International Journal of Pure and Applied Mathematics
Volume 120 No. 5 2018, 1149-1162
ISSN: 1314-3395 (on-line version)
url: http://www.acadpubl.eu/hub/
Special Issue
http://www.acadpubl.eu/hub/

Nitrogen dioxide (NO_2) Gas Sensing Characteristics of ZnO – Na CMC Thin film Prepared by Sol-Gel Dip Coating Method

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ABSTRACT

Nitrogen dioxide sensing characteristics of Zinc Oxide thin films prepared by sol-gel dip coating method are discussed in this paper. The sol-gel for dip coating was synthesized using Zinc nitrate hexahydrate (Zn (NO3)2.6H2O) and organic polymer Sodium Carboxy Methyl Cellulose (Na- CMC) as a starting material. Crystallinity and crystallite size of the prepared thin film was characterized by X-ray diffraction (XRD). Morphology was studied using Scanning Electron microscope (SEM). The gas sensing characteristics was studied using chemiresistive method, by exposing the ZnO – Na CMC film to various concentrations of NO_2 gas at room temperature. Gas sensing parameters such as response, selectivity, lowest detection limit, response/recovery time of the ZnO-Na CMC thin film towards NO_2 were also reported.

Keywords: ZnO, Na-CMC, sol-gel dip coating, thin film, NO_2 gas sensor.

INTRODUCTION

In modern days, nano materials with size less than 100nm are widely investigated by researchers because of its interesting surface, volume effects [1], large surface to volume ratio, reduced particle size etc., [2]. These nano materials have a unique physical, chemical and optical property [3] which leads to its application in abundant fields. Currently use of nano materials in the field of gas sensor has gained interest as it helps in detection of toxic and combustible gases [4]. The excess of noxious and combustible gases cause degradation to environment and are hazardous to human health. The fabrication of gas sensor with good sensitivity, selectivity, quick response and recovery time to the lowest concentration of target gas together with low operating temperature is an art of interest. From the various materials (metal oxides, organic compounds, polymers, metals., etc.,) Semiconducting metal oxide nano particles are extensively studied for gas sensing application due to tiny dimension, suitable operating temperature, more surface sites available for gas adsorption, high response for many gases, low cost, portability, non-toxicity etc., [5,6].

Zinc oxide is an intrinsic n-type semiconductor with wide band gap is one of the most widely studied materials for gas sensing application [7]. It offers several advantages like high electron mobility, nontoxic nature, copious availability and high chemical stability [8–10]. It is prepared in many forms such as single crystal, powder, pellet, thin film and thick film [11–13] among these, thin films has good sensing response towards reducing and oxidizing gases [14]. Sensing characteristics of the thin film greatly depends on surface state and morphology of semiconducting metal oxide which act as a chemical reaction centre. To get customized surface states preferable for sensing application sol gel dip coating method has selected as a film deposition technique.

Dip coating method is a simple, cost efficient and wet chemical method which is generally used for ZnO thin film fabrication. In this method thickness, porosity and morphology of the thin film can be changed by controlling sol-gel concentration, withdraw speed, dipping and drying time also superior film area can be covered when compared to spin coating. Here Dip coating was done by the automated dip coating unit (HOLMARC, HO-TH-01). Sol-gel preparation, thin film coatings was followed by heat treatment is the steps followed in sol gel dip coating method. Adhesiveness of the coated film on the substrate depends upon viscosity of sol-gel. Na-CMC is used in sol-gel preparation, because of film forming ability due to plentiful OH group and its characteristic thickening properties. Na-CMC is an inorganic green polymer which is easily soluble in water. Viscosity builder, stabilizer and emulsifier are some of the general utilities of Na-CMC. Its property mainly depends on molecular weight (MW) and degree of substitution that is number of OH groups substituted per an-hydro glucose unit. 0.7 degree of substitution of CMC is most commonly used.

Nitrogen dioxide is a chemical compound which is reddish brown gas that has a characteristic sharp, biting odor and is prominent air pollution. NO_2 is paramagnetic bent molecule with C_{2V} point group symmetry. NO_2 is a highly poisonous gas that exposure produces inflammation of lungs that many only cause slight pain or pass unnoticed, but resulting edema several days later may cause death. NO2 is a major atmospheric pollutant that is able is to absorb UV light that does not reach the earth's surface. Hence, we focus our work towards fabrication of ZnO thin film which could detect the NO_2 gas at room temperature.

MATERIALS AND METHODS

A homogeneous solution was obtained by dissolving 4.68gms of zinc nitrate hexa hydrate in 100 mL of deionized water, which acts as a precursor solution. Additionally, 2gms of Na-CMC is dissolved in 100mL of deionized water, which acts as a thickening agent. Precursor solution was added little by little to the thickening agent with the flow rate of 1mL/min. Colour change was observed when 8mL of precursor solution was added, which indicates the formation of ZnO nano particles. Throughout the entire process the solution was kept under constant stirring and the temperature maintained was 70^0C (±2^oC) at last white colour viscous solution was obtained.

The obtained solution was kept for ageing with constant stirring for 12 hours. The aged solution was used as a sol-gel for dip coating. Glass substrates are ultrasonically cleaned with deionized water, acetone and Isopropyl alcohol for 10 minutes each. ZnO – Na CMC Thin films were obtained by immersing the substrate into the sol, dip for 3minutes, draw vertically with the speed rate of 9000 μsec and dried at 75^oC for 5 minutes. The above mentioned process was repeated 10 times to get a uniform coating. It was then annealed at 350^oC, 400^oC and 450^oC for 3 hours to get crystalline ZnO thin film nano particles. Na-CMC is mostly used to get customized nano particles and to provide adhesion of ZnO nano particles on untreated glass substrate.

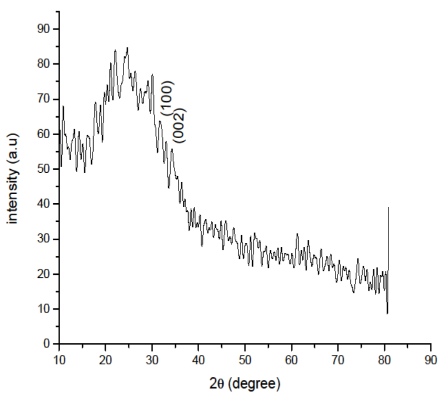
CHARACTERIZATION

X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) characterizations were done to determine Crystallinity, crystallographic structure, crystallite size and surface morphology of the ZnO- Na CMC thin film annealed at 350^{o}C, 400^{o}C and 450^{o}C. The XRD pattern was obtained by X-ray powder diffractometer (PAN analytical X-ray diffractometer) equipped with Cu Kα radiation having wavelength of 0.1548nm as a source. The crystallite size was calculated using Debye Scherrer's formula.\

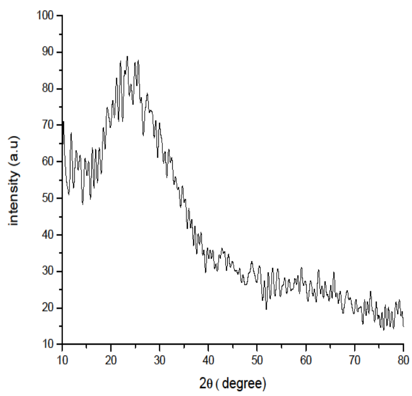
$$D = \frac{k\lambda}{\beta\cos\theta}$$

RESULTS AND DISCUSSIONX-RAY DIFFRACTION

The crystalline nature of dip coated thin film was characterized by XRD. Figure 1. Shows the XRD pattern for the films annealed at 350^{0}C, 400 and 450^{0}C, Where the peak positions 31.77^{0}and 34.42^{0}are the characteristic peaks of all ZnO films at [100], [002] plane respectively. The occurrence of hexagonal wruzite structure was confirmed using [002] plane and Peak broadening concludes the formation of nano particles. The average crystallite size of the film was measured using equation (1) and it was found to be around 25nm. Due to very thin layer of film coated on glass substrate, a strong hump was seen on XRD pattern of ZnO thin film less than 35^{0}.



(a)



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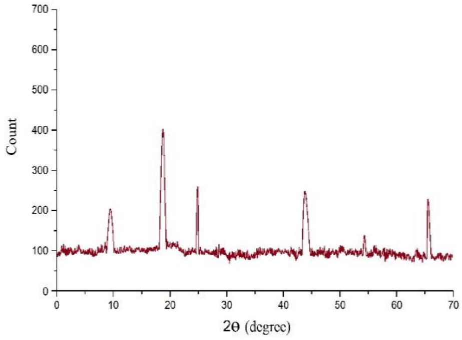
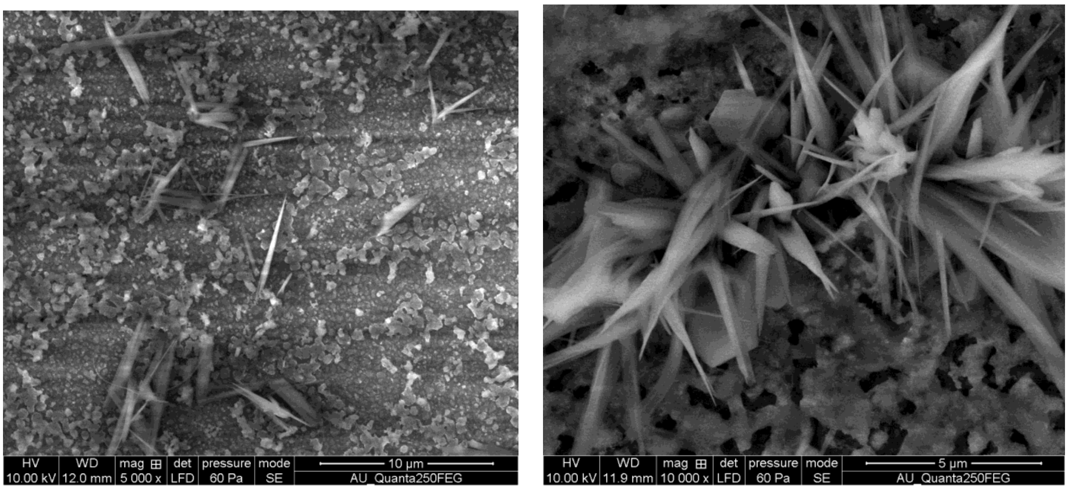


(c)

Figure 1: XRD patterns of ZnO – Na CMC film annealed at 350^0C, 400^0C and 450^0C

SEM ANALYSIS

SEM images of ZnO thin film shows a hexagonal morphology as depicted in Figure 2. Due to agglomeration, overall morphology resembles like nanotubes, nano needles and some of them are amorphous in nature.



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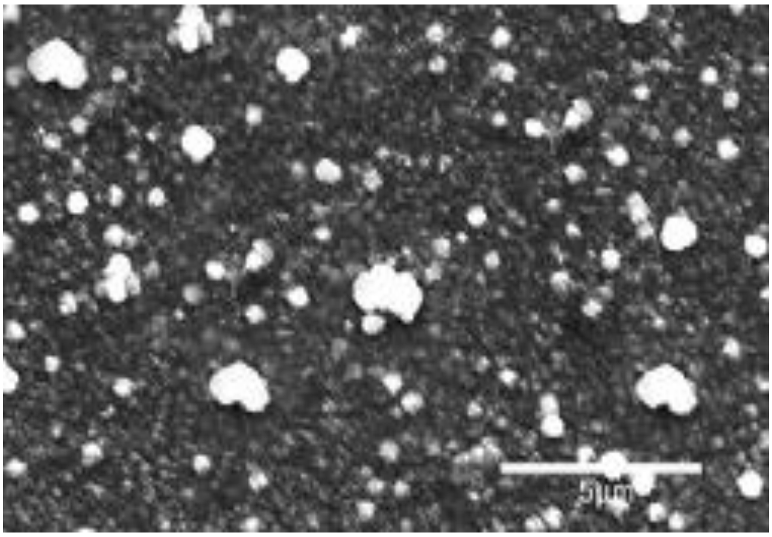

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Figure 2: SEM images of ZnO – Na CMC film annealed at 350^0C, 400^0C and 450^0C

STUDY OF GAS SENSOR PROPERTIES

Gas Sensing studies were made on basis of chemiresistive method, in which the chemical reaction between adsorbed oxygen on the material surface and the target gas results in variation of resistance.

When the thin film is exposed to air, atmospheric oxygen gets adsorbed on the film surface in any one of the form O^{2-}, O^-, O_2^-. This chemisorbed oxygen capture electron from the surface of the film, as a consequence of which an electron deficient region is formed near the film surface. It leads to enlarge in height of the potential barrier and it causes an raise in resistance of the material. The point at which the resistance remains approximately stable is considered as base resistance. When a trial gas is injected into the test chamber, they readily react with the chemisorbed oxygen. As a result of chemical reaction between chemisorbed oxygen and test gas resistance transformation occurs in two possible ways. If the test gas is an oxidizing gas, they trap more electrons from the material surface results in increase of resistance from the base resistance. While for reducing gas, the attentive electrons are released back to the film surface and hence resistance of the film decreases from the base resistance. The ratio between changes in resistance from the base resistance is said to be response of the sensing material.

For reducing gas $$S = \frac{R_a}{R_g}$$

For oxidizing gas $$S = \frac{R_g}{R_a}$$

Where R*a* is the resistance of the film in air and R*g* is the resistance of the film in the presence of test gas.

In this paper, sensor response towards test gas NO_2 was measured at room temperature using a computer interfaced dynamic gas sensing setup. The set up used was same as the one reported. To know the sensing characteristics of fabricated ZnO thin film, response of the film towards 105, 10 and 170 ppm of NO_2 was estimated. Response of the film towards test gas was calculated using above equation. Transient response of the film towards mentioned ppm is illustrated in Fig.3 and its corresponding histogram is shown in Fig.4. From the result, maximum resistance change was observed for NO_2 and its corresponding magnitude of response was 280, 390 and 500. Compared within the films annealed at 350^0C has less response and 500^0C has good response, observed for NO_2. This variation in magnitude of response arises from the amount of chemisorbed oxygen on the surface of the film and the variation in interaction strength of the test gas with the surface of the sensing element [47]. The NO_2 sensing mechanism involves the following phenomena. After attaining the base resistance, 170 ppm was injected into the closed test chamber. Due to its reducing nature, NO_2 tends to release the trapped electrons back onto the ZnO thin film surface. This leads to decrease in height of the potential barrier so the conduction increases. This causes resistance to fall from its base resistance.

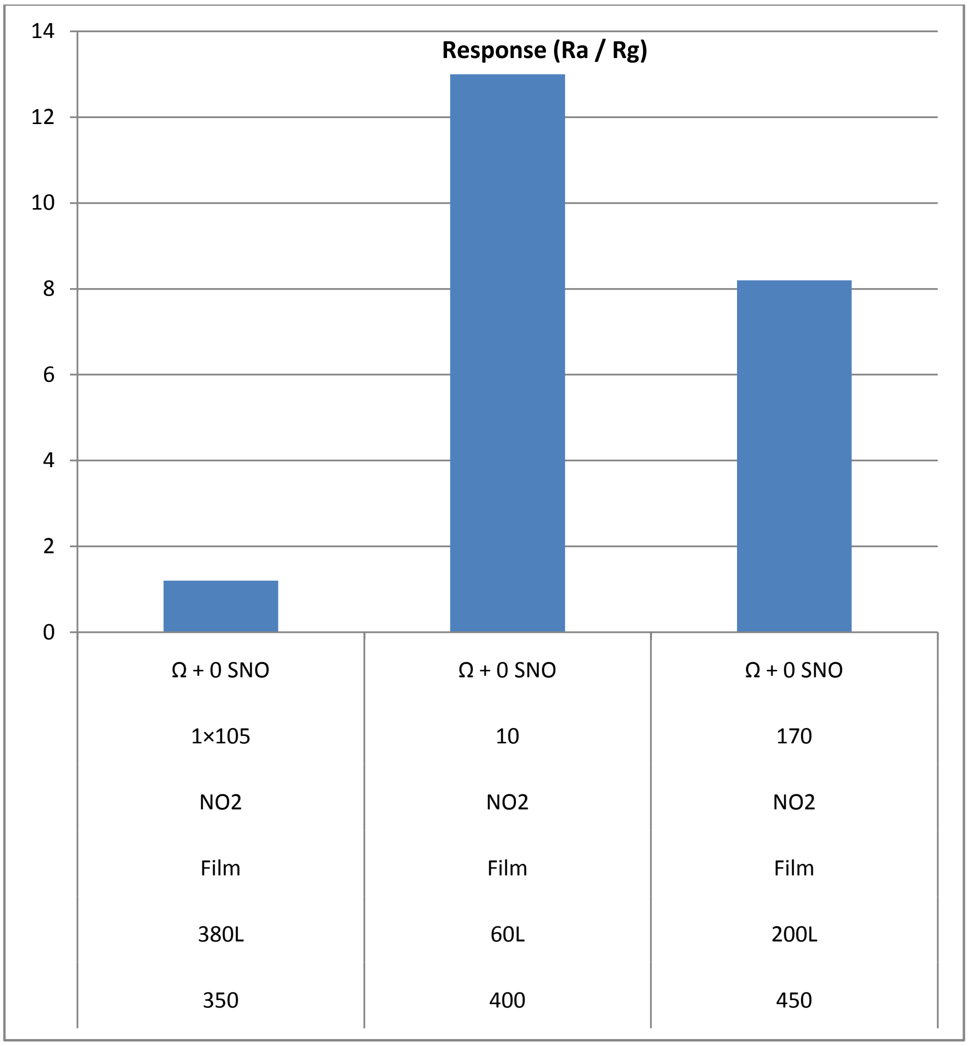
In general, the response time of the sensor towards test gas decreases with increase in test gas concentration [44,51]. In our work that was observed above 150 ppm, below which an unusual trend was observed with increase in concentration. However, in recovery time both the trends were observed for various concentration. Table 1 represents the response and recovery time for various concentrations of NO_2, from the results obtained the dip coated thin film has the lowest detection limit of 10 ppm with the response time of 10 seconds at room temperature, but it lacks high response (S = 1.20). The selective sensing mechanism of ZnO based materials to acetone is still not explained or understood. At the same time, high sensitivity of ZnO to acetone was attributed to the powerful interaction force between the spontaneous electric dipole moment of ZnO and the largest dipole moment of NO_2 compared to the other test gases used.

TABLE 1: GAS SENSOR RESULT FOR VARIOUS TEMPERATURES

Temperature	**Features nm**	**Form**	**Test Gas**	**Top^{O}c**	**Ppm**	**Sensor type**	**Response time / Recovery time**
350^{0}c	380L	Film	NO2	280	1×105	Ω + 0 SNO	1.20
400^{0}c	60L	Film	NO2	390	1x10	Ω + 0 SNO	13
450^{0}c	200L	Film	NO2	410	1x170	Ω + 0 SNO	8.2

Tdep – temperature of deposition, Top - operating temperature, Tres – response time,

Ppm – part per million, R = Ra / Rg (oxidative gas), R = Rg / Ra (reduction gas).



Responses of the sensors based column representation on ZnO (Na-CMC)

Conclusion

ZnO – Na CMC thin films have been fabricated by sol-gel dip coating technique and its gas sensing characteristics were studied. Crystallinity and the existence of most even hexagonal wurtzite structure were confirmed with X-Ray Diffraction. The sensing test was carried out in a closed chamber using chemiresistive method at room temperature ^{0}C. The results showed that the fabricated ZnO- Na CMC thinfilm can act as a NO_2 gas sensor, since it shows high response among the test gases and also it exhibit higher selectivity for nitrogen with the value of 80%. Response and recovery time for various concentration of NO_2 is in the order of seconds. The lowest detection limit of room temperature ZnO-NA CMC thin film was observed with the response of 1.20.

FINANCIAL SUPPORT AND SPONSORSHIP:

-NIL

CONFLICT ON INTEREDT:

-There are no conflicts of interest.

ACKNOWLEDGMENTS:

-The author is sincere thanks to DR. P.Gowthaman, HOD., M. Venkatachalam , M.Saroja

Erode arts and science college erode, for supporting and providing the facility of work in the lab.

References

[1] C.S. Prajapati, A. Kushwaha, P.P. Sahay, Influence of Fe doping on the structural , optical and acetone sensing properties of sprayed ZnO thin films, Mater. Res. Bull. 48 (2013) 2687–2695. doi:10.1016/j.materresbull.2013.03.026.

[2] D.P. Macwan, P.N. Dave, S. Chaturvedi, A review on nano-TiO2 sol–gel type syntheses and its applications, J. Mater. Sci. 46 (2011) 3669–3686. doi:10.1007/s10853-011-5378-y.

[3] P. Rai, S. Raj, K.-J. Ko, K.-K. Park, Y.-T. Yu, Synthesis of flower-like ZnO microstructures for gas sensor applications, Sensors Actuators B Chem. 178 (2013) 107–112. doi:10.1016/j.snb.2012.12.031.

[4] B. Lyson-sypien, A. Czapla, M. Lubecka, P. Gwizdz, K. Schneider, K. Zakrzewska, et al., Nanopowders of chromium doped Tio2 for gas sensors, Sensors Actuators B Chem. 175 (2012) 163–172. doi:10.1016/j.snb.2012.02.051.

[5] N. Kakati, S.H. Jee, S.H. Kim, J.Y. Oh, Y.S. Yoon, Thickness dependency of sol-gel derived ZnO thin films on gas sensing behaviors, Thin Solid Films. 519 (2010) 494– 498. doi:10.1016/j.tsf.2010.08.005.

[6] R.C. Pawar, J.-W. Lee, V.B. Patil, C.S. Lee, Synthesis of multi-dimensional ZnO nanostructures in aqueous medium for the application of gas sensor, Sensors Actuators B Chem. 187 (2013) 323–330. doi:10.1016/j.snb.2012.11.100.

[7] P.P. Sahay, Zinc oxide thin film gas sensor for detection of acetone, J. Mater. Sci. 40 (2005) 4383–4385. doi:10.1007/s10853-005-0738-0.

[8] S. Ozturk, N. Kıilinç, N. Tasaltin, Z.Z. Ozturk, A comparative study on the NO2 gas sensing properties of ZnO thin films, nanowires and nanorods, Thin Solid Films. 520 (2011) 932–938. doi:10.1016/j.tsf.2011.04.177.

[9] M. Aslam, V.. Chaudhary, I.. Mulla, S.. Sainkar, a. . Mandale, a. . Belhekar, et al., A highly selective ammonia gas sensor using surface-ruthenated zinc oxide, Sensors Actuators A Phys. 75 (1999) 162–167. doi:10.1016/S0924-4247(99)00050-3.

[10] A. Kulandaisamy, C. Karthek, P. Shankar, G.K. Mani, J. Balaguru Rayappan, B. Rayappan, Tuning selectivity through cobalt doping in spraypyrolysis deposited ZnO thin films, Ceram. Int. 42 (2016) 1408–1415.

[11] S. Kalpana Rajan, K.N. Marimuthu, M. Priya, Synthesis of Zno Nano Rods by Dip Coating Method, Arch. Appl. Sci. Res. 4 (2012) 1996–2001.

[12] R. Mariappan, V. Ponnuswamy, R. Suresh, P. Suresh, a. Chandra Bose, M. Ragavendar, Role of substrate temperature on the properties of Na-doped ZnO thin film nanorods and performance of ammonia gas sensors using nebulizer spray pyrolysis technique, J. Alloys Compd. 582 (2014) 387–391. doi:10.1016/j.jallcom.2013.08.048.

[13] D. Sivalingam, J.B. Gopalakrishnan, J.B.B. Rayappan, Structural, morphological, electrical and vapour sensing properties of Mn doped nanostructured ZnO thin films, Sensors Actuators B Chem. 166-167 (2012) 624–631. doi:10.1016/j.snb.2012.03.023.

[14] N. Hongsith, C. Viriyaworasakul, P. Mangkorntong, N. Mangkorntong, S. Choopun, Ethanol sensor based on ZnO and Au-doped ZnO nanowires, Ceram. Int. 34 (2008) 823–826. doi:10.1016/j.ceramint.2007.09.099.

[15] G.S.T. Rao, D.T. Rao, Gas sensitivity of ZnO based thick film sensor to NH 3 at room temperature, Sensors Actuators B. Chem. 55 (1999) 166–169.

[16] G.K. Mani, J.B.B. Rayappan, A highly selective room temperature ammonia sensor using spray deposited zinc oxide thin film, Sensors Actuators B Chem. 183 (2013) 459–466. doi:10.1016/j.snb.2013.03.132.

[17] P. Shankar, J.B.B. Rayappan, Spray Deposited Nanostructured Zinc Oxide Thin Film as Room Temperature Ethanol Sensor—Role of Annealing, Sens. Lett. 11 (2013) 1956–1959. doi:10.1166/sl.2013.3051.

[18] A. Wei, L. Pan, W. Huang, Recent progress in the ZnO nanostructure-based sensors, Mater. Sci. Eng. B. 176 (2011) 1409–1421. doi:10.1016/j.mseb.2011.09.005. [19] D. Sivalingam, J.B. Gopalakrishnan, J.B.B. Rayappan, Structural, morphological, electrical and vapour sensing properties of Mn doped nanostructured ZnO thin films, Sensors Actuators B Chem. 166-167 (2012) 624–631. doi:10.1016/j.snb.2012.03.023.

[20] R. Pandeeswari, R.K. Karn, B.G. Jeyaprakash, Ethanol sensing behaviour of sol–gel dip-coated TiO2 thin films, Sensors Actuators B Chem. 194 (2014) 470–477. doi:10.1016/j.snb.2013.12.122.

[21] C. Ge, C. Xie, S. Cai, Preparation and gas-sensing properties of Ce-doped ZnO thinfilm sensors by dip-coating, Mater. Sci. Eng. B. 137 (2007) 53–58. doi:10.1016/j.mseb.2006.10.006.

[22] S.S. Nath, M. Choudhury, D. Chakdar, G. Gope, R.K. Nath, Sensors and Actuators B : Chemical Acetone sensing property of ZnO quantum dots embedded on PVP, Sensors Actuators B. Chem. 148 (2010) 353–357. doi:10.1016/j.snb.2010.06.001.

[23] M. Vanaraja, K. Muthukrishnan, S. Boomadevi, R.K. Karn, V. Singh, P.K. Singh, et al., Dip coated nanostructured ZnO thin fi lm : Synthesis and application, Ceram. Int. 42 (2016) 4413–4420. doi:10.1016/j.ceramint.2015.11.125.

[24] Sounder. J *1, P.Gowthaman1 , M. Venkatachalam1, M. Saroja1, and V.K. Evanjelene2 A Review of Zinc Oxide Photo Anode Films for Dye-Sensitized Solar Cells based on Zinc Oxide Nanostructures ,Sounder. J et al./ Elixir Elec. Engg. 99 (2016) 43075-43078 43075

[25] Sounder. J *1, P.Gowthaman1 , M. Venkatachalam1, M. Saroja1, A Review of Gas Sensors Based on Semiconducting Metal Oxide IOSR Journal of Electrical and Electronics Engineering (IOSR-JEEE) e-ISSN: 2278-1676,p-ISSN: 2320-3331, Volume 12, Issue 2 Ver. I (Mar. – Apr. 2017), PP 47-54

[26] Sounder. J *1, P.Gowthaman1 , M. Venkatachalam1, M. Saroja1, ZNO Gas Sensor Thin Film Preapared by Sol-Gel Dip Coating Method *IOSR Journal of Applied Chemistry (IOSR-JAC)* e-ISSN: 2278-5736.Volume 10, Issue 8 Ver. I (August. 2017), PP 14-19

[27] Sounder.J1, P.Gowthaman2, M. Venkatachalam3, M.Saroja4, G.Parthasarathy5 ZNO Thin Film Prepared By Dip Coating Technique for Gas Sensing Application International Journal for Research in Applied Science & Engineering Technology (IJRASET**)** ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor:6.887 Volume 5 Issue X, October 2017- Available at www.ijraset.com

[28] Sounder. J.*, P.Gowthaman, M. Venkatachalam, M.Saroja Zno Gas Sensor Thin Film preapared by Sol-Gel Dip Coating International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.10 No.12, pp 364-371, 2017

[29] Sounder.J1, P.Gowthaman2, M. Venkatachalam3, M.Saroja3, S.Shankar4, M. kutraleeswaran4. ZnO Thin Film Acetone Sensor Prepared By Dip Coating Technique IAETSD JOURNAL FOR ADVANCED RESEARCH IN APPLIED SCIENCES VOLUME 5, ISSUE 1, JAN/2018 ISSN NO: 2394-8442