# Synthesis of Nano Gas Sensor Arrays

H. Shokry Hassan*, A.B.Kashyout*, A. A. A. Nasser**, I. Morsi**, and A. Rafaat**
*Advanced Technology and New Materials Research Institute, City for Scientific Research and technology application, new Borg el Arab City, Alexandria **Arab Academy for Science, and Technology, and Maritime Transport
Correspondence should be addressed to at menem_1954@yahoo.com.

## Abstract:-

The paper presents novel structures of Nano gas sensor arrays by using ZnO and doped with aluminum . ZnO Nanomaterial are successfully prepared using sol-gel technique . These include, similar and dissimilar structures. All used sensors are composed of zinc oxide doped with aluminum at different concentrations for dissimilar structures, and with the same concentration for similar structures. The first array (double sensor array) based on doping with percentages of 5% and 1%, while the second array (quadrature sensor array) uses 5% doping only. The resulting Nano array characterization is carried out using the scanning electron microscopy (SEM). This characterization determines the structure of the Nano element (dot, rod or wire). This is followed by the X-Ray Diffraction (XRD) characterization which indicates the purity and intensity of the Nano element within the structure. The electrical characteristic of the sensor is determined by measuring the two terminal sensor's resistance at different concentrations of the gas, for different temperature ranges. More than order of magnitude change in the resistance is found to occur in response more than 100% change in temperature for different doping concentration, which indicates that arraying results in a more than unity array factor. This is a good measure for pollution in industrial applications.

## 1. Introduction

Recently, there is a large need for low-cost production of transparent conducting films e.g.,( ZnO, SnO2, In2 O3, and Cd2SnO4) [1-3] because of their applications in various energy Efficiency specializations such as Piezoelectric devices, multilayer thermal image converter Systems, thin film transistor (TFT) ,window layer in heterojunction Solar cells, dye sensitization solar cells, heat mirrors, and gas sensors Solid State [4]. The film metal oxide gas sensors used widely because of their excellent characteristics such as low Cost, and small size, high sensitivity and fast response, and speed recovery. Greater selectivity, sensitivity and improve Stability [5]. Zinc oxide (ZnO) is not a newly discovered compound and research on its preparation and characterization has continued for several decades. However, a renewed interest of the scientific community in ZnO can be measured by the very large number of publications which have appeared on this compound in the past few years. ZnO is an oxide of group II metallic zinc [6] that exists between semiconductors and ionic materials, which gives ZnO the electrical amphoteric property as n-type semiconductor in most preparation procedures, although p-type conductivity is also reported under certain conditions [7,8].ZnO is a large band gap n-type Semiconductor which combines several advantages over its competitors such as GaN used today for production of short wavelength light-emitting devices. Its excitation energy (60 mV) is larger than the room-temperature thermal energy, and high-excitation near-UV luminescence and laser emissions can be expected. ZnO is stable under high-energy radiation and can be easily etched in acidic or alkaline solutions. The preparation of nanostructured ZnO in a large variety of shapes is an emerging field. One-dimensional (1D) ZnO nanostructures such as nanorods, nanowires, nanobelts, nanotubes and nanowhiskers are important for their physical properties arising from quantum confinement (such as electronic quantum transport and enhanced radiative recombination of carriers). Nanowires have promising potentials in extensive applications and are the fundamental building blocks for fabricating short-wavelength nanolaser, field effect transistors (FET), ultrasensitive nanosized gas sensors, nanoresonators, transducers, actuators, nanocantilevers and field emitters [8–14]. These properties could have numerous applications in various areas such as nanoscale electronics, optoelectronic devices and high-density magnetic memories [15] .Several techniques have been stated to grow doped and nondoped ZnO films as vapor condensation, thermal evaporation, spray pyrolysis, magnetron sputtering, metalorganic, chemical vapor deposition, and sol-gel among others [16–20].In this paper two structure of gas sensor array are developed by using ZnO doped with aluminum with different doping concentration , the array can sense different gases with high selectivity and sensitivity.

## 2. Experimental Work

2.1. *Preparation of ZnO/Al-Doped ZnO Nano powder and film fabrication.* The ZnO nanomaterial are prepared via sol-gel route [1] by mixing A 6 ml of 1M zinc acetate aqueous solution and a 6 ml of 10MNaOH aqueous solution are added into 15 ml alcohol. After being stirred, 1ml tri-ethanol amine (TEA) is added to the mixture [25-27], and then the mixture has been stirred for half hour .In case of preparing 1 , 5 wt% Al-doped ZnO; an equivalent amount of aluminum chloride is added to the mixture zinc acetate dehydrate ,alcohol and TEA**.** A 50 ml beaker containing the solution mixture is entered to oven for 60 minutes at temperature 70°C. Then the resulting solutions are washed with distilled water and ethanol to remove any residual salts, and , and finally dried at 60°C for 2 hours. The colloidal solution is obtained by mixing the ZnO nanomaterial with ethanol and vigorously stirred and left long time to form homogeneous suspension of 20wt% ZnO. The suspension is applied onto the substrate by wafer spinner machine (Model Polos300 AWS) at 100 rpm for 2 minutes or according to the desired thickness. The film is then allowed to dry in air for 15 minutes and sintered in airflow at 400◦C for 5 minutes.

*2.2 Preparation of solid state semiconductor gas sensor array*. The glass substrates is ultrasonically cleaned in acetone for 15 minutes, then rinsed several times with demonized water. the copper mask as shown in (figure1(a) & figure1(b)) is added on the film ,then the film and is entered to the heater (platinum heater) is deposited by a sputtering machine (Turbo Sputtering RF & DC Power Supplies Deposition System Model Hummer 8.1) [23], (*P* 100WRF, *t* =2minutes). Then, the suspension of metal oxide (ZnO or Al doped ZnO) was applied onto the substrate by wafer spinner machine (100 rpm, 2 minutes), then the film is allowed to dry in air and this is repeated for several times to achieve the desired thickness. Finally Pt contact is deposited (*P* =100WRF, *t* = 2 minutes).

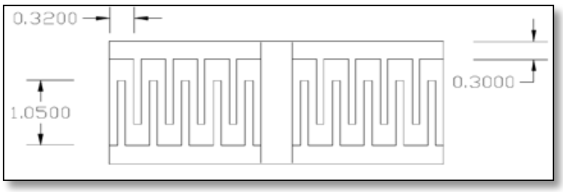

Figure1(a):Mask of double sensor array

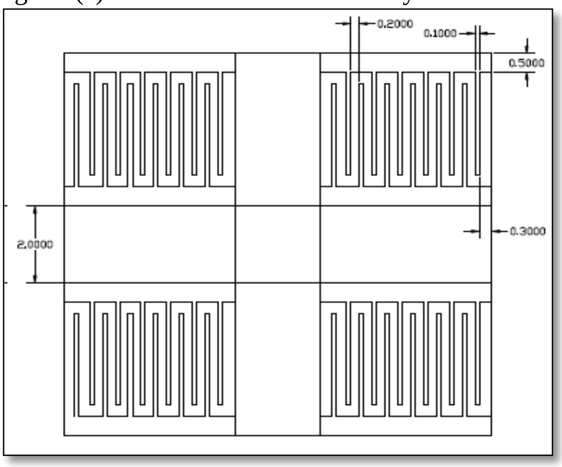

Figure1 (b) :Mask of Quadrature sensor array

*2.3 The array structure,* Two array structure are developed;The first array structure is double sensor array uses doping percentages of 1% and 5% as shown in (figure2(a)),This structure can sense different gases with different concentration. The second array structure is quadrature sensor array uses 5% doping only as shown in (figure2(b)).this structure is consists of four sensors with same concentration connected in series. The behavior of each gas sensor array structure have been studied for two application of gas sensor array ,these application is sensing the $H_2$ and $CO_2$ gas.

Figure2(a):Double gas sensor array

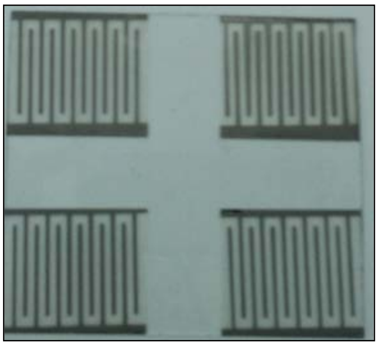

Figure2(b):Quadrature gas sensor array

*2.4 Characterization of ZnO and Al Doped ZnO Nano material.* X-ray diffraction patterns are obtained using using Schimadzu 7000 Diffractometer operating with Cu K$\alpha$ radiation ($\lambda$ = 0.15406 nm) generated at 30 kV and 30mA with scan rate of 2◦ min$^{-1}$ for 2$\theta$ values between 20 and 80 degrees.

*2.5. Electrical Properties of the Gas Sensors.* The resistivity of gas sensors are measured versus temperature utilizing different gases. The measurements are carried out in the temperature range 20–200◦C with $H_2$ and $CO_2$. The effect of Al doping on the sensitivity of gas sensor is also studied. All of these measurements have been carried out using homemade gas chamber able to work at high temperatures and pressures and under dark conditions to avoid the effect of UV radiation [21].

## 3. Results and Discussion

3.1. *X-Ray Diffraction (XRD).* XRD is used to characterize the different phases of the prepared ZnO Nano material (Figure3) shows the XRD patterns for ZnO nanomaterial the XRD patterns indicates the purity and intensity of nanomaterial.

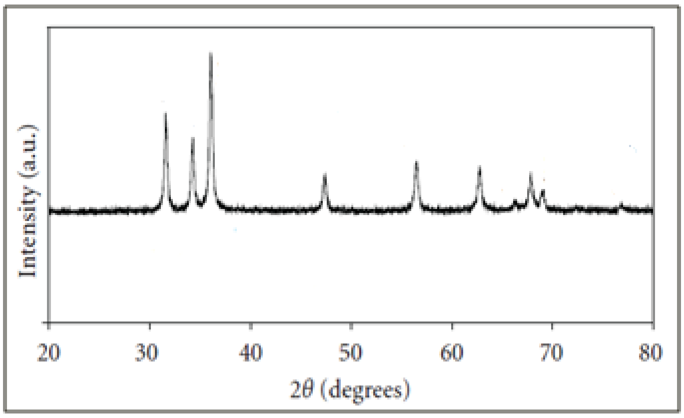


Figure3: X-ray Diffraction (XRD) Pattern of ZnO Nanomaterials

3.2 *Scanning Electron Microscope (SEM).* Figure (4) shows the SEM images of pure ZnO, ZnO doped with 1% and 5% Al, respectively. It is noted that at pure ZnO (Figure 4(a)), ZnO Nonorods [24 ]are well identified and aggregated (500nm in size). As 1 wt% of Al (Figure 4(b)), 5 wt % of Al (Figure 4(c)).

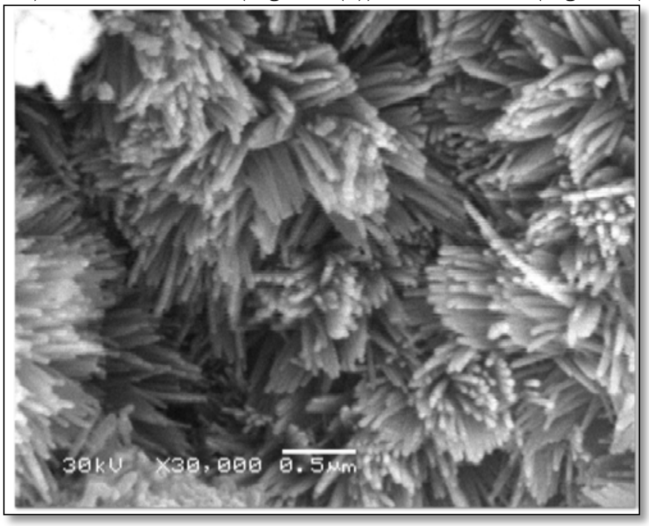


Figure4(a):SEM for pure ZnO

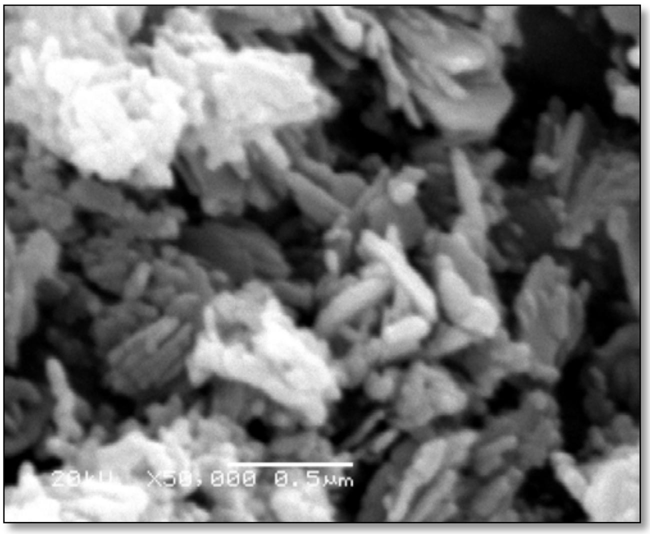


Figure4(b):SEM for ZnO Doped with 1% Al Concentration

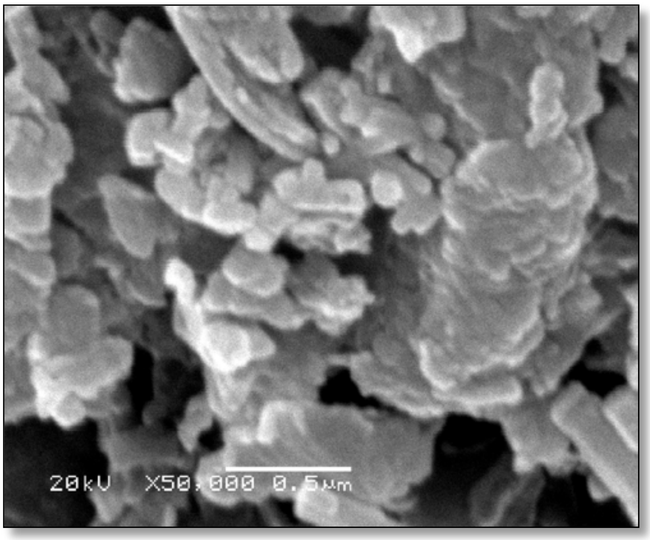


Figure4(C):SEM for ZnO Doped with 5% Al Concentration

*3.3. Electrical Measurements of Gas Sensors.*

Solid state gas sensor consists of four main components, isolated substrate (glass, ceramics, etc.), heater, semiconductor metal oxide, and two electrodes. The gas sensitivity, *S*, is given by equation (1) and (2) [22 ,28-30].

$$S = \frac{\Delta R}{Ra} \quad (1)$$

$$\Delta R = (Ra - Rg) \quad (2)$$

Where $R_a$ and Rg express the resistance of the sensor in air and in detecting gas, respectively.

*3.3.1. Sensitivity of double sensor array for $H_2$ and $CO_2$ gas*

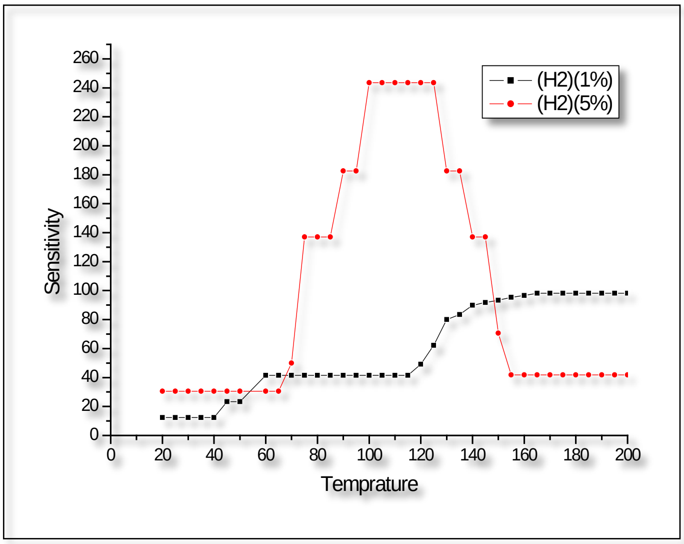


Figure5(a): Sensitivity of double gas sensor array for $H_2$ gas.

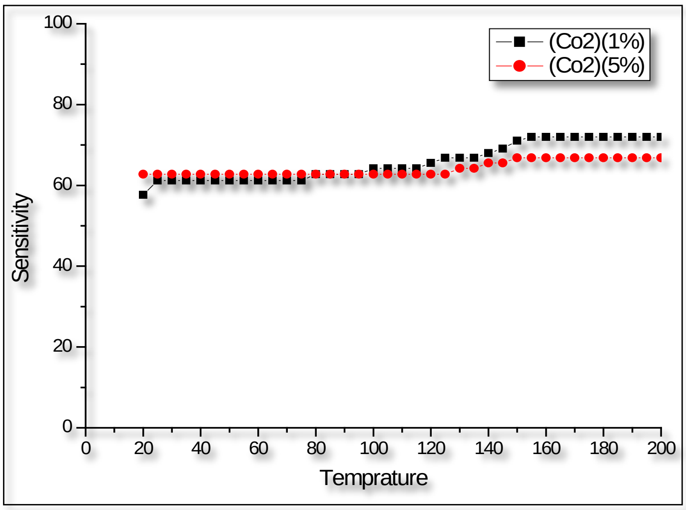


Figure5(b): Sensitivity of double gas sensor array for $CO_2$ gas

*3.3.2. Sensitivity of quadrature sensor array (series connection between four sensors) uses for $H_2$ and $CO_2$ gas.*

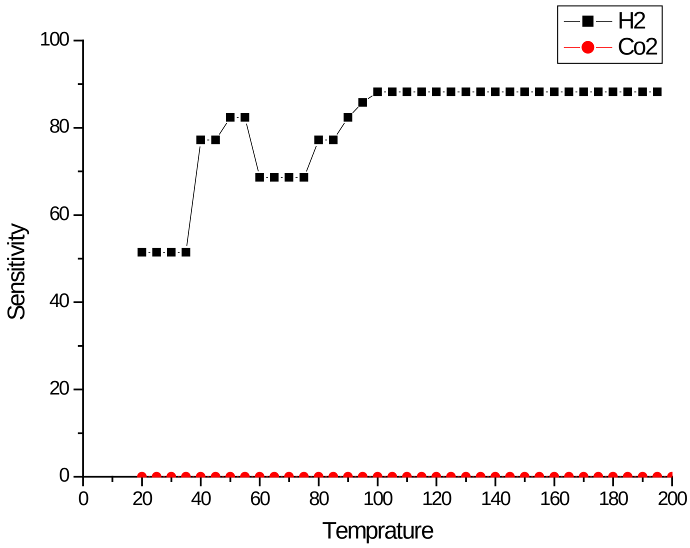


Figure5(C): Sensitivity of quadrature gas sensor array for $H_2$ and $CO_2$ gas.

Those figures indicates that ,The double sensor array has a better result for sensing of both $H_2$ and $CO_2$ gases than quadrature sensor, The $H_2$ gas sensitivity is high in (5% doping) and $CO_2$ gas sensitivity is moderate in (1% doping),The quadrature sensor array has moderate sensitivity for $H_2$ gas and has no sensitivity for $CO_2$ gas.

## 4. Conclusions

ZnO and ZnO:Al nanomaterials are prepared by sol-gel technique. Thick films are prepared using spinner coating to construct gas sensor devices. ZnO and ZnO:Al nanomaterials are characterized by SEM and X-ray diffraction , the construction of ZnO is Nanorods .Two different array structure have been developed ,the first structure is double sensor array with different doping material ZnO:1% Al and ZnO:5% AL,and the second structure is quadrature sensor array which fabricated from same material ZnO:5% Al doped. The double sensor array is the best structure of array and has better results of sensitivity compared with the sensitivity of quadrature sensor array in both gases $H_2$ and $CO_2$. Quadrature sensor array not sensitive for $CO_2$ gas . Different gases can be detected at the same time by using different doping concentration (zinc oxide with aluminum). at quadrature sensor array ,The series connection between four sensor increase the initial resistance in air which make the sensitivity for gas decreasing according to equation (1) of sensitivity.

## References

[1] A. B. Kashyout, M. Soliman, M. El Gamal, and M. Fathy,"Preparation and characterization of nano particles ZnO films for dye-sensitized solar cells,"Materials Chemistry and Physics, vol. 90, no. 2-3, pp. 230–233, 2005.

[2] G. Lu, K. L. Huebner, L. E. Ocola,M. Gajdardziska-Josifovska, and J. Chen, "Gas sensors based on tin oxide nanoparticles synthesized from a mini-arc plasma source," Journal of Nanomaterials, vol. 2006, Article ID 60828, 7 pages, 2006.

[3] M. T. Mohammad and W. A. Abdul Ghafor, "Optical properties of cadmium stannate thin film prepared by pyrolytic process," Solid State Communications, vol. 72, no. 10, pp. 1043–1046, 1989.

[4] M. G. Ambia, M. N. Islam, and M. Obaidul Hakim, "Studies on the seebeck effect in semiconducting ZnO thin films," Journal of Materials Science, vol. 27, no. 19, pp. 5169–5173,1992.

[5] W. Shen, Y. Zhao, and C. Zhang, "The preparation of ZnO based gas-sensing thin films by ink-jet printing method," Thin Solid Films, vol. 483, no. 1-2, pp. 382–387, 2005.

[6] T.Steiner, Semiconductor Nanostructures for Optoelectronic Applications, chapter 6, Barnes & Noble, 2004.

[7] K.-K. Kim, H.-S. Kim, D.-K. Hwang, J.-H. Lim, and S.-J. Park,"Realization of p-type ZnO thin films via phosphorus doping and thermal activation of the dopant," Applied Physics Letters,vol. 83, no. 1, pp. 63–65, 2003.

[8] A. K. Srivastava, B. R. Chakraborty, and S. Chandra, "Crystallographically oriented nanorods and nanowires of rfmagetron-sputtered zinc oxide," Journal of Nanomaterials, vol.2009, Article ID 310360, 2009.

[9] O¨ zgu¨r U¨ , Alivov Y I, Liu C, Teke A, Reshchikov M A, Dogan M A, Avrutin V, Cho S J, Morkoc H "A comprehensive review of ZnO materials and devices." J. Appl. Phys. 98:041301 1–041301 105,2005.

[10] Wang Z L "Nanostructures of zinc oxide. Mater." vol 7(6):26– 33,2004.

[11] Pan Z W, Dai Z R, Wang Z L"Nanobelts of semiconducting oxides." vol 291:1947–1949,2001.

[12] Wang Z L "Zinc oxide nanostructures: growth, properties and applications." J. Phys.:Condens. Matter 16:R829–R858,2004.

[13] Heo YW, Norton D P, Tien L C, Kwon Y, Kang B S, Ren F, Pearton S J, LaRoche J R "ZnO nanowire growth and devices." Mater. Sci. Eng. R 47:1–47,(2004).

[14] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R, Yang P "Room-temperature ultraviolet nanowire lasers." Science 292:1897–1899,(2001).

[15] Klingshirn C, Hauschild R, Priller H, Decker M, Zeller J, Kalt H "ZnO rediscoveredonce Superlattices Microstructures" 38:209–222,(2005).

[16] Wang Q, Wang G, Xu B, Jie J, Han X, Li G, Li Q, Hou J G "Non-aqueous cathodic electrodeposition of large-scale uniform ZnO nanowire arrays embedded in anodic alumina membrane." Mater. Lett. 59: 1378–1382,(2005).

[17] R. Martins, E. Fortunato, P. Nunes et al., "Zinc oxide as anozone sensor," Journal of Applied Physics, vol. 96, no. 3, pp.1398–1408, 2004.

[18] M. Grassi, D. A. W. Soares, A. A. A. De Queiroz, A. H. A.Bressiani, and J. C. Bressiani, "Organometallic chemical vapor deposition of compound semiconductors," Materials Science and Engineering B, vol. 112, no. 2-3, pp. 179–181, 2004.

[19] R. Al Asmar, G. Ferblantier, F. Mailly, P. Gall-Borrut, and A.Foucaran, "Effect of annealing on the electrical and optical properties of electron beam evaporated ZnO thin films," Thin Solid Films, vol. 473, no. 1, pp. 49–53, 2005.

[20] D. J. Kang, J. S. Kim, S. W. Jeong, Y. Roh, S. H. Jeong, and J. H. Boo, "Structural and electrical characteristics of R.F. magnetron sputtered ZnO films," Thin Solid Films, vol. 475, no. 1-2, pp. 160–165, 2005.

[21] X. L. Cheng, H. Zhao, L. H. Huo, S. Gao, and J. G. Zhao, "ZnO nanoparticulate thin film: preparation, characterization and gas-sensing property," Sensors and Actuators B, vol. 102, no.2, pp. 248–252, 2004.

[23] N. M. Sbrockey and S. Genesan, "ZnO thin films by MOCVD," III-Vs Review, vol. 17, no. 7, pp. 23–25, 2004.

[24] Zhengzhi Zhou • Yong Ding • Xihong Zu • Yulin Deng J Nanopart "ZnO spheres and nanorods formation: their dependence on agitation in solution synthesis" Res J Nanopart Res DOI 10.1007/s11051-010-9922-5, 2009.

[25]A. B. Kashyout,1 H. M. A. Soliman,1 H. Shokry Hassan,1 and A. M. Abousehly2 "Fabrication of ZnO and ZnO:Sb Nanoparticles forGas Sensor Applications," Journal of Nanomaterials Volume 2010, Article ID 341841, 8 pages doi:10.1155/2010/341841,2010.

[26] Yu-Jin Chena,c,∗, Chun-Ling Zhub, Gang Xiaob " Ethanol sensing characteristics of ambient temperature sonochemically synthesized ZnO nanotubes ,"Sensors and Actuators B 129 639–642,(2008).

[27] Jinxia Duan, Xintang Huang, Enke Wang "PEG-assisted synthesis of ZnO nanotubes," Materials Letters 60 1918–1921,(2006).

[28] Sandra C. Hernandez, Debangshu Chaudhuri, Wilfred Chen, Nosang V. Myung,* Ashok Mulchandani* "Single Polypyrrole Nanowire Ammonia Gas Sensor" DOI: 10.1002/elan.200703933, 2007.

[29] S K GUPTA1,*, ADITEE JOSHI2 and MANMEET KAUR1 "Development of gas sensors using ZnO nanostructures" J. Chem. Sci., Vol. 122, No. 1, pp. 57–62. ,2010.

[30] Ming-Zhi Yang 1, Ching-Liang Dai 1,* and Chyan-Chyi Wu 2 "A Zinc Oxide Nanorod Ammonia Microsensor Integrated with a Readout Circuit on-a-Chip" Sensors doi:10.3390/s111211112,2011.