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# Surface passivation effect on CO<sub>2</sub> sensitivity of spray pyrolysis deposited Pd-F: SnO<sub>2</sub> thin film gas sensor

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**Abstract:** Different thin films samples made of SnO<sub>2</sub>, F:SnO<sub>2</sub>, Pd: SnO<sub>2</sub> and and co-doped Pd-F: SnO<sub>2</sub> were deposited at a substrate temperature of 450°C using optimized doping concentrations of F and Pd, thereafter the samples were annealed and passivated in a tube furnace at 450°C. Optical and electrical methods were used in characterizing the thin film samples: The band gap energy for all samples was extracted from optical data using a proprietary software, Scout™ 98. The calculated band gap energy were found to be 4.1135eV for Pd:SnO<sub>2</sub> and 3.8014eV for F:SnO<sub>2</sub> being the highest and the lowest calculated band gap energies, respectively. The wide band gap energy has been attributed to the incorporation of Pd ions in crystal lattice of SnO<sub>2</sub> thin film for Pd:SnO<sub>2</sub> while for F:SnO<sub>2</sub> has been due to incorporation of F<sup>-</sup> ions in the crystal lattice of SnO<sub>2</sub> which gives rise to donor levels in the SnO<sub>2</sub> band gap. This causes the conduction band to lengthen resulting to a reduction in the band gap energy value. The electrical resistivity was done by measuring the sheet resistance of the SnO<sub>2</sub>, Pd:SnO<sub>2</sub>, F:SnO<sub>2</sub> and Pd-F:SnO<sub>2</sub> thin films. The undoped SnO<sub>2</sub> thin film had the highest sheet resistivity of 0.5992 Ωcm while F:SnO<sub>2</sub> had the lowest sheet resistivity of 0.0075 Ωcm. The low resistivity of F:SnO<sub>2</sub> results from substitution incorporation of F<sup>-</sup> ions in the crystal lattice of SnO<sub>2</sub> thin films, instead of O<sup>2-</sup> ions which lead to an increase in free carrier concentration. The Pd-F:SnO<sub>2</sub> gas sensor device was tested for CO<sub>2</sub> gas sensing ability using a lab assembled gas sensing unit. The performance of the gas sensor device was observed that: the as prepared device was more sensitive to CO<sub>2</sub> gas than those subjected to annealing and passivation. The decrease in the sensitivity of the annealed Pd-F: SnO<sub>2</sub> gas sensor is attributed to decrease in grain boundary potential resulting from grain growth. This causes a decrement in adsorption properties of CO<sup>-</sup> and O<sup>-</sup> species by the annealed Pd-F: SnO<sub>2</sub> thin film. The sensitivity of passivated Pd-F: SnO<sub>2</sub> gas sensor was found to be the lowest. The low sensitivity is due to the effects of nitration and decrement in grain boundary potential resulting from grain growth, nevertheless, the sensitivity of the passivated Pd-F: SnO<sub>2</sub> thin film was found to be within the range for gas sensing applications.

**Keywords:** Spray Pyrolysis, Fluorine doping, Palladium doping, co-doping, Palladium and Fluorine co-doping, Annealing, Passivation, F -co- doped Pd:SnO<sub>2</sub> (Pd-F: SnO<sub>2</sub>)

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) gas is the main component of the greenhouse gas emissions. Due to a large number of CO<sub>2</sub> gas emissions, the greenhouse effect has caused a great damage to the environment and is threatening the existence of human kind. The CO<sub>2</sub> gas is known to depress the oxygen levels in laboratories and industries. It is therefore necessary and

important to detect and determine its level of concentration [1]. To do so, thin film metal oxide semiconductor gas sensors have been designed which include TiO<sub>2</sub>, ZnO and SnO<sub>2</sub> thin films [2]. Among these, SnO<sub>2</sub> thin films are reported to have a better performance due to their desirable qualities which include: chemical inertness, mechanical hardness and high temperature resistant [3, 4]. 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 SnO<sub>2</sub> thin films can be manipulated from normal to degenerate by suitably doping SnO<sub>2</sub> with appropriate amount of noble metal (Pt, Pd), semi-metal (Sb, In, Bi) and halogens (F, Cl) [5]. Tin oxide can exist in two structures belonging to direct and indirect optical transitions, with different band gap energy; a direct band gap energy that ranges from 3.6 to 4.6 eV [6] at room temperature and indirect band gap energy of about 2.6 eV [7]. In order to improve on gas sensing properties of SnO<sub>2</sub> thin films, doping with appropriate materials is done. Doping SnO<sub>2</sub> thin films with Pd improves on their sensitivity to a number of gases [5, 8, 9]. Likewise, post deposition treatment effects e.g. annealing of SnO<sub>2</sub> thin films in air, improves on the gas sensing and optoelectronic properties of the thin films [10]. The performance of doped SnO<sub>2</sub> thin films degrades with time due to changes in the gas sensing properties of thin films resulting from corrosion of the active part of the thin film gas sensor, other factors affecting performance of gas sensor are exposure of the thin films to adverse environmental and working conditions e.g. humidity and elevated temperatures [11, 12, 13]. In order to avoid corrosion of the active part of the thin film gas sensor as well as to improve on the stability and gas sensing properties, passivation is one of the best method which improves on the longevity of the gas sensors' working lifespan. In this work, the theme was to fabricate and characterize a transparent Pd-F:SnO<sub>2</sub> thin film gas sensor, then analyze the effect of surface passivation on its CO<sub>2</sub> gas sensing ability. Spray pyrolysis technique was used to deposit the thin films. This is because the method 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 [14].

## 2. Experimental Procedure

### 2.1. Sample Preparation

The substrates 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 cleaning procedure was as follows: first the substrates were immersed in a soapy water solution and then agitated in a ultrasonic bath for 30 minutes, then 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 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, the schematic diagram is as shown in Fig 1. 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. 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°C
3	Flow rate	4 ml/min
4	Quantity of spraying solution	30 cm <sup>3</sup>
5	Nozzle to substrate distant	33 ± 3 cm

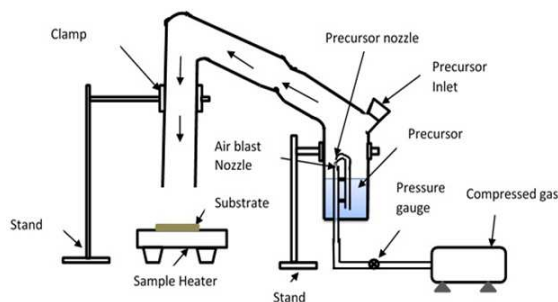


Figure 1. Spray pyrolysis experimental set up.

The undoped SnO<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub> thin films. 1.0g of ammonium fluoride (NH<sub>4</sub>F) was added to distilled water in order to make NH<sub>4</sub>F solution. NH<sub>4</sub>F solution was then added to the spraying/starting solution containing stannic chloride from 0at% to 22.74at%F and 2.7at%Pd at varying doping concentrations ranging from 0 - 19.28at%F in order to make F:SnO<sub>2</sub> and Pd-F: SnO<sub>2</sub> thin films, respectively [15].

### 2.3. 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 three pre-developed models in Scout™ 98 software. The models used were the Harmonic Oscillator model, OJL model and the Drude model. The graphs were then plotted using the Origin Pro 8.1 software.

### 2.4. 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 2.

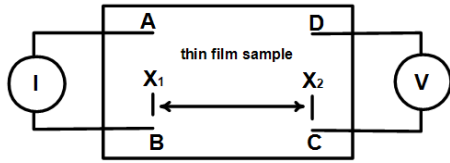


Figure 2. Schematic diagram showing the arrangement used to measure sheet resistance.

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. The values of sourced current and measured voltages were used to determine the sample resistivity. Typical probe spacing X<sub>1</sub>-X<sub>2</sub> was about 20mm.

2.5. Thin Film Annealing

Thin films were annealed in a tube furnace (schematic diagram shown in figure 3), in the presence of air at 450°C for 30 minutes. This was done in order to improve the microstructure and crystallization of the thin films. Apart from crystallization and microstructure improvement, annealing was done in order to improve on the optoelectronic and gas sensing properties of the thin films.

2.6. Thin Film Passivation

Thin films were passivated by annealing them in a nitrogen gas atmosphere for 30 minutes at 450°C in a tube furnace. This was done in order to study on the effect of surface passivation on gas sensing ability of Pd-F: SnO<sub>2</sub> thin films.

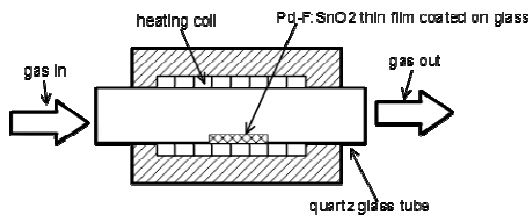


Figure 3. Horizontal tube furnace for annealing and passivation.

2.7. CO<sub>2</sub> Gas Sensitivity Test

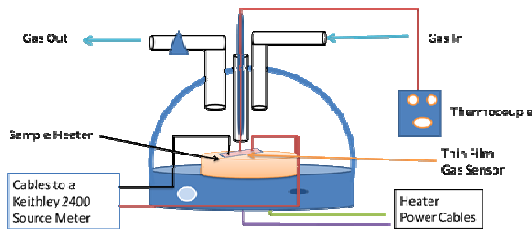


Figure 4. Lab Assembled Gas Sensing Unit

A dome shaped lab assembled gas sensing unit was used to carry out CO<sub>2</sub> gas sensitivity test using the as prepared, annealed and passivated Pd-F: SnO<sub>2</sub> thin films. A schematic diagram of the lab assembled gas sensing unit used is as shown in figure 4.

The chamber basement is metallic while the dome is made of glass. The volume of the chamber is 2.4 litres and the rating

of the heating resistant coil is 1500watts. The set up was used to measure change in resistance of the thin films on exposure to the target gas. Contacts at the end of the sample were made using silver paste and were connected to Keithley 2400 source meter for change in resistance measurement. The samples were heated using electrical resistive heating. The sample temperature was measured and controlled using a thermocouple attached to the sample. Sample resistance in air (R<sub>a</sub>) was measured at different temperatures ranging from 50°C to 250°C. A small volume of CO<sub>2</sub> gas (2000ppm) compared to the chamber volume was introduced into the chamber. The gas was allowed to diffuse in the chamber at room temperature and at 40°C for 10 minutes. The sample temperature was raised to 50°C, 100°C, 150°C, 200°C and 250°C at each sample temperature the resistance of the thin film was measured at 2000ppm of CO<sub>2</sub> gas at normal standard atmospheric pressure. The experiment was repeated for other levels of concentration of the target gas i.e. 3000ppm to 6000ppm. The electrical resistance of the sample in air (R<sub>a</sub>) and in the presence CO<sub>2</sub> gas was used to evaluate the CO<sub>2</sub> gas sensitivity. CO<sub>2</sub> gas Sensitivity S was calculated using equation 1 as done by Daniya and Nurzhan [15].

$$S = \left[ \frac{R_g - R_a}{R_a} \right] \times 100\% \quad (1)$$

CO<sub>2</sub> gas sensitivity was evaluated for as prepared, annealed and passivated Pd-F: SnO<sub>2</sub> thin films in order to determine the effect of surface passivation on the gas sensing properties of the Pd-F: SnO<sub>2</sub> thin films.

3. Results and Discussion

3.1. Analysis on Optical Properties of Doped SnO<sub>2</sub> Thin Films

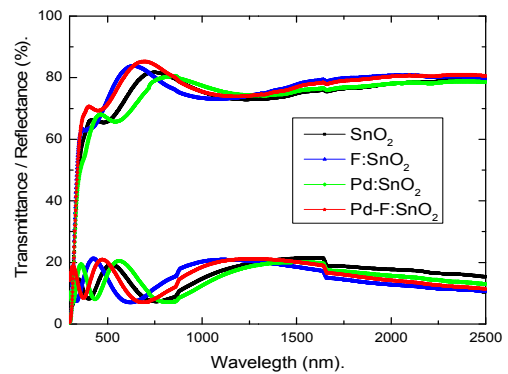


Figure 5. Transmittance and reflectance spectra for doped SnO<sub>2</sub> thin films

Figure 5 gives transmittance and reflectance spectra for as prepared and doped SnO<sub>2</sub> thin films. Each type of thin film had a different characteristics of transmittance and reflectance spectra, for example, maximum transmittance of 81.7%, 83.76%, 80.61% and 85.25% for SnO<sub>2</sub>, F:SnO<sub>2</sub>, P:SnO<sub>2</sub> and Pd-F:SnO<sub>2</sub> thin films, at wavelengths position 749nm, 639nm, 859nm and 698nm, respectively was obtained. The high transmittance results from formation of Fermi-Levels in the conduction band of the thin films [17].

A trend as a result of optimum doping of SnO<sub>2</sub> thin films with Pd and F is seen at wavelength region of 330nm to 830nm. For example doping SnO<sub>2</sub> thin films with Pd lowers the transmittance of SnO<sub>2</sub> thin films from 80.83% to 76.03% at 698 nm while at the same wavelength position, doping SnO<sub>2</sub> and Pd:SnO<sub>2</sub> with F increases the transmittance of SnO<sub>2</sub> from 80.83% to 83.85% and that of Pd:SnO<sub>2</sub> from 76.03% to 85.25%. A sharp fall in transmittance at 306 nm is due to absorption of the glass substrate [18]. In general reflectance of doped SnO<sub>2</sub> thin films was below 22% in the entire wavelength region. The visible range of the spectrum as seen from figure 5 is characterized by undulating curves with maximum and minimum points. These points are associated with interband transition where electrons from filled states at the top of valence band absorb incident photon energy almost equal to band gap energy and thus are photo-excited to empty states in the conduction band of the thin films. The energy range at which these points are attained corresponds to the band gap energy of the thin films. Photo-transitions at low energy levels are caused due to fundamental absorption. Two weird peaks at about 900nm and 1600nm occur due to change of detectors. The SolidSpec-3700DUV spectrophotometer used in this study is equipped with 3 detectors, i.e. a photomultiplier tube detector for the ultraviolet and visible regions, InGaAs and PbS detectors for near infrared region. The wavelength detection can be transitioned from photomultiplier tube detector to the InGaAs detector in any of the wavelength range from 700nm to 1000nm (the default switching wavelength is 870nm). The wavelength detection can again be transitioned from InGaAs detector to a PbS detector in any of the wavelength position from 1600nm to 1800nm (the default switching wavelength is 1650nm).

### 3.2. Effect of Annealing and Passivation on Transmittance and Reflectance of Pd-F: SnO<sub>2</sub> Thin Films

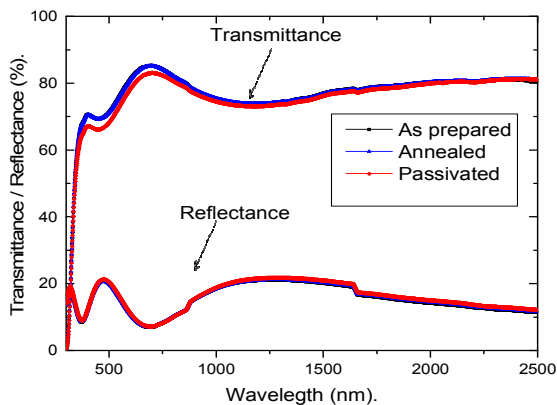


Figure 6. Transmittance and reflectance spectra for as prepared, as annealed and passivated Pd-F: SnO<sub>2</sub> thin films

In order to determine the effect of surface passivation on the optical properties of Pd-F: SnO<sub>2</sub> thin films, post deposition treatment was done on the thin films i.e. annealing and passivation. The graph shown in figure 6 compares the transmittance and reflectance of the as prepared, annealed and passivated Pd-F: SnO<sub>2</sub> thin films. There was a slight drop in

the value of transmittance of the thin films at wavelength range of 350nm to 850nm upon passivation. This means that the transparency of Pd-F:SnO<sub>2</sub> is slightly affected by its exposure to high operating temperatures.

### 3.3. Analysis on Calculated Band Gap Energy for as Prepared Doped SnO<sub>2</sub> Thin Films

Figure 7 gives calculated band gap energy for doped SnO<sub>2</sub> thin films prepared under optimized doping concentration. Calculated band gap energy for bare SnO<sub>2</sub> was 4.06564 eV. Optimum doping of SnO<sub>2</sub> with Palladium causes a widening effect on the band gap i.e. band gap for SnO<sub>2</sub> increases from 4.06564 eV to 4.1135 eV. This is ascribed to the well-known 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.*, [18].

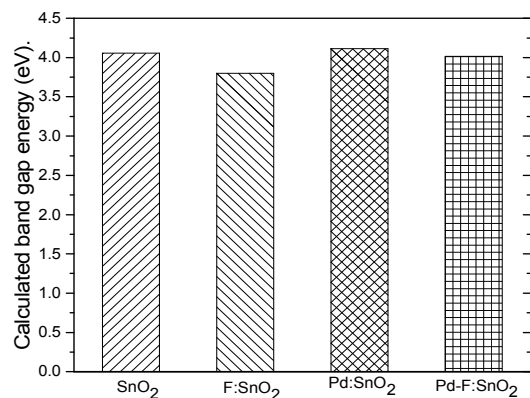


Figure 7. Calculated band gap energy for as prepared and doped SnO<sub>2</sub> thin films.

Optimum doping of SnO<sub>2</sub> and Pd: SnO<sub>2</sub> thin films with fluorine leads to a narrowing effect on the band gap. I.e. calculated band gap energy for SnO<sub>2</sub> decreases from 4.0564eV to 3.8014eV for F:SnO<sub>2</sub> while the calculated band gap energy for Pd: SnO<sub>2</sub> decreases from 4.1135 eV to 4.0143 eV for Pd-F:SnO<sub>2</sub>. The decrease in the calculated band gap energy value is due to incorporation of F<sup>-</sup> ions in the crystal lattice, which gives rise to donor levels in the SnO<sub>2</sub> and Pd: SnO<sub>2</sub> band gap. This causes the conduction band to lengthen leading to a reduction in the band gap value [20].

### 3.4. Analysis on Sheet Resistivity of as a Prepared Doped SnO<sub>2</sub> Thin Films

Figure 8 gives sheet resistivity of SnO<sub>2</sub> based thin films prepared under optimized doping concentrations. Sheet resistivity of 0.5992 Ωcm was recorded for bare SnO<sub>2</sub> thin films. This low sheet resistivity can be attributed to deviation from stoichiometry due to creation of oxygen vacancies which act like electron donors and increase free carrier concentration [7]. From figure 8, the sheet resistivity of SnO<sub>2</sub> thin film is seen to decrease significantly when SnO<sub>2</sub> is



doped with palladium at optimum condition (2.7at%Pd) from 0.5992 Ωcm to 0.0271 Ωcm. The decrease in the resistivity is due to the presence of Pd ions in the crystal lattice of SnO<sub>2</sub> thin films [21]. When SnO<sub>2</sub> and Pd:SnO<sub>2</sub> is doped with an optimum concentration of F, the resistivity of SnO<sub>2</sub> decreases from 0.5992 Ωcm to 0.00075Ωcm and that of Pd:SnO<sub>2</sub> decreases from 0.0271Ωcm to 0.000164Ωcm. The decrease in sheet resistivity is due to substitutional incorporation of F<sup>-</sup> ions in the crystal lattice of SnO<sub>2</sub> thin films, instead of O<sup>-</sup> ions which lead to an increase in free carrier concentration [21].

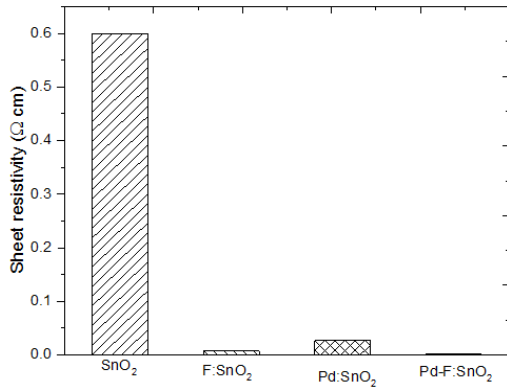


Figure 8. Sheet resistivity characteristics of SnO<sub>2</sub>, F:SnO<sub>2</sub>, Pd:SnO<sub>2</sub> and Pd-F:SnO<sub>2</sub> thin films

### 3.5. CO<sub>2</sub> Gas Sensitivity

CO<sub>2</sub> is an oxidizing gas and the gas sensing mechanism involves its disintegration into CO<sup>-</sup> and O<sup>-</sup> species. These species are adsorbed on the surface of the thin film. This process withdraws electrons from the conduction band of the thin film, leading to an increase in the resistivity of the thin film. Figure 9 shows the CO<sub>2</sub> gas sensing mechanism [22].

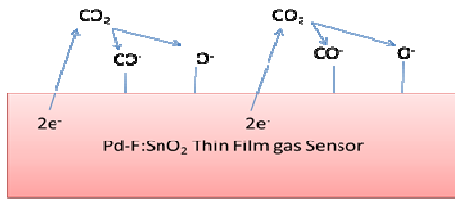


Figure 9. Desegregation of CO<sub>2</sub> in CO<sup>-</sup> and O<sup>-</sup> species.

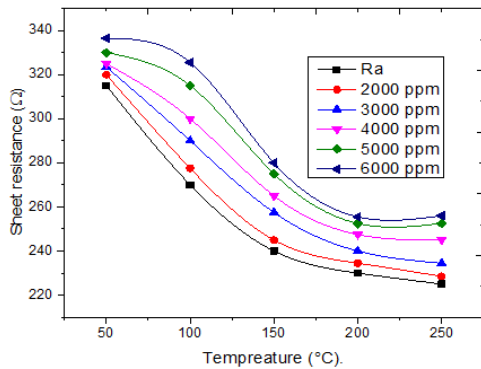


Figure 10. Sheet resistance versus temperature for the as prepared Pd-F:SnO<sub>2</sub> thin films.

Figure 10 shows the gas sensing characteristics of as prepared Pd-F: SnO<sub>2</sub> gas sensor. Two parameters were monitored during this process that is CO<sub>2</sub> gas concentration in parts per million and temperature. The results show CO<sub>2</sub> gas at different level of concentration ranging 2000ppm – 6000ppm, as well as sheet resistance measurements recorded at different temperature from 50°C to 250°C. The sheet resistance was highest at 50°C and gradually decreased to the lowest level at 250°C. The sheet resistance was recorded highest for all temperature level for CO<sub>2</sub> gas concentration of about 6000ppm and was lowest for all temperature level in the absence of CO<sub>2</sub> gas. At 100<sup>0</sup>C, change in sheet resistance for the as prepared Pd-F: SnO<sub>2</sub> thin films is more pronounced and slightly pronounced at 150<sup>0</sup>C. Saturation effects and decrease in adsorption rate start dominating at higher temperatures > 100<sup>0</sup>C [23, 24].

Similar results to those of as prepared Pd-F: SnO<sub>2</sub> gas sensor were observed for annealed Pd-F: SnO<sub>2</sub> thin film as seen in figure 11. Decrease in adsorption rate and saturation effects are more dominant at higher temperatures > 150<sup>0</sup>C. This is attributed to change in grain size of the thin films as a result of increase in the operating temperature of the thin film gas sensor [23, 24].

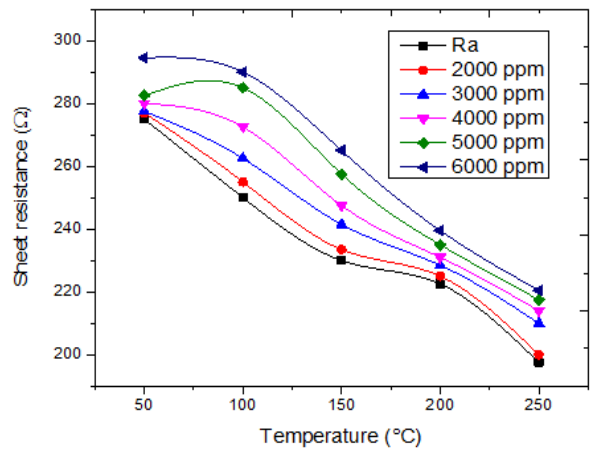


Figure 11. Sheet resistance versus temperature for the as annealed Pd-F:SnO<sub>2</sub> thin film.

For the passivated Pd-F: SnO<sub>2</sub> gas sensor as seen in figure 12, similar results to those of as prepared and annealed Pd-F: SnO<sub>2</sub> gas sensors were observed. However, the change in sheet resistance due to increase in concentration of CO<sub>2</sub> gas (ppm) was the lowest for the passivated Pd-F:SnO<sub>2</sub> gas sensor as compared to that of as prepared and annealed Pd-F:SnO<sub>2</sub> gas sensors. This is due to decrease in CO<sup>-</sup> ions and O<sup>-</sup> ions adsorption properties of the Pd-F: SnO<sub>2</sub> gas sensor resulting from its passivation. The decrease in adsorption properties of Pd-F:SnO<sub>2</sub> thin film gas sensor are ascribed to modification of surface states and nitration effects resulting from annealing of the Pd-F: SnO<sub>2</sub> gas sensor in an oxygen deficient atmosphere (nitrogen).

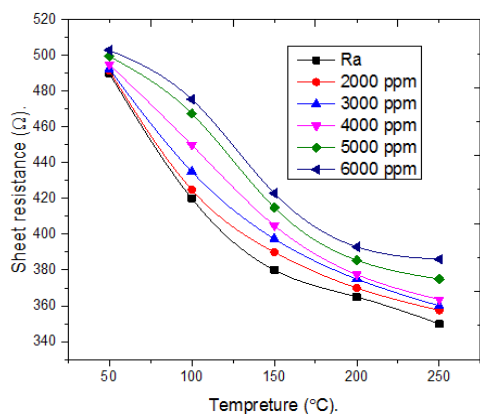


Figure 12. Sheet resistance versus temperature for the passivated Pd-F: SnO<sub>2</sub> thin film.

Figure 13 gives a comparison on the sensitivity of the as prepared, annealed and passivated Pd and F co-doped SnO<sub>2</sub> thin films. The sheet resistance of the sample in air ( $R_a$ ) and in the presence CO<sub>2</sub> gas at 100°C was used to evaluate the CO<sub>2</sub> gas sensitivity. CO<sub>2</sub> gas Sensitivity, S was calculated using equation 1.

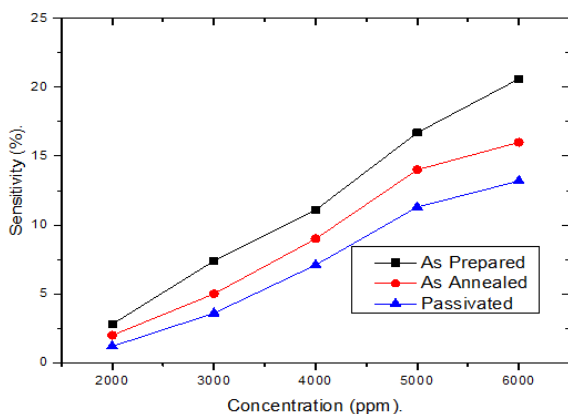


Figure 13. Sensitivity versus CO<sub>2</sub> concentration (ppm).

CO<sub>2</sub> gas sensitivity was evaluated for as prepared, annealed and passivated Pd-F: SnO<sub>2</sub> thin films in order to determine the effect of surface passivation on the gas sensing ability of Pd-F: SnO<sub>2</sub> thin films. The annealed Pd-F: SnO<sub>2</sub> thin films had low sensitivity towards CO<sub>2</sub> gas as compared to the as prepared thin films. This is attributed to improved microstructure of the thin films as a result of annealing the samples in air. Annealing of the thin films in air results in grain growth which reduces the grain boundary potential of the thin films [25, 26]. This leads to decrease in the adsorption properties of the annealed thin films towards CO<sub>2</sub> gas. The passivated thin films had the lowest sensitivity as compared to the as prepared and as annealed thin films but the sensitivity was within the range for gas sensing applications. The low sensitivity of the passivated samples can be attributed to the improved microstructure of the thin films as a result of annealing the samples in an oxygen deficient atmosphere (nitrogen), modification of surface states upon passivation [26] and effects of nitration.

## 4. Conclusions

The SnO<sub>2</sub> thin films have been found to have resistivity of about 0.5992 Ωcm, this low resistivity has been attributed to deviation from stoichiometry and creation of oxygen vacancies. On doping the SnO<sub>2</sub> with palladium, the electrical resistivity of Pd:SnO<sub>2</sub> has been observed to decrease due to the presence of Pd ions into the crystal lattice which contributes more electron ions into the lattice increasing electron carriers. Doping SnO<sub>2</sub> and Pd:SnO<sub>2</sub> with optimum concentration of F decreased their sheet resistivity to 0.00075Ωcm and 0.000164 Ωcm for resulting thin films i.e. F:SnO<sub>2</sub> and Pd-F:SnO<sub>2</sub> respectively. The decrease in sheet resistivity is due to substitutional incorporation of F<sup>-</sup> ions in the crystal lattice of SnO<sub>2</sub> thin films instead of O<sup>-</sup> ions which lead to an increase in free carrier concentration. The calculated band gap energy for undoped SnO<sub>2</sub> was 4.0564eV which increased to 4.1135eV due optimum Pd doping. The increase in calculated band gap energy value is attributed to the well-known Burstein Moss effect. On doping SnO<sub>2</sub> and Pd:SnO<sub>2</sub> with F the calculated band gap energy decreased to 3.8014eV and 4.0143eV for resulting thin films i.e. F:SnO<sub>2</sub> and Pd-F:SnO<sub>2</sub> respectively. The performance of the gas sensor device has been observed that the as prepared device was more sensitive to CO<sub>2</sub> gas than those subjected to annealing and passivation. The decrease in the sensitivity of the annealed Pd-F: SnO<sub>2</sub> gas sensor is attributed to decrease in grain boundary potential as a result of grain growth. This causes a decrement in adsorption properties of CO<sup>-</sup> and O<sup>-</sup> species by the annealed Pd-F: SnO<sub>2</sub> thin film. The sensitivity of passivated Pd-F: SnO<sub>2</sub> gas sensor was found to be the lowest. The low sensitivity is ascribed to effects of nitration and decrement in grain boundary potential resulting from grain growth, nonetheless, the sensitivity of the passivated Pd-F: SnO<sub>2</sub> thin film was found to be within the range for gas sensing applications.

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## References

- [1] Sun, B., Guangzhong, X., Jiang, Y and Xian, L. Comparative CO<sub>2</sub>-Sensing Characteristic Studies of Starch Thin Film Sensors. *Journal of Energy Procedia*, vol 12, pp 726 – 732, 2011.
- [2] Bochenkov, V. E and Sergeev, G. B. Preparation and chemiresistive properties of nanostructured materials. *Advances in Colloid and Interface Science, Russia*, vol 116, pp 245-254, 2005.

- [3] 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.
- [4] 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.
- [5] Subramanian, N.S, Santhi, B, Sundareswaran, S, Venkatakrishnan, K.S. "Studies on Spray Deposited SnO<sub>2</sub>, Pd:SnO<sub>2</sub> and F:SnO<sub>2</sub> Thin Films for Gas Sensor Applications", *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, vol 36, pp 131-135, 2006.
- [6] 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.
- [7] Mohammad, T.M. "Performance and characteristics of Al-PbS/SnO<sub>2</sub>: F selective coating system for photothermal energy conversion". *Solar Energy Mater.* Vol 20, pp 297-305, 1990.
- [8] Boshta, M., Mahmud, A. and Sayed, M. H. Characterization of sprayed SnO<sub>2</sub>: Pd thin films for gas sensing applications. *Journal of Ovonic Research*, vol 6, pp 93 – 98, 2010.
- [9] Odari, B.V., Mageto, M., Musembi, R., Othieno, H., Gaithe, F., and Muramba, V. "Optical and Electrical Properties of Pd Doped SnO<sub>2</sub> Thin Films Deposited by Spray Pyrolysis". *Australian Journal of Basic and applied Sciences*, vol 7(2), pp 89-98, 2013.
- [10] 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.
- [11] 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.
- [12] Miller, T.A., Bakrania, S.D., Perez, C and Woodriddle. *Nanostructured Tin Dioxide Materials for Gas Sensor Applications*. American Scientific Publishers, Michigan 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] Jebbari, N., Kamoun, N and Bennaceur, R. "Effect of SnCl<sub>4</sub> concentration on F: SnO<sub>2</sub>, deposited by chemical spray pyrolysis". *In the proceedings of International Renewable Energy Congress*, Sousse, Tunisia, vol 2, pp 276-279, 2010.
- [15] 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:SnO<sub>2</sub>. *International Journal of Materials Science and Applications*. Vol. 3, No. 5, pp 137-142, 2014.
- [16] Daniya M. Mukhamedshina and Nurzhan B. Beisenkhanov *Influence of Crystallization on the Properties of SnO<sub>2</sub> Thin Films, Advances in Crystallization Processes*, Dr. Yitzhak Mastai (Ed.), InTech Europe, pp 221-258, 2012.
- [17] 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.
- [18] Sandipan R, Gupta P.S. and Gurdeep S. "Electrical and Optical properties of sol-gel prepared Pd-doped SnO<sub>2</sub> 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.
- [19] Sa'nchez-Garcia, M., Maldonado, Castaneda, L., Silva-Gonzalez, R and Olvera, M.L. Characterization of SnO<sub>2</sub>: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.
- [20] Moure- Flores, F., Guillen – Gervantes, A., Nieto-Zapeda, K.E., Quinones- Galvan, JG., Hernandez- Hernandez. A., Olvera, M.G and Melendez- Lira, M. "SnO<sub>2</sub> Thin Films Deposited by RF Magnetron Sputtering: Effect of the SnF<sub>2</sub> Amount in the Target on the Physical Properties". *Revista Mexicana de Fisica*, vol 59, pp 335-338, 2013.
- [21] Yousaf, S.A and Ali, S. "The Effect of Fluorine Doping on Optoelectronic Properties of Tin-Dioxide (F:SnO<sub>2</sub>) Thin Films". *Journal of Natural Sciences and Mathematics*, vol 48, pp 43-50, 2008.
- [22] Edgar Sotter. Development of a Thick Film Gas Sensor for Oxygen Detection at Trace Levels, PhD thesis, Xavier Vilanova, Tarragona Spain, 2006.
- [23] Batzill, M and Diebold U. The surface and materials science of tin oxide. *Progress in Surface Science*, vol 79, pp 47–154, 2005.
- [24] 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.
- [25] Desale, J.D., Shaikh, S., Siddique, F., Ghosh, A., Birajdar, R., Ghale, A and Sharma, R. Effect of Annealing on Structural and Optoelectronic Properties of Cds Thin Films Prepared by SILAR Method. *Advances in Applied Research*, vol 2, pp 417-425, 2011.
- [26] Simoñes, A.Z., Riccardi, C.S., Dos Santos, M.L., Gonza' lez Garcia, F., Longo E and Varela J.A. Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films. *Materials Research Bulletin*, vol 44, pp 1747–1752, 2009.