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Full Paper

Biasing Voltage Dependence of Sensitivity of Electron Beam Evaporated SnO_2 Thin Film CO Sensor

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Abstract: Thin films of tin oxide were deposited by electron beam evaporation. The effects of the sensor biasing voltage and film thickness on the CO-sensing of tin oxide thin films were investigated. The films were characterized using X-ray diffraction and X-ray photoelectron spectroscopy All the films were found to be amorphous. The current-voltage characteristic of the sensor in air has shown that semiconductor-metal interface forms Schottky barrier. It was found that the CO-sensing properties depend on the sensor biasing voltage and film thickness. For lower biasing voltages the sensitivity was much higher than for the higher voltages. It was found that the sensitivity of the films to CO increased with the film thickness.

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. Film parameters that are widely known to affect the sensing properties of a thin film are surface roughness, stoichiometry, grain size, structure (amorphous or polycrystalline), and porosity [1-6]. Furthermore 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]. More recently while studying the effects of the electrode metals and configuration on the CO sensing of tin oxide thin films it was found that the CO-sensing properties depend both on the electrode metals and configuration [10]. Moreover while studying 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 it was shown that the CO-sensing properties strongly depend on the film thickness and preparation conditions [1]. Although various parameters of SnO_2 thin film CO sensor has been studied thoroughly in the past, however nothing or very little has been published on the dependence of electron beam evaporated thin film SnO_2 CO sensor on the sensor biasing voltages. Therefore, the aim of the present work was to study the dependence of thin film SnO_2 CO sensor sensitivity on the sensor biasing voltages.

2. Experimental Details

Thin films of tin oxide having thicknesses ranged from about 200 to 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. In the preparation of the films, oxygen was readmitted to raise the pressure of the coating chamber to 5×10^{-4} mbar. 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 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 K_α (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 K_α radiation (1.54 Å). The films deposited on BK7 glass were used for the XRD analysis. The 2θ range studied was 0-80^o. The 2θ step and step acquisition time were 0.02^o and 1.00 s, respectively.

The resistances of the films were determined from the measurement of the current passing through the sample at different bias voltages. The measurements were done in air and air-CO mixture, in the temperature range 25-500 ^{o}C. The thicknesses of the films ranged from about 200 to 400 nm. 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 ^{0}C for 4 hours under atmospheric conditions with the aim to stabilize their physical parameters.

3. Results and Discussion

3.1 Characterization of films

The X-ray 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 ^{0}C had no effect on the nature of the diffraction patterns.

Figure 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 ^{0}C).

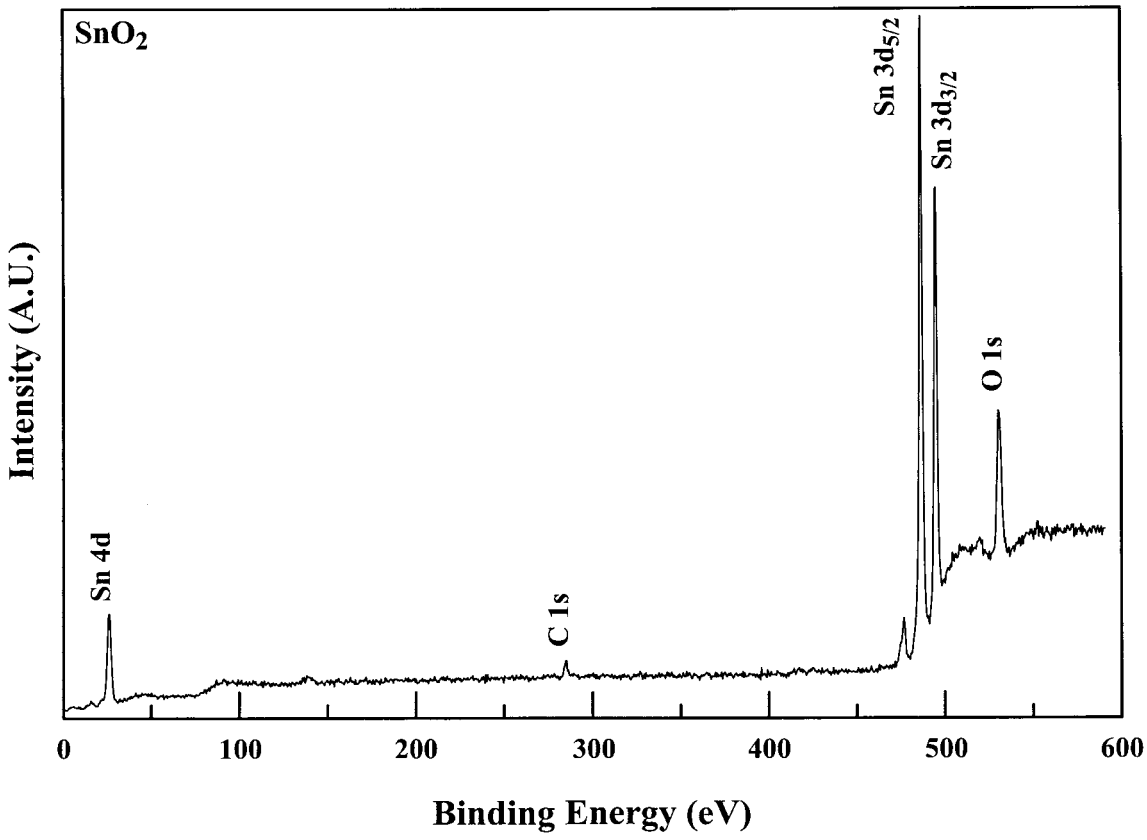

Figure 1. A wide scan x-ray photoelectron spectrum of tin oxide film.

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 [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%.

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 $\Delta R/R_{air}$ where $\Delta R=R_{air}-R_{CO}$. The sensitivity was measured as a function of sensor temperature and sensor biasing voltages. 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 Sensitivity (S) measured at a given temperature, in addition to other film preparation conditions (films prepared with or without the presence of oxygen environment during deposition, film thickness, porosity, electrode metals and configuration [1, 10]) also strongly depends on the sensor biasing voltage. Before starting with the measurements the films were thermally annealed at a temperature of 400 ^{0}C for 4 hours under atmospheric conditions with the aim to stabilize their physical parameters.

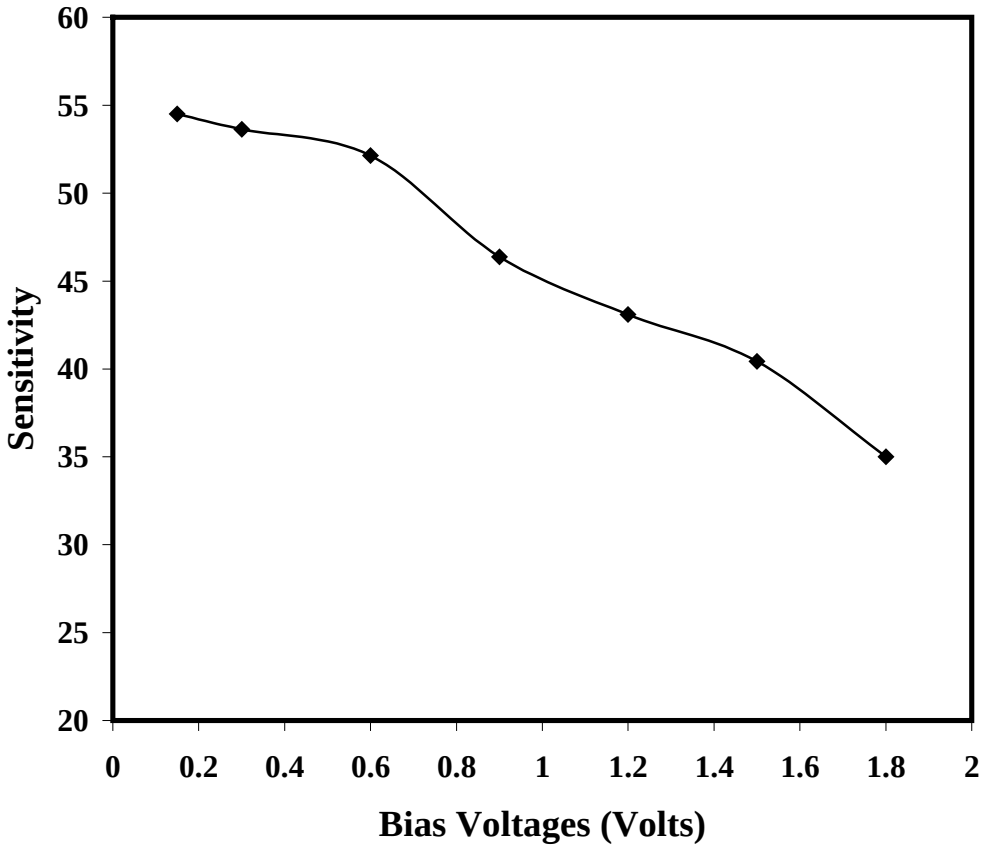

Figure 2. Sensitivity as a function of biasing voltage for SnO_2 sensor of thickness 200 nm, CO concentration of 1000 ppm and temperature of 350 ^{o}C.

Figure 2 shows sensitivity dependence on the sensor bias voltage for SnO_2 sensor of thickness 200 nm with CO concentration of 1000 ppm at temperature of 350 ^oC (optimum operating temperature of SnO_2 CO sensor [1, 10]). Figure 2 depicts that there is a significant decrease in sensitivity as the biasing voltages is increased. For the lower biasing voltages the sensitivity is almost 50 percent higher than that of higher biasing voltages. Similar results were observed for other film thicknesses of 180 nm, 300 nm and 400 nm and temperatures of 300 ^oC and 500 ^oC.

Figure 3 shows current voltage characteristics of SnO_2 film of thickness 200 nm in air at 350 ^oC. It is clear from the Figure that the current-voltage relationship is non-linear (non-Ohmic). Similar non Ohmic trend was observed when a resistance-voltage characteristic was studied for SnO_2 film of 200 nm thickness and at the temperature of 350 ^oC. The non-linearity of the current-voltage-resistance characteristics in Figures 3 and 4 clearly show that the semiconductor-metal interface forms Schottky barrier.

It is known that thick films gas sensor while sensing CO, utilizes the presence of the Schottky barrier. First oxygen from the ambient is adsorbed on the exposed surface of the sensor, extracts electron from the material to form O^-. When the sensor is exposed to a reducing gas like CO, the adsorbed CO reacts with the adsorbed O^- and releases the trapped electron back to the conduction band, and thereby lowering the barriers height and resistance.

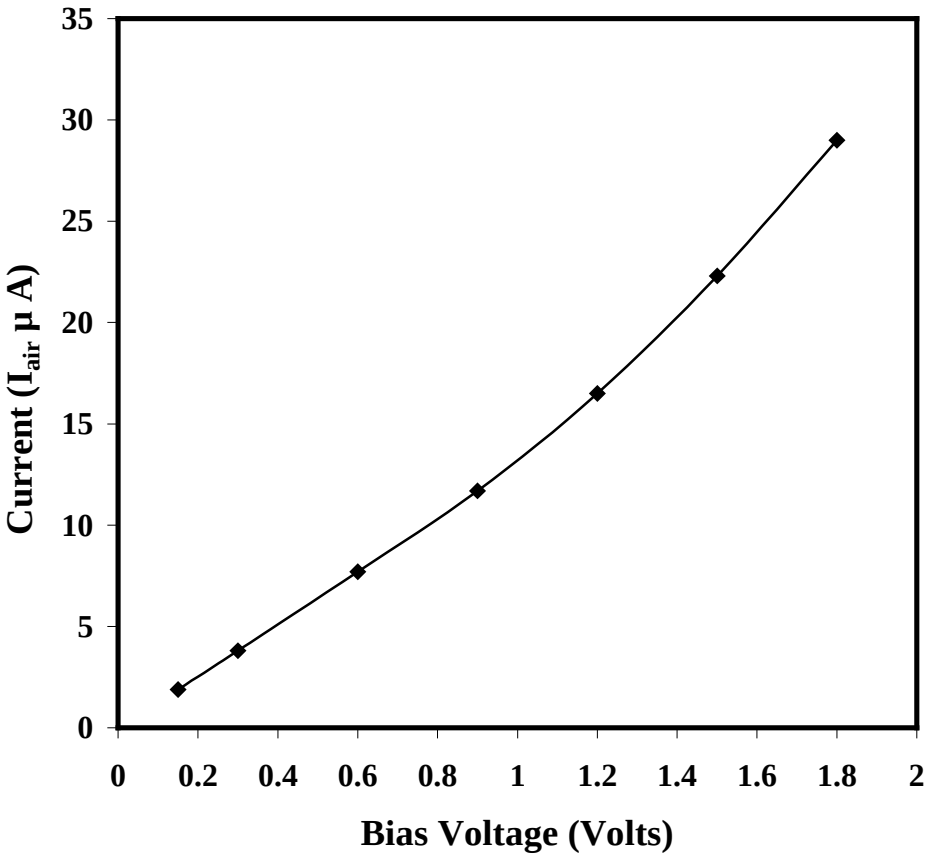

Figure 3. Current voltage characteristics of SnO_2 sensor in air at 350 ^oC for film thickness of 200 nm.

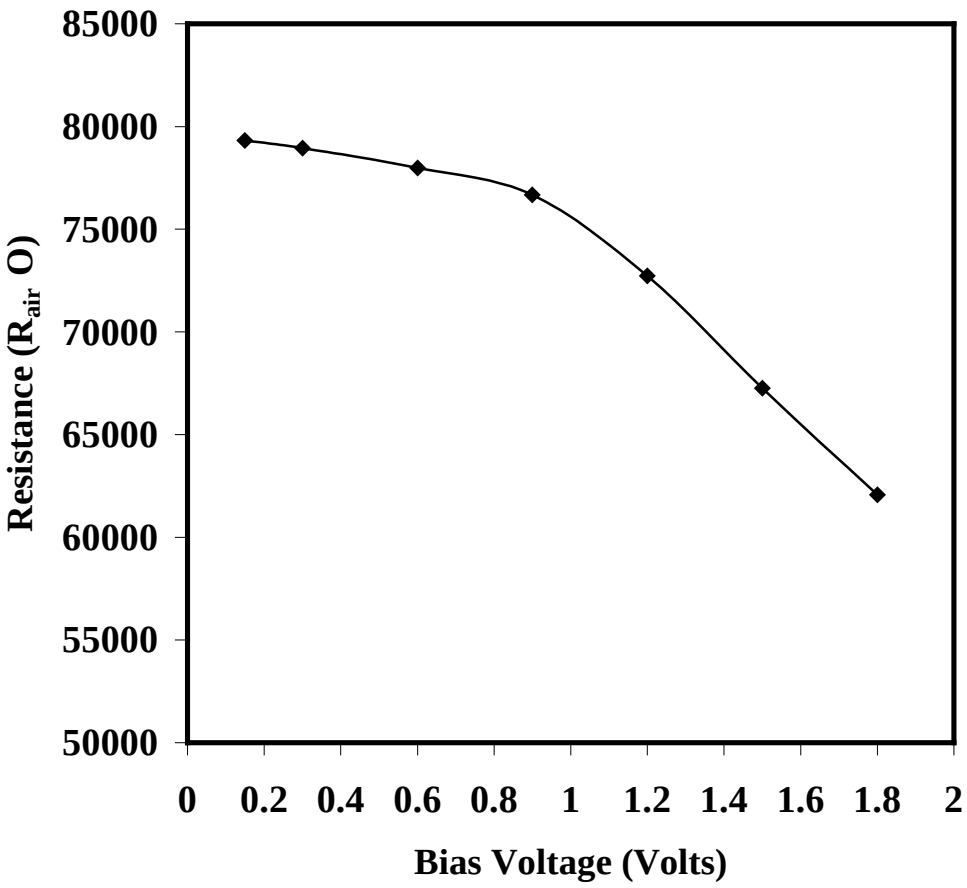

Figure 4. Variation of SnO_2 sensor resistance in air with bias voltages at 350 ^oC for film thickness of 200 nm.

This Schottky barrier controlled conduction mechanism [15-16] is applied for thick film SnO_2 and TiO_2 based CO sensors for temperatures of approximately 500 ^oC. In the present case also, Schottky barrier controlled conduction mechanism could be attributed to the sensing behavior of SnO_2 thin film sensor. Moreover, the change in the sensitivity with biasing voltage could be attributed to the influence of applied voltage in altering Schottky barrier.

Figure 5 shows the sensitivity as a function of operating temperature for the tin oxide films of different thickness. It was found that at a given operating temperature the sensitivity 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 [1]. Increase in the sensitivity for CO with thickness has been observed in thin films of HfO_2 [13]. Moreover, this observation may also find a support from a recent work of Becker et al [14] where they studied gas-sensing properties of thin (thickness 50 – 300 nm) and thick (15000 – 80000 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.

Conclusions

The effects of the biasing voltages on the CO sensing of tin oxide thin films were investigated. The current-voltage-resistance characteristic of the sensor in air has shown the formation of Schottky

barrier at semiconductor-metal interface. It was found that the CO-sensing properties depend strongly on the sensor biasing voltages. For lower biasing voltages the sensitivities were much higher (almost 50%) than the higher biasing voltages. The sensitivity of the films increases with thickness of the film.

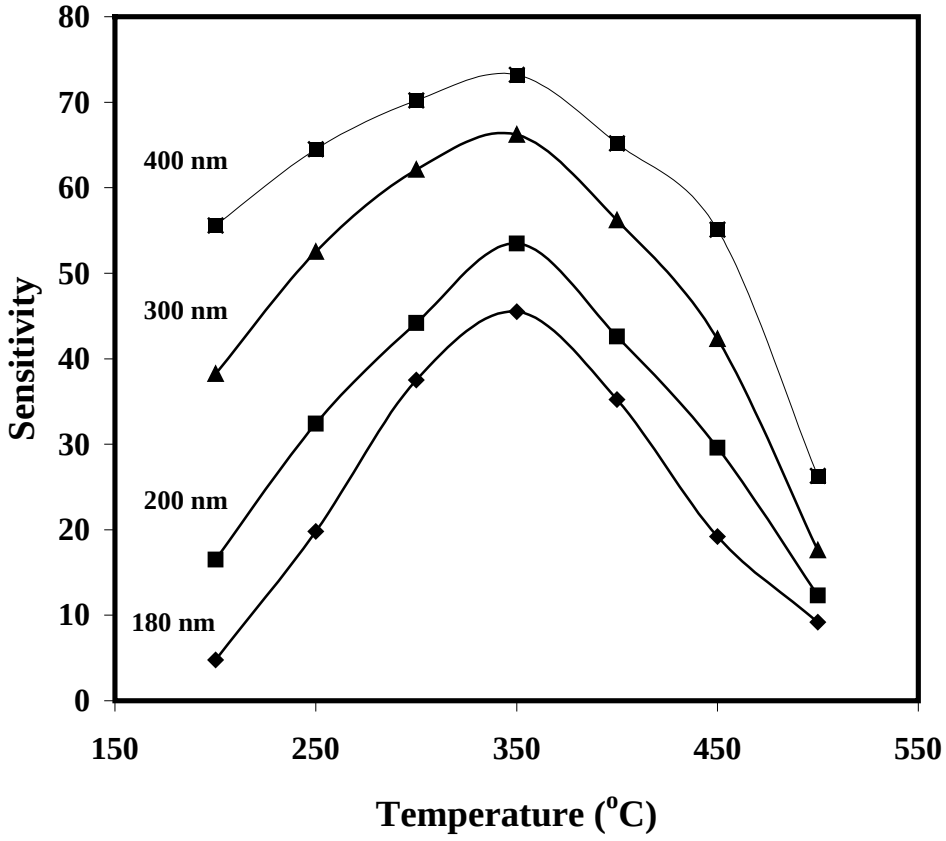

Figure 5. Effects of film thickness of a SnO_2 sensor on its sensitivity. The CO concentration was 1000 ppm and basing voltage was 0.2 volts.

Acknowledgments

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