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CHARACTERIZATION OF SPRAYED SnO_2:Pd THIN FILMS FOR GAS SENSING APPLICATIONS

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Preparation of SnO_2 doped with Pd thin films was carried out by spray pyrolysis technique on glass substrate heated at 450°C. The films thus obtained were characterized by measuring structural and optical properties. Carbon monoxide gas-sensing properties were also investigated.

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1. Introduction

Metal oxide gas sensors have been the subjects of large number of investigations during the past [1–7]. The sensors based on these materials change their conductivity in the presence of oxidizing and reducing gases as electron density at the surface gets modified due to absorption and desorption of O^{2-}, O_2^- or O^-. This adsorbed oxygen gets trapped at the grain boundary trap states thereby increasing the grain boundary potential barrier. This culminated in an increase in resistivity of the material. For reducing gases, the trap states get depleted of charged carriers and thereby reduce the resistance through lowering of the potential barrier at the grain boundaries.

Among the various metal oxides studied for gas sensor applications, SnO_2 has emerged as one of the potential material in recent years. Tin oxide has the unique properties of being transparent and at the same time conducting. The conductivity arises from the oxygen deficient sites and the conductivity could be modulated from normal semiconducting to degenerate one by suitably doping the material and manoeuvreing the oxygen deficient sites. Different techniques [1–12] were adopted to deposit SnO_2 coatings for sensor applications but spray pyrolysis technique routes seem to be the most favored one due to its inherent capability of producing stable films with reproducible properties besides the process being scalable and cost-effective.

In this study, spray pyrolysis technique was adopted to deposit Palladium doped SnO_2 coatings onto glass substrates. Films thus produced were characterized by measuring optical and structural properties. CO sensing properties were also investigated.

2. Experimental details

SnO_2 films were deposited by spray of an aqueous solution of $SnCl_4$:$5H_2O$ dissolved in ethyl alcohol for pure SnO_2 films onto the preheated glass substrates at temperatures 450 °C using compressed air as an atomization gas. The distance between the nozzle and substrate, pressure of the carrier gas, spray time and spray rate were optimized to obtain good-quality SnO_2 thin films. The substrates were ultrasonically cleaned in acetone, methanol and distilled water, respectively

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and dried in air. To get the Pd doped SnO_2 , the solution of $PdCl_2$ was added to the starting solution with different concentrations (2.5-15%).

SnO_2 film is colorless and it had very good adhesion to glass substrates. The thickness of the film was measured by a mechanical stylus and was found to be 0.3-0.4 μm. The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a Philips diffractometer with CuKα radiation (λ=1.5418 Å), at 35 kV, 30 mA. The transmission and reflection spectra of the films were measured by Jasco V-570 ultraviolet– visible spectrophotometer.

The sensitivity tests were carried out in a home made stainless steel testing chamber that measure the change in surface resistance of the samples on gas exposure as shown in Fig.(1). Silver paste contacts were made at the ends of the sensor element and the terminals are connected to a computerized multimeter (Keithly6517A) and a constant voltage source for resistance measurement. The samples were heated by using a heating resistance. The sample temperature was monitored and controlled by a thermocouple attached to the substrate. A constant amount of CO (500ppm) was injected to the testing chamber. The sensing characteristics of the sensor were then recorded by measuring the change in electrical resistance of the sensor when the latter was exposed to CO. The sensitivity $[(R_{air}-R_{gas})/R_{air}]$; R_{air} and R_{gas} being the sensor resistance in air and gas at the same temperature; defined as the percentage change of the film resistance in the presence of the CO gas [13] was calculated for each temperature and concentration of Pd dopant.

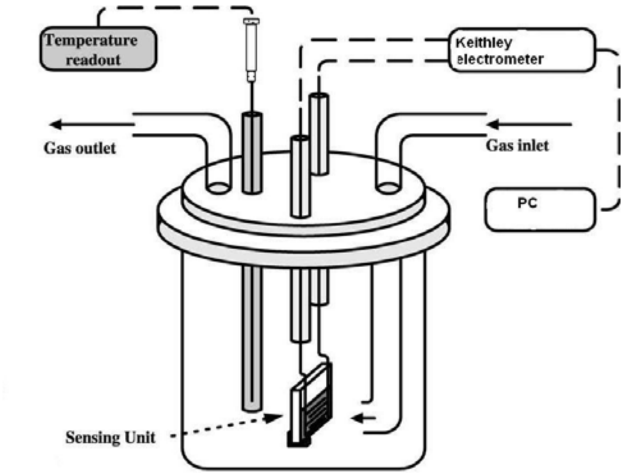

Fig. 1 Gas sensing setup.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of pristine SnO_2 and Pd:SnO_2 with various Pd concentration are shown in Fig. 2. All the diffraction patterns show characteristic tin oxide peaks with rutile structure [14] without any impurity phase or peaks corresponding to PdO, indicating formation of single phase tin oxide structure. After the incorporation of Pd there is broadening and drop off in the intensity of the peaks. Initially on doping with 10 % Pd the intensity decreases, while on further addition of Pd there is no significant difference in the peak intensity is observed. The grain size was found from peak profile and calculated from Scherrer formula [15] 20-30 nm. It is well known that a high surface to volume ratio due to nanostructures is one of the important criteria to increase the sensitivity towards a particular test gas. Thus, 10 % is the optimum concentration of Pd to get a very low crystallite size in the present method.

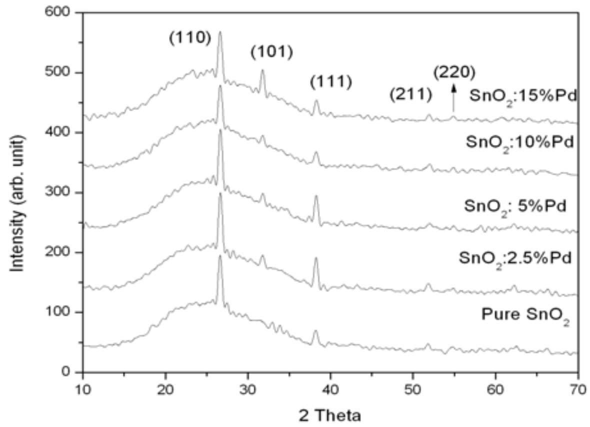

Fig. 2. XRD patterns of pure and SnO_2 doped with different Pd concentration.

3.2. Optical properties

Optical transmittance and reflection spectra of SnO_2 pure and doped with different Pd concentrations are shown in Fig. 3. The SnO_2 film shows maximum transmittance of about 80% in the near UV–Vis. region.

In order to obtain the band gap, the absorption coefficient (α) was calculated from the transmission data by using the following relation [16],

$$\alpha = \frac{\ln T}{t} \tag{1}$$

where t is the film thickness and T is the transmittance. For the direct transition, the optical band gap energy of SnO_2 film was determined by using the equation [16],

$$\alpha = cons\tan t \; \frac{(h\upsilon - E_g)^{1/2}}{h\upsilon} \tag{2}$$

where hν is the photon energy and E_g is the optical band gap which could be calculated from $(\alpha h\nu)^2$ versus hν plot. The plot of $(\alpha h\nu)^2$ against hν is shown in Fig. 4. By extrapolating the linear part of the plot to α = 0, the optical band gap of 3.9 eV was estimated for pure SnO_2 film. While the optical band gap decreases with increasing the Pd concentration.

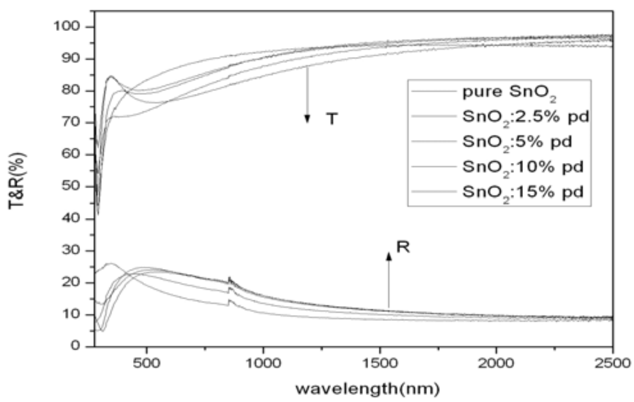

Fig. 3. Optical transmission and reflection for pure SnO_2 and SnO_2:Pd with different concentrations.

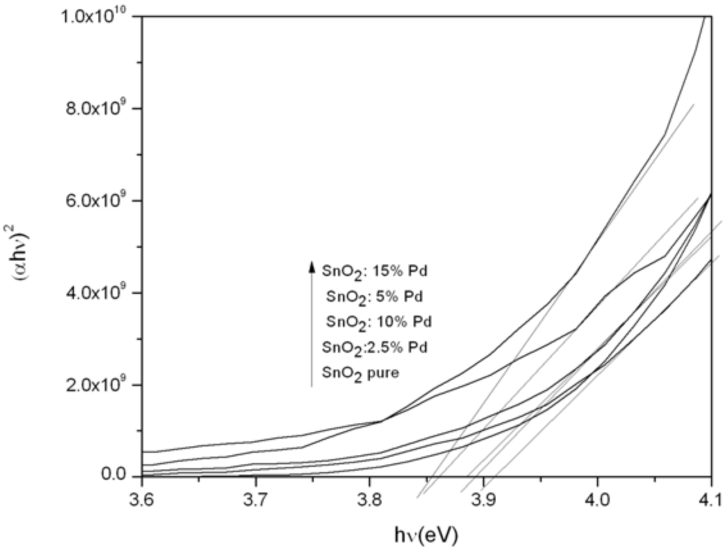

Fig. 4. $(\alpha h\nu)^2$ against hν for pure SnO_2 and SnO_2:Pd with different concentrations.

3.3. Gas sensing properties

It is well known that gas sensing is a surface phenomenon and is mainly controlled by the adsorbed oxygen species. Doping with Pd gives rise to various oxygen species and surface states causing enhancement in the gas sensing.

Resistance of tin oxide films depends mainly on various oxygen-deficient sites present after deposition as well as on the doping level. Palladium was found to reside on the grains and at the grain boundaries of SnO_2 films. Presence of Pd in the film generates surface states and provides excess electrons to them. When such a film is heated at higher temperature, oxygen is adsorbed by the tin oxide layer and abstracts electron from the surface states thereby increasing the film resistance. This results in the formation of ionic species such as O^{2-}, O_2^- and O^-. Desorption of these oxygen species at the surface due to the presence of Pd would culminate in an increase in conductance of the SnO_2 layer significantly in the presence of the sensing gas (CO). Additionally, an increase in conductivity is also due to the reduction of the electronic potential barrier in the grain boundary of SnO_2 when oxygen is adsorbed on its surface. The adsorption/desorption of oxygen causes a change in Fermi level of the grains and hence changes the grain boundary potential barrier [17, 18]. The reactions at the surface of films would be as follows:

$$O_2 + e^- \rightarrow O_2^- ; \quad (3)$$

$$O_2^- + e^- \rightarrow 2O^- ; \quad (4)$$

$$CO + O^- \leftrightarrow CO_2 \quad (5)$$

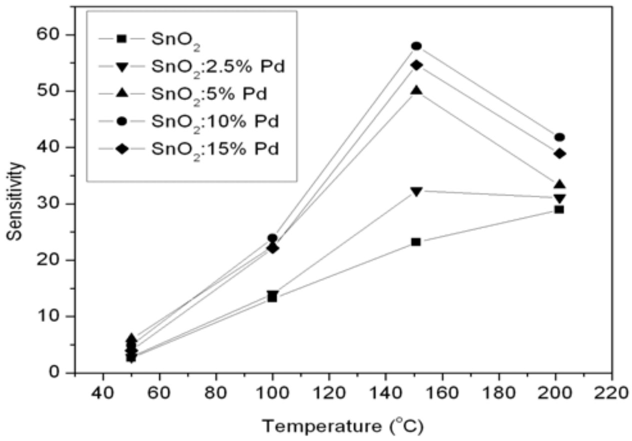

Fig. 5. The CO gas sensitivity of SnO_2 and SnO_2 doped with different Pd concentration versus the operating temperature

Fig. 5. shows the sensitivity to CO gas as a function of operation temperature for the SnO_2 doped with different Pd concentration. It can be seen that the sensitivity of SnO_2 films was increased with increasing the Pd concentration. Increase the Pd concentration within SnO_2 shows a higher surface area and smaller grains size diameters. This translated into improved dynamic gas sensing properties and also improved responses to gases. It was found that the sample of 10% Pd has the highest sensitivity for CO gas at operating temperature 150^{o}C.

4. Conclusions

SnO_2 and SnO_2: Pd films of 0.3 – 0.4 μm thickness and a doping Pd content of 2.5–15% in solution are synthesized by spray pyrolysis. XRD patterns show characteristic tin oxide peaks with rutile structure without any peaks corresponding to PdO, indicating formation of single phase tin oxide structure. There were no effects of Pd doping on the optical transmission and reflection of SnO_2. The optical energy band gap slightly decreases with increasing Pd concentration.

SnO_2 doping by Pd using spray pyrolysis technology is a very effective method for improving the gas sensing characteristics of SnO_2 thin films. Even small additives of Pd increase the gas response to reducing gases such as CO gas, optimize operating temperatures, and decreases response time.

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