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Sensitivity enhancement for CO gas detection using a SnO_2–CeO_2–PdO_x system

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Abstract

Thick film CO sensors were fabricated using SnO_2 loaded with CeO_2 and PdO_x. The composition that gave highest sensitivity for CO was in the wt.% ratio of SnO_2:CeO_2:PdO_x as 94:5:1. The nano-crystalline powders of SnO_2–CeO_2–PdO_x composites synthesized by sol–gel method were screen-printed on alumina substrates. The fabricated sensors were also tested against other gases like H_2, CH_4, C_3H_8, C_2H_5OH, NO_x and SO_2. The composite material was found sensitive against CO in the working temperature range between 120 and 180 °C, with minor interference of other gases. The CO gas as low as 40 ppm can be detected by the present fabricated sensors.

Keywords: SnO_2–CeO_2–PdO_x composites; Sol–gel method; CO selective gas sensor

1. Introduction

CO is a highly toxic gas and is produced during the burning of fossil fuels, or by malfunctioning of domestic appliances in houses, leading to fatal accidents. It affects the human beings directly, fixing haemoglobin permanently to carboxy-haemoglobin, restricting oxygen supply to the respiratory system. Thus monitoring of this gas has great environmental significance.

Tin oxide is the most used n-type semiconductor in gas sensing devices because of its capabilities to detect inflammable gases like CH_4, H_2, C_2H_5OH, CO and so on [1–9]. This material when exposed to atmosphere, the physisorbed oxygen molecules pick up electrons from the conduction band of SnO_2 [10] and create a positive space-charge layer just below the surface of SnO_2 particles leading to a potential barriers between the particles resulting in the electrical resistance of the SnO_2 film. Reducing gases such as H_2, CH_4, C_3H_8, C_2H_5OH or CO react with the physisorbed oxygen [11] increasing the electronic concentration in the material, thereby decreasing the electrical resistance. This change in resistance serves as sensing signal. The main drawback of tin oxide however is its low selectivity towards reducing gases and thus cross-sensitivity between these gases is one of the major problems [8,12].

Certain measures have been taken to overcome these difficulties in detecting CO, such as controlling the grain size and film thickness of SnO_2 [8], sintering procedures [13], applying filters [12,14,15], inserting metallic buried layers in sputtered SnO_2 micro sensors [8] and so on. It is reported that the nano-crystalline metallic oxides can provide better sensitivity in comparison to their microcrystalline counterparts [7,16]. This factor is attributed to the increased surface to bulk ratio of the nano-particles leading to the adsorption of more oxygen on the surface thereby forming a more electron depletion zone across the crystals. Another way suggested is the introduction of dopants to modify the characteristics of SnO_2 [17–19]. In terms of the catalytic aspects, it has been observed that doping of the noble metal cations increase sensitivity greatly, as these cations favor adsorption of the gaseous molecules [19–24]. Jinkawa et al. [25] showed that doping of

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the rare earth oxides in SnO_2 influence the catalytic properties of SnO_2 due to their acid/base characteristics. Teterycz et al. [26] noticed that CeO_2 when used as additive in SnO_2 does not alter conductivity and reacts faster with the reducing gases. SnO_2 being slightly acidic in nature, the basic nature of rare earth oxides may favor some catalytic aspects [27,28] and thus systems like $SnO_2{\cdot}La_2O_3{\cdot}Pd$ or $SnO_2{\cdot}La_2O_3{\cdot}Au$ are proposed for CO sensors [29,30].

In view of the oxidizing catalytic activity of CeO_2 towards reducing gases such as CO to CO_2 [31] and the catalytic aspects of the noble metals [19–24], we prepared the nano-crystalline SnO_2–CeO_2–PdO_x composite to investigate this system as CO sensing material. SnO_2 base material was synthesized by the sol–gel method and PdO_x and CeO_2 were added as sensitizers in small amounts.

2. Experimental

2.1. Sample preparation

All the chemicals were of high purity grade (semiconductor grade) and were used without further purification. The base material SnO_2 loaded with CeO_2 and PdO_x was prepared by sol–gel method using $SnCl_4$ (99.995%, Aldrich), $(NH_4)_2Ce(NO_3)_6$ (99.99%, Aldrich) and $PdCl_2$ (99.999%, Aldrich). The mixtures of solutions containing 20 wt.% of $SnCl_4$ in water and varying amounts of solution of ceric ammonium nitrate and palladium chloride (Table 1) were taken as precursors and stirred well. Ammonium hydroxide solution (25% in water) was added dropwise to each mixture so as to get a pH 9.0 followed by stirring for 20 min resulting in the formation of gels. The gels obtained were aged for one day at room temperature. The volatiles were removed under reduced pressure at 70 °C to get creamy powders.

The materials were characterized by XRD using a Rigaku X-ray diffractometer D/Max 2000-Ultima with Cu Kα radiation and their particle size were evaluated by scanning electron microscope using a Philips XL-30 model.

2.2. Sensor fabrication

Alumina substrates (1 mm thick, 5 mm × 8 mm size) were printed inter-digitally with combed structure for Au electrodes and backside for heaters as described elsewhere [32]. The pastes of the materials synthesized were then screen-printed [32] on the ultrasonically cleaned alumina substrates. The printed films were heated at 700 °C for 2 h. The two sides of the fabricated chip design with a heater on backside are shown in Fig. 1. Table 1 shows the compositions of the fabricated sensors.

Table 1
Compositions of the fabricated sensors in wt.% ratios

Sample number	Composition of the used materials (wt.%)		
	SnO_2	PdO_x	CeO_2
S-1	96	1	3
S-2	95	1	4
S-3	94	1	5
S-4	93	1	6
S-5	92	1	7
S-6	94.5	0.5	5
S-7	93.5	1.5	5
S-8	93	2.0	5

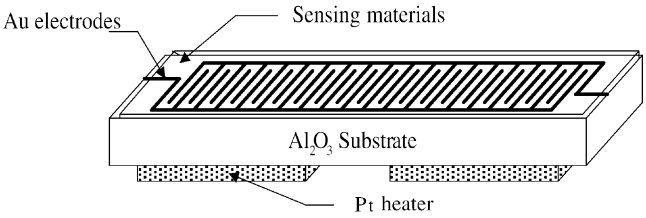

Fig. 1. The design of the fabricated sensor.

2.3. Measurement of sensor resistance

All experiments were carried out using an environmental test chamber, schematic view of which is shown in Fig. 2. The heater temperature was maintained at 170 °C with a supply of heater voltage of ~4.5 V. The measurement of the sensor temperature was made with the help of IR-0506 (Minolta Corp.) temperature analyzer. All these experiments were done at a fixed humidity of 65% RH. Fresh air with a controlled humidity of 65% RH at 22 °C (room temperature) was led and then the gas inlets and outlets of the chamber were closed. The sensor resistance was measured as the chamber reached at the desirable conditions. This experiment was repeated with

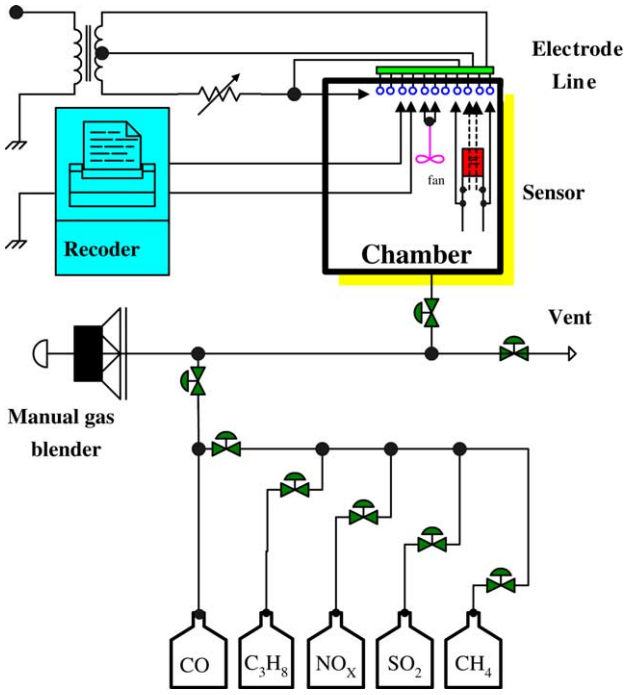

Fig. 2. Schematic view of the measuring system.