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HYSTERESIS BEHAVIOUR OF SENSITIVITY IN CH_4 DETECTION IN AIR USING Sno_2 WITH Pd AS SENSITIZING ADDITIVE

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Abstract. The sensitivity of SnO_2 with Pd as an additive showed a hysteresis behaviour when measurement was carried out as the operating temperature is increasing compared to measurement with decreasing temperature. The sensitivities of the samples that were calculated at the various operating temperatures from 200°C to 430°C were found to be higher when measuring with decreasing temperature. This observed hysteresis in sensitivity is discussed in terms of the type of oxygen species adsorbed on the SnO_2 surface.

Keywords: hysteresis, sensitivity, sensitizing additive, conductance, methane

Abstrak. Kepekaan SnO_2 dengan Pd sebagai bahan tambah menunjukkan sifat histerisis apabila pengukuran dilakukan pada suhu operasi menaik berbanding dengan pengukuran yang dilakukan pada suhu menyusut. Kepekaan sampel-sampel dikira bagi beberapa suhu operasi dari 200°C sehingga 430°C dan didapati kepekaan meningkat apabila pengukuran yang dilakukan pada suhu menurun. Histerisis yang diamati dalam kepekaan ini dibincangkan dalam konteks jenis spesies oksigen yang terjerap di atas permukaan SnO_2.

Kata Kunci: histerisis, kepekaan, bahan tambah pemekaan, konduktans, metana

1.0 INTRODUCTION

Tin (IV) oxide (SnO_2) is non-stoichiometric in that it is deficient in oxygen atoms. Charge neutrality is maintained by the presence of some tin (II) ions (Sn^{2+}) in place of some tin (IV) ions (Sn^{4+}) and these act as electron donors so that the material is predominantly an n-type semiconductor [1]. Due to this sudden interruption in the periodicity of the crystalline lattice, the atoms or ions on the semiconductor surface have incomplete coordination (incomplete number of nearest neighbours) which give them quite different properties from atoms or ions in the bulk. The disturbance of lattice periodicity at the surface creates "intrinsic" localized electronic states. The atoms on the surface, therefore, show increased reactivity towards the components of their fluid surroundings [2]. Pd is an effective oxidation catalyst for CH_4. The addition

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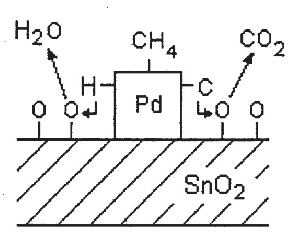
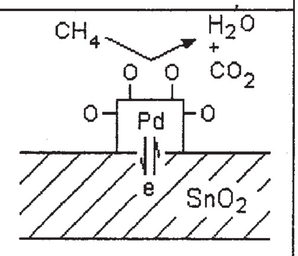
Type	Chemical	Electronic
Model		
Role of noble metal	Activation and spill-over of sample gas	Electron donor or acceptor
Origin of conductivity change	Change of oxidation state of SnO_2	Change of oxidation state of noble metal
Example	Pd-SnO_2	Pd-SnO_2

Figure 1 Model for possible CH_4 detection mechanism by SnO_2 withy a noble metal as catalyst

of Pd to SnO_2, therefore, significantly enhances its sensitivity in CH_4 detection [3]. If Pd particles are present on surface of SnO_2 crystallites, there are several ways in which the catalyst can affect the intergranular contact region of the crystallites and thus the sensor conductance as shown in Figure 1. One of them is Fermi energy pinning by the metal, while another is spillover of species from the metal to the semiconductor [4].

If a pressed pellet of SnO_2 is exposed to air, a higher Shottky energy barrier would develop between adjacent SnO_2 crystallites. This increase in the barrier energy is due to adsorption of oxygen on the surface of SnO_2 [4]. The surface of SnO_2 becomes negatively charged by the adsorption of oxygen molecules or atoms that are ionized at the expense of electrons removed from the bulk of the crystallites. According to Vancu et. al [2] there are three species of oxygen (O_2^-, O^{2-}, and O^-) that can be adsorbed on the surface of SnO_2 when it is heated to operating temperatures in the range of 200°C to 600°C [2]. The former two are adsorbed at lower temperatures and are less reactive than O^-, which is adsorbed at higher temperatures. When such a charged SnO_2 surface is exposed to CH_4, a chemical reaction occurs between the CH_4 molecules and the adsorbed oxygen ions ultimately forming H_2O and CO_2 that are then desorbed. The reaction to form H_2O and CO_2 results in the release of electrons to the solid, thus lowering the potential barrier and increasing the conductance of the sample [5].

2.0 EXPERIMENTAL PROCEDURE

SnO_2 powder (Fluka) and Pd powder (ESPI) were mechanically mixed in the required proportions of (100-x)$SnO_2 \times$ Pd (x = 10 and 15 wt%). The mixed powders were then compressed in a 40 mm die at a pressure of 40 MPa for five minutes. The disc-shaped samples were then sintered in an electric furnace at 900°C for one hour with heating and cooling rates of 20°C per minute. Ten grams batch mixture of SnO_2 and noble metal (Pd) produced a pellet of 40 mm diameter and 2 mm thickness. The pellets were then mechanically cut into $10 \times 10 \times 2$ mm^3 of dimension regular shapes. The sample was next inserted into a sample holder with electrodes that were pressed against the samples by tightening a screw as shown in Figure 2. The sample holder was attached to a probe and then was inserted into the reaction unit of a gas sensor test chamber which was described elsewhere [6].

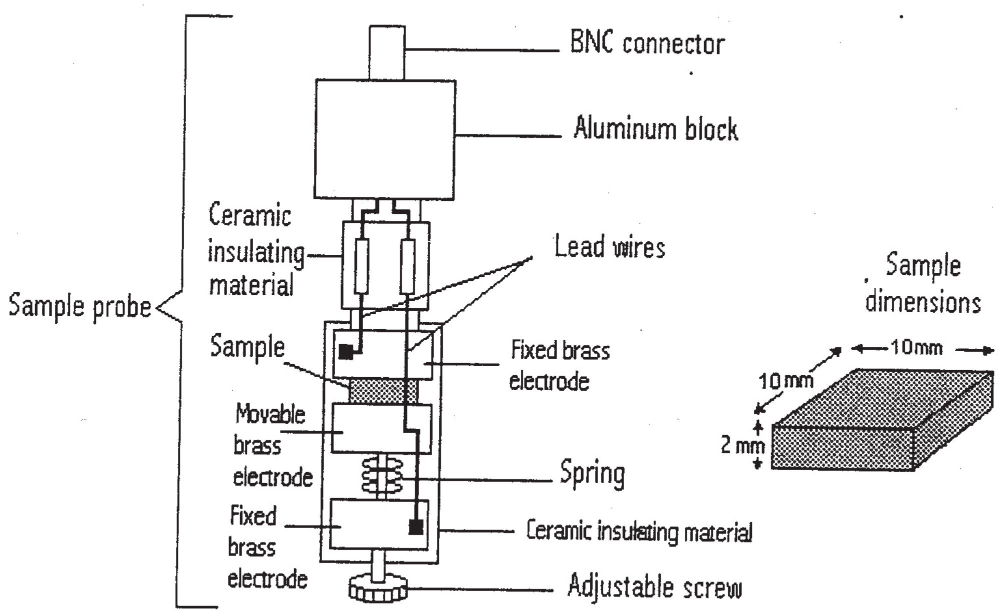


Figure 2 Sensor probe and sample dimensions

The electrical circuit used to measure the output signal is a simple sensor circuit consisting of a sensing element of resistance R_s, in series with a load resistor R_L as shown in Figure 3 [3]. A dc voltage is applied to the combination to provide the current I_s, which drops voltages, V_s and V_L across the sensor and the load , respectively. The output signal was taken as the load voltage, V_L, across the load resistor, R_L. The sensitivity, S, is then calculated from the relation

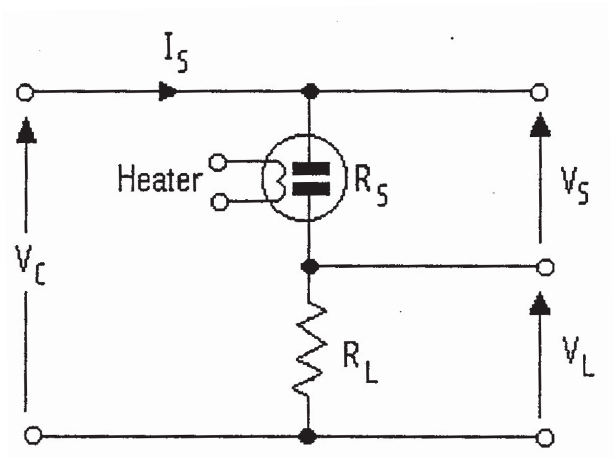


Figure 3 Sensor circuit used for measuring the output signal

$$S = [(G - G_0)/G_0] \times 100\% \quad (1)$$

where G is the conductance in test gas and G_0 is the conductance in synthetic air (<10 ppm moisture).

Commercial gas mixtures of 5000 ppm CH_4 in air and synthetic air were used in the experiments. In addition, other concentrations of CH_4 in synthetic air were achieved by using a flow controller and a gas injection port in a simple gas mixing system.

3.0 RESULTS AND DISCUSSION

Figure 4 and 5 show the sensitivity of SnO_2 samples with 10 and 15 wt% Pd, respectively, sintered at 900°C for 1 hour as a function of operating temperature from 200°C

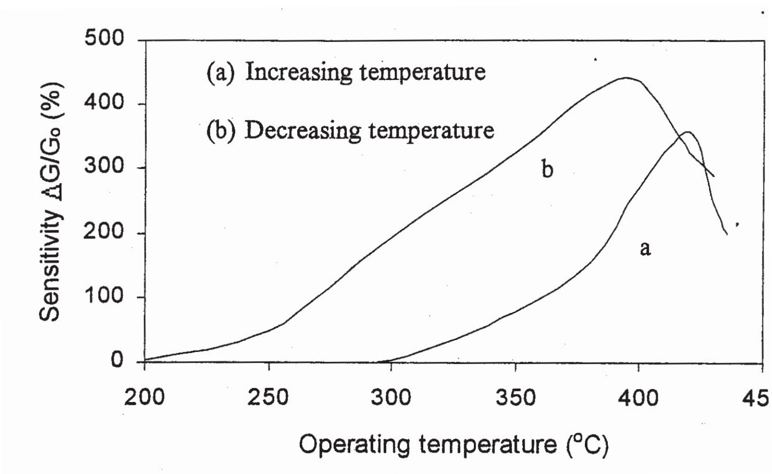


Figure 4 Sensitivity to CH_4 in air vs. operating temperature for SnO_2 with 10 wt% Pd sintered at 900°C

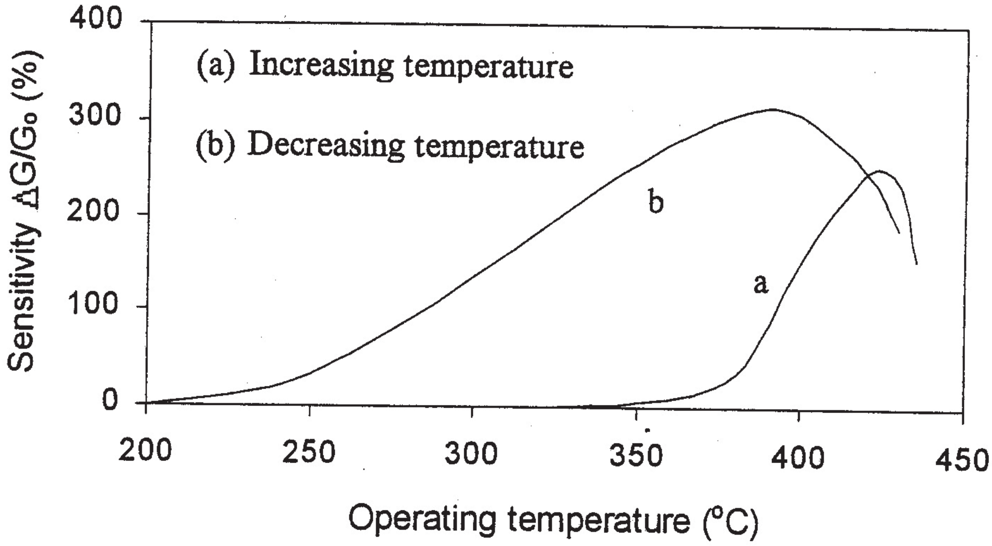


Figure 5 Sensitivity to CH_4 in air vs. operating temperature for SnO_2 with 15 wt% Pd sintered at 900°C

to 430°C for measurements taken with increasing and decreasing temperature. As can be observed in all instances, the sensitivities calculated at the various operating temperatures are higher for measurement with temperature decreasing as compared to measurement with temperature increasing. This hysteresis is explained in terms of the type of oxygen ion adsorbed on SnO_2 surface when it is heated to operating temperatures in the range of 200°C to 600°C. These adsorbed oxygen ions are either molecular (O_2^-) or atomic (O^{2-} and O^-) [2]. The former two (O_2^- and O^{2-}) are adsorbed at lower temperatures and are less reactive than the later (O–), which is adsorbed at higher temperatures. Consequently, when measurement is done while temperature is being increased in steps, the less reactive oxygen ions are encountered at each step and gradually the more reactive oxygen ions appear at higher temperatures. Conversely, when the measurement process is reversed to measurement at decreasing temperatures in steps the more reactive oxygen ions (O^-) remain adsorbed as the temperature is lowered from a higher to a lower level thus resulting in the higher sensitivities observed when measurement is done with decreasing temperature.

4.0 CONCLUSION

The mechanism underlying the hysteresis in the detection of CH_4 in air using SnO_2 with Pd as sensitizing additive was discussed in the light of the experimental results observed in this study. The higher sensitivities observed when measurement was carried out with decreasing temperature as compared to measurement with increasing temperature is attributed to the reaction of CH_4 with the more reactive O^- ions that remain adsorbed on the metal oxide surface as the operating temperature is decreased.

5.0 ACKNOWLEDGEMENT

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