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CO-sensing properties of undoped and doped tin oxide thin films prepared by electron beam evaporation

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Abstract

Undoped thin films of tin oxide and those doped with indium oxide and nickel oxides were deposited by electron beam evaporation. The effects of the film thickness and preparation conditions (films prepared with or without the presence of oxygen environment during deposition) on the optical and carbon monoxide sensing properties of the films were studied. The films were characterized using X-ray diffraction and X-ray photoelectron spectroscopy and optical spectroscopy techniques. All the films were found to be amorphous. It was found that the sensitivity of the films to CO increased with the thickness and the porosity of the films. It was found that their selectivity to CO gas relative to CO_2 and SO_2 gases could be improved upon doping the films with indium (or nickel) oxide.

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Keywords: Thin film; CO sensor; SnO_2; Semiconductor sensor

1. Introduction

There is an ever-increasing demand for gas sensors in various fields. Particular attention has been devoted to the monitoring of carbon monoxide (CO). More precise control of the air/fuel ratio in a combustion processes can yield significant gains in efficiency and result in substantial savings in fuel consumption. The flue gas concentration of CO is a reliable and accurate indication of the completeness of combustion, as it is the most sensitive indicator of unburned combustible losses. Tin oxide based gas sensors are among the most widely used semiconductors for detecting CO [1–10]. Most of the commercially available gas sensors are based on thick-film metal oxide materials deposited on ceramic heater substrates [6]. A common shortcoming of such thick-film devices is their high level of heating power consumption. This level can be reduced by about one order of magnitude using micro-machined heater substrates [6]. The established state-of-the-art in silicon micromachining is still the use of evaporated or sputtered thin-film metal oxide materials [6]. Therefore, in the present work CO gas sensing properties of thin films prepared by electron beam evaporation were studied.

The gas sensing properties were studied for films of different thickness (100–600 nm) and for films prepared in vacuum with and without introducing oxygen in the chamber. The presence of oxygen in the chamber is expected to produce films that are more porous than those prepared without the presence of oxygen in the chamber. The effects of oxygen partial pressure on the CO-sensing and optical properties of the films were studied. An attempt has been made to correlate these properties. A careful study of their optical properties can throw some light on the surface conditions and porosity of the films, which are the two main factors affecting their gas sensing properties. Tin oxide films doped with indium oxide and nickel oxide, were prepared. The doping was carried out in order to improve their selectivity. The films were characterized by X-ray diffraction and X-ray photoelectron spectroscopy.

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2. Experimental details

Thin films of tin oxide and tin oxide doped with 5% by weight with NiO or In_2O_3 were prepared in a Leybold L560 box coater pumped by a turbomolecular pump. The system was pumped to a base pressure of 4×10^{-6} mbar. The films were deposited by electron beam evaporation. Before deposition, the material was slowly outgassed with a shutter blocking the vapor from the sample surface. For different purposes of film characterization, the films were simultaneously deposited on different substrates: BK7 glass and tantalum substrates. The substrates were rotated during the deposition. A constant rate of evaporation of $0.4\,\mathrm{nm\,s^{-1}}$ was controlled by a quartz crystal thickness monitor and rate controller. The source-to-substrate distance was about 45 cm.

The deposition parameter that was varied in this work was the oxygen partial pressure. In the preparation of some of the films, oxygen was readmitted to raise the pressure of the coating chamber to 5×10^{-4} mbar. The settings used were: (a) films deposited on unheated substrates with oxygen, labeled as RO and (b) films deposited on unheated substrates without oxygen, labeled as RW. The thicknesses of the films were determined by an optical method and ranged from about 100 to 600 nm.

After the films were deposited, they were removed from the coating chamber, and a variety of characterization techniques were employed to study their various properties. The normal incidence reflectance and transmittance of the films, on BK7 glass substrates, were measured over the wavelength range of 300–2000 nm, using a JASCO V-570 double beam spectrophotometer. The chemical composition of the films was studied using X-ray photoelectron spectroscopy (XPS), and was performed in a VG Scientific ESCALAB MKII spectrometer using Al Kα (1486.6 eV) radiation. The instrumental resolution was 1.2 eV with a slit width of 6 mm. Samples were maintained at ambient temperature at a pressure of 5×10^{-9} mbar. The films deposited on tantalum substrates were used for the XPS analysis, so that charging of nonconducting samples could be reduced. Film structure was examined by X-ray diffraction (XRD), and was performed in a JEOL JDX-3530 X-ray diffractometer using Cu Kα radiation (1.54 Å). The films deposited on BK7 glass were used for the XRD analysis. The 2θ range studied was 0–80 °. The 2θ step and step acquisition time were 0.02° and 1.00 s, respectively.

The resistance of the films was determined from the measurement of the current passing through the sample at a fixed voltage. The measurements were done in air, in the temperature range 25–500 °C. Prior to the deposition of the films, gold electrodes of length 7 mm and electrode spacing of 2 mm were deposited on glass substrates by thermal evaporation. Platinum lead wires were then attached onto contact pads of the electrodes with an electrically conducting paste (Aremco-Bond 597/C). Before starting with the measurements the films were thermally annealed at a temperature of 400 °C for 4 h under atmospheric conditions with the aim to stabilize their physical parameters.

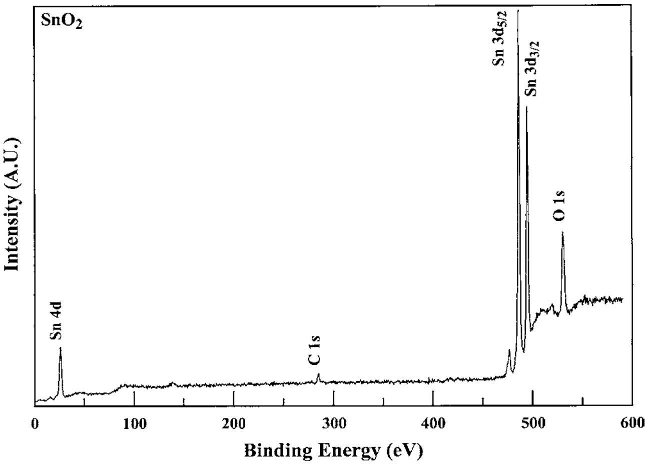

Fig. 1. A wide scan X-ray photoelectron spectrum of tin oxide film of type RW.

3. Results and discussion

3.1. Characterization of films

The diffraction patterns obtained for all the films showed a broad peak, which is typical of an amorphous structure. Annealing of the films in air at a temperature of 400 °C had no effect on the nature of the diffraction patterns.

Fig. 1 shows an XPS wide scan spectrum of a tin oxide film of the RW type. Similar spectra were obtained for the RO type of films. The scan shows sharp lines due to the main constituents (Sn and O) and the carbon C 1s peak arising from hydrocarbon contamination. The C 1s peak, at a binding energy (BE) of 284.6 eV, was used to make corrections for charge shift. The atomic ratio of oxygen to tin (O/Sn) was determined from the areas of the O 1s and Sn $3d_{3/2}$ peaks. The values of the ratio were found to be: RW-type 1.79 (as-deposited) and 1.69 (annealed in air at a temperature of 400 °C) and RO-type 2.18 (as-deposited) and 1.85 (annealed in air at a temperature of 400 °C). For the as-deposited RO films, the atomic ratio was higher than the stoichiometric value of 2. This hyper-stoichiometry may be due to the presence of tin hydroxide and/or trapped oxygen in the RO films [11–12]. XPS is a surface technique that probes only a few top monolayers, and thus, cannot reveal the O/Sn ratio in the bulk of the film. Nevertheless, the O/Sn ratio showed the expected trend, i.e. it increased with the introduction of oxygen and decreased upon annealing the films in air. The uncertainty in the measurement of the atomic ratio O/Sn was about 10%.

Measured normal incidence transmittance (T) spectra of some of the tin oxide films are shown in Fig. 2. The films were transparent down to a wavelength of about 500 nm. Normal incidence transmittance (T_f) of a transparent film (with refractive index n_f and thickness t_f) on a transparent substrate (refractive index n_s) is given by [13]

$$T_f = \frac{(n_s/n_o)(1+r_1)^2(1+r_2)^2}{1+r_1{}^2r_2{}^2+2r_1r_2\cos\delta} \qquad (1)$$

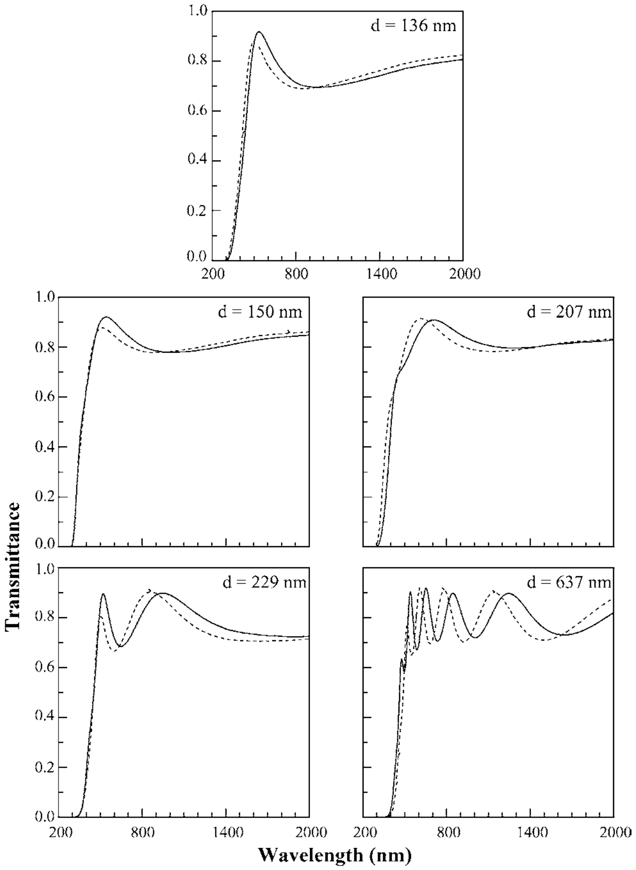

Fig. 2. Normal incident transmittance spectra for some films of the tin oxide. These spectra were taken before (solid curves) and after annealing (broken curves) the samples at 400 °C in air.

where $n_o \sim 1.0$ is the refractive index of air, $r_1 = (n_o - n_f)/(n_o + n_f)$, $r_2 = (n_f - n_s)/(n_f + n_s)$, $\delta = 4\pi n_f d/\lambda$, λ is the wavelength and d is the thickness of the film. In a dual beam spectrophotometer, if air is the medium in the reference beam and a substrate coated with a transparent film is placed in the path of the specimen beam then the measured transmittance (T) is given by

$$T = T_f T_s \tag{2}$$

here $T_s = (4n_o n_s)/(n_o + n_s)^2$, is the transmittance across the back surface of the substrate into the air. Eqs. (1) and (2) do not include the effects of multiple reflections in the substrate. The use of a wedge substrate would ensure that reflection from the back of the substrate is deflected out of the optical path of the instrument so that the multiple reflections in the substrate do not affect the measurement. If T is measured as a function of λ and d and n_s are known, then, in principle n_f can be determined from Eq. (2). An expression giving an explicit value of n_f cannot be obtained. However, the equation for T may be solved by a numerical method of [14]. Thus, a method of determining refractive index and thickness of a transparent film from the measurement of transmittance given in [14] was used in the present work for the spectral region above 500 nm. The results of the application of the above method to the tin oxide films are displayed in Fig. 3, which shows the dispersion of the refractive index averaged over films of different thickness in each of the types. The most obvious indication of the presence of change in the refractive index of a thin film is usually seen in the change that occurs in the transmittance minima, as discussed below.

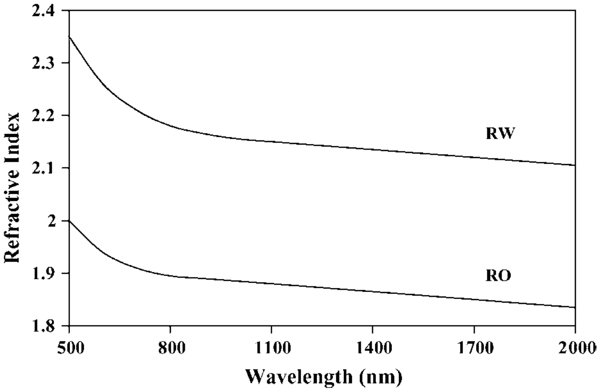

Fig. 3. Refractive index as a function of wavelength of tin oxide films deposited under different experimental conditions. RO films deposited on unheated substrates with oxygen and RW films deposited on unheated substrates without oxygen.

It can be shown from Eqs. (1) and (2) that the maximum and minimum values of the measured transmittance are

$$T_{\max} = [(4n_o n_s)/(n_o + n_s)^2]^2 \tag{3}$$

and

$$T_{\min} = \frac{(4n_o n_s)/(n_o + n_s)^2}{(4n_f^2 n_s)/(n_f^2 + n_s)^2} \tag{4}$$

The maximum in transmittance is independent of the refractive index of the film and has the same value as that of the measured transmittance of an uncoated substrate Eq. (3). The minimum in transmittance depends on the refractive index of the film and decreases in the value as n_f is increased Eq. (4). Fig. 4 is a plot of $T_{\min}$ versus n_f, calculated using Eq. (4), on the assumption that $n_s = 1.505$ (that of BK7 glass substrate

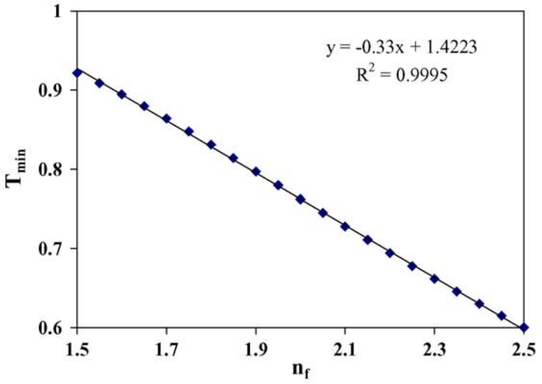

Fig. 4. A visual inspection of the spectral transmittance of a film with the aid of $T_{\min}$ vs. n_f curve can provide quick reference to the refractive index of the film.

averaged over the wavelength region from 500 to 2000 nm). It is obvious from Fig. 4 (using the results of Fig. 2) that upon annealing the films in air the refractive index increases by 1–2% in either of the two types of the films. The shifts in the minima and maxima of the transmittance curves (Fig. 2) upon annealing with respect to those of unannealed films suggest that upon annealing the film thickness decreases by about 10%.

3.2. CO gas-sensing properties

The CO gas-sensing properties of the oxide films were studied by measuring the film resistance in air (R_{air}) and in presence of dry air containing different concentrations of CO (R_{CO}). The CO gas showed a reducing effect, leading to a decrease in the electrical resistance as in most of the n-type metal oxide semiconductors [6]. For reducing gases the sensitivity S is defined as $\Delta R/R_{\text{air}}$, where $\Delta R = R_{\text{air}} - R_{\text{CO}}$. The sensitivity was measured as a function of sensor temperature. The sensor was placed in a direct contact with a heated copper disc. The heating of the disc was provided by nichrome wire (covered by alumina tubes) heater passing through the disc. The temperature of the sensor was controlled by varying the magnitude of the applied voltage to the heating element. It was found that the S, measured at a given temperature, depended on factors, such as film preparation conditions, and film thickness. These effects are discussed below. Before starting with the measurements the films were thermally annealed at a temperature of 400 °C for 4 h under atmospheric conditions with the aim to stabilize their physical parameters.

Fig. 5 shows the sensitivity as a function of operating temperature for RO-type of the tin oxide films of different thickness. Irrespective of the type of a film, it was found that at a given operating temperature the S of the film increased with its thickness. Increase in sensitivity of thin tin oxide films with thickness, for the CO detection has been recently reported [9]. Increase in the sensitivity for CO with thickness has been observed in thin films of HfO_2 [15]. Moreover, this observation may find a support from a recent work of Becker et al. [6] where they studied gas-sensing properties of thin (thickness 50–300 nm) and thick (15,000–80,000 nm) films of tin oxide. They concluded that thin films mainly respond to oxidizing gases such as O_3 and NO_2, whereas thick films preferably respond to reducing species like CO and CH_4.

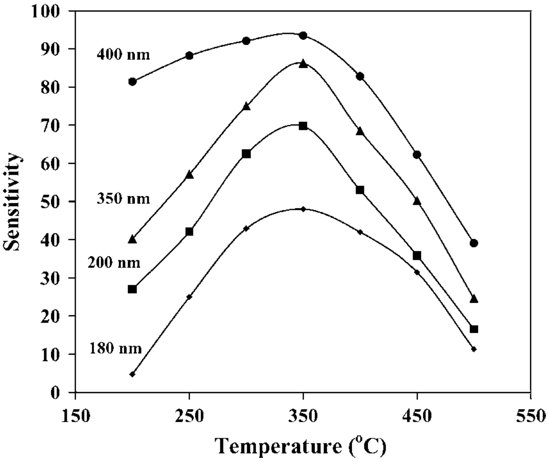

Fig. 5. Effects of film thickness of a SnO_2 (RO-type) sensor on its sensitivity. The CO concentration was 50,000 ppm.

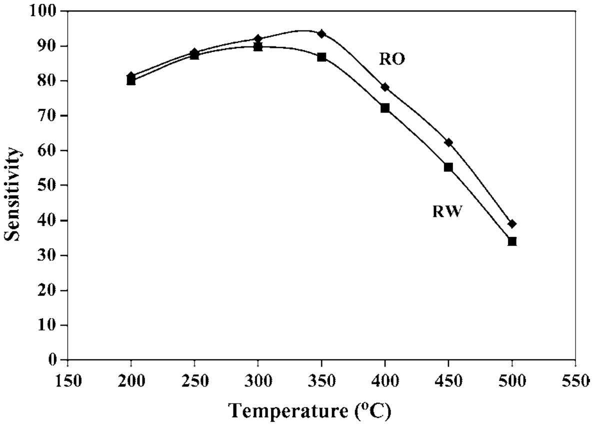

Fig. 6. Effects of film preparation conditions on the sensitivity. Sensitivity as a function of temperature for SnO_2 films deposited under different conditions but having nearly same thickness (about 400 nm): RO: films prepared on unheated substrates with introduction of oxygen; RW: films prepared on unheated substrates without introduction of oxygen.

Fig. 6 shows the sensitivity versus temperature curves for different types of films of SnO_2. The sensitivity of RO-type of films is higher than the RW-type. The RO-type of films has lower refractive index (Fig. 3) as compared with the same for the RW-type. Similar observations were made for HfO_2 [15]. The effect of oxygen can be explained as follows [16]. Oxygen induces a strong thermalization of incoming molecules. Moreover, the oxygen adsorbed on the growing film causes a reduction in the condensate (SnO_2 molecules) mobility. Therefore, the kinetic energy of the incoming molecules is reduced, and they cannot rearrange themselves on the surface of the substrate in a densely packed structure. Thus, the density of the film decreases, and, consequently, the refractive index decreases (Lorentz–Lorenz law). This indicates that the CO-sensing properties do depend on the porosity (as indicated by its refractive index) of a metal oxide film. Park and Mackenzie [17] while studying the alcohol sensing properties of tin oxide film concluded that the sensing properties strongly depend on film porosity rather than thickness or grain size. It may, therefore, be concluded that best possible sensitivity could be achieved through the use of RO-type of films.

Fig. 7 shows sensitivity as a function of temperature for different CO concentrations for a SnO_2 sensor. It shows that the CO concentration as small as 10 ppm can be easily detected. The values of the sensitivity at 350 °C (that is maxima in sensitivity versus temperature curve) are plotted in Fig. 8 as function of the CO concentration. Ferroni et al. [18] observed a similar linear behaviour in logarithmic scale for MoO_3 film.

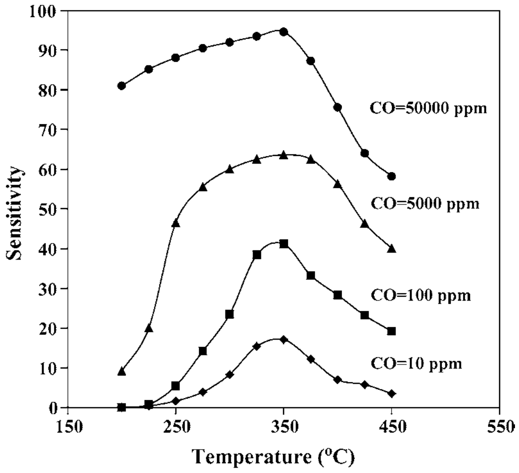

Fig. 7. Sensitivity as a function of CO concentration for a SnO_2 sensor for a RO-film of thickness of about 400 nm.

The observed linear behaviour in logarithmic scale is an indication that the current-percolation model holds true for these films [18].

Doping is the most popular method for the improvement of sensitivity and selectivity of SnO_2-based (or the other metal oxide-based) gas sensors [1,4,5]. One general strategy for tailoring materials for selective sensor response involves the modification of the surface by addition of dopants or additives during sensor fabrication. In the present work for this purpose doped films of SnO_2 were studied. The dopants used were 5% by weight of CuO, NiO and In_2O_3. The dopants in powder form were added to SnO_2 powder and pallets were formed for the mixture in each of the case. These pallets were used to form thin films. In the case of CuO doped SnO_2 films, satisfactory results could not be achieved as the vapor of the mixture (in electron beam deposition) reacted with pre-deposited Au electrodes. As a result of this reaction Au films peeled of the substrate. However, for the NiO and In_2O_3 doped films satisfactory results were obtained. Response of undoped SnO_2 thin film as a function of temperature to different gases, such as CO, SO_2, and CO_2 is shown in Fig. 9. It

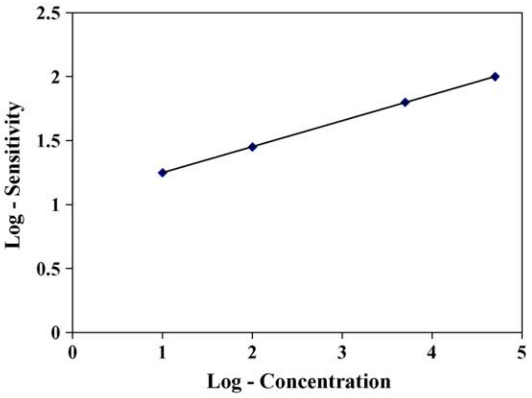

Fig. 8. Response of the SnO_2 thin film to different CO concentrations at 350 °C. The results are based on the data given in Fig. 7.

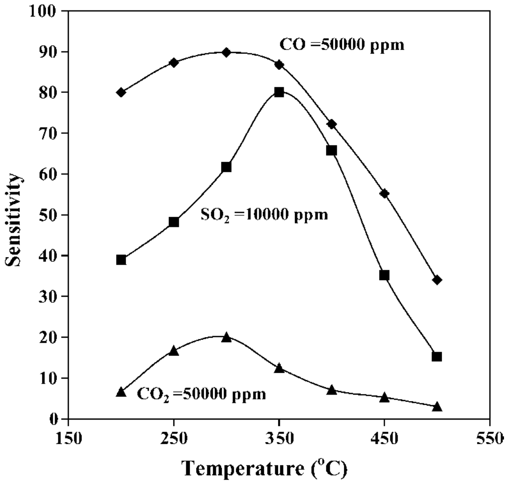

Fig. 9. Response of the undoped SnO_2 thin film to different gases, such as CO, CO_2, and SO_2.

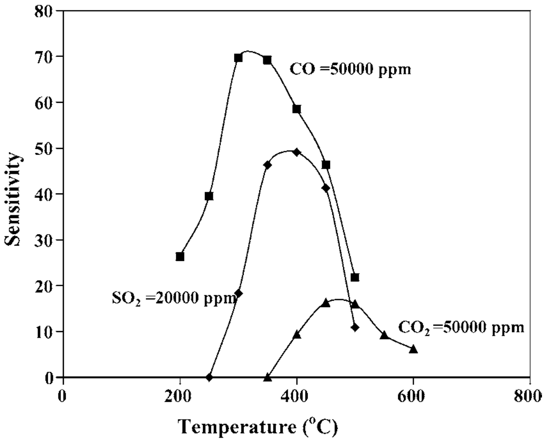

Fig. 10. Response of the SnO_2 thin film doped with In_2O_3 (5% by weight) to different gases, such as CO, CO_2, and SO_2.

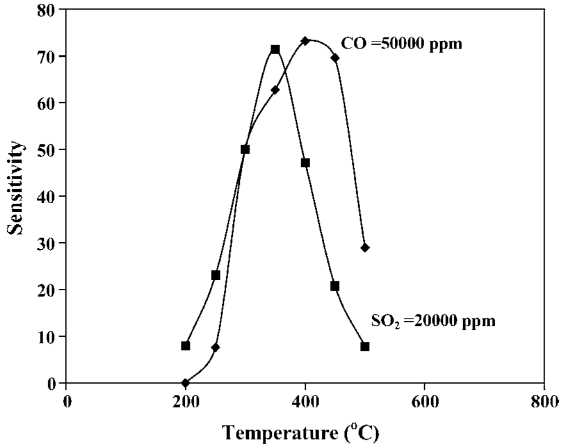

Fig. 11. Response of the SnO_2 thin film doped with NiO (5% by weight) to different gases, such as CO and SO_2. Its response for CO_2 was insignificantly small.

is clear from Fig. 9 that the sensitivity of the sensor for CO_2 gas is significantly smaller than the same for the CO and SO_2 gases. The effects of doping on the response of SnO_2 films (doped with NiO and In_2O_3) are shown in Figs. 10 and 11. In a NiO-doped sensor the sensitivity for CO_2 was too small to be detected. It is clear from Figs. 10 and 11 that maximum in sensitivity curves appeared at different temperatures (for a given gas) for undoped and Ni-doped and In-doped films. Thus, to achieve a better selectivity for CO gas as compared with for SO_2 gas, the sensors may be operated at different temperatures, for example, Ni-doped sensor temperature range of 450–500 °C (Fig. 11) and In-doped with a range of 250–270 °C (Fig. 10).

4. Conclusion

The effects of the deposition conditions on the refractive index, CO-sensing, and the compositional and structural properties of tin oxide thin films were investigated. All the films were found to be amorphous. The refractive index decreased with the introduction of oxygen. The present study showed that the CO-sensing properties strongly depend on the thickness of the film and its porosity (as indicated by its refractive index). The sensitivity of the films increases with the film porosity as well as with thickness of the film. Sensitivity of the films was tested for other gases, such as CO_2 and SO_2. Tin oxide films doped with indium oxide or nickel oxide was found to be more selective in detecting CO gas than the other two gases (while operated at an appropriate temperature) as compared with undoped films.

Acknowledgments

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