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Surface passivation effect on CO_2 sensitivity of spray pyrolysis deposited Pd-F: SnO_2 thin film gas sensor

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Abstract: Different thin films samples made of SnO_2, F:SnO_2, Pd: SnO_2 and and co-doped Pd-F: SnO_2 were deposited at a substrate temperature of 450^{o}C using optimized doping concentrations of F and Pd, thereafter the samples were annealed and passivated in a tube furnace at 450^{o}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_2 and 3.8014eV for F:SnO_2 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_2 thin film for Pd:SnO_2 while for F:SnO_2 has been due to incorporation of F^- ions in the crystal lattice of SnO_2 which gives rise to donor levels in the SnO_2 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_2, Pd:SnO_2, F:SnO_2 and Pd-F:SnO_2 thin films. The undoped SnO_2 thin film had the highest sheet resistivity of 0.5992 Ωcm while F:SnO_2 had the lowest sheet resistivity of 0.0075 Ωcm. The low resistivity of F:SnO_2 results from substitution incorporation of F^- ions in the crystal lattice of SnO_2 thin films, instead of O^- ions which lead to an increase in free carrier concentration. The Pd-F:SnO_2 gas sensor device was tested for CO_2 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_2 gas than those subjected to annealing and passivation. The decrease in the sensitivity of the annealed Pd-F: SnO_2 gas sensor is attributed to decrease in grain boundary potential resulting from grain growth. This causes a decrement in adsorption properties of CO^- and O^- species by the annealed Pd-F: SnO_2 thin film. The sensitivity of passivated Pd-F: SnO_2 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_2 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_2 (Pd-F: SnO_2)

1. Introduction

Carbon dioxide (CO_2) gas is the main component of the greenhouse gas emissions. Due to a large number of CO_2 gas emissions, the greenhouse effect has caused a great damage to the environment and is threatening the existence of human kind. The CO_2 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_2, ZnO and SnO_2 thin films [2]. Among these, SnO_2 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_2 thin films can be manipulated from normal to degenerate by suitably doping SnO_2 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_2 thin films, doping with appropriate materials is done. Doping SnO_2 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_2 thin films in air, improves on the gas sensing and optoelectronic properties of the thin films [10]. The performance of doped SnO_2 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_2 thin film gas sensor, then analyze the effect of surface passivation on its CO_2 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^{o}C
3	Flow rate	4 ml/min
4	Quantity of spraying solution	30 cm^3
5	Nozzle to substrate distant	33 ± 3 cm

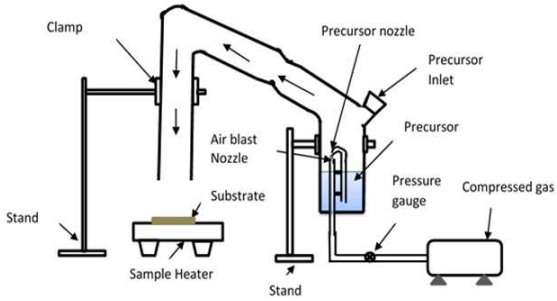

Figure 1. *Spray pyrolysis experimental set up.*

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 (NH4F) was added to distilled water in order to make NH4F solution. NH4F 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_2 and Pd-F: SnO_2 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^{0}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.

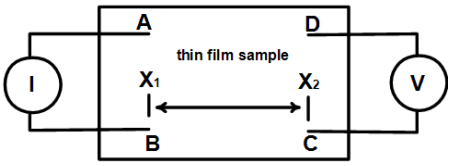

Figure 2. *Schematic diagram showing the arrangement used to measure sheet resistance.*

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_1-X_2 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^{0}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^{0}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_2 thin films.

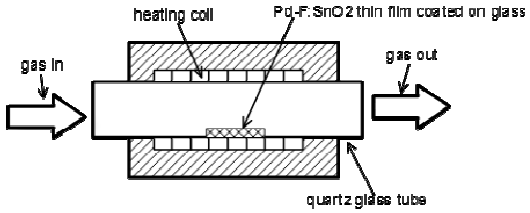

Figure 3. *Horizontal tube furnace for annealing and passivation.*

2.7. CO_2 Gas Sensitivity Test

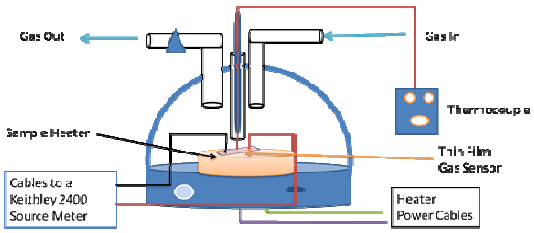

Figure 4. *Lab Assembled Gas Sensing Unit*

A dome shaped lab assembled gas sensing unit was used to carry out CO_2 gas sensitivity test using the as prepared, annealed and passivated Pd-F: SnO_2 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_a) was measured at different temperatures ranging from 50^{0}C to 250^{0}C. A small volume of CO_2 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^{0}C for 10 minutes. The sample temperature was raised to 50^{0}C, 100^{0}C, 150^{0}C, 200^{0}C and 250^{0}C at each sample temperature the resistance of the thin film was measured at 2000ppm of CO_2 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_a) and in the presence CO_2 gas was used to evaluate the CO_2 gas sensitivity. CO_2 gas Sensitivity S was calculated using equation 1 as done by Daniya and Nurzhan [15].

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

CO_2 gas sensitivity was evaluated for as prepared, annealed and passivated Pd-F: SnO_2 thin films in order to determine the effect of surface passivation on the gas sensing properties of the Pd-F: SnO_2 thin films.

3. Results and Discussion

3.1. Analysis on Optical Properties of Doped SnO_2 Thin Films

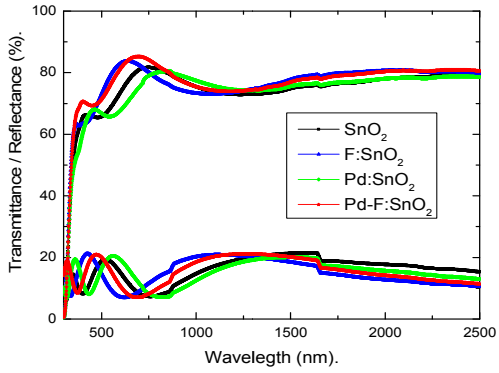

Figure 5. *Transmittance and reflectance spectra for doped SnO_2 thin films*

Figure 5 gives transmittance and reflectance spectra for as prepared and doped SnO_2 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_2 , F:SnO_2, P:SnO_2 and Pd-F:SnO_2 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_2 thin films with Pd and F is seen at wavelength region of 330nm to 830nm. For example doping SnO_2 thin films with Pd lowers the transmittance of SnO_2 thin films from 80.83% to 76.03% at 698 nm while at the same wavelength position, doping SnO_2 and Pd:SnO_2 with F increases the transmittance of SnO_2 from 80.83% to 83.85% and that of Pd:SnO_2 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_2 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_2 Thin Films

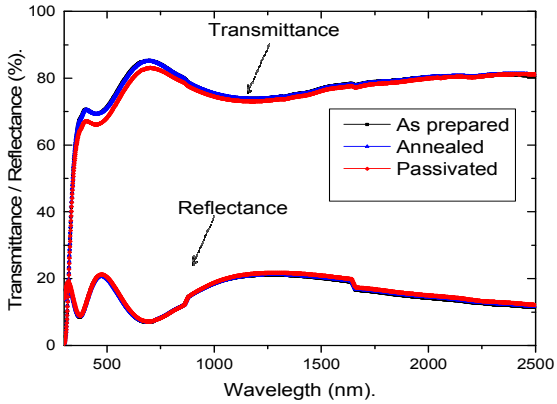

Figure 6. *Transmittance and reflectance spectra for as prepared, as annealed and passivated Pd-F: SnO_2 thin films*

In order to determine the effect of surface passivation on the optical properties of Pd-F: SnO_2 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_2 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_2 is slightly affected by its exposure to high operating temperatures.

3.3. Analysis on Calculated Band Gap Energy for as Prepared Doped SnO_2 Thin Films

Figure 7 gives calculated band gap energy for doped SnO_2 thin films prepared under optimized doping concentration. Calculated band gap energy for bare SnO_2 was 4.06564 eV. Optimum doping of SnO_2 with Palladium causes a widening effect on the band gap i.e. band gap for SnO_2 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].

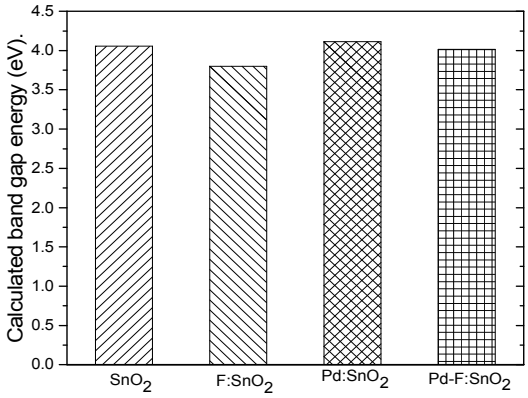

Figure 7. *Calculated band gap energy for as prepared and doped SnO_2 thin films.*

Optimum doping of SnO_2 and Pd: SnO_2 thin films with fluorine leads to a narrowing effect on the band gap. I.e. calculated band gap energy for SnO_2 decreases from 4.0564eV to 3.8014eV for F:SnO_2 while the calculated band gap energy for Pd: SnO_2 decreases from 4.1135 eV to 4.0143 eV for Pd-F:SnO_2. The decrease in the calculated band gap energy value is due to incorporation of F^- ions in the crystal lattice, which gives rise to donor levels in the SnO_2 and Pd: SnO_2 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_2 Thin Films

Figure 8 gives sheet resistivity of SnO_2 based thin films prepared under optimized doping concentrations. Sheet resistivity of 0.5992 Ωcm was recorded for bare SnO_2 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_2 thin film is seen to decrease significantly when SnO_2 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_2 thin films [21]. When SnO_2 and Pd:SnO_2 is doped with an optimum concentration of F, the resistivity of SnO_2 decreases from 0.5992 Ωcm to 0.00075Ωcm and that of Pd:SnO_2 decreases from 0.0271Ωcm to 0.000164Ωcm. The decrease in sheet resistivity is due to substitutional incorporation of F^- ions in the crystal lattice of SnO_2 thin films, instead of O^- ions which lead to an increase in free carrier concentration [21].

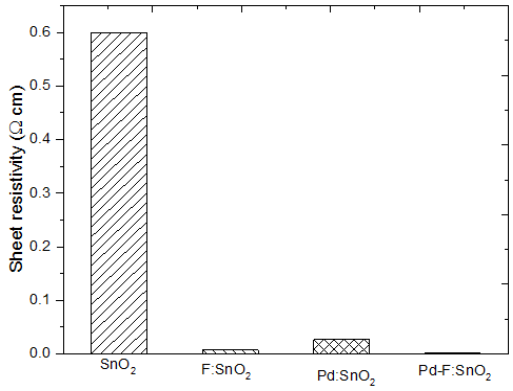

Figure 8. *Sheet resistivity characteristics of SnO_2, $F:SnO_2$, $Pd:SnO_2$ and $Pd\text{-}F:SnO_2$ thin films*

3.5. CO_2 Gas Sensitivity

CO_2 is an oxidizing gas and the gas sensing mechanism involves its disintegration into CO^- and O^- 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_2 gas sensing mechanism [22].

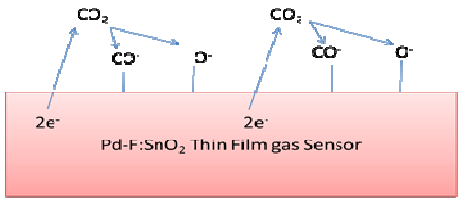

Figure 9. *Desegregation of CO_2 in CO^- and O^- species.*

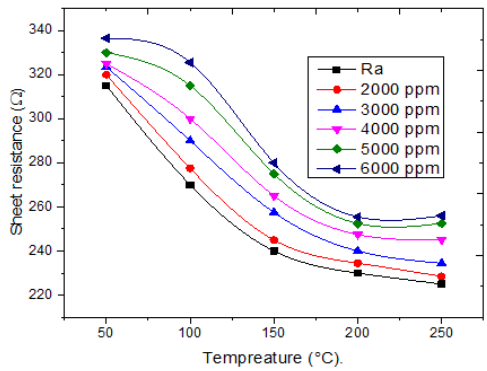

Figure 10. *Sheet resistance versus temperature for the as prepared Pd-F: SnO_2 thin films.*

Figure 10 shows the gas sensing characteristics of as prepared Pd-F: SnO_2 gas sensor. Two parameters were monitored during this process that is CO_2 gas concentration in parts per million and temperature. The results show CO_2 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_2 gas concentration of about 6000ppm and was lowest for all temperature level in the absence of CO_2 gas. At 100^0C, change in sheet resistance for the as prepared Pd-F: SnO_2 thin films is more pronounced and slightly pronounced at 150^0C. Saturation effects and decrease in adsorption rate start dominating at higher temperatures > 100^0C [23, 24].

Similar results to those of as prepared Pd-F: SnO_2 gas sensor were observed for annealed Pd-F: SnO_2 thin film as seen in figure 11. Decrease in adsorption rate and saturation effects are more dominant at higher temperatures > 150^0C. 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].

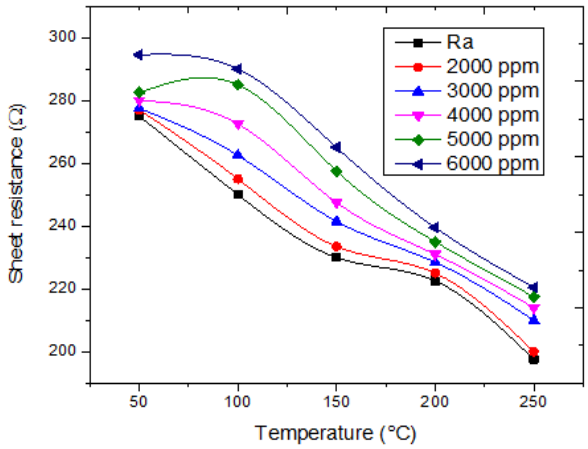

Figure 11. *Sheet resistance versus temperature for the as annealed Pd-F:SnO_2 thin film.*

For the passivated Pd-F: SnO_2 gas sensor as seen in figure 12, similar results to those of as prepared and annealed Pd-F: SnO_2 gas sensors were observed. However, the change in sheet resistance due to increase in concentration of CO_2 gas (ppm) was the lowest for the passivated Pd-F:SnO_2 gas sensor as compared to that of as prepared and annealed Pd-F:SnO_2 gas sensors. This is due to decrease in CO^- ions and O^- ions adsorption properties of the Pd-F: SnO_2 gas sensor resulting from its passivation. The decrease in adsorption properties of Pd-F:SnO_2 thin film gas sensor are ascribed to modification of surface states and nitration effects resulting from annealing of the Pd-F: SnO_2 gas sensor in an oxygen deficient atmosphere (nitrogen).

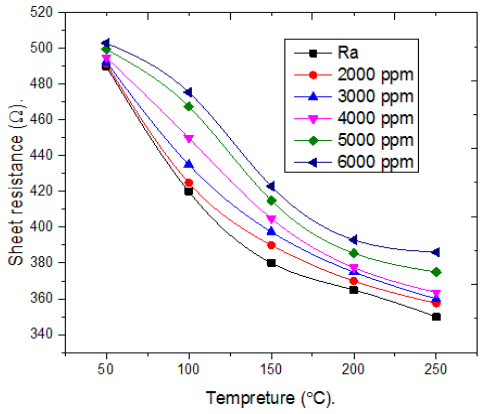

Figure 12. *Sheet resistance versus temperature for the passivated Pd-F: SnO_2 thin film.*

Figure 13 gives a comparison on the sensitivity of the as prepared, annealed and passivated Pd and F co-doped SnO_2 thin films. The sheet resistance of the sample in air (R_a) and in the presence CO_2 gas at 100^0C was used to evaluate the CO_2 gas sensitivity. CO_2 gas Sensitivity, S was calculated using equation 1.

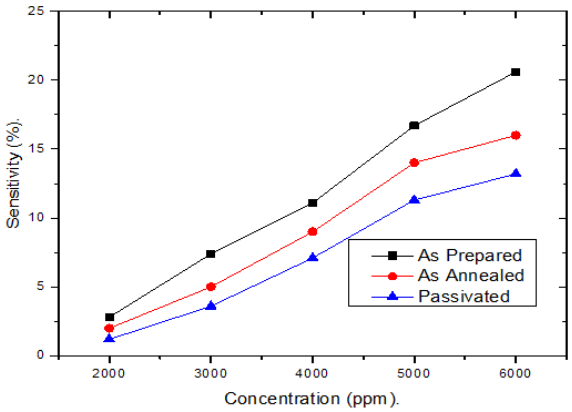

Figure 13. *Sensitivity versus CO_2 concentration (ppm).*

CO_2 gas sensitivity was evaluated for as prepared, annealed and passivated Pd-F: SnO_2 thin films in order to determine the effect of surface passivation on the gas sensing ability of Pd-F: SnO_2 thin films. The annealed Pd-F: SnO_2 thin films had low sensitivity towards CO_2 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_2 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_2 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_2 with palladium, the electrical resistivity of Pd:SnO_2 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_2 and Pd:SnO_2 with optimum concentration of F decreased their sheet resistivity to 0.00075Ωcm and 0.000164 Ωcm for resulting thin films i.e. F:SnO_2 and Pd-F:SnO_2 respectively. The decrease in sheet resistivity is due to substitutional incorporation of F^- ions in the crystal lattice of SnO_2 thin films instead of O^- ions which lead to an increase in free carrier concentration. The calculated band gap energy for undoped SnO_2 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_2 and Pd:SnO_2 with F the calculated band gap energy decreased to 3.8014eV and 4.0143eV for resulting thin films i.e. F:SnO_2 and Pd-F:SnO_2 respectively. The performance of the gas sensor device has been observed that the as prepared device was more sensitive to CO_2 gas than those subjected to annealing and passivation. The decrease in the sensitivity of the annealed Pd-F: SnO_2 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^- and O^- species by the annealed Pd-F: SnO_2 thin film. The sensitivity of passivated Pd-F: SnO_2 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_2 thin film was found to be within the range for gas sensing applications.

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