Practical type of gas sensors based on sintered semiconductor for detection of hydrogen and odor

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1. Introduction:

Practical hydrogen sensors and odor sensors were developed. The hydrogen sensors have robust performances and have been very often used for semiconductor manufacturing. Today, new needs to H_2 sensors are also growing in terms of safe utilization of hydrogen energy. On the other hand, the odor sensors are available for evaluation of odor intensity via total detection and measurements of odor, and have been utilized for convenient or continuous odor-measurements in different fields.

2. Hydrogen Sensor[1)]

Figure 1 shows "Hot-wire type semiconductor sensor", with two terminals (a) and its working circuit (b) used in this study. The sensor consists of platinum wire coil with a 0.020 mm diameter and a sintered SnO_2 bead (2 atomic% of Ce added) with a 0.50 mm diameter. The coil functions as both a heater and an electrode for the semiconductor bead: the total resistance (R_s) of the sensor is considered as a parallel electric circuit consisting of the coil resistance and the semiconductor one. A SiO_2-accumulated dense layer is formed near the bead surface to obtain a high hydrogen-selectivity. The thickness of the dense layer is estimated to be about 100μm from the depth distribution of SiO_2 obtained by ion microprobe analyzer. Besides, sensor output (V) is bridge output, as shown in Fig. 1(b); and sensitivity ΔV=V(in air mixed with target gases)-V(in clean air). **Figure 2** shows the cross sensitivity of the H_2 sensor (sensor temp., 480°C). Such extremely high selectivity to H_2 was explained by a kinetic model involving *a molecular-sieve like effect* of the dense SiO_2 layer, where the diffusion of gases could be limited according to their molecular sizes and/or weights, as shown in **Fig. 3**. In this connection, molecular diameters obtained from viscosity of H_2, H_2O, O_2, CO, CH_4 and i-C_4H_{10} are 0.218, 0.272, 0.296, 0.380, 0.38 and 0.5 nm, respectively. Specially, H_2 passes easily through the dense layer and causes the reaction with the surface oxygen species (O_2^-, O^-, O^{2-}) , resulting in decrease in resistance of the semiconductor. The H_2 sensor, thus obtained, has the following robust performances from a practical point of view: high H_2-selectivity, low humidity dependence (**Fig. 4**) and long term stability (**Fig. 5**). In the absolute humidity range from 2.4 to 46.0g/m^3, the errors were ±8.4%(at 200ppm of H_2), ±8.4%(500ppm) and ±7.6%(1000ppm), respectively. During 8 years in a room air, the error for 500ppm of H_2 has been ±10% and the sensor output to ethanol (in 2000ppm) has also been consistently depressed.

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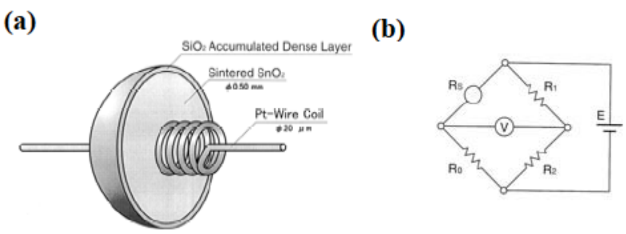

Fig. 1 Cross sectional view (a) and working circuit (b)

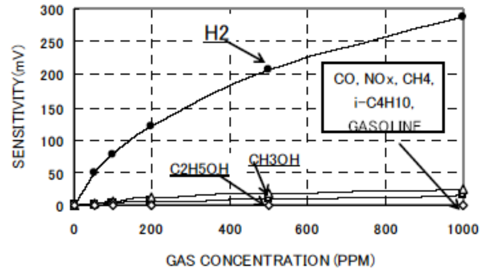

Fig. 2 Cross sensitivity

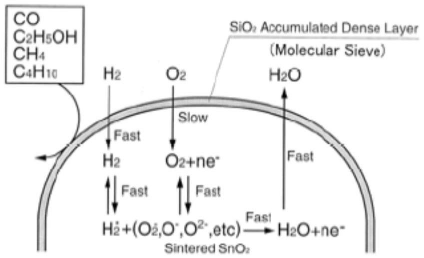

Fig. 3 Kinetic model of molecular sieve-like effect based on excellent H_2-selectivity

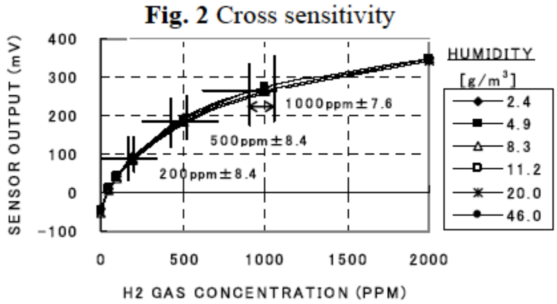

Fig.4 Humidity dependence

In addition, the 90% response times to H_2 gas decrease with increase in H_2 gas concentrations: for instance, 15, 10 and 7s to 200, 500 and 1000ppm of H_2, respectively. Finally, the H_2 sensor has also a prominent resistance against poisonous gases of SO_x, H_2S or NO_x, because the sensing layer is protected with the surface SiO_2 dense layer.

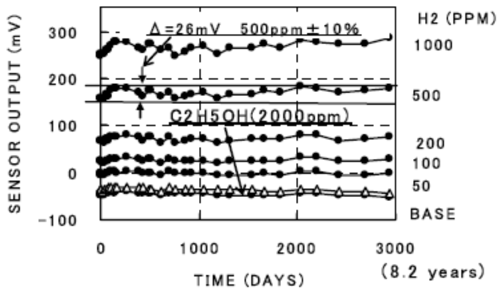

Fig.5 Long term stability

3. Odor sensor[2,3)]

The structure and working circuit of odor sensor is the same as shown in **Fig. 1**, except for composition of semiconductor layer. The sensitivity ratio of H_2 to C_2H_5OH (in 800 ppm) fell to 0.04 by the addition of above 4 mol% CaO to SnO_2. The sensitivities to more than 70 species of organic or inorganic compounds were measured in this study. **Figure 6** shows cross sensitivities to typical compounds obtained at 450°C of sensor temperature. In general, high sensitivities to compounds with functional groups or unsaturated bonds are obtained: alcohols, carbonic acids, ketones, aldehydes, esters, ethers, amines, thiols and unsaturated hydrocarbons. Several characteristic sensitivity-orders are seen in each group: increase in carbon number of alkyl groups, in number of methyl group or in degree of unsaturation increases their sensitivities; blanching in alkyl substituted groups decreases sensitivities. Lone pair electrons and π-electrons may be favorable, whereas blanching unfavorable owing to steric factor on adsorption to active sites. On the other hand, the sensitivities to H_2, CH_4, CO and saturated hydrocarbons are effectively depressed. In connection with the above results, the physicochemical properties of odor molecules well-known in odor science are summarized in **Table 1**. Odor molecules fall into organic compounds with functional groups (odor-generating groups) with polar bonds or with O, N and S (odor-generating atoms) with a large electronegativity; methyl group classified as odor-generating group or increase in carbon number in substituted group increases odor intensity. The odor molecules have, on the whole, high sensitivities, and further some partial similarities for the orders between the sensitivities and the odor intensities. As shown in **Fig. 6**, the relationship between sensitivity and gas concentration is linear on log-log graph, $\Delta V = k_1 \cdot X^n$, which is similar to Stevens' power law, $Y = k_3 \cdot X^m$, well-known in odor science: $k_{1,2}$, n and m constants. The above qualitative and quantitative similarities found between sensitivity and odor intensity is very useful for *total odor detection and measurements*. Thus, the odor sensor has been utilized for real-time or continuous monitoring of odor in different fields, because, in fact, main odorants are often fixed in each field.

Finally, odor discrimination and odor intensity are important factors to evaluate odor. The odor discrimination has been tried by different technical methods. On the other hand, the evaluation of odor intensity by the total detection and measurements of odor proposed in this study is an innovative approach from a practical point of view.

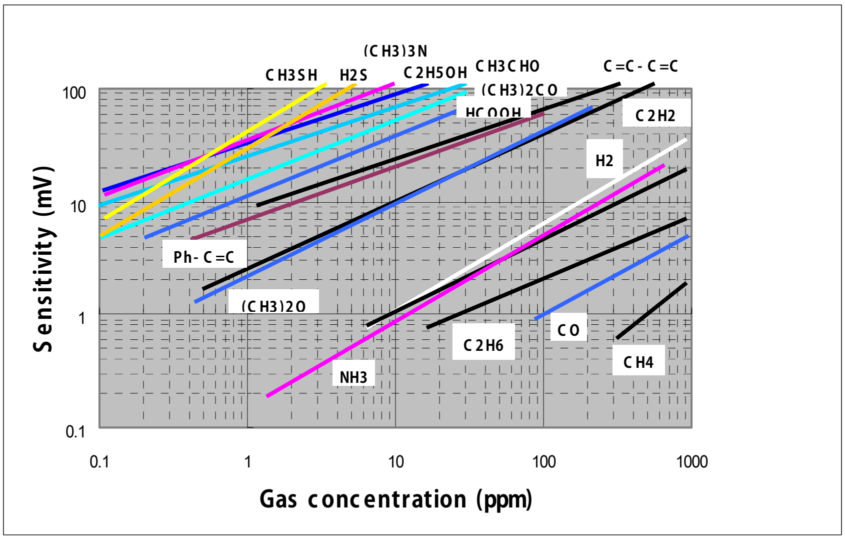

Table 1. Physicochemical properties of odor molecules governing odor intensity known in odor science

Physicochemical properties	Examples
①Odor generating atms with a large electronegativity	O, N, S
②Odor generating groups including polar bonds or functional groups	R-OH, RR'>C=O, R-(C=O)OH, R-(C=O)H, R-(C=O)OR',R-O-R', R-NH$_2$, R-SH, R-S-R', -CH$_3$(methyl group) (R stands for alkyl group)
③Unsaturation-bond number (degree of unsaturation)	>C=C<, -C≡C-, >C=C-C=C<

Physicochemical properties	Examples
④Blanching	Blanching in alkyl groups (R) weakens odor intensity.
⑤Position of hydroxyl groups (-OH)	Order of odor intensity of alcohols: primary> secondary> tertiary
⑥Number of carbons in molecules (molecular weight)	Peak of odor intensity falls into C8–C15 of carbon number in normal hydrocarbons.
⑦Molecular structures	Steric isomers (optical, geometrical)

1)Akira Katsuki and Kiyoshi Fukui, H_2 selective gas sensor based on SnO_2, Sensors & Actuators B5(1991)27-32.

2）K. Fukui and K. Komatsu, Alcohol-sensitive gas sensor using SnO_2 ceramics, Proc. 4th Int. Conf. Solid-State Sensors and Actuators (Transducers '87) Tokyo, Japan, June 2-5, 1987, pp.614-617.

3)Kiyoshi Fukui, Detection and measurements of odor by sintered tin oxide gas sensor, Sensors & Actuators B52 (1998)30-37.