
Effect of Annealing and Surface Passivation on Doped SnO₂ Thin Films Prepared by Spray Pyrolysis Technique

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Abstract: In this study doped SnO₂ thin films have been prepared by spray pyrolysis technique using an alcoholic precursor solution consisting of stannic chloride (SnCl₄.5H₂O), ammonium fluoride (NH₄F) and palladium chloride (PdCl₂). Optimization on the deposition parameters was done so as to obtain high quality thin films. The effect of varying the Fluorine content on the optoelectronic properties of F: SnO₂ thin films was studied. Data for transmittance and reflectance in the wavelength range from 300nm – 2500nm was obtained using the solid spec 3700DUV spectrophotometer. Electrical characterization of the thin films was done using the four point probe method at room temperature. Post deposition treatment of the thin films by annealing in air then passivating in nitrogen gas environment was done in a tube furnace at 450⁰C. Sheet resistivity for the as prepared F: SnO₂ was found to be 0.4599 Ωcm and 0.00075 Ωcm being the highest and lowest sheet resistivity at 22.74 at% F and 16.41at% F doping in SnO₂ respectively. Low sheet resistivity of F: SnO₂ thin films is due substitutional incorporation of F ions instead of oxygen ions into the crystal lattice of SnO₂ thin films which increases free carrier concentration. The effect of annealing generally was found to improve on the electrical conductivity of the thin films which is due to increase in carrier mobility and density. Passivation on the other hand had a slight opposite effect. Effects of annealing and passivation on doped SnO₂ thin films band gap energy and their transparency was insignificant, rendering the doped SnO₂ thin films good choice for making a transparent thin film gas sensors.

Keywords: Spray Pyrolysis, Fluorine Doping, Palladium Doping, Annealing and Passivation

1. Introduction

SnO₂ thin films are reported to belong to a class of materials that combines high optical transparency with good electrical conductivity [1]. Tin oxide is a crystalline solid with a tetragonal rutile structure. It is a wide band gap, non-stoichiometric semiconductor material of n-type conductivity. The conductivity of SnO₂ thin films can be manipulated from normal to degenerate by suitably doping SnO₂ with appropriate amount of noble metal (Pt, Pd), semi-metal (Sb, In, Bi) and halogens (F, Cl) [2]. The band gap energy for doped SnO₂ thin films is a direct one and ranges from 3.6 to 4.6eV [3, 4, 5]. Moreover, SnO₂ thin films besides other metal oxide semiconductors e.g. ZnO and TiO₂ are reported to have more desirable qualities which include mechanical hardness, chemical inertness, a wide range of

high temperature spectrum of operation, excellent resistance to strong acids and bases and of good adhesion to many substrates [1, 6]. These properties make SnO₂ based thin films good candidates for a number of applications in many fields of research and in various device fabrications. Most important is the thin film application in environmental monitoring through sensing of a number of gases. SnO₂ characteristics for gas sensing applications have been improved through catalytic and impurity doping with a view of improving on its sensitivity to a number of gases as well as its optoelectronic properties [2, 4, 7, 8]. SnO₂ based thin films have been reported to suffer from sensitivity due to the presence of ambient humidity which has been overcome by resistive heating of the thin film gas sensor element [9]. Moreover, the effect arising from instability of the doped SnO₂ thin films when exposed to adverse environmental and

weather conditions e.g. elevated temperatures, volatile organic compounds and attacks by atmospheric oxygen leading to corrosion of the active surface layer has been a challenge in the recent past [10]. To overcome this problem and to promote the adsorption of CO species by preadsorbed NO, thin films for gas sensing application are passivated by application of ultra-thin layer which prevents surface corrosion or modification of the surface states through post deposition treatment effects e.g. annealing and passivation [3, 7, 8, 9, 11, 12, 13, 14, 15, 16]. In this study we propose to passivate doped SnO₂ based thin films by annealing them in a nitrogen gas atmosphere and study the effect of annealing and surface passivation on optoelectronic properties of doped SnO₂ thin films for CO₂ gas sensing applications.

Many methods have been employed to deposit SnO₂ based thin films such as RF magnetron sputtering [17], chemical vapor deposition method [18], Electron Beam evaporation method [19], Flash evaporation technique [20], Dip coating technique [21] and the spray pyrolysis technique [22]. In this study spray pyrolysis was chosen because in it there is the advantage of controlling the grain size and growth on atomic scale by varying the precursor content, pressure of the carrier gas and substrate temperature [23]. Moreover, spray pyrolysis technique is cheap, efficient in coating large surfaces; reproducible hence, the method can be utilized for large scale production of high quality thin films [22].

2. Experimental Procedure

2.1. Sample Preparation

The substrates were microscope glass slides measuring 1.2mm in thickness and 2.5cm by 7.6cm in dimensions. Before deposition, the substrates were cleaned by first soaking them in soapy water solution and sonicated for 30 minutes; they were removed and rinsed using distilled water. Thereafter, the substrates were immersed in distilled water in a beaker and sonicated for another 30 minutes then rinsed in distilled water and left to dry at room temperature. After drying the substrates were stored in desiccation ready to be used for coating the thin films.

2.2. Thin Film Deposition

Spray pyrolysis technique was used to coat the films. The experimental set up used was a home-made spray pyrolysis system shown in figure 1. It consisted of a fume chamber, hot plate, spray nozzle of diameter ~1 mm, input gas valve, gas compressor, gas flow meter, conduit tube, thermocouple and a pressure gauge. The following table 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°C
3	Flow rate	4 ml/min
4	Quantity of spraying solution	30 cm ³
5	Nozzle to substrate distant	33.0 ± 3.0 cm

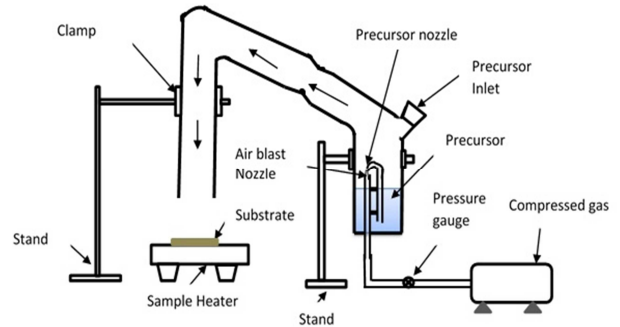


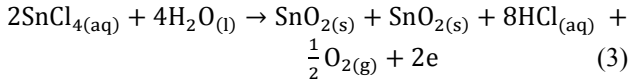
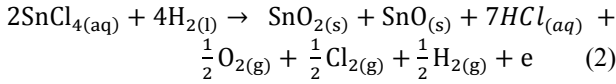
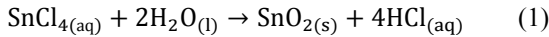
Figure 1. Spray pyrolysis experimental set up.

The undoped SnO₂ 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%). Palladium chloride solution was prepared by dissolving 0.5 g of PdCl₂ (59-60%Pd) in 60 ml of ethanol (99.9%). It was then added to stannic chloride solution at a concentration 2.7 at% Pd (optimum) in order to make Pd: SnO₂ thin films. 1.0g of ammonium fluoride (NH₄F) was dissolved in distilled water in order to make NH₄F solution which was then added to the spraying solution containing stannic chloride at varying doping concentrations ranging from 0- 22.74 at% F in order to make F: SnO₂ thin films [4, 3, 7, 8].

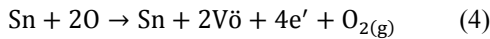
2.3. Kinetics of Thin Film Growth

The as prepared precursor was translucent and contained ionized atoms at predetermined proportions [22]. The precursor droplets are reported to undergo three major steps during the course of spray pyrolysis: Drop shrinkage due to evaporation, conversion of precursor into oxides and finally solid particle formation [24]. Substrate temperature plays a critical role in determining the quality thin films to be produced. Substrate temperatures below 260°C lead to formation of foggy thin films whose optoelectronic properties are quite poor [1]. Substrate temperatures above 500°C leads to vaporization of the spray before reaching the substrate hence the resultant thin films become almost powdery [1]. The suitable substrate temperature for deposition of SnO₂ based thin films is between 260°C to 500°C [1] with 450 °C being most suitable since Sn is oxidised at temperature above 440 °C [22]. Flow rate is another essential factor that should be controlled for production of high quality thin films. The role of the carrier gas is to transport and dry the micro particles of the metal chlorate solution before they land on the surface of the substrate. This leads to insufficient wettability between the micro particles and previously deposited film surface [25]. The particle formation may involve the following two mechanisms: one-particle-per-drop mechanism and gas-to-particle conversion [27]. In the one-particle-per-drop mechanism, each droplet is regarded as a micro reactor and converts into one solid particle when it travels towards substrate. In contrast, gas-to particle conversion occurs when the precursor is volatile and is transported across the particle-gas interface [26, 27]. Resultant thin films produced

are therefore of low packing density with many pin holes. Generally in spray pyrolysis, thin films of SnO₂ are prepared by the following reaction as shown in equations 1- 3[25].



Due to defect reaction, doubly ionized oxygen vacancies are predominant in SnO₂ thin films and can be explained in terms of reaction shown in equation 4.



Hence, the resultant thin film composition is of the form SnO_{2-x}(V_O)_{xe}'_{2x} where x is the deviation from stoichiometry, V_O, the doubly ionized oxygen vacancies and e', the electrons that are needed for charge neutrality on macroscopic scale [25].

2.4. Annealing of Thin Films

Thin films were annealed in a tube furnace as shown in figure 2, in the presence of air at 450°C for 30 minutes. This was performed to reduce intrinsic stress, improve on lattice mismatch and create longer mean paths for free electrons hence improving on electrical conductivity of the thin films [28]. Moreover, annealing was done in order to improve on stability in time for coatings during gas sensing operations [9].

2.5. Passivation

Thin films were passivated by annealing them in a nitrogen atmosphere in a tube furnace for 30 minutes at 450°C. Since passivation is known to improve on the stability of doped SnO₂ thin films without adversely affecting the gas sensitivity of the SnO₂ based thin films [8, 9, 11, 12, 13], in this study it was done in order to study its effect on optoelectronic properties of doped SnO₂ thin films.

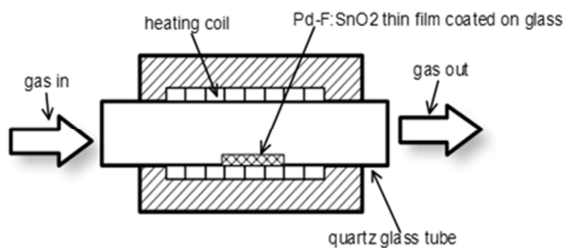


Figure 2. Horizontal tube furnace for annealing and passivation.

2.6. Electrical Characterization

Electrical characterization of thin films was done using the four point probe method at room temperature (25 °C). The measurements were taken in a square geometry using Keithley 2400 Source Meter. The four contact terminals of Keithley

2400 Source Meter were placed on the surface of the thin film as shown in figure 3. Typical probe spacing was 20 mm. A high impedance current source was used to supply current through the two probes A and B and a voltmeter was used to measure the voltage across probes C and D.

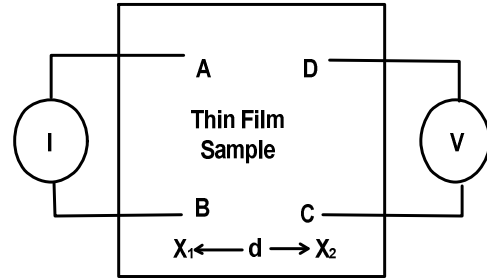


Figure 3. schematic diagram showing the arrangement used to measure sheet resistance.

The values of sourced current and measured voltages were used in determining sample resistivity using equation (5).

$$\rho_s = \beta \left(\frac{V}{I} \right) t \quad (5)$$

Where β is a geometric factor and in the case of a semi-infinite thin sheet, $\beta = 4.53$, which is just $\pi/\ln 2$ from the derivation of equation 5 and t is the thin film thickness [22].

2.7. 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 Harmonic Oscillator model, Drude Model and the OJL model. The models were used to simulate theoretical data from the experimental data from which optical constants e.g. band gap were calculated. The graphs were drawn using the Origin Pro 8.1 software.

3. Results and Discussion

3.1. SnO₂ Thin Films

Figure 4 shows transmittance and reflectance spectra for undoped SnO₂ thin films as prepared, annealed and passivated. All the films had high transmittance in the visible region of the solar spectrum. The undoped SnO₂ thin films had a transmittance of 81.73% at 749 nm. This high value of transmittance is due to formation of Fermi levels in the conduction band of SnO₂ thin films [29]. The reflectance of the thin films was below 22%. It is clear from the figure that in the entire wavelength region from 300nm to 2500nm there was hardly any noticeable change in transmittance for all the films. Passivation seems to have had little effect in reflectance only at 300nm – 350nm and another slight difference between 1000nm – 1600nm.

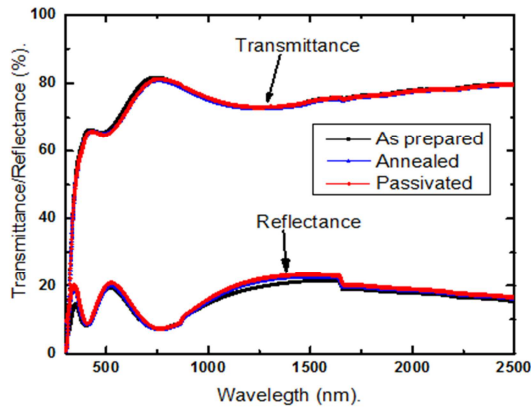


Figure 4. Transmittance and reflectance spectra for as prepared, annealed and passivated SnO₂ thin films.

In general, the change in reflectance of the thin films as a result of annealing and passivation was minimal which can be attributed to high mechanical integrity of SnO₂ based thin films [6]. Figure 5 shows a comparison on the calculated band gap energy for undoped SnO₂ thin films as prepared, annealed and passivated. The calculated band gap energy for undoped SnO₂ thin films decreased slightly after annealing due to localization of the oxygen atoms at the interstitials. The induced oxygen interstitials form separate band defects in the band gap region, causing the reduction in calculated band gap energy value [31, 32]. Upon passivating the annealed thin films, the calculated band gap energy increased slightly. The increase calculated band gap energy is attributed to increase in the formation of nanocrystalline grains [33] or effects arising from annealing the thin film in an oxygen deficient atmosphere [7].

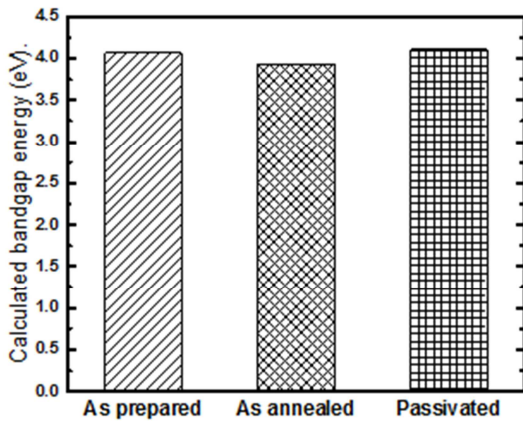


Figure 5. Calculated band gap energy for as prepared, annealed and passivated SnO₂ thin films.

Figure 6 shows the effect of annealing and passivation on sheet resistivity of undoped SnO₂ thin films. Annealing process is seen to decrease the sheet resistivity of undoped SnO₂ thin film slightly. This is because annealing process is ascribed to decrease intrinsic stress, improve on lattice mismatch and create longer mean paths for free electrons hence increasing their mobility thereby improving on the electrical conductivity of the thin films [28, 35]. When the thin

films were passivated, there was a slight increase in resistivity for the passivated samples which is attributed to increase in the formation of nanocrystalline grains [33] or effects arising from annealing the thin film in an oxygen deficient atmosphere [7].

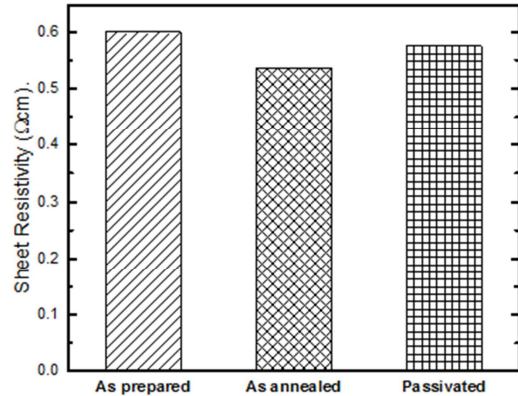


Figure 6. Sheet resistivity of the as prepared, annealed and passivated SnO₂ thin films.

3.2. SnO₂ and F: SnO₂ Thin Films

Figure 7 shows the effect of incorporating F on the sheet resistivity of SnO₂ thin films. Undoped SnO₂ has a low resistivity of the order of 10⁻¹ Ωcm which is in agreement with results obtained by [25, 34, 17]. The low resistivity of SnO₂ thin films emanates from creation of oxygen vacancies which act like donors of electrons and increase free carrier concentration [25]. When undoped SnO₂ was doped with F, the sheet resistivity was found to vary from as high as 0.5992 Ωcm to a low of 0.00075 Ωcm as seen in figure 7. When SnO₂ was doped with fluorine at 4.68at%, the sheet resistivity was observed to decrease dramatically to 0.2080 Ωcm which is more than half the sheet resistivity of undoped SnO₂ thin film. Continued doping improved the conductivity of the F: SnO₂ thin film up to a minima of 0.00075 Ωcm at doping level of about 16.41at%F. This decrease in sheet resistivity is attributed to substitutional incorporation of F⁻ ions in the crystal lattice of SnO₂ thin films, instead of O⁻ ions which lead to an increase in free carrier concentration [30].

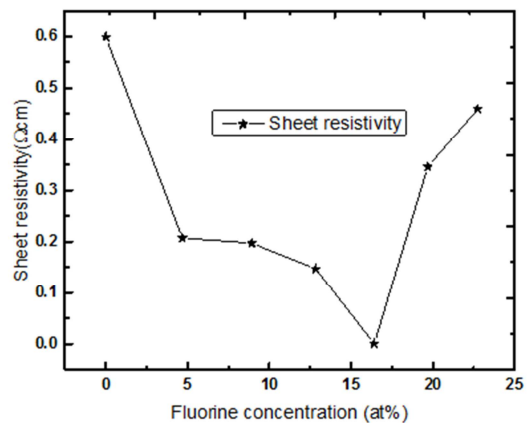


Figure 7. Sheet resistivity versus fluorine concentration.

Increase in the dopant concentration beyond the optimum level of F doping as seen in figure 7, led to an increase in the sheet resistivity of the F: SnO₂ thin films. The increase in sheet resistivity is attributed to the incorporation of fluorine ions at the interstitial sites which deteriorates the crystal structure leading to decrease in mobility of the free electrons hence, the increase in resistivity of the F: SnO₂ thin films. This deduction is in good agreement with literature work done by [30].

3.2.1. Effect of Annealing and Passivation on F:SnO₂ Thin Films

Figure 8 shows the effect of annealing and passivation on F: SnO₂ thin films prepared at 16.41 at% F which had a low resistivity of 0.00075 Ωcm.

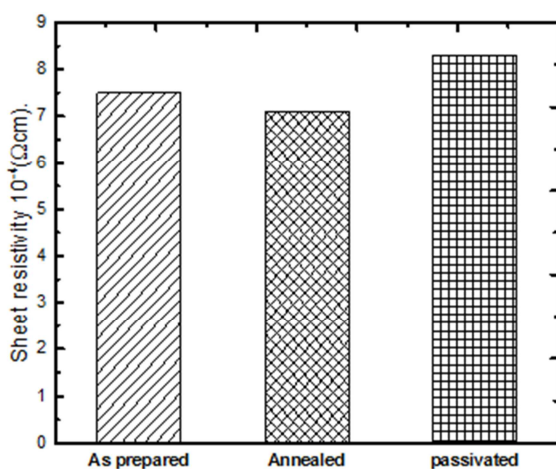


Figure 8. Sheet resistivity of the as prepared, annealed and passivated F: SnO₂ thin films.

Annealing effects led to further decrease in resistivity of F: SnO₂ thin films which is attributed to increase in crystallinity, hence mobility of free charge carriers [35, 36]. Passivation had an opposite effect which is attributed to increase in the formation of nanocrystalline grains [33] or effects arising from annealing the thin film in an oxygen deficient atmosphere [7].

3.2.2. Effect of Annealing and Passivation on Optical Properties of F: SnO₂ Thin Films

Figure 9 shows the transmittance and reflectance spectra for as prepared, annealed and passivated F:SnO₂ thin films. The transmittance and reflectance of F:SnO₂ seem to be unaffected by the exposure of the thin films to high temperatures during thermal treatment in air and in the presence nitrogen gas which is attributed to high mechanical integrity of SnO₂ based thin films [6].

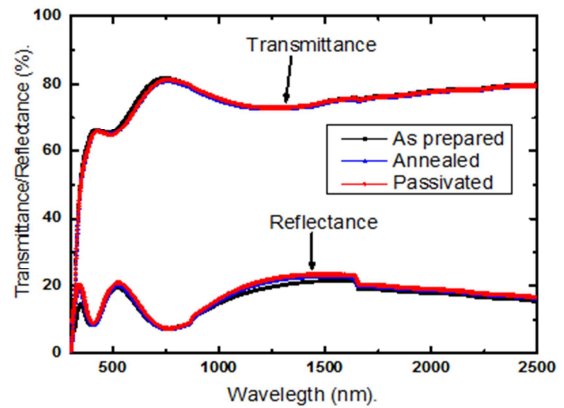


Figure 9. Transmittance and reflectance spectra for as prepared, annealed and passivated F: SnO₂ thin films.

Figure 10, shows the effect of annealing and passivation on calculated band gap energy for F: SnO₂ thin films. It can be seen from figure 10 that annealing and passivation hardly had any noticeable change on the calculated band gap energy for F:SnO₂ thin films. This means that the optical properties of F:SnO₂ are not affected by exposure of thin films to high operating temperatures which is attributed to high mechanical integrity of SnO₂ based thin films [6]. This makes F:SnO₂ thin films good candidates for optical-gas sensing application.

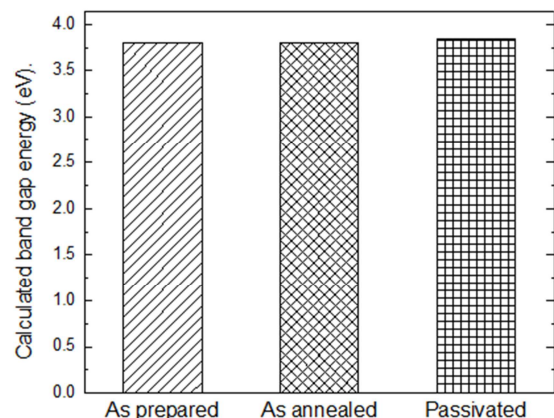


Figure 10. Calculated band gap energy for the as prepared, annealed and passivated F: SnO₂ thin films.

3.3. Pd:SnO₂ Thin Films

Figure 11 is a comparison on optical spectroscopy results for as prepared Pd: SnO₂ thin films as well as after annealing and passivation process. Optical transmittance of the thin films i.e. from 350nm to 1800nm increased slightly as a result of annealing and thereafter, it increased again slightly upon passivating the annealed thin films. Annealing and passivation process makes the Pd:SnO₂ more crystalline hence becoming more transparent [35, 36]. Annealing and passivation on the thin films caused a slight variation on the reflectance of the thin films.

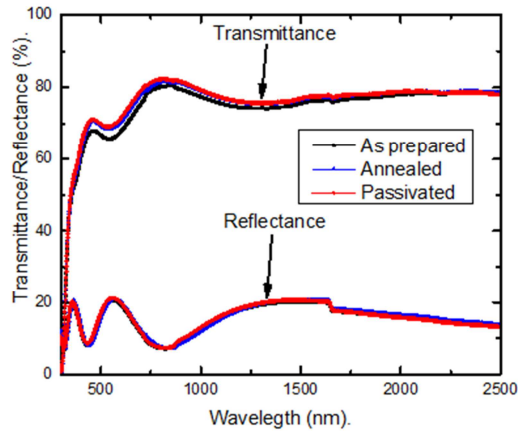


Figure 11. Transmittance and reflectance spectra for as prepared, annealed and passivated Pd: SnO₂ thin films.

The calculated band gap energy for the Pd:SnO₂ seems not to be affected by the exposure to of the thin films to high temperatures during annealing and passivation as shown in figure 12. Annealing and passivation had a significant improvement on conductivity of Pd:SnO₂ as seen in figure 13. This is attributed to increase in mobility of free charge carriers due to improved crystallinity of the thin films [35, 36].

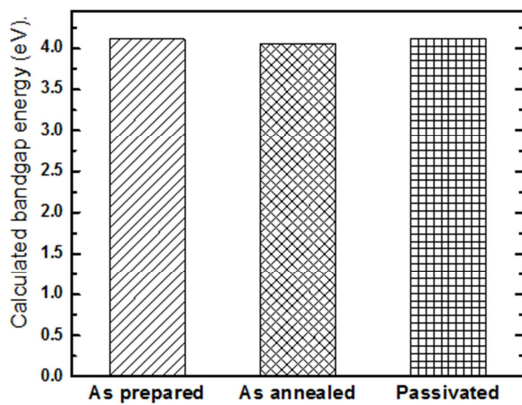


Figure 12. Calculated band gap energy for as prepared, annealed and passivated Pd:SnO₂ thin films.

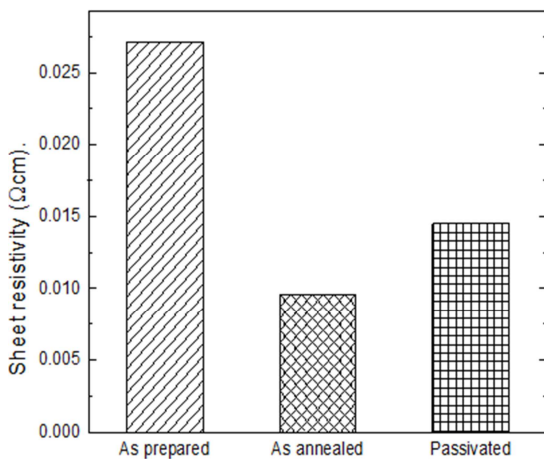


Figure 13. Sheet resistivity for the as prepared, annealed and passivated Pd: SnO₂ thin films.

4. Conclusions

Optical transmittance of undoped SnO₂ thin films was found to be 81.73% at 749 nm. The high optical transmittance of the thin films results from formation of Fermi levels in the conduction band of the thin films. When undoped SnO₂ thin films were annealed and later passivated there was hardly any noticeable change in the optical transmittance of annealed and passivated samples. Annealing and passivation was also found to have a slight variation in the calculated band gap energy for undoped SnO₂ thin films. Annealing process slightly decreased the calculated band gap energy value which is due to localization the oxygen atoms at interstitials. The induced oxygen interstitials form separate band defects in the band gap region, causing a reduction in calculated band gap energy value. Passivation resulted into a slight increase in the calculated band gap energy value for undoped SnO₂ thin films which is attributed to increase in the formation of nanocrystalline grains or effects arising from annealing the thin film in an oxygen deficient atmosphere. Calculated band gap energy for F: SnO₂ and Pd: SnO₂ thin films was found to follow a similar trend upon annealing and passivation to that of undoped SnO₂ thin films. Sheet resistivity of undoped SnO₂ thin film was found to be 0.5992Ωcm which decreased slightly upon annealing and increased slightly upon passivation. The decrease in sheet resistivity of undoped SnO₂ thin film results from increased mobility of free charge carriers while the slight increase in sheet resistivity upon passivation is attributed to increase in the formation of nanocrystalline grains or effects arising from annealing the thin film in an oxygen deficient atmosphere. On doping SnO₂ with 16.41 at% F, the sheet resistivity of F: SnO₂ decreased to a minima of 0.00075Ωcm. The decrease in sheet resistivity is due to substitutional incorporation of F ions in the crystal lattice of SnO₂ instead of oxygen vacancies thereby leading to an increase in free carrier concentration. A similar trend obtained on sheet resistivity for SnO₂ thin films after annealing and passivation processes were also obtained for F: SnO₂ and Pd: SnO₂ thin films.

Generally SnO₂ based thin films prepared by spray pyrolysis technique have good optoelectronic properties for gas sensing applications. Their exposure to high temperatures during annealing and passivation process improves on their electrical conductivity with insignificant effects on transmittance and reflectance and a slight effect on the calculated band gap energy value for SnO₂, F:SnO₂ and Pd:SnO₂ thin films. This makes doped SnO₂ thin films stable. Since passivation is known to improve on longevity of doped SnO₂ thin films, passivated SnO₂, F:SnO₂ and Pd:SnO₂ are therefore a good choice for making a transparent thin film gas sensor.

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References

- [1] 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*, 5 (4), 77-85, 2009.
- [2] Subramanian, N.S, Santhi, B, Sundareswaran, S, Venkatakrishnan, K.S. "Studies on Spray Deposited SnO₂, Pd:SnO₂ and F:SnO₂ Thin Films for Gas Sensor Applications". *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 36, 131-135, 2006.
- [3] Mwathe, P.M., Musembi, R., Munji, M., Odari, B., Munguti, L., Ntilakigwa, A, A., Nguu, J., Aduda, B., Muthoka, B. "Influence of Surface Passivation on Optical Properties of Spray Pyrolysis Deposited Pd-F:SnO₂". *International Journal of Materials Science and Applications*. 3(5), 137-142, 2014.
- [4] Odari, B.M., Musembi, R.J., Mageto, M.J., Othieno, H., Gaitho, F., Mghendi, M and Muramba, V. "Optoelectronic Properties of F-co-doped PTO Thin Films Deposited by Spray Pyrolysis". *American Journal of Materials Science* 3(4), 91-99, 2013.
- [5] Rakhshani, E.A., Makdisi, Y and Ramazaniyan, A.H. "Electronic and optical properties of fluorine-doped tin oxide films". *Journal of Applied Physics*, 83, 1049-1057, 1998.
- [6] Kim, K.S., Yoon, S.Y., Lee W.J and Kim, K.H. "Surface morphologies and electrical properties of antimony-doped tin oxide films deposited by plasma enhanced chemical vapor deposition". *Surface and Coatings technology*. 138 (2-3), 229-236, 2001.
- [7] Mwathe, P.M., Musembi, R., Munji, M., Odari, B., Munguti, L., Ntilakigwa, A, A., Nguu, J., Muthoka, B. "Effect of Surface Passivation on Electrical Properties of Pd-F:SnO₂ Thin Films Prepared by Spray Pyrolysis Technique". *Coatings*. 4, 747-755, 2014.
- [8] Mwathe, P.M., Musembi, R., Munji, M., Odari, B., Munguti, L., Ntilakigwa, A, A., Nguu, J., Aduda, B., Muthoka, B. "Surface passivation effect on CO₂ sensitivity of spray pyrolysis deposited Pd-F: SnO₂ thin film gas sensor". *Advances in Materials*. 3(5), 38-44, 2014.
- [9] 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*, 2 (3), 200-212, 2009.
- [10] Fine, G, F., Leon, M., Cavanagh, Afonja, A and Binions, R. "Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring". *Journal of Sensors*, 10, 5473-5502, 2010.
- [11] 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* 20, 1-8, 2007.
- [12] Bochenkov, V. E and Sergeev, G. B. "Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures and their Applications": American Scientific Publishers, Russia, 3, 31-52, 2010.
- [13] Ozaki, Y., Suzuki, S., Morimitsu, M and Matsunaga, M. "Enhanced long-term stability of SnO₂-based CO gas sensors modified by sulfuric acid treatment". *Sensors and Actuators B*, 62, 220-225, 2000.
- [14] Radecka, M., Zakrzewska, K. and Rekas, M. "SnO₂-TiO₂ solid solutions for gas sensors", *Sensors and Actuators B*, 47, 194-204, 1998.
- [15] Soiymosi, F and Kiss, J. "Adsorption and reduction of NO on Tin (IV) oxide catalysts". *Journal of Catalysis*, 41, 202-211, 1976.
- [16] Soiymosi, F and Kiss, J. "Adsorption and reduction of NO on tin(IV) oxide doped with chromium(III) oxide". *Journal of Catalysis*, 54, 42-51, 1978.
- [17] Moure- Flores, F., Guillen – Gervantes , A., Nieto-Zapeda, K.E., Quinones- Galvan, J.G., Hernandez- Hernandez. A., Olvera, M.G and Melendez- Lira, M. "SnO₂ Thin Films Deposited by RF Magnetron Sputtering: Effect of the SnF₂ Amount in the Target on the Physical Properties". *Revista Mexicana de Fisica*, 59, 335-338, 2013.
- [18] Al-Delaimy, S.M.; Basheer, R.J. "Annealing effects on structural and optical properties of SnO₂ thin films". *J. Edu. Sci.*, 21, 99–109, 2008.
- [19] Senthilkumara, V.; Vickramana, P.; Joseph Princeb, J.; Jayachandran, M.; Sanjeevirajad, C. "Effects of annealing temperature on structural, optical, and electrical properties of antimony-doped tin oxide thin films". *Philos. Mag. Lett.*, 90, 337–347, 2010.
- [20] Jain, V.K.; Kumar, P.; Vijay, Y.K. "Preparation of nanostructure ZnO-SnO₂ thin films for optoelectronic properties and post annealing influence". *World Acad. Sci. Eng. Technol.*, 72, 1575–1577, 2012.
- [21] Yadav, A.A.; Masumdar, E.U.; Moholkar, A.V.; Rajpure, K.Y.; Bhosale, C.H. "Gas sensing of fluorine doped tin oxide thin films prepared by spray pyrolysis". *J. Sens. Transducers*, 92, 55–60, 2008.
- [22] Jebbari, N., Kamoun, N and Bennaceur, R. "Effect of SnCl₄ concentration on F: SnO₂, deposited by chemical spray pyrolysis". *In the proceedings of International Renewable Energy Congress*, Sousse, Tunisia, 2, 276-279, 2010.
- [23] Patil, P.S. "Review Versatility of Chemical Spray Pyro-lysis Technique," *Materials Chemistry and Physics*, 59 (3), 185-198, 1999.
- [24] Ganesh, E. P., Kajale, D.D., Chavan, D.N., Pawar, N.K., Ahire, P.T., Shinde, S.D., Gaikwad, V.B and Jain, G.H. "Synthesis, characterization and gas sensing performance of SnO₂ thin films prepared by spray pyrolysis". *Bulletin of material science*, 34, 1-9, 2011.
- [25] Chacko, S., Sajeeth, N., Philip and Vaidyan, V. K. "Effect of substrate temperature on structural, optical and electrical properties of spray pyrolytically grown nanocrystalline SnO₂ thin films". *Physica Status Solid .A* 204(10) 3305–3315, 2007.
- [26] Gurav A S, Kodas T T, Joutsensaari J, Kauppinen E I and Zilliacus R. *J. Mater. Res.* 10 1644, 1995.
- [27] Kodas T T and Hampden-Smith M J. "Aerosol processing of materials". (New York: Wiley-Vch) p. 421, 1999.

- [28] Baco, S., Chik, A and Tassin, F.M.D. "Study on Optical Properties of Tin Oxide Thin Films at Different Annealing Temperatures". *Journal of Science and Technology*, 61-72, 2012.
- [29] Kilic, C & Zunger, A. "Origins of coexistence of conductivity and transparency in SnO₂". *Physics Review Letters*, 88, 095501, 2002.
- [30] Yousaf, S.A and Ali, S. "The Effect of Fluorine Doping on Optoelectronic Properties of Tin-Dioxide (F: SnO₂) Thin Films". *Journal of Natural Sciences and Mathematics*, 48, 43-50, 2008.
- [31] Saipriya, M. Sultan, R. Singh. "Effect of environment and heat treatment on the optical properties of RF-sputtered SnO₂ thin films". *Physica B*: 406, 812-817, 2011.
- [32] Igwe H.U and Ugwu E.I. "Optical Characteristics of Nanocrystalline Thermal Annealed Tin Oxide (SnO₂) Thin Film samples Prepared by Chemical Bath Deposition Technique". *Journal of Advance in Applied Science Research*, 1(3), 240-246, 2010.
- [33] Sharma, A., Prakah, D and Verma, K.D. "Post annealing effect on SnO₂ thin films grown by thermal evaporation technique". *Optoelectronics and advanced materials – Rapid communications*, 1 (12), 683-688, 2007.
- [34] Odari, B.M., Mageto, M.J., Musembi, R.J., Othieno, H., Gaitho, F., and Muramba, V. "Optical and Electrical Properties of Pd Doped SnO₂ Thin Films Deposited by Spray Pyrolysis". *Australian Journal of Basic and Applied Sciences*, 7 (2): 89-98, 2013.
- [35] Alonzo-Medina, G. M., González-González, A., Sacedón, J. L and Oliva, A. I. "Understanding the thermal annealing process on metallic thin films". *In the proceedings of IOP Confrence Series: Materials Science and Engineering*, 45, 1-6, 2013.
- [36] Luangchaisri, C., Dumrongrattana, S and Rakkwamsuk, P. "Effect of heat treatment on electrical properties of fluorine doped tin dioxide films prepared by ultrasonic spray pyrolysis technique". *Procedia Engineering*, 32, 663 – 669, 2012.