Preparation and Characterization of ZnO Nanoparticles by Chemical Route Method

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ABSTRACT

Zinc oxide nanoparticles have been developed using hexahydrated zinc nitrate by chemical route method. The white precipitate was obtained at 800C by a simple wet chemical route. Zinc oxide nanoparticles based thick film samples were prepared by standard screen printing technique and fired at 5000C for 30 minutes. The obtained ZnO nanoparticles thick films were investigated by X-ray diffraction (crystal Structural), X-ray diffraction patterns showed that ZnO nanoparticles have hexagonalwurtzite structure. The UV-VIS absorption spectra of ZnO nanoparticles sintered at 4000C shows a maximum absorption band at 259 nm. The FT-IR shows the absorption peak of ZnO nanoparticles are observed in the range 600-450 per cm is attributed to the stretching Zn-O bonds respectively. No hydrogen bonding was observed in the commercial ZnOwhereas in ZnO nanoparticles hydrogen bonding was observed at 3414 per cm.Using half bridge method the D.C resistance of the film samples measured in air atmosphere at different temperatures. The TCR, activation energy and activation energy of films were evaluated at 5000C.

Keywords: ZnO, Material behavior, UV-vis analysis, FTIR, TCR, activation energ.

INTRODUCTION:

Research in the field of synthesis methodology of nano-materials is only oriented controlling in their Size, shape and different composition. In recent times nano-material technology has been useful in reducing the size of the materials to nano-scale [1]. Nanosized semiconductors are in demand due to their significant electrical, chemical, optical, magnetic and gas sensing properties which are useful in electronic devices with various functions [2-4]. Zinc oxide has hexagonal wurtzite unit cell structure a band gap (3.37eV) with its lattice parameters a= 3.253AUand C=5.209AU with large binding energy [2,5,6]. The physical and chemical properties of nanoparticle materials depends on size, size dispersity, shape, surface state, crystal structure, organization onto a hold up and dispensability[7]. Zinc oxide is one of the most studied materials in nanotechnology that have been studied for applications such as Solar cells, Gas sensors, Photo luminescent , Photo detectors, Photo catalysis, electrical devise, acoustic devises, optoelectronics, nano-generators, biosensors [8-13], the ability to absorbance in the UV range and negligible toxicity makes zinc oxide nanoparticles very useful for sensing and optical study [14-17]. Numbers of research workers have reported that the size and shape of the material strongly affect the properties and the applications of the nano-materials. Reducing the size of the ZnO to the nano-scale changes its properties significantly [18-21]. Hence, more effort is being dedicated on controlling the size and shape of the nanoparticles; however even to this time remains a challenge in symmetric chemists in the nanotechnology and nano-science field. Different factors such as concentration, precursors, capping molecule, solvents, time, temperature and others are reported to affect the size and shape of the nanoparticles [22, 23] .The synthesis of ZnO nano-paricles may be achieved by physical and chemical route methods. Several numbers of methods for preparation of zinc oxide nanoparticles are reported in literature survey, such as sol-gel, hydrothermal, solution combustion, micro emulsion, microwave irradiation, solvo thermal and co-precipitation chemical route [24, 25]. However, chemical route methods are more suitable for production of high quality zinc oxide nanoparticles in industrial scale [24] due to its simplicity, less expensive, low cost and efficiency in obtaining nanoparticles with uniform particle size and surface morphology [25]. This technique consists of the reaction between a heated sodium hydroxide solution and a zinc nitrate solution at particular temperature. Besides, under controlled temperature, the decomposition of the reactants is initiated causing the immediate formation of ZnO nanoparticles [26, 27].Herein we have discussed the preparation and characterization of ZnO nanoparticles by simple chemical route method.

EXPERIMENTAL PROCEDURE:

Zinc oxide nanoparicles were synthesized by using simple chemical route method [28]. The ZnO nanoparticle was prepared using AR grade 0.2M hexahydrated zinc nitrate [$Zn(NO_3)_2.6H_2O$] mixed with 0.4M sodium hydroxide [NaOH] solution were prepared with distilled water respectively.The sodium hydroxide solution was slowly added in zinc nitrate solution at 80^0C temperature under vigorous stirring, which result in the formation of white color precipitation. The white color product was centrifuged at 5000 rpm for 20 minutes and washed two times with distilled water. The obtained white product was dry under IR lamp for few hours and sintered at 400^0C in air atmosphere for 1hour.

Initially Zinc oxide nanoparticles fine powder sintered at 400^0C for 2 hrs in muffle furnace. The sintered ZnO nanoparticles powder was crushed and mixed thoroughly in an acetone medium by using a mortar and pestle with a glass powder as a permanent binder [29].The paste was prepared by functional material(ZnO), glass powder and ethyl cellulose was mixed together and the mixture was then mixed with butyl carbitol acetate(BCA) to make the paste. The paste was used to prepare ZnO thick films on alumina and glass substrate by using screen-printing method. In this method 140$ mesh size screen was used for preparation of ZnO thick films. After screen printing, the prepared thick film samples were dried under infrared lamp for one hour and then fired at 500^0C for 30 minutes in muffle furnace [30, 31].

The Zinc oxide nanoparticles and its thick films were used for all necessary characterizations. The ZnO nanoparticles thick films fired at 500^0C for 30 minutes. The crystal structures were investigated using X-ray diffraction analysis by Miniflex model,Rigaku Japan, CuKα radiation (λ=1.542AU) from 20 to 80 degree.The average crystallite size of zinc oxide thick film samples were calculated by using Debye Scherrer formula[32]. To estimate optical band gap and the UV optical absorption spectra were measured in the range 200–400 nm by UV-Vis spectrophotometer (JASCO UV-VIS-NIR Model No.V-670).

The infrared spectra of the ZnO nanoparticles sample were recorded at room temperature in the wave number range 400-4000 per cm by a FT-IR spectrophotometer (Shimadzu, FT-IR-6100). By using half bridge method, the DC resistances of the ZnO nanoparticles thick film samples were measured in an air at different temperature [33]. Sheet resistivity of the ZnO nanoparticles film samples was determined from the dimensions of the film sample.To determine the TCR by using the following relation

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) /^0 C \,..\,.....\;(1)$$

Using Arrhenius relation, the activation energy of ZnO nanoparticles thick film samples were evaluated.

$$R=R_o e^{-\Delta E/KT} \quad ....\;(2)$$

Where ΔE is the activation energy of the electron transport in the conduction band, R_o is constant, K is constant and T is absolute temperature.

RESULTS AND DISCUSSION:

X-ray diffraction analysis of ZnO nanoparticle thick films:

Figure 1shows an X-ray diffraction pattern of ZnO nanoparticlesthick films firing at 500^0C in the range $20\text{-}80^0$. The X- ray diffraction pattern of ZnO nanoparticles by co-precipitation method shows several peaks of Zinc Oxide phases indicating random orientation for the polycrystalline nature.The observed peaks shows the presence of phases of ZnO nanoparticles and match well with reported ASTM data confirming hexagonal wurtzite structure[ASTM Card, 36-1451].The X-ray diffraction pattern of the ZnO thick film samples formed at 500^0C by chemical reaction between sodium hydroxide and hexahydrated zinc nitrate was examined.

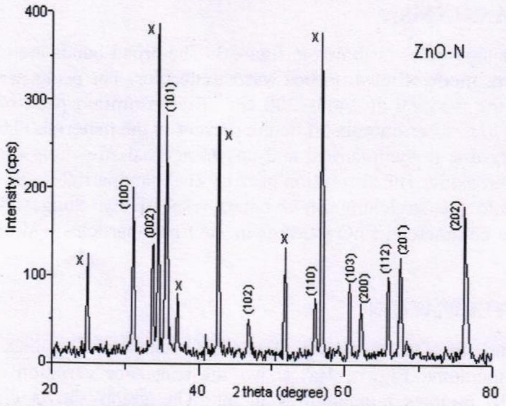

Figure1:XRD pattern of ZnO nanoparticles thick film sample fired at 500^{0}C

The X-ray diffraction pattern of the ZnO thick film samples exhibits hexagonal wurtzite structure (Space group P6$_3$mc and lattice parameters a=3.25 A^0 and C= 5.20 A^0)[34]. It has been observed that (101) reflections are of maximum intensity, which indicates that ZnO nanoparticles thick film samples have preferred orientation in the (101) plane. These peaks are associated with the crystalline planes and originating from (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) of ZnO nanoparticles thick film samples.Two reflections at an angle 2θ=58^{0}and 77.40^0 corresponding to alumina of the substrate were observed. The average crystallitesizeof ZnO nanoparticles thick films fired at 500^{0}C wasobserved as36nm[35].

UV-VIS SPECTROSCOPY ANALYSIS:

Figure 2 shows the optical absorption spectra of ZnO nanoparticlessintered at 400^{0}C in the wavelength range 200–400 nm.It shows a strong absorption band at about 259 nm due to surface Plasmon resonance inZnO nanoparticles. The small shift in the absorption band of ZnO nanoparticles powder samples is attributed to the blue shifted with respect to the bulk absorption edge appearing at 261nm [37] at room temperature. The band gap energy of ZnO nanoparticles can be calculated using the Tauc's relation [38,39].Corresponding value of energy band gap of synthesized form of ZnO is found to be 4.2eV respectively. Large band gap energy and small blue shifted absorption edge confirm that the prepared ZnO Nanoparticles exhibits strong quantum confinement effect (small size).

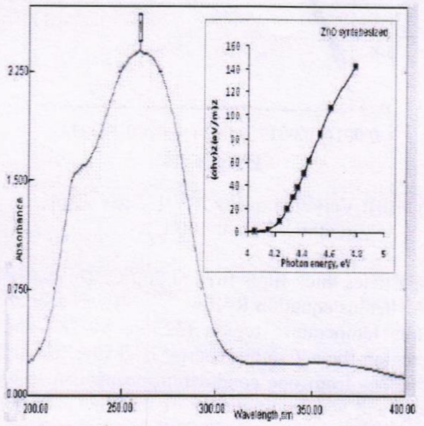

Figure 2: UV Absorption spectra and Band gap energy of ZnO nanoparticles sintered at 400^{0}C.

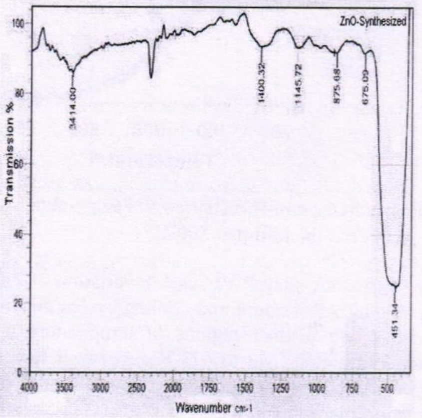

Figure 3: FTIR spectra of ZnO nanoparticles

FT-IR SPECTROSCOPY ANALYSIS:

Infrared spectrum of ZnO nanoparticles is shown in figure 3. The broad bands are observed at 3414cm^{-1} is due to Zn-OH stretching vibrations mode of the adsorbed water molecules. The peaks are due to C-H of alkene may be present as impurities in the material at 2400-2300 cm^{-1}.The absorption peak of ZnO nanoparticles peak observed at 1400 cm^{-1} is due to C=C or quinoid structure present in the materials. The absorption peaks of ZnO nanoparticles at 1145cm^{-1} are due to symmetrical and unsymmetrical stretching of carboxylate group, it may exist as an impurity in the zinc oxide. The absorption peak of ZnO nanoparticles was observed in the range 600-450 cm^{-1}. It was attributed to the stretching Zn-O bonds respectively. Suggestions from IR, no hydrogen bonding was observed in the commercial ZnO whereas in ZnO nanoparticles hydrogen bonding is observed at 3414 cm^{-1}.

ELECTRICAL CHARACTERIZATION:

By using half bridge method, the DC resistance of the ZnO nanoparticles thick films fired at 500^{0}C was measured as a function temperature. **Figure 4(a)** shows the resistance variation of ZnO nanoparticles thick films fired at 500^{0}C for 30 minutes temperatures in air. The graph shows different conduction region; continuous coming down of resistance, an exponential coming down region and (iii) finally the state of being saturated. Increase in temperature of thick film samples causes the electrons to acquire sufficient energy and cross the barrier at grain boundaries [40,41].At higher temperature, the oxygen adsorbates are desorbed from the surface of the ZnO film samples this can decrease in potential barrier at grain boundaries.There is a decrease in resistance with increase in temperature indicating semiconducting behavior, obeying $R=R_O\ e^{-\Delta E/KT}$ in the temperature range of 50 to 400^{0}C.For ZnO nanoparticles film samples fired at 500^{0}C, initially resistance is coming downs linearly up to a certain transition temperature. After the transition temperature, the resistance decreases with exponential fashion and finally saturate to steady level. The varying temperature depends on fired temperature of the ZnO films. The initially measured value of resistance of ZnO nanoparticle thick films air atmosphere (at 27^{0}C) was 428560 Mohm.

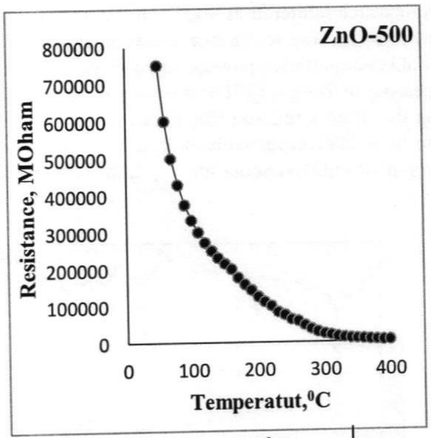

Fig.4(a): Variation of Resistances V^{s}Temperature of ZnO thick film at 500^{0}C

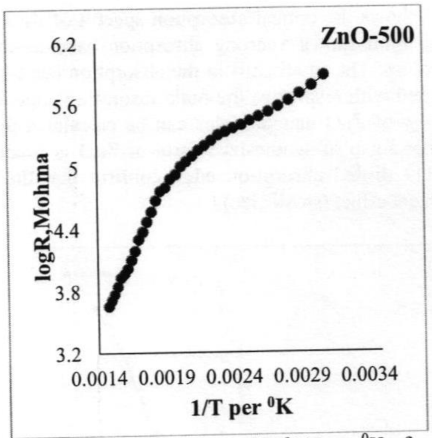

Fig.4(b): Variation of log R V^{s}1/T per ^{0}K of ZnO thick film at 500^{0}C

Figure 4 (b) shows log R versus 1/T variation of ZnO nanoparticles thick films fired at 500^{0}C. This variation is reversible in both heating and cooling cycles obeying the Arrhenius equation $R=Roe^{-\Delta E/KT}$. It was seen that the curve has two distinct regions of temperature namely low temperature region (323 to 403^{0}K) and high temperature region (543 to 673^{0}K). At lower temperature region the activation energy is always less than the energy in the higher temperature region because material passes from one conduction mechanism to another conduction mechanism. The value of TCR, Sheet resistivity and activation energy of the ZnO nanoparticles thick films fired at 500^{0}C are summarized in Table 1.

Table 1: TCR, Sheet Resistivity and Activation energy of ZnO nanoparticles Thick films fired at 500^{0}C [Thickness =10μm]

Fired Temp (^{0}C)	Temperature Coefficient Resistance (per ^{0}C)	Sheet resistivity	Activation energy in eV	
			Low Temperature Region	High Temperature Region
500	6.326x10^{-3}	0.2678 x10^{12}	0.1506	0.5640

CONCLUSION:

Zinc oxide nanoparicles were prepared by simple co-precipitation method. Polycrystalline ZnO nanoparticles -based thick films were fabricated by using standard screen printing technique. The X-ray diffraction pattern of the ZnO nanoparticles thick film samples exhibits hexagonal wurtzite structure. The average crystallite size of the zinc oxide nanoparticles thick film samples was found to be 36nm.No hydrogen bonding was observed in the commercial ZnO whereas in ZnO nanoparticles hydrogen bonding was observed at 3414 per cm.From UV-Vis absorption spectra, it exhibits a strong absorption band at about 259 nm due to surface Plasmon resonance of ZnO nanoparticles. Large band gap energy and small blue shifted absorption edge confirm that the prepared ZnO Nanoparticles exhibits strong quantum confinement effect (small size).At lower temperature region the activation energy is always less than the energy in the higher temperature region.

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REFERENCES:

M.Gusatti, G. SérgioBarroso, C. Eduardo, M. de Campos, D.Aragão, R. de Souza, J. de Almeida, R. Bohn Lima, C. Cardoso Milioli,L. Abreu Silva, H.GracherRiella, N. Cabral Kuhnen, *Effect of Different Precursors in the Chemical Synthesis of ZnONanocrystals*, Materials Research, 14(2), 264-267,2011.

M S Tokumoto, V. Briois, C. V. Santilli, S.H. Pulcinelli, "Preparation of ZnO nanoparticles: structure study of the molecular precursor, *Journal of Sol-Gel Science and Technology,* Vol. 26 (1-3), 547-551,2003.

P. Kumar, L S Panchakarla, S V Bhat, U Maitra, K S Subrahmanyam, C N R Rao, Photoluminescence, white light emitting properties and related aspects of ZnO nanoparticles admixed with graphen and GaN, Nanotechnology, 21(38) Article ID 385701, 2010.

G. Thomas, *Invisible circuits,* Nature, 389(6654), 907-908,1997.

J. Kubota, K.Haga, Y. Kashiwaba, H.Watanabe,B. Zhang, Y.Segawa, Characteristics of ZnO whiskers prepared from organic-zinc. *Applied Surface Science.* 216, 431-435, 2003. doi:10.1016/S0169-4332 (03)00388-X.

Fu Y-S, X-W. Du, J. Sun, Y – F. Song, J. Liu. Single – crystal ZnO cup based on hydrothermal decomposition route. *Journal of Physical Chemistry*. 111, 3863-3867, 2007.

H Reza Ghorbani, F. ParsaMehr, H. Pazok, B.MosavarRahmani, Synthesis of ZnONanoparticles by Precipitation Method, *Oriental Journal of Chemistry*, 31(2),1219-1221.

P. X. Gao, Y. Ding, W. Mai, W. L. Hughes, C. Lao, Z. L.Wang, Materials science: conversion of zinc oxide nanobeltsintosuperlattice-structured nanohelices, *Science*, 309(5741), 1700–1704, 2005.

X. L. Cheng, H. Zhao, L. H. Huo, S. Gao, J. G. Zhao, ZnO nano particulate thin film: preparation, characterization andgas-sensing property, *Sensors and Actuators, B*, 102, 248–252, 2004.

E. Topoglidis, A. E. G. Cass, B. O Regan, J. R. Durrant, Immobilisation and Bioelectrochemistry of proteins onnanoporous TiO_2 and ZnO films, *Journal of ElectroanalyticalChemistry*, 517, 20–27, 2001.

Y. Hames, Z. Alpaslan, A. K¨osemen, S. E. San, Y. Yerli, Electrochemically grown ZnOnanorods for hybrid solar cellapplications, *Solar Energy*, 84, 426–431, 2010.

W. Jun, X. Changsheng, B. Zikui, Z. Bailin, H. Kaijin, W. Run, Preparation of ZnO-glass varistor from tetrapod ZnOnanopowders, *Materials Science and Engineering B*, 95, 157–161, 2002.

P.Sharma, K. Sreenivas, K. V. Rao, Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalancedmagnetron sputtering, *Journal of Applied Physics*, 93, 3963–3970, 2003.

P.V.Kamat,R.Huehn, R.Nicolaescu, A 'sense and shoot' approach for photocatalytic degradation of organiccontaminants in water, *Journal of Physical Chemistry B*, 106,788–794, 2002.

Y.S. Fu, X. W. Du, S. A. Kulinichetal., Stable aqueous dispersion of ZnO quantum dots with strong blue emission via simple solution route, *Journal of the American Chemical Society,* 129, 16029–16033, 2007.

A. Becheri, M. Dürr, P. Nostro, P. Baglioni, Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers, *Journal of Nanoparticle Research,* 10, 679–689, 2008.

Y. S. Fu, X. W. Du, S. A. Kulinichetal. Stable aqueous dispersion of ZnO quantum dots with strong blue emission via simple solution route, *Journal of the American Chemical Society,* 129,16029–16033, 2007.

N. Moloto, M. J. Moloto, N. J. Coville, S. SinhaRay, Optical and structural characterization of nickel selenide nanoparticles synthesized by simple methods, *Journal of Crystal Growth,* 311, 3924–3932, 2009.

Y. W. Jun, J. S. Choi, and J. Cheon, Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes, *AngewandteChemie-International Edition,* 45, 3414–3439, 2006.

C. Tang, S. Fan, M. L. De La Chapelle, H. Dang, P. Li, Synthesis of gallium phosphide nanorods, *Advanced Materials,* 12, 1346–1348, 2000.

J. Yang, J. H. Zeng, S. H. Yu, L. Yang, G. E. Zhou, Y. T. Qian, Formation process of CdSnanorods via solvothermal route, *Chemistry of Materials,* 12, 3259–3263, 2000.

Y. W. Jun, J. S. Choi J. Cheon, Shape control of semiconductor and metal oxide nanocrystals through non hydrolytic colloidal routes, *Angewandte Chemie-International Edition,* 45, 3414–3439, 2006.

C. Tang, S. Fan, M. L. De La Chapelle, H. Dang, P. Li, Synthesis of gallium phosphide nanorods, *Advanced Materials,* 12, 1346–1348, 2000.

C.Wu, X. Qiao, J. Chen, H. Wang, F.Tan, S.Li. A novel chemical routeto prepare ZnO nanoparticles. *Materials Letters.* 60,1828-1832, 2006;. doi:10.1016/j.matlet.2005.12.046

Y.Hu,H.Chen, Preparation and characterization of Nanocrystalline ZnO particles from a hydrothermal process. *Journal of Nanoparticle Research.* 10:401-407, 2008. doi:10.1007/s11051-007-9264-0

M.Vaezi, S.Sadrnezhaad, Nanopowder synthesis of zinc oxide via solochemical processing. *Materials and Design.28,* 515-519, 2007. doi:10.1016/j.matdes.2005.08.016

M.Gusatti, J.Rosário, C.Campos, N.Kuhnen, E.Carvalho, H.Riellaet al. Production and Characterization of ZnOnanocrystalsobtainedbySolochemical processing at different temperatures. *Journal for Nanoscience and Nanotechnology.* 10,4348-4351, 010.doi:10.1166/jnn.2010.2198

D. Bahnemann, C. Kormann, M. Hoffmann, Preparation and characterization of quantum size zinc oxide: a detailed spectroscopic study, *Journal of Physical Chemistry,* 91, 3789–3798, 1987.

L I Maissel, R Glang R (Eds.) *Hand book of thin film technology,* McGraw-Hill, New York, (1974)

K. Jain , R. Pant ,S.Lakshikumar, *Effect of Ni doping on thick film SnO_2 gas sensor.* Sensors and Actuators,B 113,823- 829,2006.

A.Garje, R.Aiyer, Electrical and Gas-sensing Properties of a thick film resistor of nanosized SnO_2 with variable percentage of permanent binder. *Int.J. Appl. Ceram.Technol,* 3[6], 477-484, 2006.

B D Cullity, Elements of X-ray diffraction, Addison-Wesley Publishing Co.(1956).

G Sarladevi, S. Manoramma, V.Rao, Gas sensitivity of SnO_2/CuO heterocontact. *Journal of Electrochemical Society,* 142[8], 2574-2577, 1995.

M.Gusatti, G.SergioBarroso, D.AragdoRiberio, D. Souza, Effect of different Precursors in the Chemical Synthesis of ZnO Nanoparticles. *Material research,* 14 (2):264-267,2011 DOI: 10.1590/s1516-14392011005000035

V. T. Salunke, Synthesis and Characterization of nanostructure ZnO Thick film Gas sensors prepared by screen printing method, *Sensors and Transducer,* 9,161-170, 2010.

J. Desai, C. Lokhande, *Material chem. Physics*.34, 313-316, 1993.

S. Samual M, L. Bose, K C George, Optical properties of ZnO nanoparticles, *Academic Review* XVI: 1&2 57-65, 2009

S Kulkarni, S Joshi, C Lokhande, Facial and efficient route for preparation of nanostructured polyaniline thin films: Schematic model for simplest oxidative chemical polymerization, *Chemical Engineering Journal,* 166,1179-1185, 2011.

S. Talam, S. Karumuri, N. Gunnam, Synthesis, Characterization and Spectroscopic Properties of ZnO Nanoparicles. *ISRN Nanotechnology,* 1D, 1-6, 2012.

R.Y.Borse, A.S. Garde, Effect of Firing temperature on electrical and structural characteristics of SnO_2 thick films. *Indian J Physics*, 82 (10) 1319-1328, 2008.

H. Windichmann and P. Mark, A Model for the Operation of a Thin-Film SnO_x conductance – Modulation Carbon Monoxide Sensor. J. *Electrochem. Soc.* 126, 627-633, 1979.
