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Development of Methane Gas Sensor by Various Powder Preparation Methods

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After SnO_2 fine powder was prepared by precipitation method, Ca as crystallization inhibitor and Pd as catalyst were added to SnO_2 raw material by various methods. Thick film device was fabricated on the alumina substrate by mixing ethylene glycol and such mixed powders. The sensing characteristics of the device for methane gas were investigated. The most excellent gas sensing property was shown by the thick film device fabricated by Method 3 in which Ca and Pd doped SnO_2 powder is prepared by mixing SnO_2 powder, 0.1 wt% Ca acetate and 1 wt% $PdCl_2$ in deionized water and by calcining the mixture, after $Sn(OH)_4$ is dried at 110°C for 36h. The sensitivity of the sensor fabricated with SnO_2-0.1 wt%Ca acetate-1wt%$PdCl_2$ powder (Method 3) powder heat-treated at 700°C for 1h was about 86% for 5,000 ppm methane in air at 350°C of the operating temperature. Response time and recovery were also excellent.

Key words : Gas sensor, Thick-film sensor, Tin dioxide, Palladium, Calcium salts, Preparation methods

I. Introduction

The gas sensor is a device to sense a specific gas component in air or to make a quantitative analysis of the gas. There are several commercial types of gas sensors, which are semiconductor type and combustion type, for hydrocarbon gas. The advantages of combustion type sensor include linear sensing behaviors, stability of output for the ambient conditions such as temperature and humidity, fast short-term stability and excellent reproducibility. Its disadvantages are the limit of catalyst lifetime, weak signal at the low gas concentration and decrease in output due to nonflammability above the upper limit of explosion concentration. On the other hand, the advantages of semiconductor type sensor are good sensing behaviors due to thermal stability of metallic oxide, long-term stability, possibility of miniaturization and low cost fabrication. SnO_2 and ZnO are the host materials for the semiconductor type gas sensor and the sensors using such oxides as Fe_2O_3,[1-2] WO_3,[3] Ga_2O_3,[4] and TiO_2[5] are still studied for practical uses. SnO_2 is widely used as the host materials because of low operating temperature, high sensitivity to the hydrocarbon gas, the possibilities of simple sensor design, and light weight and inexpensive fabrication, but the SnO_2 sensor exhibits the low sensitivity and poor selectivity[6] for CH_4, a poor long-term stability,[7] inequality of physical properties, large dependence of sensitivity upon extreme humid conditions[8,9] and difficult sensibility at a low gas concentration. However, the addition of noble metal catalysts such as Pt and Pd can improve both poor selectivity for the specific gas and low sensibility at the low concentration of the gas. As operating temperature increases, the sensitivity of the methane gas varies greater than that of other hydrocarbon gases such as butane, ethane, and propane because the methane gas needs adsorption of much energy. Its sensitivity to CH_4 is high at 400°C or higher, but operating long term stability and durability still remain unsolved.

In this research, we prepare synthetic SnO_2 powder by precipitation method chemical methods and add Ca as crystallization inhibitor and Pd as catalyst by various mixing methods which can improve such sensing properties as indicated above. Then, thick film gas sensor is fabricated with the powder by screen printing method, and the sensing characteristics of methane gas are measured at 350°C. At the same time, the initial sensor resistance has been investigated.

II. Experimental Procedure

1. Mixing method of Ca and Pd additives

$SnCl_4 \cdot 5H_2O$, $Ca(CH_3CO_2)_2 \cdot H_2O$, and $PdCl_2$ were used as the starting materials to prepare the sensor materials. In this study, SnO_2 fine powder was prepared by wet chemical processing.[10-12] This method is to precipitate in the form of metallic hydroxide from Sn^{4+} ion dissolved in solution, and highly pure, active and homogeneous powders which improve the sensing characteristics of the sensor are prepared. A fixed pH value is needed to precipitate hydroxide from the metal ion dissolved in the aqueous solution. When NH_4OH was added to the aqueous solution of $SnCl_4 \cdot 5H_2O$, $Sn(OH)_4$ was precipitated. In case

Pd and Ca salts are added, $Pd(OH)_2$ and $Ca(OH)_2$ are precipitated. The pH conditions to obtain the hydroxide precipitates can be theoretically calculated as follows:

Solubility product[13] of $Sn(OH)_4$ is

$$[Sn^{4+}][OH^-]^4=1\times10^{-56} \quad (1)$$

where

$$\log[OH^-]=-14+pH \quad (2)$$

Eq. (1) can be simplified by taking the logarithm,

$$\log[Sn^{4+}]+4\log[OH^-]=-56 \quad (3)$$
$$\log[Sn^{4+}]=-4pH \quad (4)$$

As for $Pd(OH)_2$, solubility product is

$$[Pd^{2+}][OH^-]^2=10^{-24} \quad (5)$$

Pd ion concentration can be expressed in term of pH:

$$\log[Pd^{2+}]=4-2pH \quad (6)$$

Lines in Fig. 1 represent the boundaries between metal ion and hydroxide stable regions. When $SnCl_4\cdot5H_2O$ and $PdCl_2$ are used, almost all their hydroxides are precipitated at more than pH 7.

The solubility product of $Ca(OH)_2$ is 3.7×10^{-6}.

$$[Ca^{2+}][OH^-]^2=3.7\times10^{-6} \quad (7)$$

The relation between Ca ion concentration and pH is

$$\log[Ca^{2+}]=22.6-2pH \quad (8)$$

In Eq. (8), the minimum pH to precipitate $Ca(OH)_2$ is 11.3. Thus the precipitation is possible only in the strong alkali solution. To apply such strong alkali condition for precipitation to the powder processing procedure is very difficult. Therefore, Ca component as additive has to mix with SnO_2 by mixing methods other than coprecipitation. While Pd catalyst must be on the surface of thick film SnO_2, the probability which Pd is in the host materials becomes high in case of coprecipitation. So is the case of Pd.

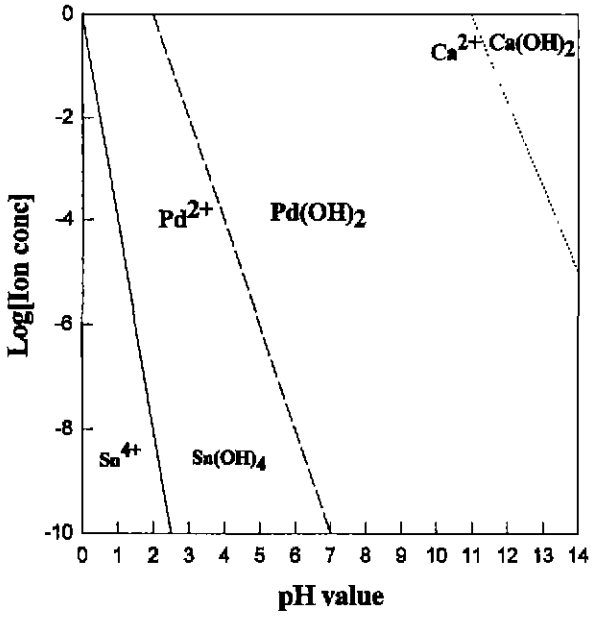


Fig. 1. pH condition to precipitate Pd and Ca hydroxides.

In this research, SnO_2 was prepared by wet chemical processing. And Ca as crystallization inhibitor and Pd as catalyst are added to improve gas sensing properties by direct addition method. Grain growth of SnO_2 powder occurs by means of a surface diffusion mechanism during calcination or sintering. Crystallization inhibitor dispersed well on the surface of SnO_2 will provide a barrier for suppressing crystal growth of SnO_2 particles during calcination or sintering. Ca acetate was well known to be an excellent crystallization inhibitor.[14]

2. Powder preparation and mixing of additives

A wet chemical method was used to prepare SnO_2 raw material powder. Meta-stannic sol was precipitated from $SnCl_4\cdot5H_2O$(0.12 M) solution by adding an aqueous ammonia solution (28%) at pH 9.5. The precipitate was filtered and washed with NH_4NO_3 until chloride was no longer detected upon addition of $AgNO_3$. SnO_2 powder was obtained by drying the precipitate at 110°C for 36 h, and crushing it. And the crushed powder was calcined at 600°C for 2 h and ball-milled for 24 h. The three different experiments were performed according to addition method of $Ca(CH_3CO_2)_2\cdot H_2O$ and $PdCl_2$ to SnO_2 powder.

Method 1: Ca and Pd doped SnO_2 powder was prepared by mixing SnO_2 powder, 0.1 wt% Ca acetate and 1 wt% $PdCl_2$ in ethyl alcohol after SnO_2 powder was calcined 600°C for 2 h.

Method 2: Ca and Pd doped SnO_2 powder was prepared by mixing SnO_2 powder, 0.1 wt% Ca acetate and 1 wt% $PdCl_2$ in ethyl alcohol and calcining the mixture after $Sn(OH)_4$ was dried at 110°C for 36 h.

Method 3: Ca and Pd doped SnO_2 powder was prepared by mixing SnO_2 powder, 0.1 wt% Ca acetate and 1 wt% $PdCl_2$ in deionized water and calcining in mixture after $Sn(OH)_4$ was dried at 110°C for 36 h. Fig. 2 shows the process procedures for preparing Ca and Pd doped SnO_2 powder.

3. Fabrication of gas sensing device and measurements of sensing characteristics

With the paste of suitable viscosity by the addition of small amounts of organic binders, ethylene glycol, to the SnO_2 powder, thick film gas sensor was fabricated on the alumina substrate where Pt electrode was already screen-printed. The interval between electrodes which were coated by an ion coater (Eiko IB-5, Japan) on the alumina substrate was 0.5 mm. The thick film device fabricated by screen printing was dried in air at 110°C for 24 h and heat-treated at 700°C, 1 h. Fig. 3 shows the thick film sensing device. It was stabilized to remove space charge presence. This treatment was done by supplying 5V for 3~4 days at the same temperature

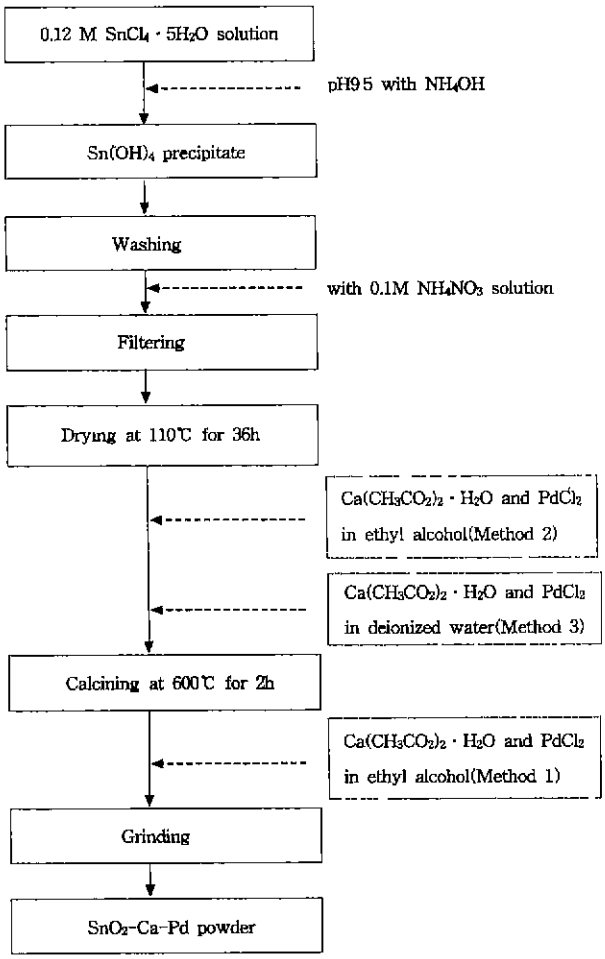


Fig. 2. Procedure for the addition of Ca acetate and $PdCl_2$ to SnO_2 powder.

of sensing property measurement. The CH_4 gas was injected with syringe into the top of the chamber and the fan was operated to make uniform atmosphere of the gas inside chamber. Then, we observed the voltage change by the recorder (Rikadenki, R-02) and multimeter(Fluke, 8085A) to measure the sensitivity to CH_4 gas. Measurement of the voltage change before and after gas injection gives the following sensor resistance.

$$R_S = R_L \times \left(\frac{V_{CC}}{V_L} - 1\right)$$

where R_S is the sensor resistance, R_L is the load resistance, V_{CC} is the operating voltage, and V_L is the output voltage.

Measured resistance change can be used to obtain gas sensitivity (S).

$$S = \frac{Ra - R_g}{R_a} \times 100(\%)$$

where Ra and Rg are the device resistance before and after gas injection, respectively. Fig. 4 shows the schematic diagram for measurements of gas sensing characteristic.

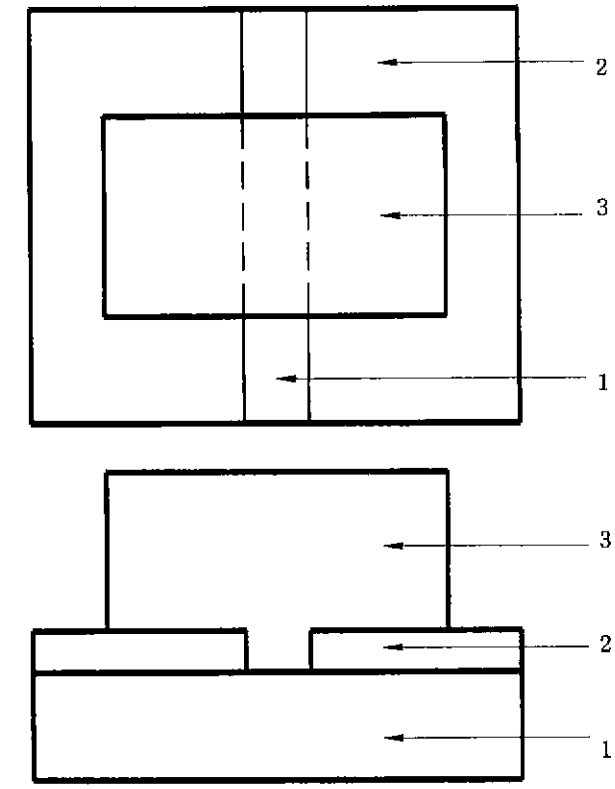


Fig. 3. Structure of the thick-film gas sensing device.
1: Alumina substrate, 2: Pt electrode, 3: Sensing material

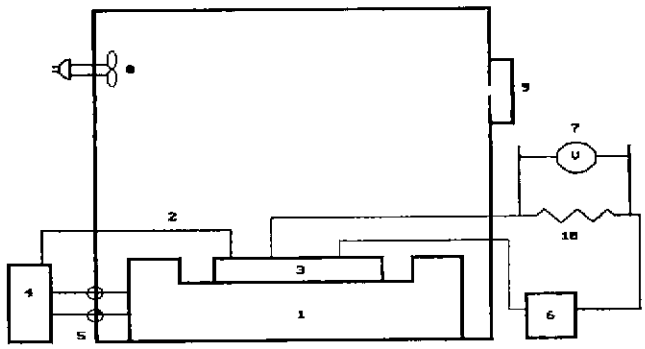


Fig. 4. Schematic diagram for measurements of gas-sensing characteristics.

1: Heater	6: Power supply
2: Thermocouple	7: Multimeter
3: Sensor	8: Fan
4: Controller	9: Gas inlet
5: Power	10: Standard resistance

4. Analysis of sensing materials

X-ray diffractometer (Rigaku Co., Japan) was used to identify phase of powder prepared by wet chemical processing. X-ray used was Cu Kα (λ=1.5405Å), scanning ratio was 4° per minute and 2θ was in the range of 20~70°. The experimental data were compared with JCPDS card. Transmission electron microscopy (TEM; Hitachi S-600, Japan) was used to observe the phase and agglomeration of the powder. The dispersion agent, aqueous solution of sodium hexametaphosphate (0.3%), was used

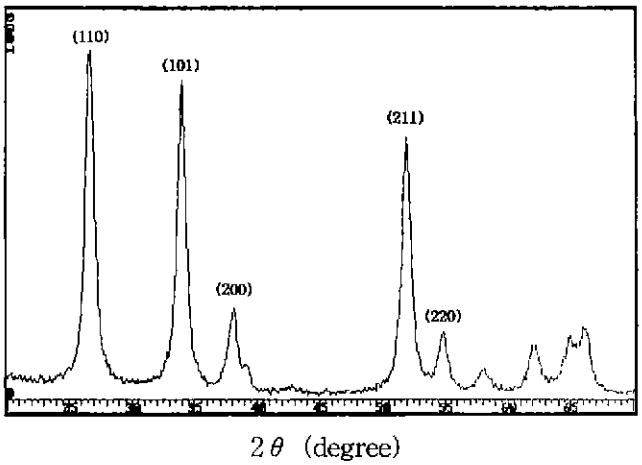


Fig. 5. XRD patterns of SnO_2 powders prepared by Method 3.

to prepare for observing the TEM specimen.

III. Results and Discussion

1. Material characteristic of sensing material powder and thick film device

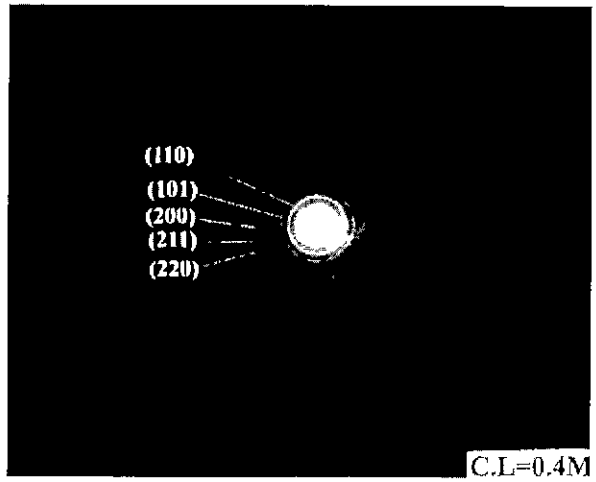
Fig. 5 shows X-ray diffraction pattern of SnO_2 powder. The peaks in the XRD pattern of the powder give the identification of the SnO_2 phase, as compared with JCPDS card. Fig. 6 shows the diffraction pattern, the phase and agglomeration of Ca and Pd doped SnO_2 powder prepared with SnO_2-0.1 wt%Ca acetate-1 wt%$PdCl_2$ powder (Method 3) powder calcined at 600°C for 2 h, observed by TEM. SnO_2 crystallites were identified from the diffraction pattern. Judging from necks between particles, we could observe huge agglomeration and spherical shape of powder.

2. Sensing characteristics

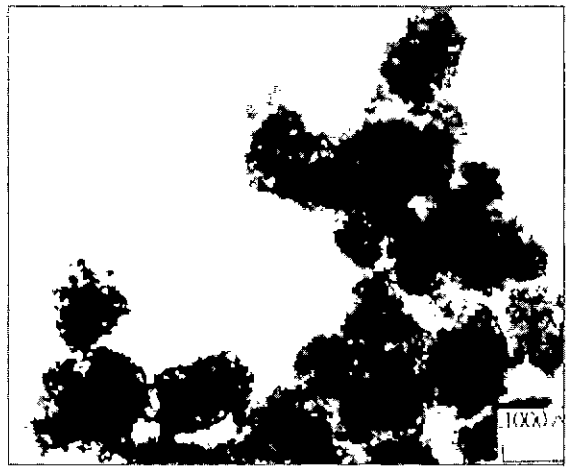
The contents of Ca acetate and $PdCl_2$ of the SnO_2 powder were 0.1 wt% and 1 wt%, respectively. The powder prepared by various mixing methods was heat-treated, and then the optimum CH_4 gas sensing condition was investigated. The change in resistance was measured after injecting CH_4 gas whose concentration was varied from 0 to 5,000 ppm in 1,000 ppm interval. In this case, the operating temperature was 350°C.

2.1. Sensing characteristics in terms of different powder mixing methods

Although the dispersion of powder by impregnation method[15] might be lower than that by coprecipitation, but the present method is simple and gives uniform distribution of catalyst. The devices fabricated by Methods 1 and 2 were heat-treated at 700°C for 1 h, and then the gas sensitivity was measured. As a result, initial resistance of the device was not stabilized as shown in Fig. 7, so the function as a sensor seems to be lost. This phenomenon in case for the powder prepared by Method 1



(a)



(b)

Fig. 6. (a) Diffraction pattern and (b) micrograph of SnO_2-0.1wt%Ca-1wt%Pd (Method 3) powders calcined at 600 °C for 2 h, observed by TEM.

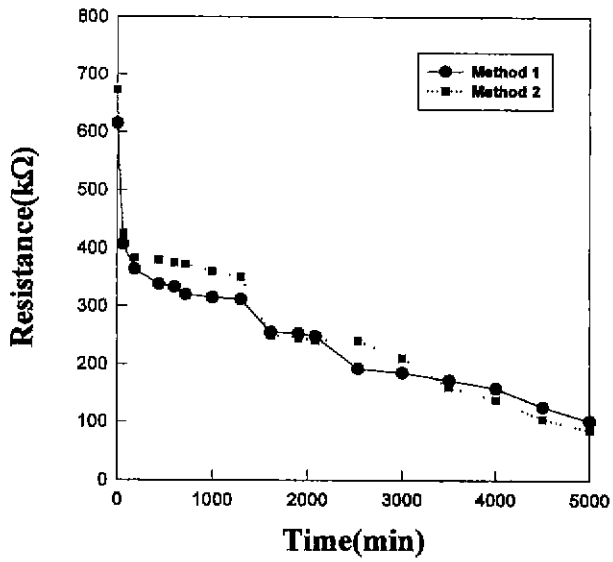


Fig. 7. The long-term resistance stability of the SnO_2-0.1 wt%Ca-1wt%Pd sensing device prepared by Methods 1 and 2.

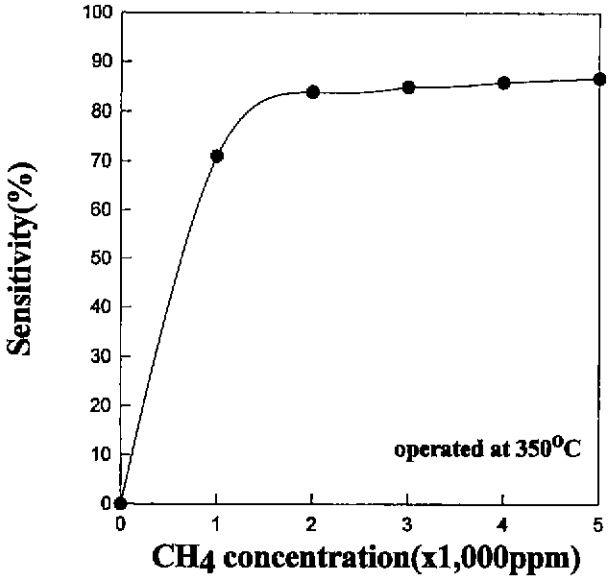


Fig. 8. Sensitivity of the CH_4 sensors prepared with the SnO_2-0.1wt%Ca acetate-1wt%$PdCl_2$ powder(Method 3) and heat-treated at 700 ℃ for 1 h to CH_4 gas in air.

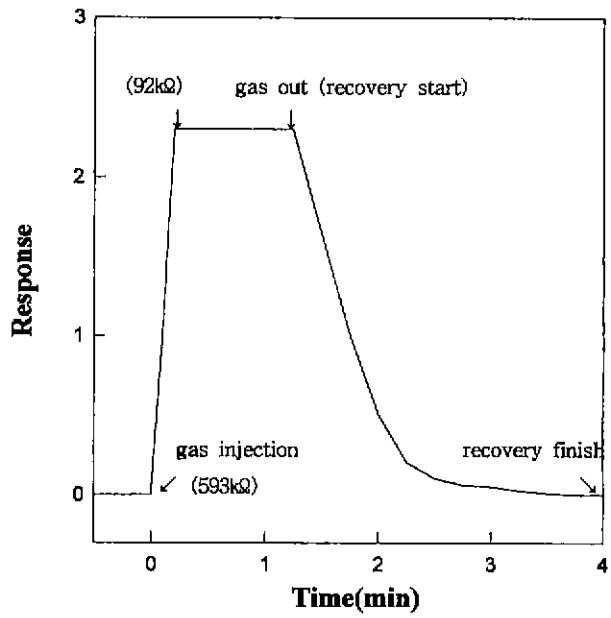


Fig. 9. Response time to methane gas.

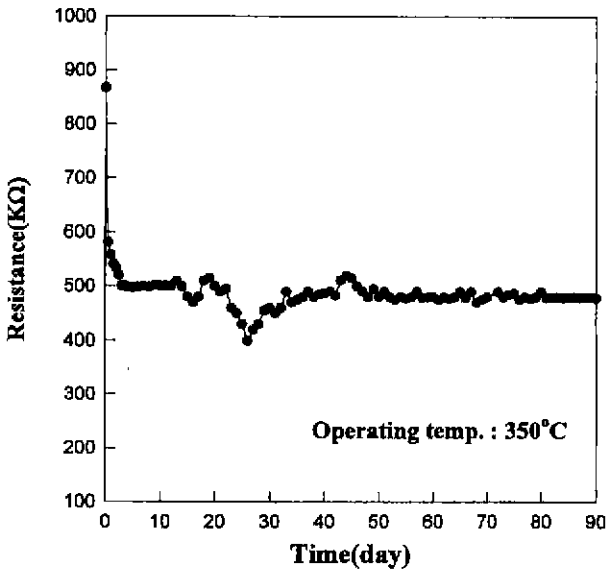


Fig. 10. Long-term resistance stability of thick film device prepared with SnO_2-0.1wt%Ca acetate-1wt%$PdCl_2$ powder (Method 3).

occurs because $PdCl_2$ was not easily decomposed to produce Pd and Cl_2 separately. In cases of Methods 1 and 2, $Ca(CH_3CO_2)_2 \cdot H_2O$ was not soluble in the ethyl alcohol. Thus complete decomposition was not achieved during heat-treated. Therefore, those compound states seem to interfere in gas sensing. But in case of Method 3, it is considered that Ca and Pd additives were well soluble in deionized water, and they were mixed enough to give homogeneous distribution of the powder. Additionally, Cl component was easily removed because of sufficient calcination, so resulting in high sensitivity. The initial resistance was 700~800 kl and sensitivity was 80% or more.

2.2. Sensing characteristics as a function of the gas concentration

Fig. 8 shows the sensitivity of device fabricated with SnO_2-0.1 wt%Ca acetate-1 wt%$PdCl_2$ powder (Method 3) heat-treated at 700°C for 1 h for 5,000 ppm methane in air. It almost approaches up to a saturation value (sensitivity 80%) at 2,000 ppm methane. Therefore, this sensor is suitable for domestic gas alarm detector.

2.3. Response and long term resistance stability

Fig. 9 shows response property of thick film device fabricated with SnO_2-0.1 wt%Ca acetate-1 wt%$PdCl_2$ powder (Method 3) heat-treated at 700°C for 1h for 5,000 ppm methane in air. The device responded immediately after gas was injected. It took only 10 seconds from injection point to the maxium sensitivity point. It tooks 1~2 minutes to recover to the initial resistance value after releasing the gas, because CH_4 gas (specific gravity: 0.54) is lighter than air. Therefore, recovery time is fast. Recovery time depends on the releasing speed of methane gas in the measuring chamber, so when methane gas is forced to be released, the response can be expected to be faster. Production of such gas sensing material on a commercial scale needs the maintenance of long-term resistance stability and high sensitivity. Fig. 10 shows the measurement of long-term resistance stability of the above-mentioned device for 90 days. Comparatively, its characteristic was stable and the change of initial resistance seems to be affected by variation of the humidity and the room temperature.

IV. Conclusions

SnO_2 fine powder prepared by wet chemical processing,

Ca as crystallization inhibitor and Pd as catalyst were mixed by various methods to fabricate a device with high sensitivity for methane gas. The sensitivity, response time, recovery, long-term resistance stability at 350°C of the fabricated CH_4 gas sensor were investigated. Conclusions are drawn as follows:

1. In case of using ethyl alcohol as mixing solution before or after calcination when Ca acetate and $PdCl_2$ are added (Methods 1 and 2), initial resistance of device was not stabilized. But in case of using deionized water as mixing solution before calcination (Method 3), its sensing property was stabilized after stabilization treatment for 2~3 days.

2. The sensitivity of device fabricated with SnO_2-0.1 wt%Ca acetate-1 wt%$PdCl_2$ powder (Method 3) heat-treated at 700°C for 1h was about 86% for 5,000 ppm methane in air at the 350°C of operating temperature.

3. The above mentioned device had fast response and recovery time. Response time was in 10 seconds and recovery time was in 1~2 minutes.

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