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Noble Metal Added Tin Oxide VOC Sensors as Nonanal Detection for Exhaled Breath Air Monitoring

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Abstract:

We have investigated the VOCs-sensing properties of Pt, Pd, Au-loaded SnO_2 thick film for exhaled breath air. It has been reported that breaths of lung cancer patients include long methylene chain-aldehydes, such as nonanal. The Pt, Pd, Au-loading for SnO_2 type gas sensors is advantage for detect to low concentration VOCs. The Pt,Pd,Au/SnO_2 element shows higher response to nonanal than a non-loaded SnO_2 element. The combustion of nonanal molecules on the surface of SnO_2 grains is assisted by added noble metals. A nonanal-sensing property of the The Pt,Pd,Au/SnO_2 depend on an annealing temperature. We installed the sensor element to a prototype of breath monitor with gas-chromatograph system, and analyzed mixed gas including three long methylene chain-aldehyde gases.

Key words: lung cancer, aldehydes, nonanal, SnO_2, multi-noble metals addition

Introduction

Human exhaled breath air includes many kinds of volatile organic compounds (VOCs), which depend on such as metabolism, mouth odor, and diseases. Parts of VOCs in exhaled breath air have been regarded as biomarkers of diseases. Many researchers have investigated the biomarkers of lung cancer [1-3], and developed analytical system for exhaled breath air [2,4]. Recently, Fuchs et al. have reported concentrations of aldehyde gases in exhaled breath airs from healthy people, smokers, and lung cancer patients. Breaths of lung cancer patients include aldehydes whose consist of aldehyde group with saturated methylene chain, such as pentanal, hexanal, octanal, and nonanal [3]. Concentration of nonanal is specifically higher than that of other aldehyde gases. Although the concentrations of these aldehyde gases are ppb level [3]. A gas chromatograph-mass spectrometer (GC/MS) with a gas condense equipment can detect low concentrate VOCs. However, the GC/MS system is so expensive that inexpensive detectors, such as portable VOC detectors, are desirable for a periodic medical inspection and a health screening.

SnO_2 is one of the best materials for VOC sensors because of its high sensitivity. In cases of sub-ppm level, the SnO_2-based gas sensors showed lower response to aliphatic hydrocarbons, halogenated hydrocarbons, and aromatic hydrocarbons than to other VOCs, such as alcohol and esters [5]. It has been reported that the addition of Pt, Pd, and Au to SnO_2 thick films improve the sensitivity to aliphatic, halogenated, and aromatic hydrocarbons, respectively [6]. Therefore, it is expected that the Pt, Pd, and Au loaded SnO_2 has advantage for the detection of the gas of long methylene chain-aldehyde group.

In this study, we have optimized film thickness and annealing temperature of the Pt, Pd, and Au loaded SnO_2-based sensors as nonanal sensors, and install the sensors in a prototype of breath monitor with gas-chromatograph system.

Experimental

(1) Sensing property

Figure 1 shows a scheme of preparation for elements. Pt, Pd, and Au colloid suspensions (particle size: 2–4 nm) were added to the SnO_2 powder (particle size: 100 nm). The contents of Pt, Pd, and Au were controlled 1 wt% relative to that of the SnO_2. The mixture was stirred and dried, subsequently burned at 400 °C for 2 h. The resulting powder was added into an organic dispersant (vehicle) to obtain a paste. The ratio powder/vehicle of the paste

was changed from 1/8 to 1/128 to control the film thickness. The pastes were subsequently dropped on 5 x 9.5 mm^2 Si substrates with comb-type Pt electrodes (10 μm gap), which was patterned on front side. On the backside of the substrate, the Pt heater was patterned. The substrates were annealed at 425 °C for 2 h. We obtained Pt,Pd,Au/SnO_2 sensor elements, as shown in Fig. 2.

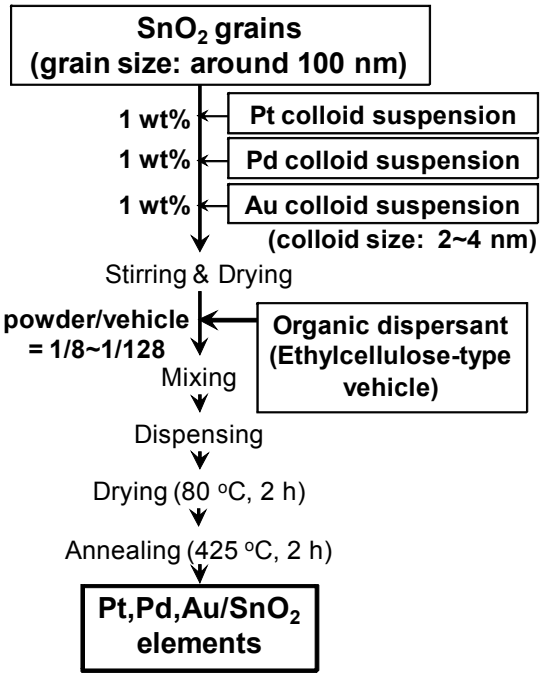

Fig. 1. Scheme of preparation for Pt,Pd,Au/SnO_2 sensor elements.

Surface and cross sections of the Pt,Pd,Au/SnO_2 thick films were observed by a JEOL JSM-6335FM field-emission scanning electron microscopy (FE-SEM). Thicknesses of the Pt,Pd,Au/SnO_2 thick films were estimated from cross sections of FE-SEM images.

The gas sensing properties of the elements were measured using a flow-type gas sensing measurement apparatus. The elements were heated at 250 and 300 °C by their Pt heaters. Nonanal gas was generated from liquid nonanal by a Gastec PD-1B permeator. The concentration of nonanal was controlled to 9.5, 1.0, 0.18, and 0.055 ppm. The total flow rate was kept at 200 mL/min. The sensor response (S) is defined as equation (1),

$$S = \frac{R_a}{R_g} \quad (1)$$

where R_a, and R_g are the electrical resistance in pure air and nonanal gas, respectively. After the nonanal-sensing property measurement, the elements were annealed at 500°C for 2 h. The 500°C–annealed–elements were measured the nonanal-sensing property again.

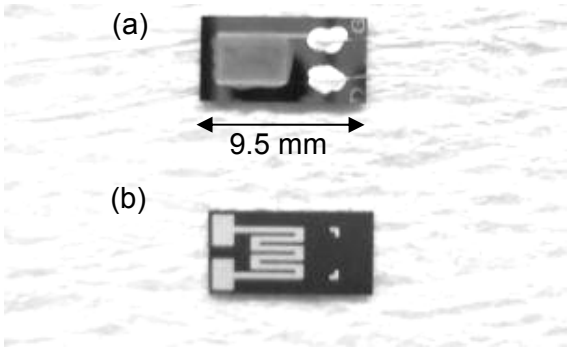

Fig. 2. Sensor elements: (a) SnO_2 thick film formed on comb-type Pt electrode (10 μm gap) on front side, (b) Pt heater on back side.

(2) Prototype system

For a prototype system, we remodeled the sensor element to 4 x 4 mm^2. The sensor element was hung on a metal stem by gold wires, as shown in Fig. 3. The Pt,Pd,Au/SnO_2 thick film and Pt heater were applied voltage via pins of the stem and the gold wires. The stem was installed in the prototype system.

Fig. 4 shows flow paths of the prototype system. The prototype system has an adsorption agent for condensation of VOCs and a gas chromatography (GC) column for separation of many kinds of VOCs. First, sample gas including VOCs in a gas bag is aspirated, and condensed to the adsorption agent. Subsequently, the adsorption agent is heated and pure air as a carrier gas is flowed to the adsorption agent. Re-gasification VOCs are separated each kind of VOC and detected by the sensor element at each retention time. In this study, we prepared a mixed gas included 500 ppb of heptanal, 500 ppb of octanal, and 500 ppb of nonanal for the evaluation of VOCs-separation.

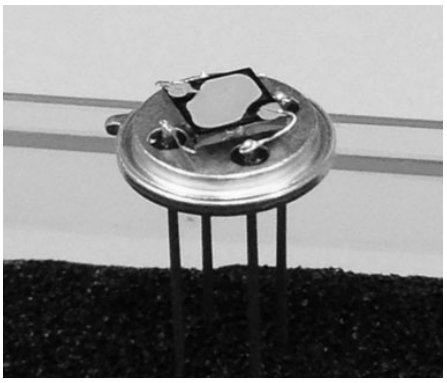

Fig. 3.Sensor element for prototype system. Size of the sensor element substrate is 4 x 4 mm^2.

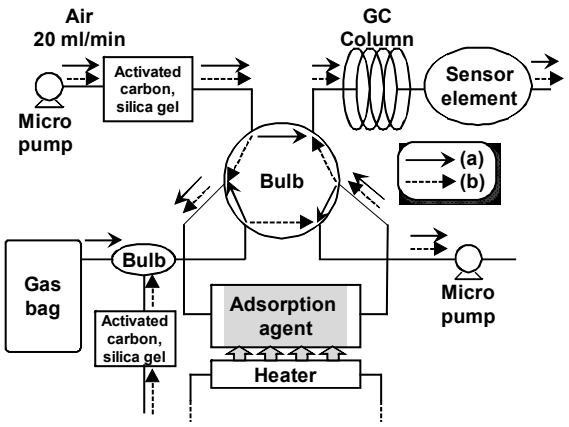

Fig. 4. Flow paths of the prototype system. Two kinds of arrows indicate flow routes: (a) VOCs-condensing path, and (b) analysis path.

Results and Discussion

(1) Sensing property

Fig. 5 shows SEM images of the Pt,Pd,Au/SnO_2 thick film on surface and edge sections. The ratio powder/vehicle of the element in Fig. 5 is 1/16. The SEM images show non-aggregation of the Pt,Pd,Au/SnO_2 grains and the Pt,Pd,Au/SnO_2 thick film has a lot of pores and uniformity thickness. We confirmed that the thickness of the Pt,Pd,Au/SnO_2 thick films can be controlled by the powder/vehicle ratios reproducibility.

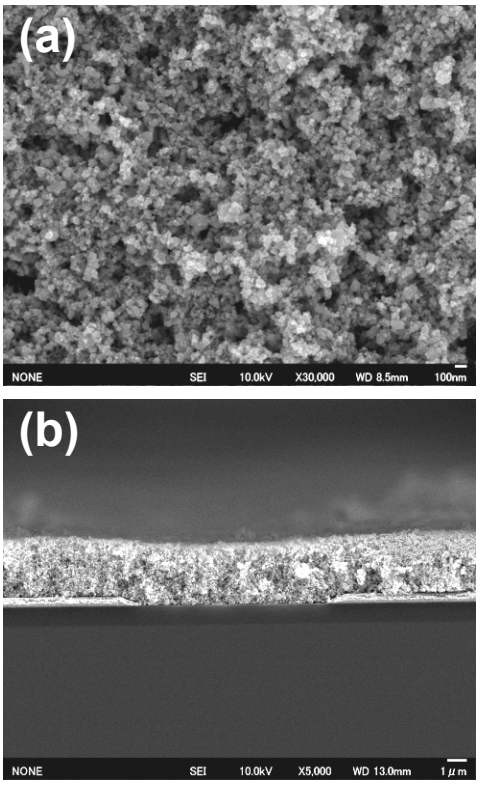

Fig. 5. SEM images of Pt,Pd,Au/SnO_2 thick film on (a) surface and (b) cross sections.

Fig. 6 shows the dynamic resistance responses of the Pt,Pd,Au/SnO_2 element. The Pt,Pd,Au/SnO_2 element was annealed at 500 °C for 2 h. The resistances of the Pt,Pd,Au/SnO_2 element decreased and reached to saturation values during flowing of nonanal gases for less than 1 min. It is found that Pt,Pd,Au/SnO_2 element exhibited distinct responses to dozen ppb of nonanal. Moreover, the Pt,Pd,Au/SnO_2 element after annealed at 500 °C shows stronger response to nonanal than the element before annealed at 500 °C.

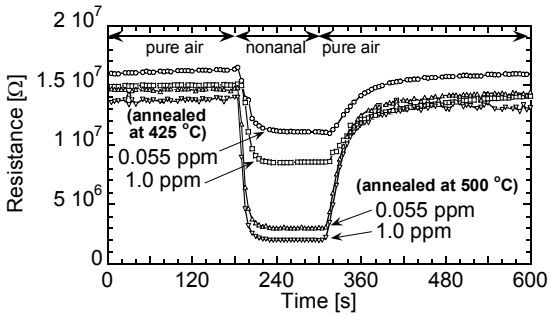

Fig. 6. Dynamic resistance responses of the Pt,Pd,Au/SnO_2 thick film (Thickness: 2.8 μm) to 1 ppm and 0.055 ppm of nonanal gases.

Fig. 7 shows the sensor responses of the Pt,Pd,Au/SnO_2 element and a non-added SnO_2 element to nonanal gases. The non-added SnO_2 as well as the Pt,Pd,Au/SnO_2 elements, after annealed at 500 °C, shows higher response to nonanal than the Pt,Pd,Au/SnO_2 before annealed at 500 °C. The results can be explained that the annealing temperature is the most important factor for detection to nonanal on the SnO_2 system.

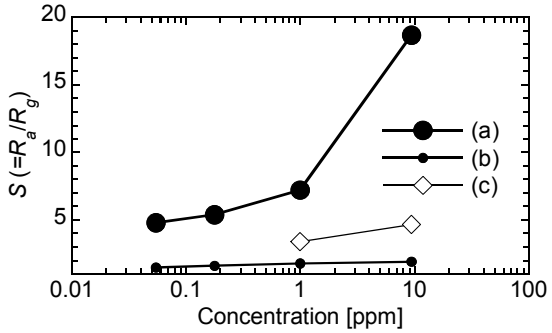

Fig. 7. Sensor response values to nonanal gas: (a) (a) Pt,Pd,Au/SnO_2 (Thickness: 2.8 μm) before annealing at 500 °C, (b) Pt,Pd,Au/SnO_2 (Thickness: 2.8 μm) after annealing at 500 °C, and (c) SnO_2 (Thickness: 1.9 μm) thick films after annealed at 500 °C. Sensor temperatures are 250 °C.

It can be explained that the decrease of electron depleted layer extremely affected the resistance change of the Pt,Pd,Au/SnO_2

because the neck growth of the SnO_2 grains seems to be promoted by annealing at 500 °C. Moreover, the Pt,Pd,Au/SnO_2 element shows higher response to nonanal than the SnO_2 element. The results suggest that the combustion of nonanal molecules on the surface of SnO_2 grains is assisted by the added noble metals.

(2) Prototype system

Fig. 8 shows sensor response from the Pt,Pd,Au/SnO_2 element in the prototype system. The prototype system can separate each VOC, which has closely resemble molecular structure; $CH_3(CH_2)_{n-2}CHO$, n=7 (heptanal), 8 (octanal), and 9 (nonanal).

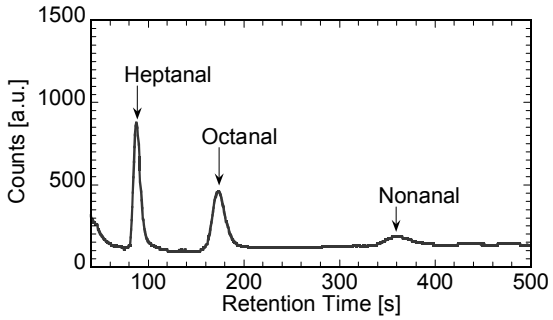

Fig. 8. Sensor response from the Pt,Pd,Au/SnO_2 element in the prototype system.

Conclusion

The Pt,Pd,Au/SnO_2 elements were prepared to drop pastes, consisting of Pt,Pd,Au/SnO_2 powder and an organic dispersant, on the substrate. We observed the Pt,Pd,Au/SnO_2 thick film has a lot of pores and uniformity thickness, and Pt,Pd,Au/SnO_2 grains do not aggregate in the Pt,Pd,Au/SnO_2 thick films. The Pt,Pd,Au/SnO_2 element shows higher response to nonanal than a non-loaded SnO_2 element. A nonanal sensing property of the Pt,Pd,Au/SnO_2 depend on an annealing temperature. The Pt,Pd,Au/SnO_2 elements after annealed at 500 °C shows higher response to nonanal than the Pt,Pd,Au/SnO_2 before annealed at 500 °C. It is plausibly explained that the combustion of nonanal molecules on the surface of SnO_2 grains is assisted by added noble metals, and the decrease of electron depleted layer extremely affected the resistance-decreased of the Pt,Pd,Au/SnO_2 because the SnO_2 grains are more combined by annealing at 500 °C. The prototype system with the Pt,Pd,Au/SnO_2 element can detect three kinds of aldehydes separately.

Acknowledgements

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