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Influence of surface passivation on optical properties of spray pyrolysis deposited Pd-F:SnO_2

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Abstract: Pd-F:SnO_2 thin films have been prepared by spray pyrolysis technique using an alcoholic precursor solution consisting of stannic chloride ($SnCl_4.5H_20$), ammonium fluoride (NH_4F) and palladium chloride ($PdCl_2$). Optimization on the deposition parameters has been done in order to obtain high quality thin films. The effect of varying the fluorine content on the optical properties of Pd-F:SnO_2 thin films were studied. Data for transmittance and reflectance in the wavelength range from 300nm – 2500nm was measured using the solid spec 3700DUV spectrophotometer. The calculated optical band gap of the as prepared thin films has been found to range from 3.8eV to 4.11eV. Fluorine incorporation for Pd-F:SnO_2 has been found to have a narrowing effect on the band gap, but at its higher concentration the band gap has been seen to increase. The band gap narrowing is due to the incorporation of F^- ions in the crystal lattice therefore giving rise to donor levels in the SnO_2 band gap which is an essential characteristic for the gas sensor applications. Both annealing and passivation have been found to have very insignificant change in optical band gap of Pd-F:SnO_2.

Keywords: Spray Pyrolysis, Fluorine Doping, Palladium Doping, Co-Doping, Palladium and Fluorine Co-Doping, Annealing, Passivation, Pd and F Co-Doped SnO_2 (Pd-F:SnO_2)

1. Introduction

Metal oxide semiconductor based devices have been a subject of a large number of scientific investigations in the recent past, especially those fabricated using ZnO, SnO_2 and TiO_2 based thin films [1]. The SnO_2 thin films have been reported in the literature to have excellent qualities which include high optical transparency, mechanical and chemical stabilities and high temperature resistant [2, 3]. SnO_2 based thin films have n-type conductivity that can be manipulated from normal to degenerate by suitably doping SnO_2 thin films with appropriate amount of noble metal (Pt, Pd), semi-metal (Sb, In, Bi) and halogens (F, Cl) [4]. SnO_2 based thin films are polycrystalline with tetragonal rutile structure and non-stoichiometric semiconductors [5, 6, 7]. Tin oxide can exist in two structures belonging to direct and indirect optical transitions, with different band gaps; a direct band gap that ranges from 3.6 to 4.6eV [8] at room temperature and indirect band gap of about 2.6eV [9]. Due to the high optical transmittance of SnO_2 based thin films they are used in many areas which are not limited to the research laboratory but are used commercially in environmental monitoring, industrial electronic sensor and liquid crystal displays [2]. They have been used as a window layer for solar cells, opacities, thin film resistors, electric conversion thin films, surface protection on layers of glass, semiconductor hetero-junction structures, heat reflective semiconductor insulator, an overcoat for thin film magnetic media overcoat and as a material for Li-ion batteries [6, 7, 10]. SnO_2 thin films do not easily react with

oxygen and water vapour and can only be dissolved by hot alkalis [11], but suffer from instability arising from three main areas of concern that is surface contamination of the active part of the sensor, changes in sensor characteristics e.g. inter-granular connectivity which occurs due to thermal expansion coefficient mismatch and/or interfacial reactions at the metal electrode/ceramic interface. Lastly, the film morphology may change over time due to the relatively high operating temperatures of the sensor, which may also cause migration of additives [12].

A number of methods have been reported to improve on the stability of doped SnO_2 thin films for gas sensor applications. Some of them include, thiourea treatment and use of metal catalysts e.g. Pd, Ru, Pt, Cu, Ag and Au [12, 13]. Annealing of the thin films in air have been reported to improve the stability of SnO_2 based thin films in time during the sensing of CO gas [14], however, annealing of thin films in air has the limitation of promoting oxidation and reduction of the oxygen vacancies which lead to loss in sensitivity of the thin films in detection of CO_2 gas. In order to improve on the stability of the thin films for CO_2 gas sensing applications while preventing the oxidation of the thin films and retaining the optimum sensitivity of the films, passivation of the doped SnO_2 thin films in a nitrogen atmosphere is proposed.

Many methods have been used to deposit SnO_2 based thin films which include RF magnetron sputtering [15], chemical vapour deposition method [16], Electron Beam evaporation method [17], Flash evaporation technique [18], Dip coating technique [10] and the Spray pyrolysis technique [19]. In this study spray pyrolysis deposition technique has been chosen because this technique is economical, promotes large area deposition allowing easy doping of the thin films hence the process is scalable and can be utilized for large scale production of high quality thin films [19]. The SnO_2 were doped with fluorine in order to improve on the charge carrier concentration and with palladium to improve on their stability and sensitivity toward CO_2 gas. Since passivation is known to improve on the stability of SnO_2 based thin films [14, 20, 21, 22], the main purpose of this study was to deposit Pd-F:SnO_2 thin films for CO_2 gas sensing and study the effect of surface passivation on the optical properties of Pd-F:SnO_2 thin films.

2. Experimental Procedure

2.1. Sample Preparation

The substrate used were ordinary microscope glass slides measuring 2.5cm by 7.6cm and 1.2mm thick. Cleaning of the substrates was done prior to deposition. The substrates were first soaked in soapy water solution and sonicated for 30 minutes. They were removed and rinsed using distilled water. After rinsing, the substrates were immersed in distilled water in a beaker and sonicated for another 30 minutes. They were removed and rinsed in distilled water and left to dry. After drying the substrates were stored in a desiccator ready to be used for coating.

2.2. Thin Film Deposition

Spray pyrolysis technique was used to coat the films. The experimental set up used is a Lab assembled spray pyrolysis system as shown in Fig 1 below. It consisted of a hot plate, spray nozzle of diameter ~1 mm, input gas valve, gas compressor, gas flow meter, conduit tube, thermocouple and a pressure gauge, and deposition was performed inside the fume chamber. The following Table 1 contains the optimized deposition parameters.

Table 1. *Optimized deposition parameters*

S/N	Deposition parameters	Optimized condition
1	Pressure of carrier gas	1.5 bar
2	Substrate temperature	450 ± 10^oC
3	Flow rate	4 ml/min
4	Quantity of spraying solution	30 cm^3
5	Nozzle to substrate distant	33 ± 3 cm

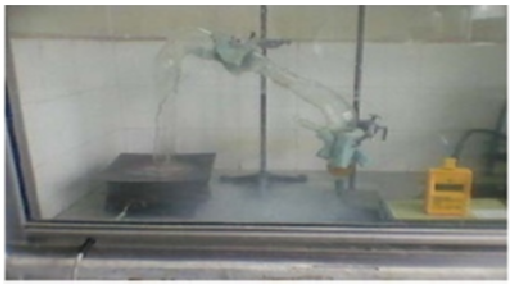

Figure 1. *Spray pyrolysis experimental set up.*

The undoped SnO_2 thin films were deposited using a precursor solution consisting of Tin (IV) chloride (98%) prepared by completely dissolving 5g of stannic chloride in 100 ml of ethanol (99.9%). 0.5 g of $PdCl_2$ (59-60%Pd) was completely dissolved in 60 ml of ethanol (99.9%). It was then added to stannic chloride solution at different doping concentrations ranging (1.8at% – 6.9at%Pd) in order to get Pd: SnO_2 thin films. 1.0g of ammonium fluoride (NH_4F) was added to distilled water in order to make NH_4F solution. NH_4Fsolution was then added to the spraying/starting solution containing stannic chloride from 0at% to 22.74at%Fand 2.7at%Pd at varying doping concentrations ranging from 0- 19.28at%F in order to make Pd-F: SnO_2 thin films.

2.3. Annealing of Thin Films

Thin films were annealed in a tube furnace (schematic diagram shown in Fig 2), in the presence of air at 450^{0}C for 30 minutes. This was done in order to improve the microstructure and crystallinity of the coatings. Apart from hardening and sintering the coatings, annealing was done in order to improve on the electrical conductivity of Pd-F:SnO_2 the thin films.

2.4. Thin Film Passivation

Thin films were passivated by annealing them in a nitrogen atmosphere in a tube furnace for 30 minutes at 450^0C. Since passivation is known to improve on the stability of doped SnO_2 thin films [13, 14, 20, 21, 22], in this study it was done in order to study its effect on optical properties of Pd-F: SnO_2 thin films.

2.5. Optical Characterization

Optical characterization of the thin films was done using Shimadzu model type DUV3700 spectrophotometer for un-polarized light. Data for both transmittance and reflectance at wavelength range 300 nm – 2500 nm was collected. Analysis of the collected data was done using pre-developed models in Scout 98 software. The models used were the Harmonic Oscillator model, Drude Model and the OJL model. The models were used to fit simulated theoretical data into experimental data and hence optical properties were calculated, that is band gap, refractive index and extinction coefficient. The graphs were drawn using the Origin Pro 8.1 software.

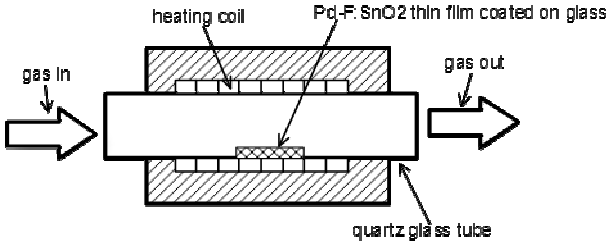

Figure 2. *Horizontal tube furnace for annealing and passivation.*

3. Results and Discussion

3.1. Optical Properties

The transmittance and reflectance measurements which were done as a function of wavelength was used to determine the effect of passivation on bare and doped SnO_2 thin films.

3.2. SnO_2 and Pd:SnO_2 Thin Films

Fig 3 shows the transmittance and reflectance spectra of both undoped and palladium doped tin oxide. The average transmittance of the thin films was 84.7% within the visible part of the spectrum. The optical transmittance was observed to decrease from 81.73% at 749 nm for undoped SnO_2 to 80.61% at 763 nm. This was as a result of 2.7at% Pd doping in SnO_2 thin films. The decrease in transmittance is due to increase in photon absorption as photon striking increases with increase in carrier concentration [23]. A maximum transmittance of 87.79% at 735nm was recorded for 1.8at% Pd doping in SnO_2 thin films. This high transmittance is attributed to decrease in diffuse and multiple reflections caused by increase in grain size and a reduction in light-scattering effect [4]. A sharp fall in transmittance at 310 nm is due to absorption of the glass substrate [24]. The reflectance of the thin films was below 22% within the visible spectrum.

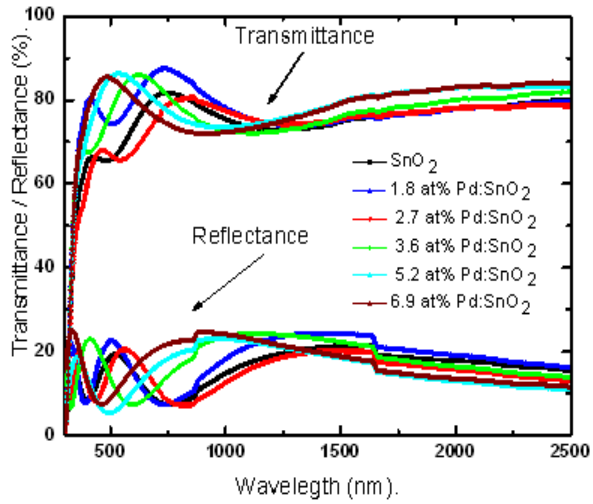

Figure 3. *Transmittance and reflectance spectra for bare and Pd:SnO_2*

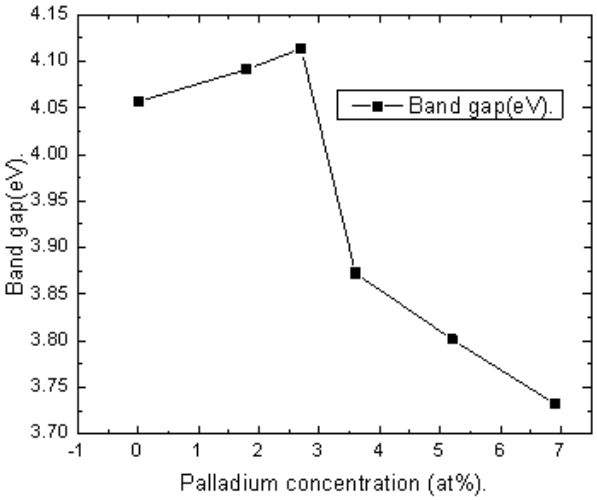

Figure 4. *Optical Band gap for Pd: SnO_2 thin films*

Fig. 4 shows a graph of optical band gaps for palladium doped tin oxide at different doping levels. The band gap of undoped SnO_2 thin film was found to be 4.0564 eV, and on doping with 1.8 at%Pd, the band gap was observed to increase slightly to 4.0913 eV. The maximum band gap widening was 4.1135 eV after doping SnO_2 with 2.7 at%Pd, the band gap widening effect can be attributed to the Burstein-Moss effect which states that: Increase in free carrier concentration, due to the high doping levels, fills empty states belonging to conduction band of the thin films thereby increasing the energy magnitude required for the valence band to conduction band transitions as reported by Sánchez-García *et al.,* 2012 [25]. Higher doping level with palladium from 3.6at%Pd – 6.9at%Pd, the band gap is observed to start decreasing which is in good agreement with results obtained by Odari *et al*., 2013 [26] and Fatema *et al.,* (2011) [27] for the similar materials.

3.3. SnO_2 and F:SnO_2 Films

Fig.5 shows the transmittance and reflectance spectra as a function of wavelength for F:SnO_2 thin films. The SnO_2 thin films were doped with fluorine. Different thin films were prepared and analyzed. The different thin films had different level of dopant concentration ranging from 0at% F doping to 22.74at%F doping.

It is clearly seen that, from 1000 nm to 2500 nm, when SnO_2 is doped with fluorine, its antireflective properties are improved. There is a slight decrease in reflectance while at the same time transmittance improves in that region. Average transmittance of the thin films was 84.28% in the visible range of the spectrum. A maximum transmittance of 89.5% was obtained at 12.83at%F doping in SnO_2 thin films. The same reasons attributed to increment and decrement of transmittance at different level of doping applies in this case as it was deduced for palladium doping. Reflectance spectra of the F:SnO_2 thin films was found to be below 22% in the measured wavelength range.

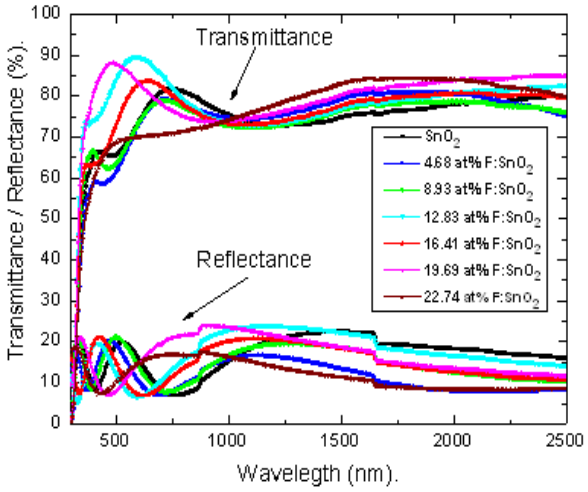

Figure 5. *Transmittance and reflectance spectra for undoped and F:SnO_2*

In fig. 6, the variation of the calculated band gap for various thin films at certain doping levels is shown. The undoped SnO_2 thin film band gap was calculated to be about 4.0564 eV. When the SnO_2 was doped with fluorine at 4.68at%F concentration, the band gap was observed to decrease to 4.0296 eV. This decrease in band gap continued upto a minima of about 3.8014 eV where the doping level was 16.41 at%F concentration. Increase in the fluorine dopant concentration from zero to the optimum level (16.41at%F) caused a narrowing effect on the band gap. The narrowing effect on the band gap can be attributed to the incorporation of F^- ions in the crystal lattice, which gives rise to donor levels in the SnO_2 band gap. This causes the conduction band to lengthen which leads to a reduction in the band gap value [15].

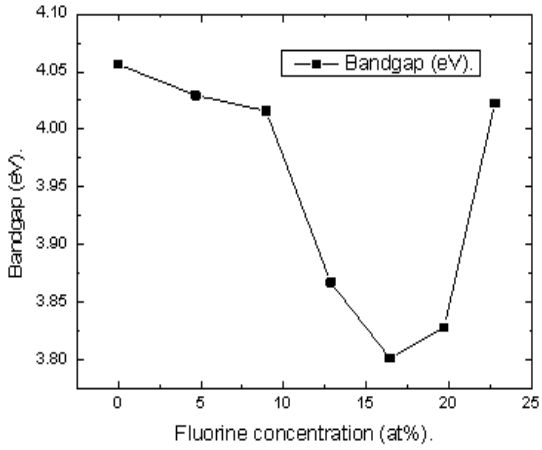

Figure 6. *Optical Band gap for F: SnO_2 thin films*

3.4. Pd-F:SnO_2 Films

Different thin films for Pd-F:SnO_2 were deposited. The film with the best optical transparency was the best choice for making a transparent thin film gas sensor. The optical band gap for 2.7at%Pd:SnO_2 thin films doped with fluorine, with the concentration of the dopant, ranging from 0at%F to 19.28at%F as shown in fig 7. It can be seen that the initial band gap of 2.7at%Pd:SnO_2 thin films was 4.1135 eV. When fluorine is incorporated to have a co-doped Pd-F:SnO_2 thin film, the band gap remains slightly above 4.05eV. Increasing the fluorine dopant concentration from zero to the optimum level of about 16.04at%F led to a narrowing effect on the band gap. The E_g was found to increase sharply for higher levels of F doping beyond this level.

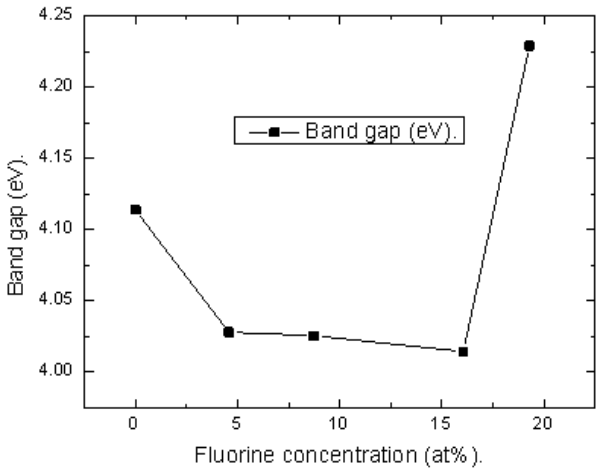

Figure 7. *Optical Band gap for Pd-F: SnO_2 thin films*

Fig 8 below shows the effect of both annealing and passivation on the band gap of Pd-F:SnO_2 thin films. On annealing the thin films, the band gap was found to decrease from 4.02eV to 3.91eV. This is because apart from eliminating the oxygen vacancies, annealing process also localizes the oxygen atoms at interstitials positions. The induced oxygen interstitials form separate band defects in the band gap region, causing the reduction in E_g value [28].

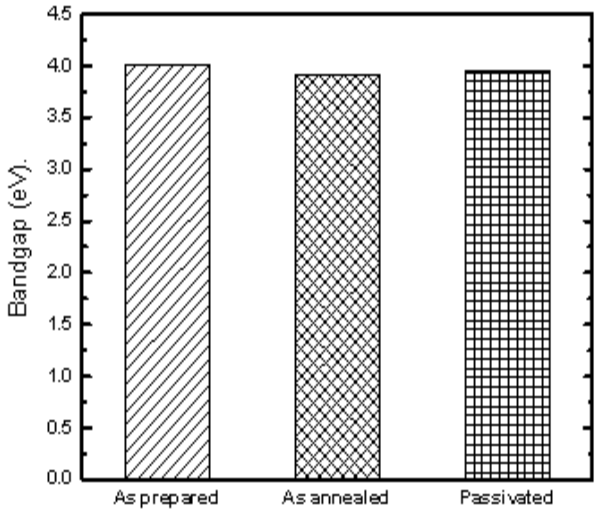

Figure 8. *Optical Band gap for Pd-F: SnO_2 thin films*

The optical band gap of Pd-F:SnO_2 thin films was found to increase from 3.91eV to 3.94eV as a result of passivation on the thin films. The increase in the value of the optical band gap can be attributed to creation of oxygen vacancies as a result of annealing of the thin films in oxygen deficient atmosphere [18].

4. Conclusion

Pd-F: SnO_2 thin films prepared by spray pyrolysis technique have good optical characteristics for gas sensing applications. The band gap has been found to narrow with increase in fluorine incorporation, this observation was ascribed to the incorporation of F^- ions in the crystal lattice, which gives rise to donor levels in the SnO_2 band gap which is an essential characteristics for the gas sensor application. Both annealing and passivation have been found to cause very insignificant change in Pd-F:SnO_2 band gap, meaning that passivated gas sensor when exposed to elevated temperature will not be severely affected.

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References

[1] Calnan, S. "Applications of Oxide Coatings in Photovoltaic Devices", *Coatings*,vol 4(1), pp 162 – 202, 2014.

[2] Mishra, R. L., Mishra, S.K and Prakash, S.G. "Optical and Gas Sensing Characteristics of Tin-Dioxide Nano-Crystalline Thin Films." *Journal of Ovonic Research*, vol 5, pp77-85, 2009.

[3] Shamala, K.S., Murthy, L.C.S and Rao, K.N. "Studies on tin oxide films prepared by electron beam evaporation and spray pyrolysis methods" *Bull. Mater. Sci.* vol 27, pp295-301, 2004.

[4] Subramanian, N.S, Santhi, B, Sundareswaran, S, Venkatakrishnan, K.S. "Studies on Spray Deposited SnO_2, Pd:SnO_2 and F:SnO_2 Thin Films for Gas Sensor Applications",*Synthesis and Reactivity in Inorganic. Metal-Organic, and Nano-Metal Chemistry*,vol 36,pp 131-135, 2006.

[5] Chowdhury, F.R., Chowdhury, S., Firozhasan and Begum, T. "Optical properties of Undoped and indium Doped Tin Oxide Thin Films". *Journal of Bangladesh Academy of Sciences,* vol 35, pp 99-111, 2011.

[6] Ikhmayies, S.J and Ahmad – Bitar, R.N. "Effect of Processing on the Electrical Properties of Spray-Deposited SnO_2:F Thin Films". *American Journal of Applied Sciences,*vol 5, pp 672-677, 2008.

[7] Salehi, H., Aryadoust, M., and Farbod, M. "Electronic and Structural Properties of Tin Dioxide in Cubic Phase". *Iranian Journal of Science & Technology, Trans.* A, vol 34, (A2), pp 131-138, 2010.

[8] Rakhshani, E.A., Makdisi, Y and Ramazaniyan, A.H. "Electronic and optical properties of fluorine-doped tin oxide films". *J. Applied Phys*. vol 83*,* pp 1049-1057, 1998.

[9] Mohammad, T.M. "Performance and characteristics of Al-PbS/SnO_2: F selective coating system for photothermal energy conversion". *Solar Energy Mater.* Vol 20,pp 297-305, 1990.

[10] Yadav, A. A., Masumdar, E. U., Moholkar, A. V., Rajpure, K. Y and Bhosale, C. H. "Gas Sensing of Fluorine Doped Tin Oxide Thin Films Prepared by Spray Pyrolysis". *Journal of Sensors & Transducers*, vol 92, pp55-60, 2008.

[11] Díaz, R (2002). *Tin oxide thin films: electronic properties and growth mechanism under electrochemical control*. University of Barcelona, Barcelona, Spain.

[12] Miller, T.A., Bakrania, S.D., Perez, C and Woondridge. *Nanostructured Tin Dioxide Materials for Gas Sensor Applications*. American Scientific Publishers, Michgan USA, , pp 1-24, 2006.

[13] Vaezi M.R. "Effects of surface modification on the recovery time and stability of nano structured tin oxide thick films gas sensors". *International Journal of electronics Transactions B: Applications*,vol 20, pp 1-8, 2007.

[14] Adamyan, A.Z., Adamyan, Z.N., Aroutiounian, V.M., Schietbaum, K.D and Han, S-D. "Improvement and Stabilization of Thin – Film Hydrogen Sensors Parameters". *Armenian Journal of Physics,* vol 2, pp 200-212, 2009.

[15] Moure- Flores, F., Guillen – Gervauntes, A., Nieto-Zapeda, K.E., Quinones- Galvan, JG., Hernandez- Hernandez. A., Olvera, M.G and Melendez- Lira, M. "SnO_2 Thin Films Deposited by RF Magnetron Sputtering: Effect of the SnF_2 Amount in the Target on the Physical Properties". *Revista Mexicana de Fisica*, vol 59*,*pp 335-338, 2013.

[16] Al-Delaimy, S.M and Basheer, R.J. "Annealing Effects on Structural and Optical Properties of SnO_2 Thin Films". *J.Edu. & Sci*.,vol 21, pp 99-109, 2008.

[17] Senthilkumara, V., Vickramana*, P., Joseph Princeb, J., Jayachandranc, M and C. Sanjeevirajad. "Effects of annealing temperature on structural, optical, and electrical properties of antimony-doped tin oxide thin films". *Philosophical Magazine Letters*,vol 90, pp 337–347, 2010.

[18] Jain, V.K., Kumar, P and Vijay, Y.K. "Preparation of Nanostructure ZnO-SnO_2 Thin Films For Optoelectronic Properties and Post Annealing Influence". *World Academy of Sciences, Engineering and Technology,* vol 72, pp 1575-1577, 2012.

[19] Jebbari, N., Kamoun, N and Bennaceur, R. "Effect of $SnCl_4$ concentration on F: SnO_2, deposited by chemical spray pyrolysis". *In the proceedings of International Renewable Energy Congress*, Souse, Tunisia,vol 2*,* pp 276-279, 2010.

[20] Bochenkov, V. E and Sergeev, G. B. "Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures and their Applications" *American Scientific Publishers, Russia*, vol 3*,* pp 31-52, 2010.

[21] Ozaki, Y., Suzuki, S., Morimitsu, M and Matsunaga, M. "Enhanced long-term stability of SnO_2-based CO gas sensors modified by sulfuric acid treatment". *Sensors and Actuators B*,vol 62*,* pp 220-225, 2000.

[22] Radecka, M., Zakrzewska, K. and Rekas, M. "SnO_2-TiO_2 solid solutions for gas sensors", *Sensors and Actuators B*,vol 47*,* pp194-204, 1998.

[23] Yousaf, S.A and Ali, S. "The Effect of Fluorine Doping on Optoelectronic Properties of Tin-Dioxide (F:SnO_2) Thin Films". *Journal of Natural Sciences and Mathematics*,vol 48*,* pp 43-50, 2008.

[24] Sandipan R, Gupta P.S. and Gurdeep S. "Electrical and Optical properties of sol-gel prepared Pd-doped SnO_2 thin films: Effect of multiple layers and its use as room temperature methane gas sensor", *Journal of Ovonic Research,*vol 6(1), pp 63-74, 2010.

[25] Sa'nchez-Garcia, M., Maldonado. Castaneda, L., Silva-Gonzalez, R and Olvera, M.L. "Characterization of SnO_2:F Thin Films Deposited by Ultrasonic Spray Pyrolysis: Effect of Water Content in Solution and Substrate Temperature". *Materials, Sciences and Applications*, vol 3, pp 690-696, 2012.

[26] Odari, B.V., Mageto, M., Musembi, R., Othieno, H., Gaitho, F., and Muramba, V. "Optical and Electrical Properties of Pd Doped SnO_2 Thin Films Deposited by Spray Pyrolysis". *Australian Journal of Basic and applied Sciences,*vol 7(2), pp 89-98, 2013.

[27] Fatema R.C, Shamima C, Firoz H and Tahmina B. "Optical properties of undoped and indium-doped tin oxide thin films", *Journal of Bangladesh Academy of Sciences,* vol 35(1): pp 99-111, 2011.

[28] Baco, S., Chik, A and Tassin , F.Md. "Study on Optical Properties of Tin Oxide Thin Films at Different Annealing Temperatures". *Journal of Science and Technology*, , vol 4, pp 61-72, 2012.