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Enhanced hydrogen sensing performance of tungsten activated ZnO nanorod arrays prepared on conductive ITO substrate

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Abstract

We report for the first time, the H_2 sensing properties of tungsten activated ZnO (W:ZnO) films prepared on electrically conductive Indium Tin Oxide (ITO) coated glass substrate by spray pyrolysis technique. Microstructure, morphology and optical properties of W:ZnO films prepared with different W dopant concentrations were investigated. All the deposited films show a hexagonal wurtzite crystal structure with preferred orientation along the *c*-axis perpendicular to the ITO substrate. The optical absorption results revealed increase in band gap and improvement in transmission upto 3% W incorporation in ZnO. The improved crystallinity of the ZnO film revealed from increase in intensity of photo emission, established the possibility of development of a sensor device with W dopant at 3% level. The energy dispersive X-ray elemental analysis of the samples confirmed the incorporation of W ions into ZnO lattice. SEM results show the influence of W catalyst on the uniform and well-aligned growth of ZnO nanorods with unique shape on ITO substrate, which provided higher capture efficiency favorable for Hydrogen (H_2) sensing. Gas sensing properties of *W*:ZnO films were studied at room temperature for different H_2 concentrations (from 100 to 400 ppm). It was demonstrated that W doping play an important role in defining the enhancement of sensor response towards H_2. Our results show fast response and recovery time for 3% W:ZnO film, suitable for high performance H_2 gas detection.

Keywords: W:ZnO thin films; ITO substrate; Spray pyrolysis; SEM; H_2 sensor

1. Introduction

Hydrogen (H_2) is regarded as one of the most promising energy carriers for its nonpolluting nature and high energy density. It has a wide range of flammability in air, which is about 4–75% by volume, and the lowest limit of H_2 concentration in air to cause explosion is 4.65% [1–3]. Accordingly, a reliable sensor is needed to detect leakage from the storage and transportation of H_2, as well as to monitor its concentration below its lower explosion limit. Metal oxide semiconductor gas sensors have drawn a great deal of attention to researchers due to their numerous advantages including lower power consumption, reproducibility, low temperature operation, ability to detect large number of gases. The sensing response of a material towards gases are strongly dependent on its structural, optical and morphological features. The formation of high active surface area and porous structure will result in a greater possibility for the gases to interact with the oxide semiconductor, which in turn increase the sensitivity of the material. Much research has been focused on increasing the sensitivity of gas detection through process, such as doping or using metal as catalyst.

Zinc oxide (ZnO) nanomaterials are promising candidates, due to its wide and direct band gap of 3.37 eV, and a large excitonic binding energy of 60 meV at room temperature [4]. ZnO thin films are promising for sensing application due to its high electrochemical stability, non-toxicity and suitability to doping. It has proved to be a highly sensitive material for flammable or toxic gas detection [5]. However, it is still demanding to design a ZnO sensor which works at room temperature. To overcome this problem, a large number of studies have been carried out in order to tune the properties of ZnO by adding impurities which can improve the sensor

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response and reduce the recovery time at near room temperature. Noble metal supported ZnO and tungsten trioxide (WO_3) has become a promising material for gas sensing devices due to their attractive electrical conductivity and good sensitivity and relative selectivity towards gases such as H_2 [6], NO_2 [7], NH_3 [8], CO [9] and O_3 [10]. Presently, WO_3 nano-structured materials have also been found to be a promising candidate for the detection of various toxic and combustible gases. However, the combination of these metal oxides with an appropriate proportion to enhance the H_2 gas sensing performance has not been reported earlier as far as we are aware. Hence in the present study, a novel transparent conducting oxide material formed by W doping in ZnO thin film was used to study the gas sensing performance towards H_2. The addition of W into ZnO is quite appealing because there is a valance difference of four between W^{6+} and Zn^{2+}, hence, each W atom can contribute more than one electron to the conductivity. The W:ZnO films are considered to be utmost an important material due to their lower cost and good transparency. In addition W doped ZnO, exhibits several advantages such as less lattice mismatch with ZnO, controllable band gap and good crystal quality with few oxygen vacancies. Several researchers have used H_2 catalyst materials, such as gold (Au), platinum (Pt) and palladium (Pd), to enhance sensor sensitivity [11–14]. However, there are no such studies on W catalytic doping of ZnO to enhance H_2 sensitivity at room temperature.

Many reports show that good quality ZnO thin films can be fabricated on glass, quartz, Si, sapphire, Ni, etc., by different techniques and under various growth condition [15]. Here, we investigate the structural, optical and morphological characteristics of W:ZnO thin films fabricated on Indium Tin Oxide (ITO) coated glass substrate, which is a new study. The novelty of growing W:ZnO nanorods on ITO substrate in our experiment is to improve the conductivity of the films that was different from previous studies. Up to date, there are no reports on the study of H_2 sensing characteristics of W:ZnO films fabricated on ITO substrate. Moreover, ITO coated glass substrate has many excellent properties, such as good conductivity, high optical transparency, low resistivity and high work function [16]. In current years, several methods including spray pyrolysis [17], sol–gel [18], thermal evaporation [19] RF sputtering [20] and pulsed laser deposition [21] have been developed for coating thin films. In the present work, we used novel pyrolytic deposition route, with specially designed spray nozzle for fabricating well-aligned W:ZnO nanostructures. Spray pyrolysis technique for synthesis of doped thin-films is an interesting option due to the use of inexpensive precursor materials, effective stoichiometric control, and no need of vacuum and low-cost equipment suitable for large-area coatings. ZnO nanorods exhibit enhanced gas sensitivity at lower operating temperatures compared with bulk materials thin films. Gas sensors that are operated at room temperature show greater advantages, such as long life, low power consumption and safe use in flammable environments [22,23]. Hence, we focused on developing ZnO nanorods as H_2 gas sensor materials that function at room temperature.

In this paper, we report the room temperature H_2 sensing characteristics of W doped ZnO thin film sensors prepared on electrically conductive ITO coated glass substrate by a spray pyrolysis method. We aimed at a better control of crystalline phase growth, surface chemistry and nanoscale dimensions in these certain films. The influence of W dopant concentration on the structural, morphological, optical and luminescence properties of ZnO thin films were investigated. The W:ZnO/ITO films of different W dopant concentration were investigated for its better sensing characteristics towards varying concentration of H_2 gas.

2. Experimental details

The W doped ZnO thin films deposited onto ITO coated glass substrate (having resistance 70–100 Ω/sq) by spray pyrolysis technique involved the decomposition of aqueous solution of high purity zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$ (A.R.grade, Aldrich)) and tungsten chloride (WCl_6), dissolved in required quantity of ethanol and deionized water as a solvent. The schematic of the spray pyrolysis experimental setup used for coating films was explained by the authors elsewhere [24]. The solution was atomized using compressed puried air. The deposition rate was kept constant at about 5 ml/1 min. The substrate-nozzle distances were maintained at 30 cm and the substrate temperature was kept constant at 350 °C for all the experiment. A specially designed spray nozzle with two concentric glass pipes was used. The precursor solution flows through the inner pipe and the air stream between the inner and outer pipes. The spray was produced by the Ventury effect at the end of both pipes. It was found that the amount of water, ethanol and the precursor solution played important roles in determining the morphology of W:ZnO films. The resultant mixed solution was sprayed in the form of a fine mist of very small fine droplets onto the preheated ITO coated glass substrate held at an optimized temperature of 350 °C. The nucleation, condensation and coalescence of the droplets resulted in the formation of W:ZnO films. In order to investigate the effect of W doping on the properties of ZnO films, dopant concentration was varied from 1% to 4%. The resultant films were found to be homogeneous, transparent and well adherent. The chemical reaction of pyrolytic process in W:ZnO film formation may be as follows:

$$Zn(CH_3COO)_2 \cdot 2H_2O \overset{\text{deposited as } 350^{\circ}C}{\Longrightarrow} ZnO + CO_2 + CH_4 \quad (1)$$

$$Wcl_6 + \frac{3}{2}O_2 \rightarrow WO_3 + 3cl_2 \quad (2)$$

$$(1-X)ZnO + WO_X \rightarrow Zn_{1-X}W_XO_{(Substrate)\downarrow} \quad (3)$$

The deposited W:ZnO/ITO films were further used to investigate the structural, optical, morphological and luminescence properties. Crystallographic and phase structure of the films were determined by X-ray diffraction (XRD) using Cu Kα radiation. The optical properties of the deposited films were investigated using ultraviolet-visible (UV) spectrophotometer. Photoluminescence