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A study of CO sensors with oscillatory response☆

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Abstract

In this paper, oscillatory changes in the conductance of catalyst-doped SnO_2 semiconductor materials in the presence of CO gas are investigated. The sensors with various transducing structures of ceramic tubes (Taguchi structure), co-axial Pt coils and substrates with deposited interdigital electrodes are compared. The results show that catalysts in the sensing materials and the sensor's operating temperature play a key role in generating an oscillatory response. A unique oscillatory response is observed when a bare Pt coil is exposed to CO gas. The relationship between the oscillation waveforms, gas concentration, operating conditions and gas flow rates for the Pt coils are preliminarily tested and discussed.

Keywords: Oscillation; Gas sensor; Carbon monoxide; Platinum catalyst

1. Introduction

Oscillatory behaviour of CO oxidation kinetics on certain metal catalysts such as Pt, Pd has received considerable attention from the surface science community during the last 20 years [1,2]. Progress has been made in experimental research on the oscillatory oxidation of CO on a catalytic surface [3]. However, current literature available has not addressed possible gas sensing applications.

It is well known that the conductivity of n-type metal oxide semiconductors generally increases when they are exposed to reducing gases such as CO, H_2. In particular, Nitta and co-workers in Japan observed a rhythmic oscillation in electric conductance when a SnO_2 (doped with Pd, ThO_2, etc.) thick film sensor was exposed to CO gas [4,5]. Since then, there has been some investigation into this type of CO sensing mechanism and its applications [6–10]. Different results and explanations have been given [11–13], however, this phenomenon is still not yet fully understood.

In this paper, oscillatory CO sensing characteristics of SnO_2 material containing Pd catalyst incorporated with various transducing structures of ceramic tubes (Taguchi structure), co-axial Pt coils and substrates with deposited interdigital electrodes were tested and compared. CO response of undoped SnO_2 painted on co-axial coils of Pt and Au were also examined.

The novel oscillatory sensing behaviour of a bare Pt coil exposed to CO was discovered and examined in detail. A new CO sensor based on this phenomenon is under development. The simplicity of the proposed sensor is highly advantageous due to the ease of fabrication.

2. Experimental

Samples with three different substrates were prepared as follows: SnO_2 mixed with 1% Pd catalyst along with 1–10% Al_2O_3, SiO_2 and MgO was ground uniformly with organic binder. The materials were then painted carefully onto the prepared substrates of ceramic tubes (Taguchi structure), co-axial Pt coils, similar to Han et al. [10] and substrates with deposited interdigital electrodes and then sintered in air for 1 h at 700 °C. These structures are presented in Fig. 1.

The fabrication of undoped SnO_2 sensors was performed by painting pure SnO_2 onto both co-axial Pt and Au coils, then sintering in air for 1 h at 700 °C. The sensors were connected in series with a load resistor and operated in test apparatus consisting of a gas chamber, a multi gas flow controller and a PC-based data acquisition system, which logged the voltage across the load resistor. A certified CO gas bottle (1000 ppm) balanced with atmospheric air at standard room conditions was used. Except where specified otherwise, the total flow rate was kept constant at 0.6 l/m.

The bare Pt coils were formed by winding 32 turns of fine Pt wire (99.999%, wire diameter 0.1 mm) with lengths of

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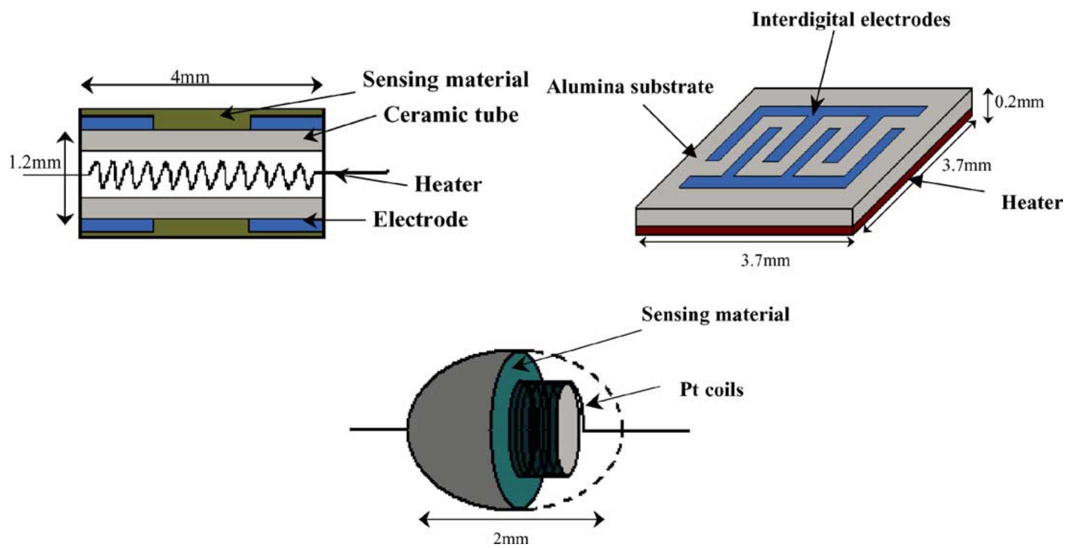

Fig. 1. Schematic diagram of the transducing structures of ceramic tube (Taguchi structure), substrates with deposited interdigital electrodes and co-axial coils.

8 mm (sample #1) and 5 mm (sample #2) and with an inner coil diameter of 0.44 mm. This was followed by cleaning and drying using acetone and distilled water. A constant operating current was applied to the coils while a multi-meter (Keithley 2550) measured the voltage as a function of time across the coils.

3. Results and discussion

3.1. *Response of Pd-doped SnO_2 sensors with various transducing structures of ceramic tubes, co-axial Pt coils and substrates with deposited interdigital electrodes*

Fig. 2 depicts typical oscillation performance for the sensors made on the three different substrates that contained Pd–SnO_2. It can be seen that the oscillatory response of the sensors with substrates of ceramic tubes (Taguchi structure) and substrates with deposited interdigital electrodes is relatively weak while that of the co-axial Pt coils is much stronger. It indicates that the transducing structure has an important influence on the oscillation mode and magnitude. The smaller the sample size and heat transfer capacity are, the higher the oscillation magnitude is. It is worth mentioning that the heater voltages at which the sensors with substrates of ceramic tubes (Taguchi structure) and substrates with deposited interdigital electrodes show oscillation response are clearly defined. It obviously represents the specific temperatures at which the sensors present oscillatory behaviour to a certain CO concentration. For instance, oscillation appears at the heating voltage of 2.0 V and oscillation ends at 2.5 V in 200 ppm CO for sensors with substrates of ceramic tubes, corresponding to the surface temperatures of approximately 150–200 °C [7]. Similar results were obtained while using Pt as doping catalyst.

From our results, it is evident that the oscillation behaviour of the doped SnO_2 materials is mainly attributed to the incorporated noble metal catalysts and operating temperature of material, while the transducing structure effects the mode and magnitude of oscillations.

3.2. *Response of undoped SnO_2 with Pt and Au co-axial coils*

This comparison was carried out to study the characteristics of undoped SnO_2 with two different coil metals of Pt and Au. Surprisingly, it can be seen from Fig. 3 that the sample

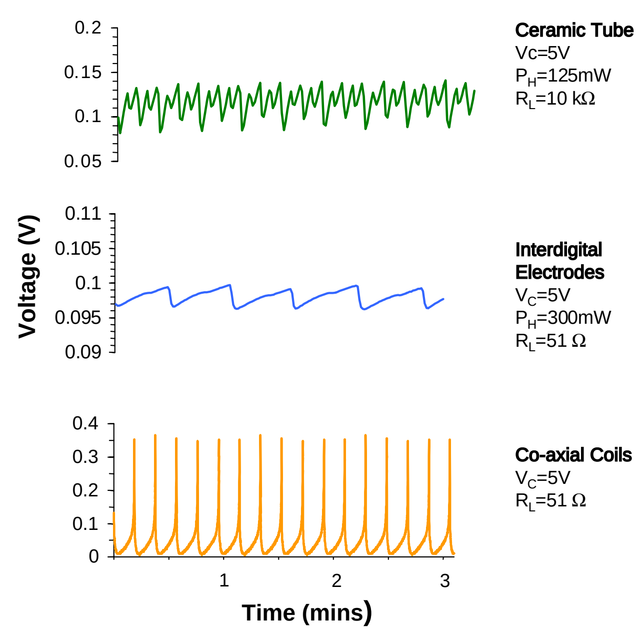

Fig. 2. Typical oscillation waveforms of Pd-doped SnO_2 with different substrates to 200 ppm CO.

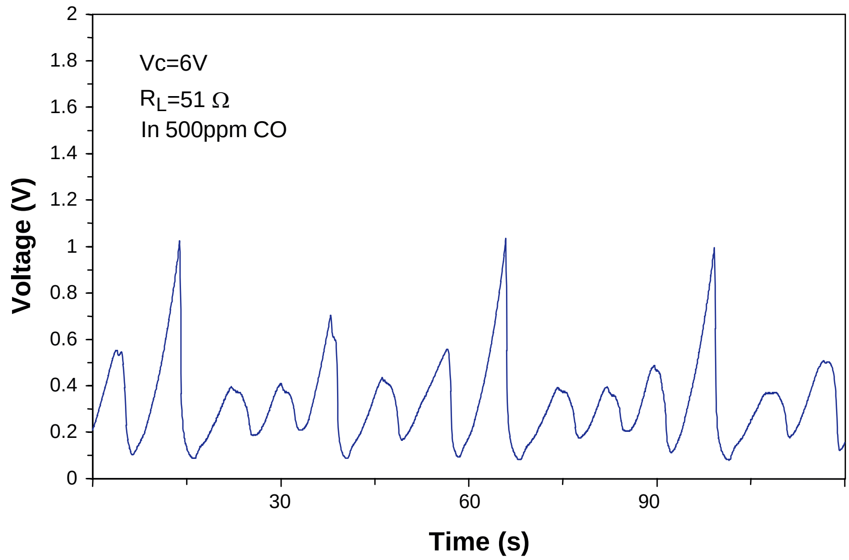

Fig. 3. Oscillatory response of undoped SnO_2 with co-axial Pt coils to 500 ppm CO.

of pure SnO_2 with Pt co-axial coils also exhibits an oscillatory response to CO gas, while no oscillation occurred with the Au co-axial coils. Pt catalyst appears to be the key material responsible for the oscillatory behaviour, and it takes part in the CO sensing reaction in SnO_2 regardless of the manner in which it is integrated into the sensor.

It was then decided to investigate the oscillatory phenomena of the oxidation of CO on bare Pt coils in order to clarify the critical role of Pt in CO sensing oscillation.

3.3. Response of bare Pt coils

Unique oscillatory sensing behaviour of bare Pt coils was observed while current (I_c) was applied to the coils. Fig. 4 depicts the dynamic properties of Pt coils at an operating current of 400 mA for the CO concentrations up to 1000 ppm. Perceptible oscillation emerges about 6 min after the sample is exposed to 300 ppm CO. It can be seen that the baseline level of the responses at 500, 700 and 1000 ppm of CO increases as the CO concentration increases. The amplitude and period of oscillation were not found to vary over this range of concentrations (see Fig. 5).

The relationship between the oscillation waveforms and I_c is illustrated in Fig. 6. It exhibits a tendency to decline in amplitude and period corresponding to the increasing I_c.

The influence of CO gas flow rates can be seen in Fig. 7. The baseline of oscillation increases with decreasing gas

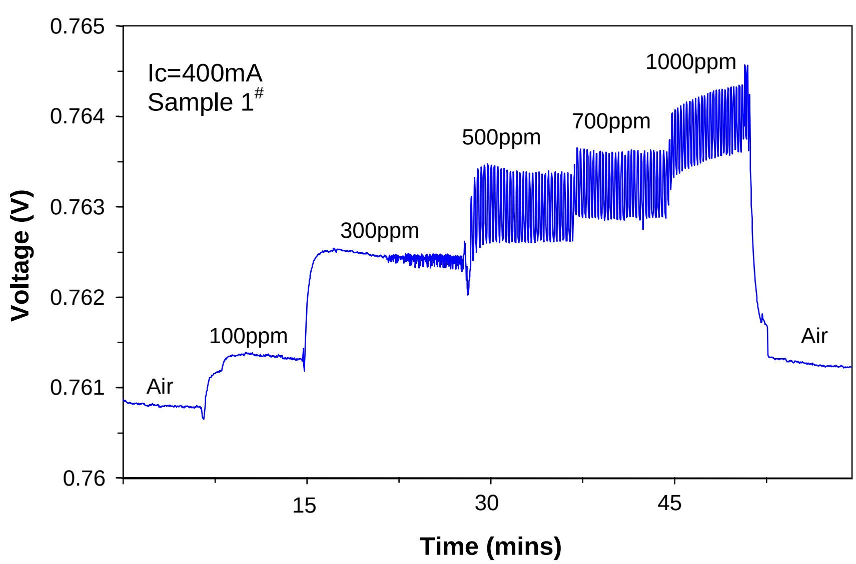

Fig. 4. Oscillatory response of bare Pt coils (sample #1) to CO at 400 mA.

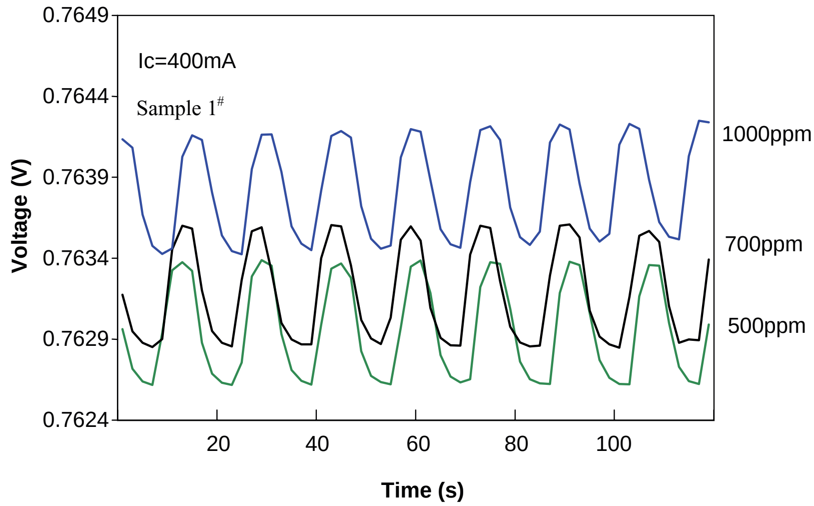

Fig. 5. Oscillation waveforms of bare Pt coils (sample #1) to 500, 700 and 1000 ppm CO at $I_c = 400$ mA.

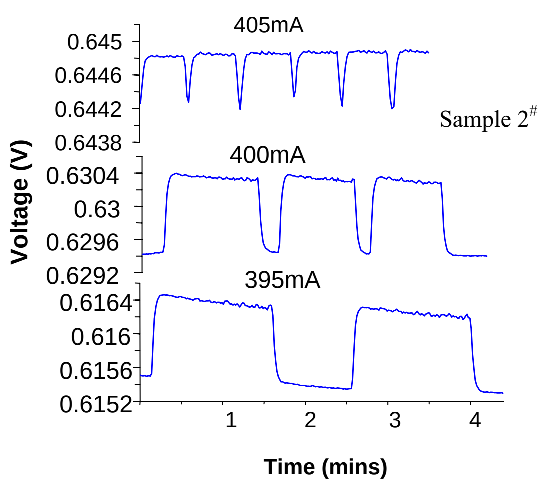

Fig. 6. Oscillation waveforms of bare Pt coils (sample #2) at different operating currents in 1000 ppm CO.

flow rates. In addition, the amplitude and period of oscillation in static gas environment was smaller than those with non-zero gas flow rates.

It is hypothesised that the coil temperature is responsible for the performance variation. When Pt coils are operated under a constant current, the amplitudes and the periods of oscillation remain consistent as a result of the stable surface temperature, as shown in Fig. 5. Decreasing the gas flow rate reduces the heat dissipation into the surrounding gas environment, which increases the coil temperature. The amplitude and period decrease accordingly, is in agreement with the results highlighted in Fig. 7.

As for the mechanism of the oscillatory CO sensing properties of Pt coils, more research is needed. However, from surface science literature, the following may be used to explain the phenomena observed in our results:

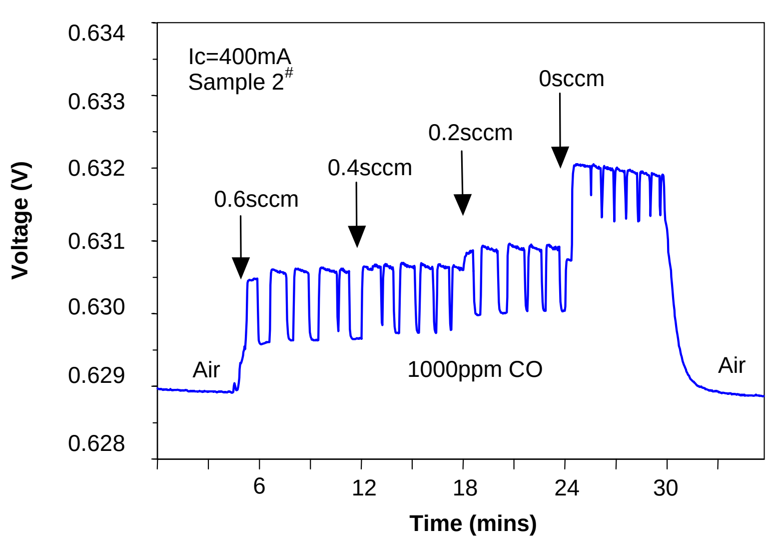

Fig. 7. Oscillation waveforms of bare Pt coils (sample #2) in different CO gas flow rates of 1000 ppm CO.

1. Langmuir–Hinshelwood (LH) reaction mechanism, which is related to the chemisorption of oxygen and CO on Pt, and CO_2 production on Pt [14].
2. The alternate oxidation and CO reduction of Pt and its coupling to the catalysed production of CO_2 on Pt [15].
3. LH mechanism and the slow formation and removal of subsurface oxygen [16].

Further investigations are being pursued to determine the underlying phenomena.

4. Conclusions

Our present results can be summarised as follows:

(1) The transducing structure employed influences the mode and magnitude of oscillations. Structures with smaller size have an increased oscillatory response.
(2) Pt catalyst is the key material responsible for the oscillatory behaviour. It takes part in the CO sensing reaction regardless of the manner in which it is integrated into the sensor.
(3) Bare Pt coils show a novel oscillatory sensing response to CO. For the samples in this paper, the concentration range in which oscillation occurs is from 300 to 1000 ppm at an operating current of 400 mA, with an amplitude of 0.8 mV and period of 15 s.
(4) Perceptible oscillations for the Pt coils could be observed at operating currents from 385 to 415 mA, when exposed to 1000 ppm CO. Operational conditions and gas flow rates influence the amplitude and period of waveforms.

The unique oscillation response of Pt to CO gas indicates the potential of using Pt as a novel gas sensing material. Platinum is only a representative among a group of noble metal catalysts associated with oscillatory behaviour. Experiments are currently being conducted with other noble metal catalysts such as Pd, Rh and Ir to detect reducing gases.

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