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THIN FILM OF COPPER DOPED ZNO FOR GAS SENSORS PREPARED BY SOL-GEL DIP COATING METHOD

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ABSTRACT

The sensing characteristics of cu- doped Zinc Oxide thin films prepared by sol-gel dip coating method were reported in this article. The sol for dip coating was synthesized using Zinc nitrate hexahydrate (Zn $(NO_3)_2.6H_2O$) and organic polymer sodium carboxy methyl cellulose (Na- CMC) as a starting material. Crystallite sizes have been shown by X-ray diffraction (XRD) and the morphology have been shown by field emission scanning electron microscopy (FESEM). The gas sensing characteristics was studied using chemiresistive method, by exposing the film to various concentrations of acetone at room temperature. Gas sensing parameters such us response/recovery time, selectivity and lowest detection limit of the thin film towards acetone were also highlighted.

KEYWORDS: Cu, ZnO, Na-CMC, Thin film, Sol-gel dip coating, Acetone, NO_2 gas sensor.

INTRODUCTION

ZnO gas sensors have been intensively investigated recently, and films have been fabricated in a variety of structures, including as single crystals, thick/thin amorphous films, nano rod arrays, and nano tube assemblies (Rout *et al*., 2006; Kim and Yong, 2011 and Bai *et al*., 2013). The general gas sensing mechanism underlying metal oxide sensor function involves a resistance change through a reaction between the oxygen species chemisorbed onto the metal oxide surface and the target gas molecules. Under ambient air conditions, the surface of a metal oxide material is covered with charged oxygen species that accept charge carriers (electrons) to form a depletion region on the surface. As these species react with reducing agents, oxygen species are desorbed from the surface and release the trapped electrons, which reduce the film thickness in the depletion region and, consequently, the resistance.

As the surface coverage of adsorbed oxygen species increases, the gas sensing response is expected to increase as well. Although the surface oxygen species density usually varies with the surface area, however, the main factors that affect the adsorption of oxygen species are the surface atomic structures related to the exposed facets and the surface defect densities, including zinc and oxygen vacancies (Tian, et al., 2012; Lee *et al.*, 2013 and Gurav *et al.*, 2014).

Nowadays use of nano materials in the field of gas sensor has gained interest as it helps in detection of toxic and combustible gases (Rai *et al.*, 2013). The excess of toxic and combustible gases cause degradation to environment and are hazardous to human health. Hence 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)

semiconducting metal oxide nano particles are extensively studied for gas sensing application due to small dimension, suitable operating temperature, more surface sites available for gas adsorption, high response towards many gases, low cost, portability, non-toxicity etc., (Kakati *et al.*, 2010 and Pawar *et al.*, 2013).

In our present work, dip coating was done by automated dip coating units. After sol prepared, thin film was coated followed by heating in furnace are the steps followed in sol-gel dip coating method (Rai *et al*., 2013).The glueness of the coated film on the substrate depend upon viscosity of sol.

MATERIALS AND METHODS

Preparation of ZnO Thin Films

To prepare the sol of 0.5mol of zinc nitrate hexahydrate Zn $(NO_3)_2 6H_2O$ was dissolved in 100 ml of deionized water and for preparing thickening agent 2g of Na (CMC) was dissolved in 100ml of deionized water and both the solutions were stirred for 30 min at room temperature, separately. After that the precursor solution was added with thickening agent at the rate of 1ml /min. After that process ZnO thin film was prepared by depositing sol on the glass substrate by using dip-coating method followed by drying at 75^0C and this was repeated for 10 times and then finally the film was annealed at 400°C.

Preparation of Cu doped ZnO Thin Films

For the 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. Then homogeneous solution was stirred for 1hour to change reaction to obtain a blue coloured sol-gel, which was used for coating (Sounder *et al.*, 2017). ZnO thin films were prepared by depositing sol on the glass substrate by using dip-coating method, followed by drying at 75^0C and this was repeated for 10 times. Then the coated films were annealed at 400^0C, 3hrs to get the Cu doped ZnO thin films.

RESULTS AND DISCUSSION

The XRD and FESEM studies were done and the results are given below.

XRD patterns of ZnO and Cu doped ZnO Thin Films

The detected (h k l) peaks are at 2θ values of 31.28°, 34.23° and 36.49° corresponding to the lattice planes (100), (002) and (101) respectively. They are in agreement with the standard JCPDS 036-1451 card for hexagonal wurtzite ZnO. The peak intensity is found to vary with the different annealing temperatures.

Figure 1 shows XRD pattern for ZnO at 400°C

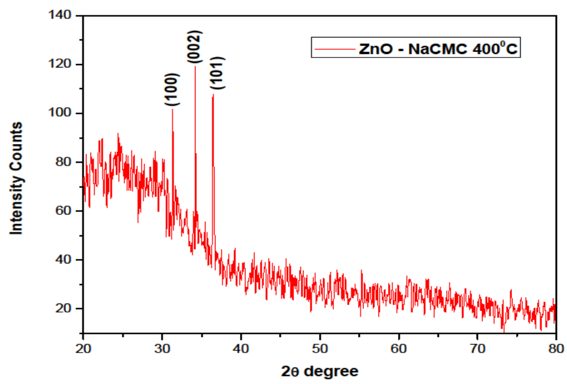
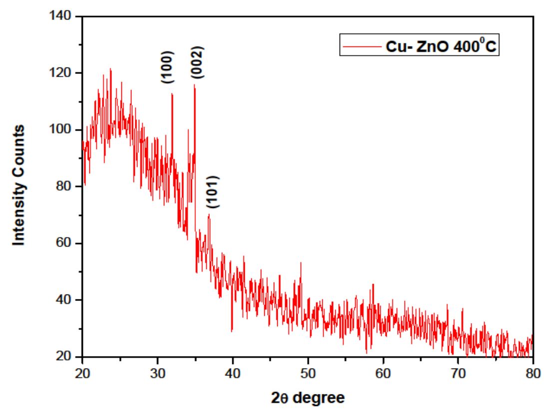


Figure 2 depicts XRD pattern for Cu doped ZnO 400°C



The detected **(**h k l) peaks are at 2θ values of 31.96°, 34.84° and 36.73° corresponding to the lattice planes (100), (002) and (101) respectively, They are in agreement with the standard JCPDS 036-1415 card .The (100) peak has lower intensity when compared with other two peak with strong (002) diffraction pear compare with (100) peaks.

The crystallite size was calculated using Debye Scherrer's formula,

$$\mathbf{D} = \frac{K\lambda}{\beta \cos\theta} \text{Å}$$

The hexagonal wurtzite structure was confirmed using [002] plane. Peak enlargement concludes that have a structure of nano particles. The particle size was found to be 4.3nm.

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 have placed in the structure located some pattern site of ZnO.

SEM Analysis

FESEM image of ZnO and Cu doped ZnO sample annealed at 400°C are given in Figure 3 and 4 respectively. The images show clusters balls and depict the observation of more agglomeration of ZnO nanoparticles. The FESEM images show nanoparticles in various diameter and basically porous in nature.

Figure 3 shows SEM Image for ZnO at 400°C

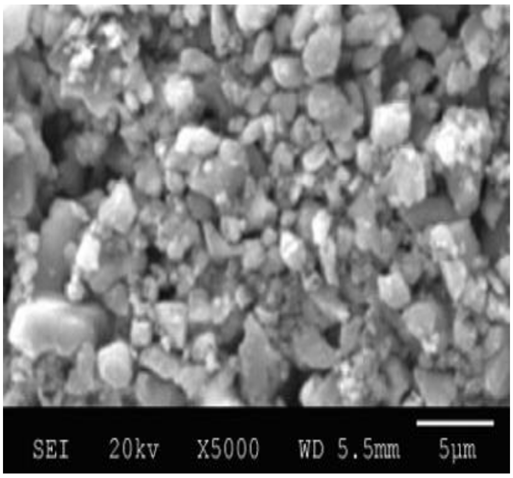
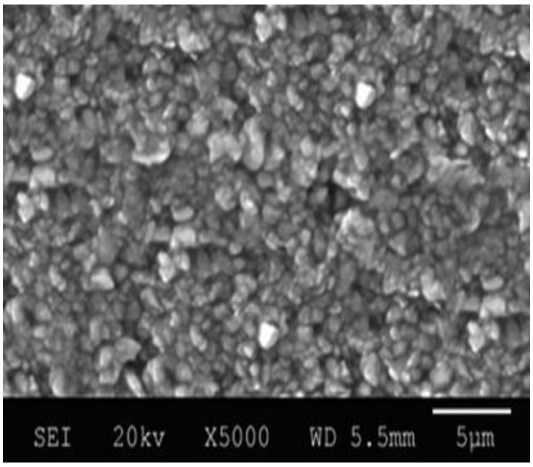


Figure 4 explains SEM Image for ZnO at 400°C



STUDY OF GAS SENSING PROPERTIES

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 ZnO and Cu doped ZnO thin films towards 200 ppm of NO_2 gas was estimated. Response of the film towards NO_2 gas was calculated using the following equation,

S=Rg/Ra

Where Ra is resistance of the film in air and Rg is the resistance of the film in presence of test gas

The No_2 sensing mechanism involves the following phenomena. After attaining the base resistance, 200ppm of NO_2 was injected in to the close testing chamber. Due to oxidizing in nature, NO_2 was tend to release the trapped electrons on back to the thin film surface.

For Cu doped ZnO thin films response time was 70s and for pure ZnO thin film it was 80s. This variation in response time 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 (Sounder *et al.*, 2017). After attaining the base resistance, 200 ppm of NO_2 was injected into the closed test chamber.

Table 1shows the Gas sensing parameters

Precursors	CVD Method	Form	Sensor type	T_{op} ^0C	P_{pm}	Gas	Ra /Rg	Response time (s)
ZnO 400^{0}C	CVD	Film	Ω + 0	400	200	NO_2	8s	80
Copper Doped ZnO 400^{0}C	CVD	Film	Ω + 0	400	200	NO_2	36s	70

T_{op} - operating temperature

ppm – part per million,

R = Ra / Rg (oxidative gas),

R = Rg / Ra (reduction gas).

CONCLUSION

The ZnO and Cu doped ZnO thin films were prepared by sol-gel dip coating method and their gas sensing characteristics were studied. The crystalline natures of dip coated thin films were characterized by XRD. The sensing property was studied using closed chamber at room temperature. The test shows that the ZnO thin film can act as NO_2 sensor. The lower detection of ZnO thin film observed to 200ppm of NO_2 with the response of 70s.

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