Preparation of ZnO and Cu doped ZnO Thin Film and compare over NO₂ Gas Sensing

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Abstract— Zinc Oxide and copper doped ZnO thin film with dip coating of gas sensing methods are we discuss in this paper .For sol gel preparation Zinc Nitrate hexahydrate (Zn (NO₃)₂.6 H_{20}) and organic polymer sodium carboxy methyl cellulose (Na-CMC) as basic material and copper nitrate as a dopant and size of the prepared thin film varied by XRD, morphology was studied by (FE-SEM) and the gas sensing was studied using acetaldehyde has been tested Keywords: ZnO, NO₂-Sensor, Sol- gel dip coating, thin film, and Gas sensors.

I.INTRODUCTION

Zinc oxide, a wide band gap intrinsic n-type semiconductor is one among the most widely studied materials for gas sensing application ^{[1].} It offers several advantages like high electron mobility, nontoxic nature, abundant availability and high chemical stability ^[2-4]. It can be prepared in many forms such as single crystal, powder, pellet, thin film and thick film ^[5-7] among which thin films has good sensing response towards reducing and oxidizing gases ^[8]. Sensing characteristics of the film greatly depends on surface state and morphology of semiconducting metal oxide ^[9]. In this present work the Dip coating was done by the automated dip coating unit (HOLMARC, HO-TH-01).

Sol preparation, thin film coating followed by heat treatment is the steps followed in sol gel dip coating method ^[10]. Adhesiveness of the coated film on the substrate depends upon viscosity of sol. Na-CMC is used in sol-preparation, because of its film forming ability due to abundant OH group ^[11] and its characteristic thickening property. Na-CMC is an inorganic green polymer which is easily soluble in water ^[12]. Viscosity builder, stabilizer, emulsifier are some of the general utilities of Na-CMC ^[13– 15]. Its property mainly depends on molecular weight and degree of substitution i.e. number of OH groups substituted per an-hydro glucose unit ^[15, 16]. Most widely used CMC has degree of substitution of 0.7 Acetone is a highly volatile and reactive compound which is colorless and flammable. It is widely used as solvent for plastics and synthetic fibers, extracting reagent, biomarker and also find applications in cosmetics, petro chemical industries ^[17] etc. At its low concentration it is non-toxic, non-carcinogen and non-neuro toxic.

II. METHODS AND MATERIALS

ZnO thin films have been prepared onto well cleaned glass substrates by sol-gel dip coating method. 4.68gms of zinc nitrate hexa hydrate, and Na-CMC and deionized water were used as starting material, were thickening agent. Precursor solution to prepare the coated solution, and the relevant volume of 2:1 ratio and added gradually to the thickening agent with the current rate of 1mL/min. Colour transform was observed when it reached 8mL of precursor solution, which indicates the formation of ZnO nano particles^[18].

For preparing copper solution for (0.5 mol) was prepared in the separate beaker by adding copper nitrate in deionized water, as the doping solution. During the entire process the solution was under constant stirring and the temperature maintained was 70°C. The above mentioned process was repeated 20 times to get a uniform coating. It was then annealed at 350°C for 3 hours to get crystalline cu-doped ZnO thin film nano particles.

II. CHARACTERIZATION

SEM characterizations are done to determine Crystallinity, crystallographic structure, and surface morphology of the ZnO and Cu doped ZnO thin film annealed at 350°C. The XRD pattern was obtained by X-ray powder diffractometer equipped with Cu K α radiation having wavelength of 22.00nm and for cu doped 4.19nm as a source. The crystallite size was calculated using Debye Scherrer's formula ^[19].

$$\mathbf{D} = \frac{\kappa\lambda}{\beta \cos \theta} \mathbf{\mathring{A}}$$

Where k is shape factor (k=0.89), λ is the wavelength of X-ray source, β is full width at half maximum (FWHM) and the θ is the diffraction angle. The morphological study was done using FE-SEM, 6701F, JEOL, JapanGas sensing behaviour of the film was studied by chemiresistive method ^[20-23].

III. RESULTS AND DISCUSSION **3.1. X-Ray Diffraction**

The crystalline nature of dip coated thin film was characterized by XRD. Fig.1 and Fig.2 shows the XRD pattern, where the peak positions 31.22°, 34.10° and 36.79 °are the characteristic peaks of ZnO at [100], [002] and [101] plane respectively. And the presence of hexagonal wruzite structure was complete using [002] plane and Peak broadening concludes the formation of nano particles. For copper doped ZnO thin film where the peak positions 31.08°,34.60° and 36.60 °are the characteristic

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peaks of ZnO at [100], [002] and [101] plane respectively. They are agreement with the standard JCPDS 036-1451.

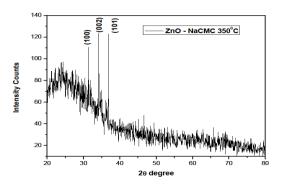


Fig.1. Sample ZnO 350°C

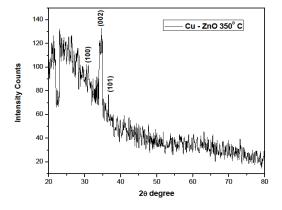
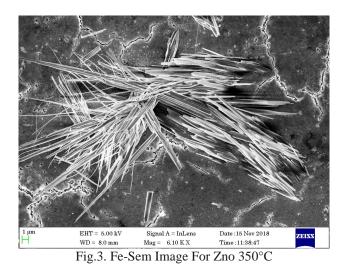


Fig.2. Sample Cu doped ZnO- 350°C

3.2. Sem Analysis

SEM images of ZnO and Cu doped thin film shows a hexagonal morphology as depicted. Due to agglomeration, overall morphology resembles like nano needles nano cluster particles were grown and some of them are amorphous in nature.



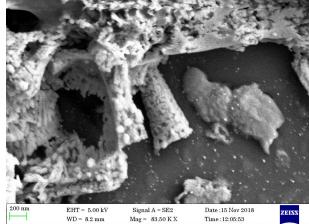


Fig.4. Fe-Sem Image For Cu Doped Zno 350°C. Gas Sensor Properties

| Prec | CVD Method | Tdep °C | Form | Sensor type | Top ⁰C | ppm | Gas | R |
|--|---------------|------------|------|----------------|-----------|-----|-----------------|----|
| Zno350 ⁰ c | CVD | 700 | Film | <u>Ω</u> +0 | 300 | 200 | NO ₂ | 38 |
| Copper Doped Zno350 ⁰ c | CVD | 700 | Film | <u>Ω</u> + 0 | 400 | 200 | NO ₂ | 22 |

Prec - precursors,

Tdep - temperature of deposition,

Top: operating temperature,

tres: response time,

ppm: partsper millon,

R = Ra/Rg (oxidative gas),

R = Rg/Ra (reductive gas)

Gas sensing mechanism involves the following phenomena. After attaining the base resistance, 200 ppm was injected into the closed test chamber. Due to its reducing 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. Gas Sensing studies were complete 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.

IV. CONCLUSION

ZnO and Cu doped ZnO 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 on closed chamber, using chemiresistive method at room temperature. The results showed that the fabricated ZnO and Cu doped ZnO thinfilm can act as a NO_2 gas sensor. The lowest detection limit of room temperature ZnO-Na CMC thin film was observed with the response of 22S.

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