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Cd Doped ZnO Thin Films By Silar For Gas Sensing Applications.

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Abstract: *Cd-ZnO thin films are prepared by Silar and are characterized by XRD, SEM and EDX. The samples are then placed inside a gas chamber kept at rotary vacuum and at pressure and temperature of 0.20 mb and 350^0C. Ethanol vapour is admitted in a controlled manner into the chamber. Resistance of the film is measured continuously before, during and after the admittance of Ethanol vapour. The experiment is repeated for different doping concentrations of Cd. And it has been observed that the resistance of the film reduces fast and considerably at the admittance of Ethanol. The response time was found to be one second and it has been noted that recovery time of the films varies with doping concentrations.*
Key words: ZnO, Response time, Silar, Ethanol Sensor

I.Introduction

Different ZnO thin films with sensing time from 20 second to 30 minutes for ethanol gas has been reported [1]. Silar method is cheap and convenient to perform doping with Al[2], Sn[3], Ga[4], N[4], Sr[5] and more others by this method and there by we can easily modify and control the properties of ZnO.

In the present study, ZnO nano structured thin films without any sensitizers coating is being used and also the time of admittance of the gas is only a few seconds. The adsorption of reducing gas molecules results in decrease in electrical resistance of oxide materials. Among oxide semiconductors, ZnO and SnO_2 are mostly studied and are known to have substantial gas sensitivity [6]. The surface resistance of metal oxide thin films is greatly influenced by chemisorption of oxygen from the air at the surface and at the grain boundaries. The conduction electrons of the materials are trapped by the chemisorbed oxygen and there forms O_2^-, O^- and O^{2-} depending on the temperature of the surface [7]. This leads to an increase in surface resistance of the thin film. When a reducing gas is introduced to the film the molecules of the reducing gas reacts with the negatively charged, chemisorbed oxygen species and thus the conduction electrons of the film becomes free. This leads to a decrease in the resistance of the film. When the reducing gas is removed from the film environment, the film regains its original high resistance again.

II.Materials And Methods

The preparation of ZnO thin film by Silar method has been reported elsewhere [8]. The process involves successive dipping of a pre-cleaned microscopic glass substrate in Sodium Zincate bath and in hot water kept at a temperature of 95^0C. A thin film of Sodium Zincate was deposited on glass substrate during the first dip, changes to ZnO during the second dip. The ZnO thin film thus formed is a white adherent film whose subsequent annealing in air leads to phase pure ZnO [9]. The annealing temperature of the film was usually 450^0 C for a duration of one hour.

In the present work, the annealed samples are put in a gas chamber for the study of sensitivity to Ethanol vapour. Cd-ZnO thin films used for the study are having a resistance varying from few Tens Ohms to a few Kilo Ohms depending on the preparation conditions. Resistance of the film was continuously measured using two probe method before, during and after the admittance of ethanol vapour into the chamber.

The gas chamber attached to a microprocessor controlled temperature controller to maintain high temperature in side the chamber. The resistance of the film is measured using Keithley digital multimeter during all course of increasing of temperature and also during the admittance and closing of Ethanol vapour. The inside of the gas chamber is kept at rotary vacuum and is attached to a digital Pirani gauge. The experiment is conducted at a pressure of 0.2 mb.

At a pressure of 0.20 mb and a temperature of 350^0C, ethanol vapour is admitted into the chamber and consequently the pressure inside the chamber increases to 2.00 mb. The ethanol vapour admitted is made transported throughout the length of the gas chamber. As Cd - ZnO is having a fast response to ethanol vapour, the resistance of the film reduces to a considerable value within one second after the admittance of the gas. The chamber is then closed and whole ethanol vapour is allowed to be removed by the vacuum pump. And as a result, the resistance of the film starts increasing and it reaches to the initial value. The response time and recovery time are noted for different admittance to a single film as well as for different films with different doping concentrations. Apart from the response time, the recovery time is found to be different for different doping concentrations. The experiment was repeated for many times to get a similar result. The same experiment is repeated for different doping concentrations of Cd from 3 atomic % to 7atomic %. The results obtained are tabulated and a graph is drawn against temperature and the resistance of the film during, before and after the admittance of the vapour. The sensitivity of the films with different doping concentrations was also determined using the relation $(R_{air} - R_{gas}) / R_{air}$

III.Results And Discussion

The Cd-Zno thin films synthesized by Silar method were used as ethanol sensor. Figure 1 represents the XRD patterns of Cd- ZnO at different doping concentrations. XRD analysis reveals that the (002) peak appears with maximum intensity at $2\theta=34.50^0$ The other peaks at 32^0 and 36.5^0 are associated with (100) and (101) reflections as for the Hexagonal Wurtzite structure (JCPDS no.36-1-1451). The average grain size of the ZnO crystals in the films were calculated by using Scherrer's formula as 29.58 nm. The SEM image showing the surface morphology of the film is given in Figure 2.

During the admittance of the gas, the response time is about 1second for 5 atomic % Cd doped ZnO thin film at a temperature and pressure of 350^0C and 0.2 mb. The relative/ resistivity becomes stable after 10-15 seconds of ethanol vapour exposure. The recovery time on the other hand was observed to be 50-55 seconds after the gas is closed. This recovery time found to be increasing according to an increase in doping concentration. The 7 atomic % doped sample shows a recovery time of 80 seconds while the 3 atomic % doped samples shows a response time of 40 seconds.

A graph showing the comparison of sensitivity of the samples is depicted in figure3. This adsorption-desorption mechanism is explained on the basis of reversible chemisorption of ethanol vapour on the nano structured ZnO surface. It produces a reversible variation in resistivity with the exchange of charges between ethanol vapour and ZnO surface leading to changes in the depletion length[10]. It is well known that Oxygen is absorbed on ZnO surface as O^- and O^{2-} by capturing electrons[12]. The sensitivity, response time and recovery time values of 3, 5and 7 at % doping with Cd on ZnO nano structured thin films are tabulated in table 1. The EDX of the 5 atomic % doped sample is depicted in figure 4.

IV.Conclusion

Cd-ZnO nano structured thin films synthesized by Silar method are found to be having fast and considerable reduction in resistance in the presence of Ethanol vapor and hence can be used as fast response sensor to ethanol vapour. The response time is found 1 second for all doping concentrations from 3 atomic % to 7 atomic %. Average sensitivity of the films are found to be 0.5033. Doping concentration of Cd increases the sensitivity of the films as well as recovery time.

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Table 1 sensitivity, response time and recovery time with doping concentrations.

Doping Concentration	Sensitivity $(R_{air} - R_{gas})/ R_{air}$	Response time	Recovery time
3 at %	0.12	1 sec	40 sec
5 at %	0.49	1sec	60 sec
7 at %	0.65	1sec	80 sec

Figure 1, XRD pattern of the samples with doping concentrations 3 at %(a), 5 at %(b) and 7at %(c)

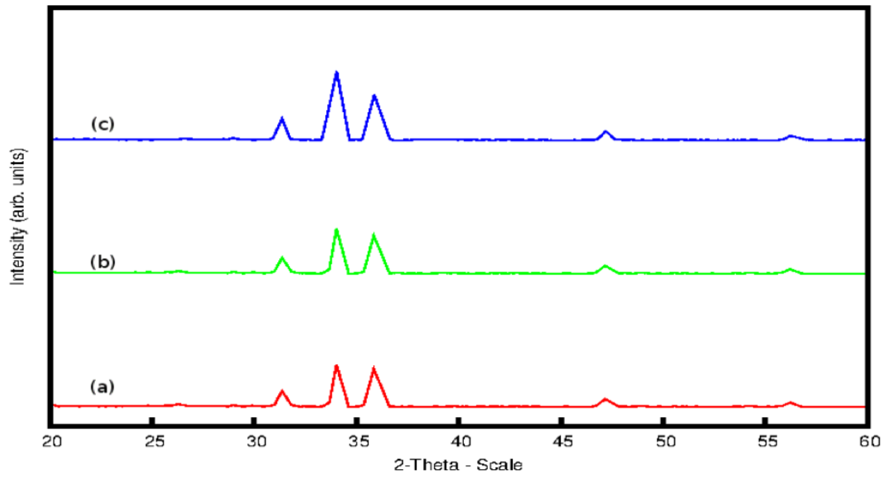

Figure 2, SEM image of Cd-ZnO

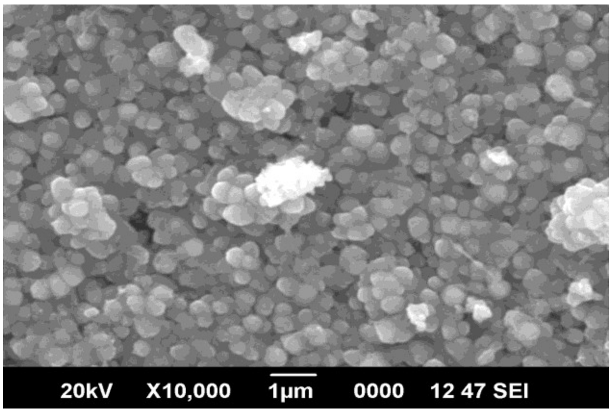

Figure 3, Resistance variation of films according to doping percentage.

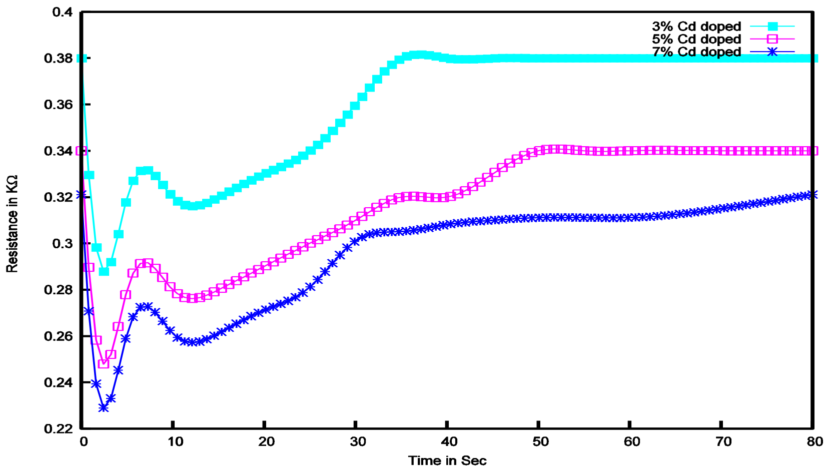

Figure 4 EDX of Cd-ZnO