

SYNTHESIS OF ZnO NANORODS BY HYDROTHERMAL METHOD FOR GAS SENSOR APPLICATIONS

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Abstract- ZnO nanorods with different sizes and shapes have been successfully synthesized via a simple hydrothermal route, using zinc acetate and Cetyltriammonium bromide (CTAB) as the reactants. The thick films of as prepared ZnO were prepared by screen-printing technique in desired pattern. The films are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The gas sensing properties of the materials have been investigated for various interfering gases such as CO_2, CO, Ethanol, NH_3 and H_2S etc at operating temperature from 30^o (room temperature) to 300^oC. The results indicate that the ZnO nanorod thick films showed much better sensitivity and stability than the conventional materials to H_2S gas at 30^oC. The nanoshaped pillar can improve the sensitivity and selectivity of the sensors. ZnO nanorods are excellent potential candidates for gas sensors.

Index terms: Hydrothermal, CTAB, ZnO nanorods, H_2S gas sensor, gas response.

I. INTRODUCTION

The hydrothermal technique is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in the processing of nanostructural materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc. The hydrothermal technique not only helps in processing monodispersed and highly homogeneous nanoparticles, but also acts as one of the most attractive techniques for processing nano-hybrid and nano composite materials. The term 'hydrothermal' is purely of geological origin. It was first used by the British geologist, Sir Roderick Murchison (1792-1871) to describe the action of water at elevated temperature and pressure, in bringing about changes in the earth's crust leading to the formation of various rocks and minerals. Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizes under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Definition for the word hydrothermal has undergone several changes from the original Greek meaning of the words 'hydros' meaning water and 'thermos' meaning heat. Recently, Byrappa and Yoshimura define hydrothermal as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system [1]. However, there is still some confusion with regard to the very usage of the term hydrothermal. For example, chemists prefer to use a term, viz. solvothermal, meaning any chemical reaction in the presence of a non-aqueous solvent or solvent in super- critical or near supercritical conditions. Similarly there are several other terms like glycothermal, alcothermal, ammonothermal, and so on. Further, the chemists working in the supercritical region dealing with the materials synthesis, extraction, degradation, treatment, alteration, phase equilibrium study, etc., prefer to use the term supercritical fluid technology. However, if we look into the history of hydrothermal research, the supercritical fluids were used to synthesize a variety of crystals and mineral species in the late 19th century and the early 20^{th} century itself [1]. So, a majority of researchers now firmly believe that supercritical fluid technology is nothing but an extension of the hydrothermal technique.

Semiconductor metal oxides as gas sensing materials have been extensively studied for a long time due to their advantageous features, such as good sensitivity to the ambient conditions and simplicity in fabrication [2–4]. Nevertheless, there are still some critical limitations to be overcome for the commercial sensors based on particulate or thin-film semiconductor metal oxides, such as limited maximum sensitivity, high working temperatures and lack of long-term stability. Recently, several groups reported the sensors based on semiconductor nanowires and nanoribbons. The results indicate that one-dimensional (1-D) nanomaterials are promising for highly sensitive chemical sensors. For example, individual single-crystalline tin dioxide nanoribbon can work at room temperature to monitor NO_2 [5]. In_2O_3 nanowire transistors can also exhibit very high sensitivity to NO_2 and NH_3 at room temperature [6]. Kolmakov et al. reported CO and O_2sensors based on SnO_2 nanowires [7]. The extremely high surface-to-volume ratios associated with 1-D nanostructures may be the reason why the sensors are much more sensitive than those from conventional materials. The microdevices based on the 1-D nanostructures have potential to overcome the limitations for this kind of sensors. Zinc oxide is also one of the earliest discovered and most widely applied oxide gas sensing materials due to its high mobility of conduction electrons, good chemical and thermal stability under operating conditions [1, 7]. But up to now, these studies were focused on the gas sensing properties of zero-dimensional ZnO; there is still no detailed report about the gas sensing properties of 1-D-ZnO nanometerials. Recently, large-scale and low-cost syntheses of ZnO nanomaterials with 1-D structure, such as nanowires and nanorods, have been achieved using a hydrothermal method [8, 9]. This brings a good chance to study its gas sensing properties. In this article, we report hydrothermal preparation of zinc oxide nanorods. The gas sensors from the 1-D nanomaterial show very high sensitivity and stability, compared to those from conventional materials. The results indicate that ZnO nanorods are potential candidates for developing stable and highly sensitive sensors.

A surfactant (CTAB) was used as the modifying and controlling agent to improve the morphology and size of products obtained in aqueous solution. Zhai et al. [10] prepared ZnO nano and micromaterials under solvothermal process using CTAB as a surfactant. Zhang et al. [11] synthesized the ZnO nanowires using a reverse microemulsion and hydrothermal methods. Recently, the gas sensing properties of 1D ZnO nanostructures to ethanol [12–15], hydrogen [16],

methanol and xylene [17] have been reported. This paper aims at preparing sensing material of 1D ZnO nanostructures using the CTAB-assisted hydrothermal process, and testing their sensing properties for detection of toxic gases. The growth mechanism, morphology, as well as gas sensing properties of the ZnO nanorods were systematically studied in this paper.

II. EXPERIMENTAL METHOD

a. Synthesis

Zinc acetate hydrated Sigma Aldrich, USA) and cetyltrimethylammonium bromide (CTAB) (AR Grade, Sigma Aldrich, USA) were used without further purification. CTAB assisted low temperature hydrothermal process: 0.182 g of CTAB and 4.80 g of sodium hydroxide (NaOH) were dissolved in 50 ml of distilled water to form a transparent solution A under stirring. 5.95 g of zinc acetate was dissolved with 50 ml of distilled water to form a transparent solution B. The 25 ml solution A and was mixed with 25 ml solution B under vigorous stirring to form 50 ml transparent solution C containing $[Zn^{+}]$ = 0.2 M, $[OH^{-}]$ = 1.2 M, [CTAB] = 0.0005 M, and the molar ratio of Zn^{2+}/OH^{-} was 1:6 after continuous stirring for 1 h at room temperature. The solution C was transferred into a 100 ml Teflon lined stainless steel autoclave and sealed tightly. Hydrothermal treatments were carried out at 200 ^{o}C for 20 h. After that, the autoclave was allowed to cool down naturally. After the reaction, the white products were harvested by centrifugation and throughout washing with distilled water, and were finally dried at 60 ^{o}C in air.

b. Characterization

The optical absorbance of the ZnO was measured using spectrophotometer (UV-visible-2450 spectrophotometer, Shimadzu) in the wavelength range 300-700 nm. The crystalline structure of the thin films was confirmed by using X-ray powder diffraction (XRD, BRUKER D8 Advanced) monochromatized and Cu.K_{α}= 0.15418 nm radiation in the range of 20^{o}–80^{o}, and field emission scanning electron microscopy (FESEM, JEOL 2300, Japan). The transmission electron microscopy (TEM, PHILIPS EM 400) and selected-area electron diffractive (SAED) were obtained on a single large rod. The thick films were prepared by screen printing technique and the gas sensing properties were measured by the static gas sensing measurement system explained elsewhere [18, 19].

III. RESULT AND DISCUSSION

a. Optical properties of ZnO rods

Figure 1 shows the variation of absorbance with wavelength of nanocrystalline ZnO nanorods thin film. The band gap energy of the sample calculated from the absorption edges of the spectra and this value is 3.40 eV, which reveals the nanocyrstalline nature.

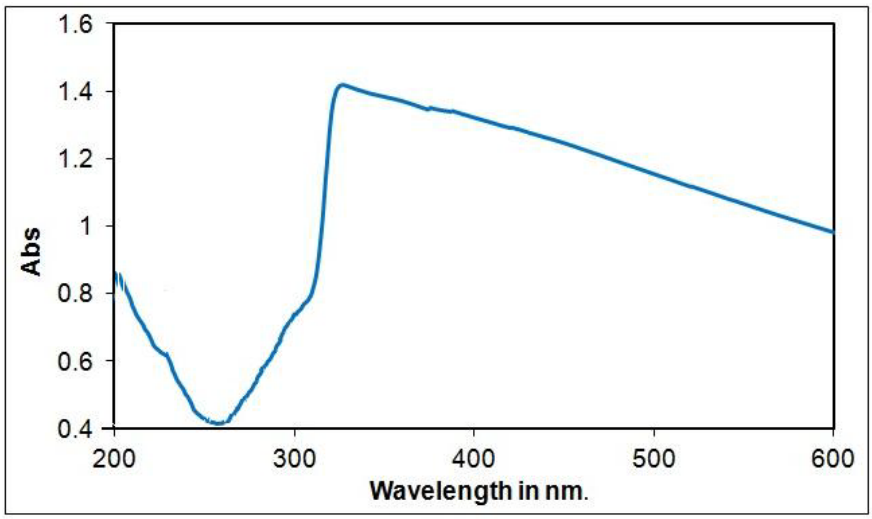


Figure 1. Absorption spectra of ZnO nanorods.

b. Growth of ZnO nanocrystals

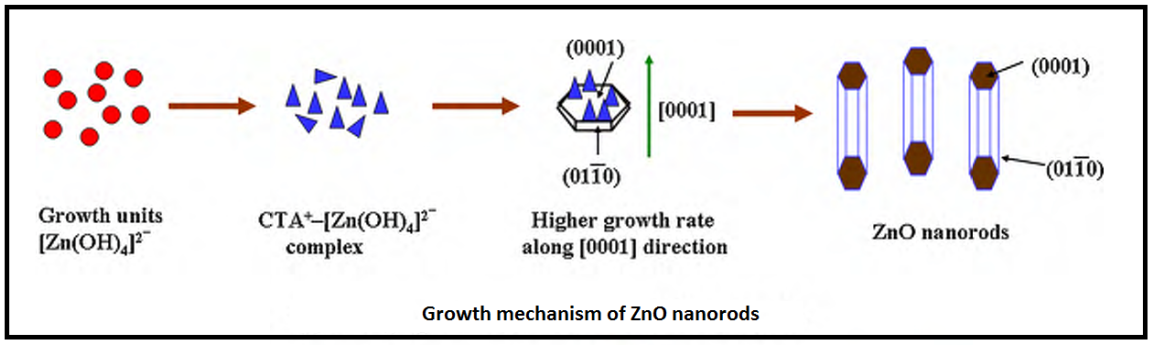


Figure 2. Scheme of growth mechanism of ZnO nanorods.

The scheme of growth mechanism of ZnO nanorods are as shown in Figure 2. Synthesis of ZnO nano- or microstructures from aqueous solution containing $Zn(OH)_4^{2-}$ ions has been reported just

from the recent years. It is generally considered a very simple and novel process. During hydrothermal process following chemical reactions may have been involved.

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (2)$$

$$Zn(OH)_2 + 2OH^{-} \leftrightarrow [Zn(OH)_4]^{2-} \quad (3)$$

$$CTAB \leftrightarrow CTA^{+} + Br^{-} \quad (4)$$

$$[Zn(OH)_4]^{2-} + CTA^{+} \leftrightarrow CTA^{+} - [Zn(OH)_4]^{2-} \quad (5)$$

$$CTA^{+} - [Zn(OH)_4]^{2-} \leftrightarrow ZnO + H_2O + CTA^{+} \quad (6)$$

We can easily understand and obviously observe that at the beginning of this process, a $Zn(OH)_2$ precipitate is obtained (reaction (1)). The possible mechanism for hydrothermal growth of ZnO nanostructures have been suggested by Wang and co-workers [20]. According to these studies, in a neutral or weakly basic solution the starting material of $Zn(OH)_2$ dissolve to smaller extent and the dissolved part exists in the form of single molecule or in a form of complex $[Zn(OH)_4]^{2-}$ (reaction (3)). Such growth units, like a polaron, are easy to incorporate on the positive (0001) and negative (000-1) faces of the crystal due to dipole interaction. So, the polar faces grow slowly and develop larger. The morphology of the crystallites grown under similar conditions should be in elongated (rod-shaped) form, bounded mainly by hexagonal prism [01-10]. This leads to the oriented growth of the $[Zn(OH)_4]^{2-}$ along [0001] direction. In addition to this, the role of surfactant should be taken into consideration. Sun et al [21] has suggested that CTAB not only accelerate the reaction of the growth units, but also leads to their oriented growth. Because of the existence of surfactant, the surface tension of solution is reduced, which decreases the energy needed to form a new phase. Therefore, ZnO crystal could form in a lower super saturation. CTAB is an ionic compound, which ionizes completely in water (reaction (4)). Since $[Zn(OH)_4]^{2-}$ exists in the form of negatively charged tetrahedron, where as CTA^{+} are positively charged with a tetrahedral head and a long hydrophobic tail. At the beginning of CTAB-assisted hydrothermal process, $CTA^{+} - [Zn(OH)_4]^{2-}$ ion pairs forms combination of CTAB and ZnO according to reaction (6). This leads to the oriented growth of the $[Zn(OH)_4]^{2-}$ along [0001] direction resulted in the formation of ZnO nanorods as shown in Figure 2.

c. The structure of the products

The XRD pattern of the as-obtained nanorods is shown in Figure 3. All the diffraction peaks could be indexed to hexagonal wurtzite ZnO (JCPDS Card No. 79-2205, a = 0.3249 nm, c = 0.5205 nm) with high crystallization. No characteristic peaks were observed for other impurities such as Zn or $Zn(OH)_2$.

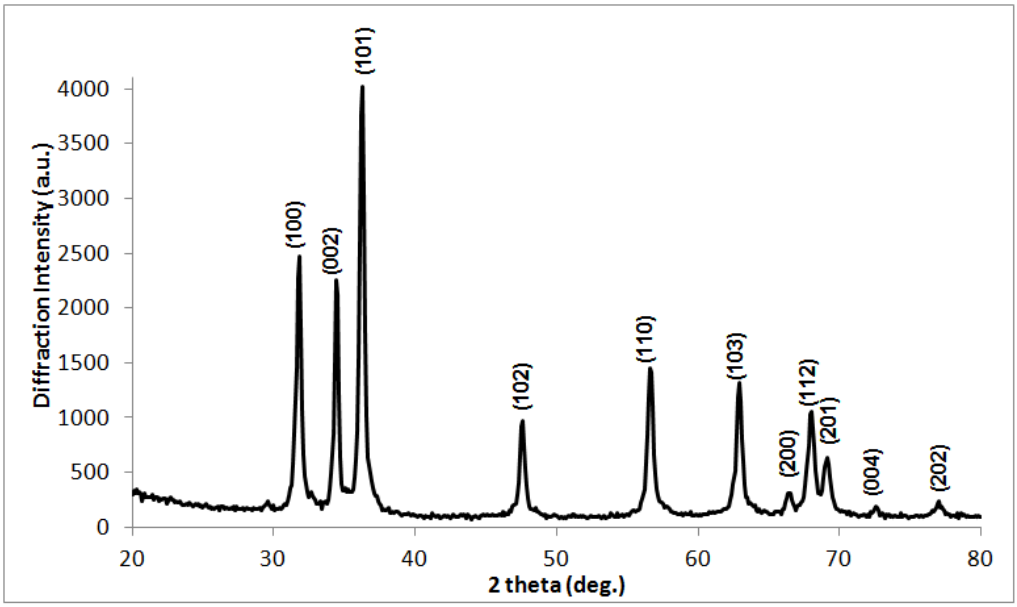
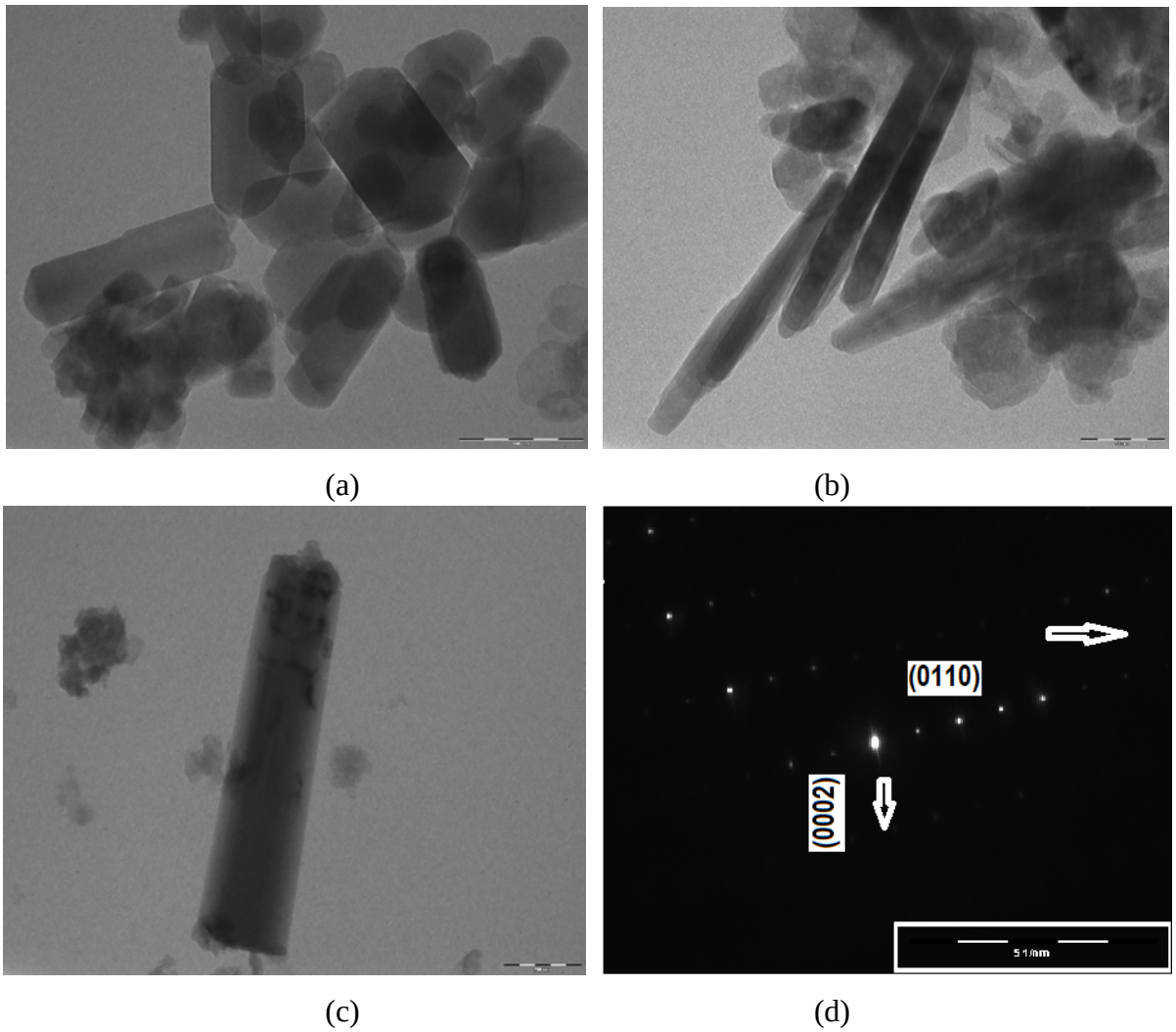


Figure 3. XRD pattern of the ZnO nanorods annealed at 600 ^{o}C.

d. Size distribution and morphology of the products

Typical TEM images of the ZnO nanorods before and after annealing are shown in Figures 4(a) and 4(b, c), respectively. ZnO nanorods with diameters ranging from 20 to 60 nm have been synthesized conveniently with this method. The length of the ZnO nanorods is about 400 nm. The materials maintained their morphology even after annealing at 600 ◦C for 1 h in air. The diameter of the nanorods increased to about 80 nm.



(a) (b)

(c) (d)

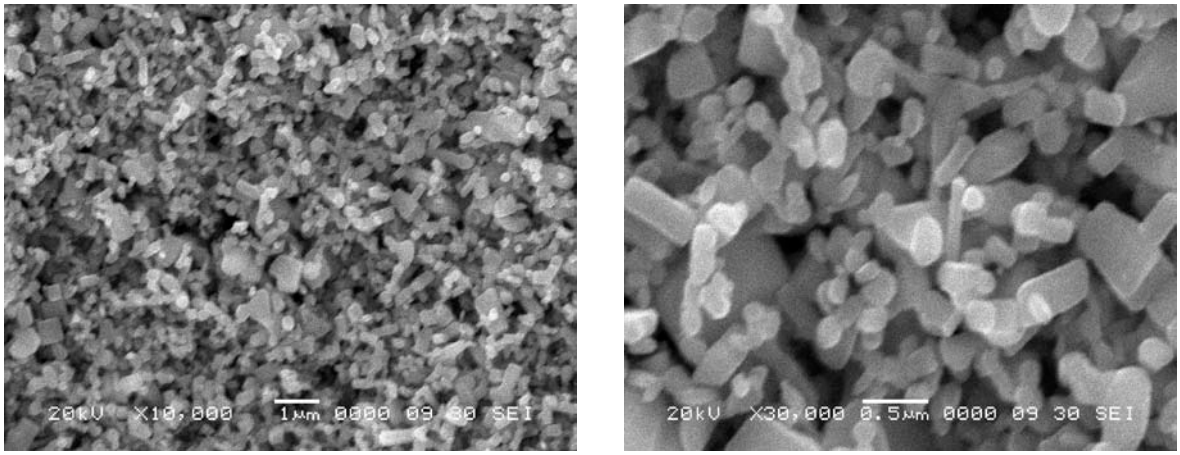
Figure 4. TEM images of the ZnO nanorods before (a), after annealing (b, c) and SAED pattern (d).

Figure 4(d) shows the SAED pattern of ZnO rod which reveal that the individual rod is single crystalline in nature preferentially grow along the [0001] direction (the c axis). The sharp spots in SAED pattern also indicate that the individual rod of ZnO microstructure is single crystalline in nature. Thus, the TEM result clearly indicates that the ZnO nanorods are wurtzite structure of ZnO.

e. Surface morphology of ZnO nanorods thick films

SEM images of the thick film prepared of ZnO nanorods are shown in Figure 5(a, b) with different magnifications. The thick films consists of various ranges of ZnO rods distributed randomly, which offers the more effective surface area to enable effective adsorption-desorption f

the oxygen. The porous nature of the film increases the in pore adsorption of the oxygen and it would increases the oxidative/reductive nature of the film.



(a) (b)

Figure 5 (a, b). SEM images of the ZnO nanorods thick film.

f. Gas response and selectivity of ZnO nanorods

The Figure 6 indicates the selectivity of ZnO nanorods thick film at room temperature and at 300^{o}C. The sensing properties of ZnO nanorods were examined to various gasses at different operating temperatures, it shows that the maximum response to H_2S gas at room temperature (30^{o}C) and ethanol at 300^{o}C for 100ppm gas concentrations. The ZnO nanorods thick film sensor has potential to detect different gasses at different temperatures with good selectivity feature. The sensor selects a H_2S gas at room temperature and ethanol at 300^{o}C. Thus by setting the temperature, one can use the sensor for particular gas detection. This can be attributed to different chemical reactivities of two gases on the sensor surface. Different gases have different energies for adsorption, desorption, and reaction on the metal oxide surface, and therefore the response of the sensor at different temperatures would depend on the gas being sensed.

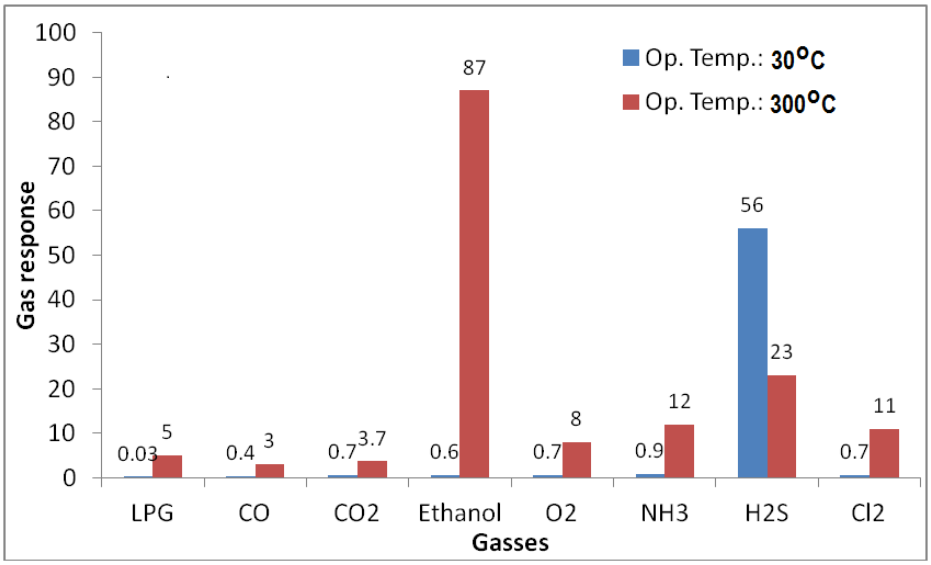


Figure 6. Selectivity of ZnO nanorods thick films at different operating temperatures.

The amount of oxygen adsorbed (O_2^-, O^-, O^{2-}) on the sensor surface goes on increasing with an increase in temperature, reaches to the maximum and then decreases with a further increase in operating temperature. The response to the gas to be detected follows the same behavior. When a reducing gas comes in contact with the sensor surface, it gets oxidized. The rate of oxidation would be the function of the amount of adsorbed oxygen on the surface and the type of gas to be detected. The larger the rate of oxidation, the larger would be the number of electrons released, and in turn the larger would be the gas response.

It is noteworthy that the ZnO nanorods thick film sensor had a high response to H_2S even at room temperature and high response to Ethanol at 300 ^oC. The decrease in resistance of a ZnO sensor upon exposure to reducing gases can be typically explained by a decrease in concentration of oxygen adsorbates ($O_{(ad)}^{2-}$) and a resultant increase in concentration of electron [22]. The gas response was mainly dependent upon two factors. The first was the amount of active sites for oxygen and the reducing gases on the surface of the sensor materials. It is seen from the TEM and SEM images in Figures 4 and 5. This could explain why the responses to Ethanol and H_2S were high compared to other gasses. The second was the reactivity of the reducing gases. The bond energy of H-SH is 381 kJ/mol [23], so that it is easy to open the bond H-SH at lower temperature. On the other hand, the bond energy for Ethanol is 452 kJ/mol [24], so that it is difficult to open the bonds in Ethanol at lower temperature. The higher temperature i.e. 300 ^oC would provide the energy to dissociate the Ethanol bonding. The reactivity of the ZnO nanorods thick films with the

target gasses would be different at different temperatures so it responses to H_2S gas at room temperature and to Ethanol at 300 ^oC.

g. Transient response of ZnO nanorods thick film sensor

The Figure 7 (a, b) indicates response and recovery of ZnO nanorods thick films for H_2S and Ethanol at 30 ^oC and 300 ^oC for 100 ppm gas concentrations respectively. The response time for H2S gas sensor is 5 s and 65 s respectively at room temperature. The response time for Ethanol sensor is 6 s and 60 s respectively at 300 ^oC.

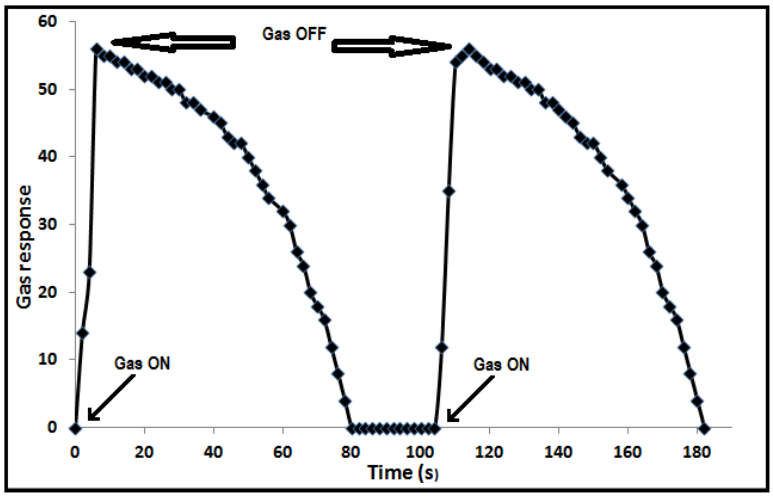


Figure 7(a). Transient response of ZnO nanorods thick film to H_2S gas.

Interestingly in the ZnO nanorods thick films, H_2S and Ethanol are found to be very sensitive, which may be credited to the large range of defects and oxygen vacancies present in the structures deposited. It is worth mentioning here that change in the resistance in semiconducting oxides is usually caused by the adsorption and desorption of the gas molecules on the surface of the film. When exposed to air, O_2 molecules are adsorbed on the surface of the ZnO film and capture electrons to form chemisorbed oxygen species (O^-). Here oxygen vacancy in ZnO nanostructures donate electron to O_2 molecules to form O^- species [24].

$$O_2(gas) + e^- \rightarrow O_2^-{}_{(ad)}$$

$$O_2^-{}_{(ad)} + e^- \rightarrow 2O^-_{(ad)}$$

The sensing mechanism for both H_2S and ethanol on the surface of metal oxides is activated by the adsorbed oxygen O present on the surface of ZnO nanostructures which is as follows:

$$CH_3CH_2OH_{(ad)} + 6O^-_{(ad)} \rightarrow 2CO_{2(g)} + 3H_2O + 6e^- \text{ (ethanol)}$$

$$H_2S + 3O^-_{(ad)} \rightarrow SO_2 + H_2O + 3e^- (H_2S)$$

As expected from the above relation, conductivity increases when H_2S or ethanol comes into contact with the ZnO nanorods thick films.

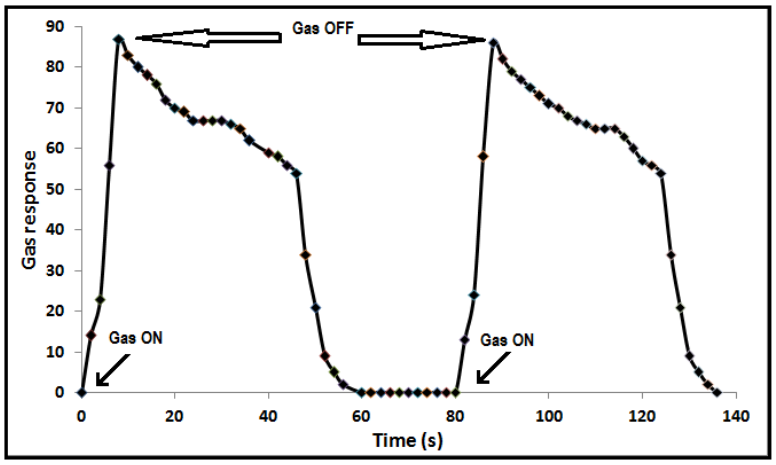


Figure 7(b). Transient response of ZnO nanorods thick film to Ethanol.

VI. CONCLUSIONS

ZnO nanorods with different sizes and shapes have been successfully synthesized via a simple hydrothermal route, using zinc acetate and Cetyltriammonium bromide (CTAB) as the reactants. The orientation of ZnO nanorods has potential to detect H_2S gas at room temperature and ethanol at 300^{o}C. At both operating temperature it showed good selectivity to the target gasses.

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REFERENCES

[1] K. Byrappa, M. Yoshimura, Handbook of Hydrothermal Technology, Noyes Publications, New Jersey, USA, 2001

[2] T. Siyama, A. Kato, A new detector for gaseous components using semiconductor thin film, Anal. Chem. 34 (1962) pp.1502–1503.

[3] J.Q. Xu, Q.Y. Pan, Y.A. Shun, Z. Li, Emulsion synthesis structure and gas sensing properties of nanometer ZnO, J. Inorg. Chem. 14 (1998) pp.355–359.

[4] A.A. Tomchenko, G.P. Harmer, B.T. Marquis, J.W. Allen, Semiconducting metal oxide sensor array for the selective detection of combustion gases, Sens. Actuators B 93 (2003) pp.126–134.

[5] M. Law, H. Kind, F. Kim, B. Messer, P. Yang, Photochemical sensing of NO_2 with SnO_2 nanoribbon nanosensors at room temperature, Angwe. Chem. Int. Ed. 41 (2002) pp.2405–2408.

[6] C. Li, D.H. Zhang, X.L. Liu, S. Han, T. Tang, J. Han, C.W. Zhou, In_2O_3 nanowires as chemical sensors, Appl. Phys. Lett. 82 (2003) pp.1613–1615.

[7] A. Kolmakov, Y.X. Zhang, G.S. Cheng, M. Moskovits, Detection of CO and O_2 using tin oxide nanowire sensors, Adv. Mater. 15 (2003) pp.997–1000.

[8] N. Yamazoe, G. Sakai, K. Shimanoe, Oxide semiconductor gas sensors, Catal. Surveys Asia 1 (2003) pp.63–75.

[9] X.M. Sun, X. Chen, Z.X. Deng, Y.D. Li, A CTAB-assisted hydrothermal orientation growth of ZnO nanorods, Mater. Chem. Phys. 78 (2002) pp.99–104.

[10] Z.Q. Li, Y.J. Xiong, Y. Xie, Selected-control synthesis of ZnO nanowires and nanorods via a PEG-assisted route, Inorg. Chem. 42 (2003) pp.8105–8109.

[11] H.J. Zhai, W.H. Wu, F. Lu, H.S. Wang, Effects of ammonia and CTAB on morphologiesof ZnO nano-and micromaterials under solvothermal process, Mater. Chem. Phys. 112 (2008) pp.1024–1028.

[12] D.F. Zhang, L.D. Sun, J.L. Yin, C.H. Yan, Attachment-driven morphology enhancement of regular ZnO nanowires, J. Phys. Chem. B 109 (2005) pp.8786–8790.

[13] R.C. Singh, O. Singh, M.P. Singh, P.S. Chandi, Synthesis of zinc oxide nanorods and nanoparticles by chemical route and their comparative study as ethanol sensors, Sens. Actuators B 135 (2008) pp.352–357.

[14] Z. Yang, Y. Huang, G. Chen, Ethanol gas sensor based on Al-doped ZnO nanomaterial with many gas diffusing channels, Sens. Actuators B 140 (2009) pp.549–556.

[15] N. Hongsith, C. Viriyaworasakul, P. Mangkorntong, N. Mangkorntong, S. Choopun, Ethanol sensor based on ZnO and Au-doped ZnO nanowires, Ceramics Int. 34 (2008) pp.823-826.

[16] O. Lupan, G. Chai, L. Chow, Novel hydrogen gas sensor based on single ZnO nanorod, Microelectron. Eng. 85 (2008) pp.2220–2225.

[17] Y.L. Cao, P.F. Hu, W.Y. Pan, Y.D. Huang, D.Z. Jia, Methanal and xylene sensors based on ZnO nanoparticles and nanorods prepared by room-temperature solid-state chemical reaction, Sens. Actuators B 134 (2008) pp.462–466.

[18] G. H. Jain, L. A. Patil, M. S. Wagh, D. R. Patil, S. A. Patil, D. P. Amalnerkar, Surface modified $BaTiO_3$ thick film resistors as H_2S gas sensors, Sensors and Actuators B: Chemical 117 (2006) pp.159-165.

[19] G. H. Jain, MOS gas sensors: What determines our choice?, Proceedings of the *Fifth International Conference on Sensing Technology 2011*, Palmerston North, New Zealand, Nov. 28 – Dec, 1, 2011, *pp. 71-77*.

[20] E. W. Shi, W.B.G. Wang, Z. Zhong, Understanding and Controlling the Morphology of ZnO Crystallites under Hydrothermal Conditions, Cryst. Res. Technol. 32 (1997) pp.659.

[21] X. M. Sun, X. Chen, Z.X. Deng, Y.D. Li, CTAB-assisted hydrothermal orientation growth of. ZnO nanorods, Mater. Chem. Phy. 78 pp. (2002) 99.

[22] O. Wan, Q.H. Li, J.Y. Chen, H.T. Wang, X.L. He, J.P. Li, C.L. Lin, Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors, Appl. Phys. Lett. 84 (2004) 3654–3656.

[23] J.A. Dean, Lange's Handbook of Chemistry, Chinese ed., Science Press, 2003, pp. 43–54 (Chapter 4).

[24] T. Zhang, Y. Zeng, H.T. Fan, L.J. Wang, R. Wang, W.Y. Fu, H.B. Yang, Synthesis, optical and gas sensitive properties of large-scale aggregative flowerlike ZnO nanostructures via simple route hydrothermal process, J. Phys. D: Appl. Phys. 42 (2009) 045103.