Sensors and Actuators B 182 (2013) 250–255

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Highly sensitive formaldehyde sensors based on catalyst added porous films fabricated by plasma spray physical vapor deposition

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ARTICLE INFO

*Article history:*
Received 22 October 2012
Received in revised form 16 January 2013
Accepted 19 February 2013
Available online 28 February 2013

*Keywords:*
Gas sensor model
Porous structure
Catalyst
Tin oxide
Formaldehyde
Physical vapor deposition

ABSTRACT

Highly sensitive formaldehyde sensors were developed using Pt-added porous $SnO_2$ films deposited by plasma spray physical vapor deposition (PS-PVD). The change in the response with Pt addition and film thickness/microstructure was investigated based on the sensor model. It is found that the magnitude of the response strongly depends on both the Pt catalytic activity and the formaldehyde gas diffusion/permeation through the $SnO_2$ film. The Pt addition enhances the increase in the film conductivity upon exposure to the gas and also accelerates the gas reaction with the $SnO_2$ films simultaneously. Especially for the porous films, due to its high gas permeation capability, Pt catalytic effect can be effectively utilized to enhance the response, by suppressing the localized gas consumption near the film surface. As a result of the optimization of these parameters, the PS-PVD porous film sensor with Pt has shown the noticeable response to formaldehyde at a concentration as low as 20 ppb.

## 1. Introduction

Highly sensitive semiconducting gas sensors have been used as devices for monitoring gaseous air pollutants such as formaldehyde (HCHO). The response of the gas sensors is known to depend on its film microstructure, design of the electrode/film, and catalyst additives [1,2]. In particular, noble metals, such as Pd, Pt, and Au, have a strong catalytic activity on the sensor response and selectivity [3–11]. Although a variety of HCHO sensors have been fabricated by various processes [12–14], they are not highly sensitive enough to detect the gas at the guideline value of the World Health Organization (80 ppb). The catalytic effect on the response possibly changes with the film structure but a correlation between the structure and catalyst is not completely understood.

We have fabricated $SnO_2$ porous film sensors by plasma spray physical vapor deposition (PS-PVD) [15,16], which has been a versatile technique for production of films with various microstructures for engineering applications (e.g., thermal barrier coatings, solid-oxide fuel cells) [17–19]. These porous film sensors successfully detected HCHO at low concentrations with no use of catalysts. In the recent study [20], we investigated synergic effects between the film structure and the sensor geometry using the sensor model, and found that higher responses are fundamentally attained with thinner porous films. It was also found that, at a fixed thickness, the response is less dependent on the applied voltage when the electrode gap is large, but it changes significantly when the gap becomes smaller than the critical gap size.

In the present paper, we aimed to enhance further the PS-PVD sensor response to HCHO by adding Pt catalyst. As a result of the optimization of the Pt concentration and the operating temperature, the sensor exhibited the noticeable response to HCHO at a concentration as low as 20 ppb. We also explain the correlation between the structure and catalyst effect using the model that takes into account temperature dependence of the oxidation reaction.

## 2. Fabrication of Pt-added porous film gas sensors

### 2.1. Experimental

Plasma spray physical vapor deposition for fabricating $SnO_2$ films was performed using a 4-MHz radio-frequency inductively coupled plasma. Plasma was generated using argon gas by a 17-kW radio-frequency power input, and oxygen gas was also introduced. Commercial $SnO_2$ raw powder (grain size: 20–50 μm) was injected into the plasma and deposition was performed under a constant total pressure of 26 kPa. The deposition condition is summarized in Table 1. This is identified to be the most favorable condition for the

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http://dx.doi.org/10.1016/j.snb.2013.02.082

**Table 1**
Deposition conditions.

| Parameter | Value |
|---|---|
| RF plasma input power (kW) | 17 |
| RF plasma Ar gas flow rate (slm) | 52 |
| RF plasma $O_2$ gas flow rate (slm) | 5 |
| Powder feeding rate ($g\,min^{-1}$) | 0.36 |
| Pressure (kPa) | 27 |
| Torch to substrate distance (mm) | 40 |
| Substrate temperature (°C) | 230 |
| Substrate revolution speed (rpm) | 50 |

fabrication of high-response sensors in our previous study. $SnO_2$ film with a thickness of 8 μm was deposited in a 3 mm × 3 mm area on an alumina substrate with platinum electrodes (electrode gap: 22 μm). The detail of the fabrication can be found elsewhere [16,20].

Following the fabrication of the $SnO_2$ films, Pt was added to the films using the pore filling method: a film was impregnated with 0.03 μL of $H_2PtCl_6{\cdot}6H_2O$ solution as a Pt precursor. The concentration of the solution was chosen to yield a nominal Pt concentration of 0.1, 0.5, or 1.0 mol%, relative to the total metal molar concentration within the film (i.e., Pt and Sn). The molar concentration of Sn had been previously estimated from the weight of the $SnO_2$ film. The impregnated films were dried at room temperature and then annealed at 600 °C for 1 h in ambient air. *S-0.1, S-0.5, and S-1* denote the films with 0.1, 0.5, and 1.0 mol% Pt, and *S-0* with no Pt addition.

The film structure was observed using a scanning electron microscope (SEM, Hitachi S-4200). The Pt molar concentration was measured using energy dispersive X-ray spectrometry (EDS, JEOL JED2300), and the average crystallite size within the film was estimated from X-ray diffraction analysis (XRD, BRUKER D2PHASER/TMK). Thermal desorption spectrometry (TDS, ESCO EMD-WA1000S/W) was employed to investigate changes in the chemical surface state of the film upon the addition of Pt. A quadrupole mass analyzer installed in the TDS system measured the gas evolved from the film as the temperature was raised to 650 °C at 6 °C $min^{-1}$ under a constant pressure of $10^{-7}$ Pa. The current of the sensors in dry synthetic air ($I_{air}$) and in the sample gas (HCHO) ($I_{gas}$) was measured (ADVANTEST TR6878) with a fixed applied voltage of 0.5 V, and the response, *S*, defined by Eq. (1), was then evaluated.

$$S = \frac{I_{gas} - I_{air}}{I_{air}}. \qquad (1)$$

The sample gas was prepared by diluting HCHO (10 or 100 ppm) from a gas cylinder with synthetic dry air with a dew point of −40 °C. The values of relative humidity of the air and the sample gas in a measuring chamber were less than 1% at room temperature. The sensor performance was evaluated over a range of temperatures between 120 and 340 °C.

## 2.2. Experimental results

### 2.2.1. Film structure

Cross-sections of *S-0* and *S-1* obtained by SEM are shown in Fig. 1. Both *S-0* and *S-1* exhibit a homogeneous porous structure at both the micro- and macro-scale. These films were identified to be tetragonal rutile crystalline phase of stannic oxide (JCPDS 41-1445) by XRD analysis. For *S-1*, no diffraction peaks related to Pt were observed. The average $SnO_2$ crystallite size was estimated from the XRD profile to be approximately 20 nm for both films. Although *S-1* was additionally annealed at 600 °C after the impregnation of the Pt chloride solution, the structure was almost the same as that of *S-0* with no Pt addition. Concentrations of Pt at arbitrarily five locations within the film are analyzed by EDS with a detection area of 1 $\mu m^2$. It turns out to be in the range of 0.8–1.1 mol% and confirms reasonably uniform dispersion of Pt elements.

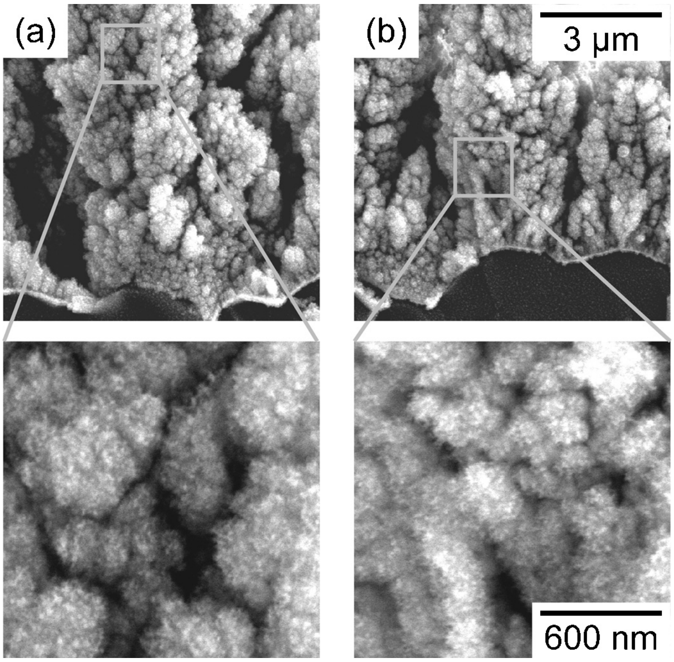

**Fig. 1.** Cross-sectional SEM images of (a) *S-0* (no Pt addition) and (b) *S-1* (1 mol% Pt).

### 2.2.2. Thermal desorption spectrometry

Thermal desorption spectra for *S-0* and *S-1* are measured as shown in Fig. 2. Mass-to-charge ratios (*m*/*z*) of 18, 32, and 44 correspond to $H_2O$, $O_2$, and $CO_2$, respectively. There is no significant difference in the $H_2O$ spectra between the two specimens. However, a noticeable difference is observed in the $O_2$ and $CO_2$ spectra. The $O_2$ signal for *S-1* increased strongly at temperatures > 500 °C,

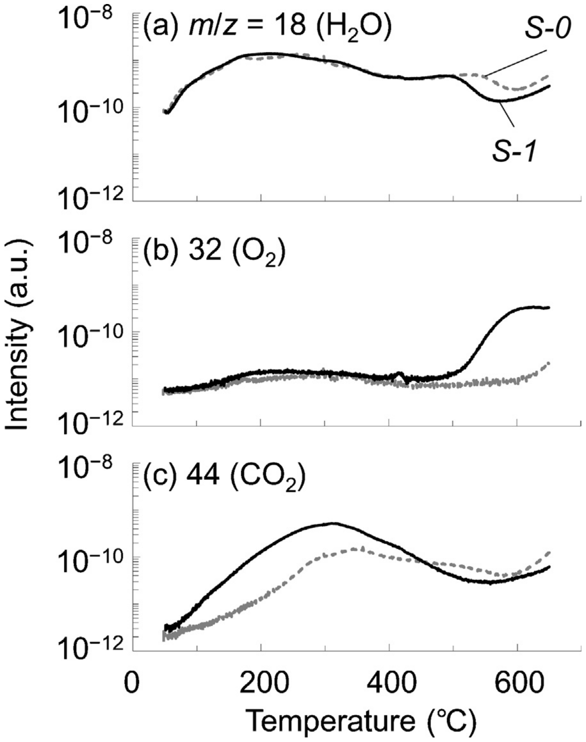

**Fig. 2.** Thermal desorption spectra of (a) $H_2O$, (b) $O_2$, and (c) $CO_2$ from *S-0* and *S-1*.