

Study of physical properties for In_2O_3 thin films produced by thermal oxidation as CO_2 , H_2 gas sensor

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ABSTRACT

Polycrystalline In_2O_3 thin films have been prepared by using thermal oxidation method. The pure In metal was evaporated by using melbedume boat at vacuum 10^{-6} torr on glass substrate. Thin films of thicknesses about 350 nm were prepared, after that we treated these films with two different temperatures and obtained In_2O_3 thin films in the presence of O_2 . The X-ray Diffraction (XRD) results refer to polycrystalline phase. Scanning Electron Microscopy (SEM) was used to study the local morphology and the surface of In_2O_3 thin films obtained by thermal oxidation method. SEM shows high homogenous morphology. AFM results show 45 nm typical sizes for the grains. The optical properties were studied by using the UV-vis spectra then the energy gap was calculated from it. The values of energy gap E_g for In_2O_3 which were obtained from heat treatment to In metallic at 200 and 300°C are 3.5 and 3.1 eV, respectively.

Keywords: Indium oxide, thermal oxidation, x-ray diffraction, scanning electron microscopy, AFM analysis.

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INTRODUCTION

Gas sensors play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. Semiconductor gas sensors in the form of thin films are highly sensitive and reliable, having a performance/price ratio comparable to that of microelectronic components. Polycrystalline tin oxide based gas sensors are commercially important for detecting reducible gases, such as hydrogen, methane, butane and carbon monoxide with high sensitivities. It is well known that the gas adsorption onto the surface of a semiconductor can influence its electrical conductivity. In fact, conductivity of semiconductor gas sensor changes by few orders of magnitude with respect to initial value in the presence of gas concentrations up to few ppm in air at ambient pressure (Makhija et al., 2005).

Metal oxide thin films like indium oxide and tin doped indium oxide have unique characteristics such as good conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability and photochemical properties. These properties are resulted from their n-type semiconductor behavior and wide band gaps. Therefore, indium oxide

and tin doped indium oxide are used in a wide range of applications including solar energy conversion and photovoltaic devices, flat panel displays and bio catalytic transformation (Wirtz et al., 2000; Martinez and Stewart, 2000; Granquist, 1993). Indium oxide (In_2O_3) as well as other transparent conducting oxides (TCO) has a wide range of applications as a top contact of various optoelectronic devices due to their special properties: a wide band gap (sufficient to be transparent in the visible range) and high carrier concentrations which make them good conductors (Fortunato et al., 2005; Iwata et al., 2003; Yoo et al., 2005; Martı́nez et al., 1997; Wang, 2008). High quality In_2O_3 films have been fabricated by various deposition methods, such as sputtering (Ryzhikov et al., 2003), sputtering (Golan et al., 2007), CVD (Penza et al., 1999), sol-gel (Poznyak and Kulak, 2000), thermal evaporation (Fechete et al., 2008) and spray pyrolysis (Ramaiah et al., 2000). We have selected reactive evaporation because this technique has several advantages: a minimum of critical parameters; elimination of sputtering damage and relative ease of operation (Gessert et al., 1990).

In this work, we studied the synthesis and

characterization of indium oxide thin films grown on a glass substrates by using a thermal evaporation simple, low-cost, and yet efficient method .

EXPERIMENTAL

Indium oxide In_2O_3 thin films were deposited according to the thermal oxidation method. At the first step thin indium metallic layers were deposited by classical vacuum thermal evaporation. The evaporation was carried out in a conventional vacuum coating unit (INFICON V90) under a vacuum of order of 6×10^{-6} torr with controlled deposition rate by using pure In, the distance of about 20 cm was kept constant between molbeduim boat and substrate. The indium thin films of thicknesses 350 nm were grown on glass substrate (total surface area 5×5 mm). A summary of the deposition conditions is shown in Table 1. The second step, involving the thermal oxidation of In thin layer was performed in 30 s at 200 and 300°C in dry air atmosphere by using a flat electric heater for substrate heating. Two thin film gold electrodes were also deposited at each end of indium oxide thin films for ohmic contact to permit electrical measurements. The crystallinity and the crystalline phases present in the films were checked by XRD using an X-ray diffractometer with $\text{CuK}\alpha$ radiation (model "Shimadzu XRD 6000"), recorded for a range of 2θ from 10 to 60° at 2° glancing angle.

The local surface morphology were investigated by scanning electron microscopy (SEM), model VEGA3 TESCAN. Grain size also was observed from the atomic force microscopy (AFM), model A2000. The absorbance and transmittance of the deposited thin film was measured using UV-VIS Spectrophotometer (Optima Sp – 300 Plus) in the wavelength region of 200 to 1100 nm.

RESULTS AND DISCUSSION

The In_2O_3 thin film polycrystalline rhombohedral structure has been investigated with XRD. Figure 1 shows a typical Bragg-Brentano spectrum taken on an identically prepared film grown on glass. Diffraction data refers to the presence of the [101] diffraction peaks from crystalline In metallic evaporated at $2\theta = 32.9822^\circ$.

Figure 2 shows the diffraction pattern of In_2O_3 thin films at two heat treatments of In, 200 and 300°C. The heat treatment of In at 200°C shows two diffraction planes of In_2O_3 thin film which are [104] and [110] at $2\theta = 30.6242^\circ$ and 32.9868° respectively, while at 300°C heat treatment.

We have the diffraction planes [104] and [110] in $2\theta = 30.6303^\circ$ and 32.9983° respectively, which perfectly matches with the In_2O_3 reference of rhombohedral structure 1997 JCPD file v.1:30. These results are the same with the other researches (Makhija et al., 2005). From Figure 2 we also see that the intensities of thin films the peaks increase with increase of the heat treatment of

Table 1. Parameters for fabrication of indium thin films.

Coating unit	INFICON V90
Materials	Indium 99.99 %
Substrates	Glass slides
Vacuum	$\sim 6 \times 10^{-6}$ torr
Substrate to film gap	20 cm

the thin films.

The SEM investigations with (1.00kx, 5.00kx, 10kx, 50kx) magnification of In_2O_3 thin films shows surface morphology of the sample with homogeneous distributions over signification surface area of continuous phase. The crystallography of In_2O_3 is as shown in Figure 3.

In Figure 4, a typical $2 \times 2 \mu\text{m}^2$ sized AFM images of In_2O_3 film surface is shown. The film crystallites are well shape and uniform in size. It was observed, from 3D image that, the films exhibit a surface columnar morphology, which can be a consequence of crystalline preferential orientation.

AFM images indicate that the used preparation conditions of the films are more favorable to obtain sample with excellent shape as shown in Figure 5. The granularity accumulation distribution chart of In_2O_3 grain size of the sample is shown in Figure 6 which is about 45 nm.

Optical properties

The optical properties were studied by measuring the transmittance and absorbance spectra are shown in the Figure 7. We have found that the film has high transmission at long wave lengths, and decreasing transmission at short wavelengths.

The energy gap (E_g) of the samples was determined by employing the following relation (Kim et al., 2008).

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (1)$$

Where α is absorption coefficient, A a constant (independent from ν) and n the exponent that depends upon the quantum selection rules for the particular material. The photon energy ($h\nu$) for y-axis can be calculated using Equation 2.

$$E = h\nu = hc/\lambda \quad (2)$$

Where h is Plank's constant (6.626×10^{-34} J.s), c is speed of light (3×10^8 m.s⁻¹) and λ is the wavelength in nm. The values of direct energy gap (E_g) for In_2O_3 which are obtained from heat treatment to In metallic at 200 and 300°C are 3.5 and 3.1 eV respectively. This is a good agreement with the values already reported by Penrose (2004). The values of energy gap increase with the

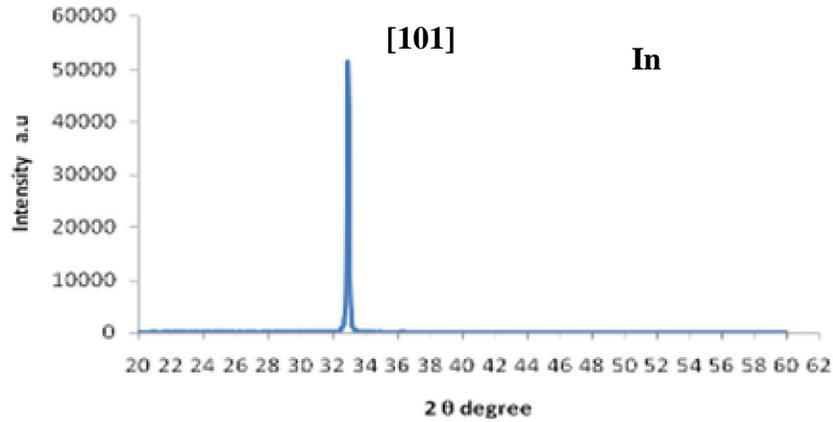


Figure 1. X-ray diffraction of In metallic sample.

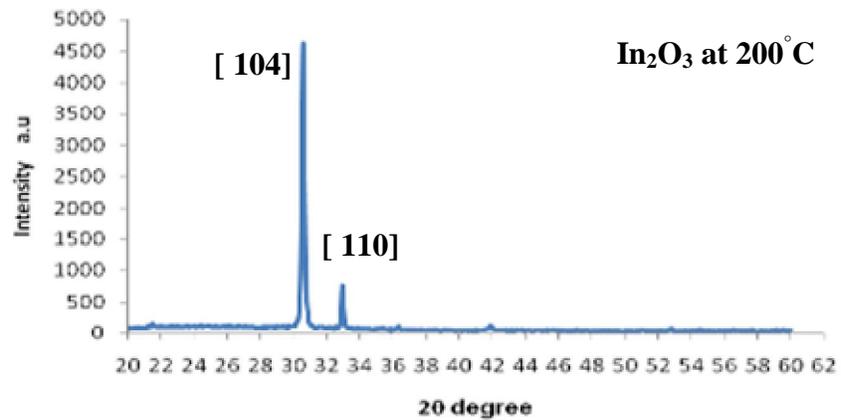
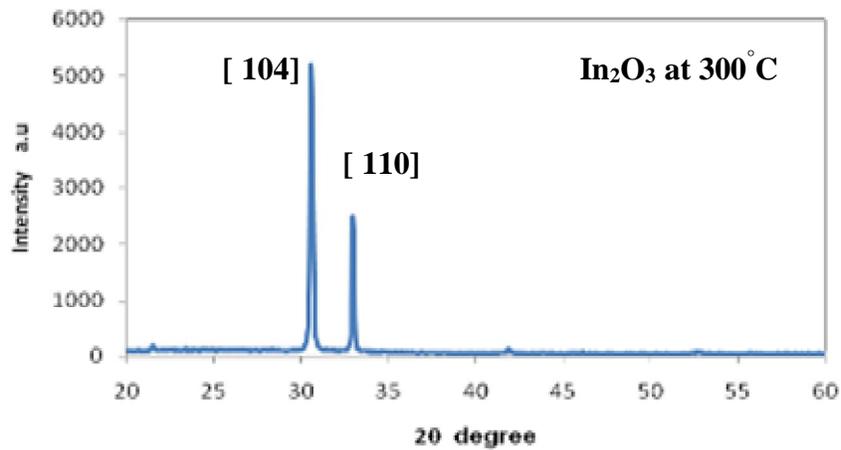


Figure 2. X-ray diffraction of In_2O_3 thin films.

decrease of thermal treatment of thin film as shown in Figure 8.

Response to gas vapor

The fabricated multipurpose sensor was mounted in a

closed chamber into which desired amount of H_2 gas/ CO_2 vapor could be injected. Nitrogen gas was purged for 15 min to clean the sample environment, examined gases was injected by micro-syringe into test chamber and sensing characteristics of the sensor were then observed. The ratio of measured resistance before and after exposing the sensor surface to gas gives sensitivity

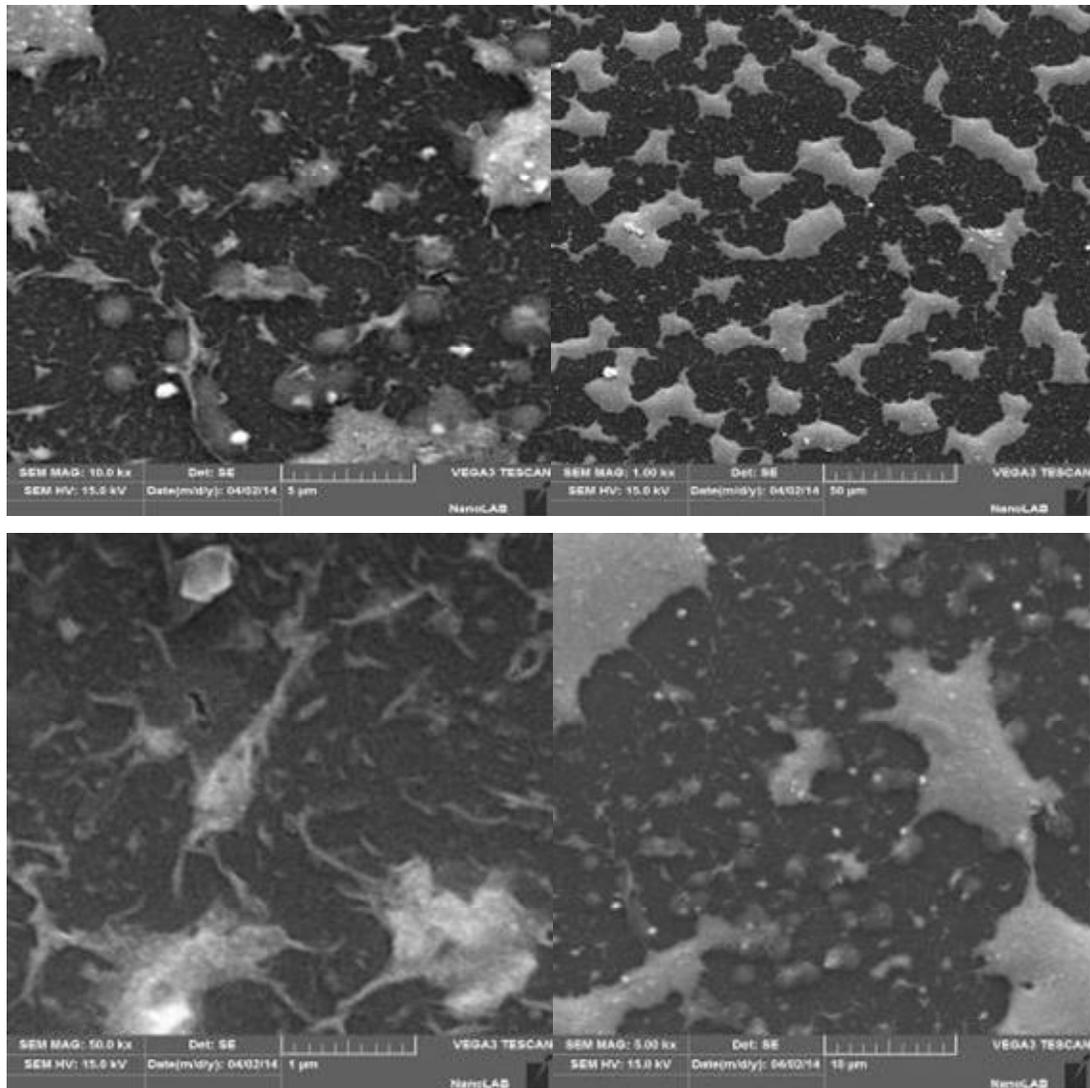


Figure 3. From the top to bottom and left to right SEM images at increasing magnification (1.00kx, 5.00kx, 10.kx, 50kx) of In_2O_3 .

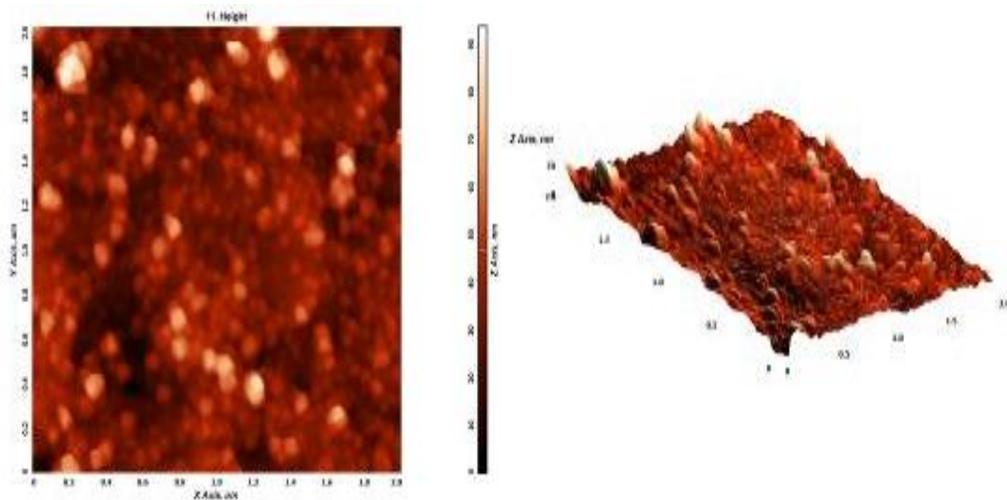


Figure 4. AFM micrographs characteristic of $\text{ZnO-In}_2\text{O}_3$ sample.

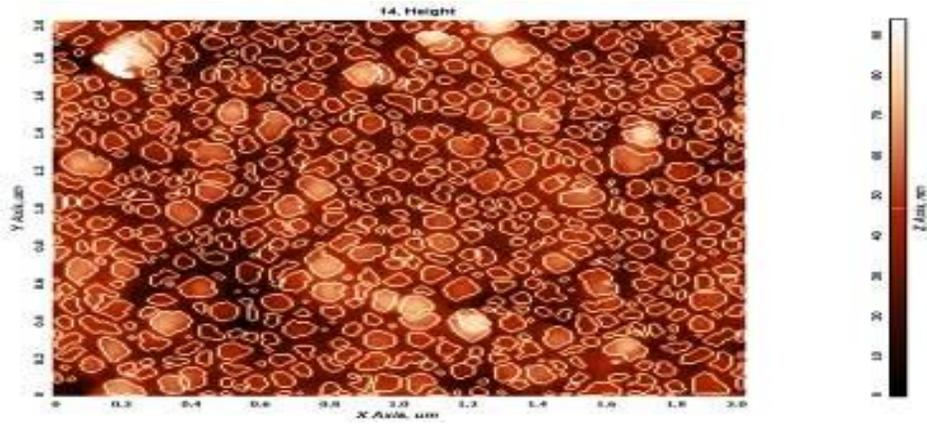


Figure 5. The shape of In_2O_3 grains.

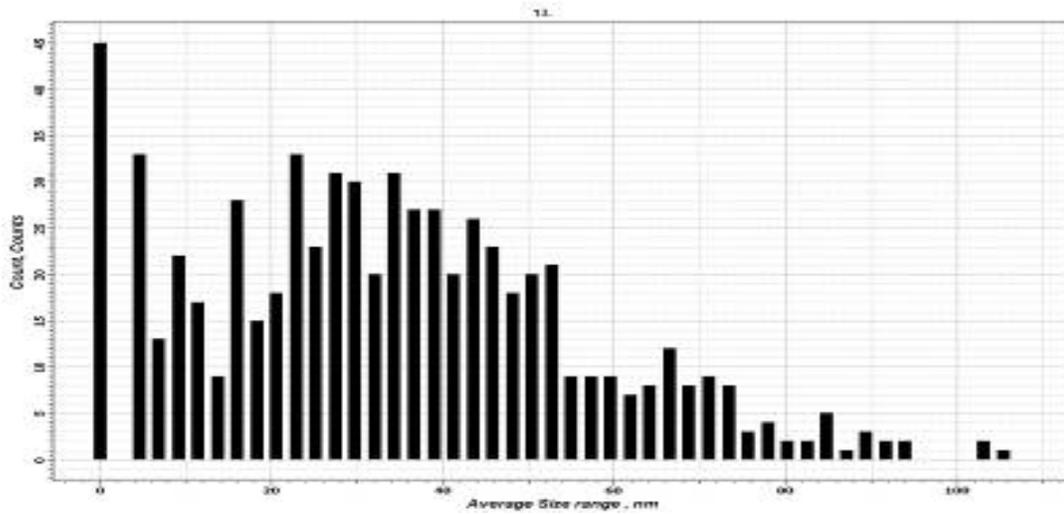
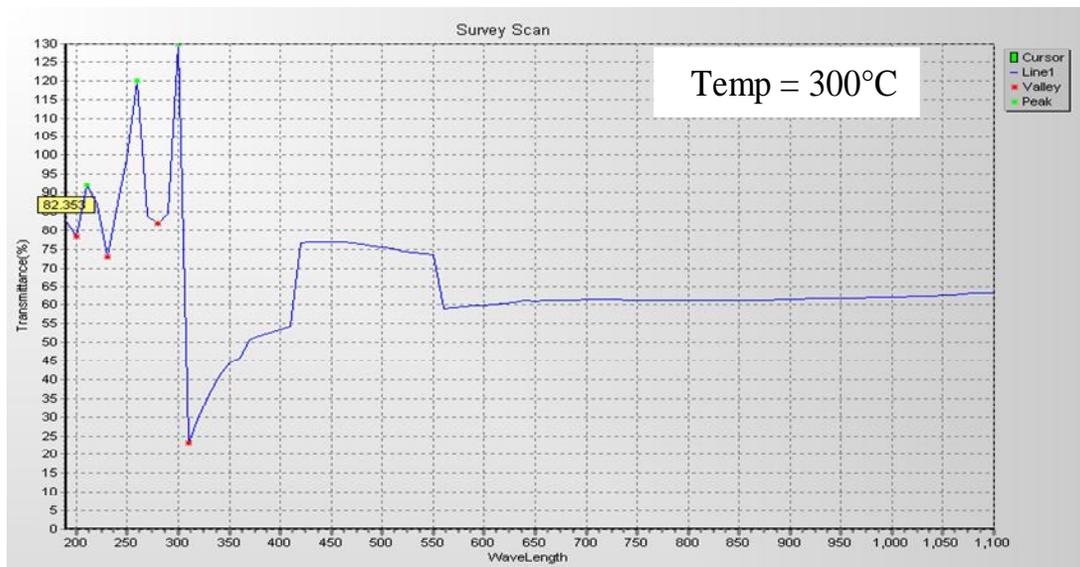


Figure 6. Granularity accumulation distribution chart of In_2O_3 sample.



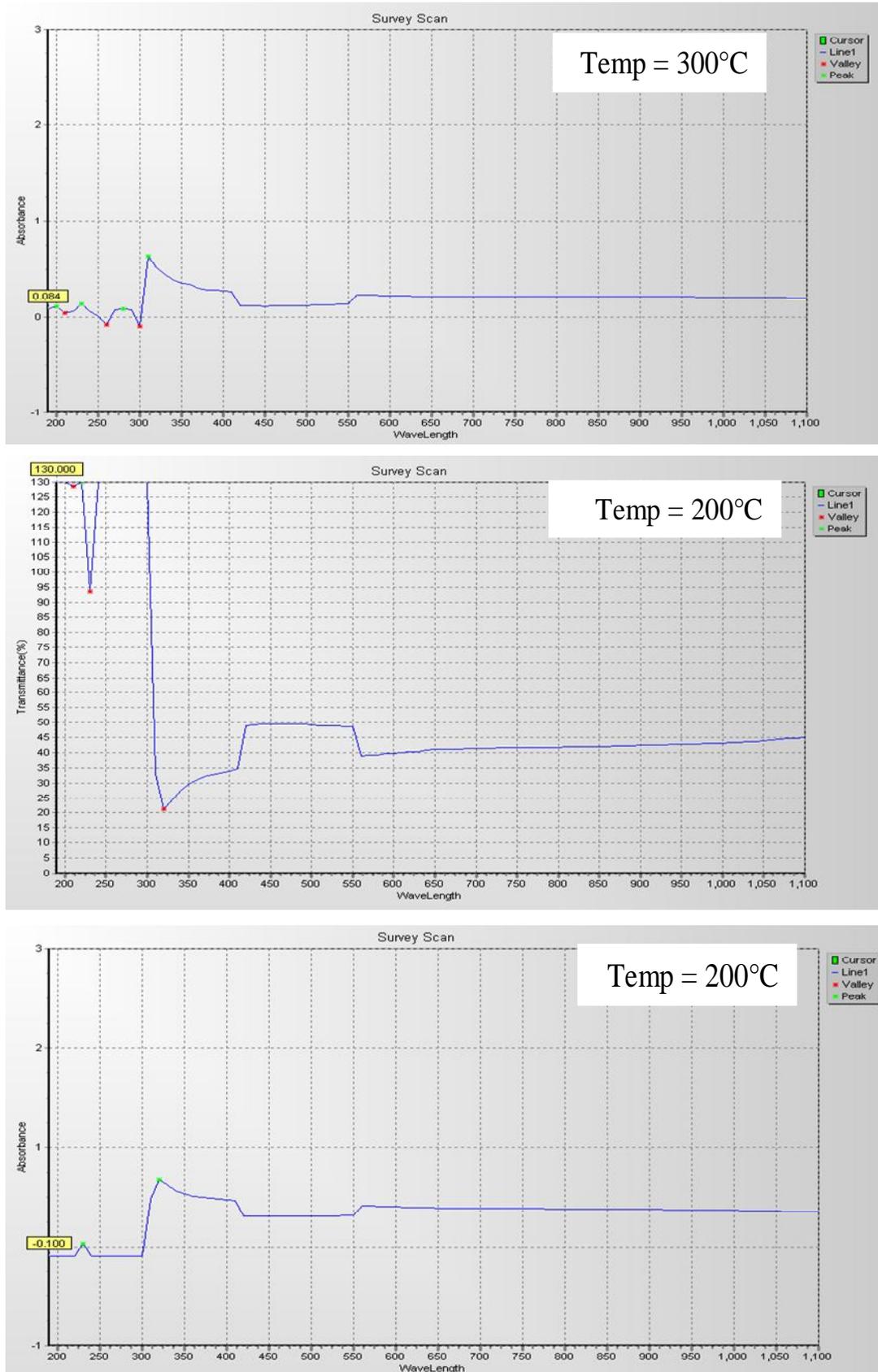


Figure 7. Transmittance and absorbance spectra of In_2O_3 thin films at heat treatment of In at 200 and 300°C.

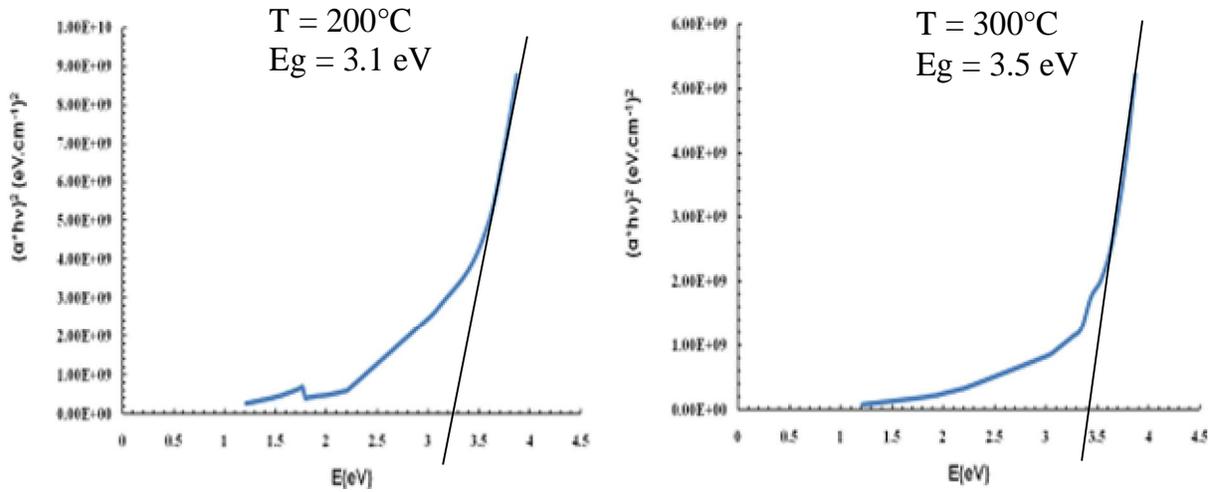


Figure 8. Plot of $(\alpha hv)^2$ versus (hv) curve of In_2O_3 thin films get from heat treatments of In metallic at 200 and 300°C.

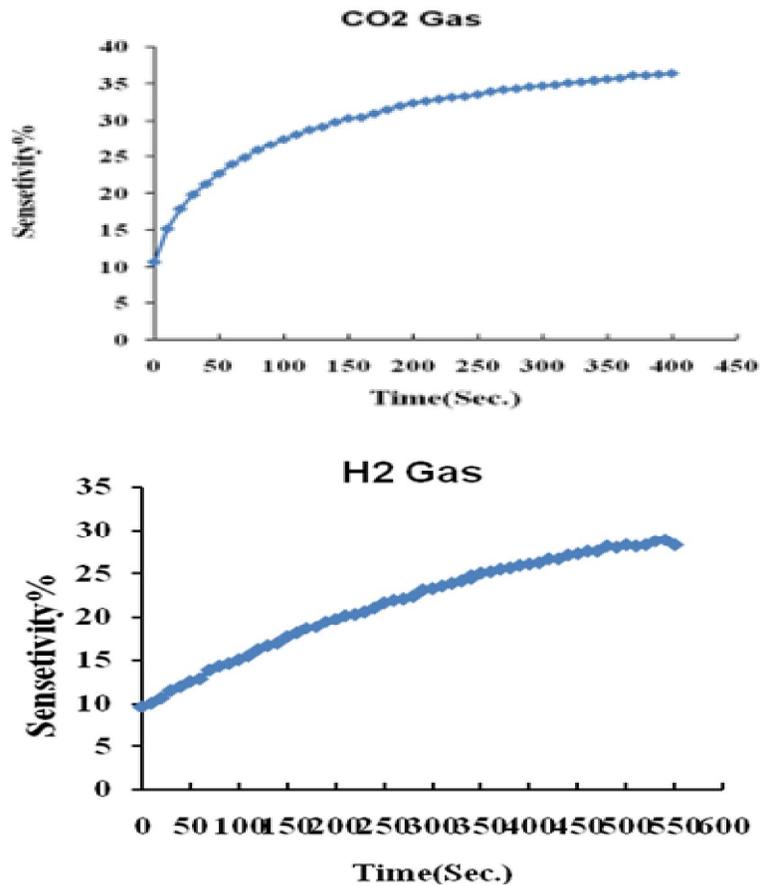


Figure 9. Sensitivity of In_2O_3 thin films get from heat treatment of In metallic at 300°C to H_2 and CO_2 gases.

(Rambu et al., 2011), the results of sensitivity is as shown in Figure 9.

$$S = \left| \frac{R_{(air)} - R_{(gas)}}{R_{(air)}} \right| \quad (3)$$

Where R_{air} , R_{gas} are the resistances in air and gas for H_2 gas/ CO_2 vapor. The sensing properties were studied at low concentrations of gases vapor (10 ppm). The results which obtained from this method are promising for the

preparation of sensitive and low cost gas sensor operating in room temperatures. From our results we conclude that the sensitivity to CO₂ gas is 35% and for H₂ gas is 28%.

CONCLUSION

Indium oxide thin film sensor for H₂ gas and CO₂ vapor were deposited by thermal deposition with 350 nm thin films thickness. The films have been characterized by x-ray diffraction, optical and electrical studies. XRD study of the atomic structure confirms the existence of In₂O₃ polycrystalline phase. From AFM results we obtained that the average grain size are about 45 nm. This film has characteristics required for application on sensor devices. The sensitivity of thin films is 35 and 28% for CO₂ and H₂ gas respectively.

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