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Short communication

A novel room temperature ethanol sensor based on catalytic Fe activated porous WO_3 microspheres

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ABSTRACT

We report the room temperature ethanol sensitivity of pristine WO_3 and Fe activated WO_3 microspheres architecture prepared by a novel spray pyrolysis method. The films exhibit single crystalline nature with preferentially oriented (200) plane along c-axis direction. Optical spectra show shift in the band edge towards longer wavelength after Fe incorporation. SEM revealed the formation of a smooth surface area of WO_3 with uniformly distributed spherical particles, which changed to porous nanostructured composition with good crystal quality after Fe doping. Gas sensing mechanism and enhancement of ethanol sensing performance of the WO_3 film with catalytic Fe addition were discussed.

1. Introduction

Ethanol sensors play an important role in medical detection, environment protection and food industries [1,2]. Detection of ethanol is an important feature of the breath alcohol analyses that is used to monitor ethanol in human breath [3]. Development of ethanol sensor with lower operating temperature and better selectivity and sensitivity is the prime objective of the present research. Metal oxide semiconductor (MOS) holds enormous promise to enable a new generation of gas sensing devices. The sensing performance of MOS film depends on the mechanism by which target gas is detected on the surface. Among different MOS reported, tungsten trioxides (WO_3) have been attracting great attention due to its inherent electrical conductivity and excellent selectivity and high sensitivity [4]. Doping of WO_3 with other elements can greatly improve the performance of the film with good efficiency. The porosity of the film can be achieved using suitable catalyst and the sensing properties can be enhanced significantly [5]. Thus, the main objective of the present work is to enhance the sensitivities of the WO_3 thin films doped with catalytic iron in the presence of ethanol. Until now there were no reports on enhancing the ethanol sensing performance of WO_3 with Fe catalytic doping.

In the present work, a novel spray pyrolysis deposition route with specially designed spray nozzle was used for film growth. The effect of Fe catalytic doping on the morphology, band gap and crystal structure of WO_3 was investigated to examine the performance of the films for room temperature ethanol detection.

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2. Experimental procedure

Pristine WO_3 and Fe activated WO_3 films of different Fe dopant concentrations were fabricated on glass substrate at 350 °C by a novel spray pyrolysis deposition route using (0.2 M) tungsten chloride (WCl_6) and (0.01 M, 0.03 M, 0.05 M) iron chloride precursors. The deposition parameters used for the preparation of WO_3 films in the present study are summarized in Table 1. The spray nozzle was specially designed with two concentric glass pipes, through the inner pipe the solution flows between the inner and outer air stream [6]. The films were then annealed at 450 °C in a muffle furnace. The chemical reaction of pyrolytic process in film formation may be as follows:

$$Wcl_6+\frac{3}{2}O_2\rightarrow WO_3+3cl_2. \quad (1)$$

The films were characterized using X-ray diffractometer (XRD), UV–vis spectrophotometer, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDXS).

The $Fe:WO_3$ sensors were fabricated with two thick silver pads on two ends of the film as electrical contacts. Fig. 1 shows the schematic diagram of the experimental setup used for measuring the sensor resistance. The resistance of the sensor was measured at room temperature in the presence of ethanol. The chamber was evacuated to a base pressure of 1.0 Pa using an oil free vacuum pump. The ethanol vapor was injected inside the chamber using a calibrated digital micropipette. The sensitivity of the sensor was determined using the standard formula for reducing gases [6,7].

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Table 1
Summary of deposition parameters for pristine WO_3 and Fe activated WO_3 thin films.

Parameters	Values
Substrate temperature	350 °C
Carrier gas flow rate	0.4 kg cm^{-2}
Precursor volume	100 ml
Solvent	Ethanol
Solution feeding rate	5 ml/min
Spray nozzle to substrate distance	30 cm
Deposition time	10 min
Temperature of annealing	450 °C
Substrate	Glass
Duration of annealing	1 h

3. Results and discussion

Fig. 2 shows the XRD patterns of pristine WO_3 and Fe activated WO_3 films. All the films exhibit single crystalline nature with hexagonal structure. A strong peak at 2θ ~24.8° belongs to the (200) phase of WO_3, orientated preferentially along the c-axis. The patterns show sharp and strong peaks, indicating high crystal quality of the film. Neither Fe nor Fe_2O_3 peak was detected. The presence of Fe was proved later by EDXS characterization. The intensity of (200) peak was much stronger for WO_3 and got suppressed by Fe addition, this may be due to the disappearance of the defeat of periodicity, textured structure and deformation in the lattice [8]. Another reason may be due to the small difference between the ionic radii of W^{6+} compared to Fe^{3+}. Fe^{3+} can fulfill the same coordination as that of W^{6+}, as W^{6+} is octahedrally co-ordinate with O^{2-}.

In Fe:WO_3 films, the (200) peak show a slight shifting towards the lower diffraction angle compared to WO_3. This slight shift may be attributed to the good Fe intercalation on W site and slight distortion in the crystal lattice. Such distortions can create a number of defects in the film which is favorable for gas sensing. Average crystallite size (D), dislocation density (δ), microstrain (ε) and number of crystallites per unit area (N) have been estimated by using standard expression [9, 10]. The value of D for pristine WO_3 film was found to be ~47 nm, which increased from ~49 to ~54 nm with an increase in Fe percentage. This significant improvement in the crystallite size after Fe doping leads to increase in the amount of oxygen vacancies. An increase in oxygen vacancies is considered to be greatly beneficial for gas sensing. Table 2 shows the structural parameters for (200) plane of the pristine WO_3 and Fe:WO_3 films. The decrease in δ obtained for Fe:WO_3 films confirmed the improvement in crystallinity of the films [11]. Moreover, the decrease in strain indicates the reduction in concentration of the lattice imperfections, and the formation of films with high crystal

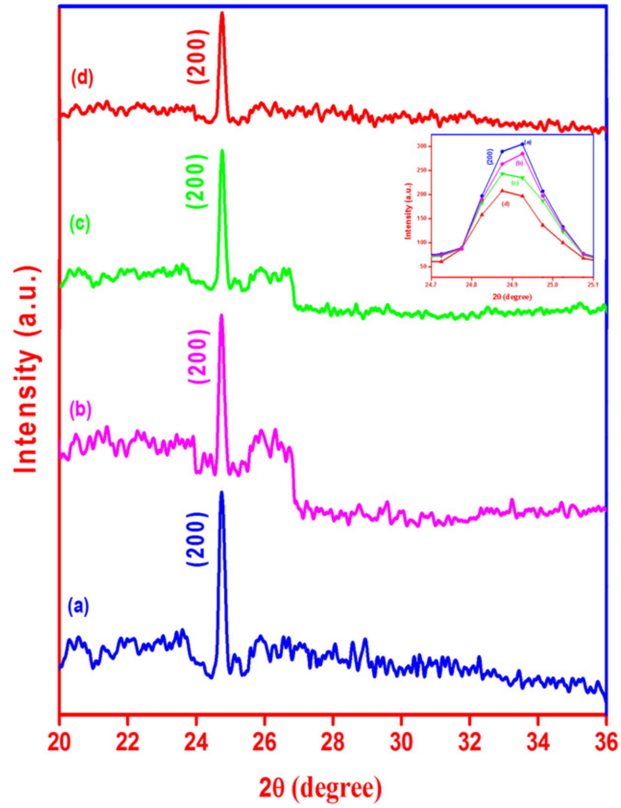

Fig. 2. X-ray diffraction patterns of Fe activated WO_3 thin films: (a) pristine WO_3; (b) 1 wt.% Fe:WO_3; (c) 3 wt.% Fe:WO_3; (d) 5 wt.% Fe:WO_3.

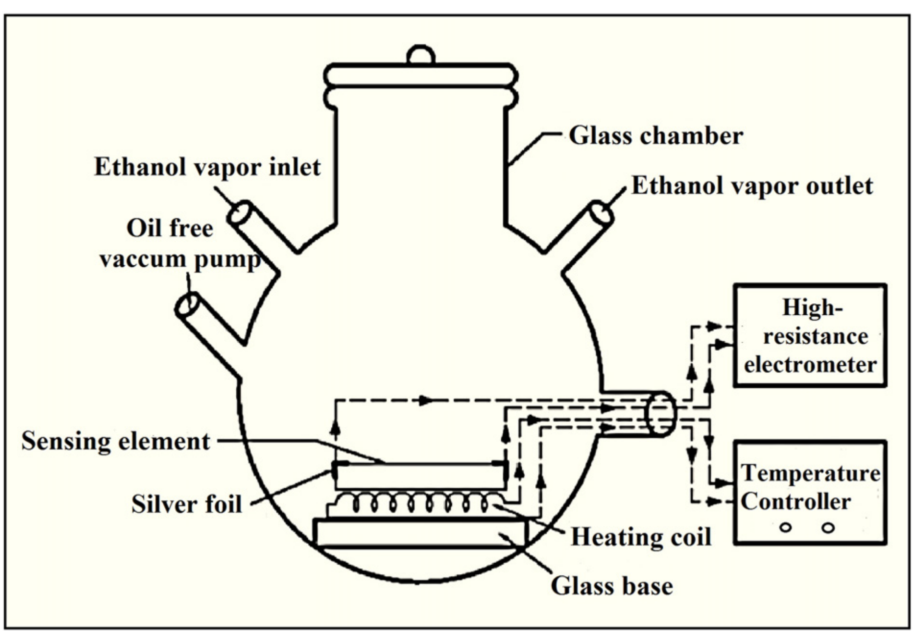

Fig. 1. Schematic of the experimental setup used for gas sensing measurement.