivity, and ability to work at sufficiently low temperature.[21] To design and fabricate an effective hydrogen sensor, many approaches have been adopted. Normally, available H_2 sensors are based on metal oxide semiconductors because they have better de-

*Projected supported by the HEC of Pakistan for international initiative research support programme (IRSIP).
†Corresponding author. E-mail: musarrat95@hotmail.com
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tecting characteristics. The present paper presents the creation of a hydrogen sensor using hexagonal ZnO nanorods that have high response and selectivity for H_2 in ambient air conditions.

2. Experimental details

ZnO nanorods have been synthesized by a hydrothermal method that is simple and bio-safe. In the growth process of ZnO nanorods, the reagents HMTA ($C_6H_{12}N_4$) hexamethylenetetramine and zinc nitrate hexahydrate dissolved in de-ionized (DI) water were used. An equimolar solution from the precursors was prepared. A 0.02 M of $C_6H_{12}N_4$ and $Zn(NO_3)_2{\cdot}6H_2O$ was mixed in deionized water (18 MΩ). The pH of the equimolar solution was measured with a portable pH meter (291A Orion). The beaker was placed in an electric oven with a temperature of 80 °C for 12 h.[22] When the reaction was completed, the beaker was cooled down at room temperature. Finally, the ZnO precipitates were separated from the reaction mixture by centrifuging for 20 min with rotation speed of 23000 rpm , and washed several times with deionized water (18 MΩ). Impurities were adsorbed on ZnO surface in the form of ions that may be organic or inorganic. Finally, white garnish powder was obtained that dried in an electric oven at a temperature of 70 °C.[23]

The interdigitated electrodes of platinum were prepared on the surface of an aluminum oxidized substrate by sputtering in the sputter coater (EMITECH K 575). About 25-mg ZnO nanorods were dispersed in ethanol and ultrasonicated for a few minutes. The suspensions of ethanol and ZnO nanorods were then dropped onto the Pt electrodes (interdigitated 2–3 μm thickness). The distance between two Pt fingers was maintained 30 μm. A quartz tube furnace was used for hydrogen sensing test. As a reference gas, the synthetic dry air was used, and with a mass flow controller, the gas flow was controlled. The resistance of the sensor was measured by a current that was generated by applying a voltage of 0.5 V to the electrodes using Agilent 34970A computerized multimeter. Identification of the crystal structure was explored by XRD (X-ray diffraction, Bruker D8) using Cu K_α ($k = 0.15418$ nm) radiation.

We scanned the sample from 0–80 °C at a rate of 0.02°/s with an accelerating voltage 40 kV and current 40 mA. General morphologies of the surfaces of ZnO nanorods were investigated with field emission scanning electron microscope (JEOL-6340F, FESEM). The optical properties were explored at room temperature in the wavelength range of 200 nm–900 nm with a UV–visible spectrophotometer.

2.1. Synthesis mechanism

HMTA and zinc nitrate decompose into Zn^{2+} and OH^- ions due to the rise in temperature. The ion concentration increases and ZnO nuclei are produced gradually. Although several processes can affect the growth of nanorods, the Oswald's ripening is an important one. The geminate crystal of ZnO nuclei in the aqueous solution forms gradually under a low concentration of precursor. Hexagonal crystal with central interface formed in the presence of HMTA. In the aqueous solution, the growth of ZnO depends on subsequent synthesis under kinetic growth and heterogeneous nucleation parameters. HMTA produces hydroxide (OH^-) and NH_3 molecules in the solution.[30] Hence, tetra amine zinc (II) $[Zn(NH_3)_4]^{2+}$ and $[Zn(OH)_4]^{2-}$ determine the morphologies of ZnO nanorods that have formed in the complex solution.

The chemical reactions involved in synthesis of ZnO nanorods are

$$Zn^{2+} + 4OH^- \rightarrow [Zn(OH)_4]^{2-}, \quad (1)$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}, \quad (2)$$

$$[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O, \quad (3)$$

$$[Zn(OH)_4]^{2-} \rightarrow ZnO + H_2O + 2OH^-. \quad (4)$$

3. Results and discussion

3.1. ZnO nanorod structure

Figure 1 illustrates the X-ray diffraction patterns, indicating that the ZnO presents a hexagonal wurtzite structure. Lattice parameters are $a = b = 0.3288$ nm and $c = 5.2054$ nm, which are in agreement with those in the standard card (space group: $P63mc$ (1996) and all data in accordance with JCPDS card number 01-089-0510 for ZnO). The calculated density of the nanorods is 5.68 g/cm^3. The peak with 100% intensity appears at $2\theta = 36.26°$ with indices $(khl) = (101)$, the second peak with 57% intensity appears at $2\theta = 31.8°$ with indices $(khl) = (100)$, and the third peak (main peak) with intensity 41.4% appears at $2\theta = 34.4°$ having indices $(khl) = (002)$. The other peaks lie in different planes due to back scattered radiations. As nanorods are randomly oriented, they do not have any specific orientation, which is confirmed from indices. No impurity peaks are detected.[24]

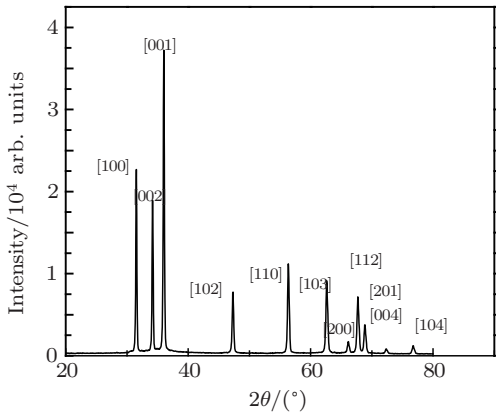


Fig. 1. XRD patterns of hexagonal ZnO nanorods.

The surface morphologies of as-grown ZnO nanorods are explored using FESEM (JEOL-6340F), format JEOL/EO and

version 0.1. The synthesized ZnO nanorods have a smooth surface. Figure 2 shows the FESEM images of high-density ZnO nanorods, and a special image of hexagonal ZnO nanorods. The diameters of nanorods are in the range of 100–130 nm and their lengths are more than 1 μm.

In Fig. 2, all the SEM images are recorded from the secondary electron images (SEI) under the conditions of accelerating voltage 5 kV in a standard mode, working distance (WD) ranging from 9 mm to 10 mm, and magnifications of 450, 850, 1800, and 1300, respectively.

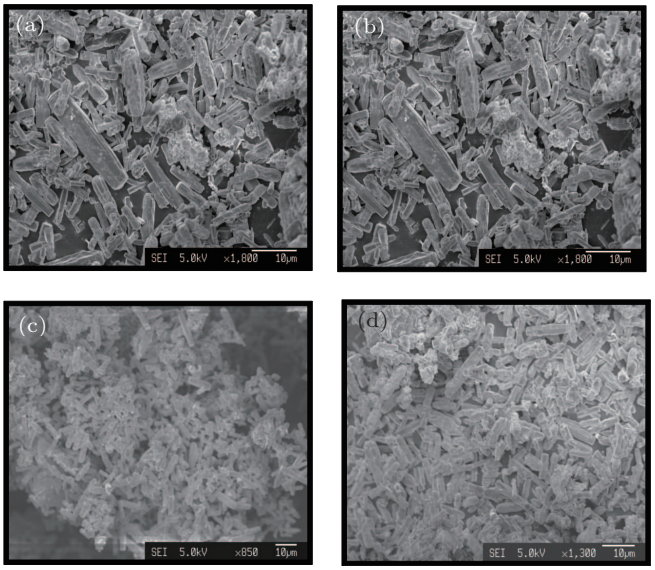


Fig. 2. Low ((a), (b)) and high ((c), (d)) magnification SEM images of randomly dispersed hexagonal ZnO nanorods.

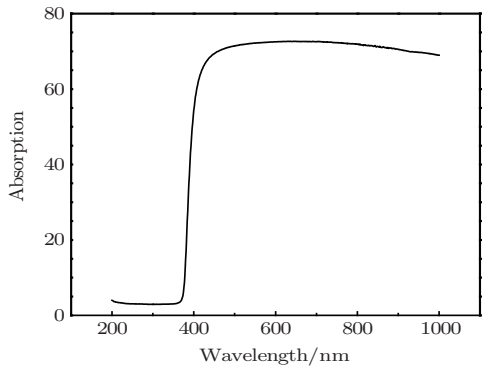


Fig. 3. Ultraviolet visible spectrum of ZnO nanorods recorded by Lambda 750.

ZnO is very important in the optoelectronics because of its wide band gap similar to UV-emission in photonic applications. Figure 3 shows the ultraviolet visible spectrum of ZnO nanorods. The absorption spectrum shows that a sharp increase at about 380 nm in the exciton region appears, which is corresponding to $E = 3.30$ eV.[25] Srikant and Clarke[26] adopted different techniques to explore the band gap of ZnO single crystal and reported that ZnO has a 3.3-eV band gap at room temperature. The lower values correspond to the existence of valance band donor transitions. Due to different defects, the absorption spectrum is normally quite broad.[27–29] The sharp increase of the absorption spectrum means that the ZnO nanorods have good crystalline quality and purity.

3.2. Gas sensing results

The gas sensor fabricated by hexagonal ZnO nanorods for sensing hydrogen gas in ambient air is placed in a test chamber. Its resistance varies linearly with the concentration of hydrogen gas. Normal resistance of ZnO decreases with concentration increasing to 5000 ppm. Figure 4(a) shows the hydrogen gas at 150 °C with concentration 1000 ppm, detected by the hexagonal ZnO nanorods. When hydrogen gas is injected with a concentration of 1000 ppm, the sensor in the ambient air shows the fast and reversible response. The resistance decays in two stages. During the first 150 s the sensor resistance decreases by a factor of 2 followed by a slower decay in more than 350 s of gas exposure (25%). After removal of hydrogen gas the sensor specifies a two-step recovery process. It is observed that resistance of the sensor 100% increases in 280 s after removal of hydrogen gas that is followed by slowly decreasing towards its initial value. The oxygen gas adsorbed on the surface of ZnO nanorods forms a depletion layer which affects the resistance of nanorods. Li *et al.*[31] studied the oxygen adsorption/desorption in ZnO nanorods under air, vacuum, and other different conditions of illumination separately. When hydrogen passes on the sensor surface the interaction between hydrogen and oxygen ions takes place, resulting in the formation of H_2O molecules. Consequently, depletion width decreases on the surface. As a result, the region of nanorod conduction near the surface is enhanced. On the surfaces of nanorods, both chemisorbed and physisorbed oxygen atoms are present. Therefore, the resistance decreases rapidly during the first phase of hydrogen exposure that is related to physisorbed oxygen removal. While oxygen atoms removed from the surface through a chemisorbed process. After the complete removal of surface charge, the further conduction variation requires more changes in the lattice of ZnO. This kind of change occurs through a slower process like the diffusion of oxygen vacancies and the diffusion of interstitial donor atoms of H_2. The temperature has an important influence on the sensor resistance after the removal of adsorbed oxygen and the hydrogen exposure on the ZnO nanorod surfaces. Figure 4(a) shows that with the increase of temperature, the resistance of the sensor drops quickly and attains 10 MΩ in the presence of H_2 gas. The resistance starts to increase with the removal of H_2 gas, and after 800 it almost behaves linearly.

Figure 4(b) demonstrates the response of the sensor under ambient conditions. The sensitivity of ZnO nanorods versus operating temperatures from 50–150 °C is illustrated. The

ratio of resistance of the sensor in air to the resistance in the presence of H_2 is defined as sensitivity (S).

The sensitivity is enhanced with the operating temperature increasing and reaches its highest limit at 150 °C and decreases as temperature further increases. The sensitivity of the sensor reaches the highest value 2.4 at 150 °C and then decreases with temperature further increasing.

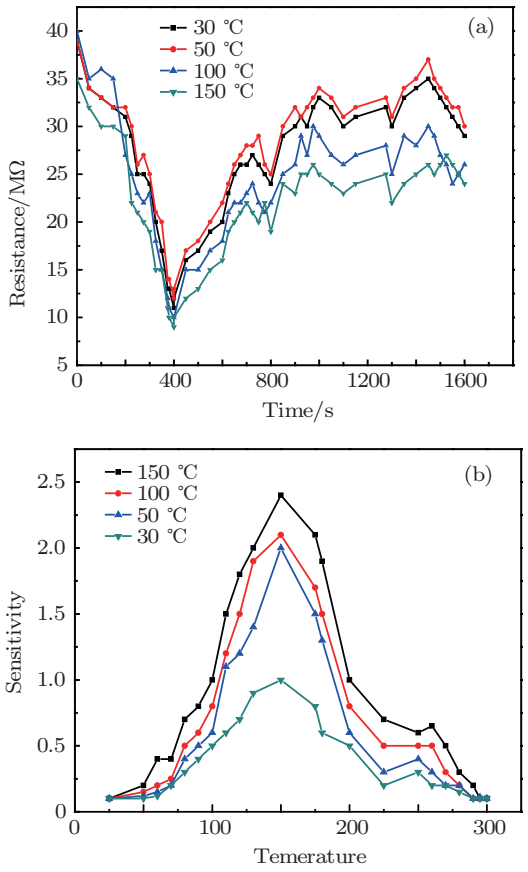


Fig. 4. (color online) (a) Resistance of ZnO nanorod gas sensor versus time at 150 °C, and (b) resistivity of hexagonal ZnO nanorods against temperature for different sensitivities.

4. Conclusions

Random oriented hexagonal ZnO nanorods are successfully synthesized by a simple chemical technique at low temperature. It is demonstrated by FESEM and XRD analysis, indicating that nanorods have a wurtzite structure and good crystal quality. UV-vis spectrometer results show optical parameters measured at room temperature. A suitable synthesis mechanism is proposed to fabricate ZnO hexagonal nanorods. The H_2 gas sensor fabricated by ZnO nanorods shows a good selectivity and reversible response under the ambient condition. The gas sensor has a sensitivity of 2.4 at a temperature of 150 °C. The resistance of the sensor decreases rapidly with H_2 gas in, and attains an original value with H_2 gas out, so it has a reversible cycle. The influence of working temperature on gas detection property is also investigated.

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