Indium doped ZnO Thin Films as CO Gas Sensor

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Abstract: **As CO is extremely dangerous its detection and monitoring is highly essential. In this work 0.1 wt% indium doped ZnO thin films are grown by sol-gel method. Structural and micro structural characteristics of the grown films are investigated from XRD pattern and FESEM micrographs respectively. Gas sensing properties of these films are studied in presence of CO gas by varying the operating temperature and gas concentration. It is observed that these indium doped ZnO thin films can detect the presence of a very low concentration of CO (~ 2 ppm) and exhibit a stable sensing performance. The gas sensing mechanism of these films is discussed.**

I. INTRODUCTION

Semiconducting metal oxides such as SnO_2, ZnO and In_2O_3 are used as gas sensing materials for detection of toxic and combustible gases for safety and environmental control [1-3]. ZnO is one of the most promising materials for gas sensing application. It is a non toxic and low cost material having high chemical stability. Recently, studied are devoted to improve the performance of ZnO by several ways. Addition of small amount of dopants, such as Al, In, Co, etc. is an effective way for improvement of gas sensing performance of ZnO. Thin films of ZnO have demonstrated high sensitivity for toxic gases [4]. Various deposition techniques such as sol gel route [5], sputtering [6], pulsed-laser deposition (PLD) [7], metal organic chemical vapor deposition (MOCVD) [8], and so on are used to grow ZnO and doped ZnO thin films.

In the present work, we have grown indium doped ZnO thin films by sol gel route. The grown films are characterized in terms of their structure, microstructure and gas sensing characteristics. Finally, an attempt has been made to understand the gas sensing mechanism of these porous indium doped ZnO thin films.

II. EXPERIMENTAL PROCEDURE

First zinc acetate dihydrate and indium nitrate dehydrate powders were mixed in 99: 1 molar ratios. The mixed powder was dissolved in a mixture of 2-methoxyethanol and MEA (monoethanolamine) solution at room temperature. The solution was heated to 60 °C and stirred continuously for 2 h. The concentration of the solution was maintained at ~ 0.4M. The solution was then spin cast onto quartz substrates using a spin coater unit (SCU 2007, apex instruments co.). The spin speed was maintained at 3000 rpm and spin time was kept for 30 s. The films were heat treated at 300 °C for 5 min after deposition. The coating and heating was repeated 15 times to get films with desired thickness. The films were finally annealed at 600 °C for 1 h in air. The phase formation behavior of the deposited thin films were studied by X-ray diffraction (Ultima III, Rigaku, Japan) analyses using Cu Ka radiation in 2θ range 20 - 80 at a scanning rate 3° /min. The micro structural characteristics of the films were investigated using field emission scanning electron microscope (FESEM) (SUPRA-40, Carl Zeiss, Germany). The gas sensing performance in presence of CO gas was characterized using an automated dynamic flow gas sensing measurement set-up developed in our laboratory. The details of the measurement set up are reported, elsewhere [9].

III. RESULTS AND DISCUSSION

A. *Structural characterization*

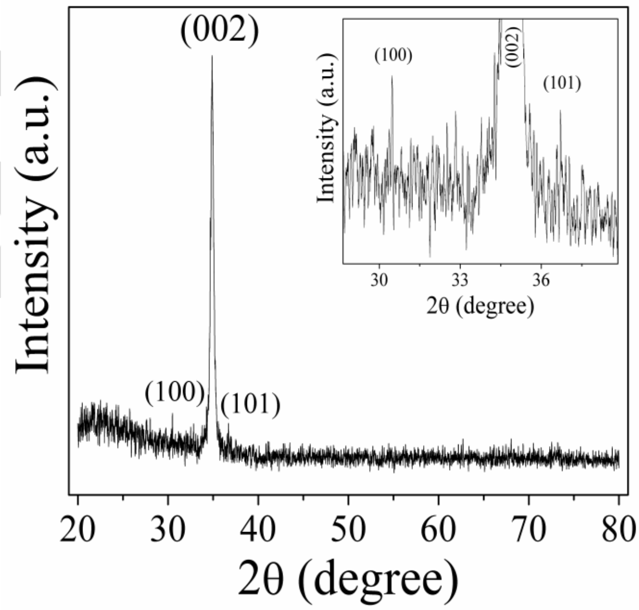

Fig. 1: X-ray diffraction pattern of indium doped ZnO thin film in the 2θ range (20-80) degree. Inset shows the magnified image of diffraction peaks.

Fig. 1 shows the X-ray diffraction pattern of indium doped ZnO thin films grown by sol gel spin coating technique. Presence of a prominent (002) peak at 2θ value 34.8 degree indicates the textured behavior of the grown films [10]. In addition to (002) peak another two peaks (100) and (101) having diminishing intensity is also observed in the pattern. However, no other impurity phase is observed which is also confirmed from the EDs measurement shown in Fig. 2.

Element	Weight%	Atomic%
O K	20.54	51.36
Zn K	79.46	48.64
In L	0.00	0.00
Totals	100.00	

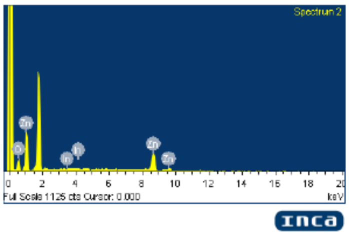

Fig.2: EDs measurement of indium doped ZnO thin films showing no other impurity phases

Absence of other impurity phases in the XRD pattern indicates the substitutional doping of indium in ZnO lattice. From the XRD pattern, the average crystallite size (D) was estimated using the Debye Scherer relation [11]

$$D = {}^{0.9\lambda}/_{\beta \cos\theta} \tag{1}$$

where λ (= 0.154 nm) is the wavelength of the X-ray radiation used, θ is the Bragg diffraction angle of the XRD peak and β is the broadening of the diffraction line at half maxima measured in radian. Using this relation the crystallite size is estimated to be ~31.8 nm.

3.2: Micro structural characterization

Fig. 3 shows a typical surface morphology of the indium doped ZnO thin films grown on quartz substrate. From the image it is observed that the film exhibits uniform and granular microstructure. It also reflects the presence of pores uniformly throughout the film which is beneficial for gas sensing. This uniformity in surface morphology is attributed to the orderly arrangement of indium atoms inside ZnO lattice.

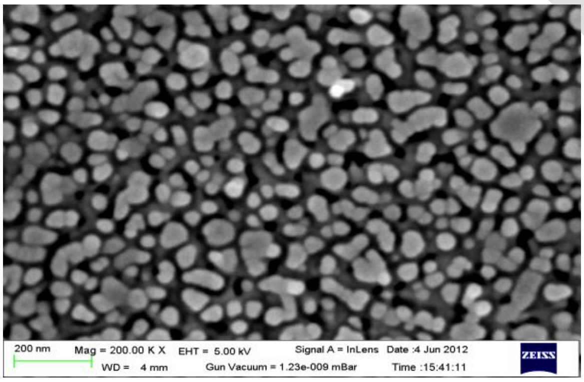

Fig. 3: FESEM image of ZnO thin films grown on quartz substrates by sol gel spin coating method.

3.3: Gas sensing characteristics

The grown indium doped ZnO thin films are characterized in terms of their CO gas sensing characteristics. It is known that ZnO is an n-type semiconductor and by doping it with indium further increases this n-type conductivity. The gas sensing mechanism for n-type semiconducting metal oxide gas sensor is reported in the literature [8]. When the metal oxide sensors are heated to high temperature oxygen present in the atmosphere are adsorbed on it. These adsorbed oxygen attracts electron from the conduction band of metal oxide, which increases the resistance. After some time this resistance (Ra) attains saturation. Now when the reducing gas is passed onto it, it reacts with adsorbed oxygen and returns the electron back to the conduction band of metal oxide. As a result the resistance (R_g) again decreases. Now the sensor response (S) is estimated from the following relation [8]:

$$s = \left(\frac{R_a - R_g}{R_a}\right) \times 100 \tag{2}$$

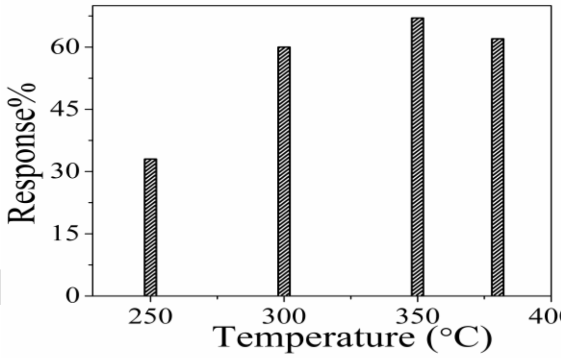

Fig. 4: Variation of response% of indium doped ZnO thin film towards the detection of 1660 ppm of CO gas as a function of operating temperature

Fig.4 shows the variation of response% of the grown thin films with the variation of operating temperature in presence of 1660 ppm of CO gas. As observed the response% first increases with the increase in operating temperature, attains its maximum value (67%) at optimum temperature (350 °C) and then decreases with further increase in temperature. This can be explained from the concept that at optimum temperature the gas molecules may have required energy to overcome the activation energy barrier of the reaction, thus giving the highest response. However, decrease in response beyond the optimum temperature is attributed to the desorption of adsorbed oxygen from the sensor surface [12].

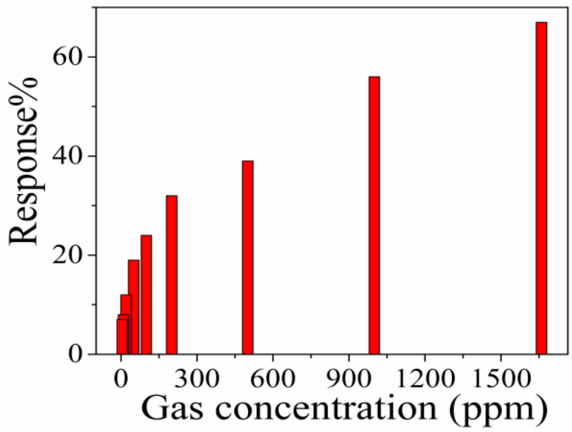

Fig. 5: Variation of response% of indium doped ZnO thin film towards the detection of various concentrations of CO gas at their optimum temperature, 350°C

First the resistance transients for detection of CO gas are recorded in presence of various concentrations at the optimum temperature, and the responses% are calculated from the measured resistance transients Fig. 5 shows the variation of response% of indium doped ZnO thin film as a function of gas concentration keeping the operating temperatures fixed at its optimum value (350^{o}C). From the figure it is observed that response% of the sensors increases with increase in gas concentration and these thin films are able to detect as low as 2 ppm (shown up to 5 ppm) of the CO gas. Understanding the sensing mechanism, it is argued that owing to the porous nature of the film the gas solid interaction takes place at the surface of individual grains, at grain boundaries and film substrate interface, thus enhancing the response.

IV. CONCLUSION

Indium doped ZnO thin films are grown on quartz substrates using the cost effective sol gel spin coating technique. XRD pattern of the grown films confirms the crystallization of the film into hexagonal wurtzite structure with its (002) peaks oriented along c-axis. The film is nano crystalline with a crystallite size of 31.8 nm. Gas sensing performance of the films is studied at different temperatures and at various concentrations of CO gas. At optimum temperature the response% is found to improve markedly. It is also observed that with increase in gas concentration the response% increases linearly. Finally, the sensing mechanism is understood from the gas solid interaction on the thin films.

ACKNOWLEDGEMENT

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