

(NO₂) Gas Sensing Characteristics of ZnO – Na CMC Thin film Prepared by Sol-Gel Dip Coating Method

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ABSTRACT : *No₂ sensing characteristics of Zinc Oxide with copper doped thin films prepared by sol-gel dip coating method are discussed in this paper. For sol gel preparation the researcher using copper nitrate and Zinc Nitrate hexahydrate (Zn (NO₃)₂ .6 H₂O) and sodium carboxy methyl cellulose (Na-CMC) and the 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. Gas sensing parameters such as response, selectivity, response/recovery time of the Cu-doped ZnO-(Na CMC) thin film towards NO₂ were also reported.*

Keywords: *Cu doped ZnO, Na-CMC, Sol- gel dip coating, thin film, NO₂ sensors.*

I.INTRODUCTION

In the last few years, the research is more agreed out on energy conservation and green technologies. This research involves the eco friendly semiconductor metal oxide such as ZnO, SnO₂, TiO₂, etc., [1, 2]. ZnO can be used either in the form of a thinfilm or as a powder. Here the demanding application of ZnO thin films is to make better the self-cleaning properties of glasses or window glass. ZnO can be coated onto glass and hold on to their gas sensing properties. The thin film nano material surface volumes will more effects. The nano materials have unique separate physical, chemical and optical properties. (P. Rai & others, 2013)³⁻⁴.

The Reason that the researcher could choose dip-coating is a simple, cost effective and also the wet chemical method which widely used.^[5]

In our present work dip coating was prepared by automated dip coating units. After sol prepared, thin film coated followed by heating furnace are step followed in sol-gel dip coating method ^[6]. The gluiness of the coated film on the substrate depend upon viscosity of sol.

II. EXPERIMENTAL WORK

Preparation of ZnO Thin Films

The sol of 0.5mol of zinc nitrate hexahydrate Zn(NO₃)₂.6H₂O is dissolved in 100 ml of de ionized water and also for preparing thickening agent 2g of Na(CMC) is dissolved in 100ml, of deionized water both the solution is stirring for 30 min at room temperature after that the precursor solution is added with thickening agent at flow rate of 1ml /min. After that process ZnO thin films are prepared by depositing sol on the glass substrate by using dip-coating method, that time duration as 10 cycle of dip and 10 cycle of dry at 75°C and this is repeated for 10times and then annealed at 400°C^[7]

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 and copper nitrate hexahydrate into 20ml of ethanol is used as dopant precursors. Then homogeneous solution was stirred for 1hour to change reaction to obtain a blue coloured sol-gel, which is used for coating ^[8]. ZnO thin films are prepared by depositing sol on the glass substrate by using dip-coating method, that time duration as 10 cycle of dip and 5 cycle dry at 75°C and this is repeated for 10times. Then the coated films are calcinated by annealing at 400°C, 3hrs to get the Cu doped ZnO thin films.

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 400°C annealing temperatures. The detected (h k l) peaks are at 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 ZnO.

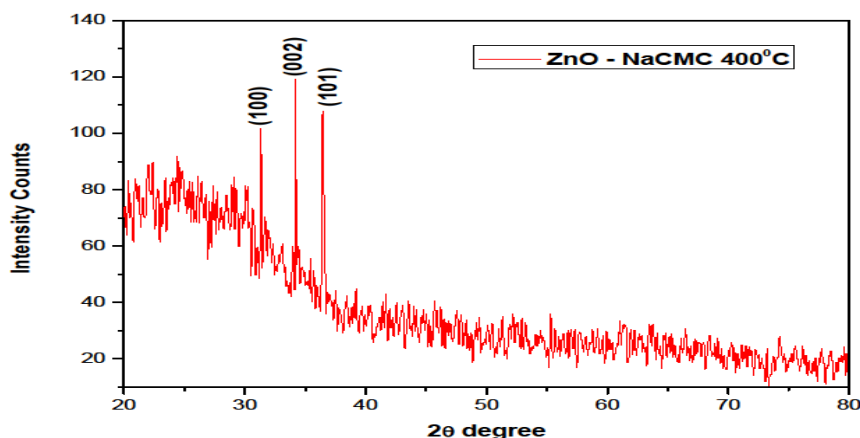


Fig- 1 XRD pattern for ZnO 400°C

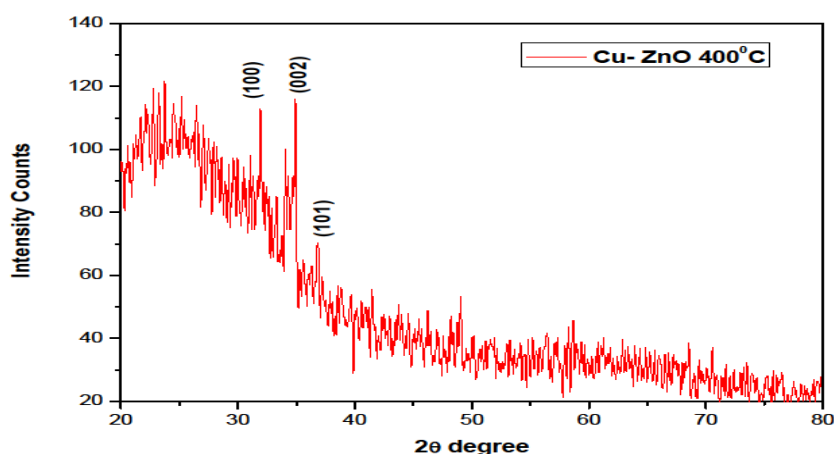


Fig- 2 XRD pattern for Cu doped ZnO 400°C

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,

$$D = K\lambda / (\beta \cos \theta) \text{ \AA}$$

The presence of hexagonal wurzite 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.

Comparing Undoped and Cu doped ZnO Thin films, Cu doped ZnO film have higher peak intensity. It may be due to secondary copper ions might placed in the structure located some pattern site of ZnO.

SEM Analysis

Shows FESEM image of ZnO and Cu doped ZnO Sample annealed at 400°C. The image shows the structure consisting of clusters balls and depicts the observation of more agglomeration of ZnO nanoparticles.

The FE-SEM image reveals the product consist of a large quantity of nanoparticles in various diameter and porous in nature.

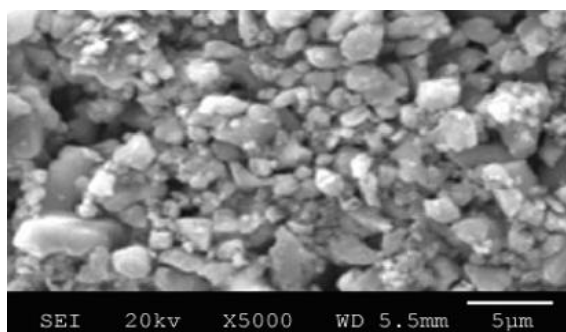


Fig- 3 SEM Image for ZnO 400°C

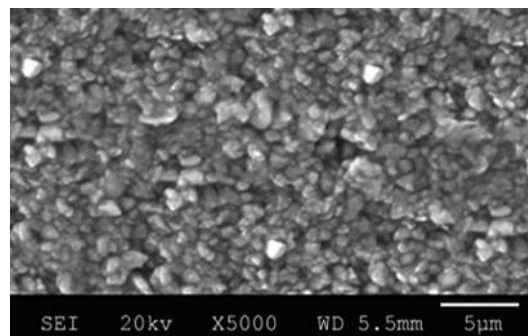


Fig- 4 SEM Image for Cu doped ZnO 400°C

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 NO₂ gas was measured at room temperature using a computer interfaced dynamic gas sensing setup. The sensing characteristics of prepared ZnO and Cu doped ZnO thin film annealed at 400°C response of those films towards 200ppm of NO₂ gas was estimated. Response of the film towards NO₂ gas was calculated using equation $S = R_g/R_a$ ^[9].

Table: Gas sensor result for 400°C temperatures

Precursors	CVD Method	Form	Features nm	Sensor type	T_{op} °C	P_{pm}	Gas	Ra/Rg	Response time (s)
ZnO 400°C	CVD	Film	780L	$\Omega + 0$	400	200	NO ₂	8s	80
Copper Doped ZnO 400°C	CVD	Film	780L	$\Omega + 0$	400	200	NO ₂	36s	70

Tdep – temperature of deposition, Top - operating temperature, Tres – response time,
 Ppm – part per million,
 $R = R_a / R_g$ (oxidative gas),
 $R = R_g / R_a$ (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, NO₂. The computer dynamic gas sensing setup was used in same one of paper.^[10]

From the result, maximum resistance change was observed in Cu doped ZnO thin films. Its corresponding magnitude of response was 70s for Cu doped ZnO 400°C and for pure ZnO 80s. These variations in magnitude of response arise 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.^[11] After attaining the base resistance, 200 ppm of NO₂ was injected into the closed test chamber. Due to its oxidizing nature, NO₂ 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.

CONCLUSION

The ZnO thin film sol-gel dip coating method and its gas sensing characteristics were studied. The most stable Nano balls in shape nano structure were conformed with XRD. The sensor test was done by closed chamber at room temperature. The test shown that the ZnO thin film can act as an NO₂ sensor for a selectivity of constant values. The limit of room temperature lower detection of ZnO thin film observed to 200ppm of NO₂ with the response of 70S. Hence the Researcher could show that it has identified diabetes.

REFERENCES

1. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J.Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.
2. K. Rajeshwar, M.E. Osugi, W. Chanmanee, C.R. Chenthamarakshan, M.V.B.Zanoni, P.Kajitvichyanukul, R. Krishnan-Ayer, Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media, J. Photochem. Photobiol.C: Photochem. Rev. 9 (2008) 171–192.
3. 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.
4. 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.
5. 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.
6. 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.
7. Sounder. J.*, P.Gowthaman, M. Venkatachalam, M.Saroja ZnO Gas Sensor Thin Film prepared 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
8. T.T. Trinh, N.H. Tu, H.H. Le, K.Y. Ryu, K.B. Le, K. Pillai, et al., Improving the ethanol sensing of ZnOnano-particle thin films—The correlation between the grainsize and the sensing mechanism, Sensors Actuators B Chem. 152 (2011) 73–81. doi:10.1016/j.snb.2010.09.045.
9. 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
10. 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
11. Sounder.J1, P.Gowthaman2, M. Venkatachalam3, M.Saroja3.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