Chemical gaseous treatment of SnO2 for a selective detection of gas

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(A010)

CHEMICAL GASEOUS TREATMENT OF SnO_2 FOR A SELECTIVE DETECTION OF GAS

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ABSTRACT: Heated at 500°C under a SO_2 air mixture, tin dioxyde is sensitized for different gaseous compounds. Selective detector devices can be imagined with sensors heated at different temperatures or with sensors with time programmed cycling temperature.

An interpretation of the electrical phenomenon based on a potential barrier effect associated with a chemical reaction process is proposed.

1. INTRODUCTION

Tin oxide is certainly the most important material used for gas detection[1-2] and its electrical properties have long been studied[3]. In fact, the electrical changes of the material by gas adsorption is very complex and it appears difficult until now to develop a reliable and a selective SnO_2 detector. Surface quality of the sample[4], influence of doping[1,5] or temperature dependence[6] were considered by several authors as important parameters on the electrical response of the sensors, but never gaseous treatments were investigated. Now it is well known that some gaseous compounds act as a poison or as a prometing on the activity of some catalysis. Amid these compounds sulfur or sulfur dioxide is certainly very active. In a recent paper[7] we pointed out the effects of a SO_2 treatment on the electrical properties of SnO_2. After few minutes of such a treatment at 500°C under a 1000 ppm sulfur dioxide-air mixture, the electrical conductance of the sample as a function of the temperature is strongly modified under some organic vapour compound -air mixtures or under some inorganic gas. In order to exploit such distinctive results our purpose is to present now a new approach for a selective detection of gas by SnO_2. According to the chemical and the electrical investigations performed on the sample, an interpretation of the phenomenon is also considered.

2. EXPERIMENTAL

2.1. Materials

Our experiments were performed with a sample of SnO_2 manufactured by the prolabo compagny (80273). The solid was cold pressed to a disk of 10 mm in diameter and 2-3 thick at a pressure of 4 tonns/cm^2. The pellets were then sintered in air at 500°C for 10 minutes. Initially two different proceedings were used for electrical contacts:

a) contacts made with gold wires were soldered onto the sample by means of gold paste

b) contacts made with platinium or gold wires were directly cold pressed with the pellet

2.2. Sulfur dioxide treatment

1000 ppm of SO_2 in pure air were introduced in the chamber during 15 minutes.

The most interesting results were obtained in the temperature range 350-500°C, and the experimental procedure adopted was 500°C.

2.3. Measurements

Conductivity measurements $G(\Omega^{-1})$ were made using a WAYNE-KERR bridge at a frequency of 1592 Hz. Direct voltage measurements have been carried out also.

3. ELECTRICAL RESULTS

Before and after treatment in SO_2, the electrical conductance of the sample measured in air is pratically inchanged, whereas it is strongly modified in an air C_6H_6 mixture after treatment. The response of the sensor under different C_6H_6 concentrations in the temperature range 20-500°C is illustrated in figure 1 and a maximum is observed at 400°C. These results have been obtained both by a continuous recording of G when the temperature decreased with a cooling rate of 10°C/mn and by isotherm measurements at different temperatures. The sensibility and the reversibility of the sensor at 400°C are illustrated in figure 2.

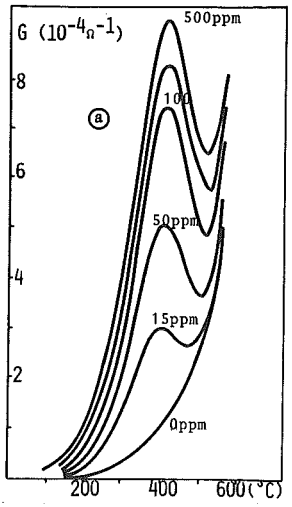

Fig. 1. Electrical performance of the sensor for different values of the concentration of benzene Conductance-temperature curves (cooling rate 50°C/mn)

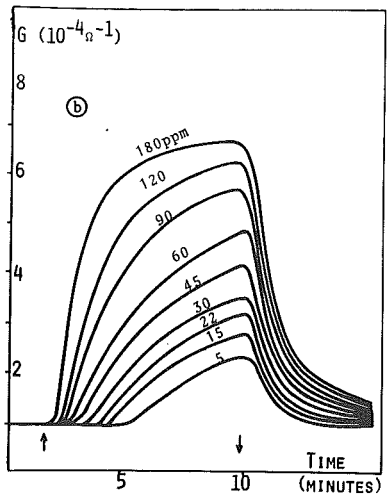

Fig. 2. Electrical performance of the sensor for different values of the concentration of benzene Isotherm measurements at 400°C

In order to check the selectivity of this material, a large number of gases were tested. With organic gaseous compounds, such as ethylene, butane, pentane, toluène or methylalcohol for example, similar results those of benzene were obtained in the temperature range 350-450°C (Fig. 3.). On the contrary methane or ethane induce no maximum.

Under inorganic compounds, such as H_2O, CO_2, NO_x or NH_3, no particular phenomena were observed, but H_2S, SO_2, H_2 and CO induce a maximum at 100°C, 250°C, 400°C and 400°C respectively (Fig. 4.). It is interesting to note that H_2S is the only gas which gives a maximum at 100°C, and that the electrical response of the sensor is not affected by water vapour.

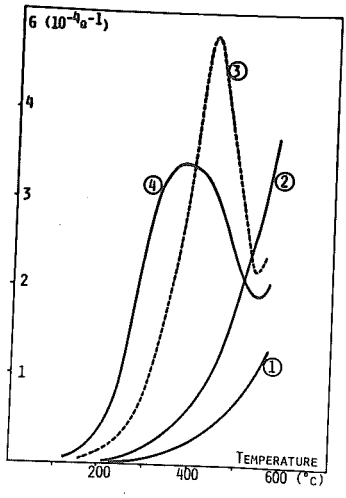

Fig. 3. Electrical response of the sensor with organic compounds (cooling rate 50°C/mn)
1 pure air
2 CH_4 or C_2H_6 (1000 ppm)
3 C_2H_4 or C_4H_{10} (0,7%)
4 n C_5H_{12} (1000 ppm)

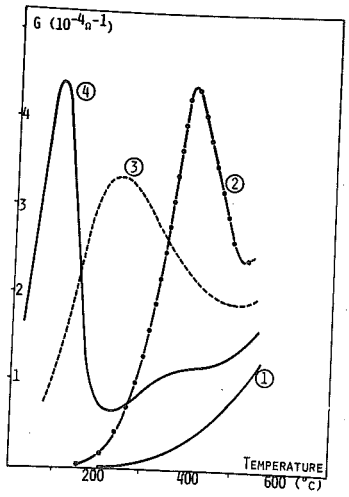

Fig. 4. Electrical response of the sensor with inorganic gases (cooling rate 50°C/mn)
1 air or NH_3(300 ppm) or CO_2(50%) or No_x(50 ppm) or H_2O(80% RH)
2 H_2 (500 ppm) or CO (3%)
3 SO_2 (1000 ppm)
4 H_2S (40 ppm)

4. SENSOR FOR A SELECTIVE DETECTION[8]

4.1. Process

If we take into account the different results obtained with different gas or vapour compounds and with benzene in particular, it is possible to produce a reliable sensor with a relative selectivity around a large number of gas. In order to exploit the maximum at 400°C, we have used two sensors A and B, treated at 400 and 500°C respectively. According to the nature of the gaseous compounds studied, two cases may be considered :

1st: gas induces a maximum near 400°C (curve b in figure 5). Under such conditions, and if pure air is considered as a reference, the electrical conductance variations for sensors A and B are represented by $\Delta G_A = A_2 - A_1$ and $\Delta G_B = B_2 - B_1$ respectively, with necessarily $\Delta G_A > \Delta G_B$

2nd: gas induces no maximum near 400°C (curve c in figure 5). Under such conditions, the electrical conductance variations for sensors A and B are represented by $\Delta G_A = A_3 - A_1$ and $\Delta G_B = B_3 - B_1$ respectively, with necessarily $\Delta G_A < \Delta G_B$

It follows that the comparison of ΔG_A and ΔG_B appears as a test for a selective detection.

4.2. Apparatus

In order to reduce the dimensions of the sensor, small rules (3×1×1mm) are mechanically cut out of a SnO_2 pellet. By means of gold paste, the sample is soldered on an alumina substratum (8×8×0,5mm) equiped on one face with a thick platinium serigraphic film as heating element. The temperature of the sensor controlled by a thermocouple, is stabilized by a special electrical circuit.

The electrical power is about 4,5 watts for sensor A and 5 watts for sensor B. An industrial prototype consists of two sensors located in a cylindric steel chamber closed on one face by a steel sintering disk.

5. ELECTRICAL PHENOMENON INVESTIGATIONS

5.1. Role of the SnO_2-metal junctions

The preceding experimental results were obtained with gold wires soldered on the sample by means of gold paste, but as mentionned above different electrodes were used and a correlation has been established between the phenomenon and the nature of the metal wires[7]. With platinium contacts and by comparison with experimental results obtained with gold contacts, we have observed that the electrical maximum is shifted to the low temperature range. Under benzene-air mixture for example, the temperature shift is about 200°C. Such results implie an important contribution of the potential barrier at the SnO_2-metal junctions. In order to study and to minimize this contribution, we have realized contacts with a thin film of gold by means of a process of evaporation. Under 1000 ppm of an SO_2-air mixture, electrical results are presented in figure 6 curve 3. In such a condition no maximum is observed and the high conductance value of SnO_2 at 20°C may be ascribe to a chemical reaction only with a reversible feature in the high temperature range (T>400°C). Results concerning electrical contacts with gold paste (curve 1 in figure 6), with gold wire cold pressed (curve 2 in figure 6) and with gold thin film, show the part of the potential-barrier and consequently the part of the chemical process on the electrical response of the sensor as a function of the temperature.

Similar results were obtained with other gas and with benzene in particular after an SO_2 treatment of SnO_2

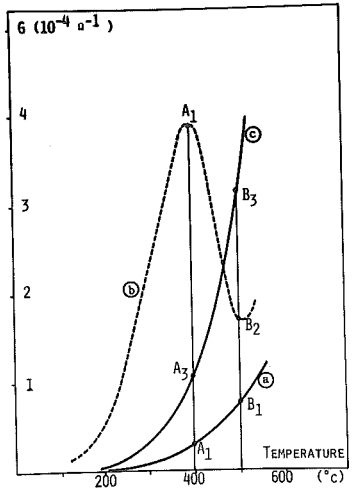

Fig. 5. Electrical working point of sensor A(400°C) and sensor B(500°C)
a pure air
b 500ppm of benzene
c 1000ppm of methane

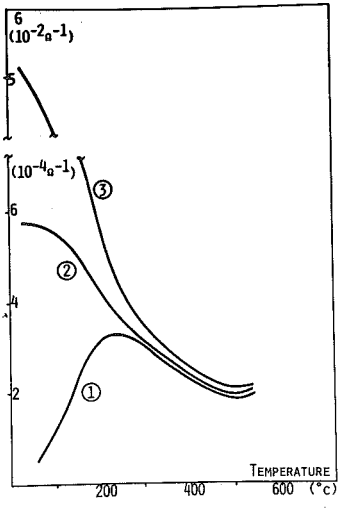

Fig. 6. Influence of the potential-barrier at the electrical contacts
1 gold paste
2 gold wire cold pressed
3 thin film of gold

The high potential barrier effect with gold paste may be explain by the presence of bismuth oxide in the paste. After annealing at 500°C, a thin film of Bi_2O_3 is created between gold and SnO_2.

5.2. Chemical investigations

In an attempt to interpret the origin of the chemical phenomenon which induces a high conductance value of SnO_2 at 20°C, we have tried to demonstrate a possible reduction of SnO_2 according the following reaction: $Sn^{4+}+4e^- \rightarrow Sn$.

In fact on the basis of infrared experiments, ESCA results[7] or RX diagrams, it appears difficult to give a satisfactory interpretation. Until now formation of metallic tin has not been observed. However we can suppose that a partial reduction in a Sn^{2+} stale may occurs. This is in a good agreement with the high conductivity value of SnO at 20°C and with a phase transition of tin oxide at 400°C: $SnO \rightarrow SnO_2$. On the other hand, sulfur in a SO_x coordination has been detected on the surface of the sample. Furthermore no correlation has been found between the maximum and an evolution of the catalytic properties of SnO_2 before and after treatment.

6. CONCLUSION

In conclusion SO_2 gaseous treatment appears as a very active proceeding and may constitute an attempt to solve the problem of the selectivity for chemical sensor. Our investigations shows that the electrical conductance maximum observed with different gas or vapour compounds, may be interpretated in terms of a potential barrier at the SnO_2 metal junctions and in terms of a chemical reaction which induces an increase of the conductance of the sample at low temperature.

Until now the chemical process is not clearly defined and a better understanding of the phenomena should allow us a more rational valorization of the results.

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