Gas Sensing Activity of Cu doped ZnO Thin Films Prepared by Sol-Gel Dip-Coating Method

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ABSTRACT : No_2 sensing characteristics of Zinc Oxide thin films prepared by sol-gel dip coating method are discussed in this paper. For sol gel preparation the researcher using Zinc Nitrate hexahydrate (Zn $(NO_3)_2$ .6 H_2o) and sodium carboxy methyl cellulose (Na-CMC) as basic material the crystallite size of the prepared thin film was characterized by X-ray diffraction (XRD). Morphology was studied using Scanning Electron microscope (SEM). The main gas sensing characteristics was studied by using chemiresistive method. Gas sensing parameters such as selectivity, response or recovery, response, time of the Cu-doped ZnO-(Na CMC) thin film towards NO_2 were also reported.

I.INTRODUCTION

The thin film nano material surface volume will more effects (C.S. Prajapati & others2013). The nano materials have unique separate physical, chemical and optical properties (B. Lyson-sypien & others, 2012). Now days we use nano material in the field of gas sensors it help in toxic and combustible gases (P. Rai& others, 2013)

The Reason for choose dip-coating is a simple, cost effective and also the wed chemical method which widely used for ZnO (T.T. Trinh &others, 2011). In this present work the dip coating was prepared by automated dip coating units. After the sol prepared, thin film coated followed by heating furnace are step followed in sol-gel dip coating method (C.H. Chia & others ,2013). From this method the thickness, uniformity porosity and morphology are altered by controlling sol-gel concentration, withdraw speed timing and dipping and drying time (K. Thongsuriwong & others,2013).

The glueness of the thin coated film on the substrate depends upon the viscosity of solution. The (Na-CMC) is used for sol-gel preparation because of it film forming ability due to were rich OH –group (K. Shao & others, 2008)

II.MATERIALS AND METHODS

Preparation of Cu doped ZnO Thin Films

Preparation of Cu doped ZnO thin film The sol of 0.3Mol concentration was prepared by dissolving the required amount of Zinc nitrate hexahydrate ($Zn(NO_3)2.6H_2O$) and copper nitrate hexahydrate (Cu(NO3)2.6H2O) into 100ml of ethanol is used as the host and dopant precursors. Then homogeneous solution was start stirred for 1hr to accelerate hydrolysis reaction to change it as blue colored sol-gel, which is used for coating. ZnO thin films are prepared and depositing sol on the glass substrate by using dip-coating method, that time duration as 5 minute of dip and 5 minute dry at 75^0C and this is repeated for 10 times. Then subsequently coated films are calcinated by annealing at 350^0C, 3hrs to achieve the Cu doped ZnO thin films. Finally the Cu-ZnO thin films are allowed to further it has taken for studies (N. Kakati, S.H. Jee, S.H. Kim et al.,2010).

III. RESULTS AND DISCUSSION

Structural characterizations were carried out via XRD, FESEM and Gas Sensor for sample of Cu doped ZnO thin films are discussed below.

XRD patterns for Cu doped ZnO Thin Films

The peak is found to vary with 350^0C annealing temperatures. The detected (h k l) peaks are 2θ values of

31.08°, 34.60° and 36.60° corresponding to the lattice planes (100), (002) and (101) respectively. They are in agreement with the standard JCPDS 036-1451 card for hexagonal wurzite structure from ZnO.

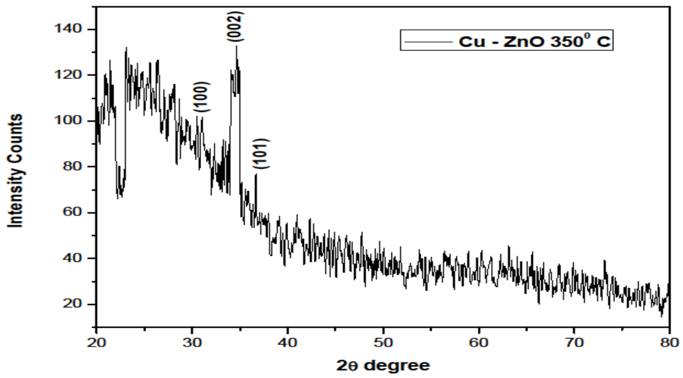

Fig- 1 XRD Image for 350°C

X-ray powder diffractometer equipped with Cu Kα radiation having wavelength of 0.1548nm as a source. The crystallite size was calculated using Debye Scherrer's formula,

$$D = \frac{K\lambda}{\beta \, \mathrm{Cos}\,\theta} \, \text{Å}$$

The incidence 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 (Debye Scherrer's) formula and it was found to be 20 nm.

SEM Analysis

Shows FESEM image of ZnO Sample annealed at 350°C. The image shows the structure consisting of clusters balls and depicts the observation of more agglomeration of ZnO nanoparticles.

FE-SEM consist of a large quantity of nanoparticles in various diameter and porous in nature.

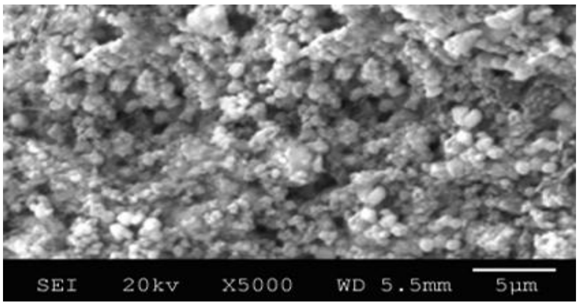

Fig-2 SEM image for 350°c

Electrical resistivity for Cu doped ZnO 350°C

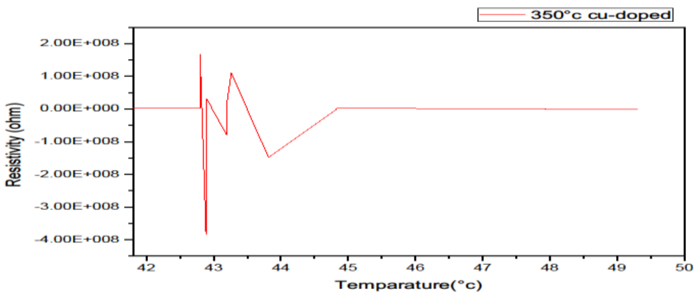

Fig-3 Electrical resistivity for Cu doped ZnO 350°C

The electrical resistivity of the Cu doped ZnO thin films annealed at 350°C are obtained. The Cu doped ZnO sample prepared at 350°C shows a NTCR resistivity of $1.5x10^{-4}$ M Ωm at 42.80°C. The samples Cu doped ZnO 350°C the evolution of resistivity with temperature have three different distinct regions. In region I, the resistivity of the sample is observed sharply increasing with temperature to ~42.7°C. The sample exhibits PTCR character in this region. On further heating, the resistivity of the sample starts decreasing with a maximum resistivity of $1.5x10^{-4}$ M Ωm at around 42.9°C in region II. The change in resistivity is observed to be from $1.5x10^{-4}$ M Ωm x to$1.5x10^{3}$ M Ωm and exhibits PTCR behavior. In region III, a decrease in resistivity with an increase in temperature (i.e. NTCR behavior) is observed for the sample up to the present experimental range $1.5x10^{1}$ M Ωm x to$1.5x10^{-2.9}$ M Ωm.

For resistivity properties, when the film is act as a resistor, so when the temperature is increases the resistivity get decreases, so it confirm that the film have good resistivity properties.

V-I CHARACTERISTICS

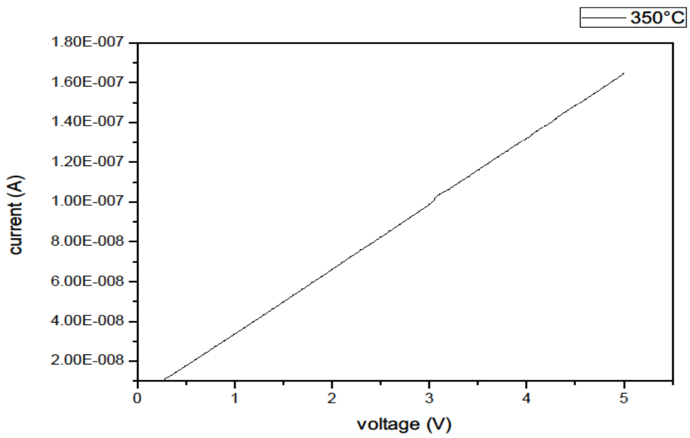

Fig -4 V-I CHARACTERISTICS for Cu doped ZnO 350°C

The electrical property of the Cu doped ZnO thin films annealed at 350°C are obtained. The Cu doped ZnO sample prepared at 350°C shows a voltage of 0v to + 5v at current 1.60E -007. For electrical properties when the voltage is increase current also get increase due to in conducting properties, so when the film is suitable for gas sensing applications.

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. In our work, sensor response towards NO_2 gas was measured at room temperature using a computer interfaced dynamic gas sensing setup. The sensing characteristics of prepared Cu doped ZnO thin film annealed at 350°C response of those films towards 200ppm of NO_2 gas was estimated.

Table: Gas sensor result for 350^0C temperatures

Precursors	***CVD Method***	***Form***	***Features nm***	***Sensor type***	***T_{op} ^0C***	***P_{pm}***	***Gas***	***Ra/Rg***
Copper Doped Zno350^0c	***CVD***	***Film***	***780L***	***Ω + 0***	***350***	***200***	***NO_2***	***45s***

Tdep – temperature of deposition, Top - operating temperature, Tres – response time,
Ppm – part per million,
R = Ra / Rg (oxidative gas),
R = Rg / Ra (reduction gas).

Where Ra is resistance of the film in air and Rg is the resistance of the film in presence of test gas. In the researcher work that the sensor response target gases such as acetone, NO_2. The computer dynamic gas sensing setup was used in same one of paper (D. Sivalingam, J.B. Gopalakrishnan et al., 2010)

From the result, the maximum resistance changes was observed in Cu doped ZnO thin films. Its corresponding magnitude of response was 45s for ZnO 350°C. These variations in amount of response arise from the amount of chemisorbed oxygen on the surface of the Film and its variations in interaction strength the test gas with the surface of the sensing element (Sounder. J, P.Gowthaman et al., 2017). After attaining the base resistance, 200 ppm of NO_2 was injected into the closed test chamber. Due to its oxidizing nature, NO_2 tends to release the trapped electrons back onto the ZnO thin film surface. This will be leads to decrease in height of the potential obstruction so the conduction increases. This make resistance to fall from its base resistance.

IV. CONCLUSION

The ZnO thin films of sol-gel dip coating method and its gas sensing characteristics were studied. The most stable Nano balls in shape nano structure were confirmed by XRD. The sensor test was done by closed chamber at room temperature. The test shown that ZnO thin film can act as a No_2 sensor for an selectivity of constant values. The limit of room temperature lower detection of ZnO thin film observed to 200ppm of NO_2 with the response of 45S. Hence the Researcher could show that it has identified diabetes.

REFERENCES

1. D.P. Macwan, P.N. Dave, S. Chaturvedi, (2011) A review on nano-TiO2 sol–gel type syntheses and its applications, J. Mater. Sci. 46 3669–3686. doi:10.1007/s10853-011-5378-y.
2. C.S. Prajapati, A. Kushwaha, P.P. Sahay, (2013). Influence of Fe doping on the structural , optical and acetone sensing properties of sprayed ZnO thin films, Mater. Res. Bull. 48 doi:10.1016/j.materresbull.2013.03.026. PP-2687–2695
3. B. Lyson-sypien, A. Czapla, M. Lubecka, P. Gwizdz, K. Schneider, K. Zakrzewska, et al., (2012). Nanopowders of chromium doped Tio2 for gas sensors, Sensors Actuators B Chem. 175 doi:10.1016/j.snb.2012.02.051.,PP-163– 172
4. P. Rai, S. Raj, K.-J.Ko, K.-K. Park, Y.-T. Yu, (2013)Synthesis of flower-like ZnO microstructures for gas sensor applications, Sensors Actuators B Chem. 178 (2013 doi:10.1016/j.snb.2012.12.031.PP- 107–112.
5. T.T. Trinh, N.H. Tu, H.H. Le, K.Y. Ryu, K.B. Le, K. Pillai, et al., (2011) Improving the ethanol sensing of ZnO nano-particle thin films—The correlation between the grainsize and the sensing mechanism, Sensors Actuators B Chem. 152 doi:10.1016/j. snb.2010.09.045. PP-73–81.
6. K. Thongsuriwong, P. Amornpitoksuk, S. Suwanboon, (2013) Structure, morphology, photocatalytic and antibacterial activities of ZnO thin films prepared by sol–gel dipcoating method, Adv. Powder Technol. doi:10.1016/j.apt.2012.07. 002.PP-275–280
8. S. Kim, H. Yoon, D.Y. Kim, S.O. Kim, J.Y. Leem, (2013). Optical properties and electrical resistivity of borondoped ZnO thin films grown by sol–gel dip-coating method, Opt. Mater.(Amst). 35 doi:10.1016/j.optmat.2013.06.048.PP-2418–2424.
9. C.H. Chia, W.C. Tsai, J.W. Chiou, (2013) Thickness effect on luminescent properties of sol– gel derived ZnO thin films, J. Lumin. 136 doi:10.1016/j.jlumin.2012.11.019. PP-160–164.
10. K. Shao, S. Liao, H. Luo, M. Wang, (2008). Self-assembly of polymer and molybdenum oxide into lamellar hybrid materials., J. Colloid Interface Sci. 320 doi:10.1016/j. .2008.01 .010, PP-445–51
11. N. Kakati, S.H. Jee, S.H. Kim, J.Y. Oh, Y.S. Yoon, (2010) “Thickness dependency of sol-gel derived ZnO thin films on gas sensing behaviors”, Thin Solid Films., 519, PP-494– 498.
12. S.S. Nath, M. Choudhury, D. Chakdar, G. Gope, R.K. Nath (2010), “Chemical Acetone sensing property of ZnO quantum dots embedded on PVP”, Sensors Actuators B. Chem., 148 ,PP-353–357.
13. D. Sivalingam, J.B. Gopalakrishnan, J.B.B. Rayappan,(2012) Structural, morphological, electrical and vapour sensing properties of Mn doped nanostructured ZnO thin films, Sensors Actuators B Chem. 166-167 doi:10.1016/j.snb.2012.03.023.PP-624–631.
14. Sounder. J.*, P.Gowthaman, M. Venkatachalam, M.Saroja,(2017) 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
15. Sounder.J1, P.Gowthaman2, M. Venkatachalam3, M.Saroja3.(JAN/2018) ZnO Thin Film Acetone Sensor Prepared By Dip Coating Technique