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Short communication

The influence of electrode metals and its configuration on the response of tin oxide thin film CO sensor

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Abstract

Thin films of tin oxide were deposited by electron beam evaporation. The effects of the electrode materials (Ag, Al, Au and Pt) and different electrode configurations on the CO-sensing of tin oxide thin films were investigated. The Pt and Au electrodes with bottom electrode configuration show much higher response than Ag and Al electrodes. The sensor response and recovery times have also been measured. The films were characterized using X-ray diffraction and X-ray photoelectron spectroscopy. All the films were found to be amorphous. It was found that the CO-sensing properties depend both on the electrode materials and configuration.

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

1. Introduction

Tin oxide based semiconductor gas sensors have been widely used for detection of the environmentally hazardous pollutant gases in general and carbon monoxide gas in particular [1–6]. However, their detecting mechanism is not fully yet established. Depending on the preparation conditions of the sensing layers (physical vapor deposition, chemical vapor deposition, screen-printed and sintered materials) and also on the sensor design (nature and geometry of the electrodes), large differences of behavior concerning gas response and selectivity are observed [7–9]. For screen printed thick film tin oxide CO sensor it has been reported that the electrode materials of silver and gold influences the detection property [8,9]. Since various deposition techniques with their associated parameters yields films of different properties, we explore the optimum condition for the electron beam evaporated SnO_2 thin film sensor in the detection of carbon monoxide by studying dependence of response and response time on the electrode material and configuration.

2. Experimental details

Thin films of tin oxide having thickness of 400 nm 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 under the oxygen partial pressure of 5×10^{-4} mbar. Before deposition, the material was slowly outgassed with a shutter blocking the vapor from the sample surface. For different purposes of film characterization (XPS, XRD), 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 nm/s was controlled by a quartz crystal thickness monitor and rate controller. The source-to-substrate distance was about 45 cm.

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

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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, various metals such as Ag, Al, Au and Pt electrodes of length 7 mm and electrode spacing of 2 mm were deposited on glass substrates by thermal evaporation. After each deposition of electrode layers, the vacuum system was exposed to atmospheric conditions in order to change the mask for deposition of the metal oxide layer (sensing layer). 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.

3. Results and discussion

3.1. Characterization of films

Fig. 1 shows an XPS wide scan spectrum of a tin oxide film. 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 2.18 (as-deposited) and 1.85 (annealed in air at a temperature of 400 °C). For the as-deposited 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 films [10–11]. 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. The uncertainty in the measurement of the atomic ratio O/Sn was about 10%.

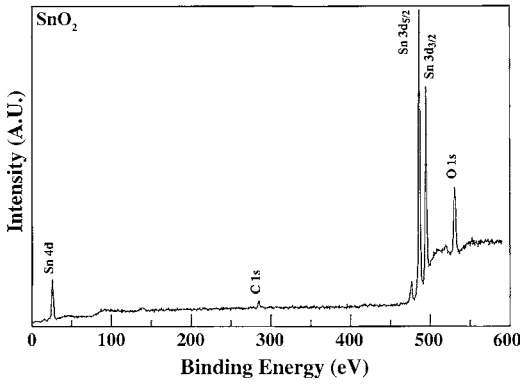

Fig. 1. A wide scan X-ray photoelectron spectrum of tin oxide film.

The XRD 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.

3.2. CO gas-sensing properties

The CO gas-sensing properties of the oxide films were studied by measuring the electrical resistance of the film in air (R_{air}) and the same at different concentrations of CO in dry air (R_{CO}). In the case of CO gas, we noticed a reduction in electrical resistance as in most of the n-type metal oxide semiconductors [6]. For such gases, showing reduction in electrical resistance, the response S is simply defined as $\Delta R/R_{air}$ where $\Delta R = R_{CO} - R_{air}$. The response measurements for sensors with various electrode materials and configurations were carried out for a set of sensor temperatures and it was observed that for any given temperature, the choice of electrode material and configuration has a strong effect on the response. The sensor was placed directly on a hot copper disc, heated with nichrome wire heater, and the temperature was controlled by applied voltage. In order to stabilize the physical parameters, all the films were thermally annealed at 400 °C under atmospheric conditions for 4 h prior to the measurements.

The response measurements of SnO_2 film with three different electrode configurations: bottom, top, and top-bottom

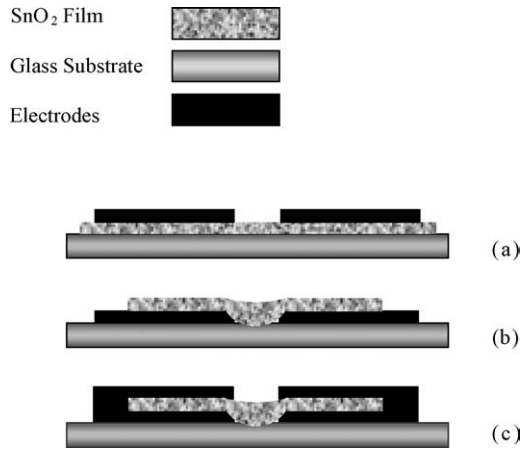

Fig. 2. Schematic of electrode configurations: (a) top-electrodes, (b) bottom-electrodes and top-bottom electrodes.

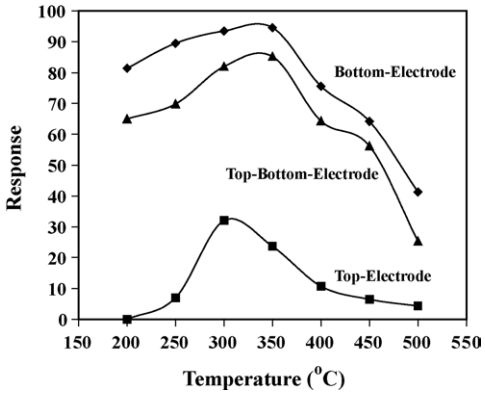

Fig. 3. Effects of electrode configurations (of Fig. 2) on the response of a SnO_2 sensor. Au-films were used as electrodes and CO concentration was 50,000 ppm.

(as sketched in Fig. 2) were carried out for Au, Pt, Ag, and Al metals, as a function of temperature, with a CO concentration of 50,000 ppm. Fig. 3 depicts the response dependence on electrode configuration for Au and it is quite clear that the bottom electrode configuration is the most sensitive; similar results were obtained for the other metals. It has been observed that when the metal film is deposited on the top (air side) of oxide films, the metal diffuses inside the sensing layer of the oxide films and thereby increases the conductivity of the oxide films [12–13] and hence lowers the sensor response for the top configuration. On the other hand, with oxide film on the top such diffusion does not take place [12,13]. In addition coupled with diffusion the roughness of the film surface (air side), which is quite inherent for SnO_2 films [14] may also contribute in lowering the sensor response. Metal films of Al, Ag, Au, and Pt were used as bottom electrodes and their effect on response of SnO_2 sensor was studied. Fig. 4 shows the responses of sensors with various electrodes in bottom configuration, as a function of temperature for 50,000 ppm

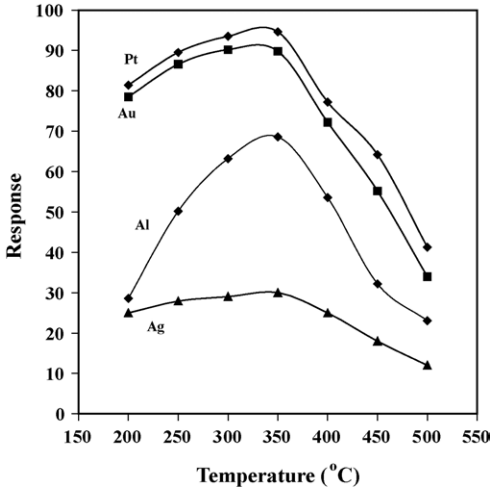

Fig. 4. Effects of electrode metal on the response of a SnO_2 sensor. Thin films of Al, Ag, Au, and Pt were used as bottom electrodes and the CO concentration was 50,000 ppm.

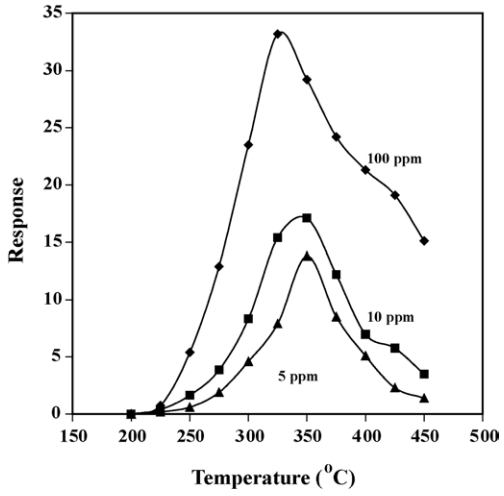

Fig. 5. Response as a function of CO-concentration for a SnO_2 sensor using the Optimum conditions: bottom Pt electrodes.

of CO. The Pt and Au electrodes show much higher response than Ag and Al electrodes. Metals whose oxidizing temperatures are less than the operating temperature of the sensors are avoided to use as electrodes due to the formation of thin oxide layer between the sensing layer and metal electrodes. Al and Ag forms the oxide films even at room temperature when exposed to the atmosphere while changing the mask for deposition of sensing layer. This oxide formation reduces the response of the gas sensor thereby limiting the use of Al and Ag as bottom electrodes. Moreover, response as a function of temperature for different CO-concentrations for a SnO_2 sensor was also studied and is shown in Fig. 5. It is quite clear from Fig. 5 that the CO-concentration as small as 5 ppm can easily be detected, provided the optimum conditions such as bottom electrode configuration and Pt as electrode material are met. Finally, Fig. 6 illustrates the dynamic resistance response of the sensor, when 100 ppm of CO mixed in dry air was directed on the sensor through a needle valve. It is clear that it takes less than 8 s for the sensor resistance to drop to its minimum value (peak response) and the sensor recovery time (the time it reaches 10% of the initial value) is about 300 s.

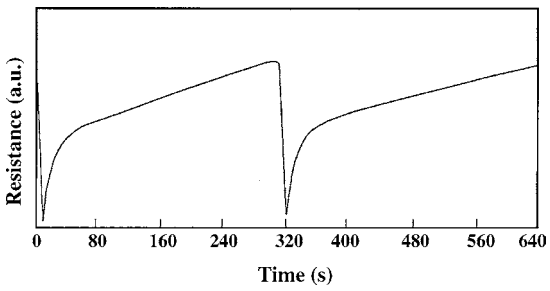

Fig. 6. Resistance response in time of SnO_2 sensor for 100 ppm of CO, measured at a temperature of 350 °C and Pt bottom electrodes.

4. Conclusion

The effects of the electrode metals and configuration on the CO sensing of tin oxide thin films were investigated and it was found that the CO-sensing properties depend both on the electrode metals and configuration. In the case of electrode metals, Ag and Al showed relatively less response, whereas Au or Pt electrodes, exhibited much higher response. Between Pt and Au, there is not much difference in terms of their response, however using Au as an electrode material could be more economical. The dependence of response on electrode configurations showed that the bottom electrode configuration exhibited much more response than the top configurations. The lower detection limit with the optimum configuration of Pt bottom electrodes, outlined in the present work is as low as 5 ppm and the response time is as fast as 8 s.

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