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Effect of Fluorine doping on H_2S gas sensing properties of Zinc Oxide thin films deposited by Spray CVD Technique

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Abstract

Structural, morphological and topographical properties of fluorine-doped ZnO nanostructure semiconductor thin films have been investigated by novel spray CVD technique. The properties of these thin films are governed by the additives of Ammonium Fluoride in non-aqueous solution of Zinc Acetate as a starting material. The crystalline structure and orientation of ZnO thin films have been investigated by X- ray diffraction (XRD) technique for varying Fluorine doping concentration in the range of 0.2 at% to 1 at% in steps of 0.2. The grain size for the films was found to be in the range of 19–23nm. Synthesis of Fluorine doping inducing transition of surface morphology is helpful in studying crystallite size, structure and phase formation by X ray diffraction pattern. For both ZnO and F: ZnO films, the dominant diffraction peak is the (002) peak at around 34.4^0, confirming the strong (002) texture of these films. The surface morphology investigated by FESEM was very smooth, more compact, dense with uniform spherical grains supporting the (002) intensity maxima.

The H_2S gas sensing properties of the films were investigated by using homemade gas sensing unit. The dependence of H_2S gas detection on the doping concentration of Fluorine doped Zinc oxide film was studied at 300^0C. It is observed that response time and recovery time increases with increase in doping concentration. It is further seen that deteriorated crystallinity and surface morphology with increase in doping concentration improve the gas detection properties of Flourine doped Zinc oxide thin film.

Keywords: spray CVD technique, thin films, X-ray diffraction and scanning electron microscopy, response time, recovery time.

Introduction

Recently, various nanocomposite thin films consisting of metal oxide semiconductors such as ZnO, In_2O_3, and SnO_2 etc have applications for the detection and monitor the various toxic & inflammable gases present in the atmosphere. Among these, ZnO is one of the earliest discovered and the most widely applied gas sensing material. But, ZnO-based gas sensors have shown some limitations, like low sensitivity, high response and recovery time towards low gas concentrations. The physical and chemical properties of zinc oxide can be easily tailored by using suitable impurity material. The gas sensing properties of zinc oxides depend naturally on their surface chemical properties, in addition to their physical or morphological properties. Therefore, incorporation of particular dopants/impurities was reported to make it selective, bring down its operating temperature and decrease the response time. Recently, different cationic dopants like Al, Sn, Pd, In, and Sb [1,2,3,4] were reported to enhance the sensing performances.

However, fluorine can be a promising anion doping candidate owing to its ionic radius similar to that of oxygen (F^{-1} 1.31 ˚A; O^{-2} 1.38 ˚A). It seems to be appropriate substitution impurity in the ZnO wurtzite structure to modify its electrical properties. A significant resistance change can be obtained in doped ZnO rather than in undoped ZnO, which results in a higher sensor response. The potential to increase the gas response of doped ZnO films is directly related to the exposed surface area, electrical and sensitivity characteristics. In order to enhance the gas performance, morphological features of the materials should be controlled during chemical synthesis resulting in high specific surface areas higher probability for a gas to interact with the semiconductor increasing the sensitivity of the materials. Several techniques for synthesis of thin film from nonaqueous route at low temperatures have been developed. In this paper, we are trying to detect low concentration of H_2S by F doped ZnO nanocrystalline films with the help of newly fabricated spray CVD technique to investigate the influence of different doping concentrations on the gas sensing properties.

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Experimental technique

The standandared conditions for the synthesis of ZnO thin film are as follows. The starting spraying solution was of 0.075 M zinc acetate dehydrate (Zn $(CH_3COO)_2$, $2H_2O$) in methanol (A.R. grade). For doping, 2M solution of ammonium fluoride in methanol was used as a source of fluorine. The solution was sprayed onto hot glass substrates using compressed air as a carrier gas. To vary concentrations of fluorine from 0.2at% to 0.8at% in steps of 0.2at% corresponding volumes of solution of ammonium fluoride were added to the main solution. To study H_2S sensing behavior ZnO resistance is measured in presence of gas as a function of time. The steady- state resistance were investigated in the temperature range 300^0C for 20 ppm H_2S in air.

Characterization Techniques

The structural investigations on ZnO thin films were carried out using a Bruker AXS X-ray diffractometer (German make Bruker axs D-8 Advance Model) with Cu–Kα (λ = 1.54 Å) as radiation source operating at 40 kV and 30 mA. The diffraction angle '2θ' was varied from 200 to1000 with a step of 0.02^0/min. The films thickness and roughness was measured by surface profilometer (model Ambios XP-1). The films surface morphology was studied with the Field emission scanning electron micrographs (FESEM) with 50,000X magnification. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments, USA in contact mode, with V shape silicon nitride cantilever of length 100μm and spring constant 0.58N/m.

Results & discussion

Structural Properties

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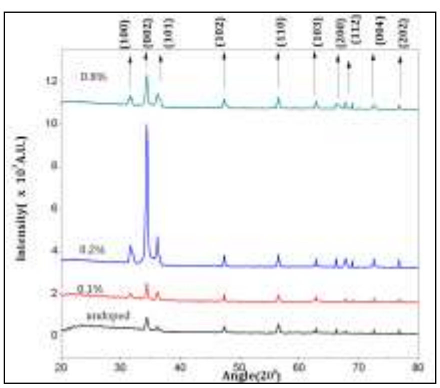

Fig.1X ray diffraction spectra of F:ZnO thin film

Fig.1 depicts the X ray diffraction pattern for F doped ZnO thin films. All the peaks correspond to the hexagonal wurtzite structure of ZnO. They are indexed according to the JCPDS80-0075. All the films show preferential growth along (002) plane. At initial stage, the intensity of (002) peak was increased with F doping, reached to its optimum value for 0.2at% and then suppressed for excess F doping. The films crystalline properties are characterized by the crystallite size. It is calculated by using the well known Debye-Scherrer formula. (Table 1)

Morphological Properties

Figure 2a & 2b illustrates scanning electron micrographs of F:ZnO thin films.

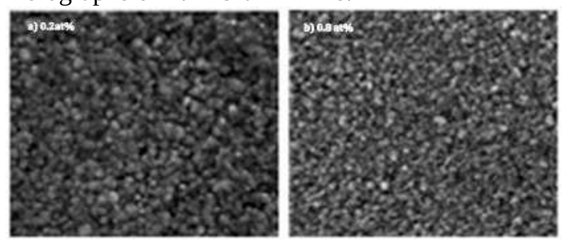

Fig.2 SEM morphology of F;ZnO thin film

It reveals that for 0.2 at % of fluorine, the surface morphology was very smooth, more compact, and dense with uniform spherical grains. However the grain size decreases for 0.8 at% F doping, showing uniform tiny, spherical bead like morphology. It shows that the mean crystallite size calculated by Scherrer formula is substantially smaller than the grain size observed by SEM. It indicates that these grains are probably aggregation of crystallites.

Topographical Properties

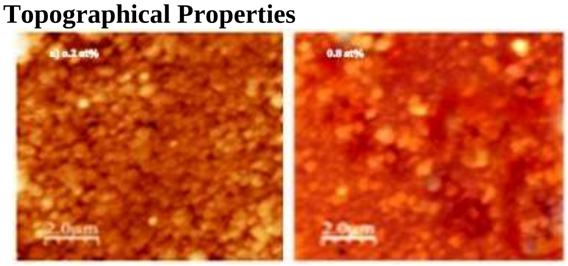

Fig.3 AFM morphology of F:ZnO thin films

Figure 3a and 3b reveals topographical properties of 0.2at% and 0.8at% fluorine doping concentration. It shows slightly large grain size distribution compared with SEM micrographs. A reasonably rounded geometry with non porous, regular and uniform texture is observed for all samples.

Gas sensing properties

The gas response of F doped ZnO nano-crystallites to 20ppm H_2S gas was investigated for 300^0C operating temperature by using the in house fabricated gas sensing unit and the results are mentioned in table1. We tested response of F doped ZnO towards H_2S reducing gas. The resistance response of this

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sensor structure was transformed into a sensitivity value using commonly used formula for the gases:

$$S=(R_a-R_g)/R_g \quad \ldots\ldots\ldots \quad (1)$$

where R_g is sensor resistance influenced by the H_2S gas and R_a is the sensor resistance in the air. Table 1 shows H_2S gas response of F doped ZnO nano-crystallites. It is observed that sensitivity increased with increase in doping concentration.

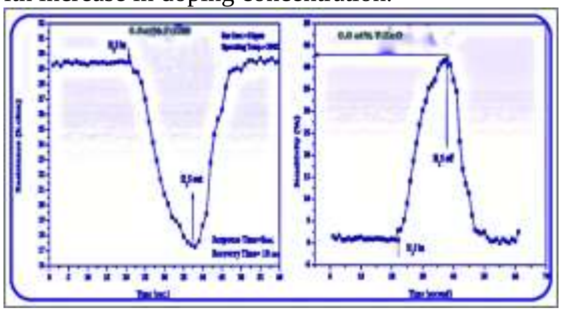

Fig.4 A typical H_2S gas response

The 0.8at% F doping concentration shows maximum sensitivity of 45% with very short response and recovery time. Thus the smaller grain size provides greater surface area for the materials which causes stronger interaction between the adsorbed gases and the sensor surface, i.e. higher the gas sensing sensitivity. It provides the large number of adsorption sites, the sensitivity could be improved by the significant change in surface area. The gas response of sensor depends on the surface reaction between the metal oxide and the gas molecules in the ambient; therefore microstructure of material plays a critical role in determining sensor response.

Table1 H2S gas sensing properties of F:ZnO

Doping concentration	Grain size	% Sensitivity	Response Time	Recovery Time
0.2at%	23nm	13%	3sec	30sec
0.6at%	18nm	20%	7sec	35ec
0.8at%	19nm	25%	8sec	20sec

Conclusion

The uniform thin films of F doped ZnO with different doping concentrations were deposited by spray CVD technique. It is clear that the gas response of sensor increases with decrease in the grain size. It provides a larger surface to volume ratio. More specifically the 0.8 at% F doped ZnO thin films show relatively small and uniform particle size which exhibits high sensitivity towards hydrogen sulfide gas with rapid response to the test gas. It also shows good recovery time for the test gas. This exhibits that the nano sized F-doped ZnO thin films for 0.8at% doping concentration deposited by spray CVD technique have a potential to become a good H_2S gas sensing material.

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