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The effect of pressure and temperature on the conductivity and sensitivity of SnO_2/Pt based gas sensors

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Abstract The temperature dependence of conductance of SnO_2 thin film (doped with 10 nm Pt) gas sensors is obtained in the temperature range 300K to 700K at different partial pressures of NH_3 and CO in nitrogen. The measurements are carried out using different heating and cooling rates. The proposed model takes into account the dependence of film conductivity on both the partial pressure and environment-temperature. The sensor-sensitivities were studied in (10^{-4} vacuum mbar), in air and in N_2. The sensitivities to NH_3/N_2 and CO/N_2 gases were studied in the temperature range 313 to 673K with different ambient temperatures and pressures. The best sensitivity, stability, and optimum work temperature were obtained with CO/N_2 at a pressure ~ 100 mbar and ambient temperature 433K.

Keywords Thin films, conductivity, gas sensors

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1. Introduction

Tin oxide based films are widely used as gas sensors due to their high sensitivity in the presence of small amounts of some gases, namely carbon monoxide. Tin oxide is a wide band gap (3.6 eV) n-type semiconductor, whose conductivity is due to oxygen vacancies [1]. The addition of small amounts of noble metals such as Pd, Pt, Ag to SnO_2 can promote gas sensitivity and selectivity. To explain why additives lead to the increase of selectivity, two possible mechanisms were proposed [2]. One is chemical sensitisation, the other is electronic sensitisation. The chemical sensitisation is mediated by the direct exchange of electrons between the semiconductor and metal additives [3]. The electronic sensitisation is due to transfer from one particle to the next across the gaps. The doping of SnO_2 with Pt reduces, in particular, the optimum operating temperature for CO. On the other hand, the doping of SnO_2 with trivalent additives favours the detection of oxidant gases [4, 5].

The aim of this work is to study the effect of both pressure and ambient temperature on the conductivity, sensitivity and stability of SnO_2/Pt thin film gas sensors.

2. Experimental

Synthesis of the material was performed using a rpcess Rheotaxial growth Thermal Oxidation (RGTO) [6, 7] method at Daimler Benz Research Laboratory, Munich, Germany as shown in Figure 1a. Tin is deposited on a silicon nitride membrane kept

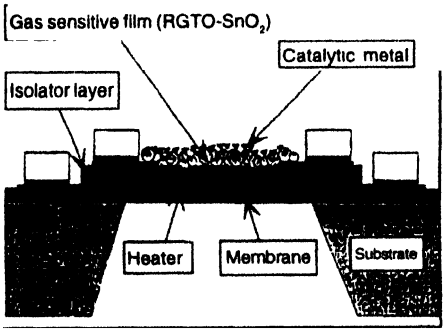

Figure 1(a). Schematic diagram of the sensor containing catalytic metal

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at 290°C, the melting point of the metal which forms microspheres with diameters of 1-6 μm. This is followed by a thermal oxidation step at 793k for 18 h, to transform the tin microspheres into SnO_2 grains of increased size, which thereby provides an electric contact *via* grain boundaries. The tin oxide layers have been activated by physical vapor deposition of 10 nm of Pt at 773K. These layers were annealed at 500°C for 1h in air. The schematic diagram of the measuring set up is shown in Figure 1b. The films were provided with two planer electrodes of gold. An insulated

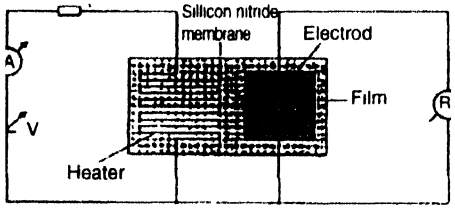

Figure 1(b). Schematic circuit of the device conductivity

Pt heater was located beneath the film. The sensors were mounted inside a vacuum chamber evacuated to $\approx 10^{-6}$ mbar by using a rotary and a turbo pump as shown in Figure 1c. The pressure was recorded by a combitron (CM 330). A gas cylinder was connected to the vacuum chamber by a pipe through which the gas flow to the bell jar was controlled by a spiral spring

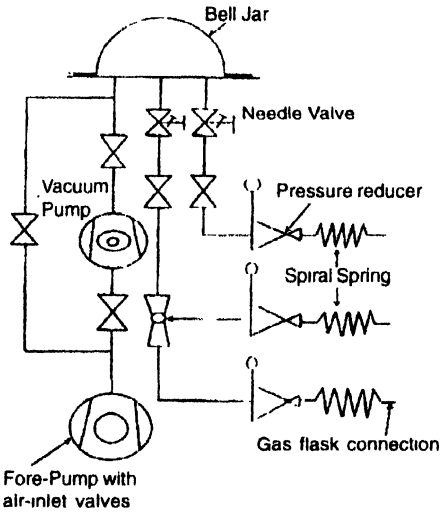

Figure 1(c). Schematic design of vacuum pump

pressure reducing valve and a needle valve. The bell jar was connected electrically with three cables. These cables were connected to the sample holder (used to carry the samples) and insulated heater (used to control the ambient temperature). The insulated heater current was adjusted to give the ambient temperatures at 303, 373 and 433K. A load resistor R_L was connected in series with the device and d.c. voltage was applied to the circuit. The voltage applied to the heater was kept below 11V to avoid the breaking of silicon diaphragms due to the temperature-induced stress. Electrical measurements were performed as follows :

(i) Electrical heating of the silicon nitride membrane,

(ii) Ohmic measurement of the sensitive layer,

(iii) Electric contact between heater and film to avoid electric breakthrough, which destroys the membrane

The measurements were performed to study the effect of pressure on the film conductivity at ambient temperatures 303, 373 and 433 k in NH_3/N_2 (100 ppm) and CO/N_2 (1000 ppm) atmospheres as a function of operating temperature. The SnO_2/Pt film was heated to 670K at first for 10 minutes to clean the samples from water vapor and hydroxyl species adsorbed on its surface.

3. Results and discussion

Tin oxide is an n-type semiconductor. According to Morrison [8, 9], the conductance σ of a pellet of an n-type material at a temperature T may be described by

$$\sigma = \sigma_0 \exp[-eV_s / KT], \qquad (1)$$

where eV_s is the surface potential barrier energy between particles and σ_0 is a factor that includes the bulk intergranular conductance. Figure 2 shows a relation between ln σ as a

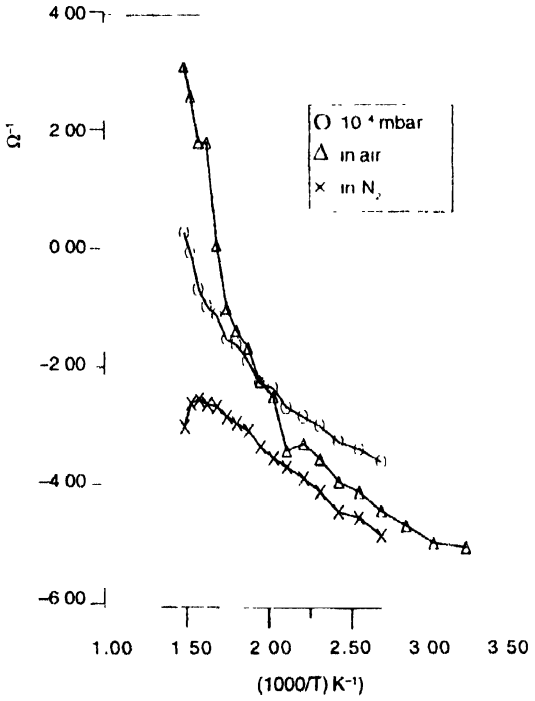

Figure 2. Conductance of SnO_2/Pt thin film as a function of inverse temperature in 10^{-4} mbar, air and N_2.

function of inverse of temperature with three different conditions (in 10^{-4} mbar, air and N_2). We note from the figure that the conductance increases with increasing temperature (semiconducting behaviour). At low temperatures, the conductance values of 10^{-4} mbar curve is higher than those in air and N_2. However at higher temperatures, the conductance values of air curve is higher than that in 10^{-4} mbar and N_2. Figures 3 (a,b,c) show the conductance of SnO_2/Pt film against reciprocal of the working temperature in (100 ppm) NH_3/N_2 under

pressures 10^{-4} mbar, 1 mbar and 100 mbar respectively, at ambient temperatures 303, 373 and 433K. For the gas sensors studied, it may be assumed that the conductance of the sensor consists of

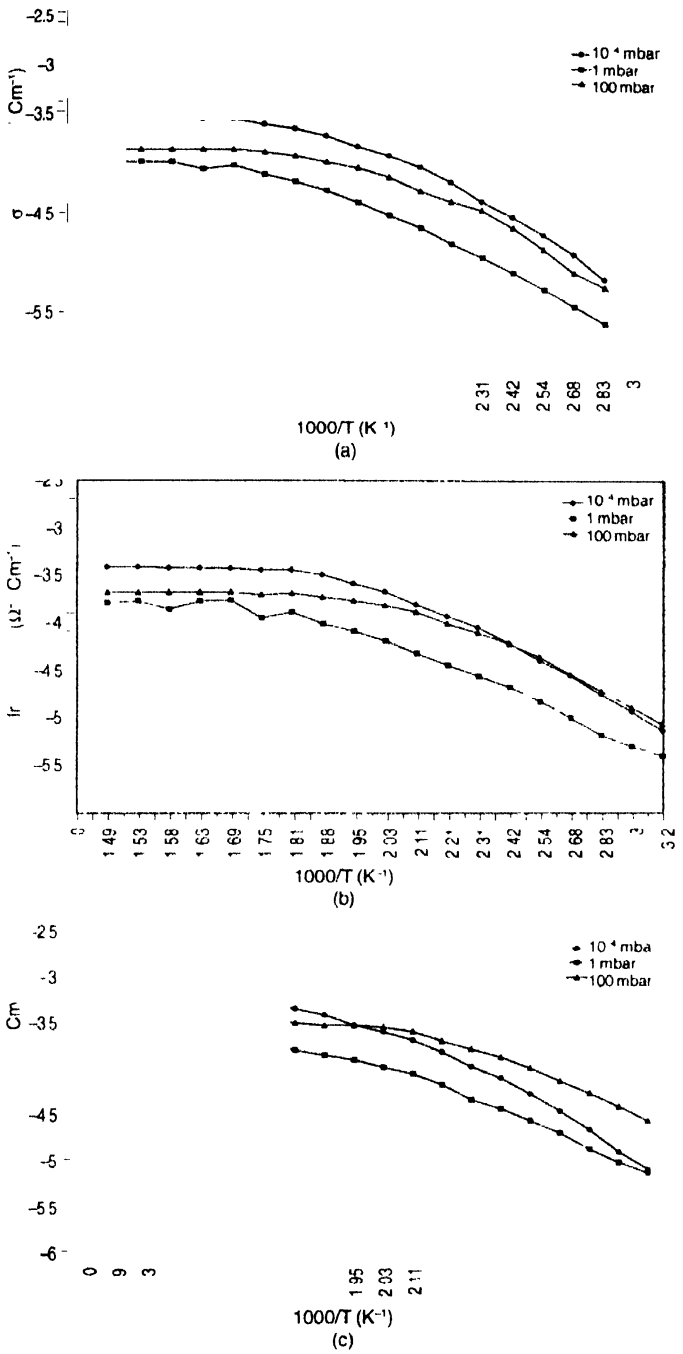

Figure 3. Conductance of SnO_2/Pt thin film as a function of inverse temperature in NH_3/N_2 (100 ppm) at ambient temperatures (a) 303 K, (b) 373 K and (c) 433 K

two parts. The first part is due to bulk conductivity and the second part is due to electron transport mechanisms between the surface particles, which might be due to activated charge carrier creation and tunneling [10]. For electrical conduction to occur, electrons have to be transferred from one particle to the next across the gaps, and it is the mechanism of this transfer that will determine the resistance of the film. For bulk conductivity, it is known that conductivity of tin oxide is due to the existence of a relatively high concentration of conduction electrons resulting from oxygen vacancies. When oxygen is present at a relatively high partial pressure in ambient atmosphere, vacant sites can be occupied by adsorbed oxygen species with simultaneous trapping of conduction electrons [10, 11]. Figure 3a shows the measured conductance values of SnO_2/Pt at different NH_3 partial pressures 10^{-4}, 1 and 100 mbar in N_2 at a temperature 30°C. The observed increase of conductivity with increasing operating temperature might be due to a decrease in the concentration of adsorbed oxygen in all cases. The conductivity at 1 mbar is lower than that at 10^{-4} mbar in the whole tested temperature range. This might be due to increase of adsorbed oxygen (Figure 3a). The conductivity at 100 mbar is higher than that at 1 mbar. This might be the result of Pt surface which seems to be a favoured surface for oxygen adsorption than that of the film surface. This leads to the observed increase of the film conductivity at 100 mbar in the whole temperature range. The conductivity is saturated at a high temperature as shown in Figure 3a. Figure 3b shows the temperature dependence of conductivity for SnO_2/Pt at the ambient temperature 373 K. Also, the conductivity at a pressure of 1 mbar is lower than that at 10^{-4} mbar in the temperature range 300–400K, which might be above due to the suggested tendency of oxygen absorption on Pt surface. Above 400K, the conductivity at 100 mbar is lower than that at 10^{-4} mbar, which may be due to the increasing thermally activated oxygen absorption of the film with increasing operating temperature. Figure 3c shows the conductivity of SnO_2/Pt at ambient temperature 433 K. The conductivity at 1 mbar as previously observed is lower than that of 10^{-4} mbar due to increase of adsorbed oxygen on semiconductor surface. The conductivity at 100 mbar is higher than that at 10^{-4} mbar in the temperature range 300-500K as mentioned before, due to the adsorbed oxygen on Pt surface. The value of the barrier energy as estimated from the above conductance curves on the basis of eq. (1), is found to lie in the range 0.12–0.19 eV.

The temperature dependence of conductivity in the temperature range 300–700 and at diffrent CO partial pressures in nitrogen of SnO_2/Pt gas sensor has also been studied. Figure 4a shows that the conductivity increases with increasing operating temperature at ambient temperature 303 K. When the SnO_2/Pt thin film is exposed to a reducing gas like CO in a N_2 environment, the reaction of CO with the adsorbed oxygen generates CO_2, while the electrons return to the conduction band of the tin oxide and leads to the increased conductivity [12]. The conductivity at 1 mbar is lower than that at 10^{-4} mbar due to the increase of the adsorbed oxygen on the semiconductor surface. At 100 mbar, the conductivity is higher than that at 10^{-4} mbar due to very high sensitivity of SnO_2/Pt for CO [3]. Figure 4b illustrates the conductivity as a function of reciprocal temperature for SnO_2/Pt at environment temperature 373 K. The increase of conductivity with increasing pressure in

the temperature range 300-530K, may be due to the increased effect of either catalytic element Pt or the absorbing gas CO on adsorbed oxygen, which decreases the surface barrier. This effect disappears above 530K. Figure 4c shows the conductance of

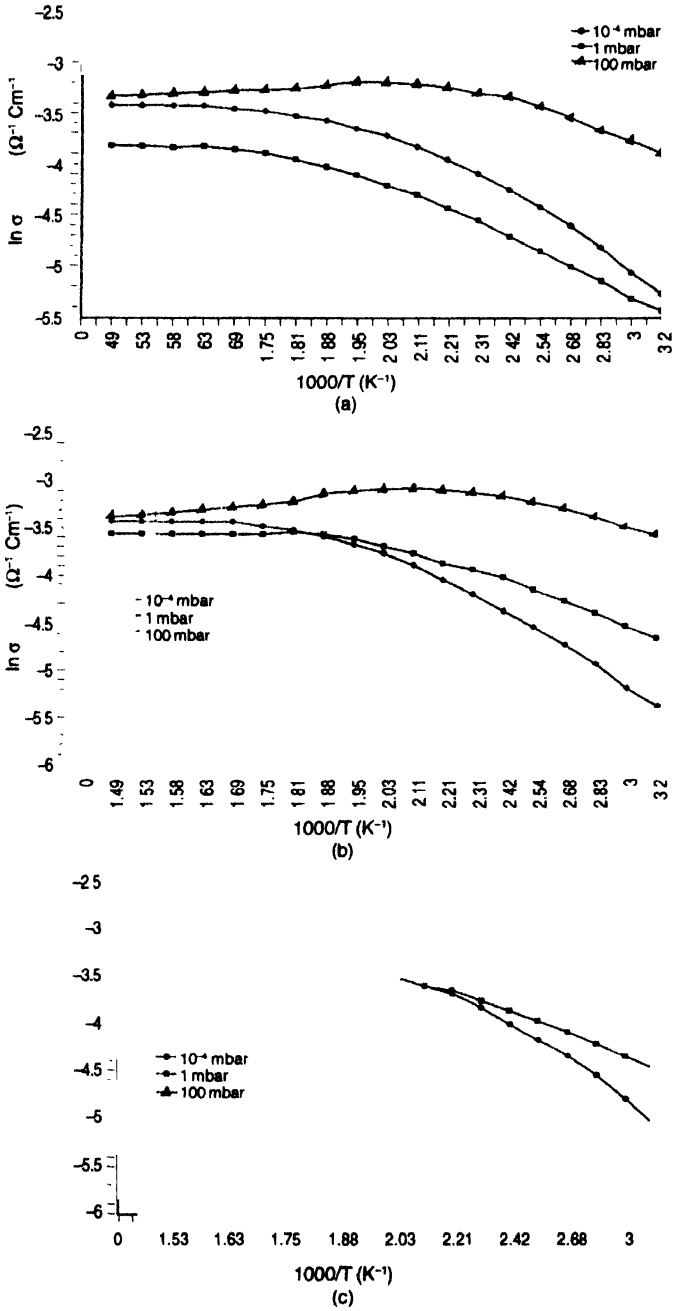

Figure 4. Conductance of SnO_2/Pt thin film as a function of inverse temperature in NH_3/N_2 (100 ppm) at ambient temperature (a) 303 K, (b) 373 K and (c) 433 K.

the Pt-doped SnO_2 film against reciprocal temperature. The conductance at 10^{-4} mbar and 1 mbar increase with the increasing temperature where oxygen is absorbed on the surface of the semiconductor. Moreover, as it is known that the electron surface state is located more deeply in O^- than in O^-_2, it is expected that at low temperature, oxygen is adsorbed in the O^-_2 form, and at higher temperatures, O^-_2 ions change to O^- ion [13]. The conductivity at a pressure of 100 mbar is higher than that at 10^{-4} mbar and 1 mbar in the temperature range 300 to around 460K. At high partial pressure, adsorbed oxygen species exhibit a high concentration, resulting in high carrier concentration and consequently, high bulk conductance [3]. Figure 5 shows the

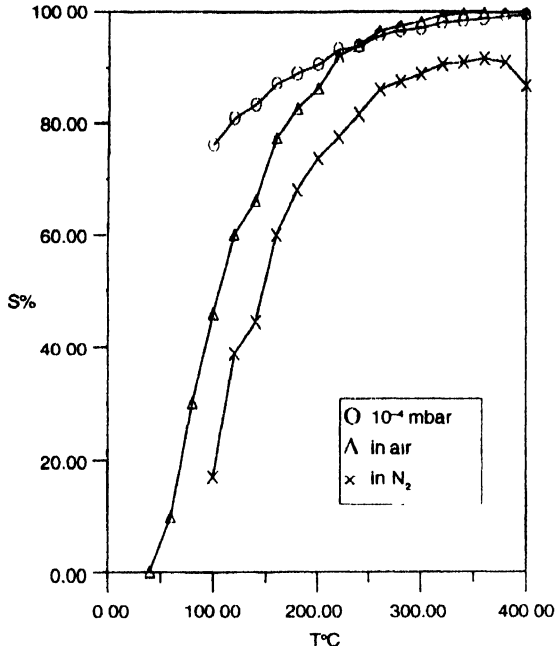

Figure 5. The relation between the sensitivity and the temperature of SnO_2/Pt thin film in 10^{-4} mbar, air and N_2 at ambient temperature 303 K (30°C).

temperature dependence of SnO_2/Pt film sensitivities. In this figure, the sensitivity (S) at the pressure 10^{-4} mbar is higher than that in air and N_2 in the measured temperature range. Also, the sensitivity increases with increasing temperature until 513 K and after this, all conditions have a stable value. The sensitivity reaches a maximum value (100 %) for a pressure of 10^{-4} mbar and in air. The sensitivity to gas (S) is defined as [14]

$$S = \frac{R_i - R_g}{R_i} \quad \frac{\Delta R}{R_i}, \tag{2}$$

where R_g is the sample resistance in the presence of the test gas and R_i is the sample resistance in air. For stabilization, the energized sensors were left in air for 6 h at 873 K in this measurement.

Figures 6 (a, b, c) show, the sensitivity of SnO_2/Pt film against the temperature in NH_3/N_2 (100 ppm) under pressures 10^4 mbar, 1 mbar and 100 mbar respectively, at ambient temperatures 30, 100 and 160°C. It is found that the sensitivity increases with the increasing temperature for all sample pressures. The pressure of 10^{-4} mbar has a maximum stable value of sensitivity (97.7% for ambient temperature = 303 K, 98% for 373 K and 98.3% for 433 K after working temperature 343 K. Figures 7 (a, b, c) show, the variation of sensitivity of SnO_2/Pt film with the working

temperature in CO/N_2 (1000 ppm) under pressures 10^{-4} mbar, 1 mbar and 100 mbar and at ambient temperatures 303, 373 and 433 K respectively. From the figure, we noted that the initial value of the sensitivity (at 313 K working temperature) increased with the increase of the ambient temperatures (303, 373 and 433 K). The pressure of 100 mbar has maximum stable values of sensitivity (98.3% for ambient temperature = 303 K, 98.5% for 373 K and 98.7% for 433 K).

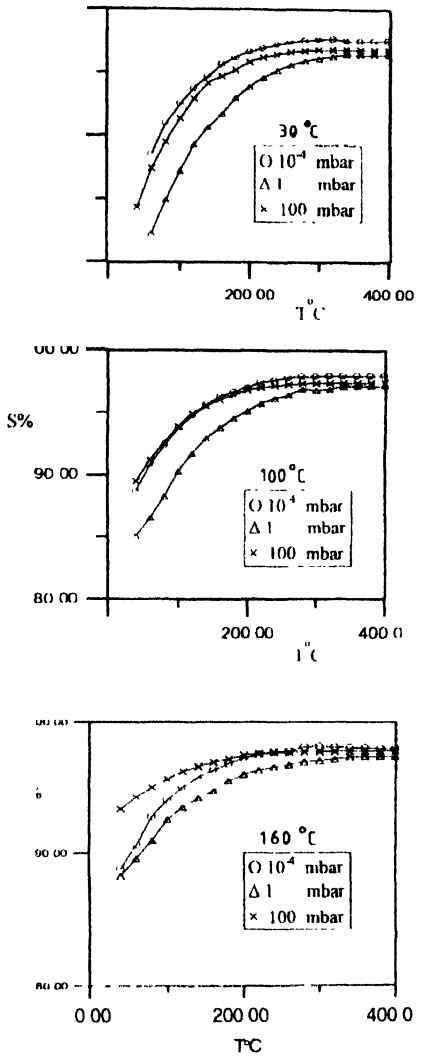

Figure 6. The relation between the sensitivity and the temperature of SnO_2/Pt thin film in (100 ppm) NH_3/N_2 in vacuum ~ 10^{-4} mbar, 1 mbar and 100 mbar, at ambient temperatures (a) 303 K (30°c), (b) 373 K (100°c) and (c) 433 K (160°c).

The increase of conductance in the presence of CO may be explained [15,16] by the reaction between CO and the chemisorbed oxygen on the surface of SnO_2,

$$2\,CO\,(g) + \bar{O}_2 \rightarrow 2\,CO_2 + e. \qquad (3)$$

This reaction reduces the band bending of the intergranular depletion layers and subsequently leads to an increase of sample's conductance.

4. Conclusions

SnO_2 sensors for CO and NH_3 have been developed on nitride substrates using Pt catalysts. In order to explain why the

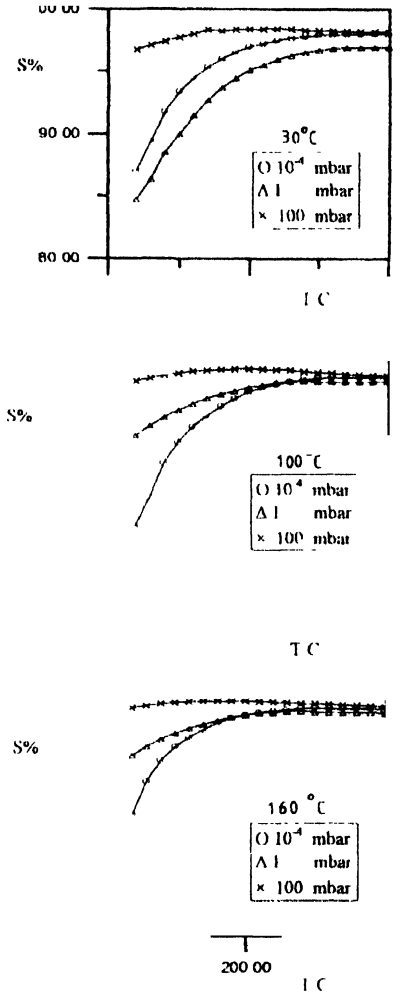

Figure 7. The relation between the sensitivity and the temperature of SnO_2/Pt thin film in (1000 ppm) CO/N, in vacuum ~ 10^{-4} mbar, 1 mbar and 100 mbar at ambient temperatures (a) 303K (30°C), (b) 373K (100°C) and (c) 433K (160°C)

conductivity at 10^{-4} mbar is high at low environment temperature, a semi-empirical model has been proposed. According to this model, film conductance is assumed to consist of two parts. One is the conventional bulk conductance due to the electron transport across semiconducting SnO_2 grains and the second is the surface conductance due to the electronic tunneling between metal particles across surface potential barriers. It has been found that the conductivity increases with increasing both partial pressure and environment temperature.

The results obtained show that SnO_2/Pt film sensors are sensitive to NH_3/N_2 and CO/N_2, but their responses are slightly different. The processes of detection of CO/N_2 are fast; dopants lower the maximum response temperature and they raise the sensitivity at low temperatures (especially at 100 mbar). The sensitivity of the sensors is higher with the CO/N_2 gas at 100

mbar pressure. The stability of the CO/N_2 gas sensors increases with the increasing ambient temperature. Also, the best stability for CO/N_2 gas sensors was obtained at 100 mbar pressure at an ambient temperature of 433 K.

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