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CO gas sensing properties of screen printed SnO_2 thick films

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The present investigation deals with the preparation of CO sensor based on SnO_2. In this work, SnO_2 films were prepared by standard screen-printing method. These films were characterized by x-ray diffraction (XRD) measurements, spectroscopy and scanning electron microscopy (SEM). These films exhibit high sensitivity, excellent selectivity, fast response and recovery to CO gas at 300 ^oC in air atmosphere.

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1. Introduction

Since half a century ago, it was discovered that the charge carrier concentration on the surface of a semiconductor is sensitive to the composition of the surrounding atmosphere [1]. Much effort has been made to develop novel solid state gas sensors based on semi-conducting metal oxides [2-5]. Many researchers are involved in the development of semiconductor oxide gas sensors based on the development of gas sensors based on ZnO, SnO_2, Fe_2O_3, TiO_2, WO_3 and In_2O_3 etc. in the detection and control of gases and organic vapors like CO, CO_2, H_2, H_2S, NH_3, NO_2, NO, LPG, ethanol, methanol and acetone [6-21].

SnO_2 is n-type semiconductor and sensors based on it have received much attention since they can detect a wide variety of gases with high sensitivity, good stability and low production cost. Thick film technology has been used to obtain inexpensive semiconductor oxide gas sensors with good sensitivity and selectivity to hazardous gas [22-24]. From last few years, SnO_2 thick films have been considered to be the most promising material for detecting different gases [17-21].

Numerous kinds of gases are emitted from various sources into our living space, working space or outdoors. Many of them are hazardous to human being and the environment. Carbon monoxide is formed as a product of incomplete combustion when not enough oxygen is available to react completely with hydrocarbons. Carbon monoxide is a colorless, odorless, tasteless and poisonous gas that can be very harmful since it lowers the oxygen delivery to the body's organs and tissue. Exposure to higher concentration of carbon monoxide can cause many problems such as visual impairment, headache and learning disabilities. Exposure to very large concentration of CO can cause death. Even small concentration of CO is harmful to the peoples with heart disease. CO also contributes to the formation of ground level ozone and hence smog as well, which cause respiratory problems. Hence detection of such harmful carbon mono oxide gas is necessary in environmental monitoring.

Comini et al [25] have reported about carbon monoxide response of molybdenum oxide thin films deposited by different techniques whereas CO gas sensing properties of Fe_2O_3 thin film sensor element was reported by Neri et al [26]. Also, Maosong et al [27] has focused on CO sensing of SnO_2 thin films and Williams et al [28] has reported the use of SnO_2 thin film for detection of CO gas from a car exhaust. Recently, Gong et al [29] fabricated ZnO thin film sensor and Niu et al [30] developed In_2O_3 based sensor to detect CO gas.

The aim of the present study was to prepare SnO_2 thick films by using screen printing onto alumina substrates and to investigate their gas sensing properties for carbon mono oxide (CO) gas.

2. Experimental

The SnO_2 powder (purity ~ 99.99%) was mechanically milled in an acetone medium using Fisher type electric agate pestle and mortar for 24 hours. After drying at 200^0c for 20 min, the powder (99 %) was thoroughly mixed with a permanent binder (lead boro-silicate glass frit with composition 70 wt% PbO, 18 wt% Al_2O_3, 9 wt% SiO_2 and 3 wt % B_2O_3). The organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose were added to this mixture to achieve proper thixotropic properties of the paste. The paste, thus formed was screen printed onto an alumina substrate. The films were allowed to stabilize at room temperature for 24 hours and then the films were cured at 900 ^0C for ½ h. During this process the glass frit melts and the functional material sintered. The thickness of the SnO_2 thick film was found to be ~ 15 μm.

The structural properties of the SnO_2 thick films were investigated using X-ray diffraction (XRD) technique. The X-ray diffraction patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having Cu K_α (λ = 0.1542 nm). Scanning electron microscopy (SEM) was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (U.K.). The thickness of the SnO_2 thick film was measured by a light section microscope (Nikon Optical Microscope, M44).

The SnO_2 thick films were used as the sensing elements. The electrical contacts were fixed 1cm apart on the surface of the SnO_2 thick films with the help of silver paste to form sensing element. The gas sensing studies were carried out using in a static gas chamber to sense the Carbon Mono Oxide (CO) in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensing element. The known volume of the CO was introduced into the gas chamber pre-filled with air and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured by using a simple two probe configuration, before and after exposure to CO using a sensitive digital multi meter (METRAVI 603). The sensitivity (S) of the sensing element is defined as:

$$S(\%) = \frac{R_a - R_g}{R_g} \times 100$$

where R_a and R_g are the resistance values of the sensor element in air and in the presence of CO, respectively.

3. Results and discussions

The XRD pattern of the SnO_2 thick film is shown in Fig.1. It indicates the diffraction peaks at 2θ values of 27°, 34.2°, 52.2°, 55.2°, 61.6°, 65.2°, 66°, 71.8°, 78.8°, 81°, 84.2°, 89.2°, 90.4°, and 95.6° which reveal the formation of the SnO_2 film (JCPDS data card). The average grain size calculated by using D and S equation as follows

$$d = 0.9 \lambda / B \cos \theta$$

where λ, B and θ are the X-ray wavelength (1.5405 Å for Cu Kα), the full width at half-maximum of the diffraction peak (FWHM) and Bragg diffraction angle, respectively. The average grain size is found to be ~ 12 nm.

The surface morphology of the screen printed SnO_2 thick film deposited on the alumina substrate is as shown in Fig 2(a). It clearly shows the surface of SnO_2 films is porous and forms a channel with the bundles of grains. Therefore, the screen printed SnO_2 film can adsorb atmospheric oxygen very easily and its amount depends on the area of the exposed surface of the film. The grains observed on the surface having granular structure. The channel formation on thick film occurs due to the softening of the glass frit as a permanent binder. The EDX analysis [Fig.2 b] indicates that the matrix contains only Sn and O with the atomic percent of 57.87 % and 42.13 % respectively. This suggests that the screen printed SnO_2 thick film is non-stoichiometric.

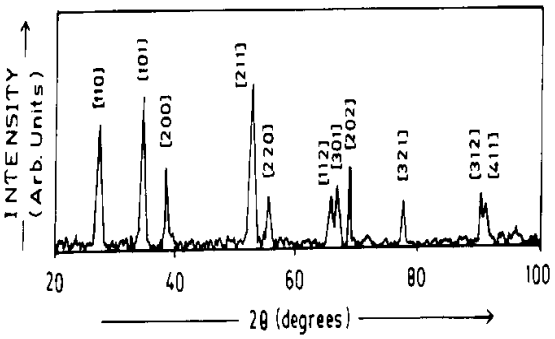
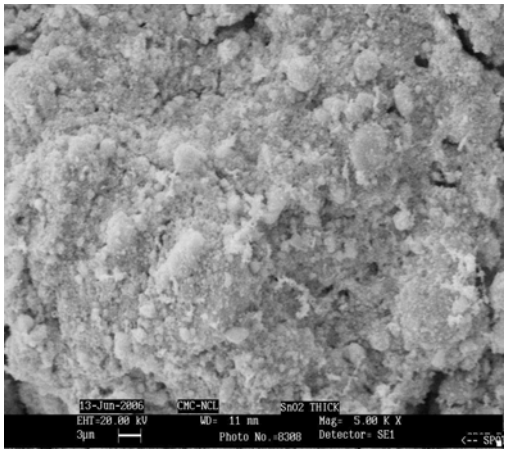
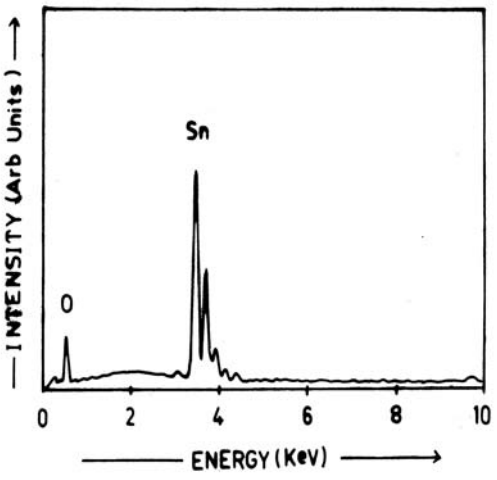


Fig. 1. X-ray diffraction pattern of the SnO_2 thick film.



a



b

Fig. 2. (a) SEM image and (b) EDX spectrum of the screen printed SnO_2 thick film on the alumina substrate.

The dependence of the sensitivity of the SnO_2 thick film towards 50 ppm CO gas on the operating temperature

is shown in Fig.3. It is observed that the sensitivity of the SnO_2 thick film to 50 ppm CO gas slowly increases from ~ 25 % to ~ 39.4 % as the operating temperature is raised from 200 to 250 ^oC. Beyond 250^oC, the sensitivity suddenly increases to a maximum value and it is found to be ~ 84.2 % at 300^oC. With further increase in the operating temperature, the sensitivity significantly decreases and it is observed to be ~ 54.5 % at 350 ^oC and then ~24.3% at 400^oC. Thus, the sensitivity to 50 ppm CO gas is maximum at 300^o C and it is found to be ~ 84.2%. The response time of the SnO_2 thick film to CO gas was nearly 3 to 5 sec and the recovery time was found to be 8 to10 sec.

The CO gas sensing mechanism based on the changes in the resistance of the SnO_2 thick film, which is controlled by the CO gas species and the amount of the chemisorbed oxygen on the surface [18, 30-32]. As mentioned earlier, the screen printed SnO_2 thick film is porous and non-stiochiometric in nature. Therefore, the oxygen chemisorption centers viz. oxygen vacancies, localized donor and acceptor states and other defects are formed on the surface during synthesis. These centers are filled by adsorbing oxygen from air. The SnO_2 film interacts with the oxygen, by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O^{2-} or O^-. The reaction kinetics may be explained by the following reactions [18, 30-33]

$$O_2(gas) \Leftrightarrow (absorbed)$$
$$O_2(absorbed) + e^- \Leftrightarrow O_2^-$$
$$O_2^- + e^- \Leftrightarrow 2O^-$$

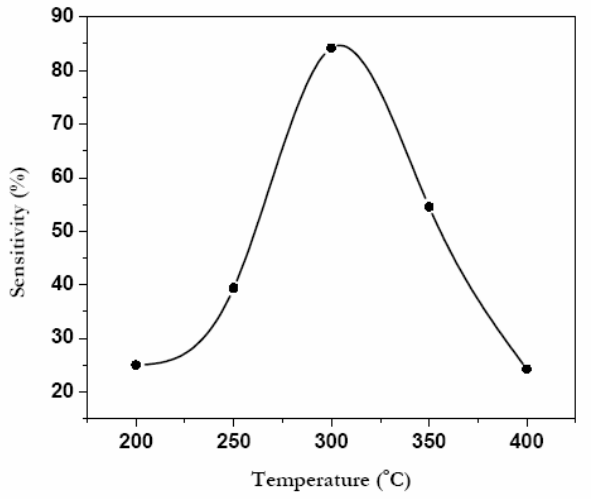
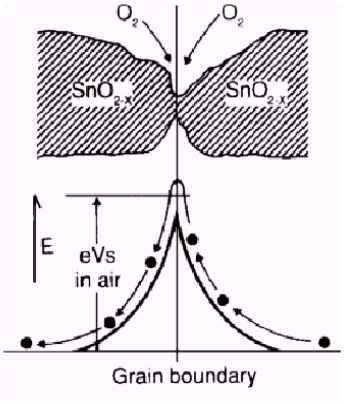


Fig. 3. Relationship between operating temperature and the sensitivity of screen printed SnO_2 thick film for 50 ppm CO in air.



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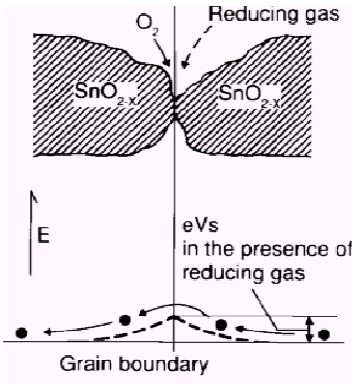

b

Fig. 4. Model of inter grain potential barrier (a) In the absence of reducing gas (b) In the presence of reducing gas.

These adsorbed oxygen species induce a subsequent potential barrier at a grain contact and a resistive depletion layer is formed, which determines most of the sensor resistance. Fig. 4. shows model of inter grain potential barrier for n-type oxide semiconductor (typically of SnO_2).

When the screen printed SnO_2 thick film is exposed to reducing gas like CO, the adsorbed oxygen is removed by oxidation of the gas and the captured electrons are injected into the conduction band. This results in the reduction of potential barrier height and a decrease in the resistance of the sensor elements [18, 30-34]. The overall reaction of the CO gas with the chemisorbed oxygen can be explained as follows [29]

$$2\,CO + O_2^- \rightarrow 2\,CO_2 + e^-$$
$$CO + O^- \rightarrow CO_2 + e^-$$

When the screen printed SnO_2 thick film is heated at a temperature of 200-250 ^oC, the reaction products do not desorb from the film surface. Nevertheless, they cover the sensing sites on the surface of the film which prevents the further reaction of the CO gas with chemisorbed oxygen. Subsequently, no appreciable change in the resistance of

the film is observed. At 250°C, the reaction product may be slightly desorb, allowing some more reaction of CO gas with chemisorbed oxygen.

At temperature 300°C, the reaction products may get desorbed immediately after their formation providing the maximum opportunity for new gas species to react with the sensing sites on the film surface. Thus, the CO gas reacts most effectively with chemisorbed oxygen at such particular temperature, which results in the significant decrease in the resistance of the film. Therefore, the maximum sensitivity of the SnO_2 thick film towards CO gas is expected at such particular temperature.

At higher temperatures (greater than 300°C), the amount of the adsorbed oxygen is less and therefore, a lesser amount of ionic species are formed. Therefore, in presence of the CO gas, the probability of the reduction reaction of the gas with chemisorbed oxygen is less, which results into a very small change in resistance of the film at higher temperatures. Therefore, the screen printed SnO_2 thick film operates as a sensing element to the CO gas only within a specific temperature window. In the present case, the optimum operating temperature for the SnO_2 thick films is 300°C at which the sensor sensitivity attains its maximum value.

The relationship between the sensitivity of the SnO_2 thick film and the CO gas concentration for an operating temperature 300 °C is shown in Fig. 5. It is observed that the sensitivity increases linearly up to 75 ppm of the CO gas concentration and after that it saturates. The linear relationship between the sensitivity and the CO gas concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the CO. The low gas concentration implies a lower surface coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in the gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at an operating temperature of 300°C for the exposure of 75 ppm of CO gas. It is obvious from Fig. 5 that not only temperature but also the CO gas concentration plays a role in determining the sensitivity of the SnO_2 thick film. The SnO_2 thick film is able to detect up to 25 ppm for CO gas with reasonable sensitivity at an operating temperature 300°C. The linearity of the sensitivity in the low CO gas concentration range (25-75 ppm) suggests that the screen printed SnO_2 thick films can be reliably used to monitor the concentration of CO gas over this range.

Fig. 6. shows the bar diagram (histogram) indicating the selectivity of the SnO_2 thick film sensor operated at 300°C towards CO gas against CH_4, LPG, H_2. It clearly indicates that the prepared SnO_2 thick film shows maximum sensitivity to CO gas than other gases, i. e. the prepared film shows selectivity towards CO gas. It may be due to maximum number of CO molecules react with adsorbed oxygen species as compared to other gases at 300°C.

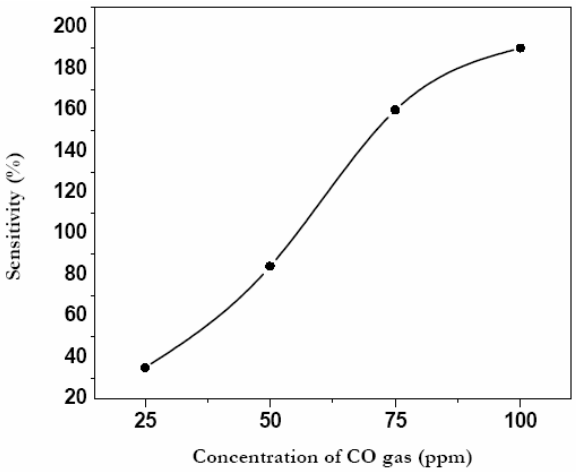

Fig. 5. Dependence of sensitivity on CO gas concentration of the screen printed SnO_2 thick film

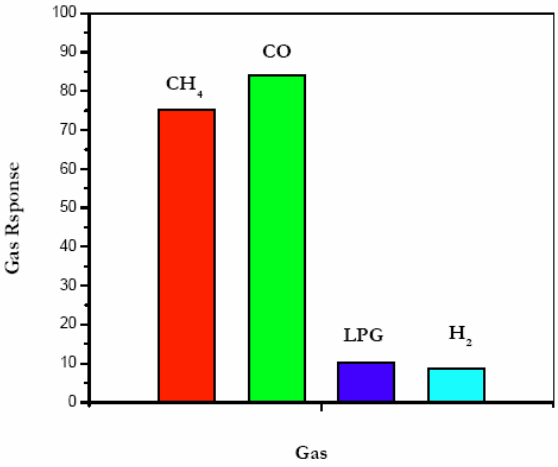

Fig. 6. Histogram of the screen printed the SnO_2 thick film showing highest sensitivity towards CO gas over LPG, CH_4 and H_2.

4. Conclusions

In this work, SnO_2 thick films were prepared by using screen printing method. These thick films were characterized by using XRD and SEM coupled with EDX. The CO gas sensing properties were investigated at different operating temperatures and gas concentrations. The SnO_2 thick films exhibit excellent CO gas sensing properties with the maximum sensitivity ~ 84.2 % at 300°C with fast response and recovery time. Further, it was shown that the screen printed SnO_2 thick films can be reliably used to monitor the concentration of CO over the range (25-75 ppm). The prepared SnO_2 thick films shows selectivity towards CO gas against LPG, CH_4 and H_2 Therefore, this study demonstrated the possibility of utilizing SnO_2 thick films as a sensor element for the detection of CO gas.

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