January - February 2020
ISSN: 0193 - 4120 Page No. 2896 - 2901

Study of metal oxide (ZnO) nanostructure based chemical sensor

Suresh Kumar Dash*, Department of Chemistry, Institute of Technical Education and Research, S 'O' A(Deemed to be University), Bhubaneswar, Odisha, India.
Ms. Suryasnata Dash,Department of Electrical Engineering, CollegeofEngineering and Technology, Bhubaneswar.
Jyoti Prakash Kar, Department of Physics and Astronomy, National Institute of Technology, Rourkela.

Article Info
Volume 82
Page Number: 2896 - 2901
Publication Issue:
January-February 2020

Abstract:
Since the beginning of the technology era, sensors have been used in medical diagnosis,
space, industry etc. The recent years have witnessed a demand of low-cost, portable, low-power consumption sensors which do not emphasize space. Technological advances have allowed sensors based on MEMS technology. Extensive research on metal oxide (ZnO) based resistive sensors is beingdone for sensor applications due to its semi-conducting nature, wide band gap, low cost, easyfabrication process.The operation of sensors at room temperature is in increasing demand asit can be operated easily. Yet, operation at low temperatures doesn’t give proper response forthe material to be sensed. Hence, the sensing activities can be enhanced by increasing thesurface of the material, and reducing the size which enhances electrical, physical andmagnetic properties. This work is based on synthesis of zinc-oxide nanowires for Hydrogenand Ethanol sensing at room temperature. Seed layer was deposited on the Silicon substratefor growth of ZnO nanowires were grown at different temperatures and theirmorphologies were observed. Electrical contacts were made by Ag particles. Hydrogen andEthanol sensing was done and their I-V and I-T characteristics were plotted respectively. Maximum sensitivity was found for ZnO NW grown at 85˚C with a good response time of 11.42 seconds. Ethanol sensing by ZnO NWs grown at 90˚C was found to have maximum sensitivity with a response time less than 41.19 seconds. Thus the above result gives future scope to a develop a real time efficient gas sensor.

Article History
Article Received*: 14 March 2019*
Revised*: 27 May 2019*
Accepted*: 16 October 2019*
Publication*: 18 January 2020*

Keywords:*ZnO nanowire, Sensing, Hydrogen, Ethanol.*

I. INTRODUCTION

The extensive use of speed sensors in controlling the speed of AC servo motors, temperature sensors to monitors the temperature of environment in laboratories, industries have drawn attention to low-cost, portable, low-power consumption sensors [1]. Sensor is a device that detects change of parameters in the environment and transforms it to a suitable signal. Different types of sensors like humidity sensors, proximity sensors, temperature sensors, light sensors, chemical sensors have been developed to find various applications in different sectors. Sensors can be classified as active and passive. An active sensor converts the input to corresponding signal without the need of an external source[2-5]. Technological advances have allowed sensors based on MEMS technology [6,7]. Sensors with high sensitivity, high response nature, are preferred. ZnO nanostructures are used as photo-catalysts, gas sensors, bio-sensors. . Various nanostructures based sensors have been developed for hydrogen sensing[13,14]. Chemical sensors are extensively used in industries, hospitals, laboratories etc. Chemical sensors detect the concentration of the analyte and convert it into appropriate signal. Chemicals like Ethanol, Acetone are detected by various metal oxide semiconductors [15,16]. In chemical sensors, gas sensors are used widely for not only leakage detection purpose but to monitor the environmental pollution and atmospheric composition. Gas sensors, sub-category of chemical sensors, can be resistive type, optical, acoustic type sensors etc. [3]. Nanostructures of ZnO can be synthesised into various morphologies like nanorods,

January - February 2020
ISSN: 0193 - 4120 Page No. 2896 - 2901

nanowires, nanoparticles, mesh-like structures etc. by various methods[17-19]. By varying the parameters various structures can be formed. Mishra et al. reviewed that ZnOnanotetrapods have been used for sensing, treatment against viral infection and fabrication of ceramics and action as good filters in purifying liquids[20]. Pauporté et al. reported that Ag doped ZnO nanowire arrays may have applications as Light Emitting Diode with a low threshold 'on' voltage of ~5V and emission of violet-blue light at 8V[21]. Kim et al. reported that MgO with ZnO nanowires can be used as UV photo-detector [22].

II. MATERIALS AND METHODS

For hydrothermal growth of ZnO, Zinc Acetate ($Zn(CH_3COO)_2$) and Hexamethylenetetramine(HMTA or $C_6H_{12}N_4$) are used as precursors. The precursor solution with the substrate present were heated for 4 hours by global heating. HMTA reacts with water to form ammonia (NH_3) and formaldehyde (HCHO) . The production of NH_3 is essential as it helps in formation of OH^- ions and forms a complex of Zn which inhibits the free concentration of Zn^{2+} and prevents supersaturation of the solution. This also results in controlled replenishment of Zn^{2+} ions. The formation of OH^- ions results in reaction with Zn and forms $Zn(OH)_2$, which again decomposes to form ZnO seeds. The nano wires of ZnO is formed by global heating method. The temperature rise takes place throughout the solution. The substrate where ZnO is to be deposited is kept upside down inclined at 45˚ to the vertical, resulting in convenient deposition.

Hydrothermal Growth of ZnO Nanowires

For hydrothermal growth of ZnO, Zinc Acetate ,$Zn(CH_3COO)_2$ and hexamethylenetetramine(HMTA or $C_6H_{12}N_4$) are used as precursors. The precursor solution with the substrate present were heated for 4 hours by global heating. The production of NH_3 is essential as it helps in formation of OH- ions and forms a complex of Zn which inhibits the free concentration of Zn^{2+} and prevents super saturation of the solution. This also results in controlled replenishment of Zn^{2+} ions. The formation of OH^- ions results in reaction with Zn and forms $Zn(OH)_2$, which again decomposes to form ZnO. ZnO is formed by global heating method. Global heating refers to overall heating of the solution. The temperature rise takes place throughout the solution. The substrate where ZnO is to be deposited is kept upside down inclined at 45˚ to the vertical, resulting in convenient deposition.

H_2 Sensing of ZnO Nanowire

H_2 is sensed by ZnO through adsorption of H_2. ZnO is an n-type semiconductor, having electrons as majority charge carriers. In normal conditions, O_2 is adsorbed on the surface forming O_2^- ions. This results in decrease of electron concentration which decreases the flow of current. When Hydrogen is adsorbed on the surface, it reacts with O_2^- atoms forming H_2O. The release of electrons increases the current and hence, it is used in H_2 sensing.H_2 sensing of ZnO nanowire is obtained by measuring the current change in the device. Since ZnO forms a resistive type sensor, change in electron concentration determines the rate ofsensing.

Thermal Evaporation Method

Before sensing, Metallization by thermal evaporation is done. Thermal evaporation is a Physical Vapour Deposition method by which materials are deposited by simple evaporation and condensation process. In thermal evaporation technique, the source evaporates and due to temperature difference, the particles evaporate and condense at the substrate. The chamber of the apparatus is filled with vacuum. A filament is used as a heater in which source material is heated. The heat produced by the filament vaporizes the material which moves from high temperature to low temperature area, where it condenses and gets deposited on the substrate. This method is used for depositing metals as electric contacts. It is also used for depositing metallic contact layers for thin film devices like solar cells, OLEDs etc.

January - February 2020
ISSN: 0193 - 4120 Page No. 2896 - 2901

Need for Ethanol Sensing

Ethanol is the main constituent in alcoholic drinks. It is used in a variety of ways starting from being a constituent material in sanitizers, antiseptics to being used as fuel. Pure ethanol causes irritation in eyes and skin. Ethanol has high flammability and it flash point is low (13 ˚C for pure ethanol). Hence it's important to detect concentrations of Ethanol. Ethanol sensing mechanism is the same as Hydrogen sensing. O_2 is adsorbed on the surface and exposure to Ethanol instigates a reaction releasing CO_2 and H_2O as products.

III. RESULTS AND DISCUSSION

Spectral characterization of ZnO Nanowire

Fig.1. reveals XRD analysis of ZnO seed layer and ZnO nanowires grown at different temperatures 85˚C, 90˚C and 95˚C. For all samples, a distinct peak at 34.5˚ was obtained. The peak was obtained for (002) plane. It was inferred that the nanowires grown were c-axis oriented. Also for increasing temperatures, the peak intensity increased. With increasing temperature, the growth of ZnO nanowires improved. The growth was seen to be dense. Nanowires grown at 85˚C have an approximate length of 1.2µm,while the length of nanowires grown at 90˚C is 1.1µm, and 2.5 µm for that 95˚C. Fig.2. shows the Raman spectra of ZnO nanowire grown at 95˚C, which show peaks for Silicon at shift of 0.002cm and 0.003 cm.

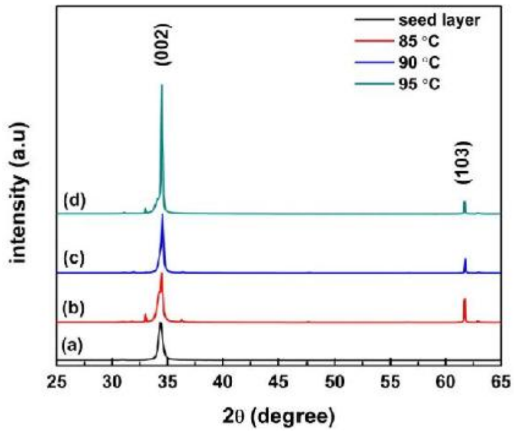

Fig.1. XRD analysis of (a) ZnO seed layer (b) ZnO nanowire grown at 85˚C (c) ZnO nanowire grown at 90˚C (d) ZnO nanowire grown at 95˚C.

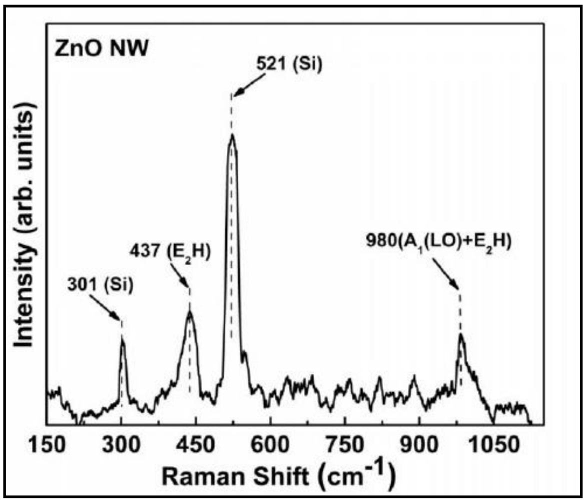

Fig.2. shows the Raman spectra of ZnO nanowire grown at 95˚C, which show peaks for Silicon at shift of 0.002cm and 0.003 cm.

Measurement of Current for H_2&EtOH Sensing

Keitheley 6487 Picoammeter Voltage Source is used to find the current response with respect to time and voltage. Current increased with increase in voltage. When H_2 was supplied, there was increase in current with respect to Vacuum conditions. Current response with respect to time, is measured by exposing the material to Vacuum and H_2 in periodic intervals. The current remained almost constant in Vacuum, while it gradually increased when exposed to H_2. The Current again decreased gradually when Vacuum was created.

January - February 2020
ISSN: 0193 - 4120 Page No. 2896 - 2901

Results of Sensing

Sensitivity can be defined as the change in resistance of the material or the current when the chemical or gas is exposed. It can be mathematically defined as:

$$S= Ra/Rg \text{ or } S=Ig/Ia$$

The effective response is determined by measuring response and recovery time. Response time is defined as the time required to reach the 90% of the maximum value of current during the gas/chemical sensing state. Recovery time is defined as time taken for the the current to reach 10% of its maximum value when the environment switches to ambient air conditions. The response curve for H_2 gas sensing, where maximum sensitivity is shown for ZnO nanowire grown at 85˚C[23]. the sensitivity was found to be 411.04 (~411) at room temperature. The response time and recovery time were recorded to be 11.42 seconds and 16.7 seconds respectively.

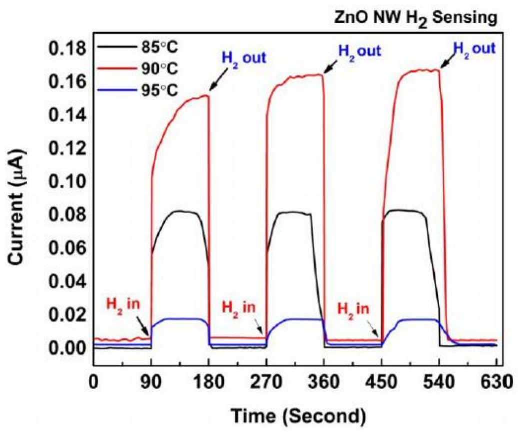

Fig. 3. I-T curve for H_2 sensing by ZnO Nanowire grown at 85˚C, 90˚C, 95˚C.

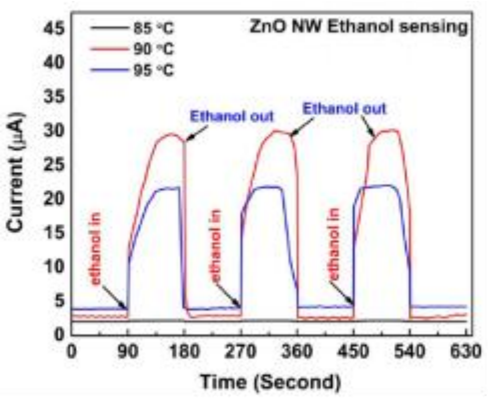

Fig.4. I-T curve showing Ethanol sensing by ZnO nanowires grown at different temperatures (85˚C, 90˚C, 95˚C).

Table1, indicates the H_2 sensing response of ZnO nanowires grown at different temperatures. The sensitivity of sensors greatly depends on the morphology of the nanowires. For the ZnO nanowire grown at 95˚C, when the material was exposed to normal air environment, it could recover 12% of its maximum current value[24]. Fig.5 shows the sensing response of ZnO nanowires to Ethanol at room temperature. The maximum sensitivity was found for ZnO nanowire grown at 90˚C with sensitivity being 10.75 with response time and recovery time being 41.19 seconds and 10.8 seconds respectively[25]. For NW-3(ZnO NW grown at 95˚C), the material was able to recover till 18% of its maximum current value, while there was no significant sensing for NW-1(ZnO grown at 85˚C)[26,27].

Table1: H_2 sensing response of ZnO nanowires grown at different temperatures.

ZnO NW	Sensitivity (S)	Response Time(sec)	Recovery Time(sec)
NW-1 (85˚C)	411.04	11.42	1.62
NW-2 (90˚C)	24.7	29.17	3.37
NW-3(95˚C)	6.20	12.88	-

IV. CONCLUSION

The growth of ZnO nanowires by hydrothermal method was significant for hydrogen and ethanol sensing. The growth of ZnO seed layer was carried by RF magnetron sputtering followed by ZnO nanowires at different growth temperatures. X-ray diffraction pattern showed highly crystalline c-axis oriented (002) peak for both seed layer and ZnO nanowires. SEM micrograph depicts well aligned nanowires like morphology grown at different temperatures. The average length and diameter of ZnO nanowires was found to be around 2.5µm and about 35nm respectively. In addition, Raman peak at 437cm^{-1} confirms the Wurtzite crystallite structure of ZnO. Furthermore in order to develop a compatible chemical and gas sensor, ethanol and hydrogen sensing measurement has been carried out. Maximum sensitivity was found for ZnO NW grown at 85˚C with a good response time of 11.42 seconds. Ethanol sensing by ZnO NWs grown at 90˚C was found to have maximum sensitivity with a response time less than 41.19 seconds. Thus the above result gives future scope to a develop a real time efficient gas sensor.

V. REFERENCES

[1] A. Dey, "Semiconductor metal oxide gas sensors: A review", Mater. Sci. Eng. B, vol. 229, 2018, pp 206–217.

[2] S. Phanchiphant, "Semiconductor Metal Oxides as Hydrogen Gas Sensors" Procedia Eng., vol. 87, 2014,pp 795 – 802.

[3] H. Gu, Z. Wang, Y. Hu, "Hydrogen Gas Sensors Based on Semiconductor Oxide" Nanostr. Sensors, vol. 12, 2012, pp 5517-5550.

[4] M. Sinha, R. Mahapatra, B. Mondal, T. Maruyama, R. Ghosh, "Ultrafast and ReversibleGas-Sensing Properties of ZnO Nanowire Arrays Grown by Hydrothermal Technique" J. Phys. Chem. C, vol. 120, 2016, pp 3019−3025.

[5] T.F. Choo, N. U. Saidin, K.Y. Kok, "Hydrogen sensing enhancement of zinc oxide nanorods via voltage biasing". R. Soc. open sci., vol. 5, 2018, pp 172372-75.

[6] M. Aslam, V. S. Palaparthy, H. Kalita, S. G. Surya, M. S. Baghini, "Graphene oxide based soil moisture microsensor for in situ agriculture applications".Sensors& Actuators: B. Chemical, vol. 273, 2018, pp 1660–1669.

[7] A.A. Vasiliev, A.V. Pisliakov, A.V. Sokolov, N.N. Samotaev, S.A. Soloviev, K. Oblov,V. Guarnieri, L. Lorenzelli, J. Brunelli, A. Maglione, A.S. Lipilin, A. Mozalev, A.V.Legin. "Non-silicon MEMS Platforms for gas sensors". Sensors And Actuators, vol. B 224,2016, pp700–713.

[8] D. Sett, D. Basak, "Highly enhanced H2 gas sensing characteristics of Co:ZnOnanorods and its mechanism" Sensors and Actuators, vol.B 243, 2017, pp475–483.

[9] K. Yadav, S.K. Gahlaut, B. R. Mehta, J. P. Singh, "Photoluminescence based H2 and O2 gas sensing by ZnO nanowires" Applied physics letters, vol.108, 2016, pp071602..

[10] F. Teimooria, K. Khojiera, N.Z. Dehnavia, "On the Dependence of H2 Gas Sensitivity of ZnO Thin Films on Film Thickness" Procedia Materials Science, vol.11,2015, pp474 – 479.

[11] H. Zhitao, L. Sisi, C. Jinkuia, C.Yong, "Controlled growth of well-aligned ZnO nanowire arrays using the improved hydrothermal method" J. Semicond. vol.34(6),2013,pp1-5.

[12] S. Ranwa, P. K. Kulriya, V. K. Sahu, L. M. Kukreja, M. Kumar, "Defect-free ZnOnanorods for low temperature hydrogen sensor applications". Applied Physics Letters, vol. 105, 2014, pp213103.

[13] N. U. Saidin, T. F. Choo, K. Y. Kok, "Hydrothermal growth of ZnO: a substrate-dependent study on nanostructures formation", Mater. Sci. Eng., vol.298, 2018, pp012016.

[14] N.S. Harale, A.S. Kamble, N.L. Tarwal, I.S. Mulla, V.K. Rao, J.H. Kim, P.S. Patil,
"Hydrothermally grown ZnOnanorods arrays for selective NO2 gas sensing: Effect of anion generating agents", Ceramics International, vol.42, 2016, pp12807–12814.

[15] T-J. Hsueh, C-L. Hsu, S-J. Chang, I-C. Chen, "Laterally grown ZnO nanowire ethanol gas sensors" Sensors and Actuators B, vol.126, 2007, pp473–477.

[16] Q. Wan, Q. H. Li, Y. J. Chen, and T. H. Wang, X. L. He, J. P. Li, C. L. Lin, "Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors", Appl. Phys. Lett.,Vol.84(18), 2004, pp1-5.

[17] N.S. Harale, A.S. Kamble, N.L. Tarwal, I.S. Mulla, V.K. Rao, J.H. Kim, P.S. Patil."Hydrothermally grown ZnOnanorods arrays for selective NO2 gas sensing: Effect of anion generating agents", Ceramics International, vol.42, 2016, pp12807–12814.

[18] O. Lupan, V. Posticab, F. Labatc, I.Ciofinic, T.Pauportéc ,R. Adelung, "Ultra-sensitive and selective hydrogen nanosensor with fast response at room temperature based on a single Pd/ZnO nanowire", Sensors and Actuators, B 254,2018, pp1259– 1270.

[19]V. Galstyan, E. Comini, C. Baratto, G. Faglia, G. Sberveglieri, "Nanostructured ZnO chemical gas sensors", Ceramics International, vol.41,2015, pp14239–14244.

[20]Y. K. Mishra, R. Adelung, "ZnO tetrapod materials for functional applications", Materials Today, Vol.21(6),2018,pp1-5.

[21]T. Pauporte, O. Lupan, J. Zhang, T. Tugsuz, I. Ciofini, F. Labat, B. Viana, "Low-Temperature Preparation of Ag-Doped ZnO Nanowire Arrays, DFT Study,and Application to Light-Emitting Diode", ACS Appl. Mater. Interfaces, vol. 7, 2015, pp11871−11880.

January - February 2020
ISSN: 0193 - 4120 Page No. 2896 - 2901

[22]D. C. Kim, B. O.Jung, J. H.Lee, H. K. Cho, J. Y. Lee, J. H. Lee, "Dramatically enhanced ultraviolet photosensing mechanism in a n-ZnO nanowires/i-MgO/n-Si structure with highly dense nanowires and ultrathin MgO layers", Nanotechnology, vol. 22,2011, pp265506.

[23]G. Wisz, I. Virt, P. Sagan, P. Potera, R. Yavorskyi, "Structural, Optical and Electrical Properties of Zinc Oxide Layers Produced by Pulsed Laser Deposition Method", Nanoscale Research Letters, vol.12,2017,pp253-258.

[24]P. Chelvanathan, Y. Yusoff, F. Haque, M. Akhtaruzzaman, M.M. Alam, Z.A. Alothman, M.J.Rashid, K. Sopian, N. Amin, "Growth and characterization of RF-sputtered at ZnS Thin film deposited various substrate temperatures for photovoltaic application", Applied Surface Science, vol. 334,2015, pp138–144.

[25]J.P. Kar, S. Kim, B. Shin, K.I. Park, K.J. Ahn, W. Lee, J.H. Cho, J.M. Myoung, "Influence of sputtering pressure on morphological, mechanical and electrical properties of Al-doped ZnO films", Solid-State Electronics, vol. 54,2010, pp1447–1450.

[26]S. Cao, Z. Kang, X. Yan, Y. Wang, Y. Zhao, Z. Bai, Y. Liu, K. Zhao, Y. Zhang, "Self-powered photo electrochemical biosensing platform based on Au NPs@ZnOnanorods array", Nano Research, vol. 9(2),2016, pp344–352.

[27]T. Tharsika, M. Thanihaichelvan, A. S. M. A. Haseeb, S. A. Akbar, "Highly Sensitive and Selective Ethanol Sensor Based on ZnONanorod on SnO2 Thin Film Fabricated by Spray Pyrolysis", Frontiers in Materials, Vol. 6, 2019,pp1-5.