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H_2S gas sensitive Sn-doped ZnO thin films: Synthesis and characterization

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ABSTRACT

Tin doped zinc oxide thin films were synthesized at low substrate temperature (473 K) by advanced spray pyrolysis technique for H_2S gas sensing application. Equimolar solution of zinc acetate and tin chloride were used to grow Sn doped ZnO thin films. The effects of tin doping concentration on the structural, morphological, and gas sensing properties of Sn doped ZnO films were investigated. It is revealed that all films exhibit wurtzite structure and the average crystallite size reduce with increasing Sn doping concentration. With an increase in Sn doping, the peak position of the (0 0 2) plane was shifted to the low 2θ values indicating the lattice distortion incorporated into the film due to Sn doping. The results obtained from TEM and FESEM characterizations confirmed the XRD observations. Further, the as-characterized Sn doped ZnO films were profoundly studied for their H_2S sensing performance. The H_2S gas sensing characteristics that are mainly governed by an operating temperature were found to be optimum at 473 K. A maximum response of ~31% to 30 ppm H_2S was obtained at 473 K with reasonably fast response and recovery. Particularly, the 4 wt.% Sn doped ZnO sample exhibits selective behavior towards H_2S on account of its surface morphological features. The H_2S detection properties of the 4 wt.% Sn doped ZnO film were improved significantly on palladium (Pd) sensitization and the film demonstrated adequately stable sensing performance.

1. Introduction

Nowadays, ecologists and researchers in the field become attentive towards semiconducting metal oxide based gas sensors, due to their small dimensions, low cost, and high compatibility with microelectronic processing and malleability to different poisonous and inflammable gases [1]. Hydrogen sulfide (H_2S) is one of the noxious, colorless and aromatic gases that often produces in the sewage, coal, coal-oil or natural gas industries and other industrially important hydrocarbon feedstocks [2,3]. It is badly harmful to human being since inhalation of excessive levels of H_2S gas in a confined space can result in loss of consciousness, respiratory failure or death. Therefore, real-time detection and monitoring over traces of such harmful gas has become particularly imperative for both resource exploitation and human health.

Hitherto, several metal oxide compound semiconductors, such as SnO_2, WO_3, TiO_2, In_2O_3, ZnO etc., has been found to be competent gas sensitive materials [4–8]. Among these, zinc oxide (ZnO) is a multifunctional semiconducting metal oxide. It is one of the most prominent and extensively studied metal-oxides for gas sensing applications. However, undoped ZnO based gas sensors operate at high operating temperature and shows poor response at low gas concentrations and poor selectivity towards similar reducing gases, which limits its use in instantaneous gas sensing. An improvement in the performance of ZnO thin film gas sensors at low operating temperatures are possible through enhancement in surface reaction kinetics by increasing available gas absorptions sites on the film surface. Nano-crystalline thin film may be the solution to this problem, because this will provide greater surfaces to volume ratios. During the last two decades, many research groups made an effort to address the issue and synthesized nano-crystalline thin films of ZnO by using various techniques such as sol–gel [9], thermal evaporation [10], magnetron sputtering [11,12] and chemical

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spray pyrolysis [13,14]. Amongst these, chemical spray pyrolysis is a simple and low cost deposition technique that offers mass production capability with uniform coatings. Recently, the conventional spray pyrolysis system has been modified by retaining all its indigenous advantages to deposit metal oxide thin films at relatively low substrate temperatures [15]. On account of its solid–vapor phase growth process this modified technique is able to produce fine nanocrystallites and thereby a large surface area, useful for gas sensing applications.

In addition to modification of synthesis processes, an impurity doping is considered as another effective way to improve the performance of metal oxide gas sensors. Among the various dopants, tin (with an ionic radius of 0.69 Å comparable to zinc 0.74 Å) [16] appears to be an appropriate substitutional impurity in the wurtzite ZnO. The difference in ionic radii of Sn and Zn is expected to degrade film crystallinity and thereby lower the grain size. In addition, a significant resistance change can be achieved by Sn incorporation in ZnO, which results in a higher sensor response. Previously, Sn impurities in ZnO films successfully demonstrated to improve the sensing properties of ZnO film to formaldehyde, ethanol and NO_2 [17–19]. However, to the best of our knowledge, the detection of H_2S gas using Sn-doped ZnO thin films has hardly ever been reported to date.

The present work reports on the synthesis and gas sensing properties of Sn-doped ZnO (SZO) thin films. The films were deposited by advanced spray pyrolysis technique onto the glass at low substrate temperature. Structure and surface morphology of the films were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. Gas sensing experiments of as-characterized SZO films were performed for H_2S as a probe gas. The H_2S gas sensing response of the films was studied as a function of operating temperature, Sn doping concentration and gas concentration. The selectivity of H_2S gas was tested against the reducing gases and alcoholic vapors. Finally, an improvement in H_2S sensing performance of SZO films by Pd-sensitization was studied and described.

2. Experimental details

The methodology adopted to prepare SZO films at low substrate temperature, their characterization and the assemblies used to study gas sensing properties are described as below:

2.1. Synthesis of sensing films and characterization

The advanced spray pyrolysis system with pneumatic glass atomizer has been used for deposition of SZO thin films. The experimental setup and other details have been reported elsewhere [15]. For deposition of SZO thin films, initially, the spraying solution was prepared by mixing the appropriate volumes of equimolar (0.1 M) non-aqueous solutions of high purity zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] (Thomas Baker) and stannic chloride [$SnCl_4{\cdot}5H_2O$] (Loba Chemie) in methanol. Three different concentrations (1, 3 and 4 wt.% measured as an atomic weight percentage) of stannic chloride were selected to dope Sn in ZnO thin films. In the deposition process, when non-aqueous solution is sprayed through the nozzle the atomized droplets arrive in the reaction chamber and pyrolytic decomposition of solution takes place and result into zinc oxide particles. These particles are then pushed in upward direction and get deposited on the glass substrates kept above the reaction chamber. The possible chemical reaction of ZnO film formation from zinc acetate solution is as follows [20],

$$Zn(CH_3COO)_2 \cdot 2H_2O + 2CH_3OH \xrightarrow{\Delta} ZnO + 2(CH_3COCH_3) + 3H_2 + O_2 \quad (1)$$

In the course of film synthesis, the other pre-optimized deposition parameters viz. core temperature (598 K), substrate temperature (473 K), spray rate (6 ml min^{-1}), nozzle to substrate distance (38 cm) and air pressure (10 LPM) were kept same. Electronic temperature controllers were used to control the substrate and core temperature throughout the experimentation. Harmful gases evolved during the thermal decomposition process within the system were expelled out. For our convenience, the 1, 3 and 4 wt.% Sn doped ZnO thin films were represented as 1SZO, 3SZO and 4SZO, respectively.

The crystalline structure of SZO thin films was analyzed by using X-ray diffractometer (German make Bruker axs D-8 Advance Model: operating at 40 kV and 30 mA) with Cu Kα (λ = 1.54 Å) radiation. The microstructure of the ZnO film was further resolved by using conventional transmission electron microscope (TEM, JEM 2000EX, JEOL, Tokyo, Japan) and selected area electron diffraction (SAED). The surface morphology of the SZO thin films was studied at room temperature by obtaining micrographs using a field emission scanning electron microscope (FE-SEM, Model: JSM-6701F).

2.2. Gas sensing measurements

To measure the H_2S gas response, the ohmic contacts were prepared by using pressed aluminium foil and such films were mounted in an airtight housing of specially fabricated gas sensing measurement unit described elsewhere in detail [21]. A measured quantity of gas concentration (ppm) was introduced into the housing by means of a syringe and corresponding variations in film resistance was measured as a function of time. The response of the film towards H_2S gas was tested at different operating temperatures in the range of 423–523 K for different H_2S gas concentrations in the air. The film selectivity to H_2S was tested against LPG, NH_3 and different alcoholic vapors. In this, the gas percentage response (S) was defined as $S = [(R_a - R_g)/R_a] \times 100\%$, where R_a is the film resistance in the air and R_g is the film resistance in a test gas or vapor. The response and recovery time are defined as the time taken by the film sensor to achieve 90% of the total resistance change in case of adsorption and desorption process, respectively. The selectivity coefficient (Q_{H_2S}) of H_2S gas to another gas was defined as, $Q_{H_2S} = S_{H_2S}/S_X$ where S_{H_2S} and S_X are the response of sensors in H_2S and 'X' gas, respectively.

For electronic sensitization, we adopted the palladium sensitization method similar to that of Mitra et al. [22–24]. The 0.01 M palladium chloride ($PdCl_2$) solution was prepared in methanol. Then, the SZO film was immersed in this as-prepared methanolic solution of $PdCl_2$ for 5 s and subsequently dried in air flow. Such dip-dry process was repeated 10 times. Finally, in order to extract the chloride from the sensitized film, the film was annealed at 473 K for 1 h. These Pd-sensitized ZnO thin films were then tested for H_2S sensing.

3. Results and discussion

3.1. Structural and surface morphological properties

Fig. 1 shows the XRD patterns of the 1SZO 3SZO and 4SZO films. Peaks with the Miller indices (1 0 0), (0 0 2) and (1 0 1) belong to the ZnO [25]. The XRD exhibits the hexagonal wurtzite structure with a polycrystalline nature. Importantly, no other peaks corresponding to tin oxide or tin are observed even at high doping percentages; which confirms that tin substitutes zinc in the hexagonal lattice and/or tin segregates to the non-crystalline region in grain boundary. It is seen that, the orientation of 1SZO film is along (1 0 1) plane; however, for further increase in Sn doping, the films possess dominant orientation along (0 0 2) plane. No change in position of (1 0 0)