Indian Journal of Science and Technology Vol. 3 No. 1 (Jan 2010) ISSN: 0974- 6846

Hydrogen sensing properties of indium doped tin oxide thin films deposited by spray pyrolysis

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Abstract

In this article the effect of indium impurity on tin oxide layers sensitivity have been studied. Tin oxide thin films without impurity and with different impurities are deposited by spray pyrolysis method and their structural layers have been characterized by x-ray diffraction spectrum and SEM technology. In different temperature we have calculated layer sensitivity. It is found that the most sensitivity is in the sample of 6% impurity at temperature of 200 °C. With increasing of impurity concentration the work temperature is decreased until in the 15% impurity sample the work temperature is decreased to 100 °C.

Keywords: Tin oxide, spray pyrolysis, thin films.

Introduction

Gas detectors have applications in fuel controllers, dangerous gas detecting in an environment and determining gas leakages. Semiconductor gas sensors are of interest which includes metal oxides of SnO_2, In_2O_3, ZnO and TiO_2 (Pielartzik *et al.*, 1999). Tin oxide semiconductor has advantageous use in sensing background. There are various techniques for depositing Tin oxide thin films on different substrates including spray pyrolysis (Aasmundtveit *et al.*, 1999), sputtering (Pankove, 1978), sol-gel process (Pankove, 1991) and organo metallic chemical vapor deposition (Keshmiri & Rezaee, 2002). Among these, the spray pyrolysis technique has several advantages such as deposition of high purity, homogeneous, cheaper and large-area films at relatively low temperatures. Aluminum and Indium doped ZnO are of interest as doping improves conductivity of ZnO thin films. Various techniques have been used to deposit undoped and doped ZnO films on different substrates, including spraypyrolysis, organometallic chemical vapour deposition (Raniero, 2006), pulsed laser deposition (Swanepoel, 1980), sputtering Schubert, 1993), and sol-gel process.

Metal-oxide sensors are based on decreasing resistance of metal-oxide thin films in presence of a gas (Wagner, 2003). Continuous efforts for parameter optimization of sensitivity, work temperature selections and steadying have been made over the last decades. Increasing the impurities has improved these parameters in a sensor (Lewis & Paine, 2000). Here we have used indium impurity to improve tin oxide layer sensitivity in the presence of hydrogen gas (Poortmans *et al.*, 1995).

Experimental procedure

Tin oxide thin films were prepared by dissolving $Sncl_4$-$5H_2O$ (33% wt), CH_3CH_2OH (33% wt) in H_2O (33% wt) and HCl (1% wt) as well. The weight ratio of 0, 2, 6, 8 and 15 of indium impurity are prepared by including 0.2, 0.6, 0.8 and 1.5 mil-gr of $InCl_3$ to 10 gr of main solution.

The solution is sprayed on hot glass substrate with dimensions of 2.5×7.5 cm. During the solution spray, carrying gas has a of 2 atm, flux rate 15 min/mm and substrate temperature 500 °C. The main reaction for creating SnO_2 thin film is as follows:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \qquad (1)$$

After depositing, both sides of samples are connected to electrodes. To measure tin oxide layer's sensitivity, a disicator is used (Keshmiri, 1996). After inputting hydrogen gas of 2000 ppm to disicator, the variation of sample resistance at various temperatures is measured and using the following formula sensitivity is calculated by,

$$S = \left[\frac{R_a - R_g}{R_a}\right] \times 100 \qquad (2)$$

where R_a is the sample resistance in air and R_g is the sample resistance in the presence of hydrogen gas. The procedure was repeated several times for temperatures between 50-300 °C. X-ray diffraction is used to study phase compositions and thin film deposition crystal structures with different impurity concentrations ($Cu\text{-}k_\alpha$, λ=0.15418 nm).

The XRD pattern has been recorded in the range of 2θ =20-70°, where the peak of intensity and width of maximum peaks can determine the main orientation of crystal growth as well as crystal structure variations with impurity concentrations. In addition, we have used SEM for samples with 2% indium impurity.

Results and discussion

Fig. 1 to 5 shows the XRD spectrum of tin oxide crystals as function of diffraction angle. It can be seen from the figures that the orientation of crystal growth is in the [110] direction and at angle of 13.24 degree. Also, there is a number of peaks in directions of (200), (211), (311) and (310) which are in diffraction angles of 16.96°, 19.12°, 25.92° and 32.84°. These diffraction patterns

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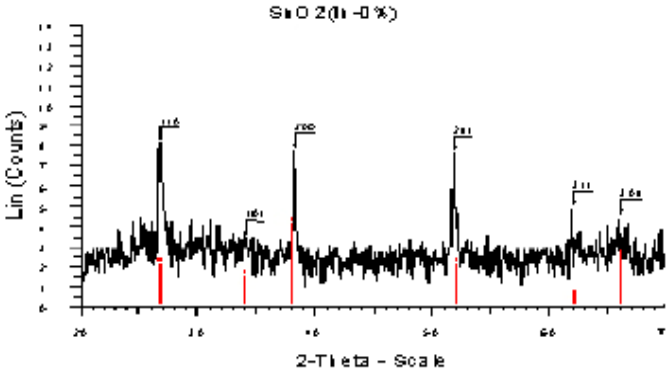
show that crystal growth is happened in these directions as well.

Fig. 1. X-ray diffraction pattern of pure Tin oxide sample.



From Fig. 1 and 2, we note that for 2% impurity the structure of Tin oxide layers are crystalline while in regards to Fig. 3 and 4, it can be seen that with increasing impurity, Indium atoms change the crystal structure of tin oxide layers to amorphs where the crystal growth orientation is not clear. In 15% impurity (Fig. 5) again, there is a number of peak in diffraction pattern which shows indium impurity in tin oxide is increased and layer structures have crystalline forms.

Fig. 2. X-ray diffraction pattern of tin oxide sample with 2% indium impurity.

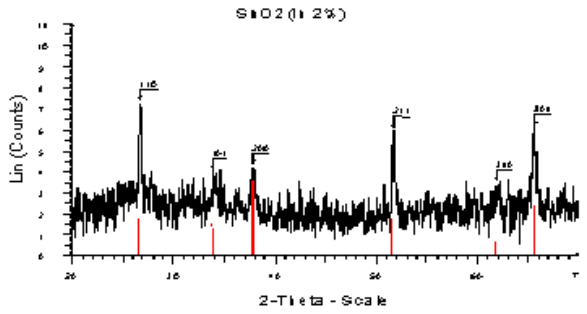


Fig. 3. X-ray diffraction pattern of tin oxide sample with 6% Indium impurity.

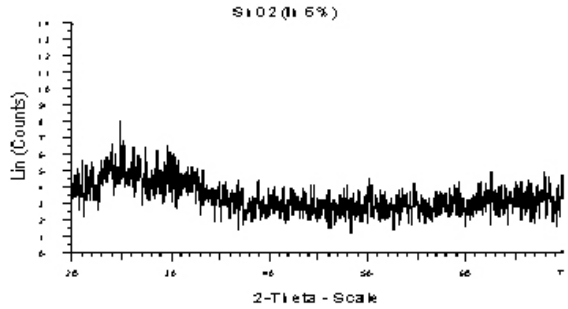


Fig. 6 shows the SEM image of sample with 2% impurity. White spots in the dark background are the single crystals which have dimensions of 7-8 μm.

Fig. 7a to 7e show sensitivity of tin oxide samples with impurity concentrations of 0, 2%, 6%, 8% and 15%, respectively. It can be seen that in sample without indium impurity (Fig.7a), with increasing temperature, sensitivity is increased and maximum sensitivity is <10% at room temperature. In this sample, layer structure is not changed with temperature variations and with increasing temperature, surface layer will attract more hydrogen. At low temperature, the behavior of sample with 2% impurity (Fig.7b) is similar to sample without impurity while at higher temperatures (200°C) less hydrogen is attracted and therefore the sensitivity is reduced. This is due to the displacement of indium atoms from surface to depth. Maximum sensitivity is for samples with 6% impurity where at sensor work temperature of 200°C the sensitivity is about 18.43%. This is largely due to small grain size which increases the active surface of layer.

Fig. 4. X-ray diffraction pattern of tin oxide sample with 8% indium impurity.

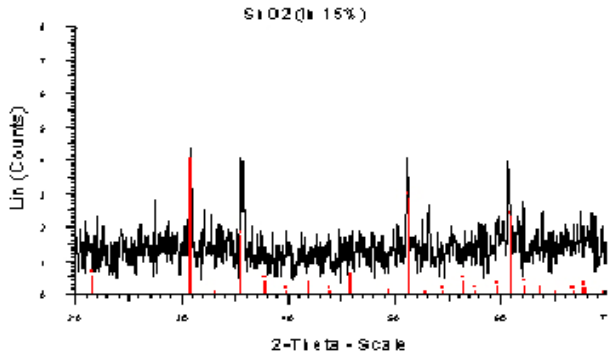


Fig. 5. X-ray diffraction pattern of tin oxide sample with 15% indium impurity.

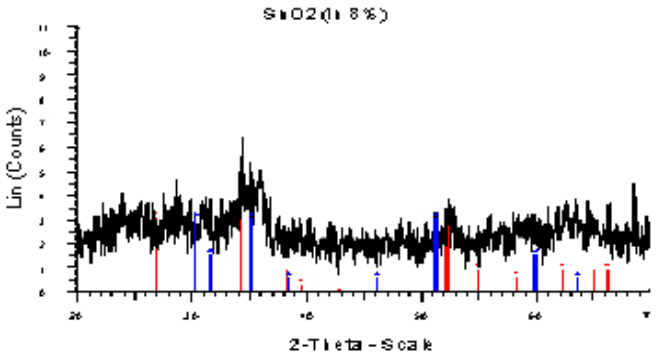


Fig. 6. SEM image of tin oxide sample with 2% indium impurity.

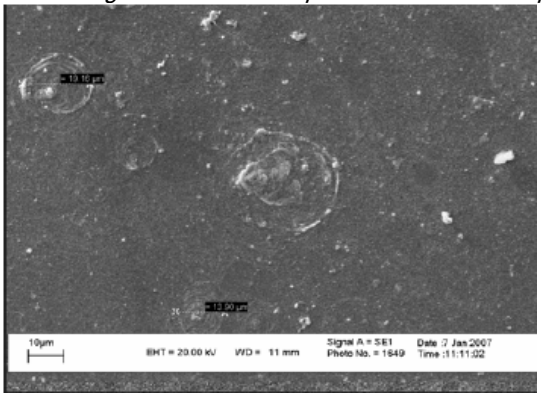


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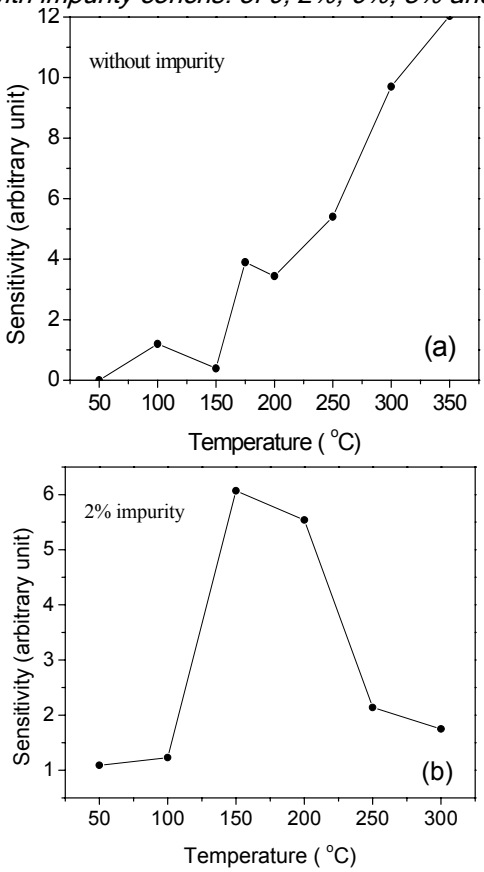
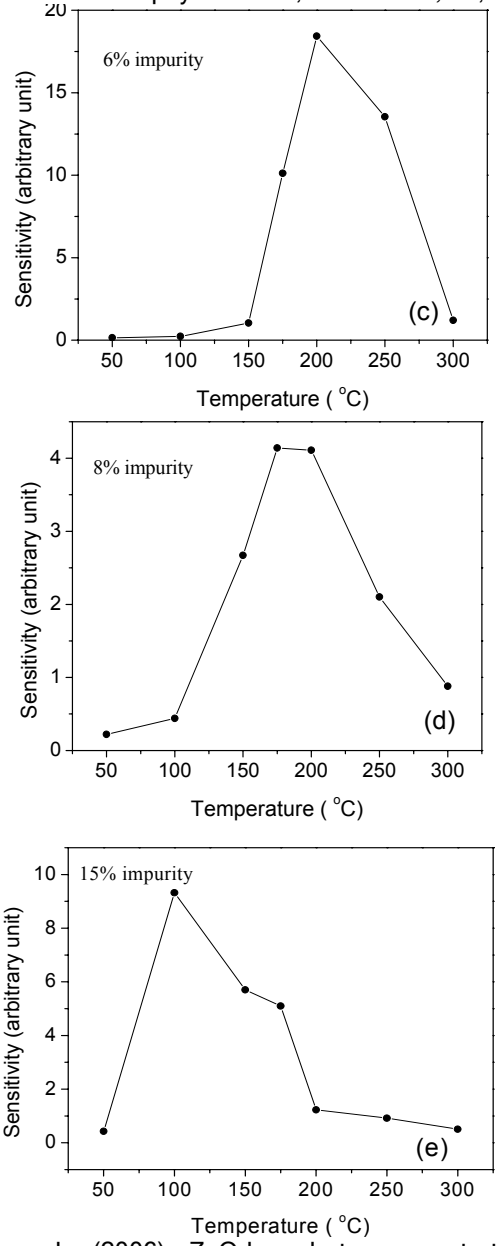
Fig. 7a-d. Tin oxide layer sensitivity in different temperature in the presence of 2000 ppm hydrogen gas and with impurity concns. of 0, 2%, 6%, 8% and 15%.





Conclusion

Indium impurity in tin oxide layers effects crystal ordering and sensitivity improvement. The maximum sensitivity is in 6% indium impurity and the minimum is in 8%. The maximum sensitivity at 200 °C was about 18.43%. With increasing indium impurity the work temperature of layers is increased and in 15% impurity concen. the work temperature is near to 100 °C.

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