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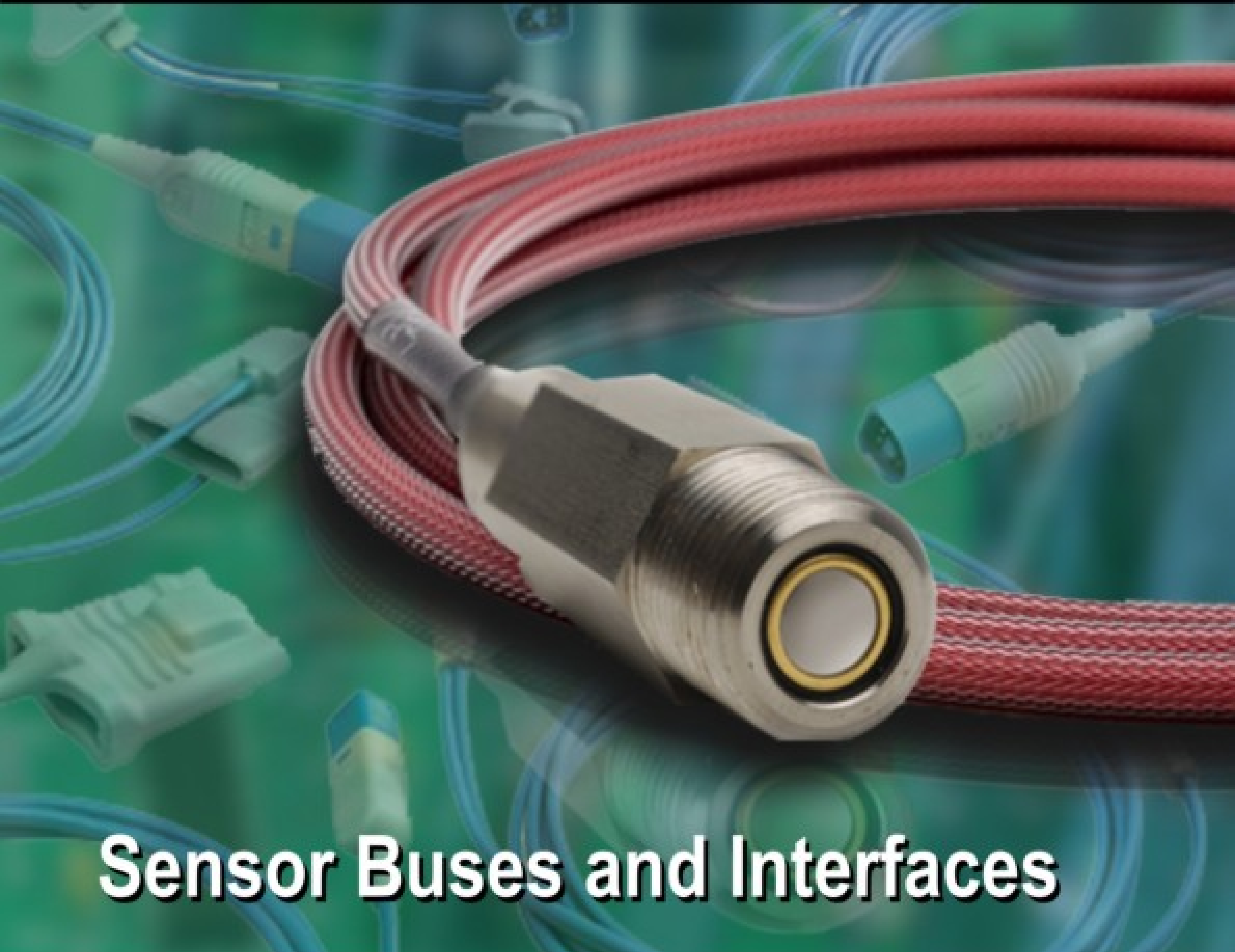

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Gas Sensing of Fluorine Doped Tin Oxide Thin Films Prepared by Spray Pyrolysis

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Abstract: Fluorine doped tin oxide (F: SnO_2) films have been prepared onto the amorphous glass substrates by a spray pyrolysis. XRD studies reveal that the material deposited is polycrystalline SnO_2 and have tetragonal structure. It is observed that films are highly orientated along (200) direction. The direct optical band gap energy for the F: SnO_2 films are found to be 4.15 eV. Gas sensing properties of the sensor were checked against combustible gases like H_2, CO_2 CO, C_3H_8, CH_4.The H_2 sensitivity of the F-doped SnO_2 sensor was found to be increased. The increase in the sensitivity is discussed in terms of increased resistivity and reduced permeation of gaseous oxygen into the underlying sensing layer due to the surface modification of the sensor. *Copyright © 2008 IFSA.*

Keywords: Fluorine doped tin oxide, XRD, Band gap energy, Sensor

1. Introduction

Transparent electrically conductive materials with high optical transmittance and low electrical resistivity are key elements for gas sensors, thin film solar cells and display devices. Amongst them, transparent conductive oxides (TCO), based on high bandgap, degenerate semiconductors, are mechanically hard and can withstand high temperature. They can be used as window layers in heterojunction photovoltaic cells [1], gas sensors [2], substrates for electrodeposition [3, 4], transparent contacts in photovoltaic and optoelectronic devices or as special coatings [5, 6, 7, 8]. Literature survey reveals that SnO_2 is a promising material, used in different gas sensors. The reaction of SnO_2 in air with different test gases is relatively extensively studied. Generally CO, CH_4 and NO_x are the most used gases to characterize the performance of sensor, because of their different sensing mechanisms [9]. CO and CH_4 introduce electrons in the conduction band (decrease sensor resistance) by reacting with the SnO_2 surface, whereas NO_x removes electrons and increase sensor resistance [10].

In the present investigation, F:SnO_2 films were deposited at optimized substrate temperature by spray pyrolysis, using an aqueous/organic solvent (water/ propan-2-ol) mixture for the first time in order to see the effect of having a large proportion of water in the spraying solution. The various properties like crystal structure, surface morphology, optical transmittance and gas sensing were studied and results obtained are compared and discussed.

2. Experimental

Stannic chloride, ammonium fluoride, oxalic acid, and solvents were obtained from Loba Chemie, Mumbai. Doubly distilled water was used throughout. To 100 ml of 2 M stannic chloride and 3.785 M ammonium fluoride, 24 ml of 0.01 M oxalic acid were added (it has been observed that the optical transmission of SnO_2 films could be increased by the addition of acid to the spray solution [11]. The final spraying solution was made up by mixing 10 ml of this solution with 10 ml of propan-2-ol. The resulting concentrations of various ingredients in the spraying solution (20 ml) were: 0.806 M $SnCl_4$, 1.527 M NH_4F. The 1.5 mm thick glass plates (2.4 x 7.4 cm), obtained from Blue Star Polar Industrial Corporation, Mumbai and quartz plates were used as substrates. Prior to deposition, the substrates were degreased with trichloroethylene, followed by rinsing with acetone, ethanol and water. Spray pyrolysis involved the spraying of a precursor solution through a pneumatic nozzle onto a substrate located on a temperature controlled heating plate. The apparatus has been described elsewhere in detail [12]. For film formation, the solution (10 ml of aqueous stock solution plus 10 ml propan-2-ol) was sprayed onto the substrates positioned horizontally on the temperature controlled heating plate at optimized substrate temperature 475 ^oC. The fixed parameters were: ($SnCl_4 \cdot 5\ H_2O$): 0.806 M, (NH_4F): 1.527 M, ($(COOH)_2$): 0.96 mM, spray rate: 5 ml/min, quantity of the spraying solution: 20 ml.

3. Results and Discussion

3.1. XRD Analysis

The as-grown film is characterized by XRD using Cu-K_α radiation. The XRD patterns obtained for the film grown on glass substrates is studied in the 2θ range of 20° to 100^o. Fig. 1 depicts the XRD pattern of F: SnO_2 film deposited at substrate temperature of 475^{o}C and shows that the material is polycrystalline and highly oriented along the (200) plane. The matching of the observed and the standard *d*-values is confirms that the deposited films are of SnO_2 with tetragonal structure (Powder Diffraction File Alphabetic PDF-2 Data Base, file 41-1445). The crystallite size estimated from diffraction line broadening by using Scherrer's formula [13] is found to be 180 nm.

3.2. Scanning Electron Microscopy (SEM) Studies

The surface morphology of the F: SnO_2 film deposited at 475 ^{o}C was studied by SEM. The micrographs of film at three different magnifications (25,000x, 55,000x and 1, 00,000x) are shown in Fig. 2. The micrograph at 25,000x (Fig. 2(a)) shows that the film is continuous with the continuous distribution of grains. At 55,000x and 1, 00,000 magnifications (Fig. 2 (b) and (c)), it shows that the sample has grains with different size whereas intergranular regions appear dark. The fine grains cover the entire surface of the substrate. The observed grain size from SEM studies is of the order of 200 nm.

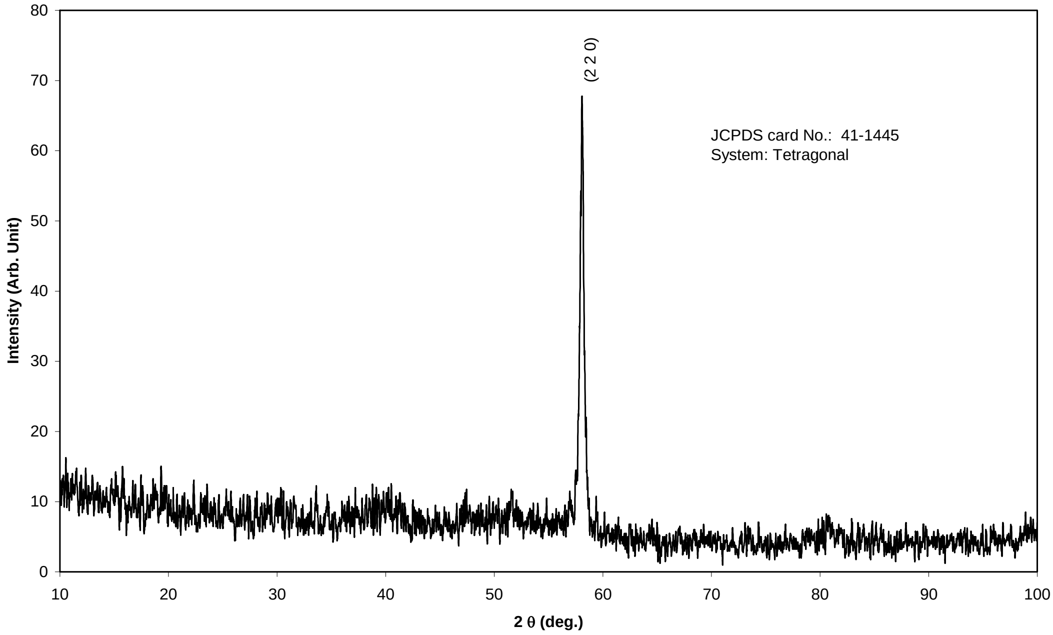
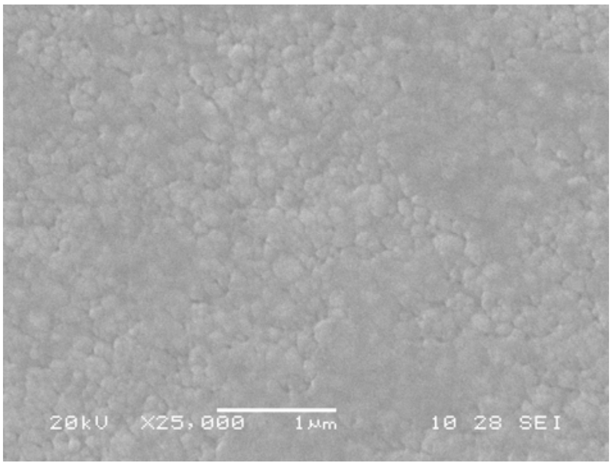
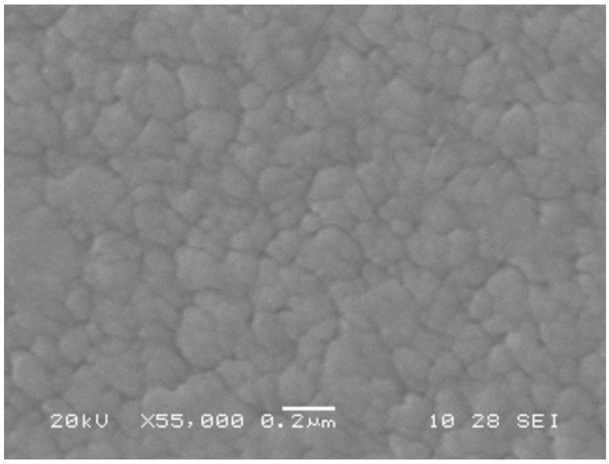


Fig.1. XRD pattern of the F: SnO_2 thin film deposited at 475^oC.



(a)



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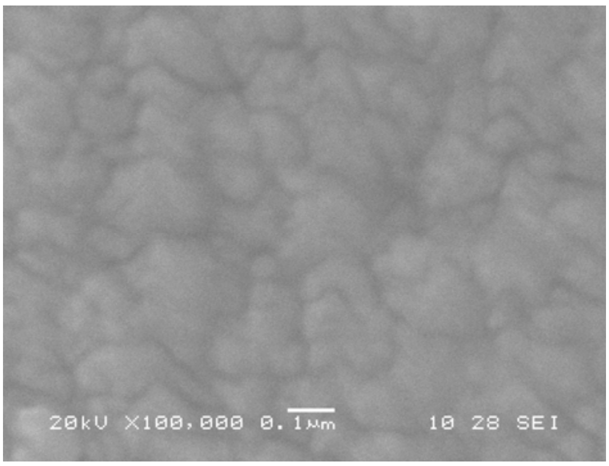
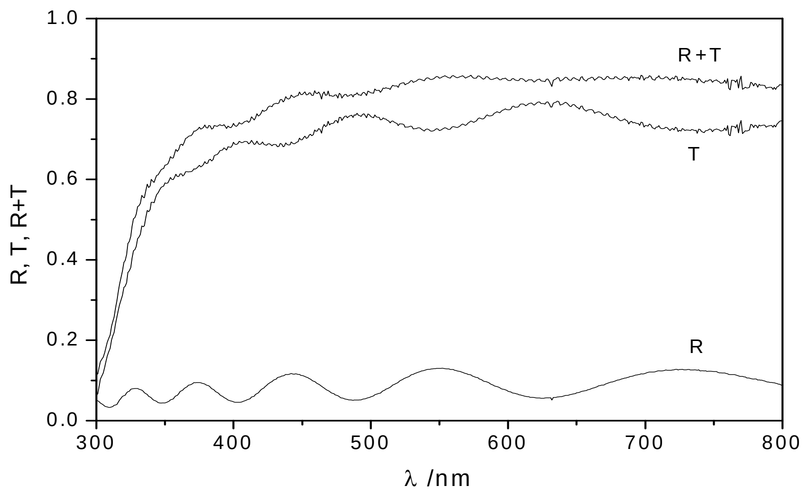


(c)

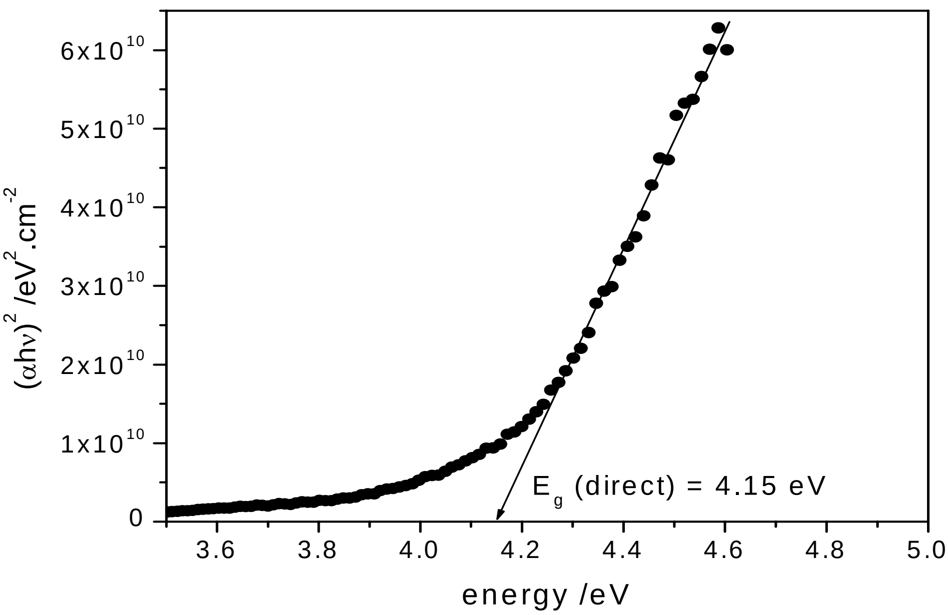
Fig. 2. The SEM micrographs of F: SnO_2 films prepared at 475^oC; magnifications: (a) 25,000x, (b) 55,000x and (c) 1,00,000x.

3.3. Optical Properties

Fig. 3 (a) shows the variation of reflectance (*R*), transmittance (*T*) and *R* + *T* with wavelength for an F:SnO_2 film deposited at 475°C. The well developed interference patterns in *R* and in *T* show that the film is specular to a great extent. However, upon adding up *R* and *T*, the resulting *R* + *T* curve is well below 1 (by 15%). In the high wavelength region, this can be ascribed to scattering, as the interferences are almost entirely averaged out, pointing to the absence substantial absorption, which would lead to a phase shift. A direct bandgap of F: SnO_2 films on quartz substrate were derived from transmission and reflection measurements. The absorption coefficient (α) was around 15000 cm^{-1} at 320 nm. The variation of $(\alpha \cdot h\nu)^2$ with hν, shown in Fig. 3 (b), has a straight line portion indicating that the transition involved is direct. The direct gap, determined by extrapolating the straight portion to the energy axis to $(\alpha \cdot h\nu)^2 = 0$, is found to be 4.15 eV, which is higher than the value of E_g = 3.57 eV reported for single crystal SnO_2 [14] and is comparable to the value of E_g = 4.3 eV reported for F:SnO_x films [15].



(a)



(b)

Fig. 3. (a) Variation of reflectance (*R*), transmittance (*T*) and *R* + *T* with wavelength, (b) Plot of $(\alpha \cdot h\nu)^2$ vs. hν for a spray deposited F:SnO_2 thin film.

3.4. Sensitivity Measurement

Gas sensing properties were evaluated in a gas chamber. The sensing activity was tested by keeping the test chamber at room temperature. In the beginning, pure nitrogen gas was passed through the test chamber to remove any residual gas or water vapors then fresh air was passed and maintained till constant sensor resistance was obtained as Ra. The test gas was then admitted along with air and Rg was measured, till a constant value of Rg was obtained. Sample gases containing CO_2, CO, CH_4, C_3H_8, and H_2 were mixed by manual gas blender and led to the measuring chamber. (Size: 250 mm × 250 mm × 160 mm). The electrical resistances of each sensor element in air (Ra) and in a gas (Rg) were measured to evaluate gas sensitivity. Gas sensitivity was defined as

$$S = \frac{Rg - Ra}{Ra} = \frac{\Delta R}{Ra}, \qquad (1)$$

where Ra is the electrical resistance of sensor in air, and Rg is electrical resistance of sensor in a particular sample gas. In this investigation, the detection of low concentration of gas (ppm level) was kept as a target. Concentrations ranging from 100 to 1000 ppm of H_2, CH_4, C_3H_8, CO_2 and CO were injected in the test chamber and the sensing signals were recorded. Sensitivities of the sensor made with nano-crystalline F-doped SnO_2 against various reducing gases were recorded. Figure 4 shows that F-doped SnO_2 based sensor has very high sensitivity for H_2. On the other hand, the sensitivities to C_3H_8, CO, CO_2 and CH_4 were relatively low, as seen in Fig. 4. F-doped SnO_2 has shown higher sensitivity to hydrogen gas in comparison to the commercially available SnO_2 sensor [16]. The higher sensitivity and selectivity of the nano-crystalline F-doped SnO_2 for hydrogen gas may be due to the greater adsorption of hydrogen molecules on the favorable sites at fluorine atoms of the materials or the increased n-type property of SnO_2 by fluorine doping. Higher sensitivity shown by nano-crystalline F-doped SnO_2 is also because of its higher surface area. Similar results have been obtained on SnO_2 nano-crystalline H_2 gas sensors for their sensitivities by Seal and Shukla [17] and Gong et al. [18].

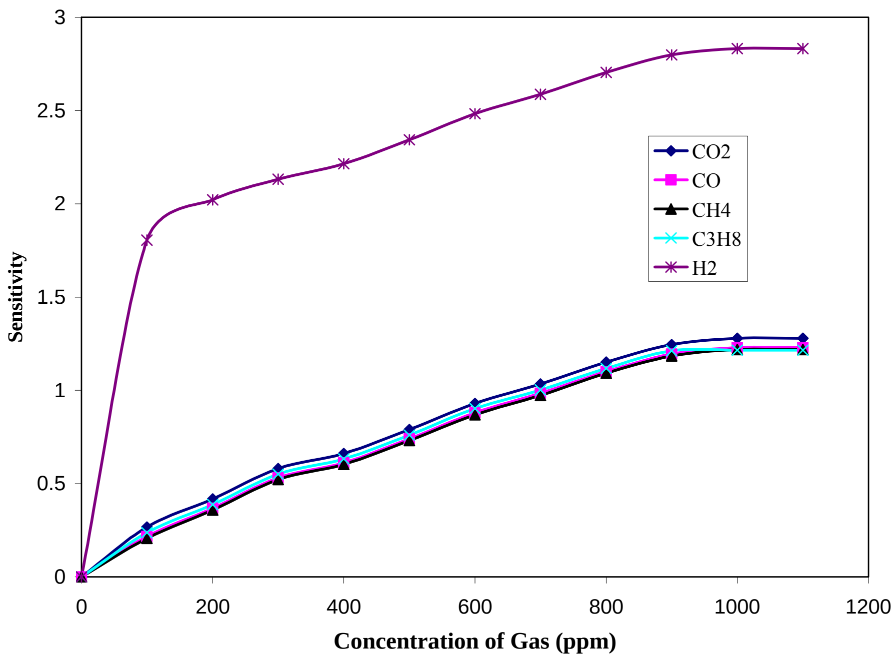


Fig. 4. Sensitivity of F: SnO_2 sensor as a function of gas concentration at room temperature.

4. Conclusions

Good quality thin film of F: SnO_2 can be deposited onto glass at a substrate temperature of 475^oC using a mixed organic/aqueous solvent (H_2O: i- PrOH = 55:45 by volume) by the simple and low cost spray pyrolysis technique. The material in thin film form is polycrystalline with tetragonal structure and highly textured. F: SnO_2 film had optical band gap energy due to a direct transition at 4.15 eV. The sensor formed by thin film of F: SnO_2 deposited at optimized parameters is very sensitive to the hydrogen gas.

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