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Preparation of multi-compositional gas sensing films by combinatorial solution deposition

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Abstract

Various compositions of gas sensing films were prepared by the combinatorial deposition of SnO_2, ZnO, and WO_3 sol solutions and their gas sensing behaviors were investigated. The film composition could be manipulated conveniently via the alternate dropping of different oxide sol solutions. From the correlation between film compositions and gas sensitivities, the selective detection of C_2H_5OH and CH_3COCH_3 in the presence of CO, C_3H_8, H_2, and NO_2 could be attained. In addition, the discrimination between C_2H_5OH and CH_3COCH_3, which is a challenging issue due to their similar chemical nature, becomes possible. This research demonstrates the precise design of the sensor-material composition for the selective gas detection via the combinatorial approach.

Keywords: A. Films; B. Composites; C. Electrical properties; E. Sensors

1. Introduction

The oxide semiconductors have been widely used as the gas sensing materials due to their high sensitivity to a small concentration of gas. However, the selective detection of a specific gas remains a challenging issue. The variation of catalyst materials [1], surface modification [2], and sensing temperature [3] are the representative approaches to achieve selective gas sensing. The manipulation of sensor composition can be considered as another effective route to enhance the gas selectivity. The selective detection becomes difficult especially when the target gases show similar chemical nature. For example, most oxide semiconductor gas sensors show similar sensing behaviors to C_2H_5OH and CH_3COCH_3 [4,5]. Thus, the discrimination between C_2H_5OH and CH_3COCH_3 is hard to accomplish.

In this contribution, we prepared various compositions of sensor films by the combinatorial deposition of SnO_2, ZnO, and WO_3 sol to the alumina substrates. The sensing materials employed include SnO_2, ZnO, WO_3, SnO_2–ZnO, SnO_2–WO_3, and ZnO–WO_3. The main focus was placed on the precise design of a gas sensor composition for the selective gas detection of C_2H_5OH and CH_3COCH_3 in the presence of CO, C_3H_8, H_2, NO_2, and C_2H_5OH and for the discrimination of C_2H_5OH and CH_3COCH_3 with similar chemical natures.

2. Experimental procedure

Hydrated tin oxide precipitates were prepared by mixing ammonium bicarbonate (NH_4HCO_3, ~95%, Junsei Chemical Co. Ltd., Japan) and tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, GR, Kanto Chemical Co. Inc., Japan) aqueous solutions. After washing the precipitate with distilled water using a centrifuge, a designated amount of hydrated tin oxide gel was suspended in 55 ml of an aqueous ammonia solution (pH 10.5). The suspension was transferred to a Teflon-lined stainless steel autoclave and treated hydrothermally at 200 °C for 3 h. This hydrothermal treatment resulted in a clear and homogeneous SnO_2 sol solution. The concentration was adjusted to 0.065 M by evaporating the solvent with constant stirring at ~70 °C. Two hundred milliliters of a zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 98+%, Sigma–Aldrich, USA) solution ($[Zn(CH_3COO)_2]$ =

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Table 1
The specifications, compositions, and phases of the sensor film

Specification	SnO_2 sol (droplets)	ZnO sol (droplets)	WO_3 sol (droplets)	Phase after heat treatment at 600 °C for 5 h
S	20			SnO_2 (tetragonal)
SZ	10	10		ZnO (hexagonal) + SnO_2 (tetragonal)
Z		20		ZnO (hexagonal)
ZW		10	10	$ZnWO_4$ (monoclinic) + minor WO_3 (monoclinic)
W			20	WO_3 (monoclinic)
SW	10		10	WO_3 (monoclinic) + SnO_2 (tetragonal)

0.35 M, solvent: 2-methoxyethanol) was added to 200 ml of a MEA solution ([MEA] = 0.35 M, solvent: 2-methoxyethanol) dropwise while stirring, which produced a solution containing white precipitate. It was heated to 60 °C and stirred for 2 h to obtain a clear and homogeneous solution. The concentration of [Zn^{2+}] in the clear stock solution was 0.175 M. The WCl_6 was dissolved in ethanol solvent. By the addition of 100 ml of distilled water, blue gel was precipitated. The Cl^- ions were washed with distilled water using centrifuge. The gel was added to 30 ml of 30% NH_4OH solution and was stirred for 24 h, which resulted in clear stock solution. The concentration was 0.27 M. Hereinafter, for simplicity, above three stock solutions will be referred as SnO_2, ZnO, and WO_3 sols.

The sensor was fabricated by the combinatorial dropping of source SnO_2, ZnO, and WO_3 sols on an alumina substrate with two Au electrodes (substrate: 1.5 mm × 1.5 mm, spacing

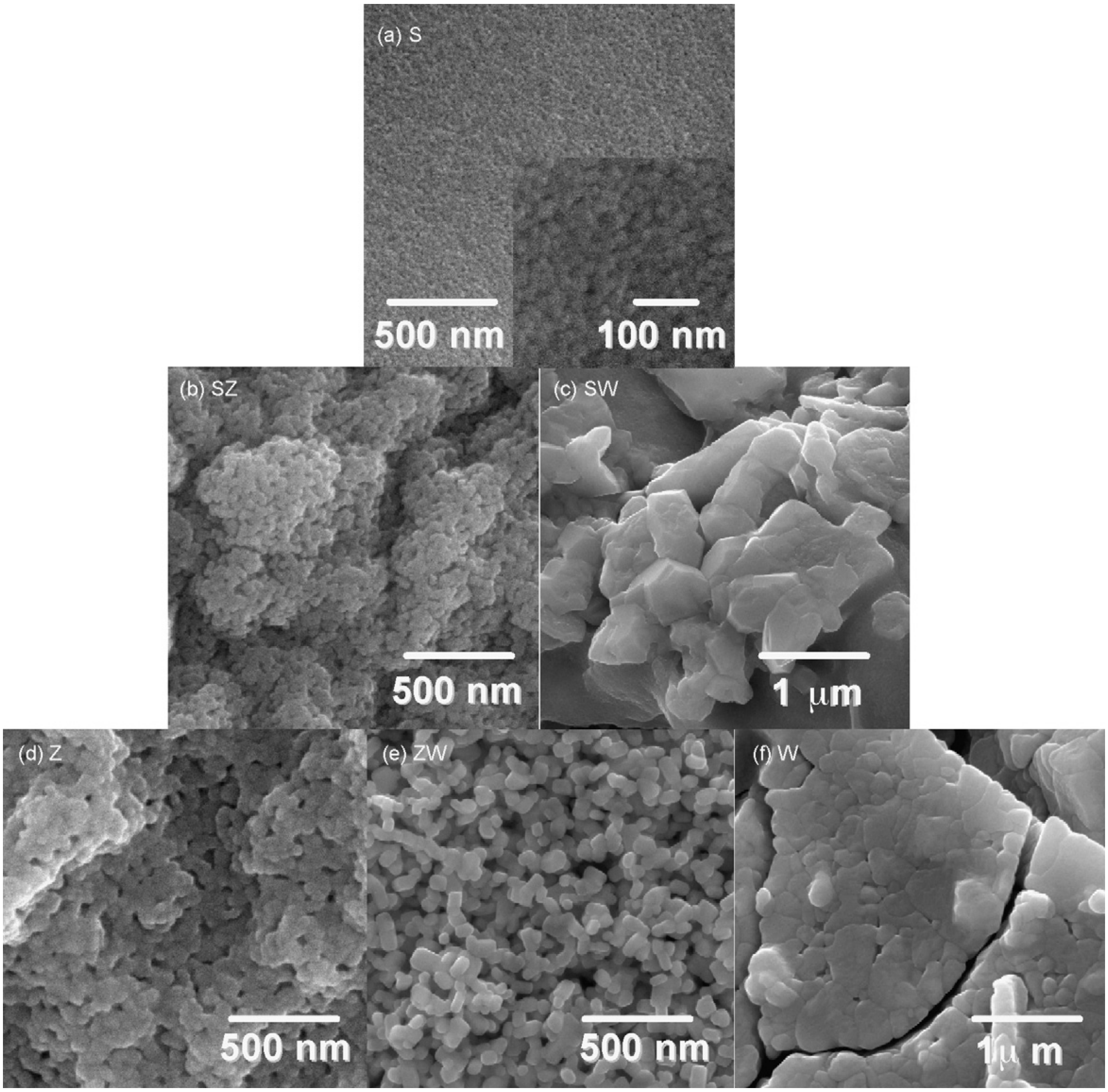

Fig. 1. Scanning electron micrographs of (a) S, (b) SZ, (c) SW, (d) Z, (e) ZW, and (f) W sensors. The sample specification was given in Table 1.

Table 2
The gas responses of sensors at 300 °C

Gas	Sensitivity					
	S	SZ	Z	ZW	W	SW
C_2H_5OH 200 ppm	13.18	4.69	1.61	1.86	3.78	1.39
CH_3COCH_3 200 ppm	12.36	2.31	1.55	1.97	4.31	1.17
C_3H_8 200 ppm	1.05	1.13	1.13	1.11	1.26	1.07
CO 100 ppm	1.95	1.19	1.08	1.38	1.39	1.20
H_2 200 ppm	1.24	1.13	1.33	1.09	1.33	1.09
NO_2 5 ppm	1.59	1.11	–	1.17	1.57	–

The responses to C_2H_5OH, CH_3COCH_3, C_3H_8, H_2, and CO are R_a/R_g and that to NO_2 is R_g/R_a.

between two electrodes: 0.2 mm). A precise micropipette (SDV10, High Tech Labs) was used to deposit the solution. Five thin-film sensors of different compositions were fabricated by the dropping of SnO_2, ZnO, and WO_3 sols. Table 1 shows the notations of the sensor materials and their corresponding compositions. After dropping of a droplet (1 droplet = ~0.87 μl), the substrate was dried on a heated hot plate (T = 70 °C) before the next step. For the homogeneous composition, the composite sensor films (SZ, SW, and SW) were made by alternative dropping of different sols.

The sensor element was heat-treated at 600 °C for 5 h for getting a crystalline thin film. The thin films after heat treatment were 5–6 μm thick. The sensor was installed in a quartz tube and the temperature of furnace was stabilized at a constant sensing temperature (300–400 °C). The gas concentration was controlled by changing the mixing ratio of parent gases and dry synthetic air. A flow-through technique with a constant flow rate (500 ml/min) was employed. Gas response (R_a/R_g) was measured at 300–400 °C by comparing the resistance of the sensor in high-purity air (R_a) and those in target gases (R_g).

3. Results and discussion

The phase of the sensor films were analyzed by X-ray diffraction pattern and the results were summarized in Table 1. The SZ and SW sensors showed the mixed phase configuration. In contrast, the $ZnWO_4$ phase was formed with minor WO_3 in ZW sensor. The formation of residual WO_3 phase emanates from the higher concentration of WO_3 sol than that of ZnO sols. Fig. 1 shows the microstructures of the films after heat treatment at 600 °C for 5 h. The S (SnO_2) sensor shows the most fine structure and is composed of primary particles of 10–15 nm. The average sizes of primary particles of SZ, Z, ZW, SW, and W sensors were approximately estimated as 30, 40, 70, 500, and 200 nm, respectively.

For all the sensors, the gas sensing behaviors to various gases were analyzed at 300 °C. (Table 2) Except SW sensors with the small responses (R_a/R_g) to all gases, most of sensors showed high responses to 200 ppm of C_2H_5OH and 200 ppm of CH_3COCH_3 and relatively small responses to C_3H_8 200 ppm, CO 100 ppm, H_2 200 ppm, and NO_2 5 ppm. Note that the

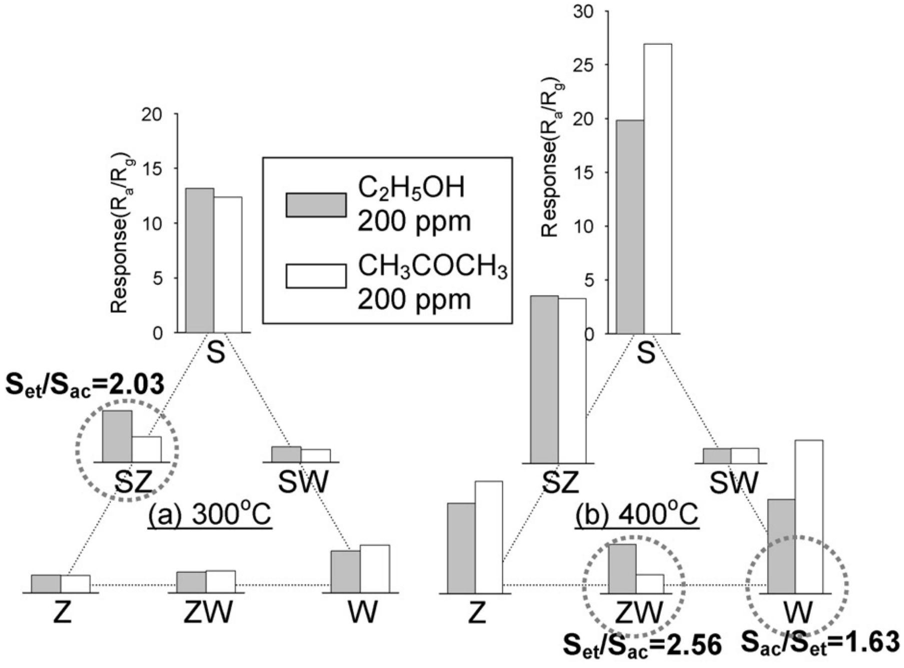

Fig. 2. The responses of the sensors to C_2H_5OH 200 ppm and CH_3COCH_3 200 ppm at (a) 300 °C and (b) 400 °C.

response to oxidizing gas (NO_2) was defined as R_g/R_a. This says that the selective detection of C_2H_5OH and CH_3COCH_3 is possible in this group of sensors. The detection of C_2H_5OH is necessary to screen intoxicated driver on the road. For this, $[C_2H_5OH] > 200$ ppm, which corresponds >0.5 g of C_2H_5OH per liter of blood, should be detected [6]. Under the heavy traffic conditions, the concentration of CO and NO_2 concentrations can increase locally up to 100 and 10 ppm [7], respectively, due to automotive emission. Accordingly, the results in Table 2 demonstrate that the present sensors can be used to screen intoxicated driver in the heavy traffic conditions.

Although all the sensors in Table 2 showed the different responses to 200 ppm of C_2H_5OH (S_{et}) and 200 ppm of CH_3COCH_3 (S_{ac}), the S_{et} and S_{ac} values for each sensor are similar with each other except the case of SZ sensor. The responses to C_2H_5OH and CH_3COCH_3 are generally reported to be similar with each other in many oxide semiconductor sensors [4,5], which is explained by their similar chemical nature. Currently, the oxide semiconductor-type C_2H_5OH sensors are being used only for screening not for legal testing. Moreover, the CH_3COCH_3 vapor in the expiration as well as ambient atmosphere is scare. Accordingly, the sensor in the present form can be employed as breath alcohol detector. However, for more precise and reliable screening, the discrimination between C_2H_5OH and CH_3COCH_3 is essential. For example, up to 300 ppm CH_3COCH_3 can be included in the expiration from a diabetes patient [8]. Thus, the selective detection of C_2H_5OH in the presence of CH_3COCH_3 is desirable for preventing the mistaking the diabetes patient as a drunken driver. On the contrary, the selective detection of CH_3COCH_3 in the presence of C_2H_5OH is necessary for the medical checking of diabetes patient.

In order to tune the gas selectivity further, the sensor responses toward C_2H_5OH and CH_3COCH_3 were measured at 300 and 400 °C and the results were summarized in Fig. 2. At both temperatures, the responses of S sensor showed the highest values, which can be attributed to its fine particle size. However, the selective detection of C_2H_5OH was effective in the SZ sensor at 300 °C ($S_{et}/S_{ac} = 2.03$) and ZW sensor at 400 °C ($S_{et}/S_{ac} = 2.56$). In comparison, the selective detection of CH_3COCH_3 was found in the W sensor at 400 °C ($S_{ac}/S_{et} = 1.63$). Fig. 3 shows the sensor response transients for these three sensors. The 90% response time to 200 ppm C_2H_5OH was ~72 s in the SZ sensor at 300 °C (Fig. 3a), while it was as small as ~3.5 s in the ZW sensor at 400 °C (Fig. 3b). Although the reason for the significant difference in sensor response time should be studied further, the uniform size of primary particles and pores with the agglomeration-free configuration in the ZW sensor seems to be responsible for the short response time. Accordingly, the ZW sensor is considered at the optimum composition for the high response as well as the short response time. The response transient of W sensor to 200 ppm CH_3COCH_3 showed a fast response and good recovery character. The response was ~14.3 and 90% of response time was ~5 s, which demonstrates that the present W sensor is a promising material to detect the trace concentration of CH_3COCH_3.

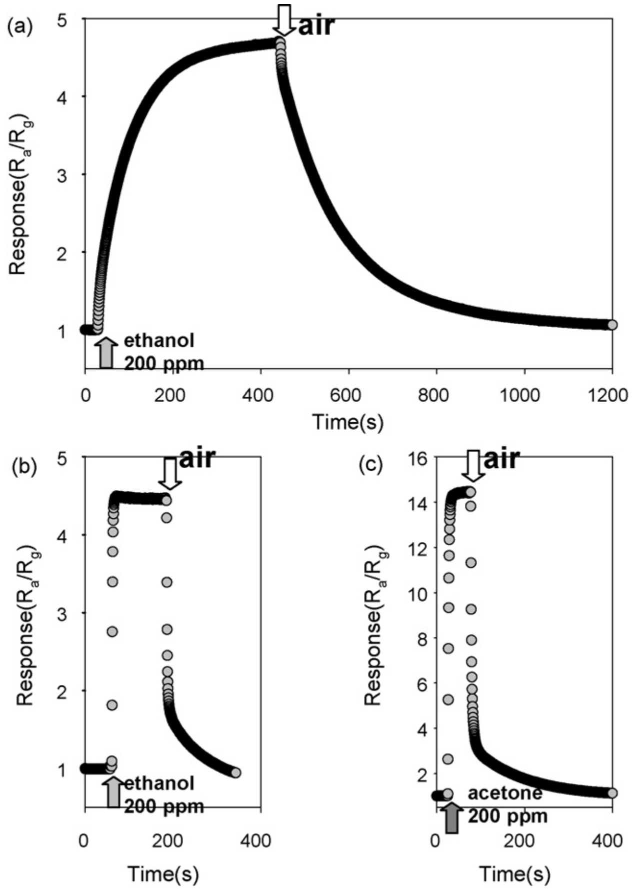

Fig. 3. Response transients of (a) SZ sensor to 200 ppm of C_2H_5OH at 300 °C, (b) ZW sensor to 200 ppm of C_2H_5OH at 400 °C, and (c) W sensor to 200 ppm of CH_3COCH_3 at 400 °C.

The sensing of C_2H_5OH is related to its oxidation or decomposition reaction. Jinkawa et al. [9] reported that the decomposition of C_2H_5OH at elevated temperature depends on the acid–base properties of the oxide catalyst used:

$$C_2H_5OH(g) \rightarrow CH_3CHO(g) + H_2(g) \quad \text{for basic oxide} \qquad (1)$$

and

$$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g) \quad \text{for acidic oxide} \qquad (2)$$

On the other hand, the CH_3COCH_3 is thermally oxidized according to the following intermediate [10]:

$$CH_3COCH_3 \rightarrow CH_3COCH_2* \rightarrow (CH_3CHO, CH_3) \rightarrow H_2C_2O \rightarrow H_2CO \rightarrow CO \rightarrow CO_2 \qquad (3)$$

The similar sensing behaviors to C_2H_5OH and CH_3COCH_3 emanate from the similar intermediate phase (CH_3CHO) and oxidation reactions. In this respect, the approximately the same S_{et} and S_{ac} values for most of sensors can be understood. It should be noted that the decomposition of CH_3COCH_3 is also influenced by the acid–base properties of the oxide catalyst.

The electronegativities of W^{6+}, Sn^{4+}, and Zn^{2+} are 2.36, 2.0, and 1.7, respectively. In the sole viewpoint of electronegativity, the acidic WO_3 promotes the (reaction (2)) more in comparison to the (reaction (1)), which can decrease S_{et} because the oxidation of C_2H_4 with negatively charged surface oxygen induces a smaller increase in conductance than that of $CH_3CHO + H_2$. This is consistent with the selective detection of CH_3COCH_3 by W sensor at 400 °C. However, the S and Z sensors did not show any significant correlation between electronegativity and S_{et}/S_{ac}. It is interesting that the S and Z sensors showed the similar S_{et} and S_{ac} values at 300 °C, while the SZ sensor shows the higher S_{et} in comparison to S_{ac}. The promotion of the adsorption and oxidation of C_2H_5OH due to the presence of the two types of centers with different reductive–oxidative and acid–base properties were suggested to be a possible reason although further studies are necessary. The high S_{et}/S_{ac} ratio in SZ sensor can be understood in the same viewpoint. However, the results in Fig. 2 could not be explained completely using one or two factors. This indicates that, besides the electronegativity and heterostructure effect, there are many other parameters that influence the selective detection of C_2H_5OH and CH_3COCH_3. The formation of new phase (for example, $ZnWO_4$ in ZW sensor), the configuration of nano-composite, crystallite size, and the agglomeration between primary particles should be taken into account for the comprehension of the overall sensing mechanisms.

4. Conclusions

It has been shown that the sensor composition can be conveniently optimized for the selective gas detection by the combinatorial deposition of SnO_2, ZnO, and WO_3 oxide sols. From the gas responses to C_2H_5OH, CH_3COCH_3, CO, C_3H_8, H_2, and NO_2, it was found that the selective detection of C_2H_5OH could be attained in the SnO_2–ZnO composite sensor at 300 °C and ZnO–WO_3 composite sensor at 400 °C. And WO_3 sensors could detect CH_3COCH_3 in the presence of C_2H_5OH. The discrimination between C_2H_5OH and CH_3COCH_3 was discussed in the viewpoints of electronegativity, heterostructure effect, and other factors. The combinatorial approach provides a promising tool for the precise design of sensor materials.

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