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## HYSTERESIS BEHAVIOUR OF SENSITIVITY IN CH<sub>4</sub> DETECTION IN AIR USING SnO<sub>2</sub> WITH Pd AS SENSITIZING ADDITIVE

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**Abstract.** The sensitivity of SnO<sub>2</sub> 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<sub>2</sub> surface.

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

**Abstrak.** Kepekaan SnO<sub>2</sub> 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<sub>2</sub>.

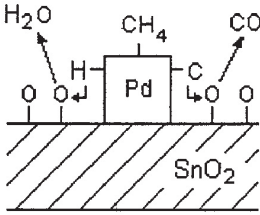
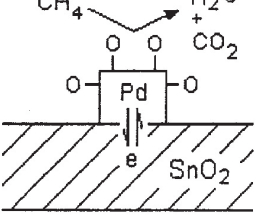
*Kata Kunci:* histerisis, kepekaan, bahan tambah pemekaan, konduktans, metana

### 1.0 INTRODUCTION

Tin (IV) oxide (SnO<sub>2</sub>) is non-stoichiometric in that it is deficient in oxygen atoms. Charge neutrality is maintained by the presence of some tin (II) ions (Sn<sup>2+</sup>) in place of some tin (IV) ions (Sn<sup>4+</sup>) 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<sub>4</sub>. 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 <sub>2</sub>	Change of oxidation state of noble metal
Example	Pd-SnO <sub>2</sub>	Pd-SnO <sub>2</sub>

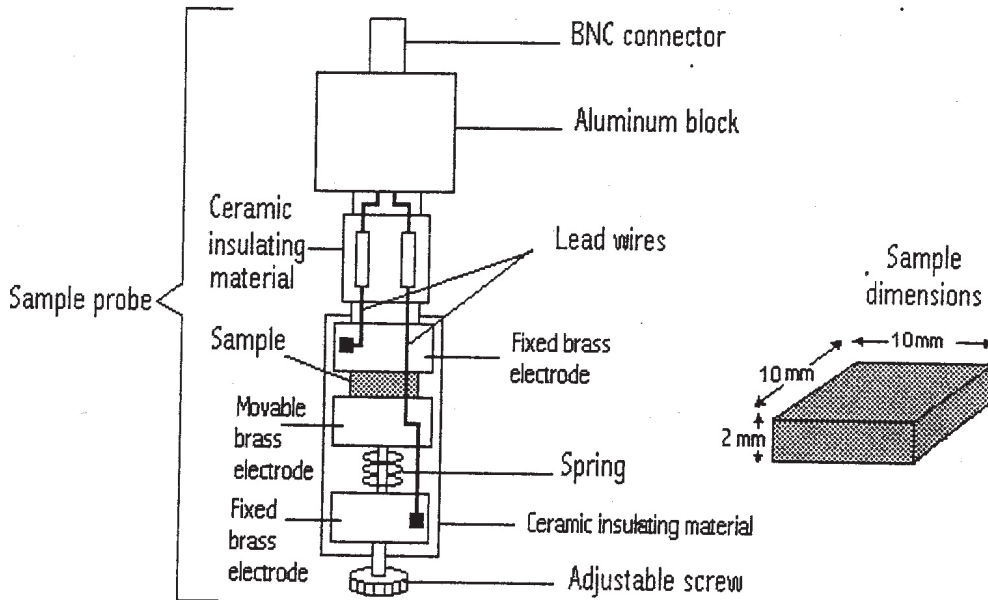
**Figure 1** Model for possible CH<sub>4</sub> detection mechanism by SnO<sub>2</sub> with a noble metal as catalyst

of Pd to SnO<sub>2</sub>, therefore, significantly enhances its sensitivity in CH<sub>4</sub> detection [3]. If Pd particles are present on surface of SnO<sub>2</sub> 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<sub>2</sub> is exposed to air, a higher Schottky energy barrier would develop between adjacent SnO<sub>2</sub> crystallites. This increase in the barrier energy is due to adsorption of oxygen on the surface of SnO<sub>2</sub> [4]. The surface of SnO<sub>2</sub> 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<sub>2</sub><sup>-</sup>, O<sup>2-</sup>, and O<sup>-</sup>) that can be adsorbed on the surface of SnO<sub>2</sub> 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<sup>-</sup>, which is adsorbed at higher temperatures. When such a charged SnO<sub>2</sub> surface is exposed to CH<sub>4</sub>, a chemical reaction occurs between the CH<sub>4</sub> molecules and the adsorbed oxygen ions ultimately forming H<sub>2</sub>O and CO<sub>2</sub> that are then desorbed. The reaction to form H<sub>2</sub>O and CO<sub>2</sub> results in the release of electrons to the solid, thus lowering the potential barrier and increasing the conductance of the sample [5].

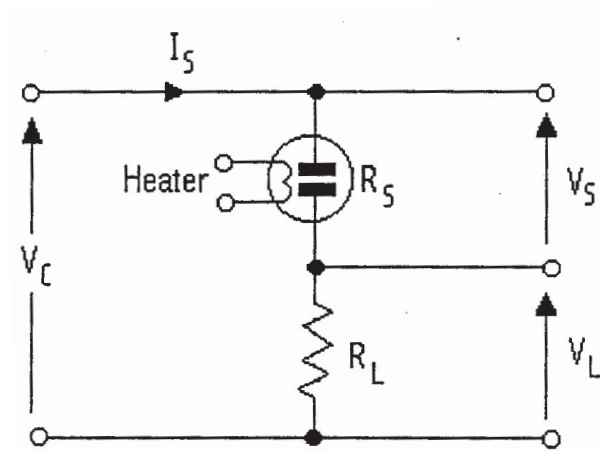
## 2.0 EXPERIMENTAL PROCEDURE

SnO<sub>2</sub> powder (Fluka) and Pd powder (ESPI) were mechanically mixed in the required proportions of (100-x)SnO<sub>2</sub> × 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<sub>2</sub> and noble metal (Pd) produced a pellet of 40 mm diameter and 2 mm thickness. The pellets were then mechanically cut into 10 × 10 × 2 mm<sup>3</sup> 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

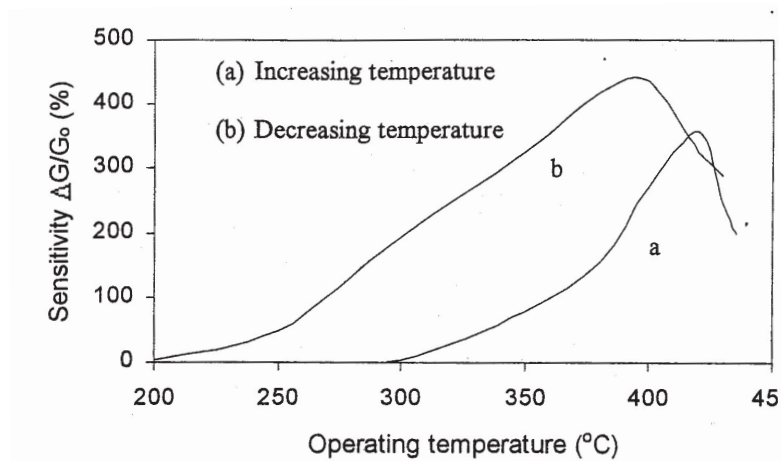
$$S = [(G - G_0)/G_0] \times 100\% \quad (1)$$

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

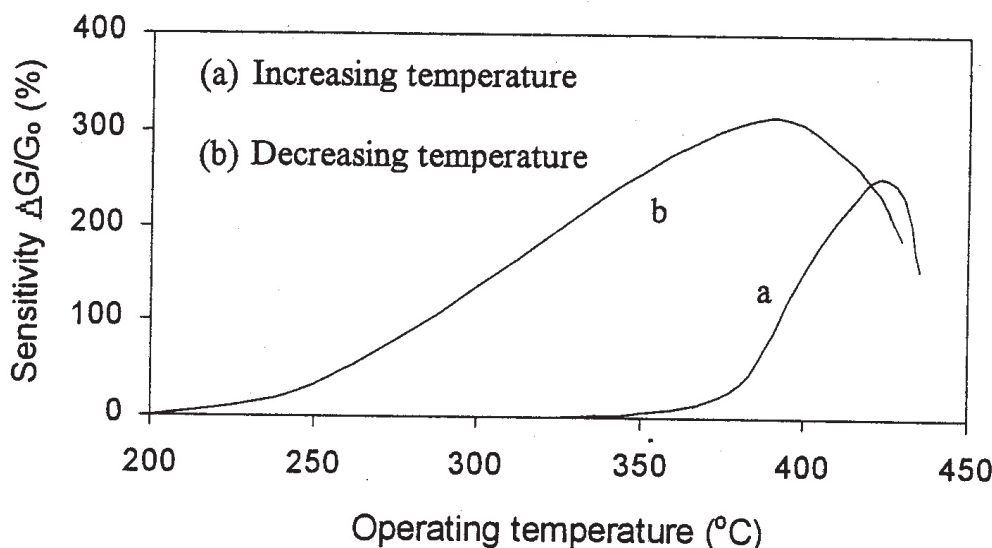
Commercial gas mixtures of 5000 ppm  $\text{CH}_4$  in air and synthetic air were used in the experiments. In addition, other concentrations of  $\text{CH}_4$  in synthetic air were achieved by using a flow controller and a gas injection port in a simple gas mixing system.

### 3.0 RESULTS AND DISCUSSION

Figure 4 and 5 show the sensitivity of  $\text{SnO}_2$  samples with 10 and 15 wt% Pd, respectively, sintered at  $900^\circ\text{C}$  for 1 hour as a function of operating temperature from  $200^\circ\text{C}$



**Figure 4** Sensitivity to  $\text{CH}_4$  in air vs. operating temperature for  $\text{SnO}_2$  with 10 wt% Pd sintered at  $900^\circ\text{C}$



**Figure 5** Sensitivity to CH<sub>4</sub> in air vs. operating temperature for SnO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub><sup>-</sup>) or atomic (O<sup>2-</sup> and O<sup>-</sup>) [2]. The former two (O<sub>2</sub><sup>-</sup> and O<sup>2-</sup>) are adsorbed at lower temperatures and are less reactive than the later (O<sup>-</sup>), 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<sup>-</sup>) 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<sub>4</sub> in air using SnO<sub>2</sub> 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 increas-

ing temperature is attributed to the reaction of  $\text{CH}_4$  with the more reactive  $\text{O}^-$  ions that remain adsorbed on the metal oxide surface as the operating temperature is decreased.

## 5.0 ACKNOWLEDGEMENT

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