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Undoped and Cobalt Doped ZnO Thin Films Ethanol Gas Sensors

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Abstract: In this research, undoped ZnO and doped with cobalt ZnO:Co thin films with different weight percentages of (1, 3, 5,7)% have been prepared on pre-heated glass substrates up to (400°C) with average thickens (300nm) by using Atmospheric Pressure Chemical Vapor Deposition (APCVD) technique. The effect of Co-doping on structural properties and the ethanol vapor gas sensing has been investigated. The results of XRD showed that the all deposited films are polycrystalline hexagonal structure with a preferred orientation in the (002) direction, the doping with Co does not change crystal structure of ZnO. The increase in the dopant concentration into the ZnO leads to an increase of the crystallite size of the films which is well known causes to increase the gas sensitivity. The effect of operating temperature on performance of the sensor material has been investigated and a choice of optimum temperature was made at around 300 °C.

Introduction

Metal oxide semiconductor sensors have advantages of small size, low mass, good sensitivity and low cost [1-4]. ZnO which is an n-type II-VI group compound with a wurtzite structure semiconductor (band-gap = 3.2 eV). Zinc oxide thin films have a wide range of applications such as gas sensors, solar cell windows, and surface acoustic-wave devices [5-7]. Pure and doped ZnO films have been investigated as sensors for O2 [8,9], H2 [10], O3 [11-12], humidity [13] and ethanol [3]. One of the requirements of the gas sensors is low power consumption, because the sensors need to work reliably and continuously. It is well known that the sensing mechanism of semiconducting oxide gas sensors is based on the surface reaction and a high surface– volume ratio. The grain size and the porosity of the sensing material are the most important factors for high sensitivity and short response time sensors. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. Nanto et al. showed that a lower operating temperature may be achieved by the doping effect, and a significant resistance change can be obtained in the doped ZnO rather than the undoped ZnO sensor, which results in a higher sensitivity [14]. The aim of this work is to produce high-quality Co doped ZnO thin films for gas sensor application by APCVD method. Special attention was paid to the influence of the operating temperature and dopant concentration.

Experimental part

Undoped and Co-doped ZnO thin films are prepared on a heated (400 oC) glass substrate by atmospheric pressure chemical vapor deposition (APCVD) technique. The base material in the preparation of undoped zinc oxide thin films was zinc acetate dehydrate [Zn (CH3COO)2 2H2O] high purity 99.9%, supplied by (B.D.H. Laboratory chemicals group, Poole England). The dopant source of Cobalt is [Co (CH3COO)2. 4H2O] high purity 99.9%, supplied by (BDH Chemicals Ltd Poole England). The thickness is calculated by weight difference method. The gas sensing properties were evaluated at various operating temperatures, from 100 to 400°C, by measuring the changes of resistance of the sensor in air and in ethanol gas. The sensitivity in the experiment was defined as S=Ra/Rg where Ra is the sample resistance measured in the ambient environment while Rg is that under the test gas.

Results and discussion

The crystal structure and orientation of the ZnO thin film of the Zno and Co:Zno samples were investigated using X-ray diffraction (XRD) patterns. The X-ray diffraction patterns for all films are shown in Fig.1 which indicates that the films are of polycrystalline in nature and exhibit single phase hexagonal wurtzite structure with a (002) preferred orientations, which suggests that the film is aligned with the c-axis oriented perpendicularly to the substrate surface. Doped sample, showed that the intensity of (002) peak is increased and peak becomes sharper, this can be explained by improvement of crystallinity. This suggests that the grain size becomes larger. The crystallite size was calculated using the Scherrer's equation and the estimated values are presented in table 1.

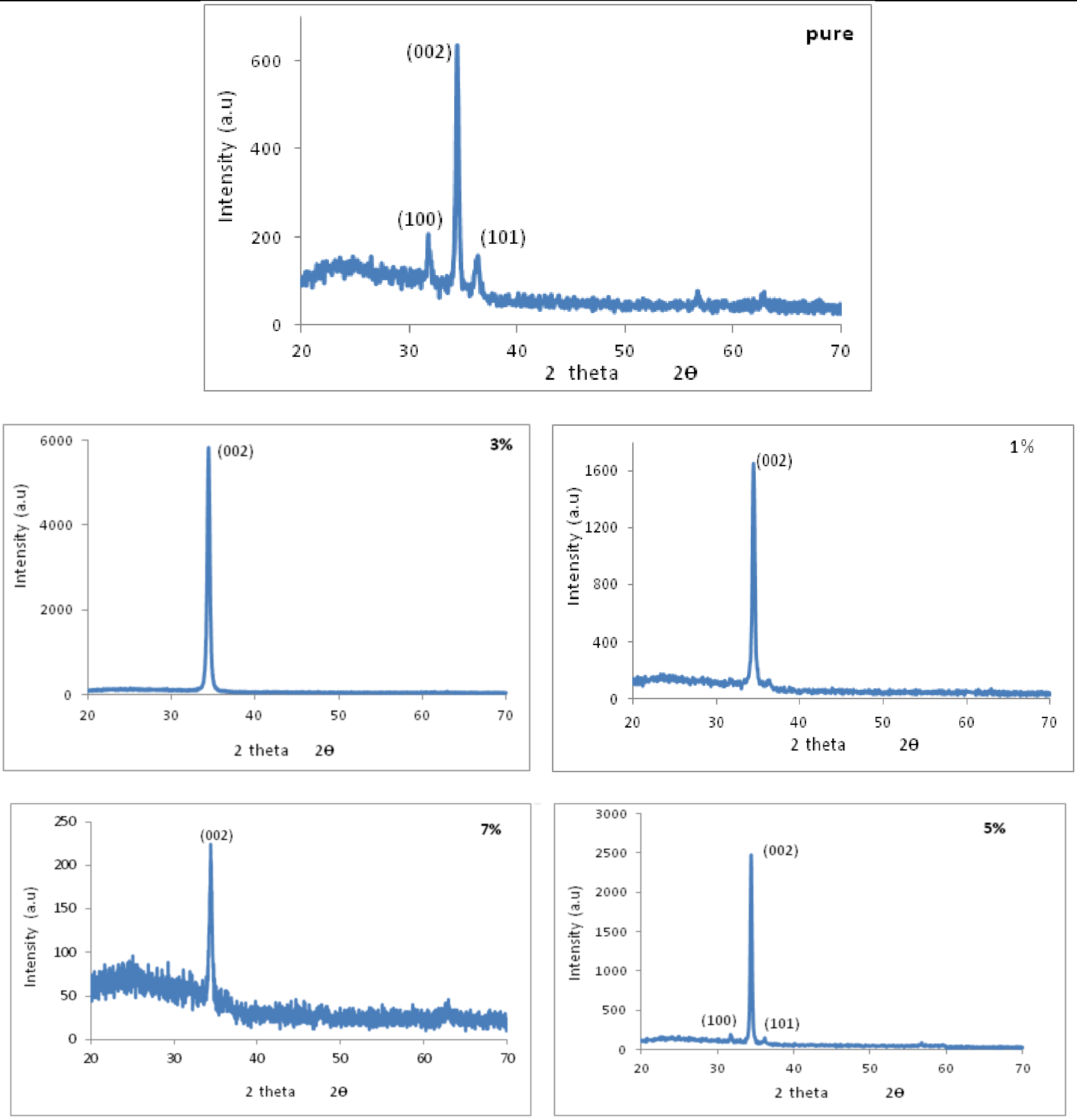

Fig (1) XRD patterns of ZnO and Co:ZnO thin films at different Co concentration

Table (1) crystallite size as a function of Co concentration

C%	0	1	3	5	7
G nm	25.7	28.9	33.1	30.2	27.4

In order to identify the optimum working temperature for Co:ZnO ethanol sensor, the sensor investigated as a function of sensor temperature from 100℃ to 400℃ for 20 ppm ethanol concentration as shown in Fig. 2. It is clearly seen that the resistance of all films decrease as operating temperature increase and when it exposed to the ethanol vapor. Also it is clear that the resistance decrease as doping concentration increasing upto 5%. When the Co concentration is above 5%, the resistance of the films increased.

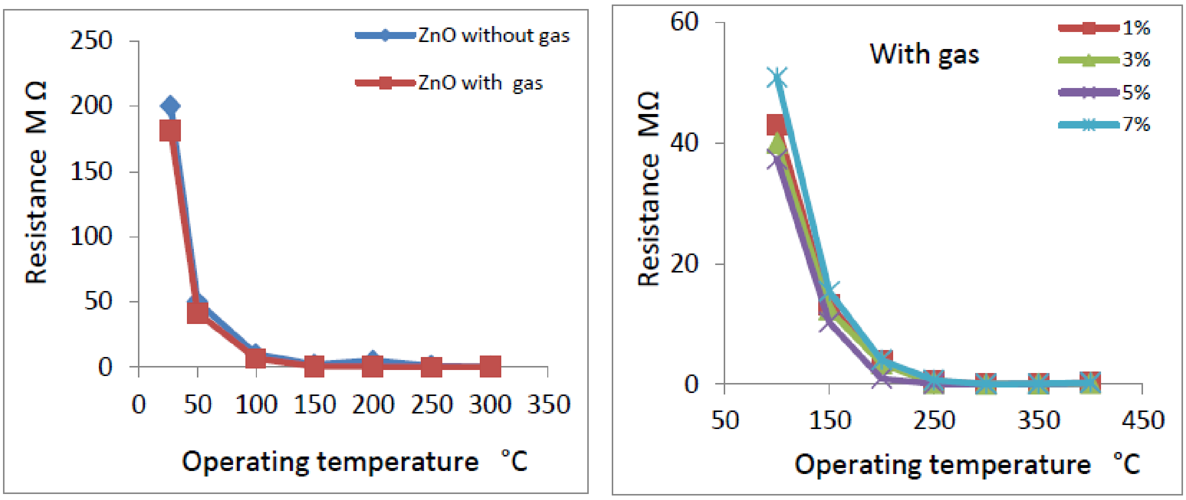

Fig (2) variation of Co:Zno thin films as a function of operating temperature at different concentration of Co

The sensitivity of the gas sensor is defined as the capability of the sensor to espond the presence of a given gas concentration. Mathematically, the sensitivity S is defined by the formula; S= Rg/Rair for redactor gas, and S= Rair/Rg , for oxidator gas, where *Rg* and *Rair* is the resistance of the sensor after and before passing the gas and reaches the saturation [15].

Fig. 3 shows the variation of sensitivity of the cobalt zinc oxide sensor with operating temperature in the range 100 ℃– 400℃ . The sensitivity of the Co:ZnO ethanol sensor increases with the operating temperature upto 300 ℃ which is attributed to increase of crystallinity of films (mobility carriers increased). When the operating temperature is above 300℃, the sensitivity of the films decreased.

The exothermic effect in the surface reaction of the oxide film with ethanol is difficult to proceed with increasing operating temperature above 300℃, thus decreasing. Also Fig. 4 has shown an increase in sensitivity value as the doping percentage increase up to 5% at operating temperature 300℃.

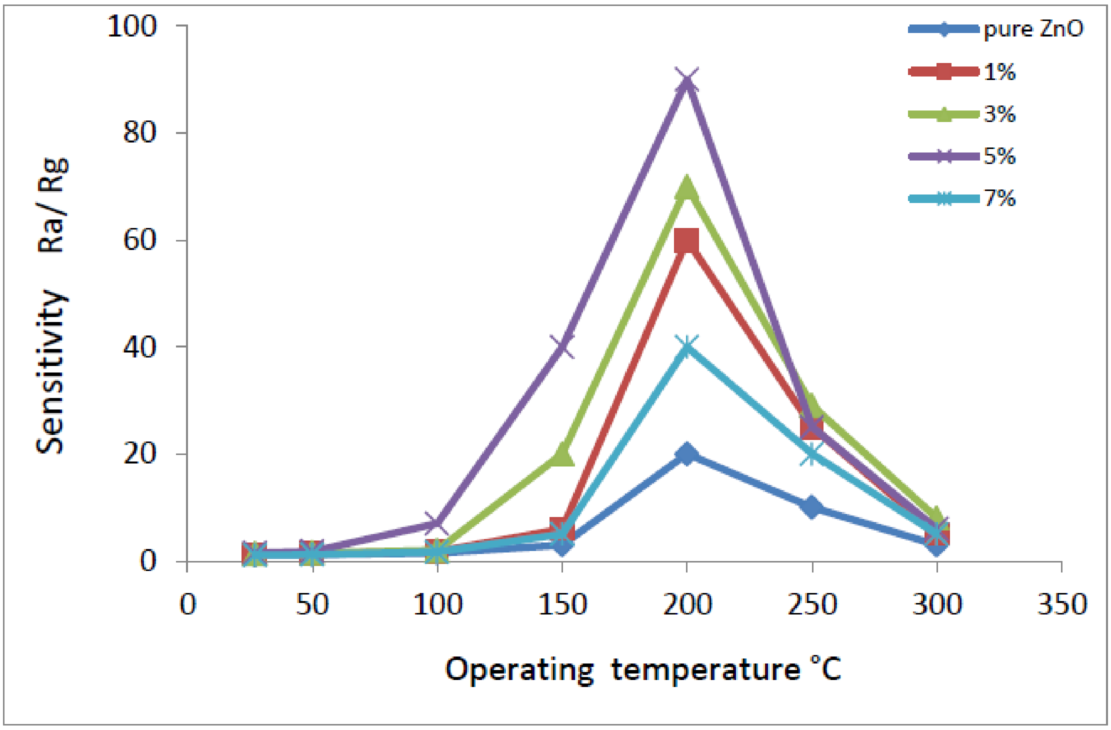

Fig (3) variation of sensitivity as a function of operating temperature at different concentration of Co

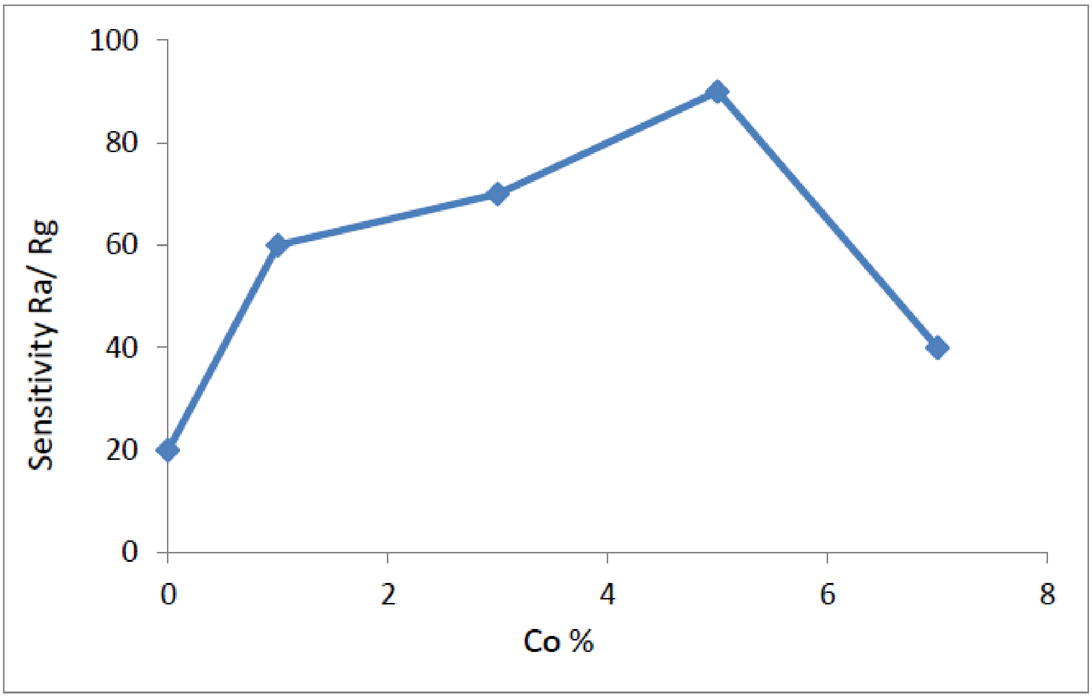

Fig (4) variation of sensitivity as concentration of Co at 200°C operating temperature

CONCLUSION

Highly textured pure and Co doped ZnO films were prepared by PACVD. Gas sensing investigation reveals that Co-doping can enhance the sensing properties of ZnO films gas sensor efficiently. From the gas sensor characterization studies, it is clear that the cobalt zinc oxide can be used as an ethanol sensor effectively. The optimized operating temperature for the cobalt zinc oxide film is 300°C and cobalt concentration 5%.

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