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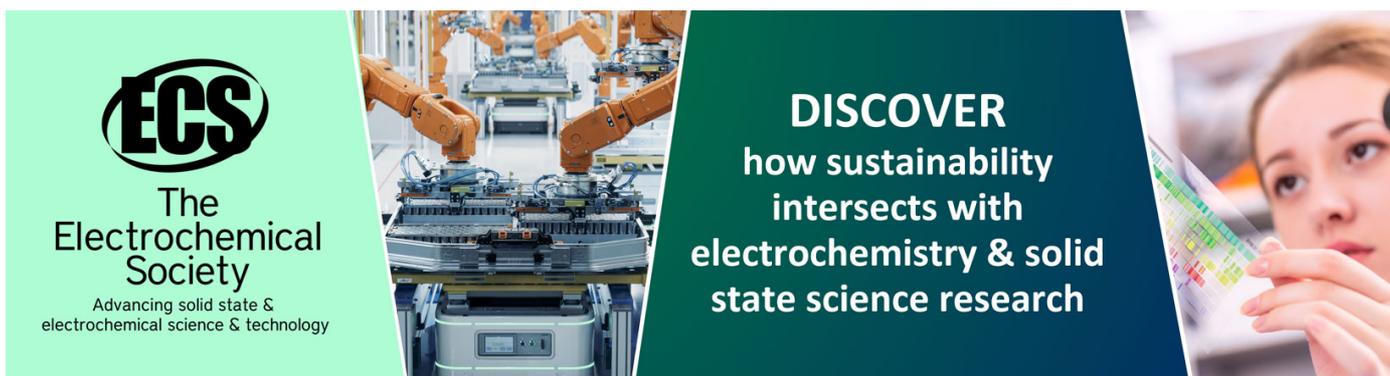
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Impact of Tin concentration in ITO films on Optoelectronic sensor performance

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Abstract: In viewing the opportunity to enhance Photovoltaic application, nine samples having different concentrations (5%, to 70%) were synthesized by sol gel Acrylamide route. XRD study indicates the entire films exhibited single phase with bixbyte structure for all films. EDXA studies confirm the existence SnO₂ enclosures in the entire samples. Atomic force micrographs of ITO films conclude that the grain size decreases with increase of tin concentration. Hot probe measurements reinforce the optimum concentration of tin (10%) for its transport properties, their optoelectronic application of DSSC. This paper focuses on the DSSC performance. In this work ITO films and their gas sensing characteristics are studied and their results are reported. ITO based H₂S sensor with 70% tin concentration exhibited maximum sensitivity at 100 °C with higher recovery time than the response times. After a long time, ITO films with different concentrations of tin (450 °C) return to the original state.

1. INTRODUCTION

All the transparent conducting materials are anion deficient and hence are always n-type semiconductors. ITO semiconductors are large band gap (3.5 eV-4.3 eV) it has low resistivity, high optical transmittance and excellent adhesion to substrate and chemical stability. [1] For obtaining high transparency in the transparent region and high reflectance in near IR region, the following parameter are effectively controlled, they are film thickness, substrate temperature, doped type and its amount, annealing temperature and other deposition condition. Surface coating can be produced by many methods such as evaporation [2], sol gel technique [3], pulsed laser deposition [4] and electron beam evaporation [5]. There is several synthesis methods have been employed for making ITO thin films, chemical methods are the best to synthesize ITO films. ITO films are widely used for variety of optoelectronics devices [6-7], energy efficient windows [8], flat panel displays [9], solar cell [10], gas sensor [11], photo catalysts [12] and surface layers in electroluminescent application [13].

The detection in leakage of gases and monitoring the air quality in our atmosphere is measured by using gas sensors. Chemical sensor is an analyzer that convert the composition of a particular element, concentration chemical activity into useful signal. Now-a days it is used in different fields such as bio-chemistry, semiconductor technology, thermology and membrane technology. It has many excellent properties such as sensitivity, selectivity, stability, detection time dynamic range, resolution, response time, recovery time, life cycle, low cost easy to realize automatic measurement. Gas sensor setup has a sensitive element made by metal oxide (M-O) or M-O semiconducting materials. The resistance of their active sensing layer changes when it is exposed to the gas to be detected. There are several gas sensor to detect gases like oxygen, CO₂, nitrogen methane etc. M-O semiconductor sensors are wide band gap semiconductor and exhibit a change in electrical conductivity proportional



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to the concentration of the gas surrounding them. The details of preparation of nano crystalline ITO films by the sol gel dip coating method have been reported in our earlier paper [16]. After the samples preparation they were characterized by different studies and their results are reported in the previous paper [14-16]. This paper mainly focuses on DSSC and sensor studies of all samples and their results are reported in this paper.

2. EXPERIMENTAL

2.1. DSSC preparation:

The detailed preparation procedure of ITO thin films has been reported by us earlier [16]. There are several inexpensive methods to prepare films for DSSC application for example screen printing, doctor blade technique etc [17-24]. The synthesized ITO powder was mixed homogeneously in an aqueous or non aqueous medium with organic additives to form a paste, this paste was coated on cleaned and dried conducting glass substrate. Followed by drying and sintering at a temperature 450 °C to remove organic additives and particles to get sufficiently connected to each other allowing better conduction of electron through the films. These sintered film were immersed in a dye solution (cis-di (thiocyanate) bis (2, 2'-bipyridyl-4,4'-di-carboxylate) ruthenium (II)) for nearly 24h at room temperature for adsorption of dye molecules on the ITO surface. The two electrodes (viz., dye soaked ITO photo anode and ITO cathode counter electrode) were sealed together with a 25 micrometer thick surlyn (a polymer) spacer on all four sides, the electrolyte (0.5 M KI, 0.05 M I₂ and 0.05 M 4-tert-butylpyridine) through a hole made on the cathodes, finally this hole was filled and sealed with surlyn. Xenon lamp (Intensity =100 m W cm⁻² & power=250 W) with ultraviolet and an infrared-blocking filter, was focused on the active cell area (0.25 cm²)

2.2. Sensors preparation:

'Figure 1' shows that basis block diagram of the gas sensing system. The system consists of electrical feeds through the base plate, connected to the heater to heat the sample under test to desired operating temperature. Relay is used to control the current passing through the heating element. A Chromium Aluminum Thermocouple was used to measure the operating temperature (connected to digital temperature indicator). The test gas was allowed through an inlet valve fitted to the base plate. A known volume of test gas was injected into the chamber by a syringe. The current through the sensor was measured by applying a constant voltage. After every exposure cycle, air was admitted into the chamber.

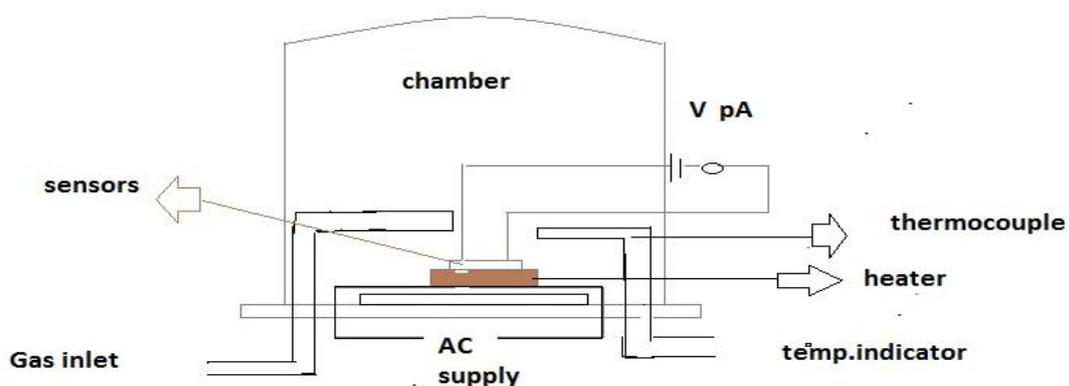


Figure 1 shows block diagram sensor arrangement

Metal oxide semiconductor (n-type is the sensing element), a potential barrier forms when the electron is transported from the ionized donors through the conduction band takes place causing a reduction in the charge carrier density interface. Further adsorption of gas is inhibited due to development of

surface charge. Reducing the rate of gas adsorption [31]. This leads to high resistance contacts at the junction between the grains which contribute to the resistance of the solid film. The resistance is sensitive to changes of the surface by gas molecules. The following equation relates the sensor resistance to the concentration of deoxidizing gas.

$$R_s = A\{C\}^{-\alpha}$$

where R_s denotes the sensor resistance,

A - constant, C - Gas concentration, α - slope of R_s curve.

3. RESULTS

The main element of the DSSC is the photo anode, generally TiO_2 is a preferred candidate, although other wide band gap materials like ZnO and Nb_2O_5 have been studied [25, 26]. Adsorption of photons on the dye creates charge carriers; the electron is anchored to the conduction band of the semiconductor in contact with dye molecule. Dye attains its original state by electron injection from the electrolyte, which comprises of an organic solvent containing redox system.

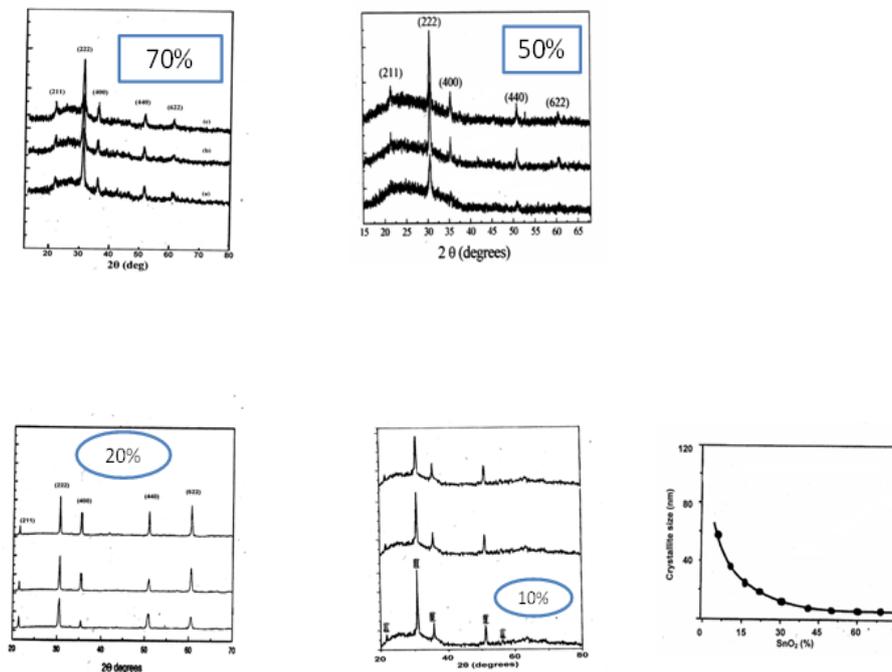


Figure. 2 shows X-ray diffraction pattern of different concentration of tin oxide in ITO films formed at different temperature (a) 350°C (b) 400°C (c) 450°C

ITO films were formed with different concentration of tin in the range of 5% to 70%. The films were single phase with bixbyte structure [16]. The crystallite size decreased with increase of tin concentration as shown in 'figure.2.' EDXA conforms of SnO_2 content present in all the samples as shown in 'figure 3'. Surface roughness increased from 0.20 nm to 1.25 nm as the tin concentration decreases, the films surface is porous. It is observed in the 'figure 4' [16]. The value of conductivity, mobility of the films increases up to 10 at% beyond which the conductivity, mobility were decreases.

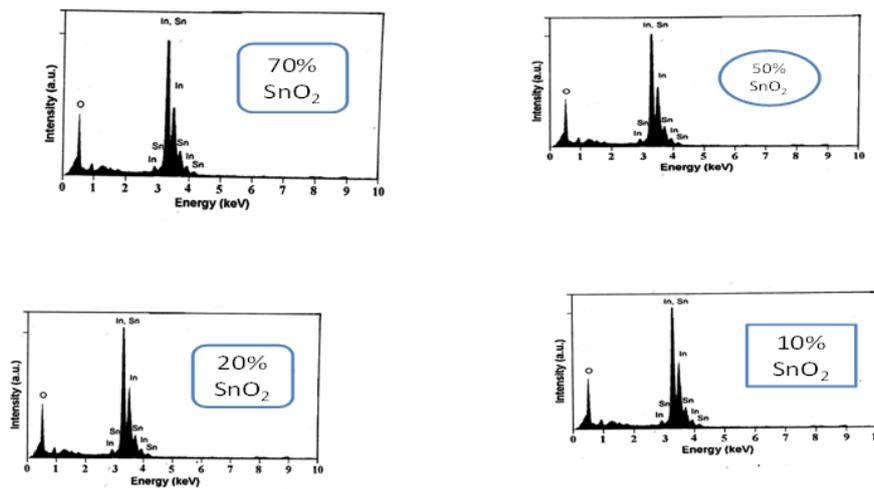


Figure. 3 shows EDAX spectrum of ITO films

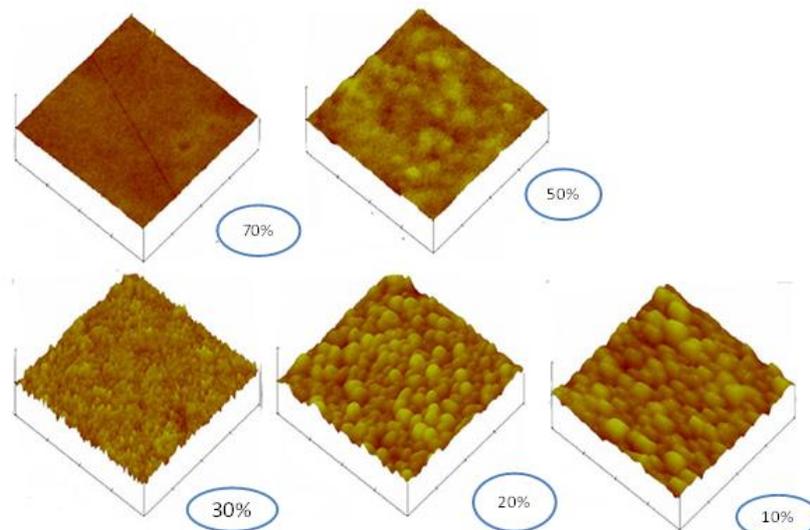


Figure. 4 shows AFM of ITO films with different concentration of Tin formed at 450°C

'Figure 5' shows the V-I characteristic curve of DSSCs using the ITO films. The η , FF, V_{OC} , and J_{SC} of the DSSCs are encapsulated in the Table 1. From the figures, it is observed that the DSSC with the ITO photo electrodes formed at 450°C, shows the maximum photo output irrespective of tin concentration. Amongst the different ITO photo electrodes, those deposited with 10 % Sn concentration showed the maximum efficiency.

The incident photon to current efficiency (IPCE) is a measure of the performance of the DSSC given by the following expression [27]

$$IPCE (\%) = 1240 \times J_{SC} / (\lambda \times P_{in}) \times 100\%$$

λ - wavelength of the incident light.

Figure.6 represents the IPCE curve for ITO films heat treated at 450°C. A broad peak is observed between 450 – 550 nm due to the absorption by ITO films. Photo generated electrons diffuse through the ITO film and the hole in the conduction band is replenished by the charge transfer from the electrolyte [28]. The contribution from the dye absorption is the IPCE value observed around 526 nm due to the visible $t_2 \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT). The IPCE spectrum shows one peaks at 410 nm and another broad peak centred at 526 nm, which are close to ruthenium-based dye (N3-dye) absorbance

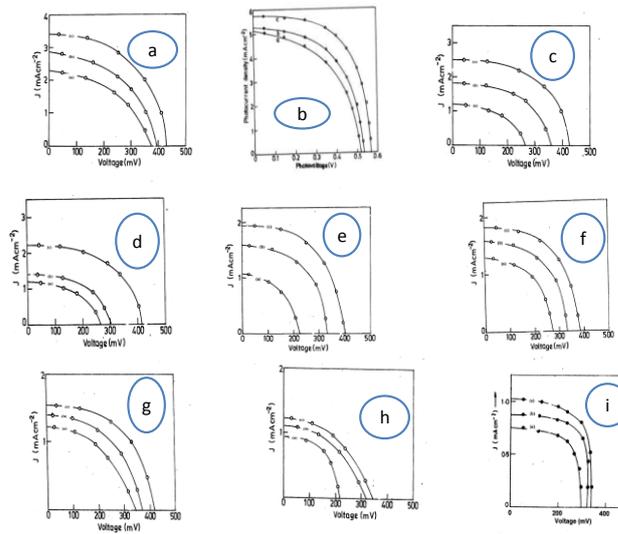


Figure 5. Shows V-I characteristics of ITO photo electrodes containing 5%,10%,15%,20%,30%,40%,50%,60%,70 % SnO₂ and formed at different temperatures (a) 350°C (b) 400°C (c) 450°C

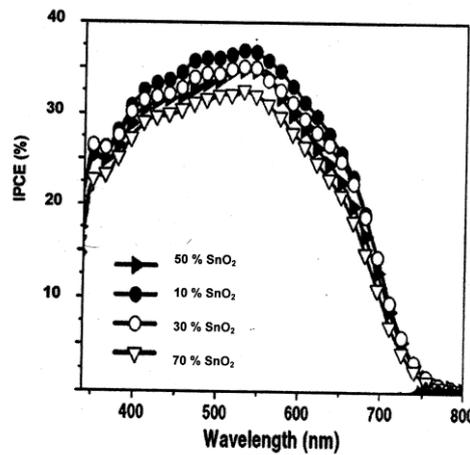


Figure 6. Shows IPCE of ITO photo electrodes containing different concentrations of SnO₂ formed at 500°C

TABLE 1. Photovoltaic performance of ITO photo electrode with different concentration of tin formed at 450 °C

Tin concentration (atomic %)	Resistivity (ohm cm)	Voc (mV)	J _{sc} (mA m ⁻²)	Ff	Efficiency (η)
70	250	0.33	1.05	0.73	0.256
60	176.2	0.34	0.25	0.51	0.220
50	72.9	0.42	1.55	0.62	0.403
40	56.8	0.38	1.81	0.68	0.467
30	17.45	0.40	1.95	0.68	0.530
20	2.64	0.41	2.20	0.70	0.631
15	0.62	0.43	2.50	0.68	0.731
10	0.10	0.57	5.75	0.70	2.294
5	0.01	0.43	3.40	0.68	0.994

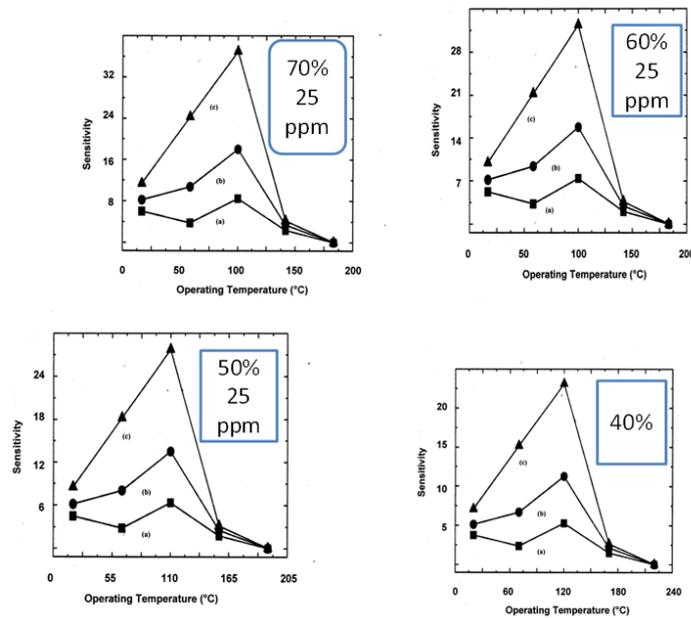


Figure 7. Sensitivity of ITO films with different tin concentration formed at different temperatures (a) 350°C (b) 400°C (c) 450°C exposed to H₂S gas (25 ppm) at different operating temperatures of the sensors.

3.1. Gas sensors:

When H₂S gas is incident on the sensor surface, the responses of all the samples increase and the operating temperature were 120°C, 110°C and 100°C respectively for the ITO films with different tin concentrations (40%, 50%, 60% and 70%). Further increase of operating temperature caused a decrease in response. Comparison of the performance of the sensors was made at the operating temperatures of 120°C, 110°C and 100°C and maximum response values were 38, 33, 29 and 23.5 respectively. The sensor responses result in familiar volcano-shaped correlation. This is based on the analysis by the reaction-diffusion equation [29], with increase of grain size, the height of the volcano top increases. An increase of the sensitivity is observed with the concentration of a test gas. The responses of ITO sensors with different tin concentrations formed at different temperatures are shown as a function of the gas concentration in 'Figure.7 & 8'. The results indicate the sensitivity of the ITO films to reducing gas H₂S. The highest surface activity results in highest response, contributing to a stronger interaction between H₂S molecules and the surface active sites. Very fine grains are obtained for films formed at low temperature, whereas high temperature formed films exhibit larger grains, which results in the increase of surface diffusion rate of adatoms during heat treatment [30] and higher surface densification. As formation temperature increases, adsorption rate also increases. Different ways of interaction takes place between the exposed H₂S gas and the surface chemisorbed oxygen. As an illustration, [31]



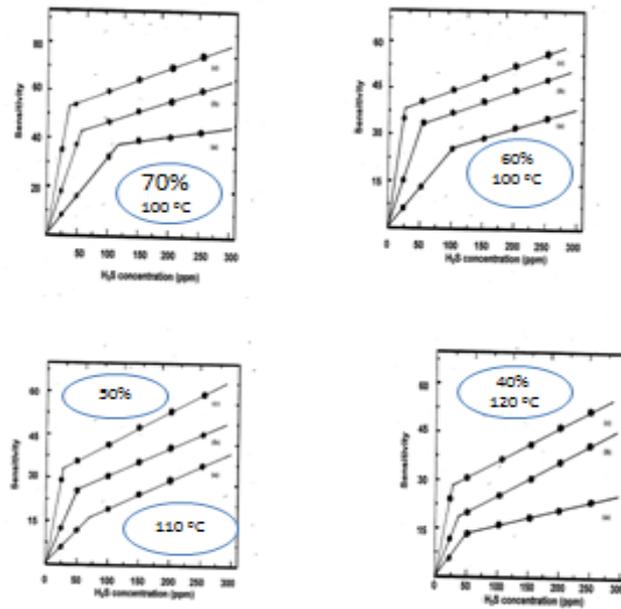


Figure 8. shows - sensitivity of ITO films with different tin concentration formed at different temperatures (a) 350°C (b) 400°C (c) 450°C exposed to different concentrations of H₂S gas at an operating temperature

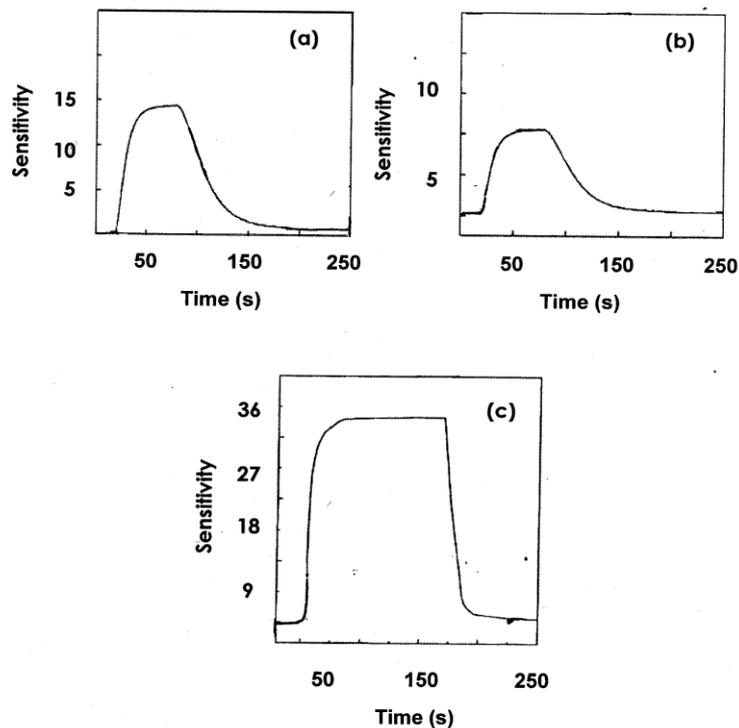


Figure 9. shows - response and recovery times of ITO films with 70 % SnO₂ formed at different temperatures (a) 350°C (b) 400°C (c) 450°C at an operating temperature of 120°C

A particular reaction on the surface is favoured by the surface acid – base property. Response time, recovery time and the chemical composition of the sensor indicates the response of the sensor to gas. As is shown in ‘Figure 9’. the fast responses to 25 ppm H₂S gas of ITO films with different

concentration of tin at the operating temperature corresponding to the maximum response for that tin concentration (120°C, 110°C and 100°C) was observed with higher recovery times than the response times, it was in the range of 70 s to 90 s for the ITO films with different concentrations of tin formed at 450°C. Though the changes are not permanent, it took long time to retrieve to the original state. The films formed with 70% tin concentration possess excellent characteristics due to the fact that, the value of time constant diminishes with decreasing particle size. The fast response for these films also indicates that the ITO nanoparticles are properly connected in the layer. Due to the high reactive surface of the nanoparticles, the measured response time values of the gas sensors are smaller and the surface of the layer dictates the dynamic behaviour of the sensor [32]. The decrease in the surface state density for smaller particle sizes also leads to an increase of the sensitivity due to a lower Fermi-level pinning and consequently, an increase in the charge depletion layer [33]. Comparable results were obtained by changing the mean particle size in the range 5 nm to 32 nm via the calcination temperature and by using metal additives [34].

4. CONCLUSION

Using sol gel method the ITO films can be easily synthesised. Dye sensitized solar cell (DSSC) application is used to find the photoelectric conversion efficiency, observed in all tin concentration of ITO films. Among the different ITO photoelectrode those deposited with 10% Sn concentration showed maximum efficiency of 2.294%. Results obtained on DSSC solar cells are very encouraging in future work. The ITO sensors with 70 % tin concentration exhibited maximum sensitivity observed in the temperature of 100°C. Sensors with lower tin concentrations rise to 40 % exhibited sensitivity to H₂S gas obtained in the temperature of 110°C and 120°C. The maximum response values are 38,33,29, 23.5. the responses to 25 ppm H₂S gas of ITO films with different concentration of tin at the operating temperature corresponding to the maximum response for that tin concentration (120°C, 110°C and 100°C) the response times were smaller than the recovery time., it was in the range of 70s to 90s for the ITO films with different concentrations of tin formed at 450°C, It takes a long time to return to normal state. Moreover, the sensor results obtain from the point toward the possibility of using them for sensing hazardous gases. The decreasing operation temperature is very useful for the industrial applications.

REFERENCES

- [1] Raoufi D, Kiasatpour A, Fallah H R, Rosatian A.S.H, 2007 *Applied Surface Science* **253** 9085
- [2] De Carvalho C N, do Rego A M B, Amaral A, Broguerira P, Lavareda G *Surface and Coating Technology*, 2000 **70** 124
- [3] Alam M J, Cameron D C 2000 *Thin Solid Films* **377** 455
- [4] Adurodija F O, Izumi H, T Ishihara, Yoshioka H, Yamada K, Matsui et al.1999, *Thin Solid Films* **79** 350
- [5] Mori N, Ooki S, Masubuchi N, Tanaka A, Kogoma M, Ito T 2002 *Thin Solid Films* **6**. 411.
- [6] Parker D G, P G Say P G, 1986, *Electronics Letters*, **22** 1266
- [7] De Andrade M C, Moehlecke S 1994 *Applied Physics A* **58** 503
- [8] Hamberg, C G. Granqvist, K F Berggren, B E Sernelius, L Engstrom, 1985 *Vacuum*, **35** 207
- [9] Pankove J I *Display devices. Berlin Heidelberg: Springer*, 1980, Verlag
- [10] Tousekova, J Kovanda J, Dobiasova L, Parizek V, Kielar P, 1995 *Solar Energy Materials and Solar Cells* ,**37** 357
- [11] Luff B J, Wilkinson J S, Perrone G 1997 *Applied Optics* **36** 7066
- [12] Poznyak S K, Golubev A N, Kulak A L, 2000 *Surface Science* **454** 396
- [13] Tueta R, Braguier M, 1981 *Thin Solid Films* **80** 143
- [14] Ramanathan G, John Xavier R, Murali K.R, 2012 *ECS transaction* **41** 33-5
- [15] Ramanathan G, Murali K.R, 2016 *Jour. of Appl.Phy.Sci.International* **7** (1) 1-7

- [16] Ramanathan G, Murali K R 2015, *International Jr. of ChemTech Research* 8 (8) 260-4
- [17] Murakami T N, Comte P, Liska P, Gratzel, Nazeeruddin C M K and Gratzel M, 2008, *Thin Solid Films*, **516** 4613-6
- [18] Chen P, Comte P, Nazeeruddin M K, Liska P, Pechy and Gratzel M, *Prog. Photovolt. Res Appl.*, 2007, **15** 603-9
- [19] Kida T, Akiyama, M Inoue, Teunematsu K S, Yao K, Noma H and Ab Ee, *Electrochem. Commun.*, 2003 369-3
- [20] Miyasaka T, Ikegami M and Kijitori, J. *Electrochem. Soc.*, 2008 **154** A455-A461 2008
- [21] Han H, Zhao X and Liu J, *J. Electrochem. Soc.*, 2005 **152** A164- 24
- [22] Zhang Y, Wu L, Xie E, Duan H, HenW and Zhao J *J. Power Sources* 2009, **189** 1256-7
- [23] Miyasaka T, Ikegamiand M, Kijitori Y, *J. Electrochem. Soc.*, 2004 **151**, A1767-6
- [24] Lancelle Beltran, Prene P, Boscher C, Belleville P, Buvai P, Lamblet S, Boissiers C, Grosso D and Sanchez C. *Chem. Mater* 2006 **18** 6152-4
- [25] Tennakone K, Kumara G.R.R, Kottegoda I R M, Perera V S P, *Chem. Commun.* 1999, **15**
- [26] Sayama K, Suguhara H, Arakawa H, *Chem. Mater.* 1998, **10** 3825.
- [27] Fang G J, Liu Z L, Zhang Z C, *J. Chinese Rare Earth Soc.* 1997 **15** 10
- [28] Huynh W U, Dittme J J, Alivisatos A P, *Science* 2002 **295** 2425
- [29] Sakai G, Matsunaga N, Shimano K, Yamazoe N, *Sens. Actuators B*, 2001 **80** 125
- [30] Kim K H, Park C G, *J. Electrochem. Soc.* 1991, **138** 2408
- [31] Tu J, Li N, Lai X, Chi Y, Zhang Y, Wang W, Li X, Li J, Qiu S, *Applied Surface Science*, **256** 2010 5051
- [32] Chung W Y, Lim J W, Lee D D, Miura N, Yamazoe N, *sensors and Actuators B*, 2000 **64** 118
- [33] Figaro UA Inc, Glenview, II *General Information for TGS Sensors*, Rev 6.98, 1998
- [34] Xu C, J Tamak Ji, Miura N, Yamazoe N, *Sensors and Actuators* 1991 **B3** 147