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A Novel Cold-Wall MOCVD Method for Fabrication of a Durable Micro-Machined SnO_2 Gas Sensor

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A novel cold-wall metal organic chemical vapor deposition (MOCVD) method has been developed to fabricate a durable micro-machined SnO_2 thin-film gas sensor. Instead of using a hot plate or a heater around a reactor, a microheater fabricated using micro-machining technology is put into the reactor and used as the heat source for thermal decomposition of the metal organic source. Since SnO_2 film is selectively deposited on the microheater using this method, no patterning process for the SnO_2 film is necessary. Moreover, the durability of the sensor fabricated using this method (N-sensor) is considerably improved compared with that of a sensor fabricated by a conventional hot-wall MOCVD method (C-sensor). The N-sensor outlasted over seven million heat cycles (500°C for 100 ms and room temperature for 100 ms), while the C-sensors were broken after a few hundred thousand heat cycles. Although the N-sensor demonstrated excellent durability, its sensitivity for methane gas was low. However, the sensitivity of the method may be improved by optimizing the deposition conditions.

1. Introduction

Semiconductor gas sensors, for example SnO_2 gas sensors, are widely used to detect various flammable gases. The sensors generally consume large amounts of electric power because most of them are fabricated using bulk technology.

There has been great interest in the fabrication of micro-machined gas sensors[1–3] because micro-machining technology effectively reduces power consumption. The sensors usually require construction of a micro-diaphragm or a micro-bridge because a cavity under the heater is indispensable for thermal insulation between the heater and the substrate. The power consumption of the sensors is reported to be reduced to 55 mW at 250°C with continuous operation.[3]

The ultimate purpose of our study is to develop a gas sensor that can detect methane and be operated with dry batteries in city gas leak detectors. The sensor should have a lifetime of at least five years and power consumption of less than 0.2 mW. Using the conventional fabrication technique, we successfully fabricated a micro-machined SnO_2 gas sensor that consumed 15 mW at 500°C with continuous operation. Therefore, it could be operated with less than 0.2 mW of power consumption when it was heated for 400 ms every 30 seconds. However, durability of the sensor was not sufficient. Durability of over five million heat cycles, which correspond to five years when intermittently operated every 30 seconds, is required for our purpose; however, the sensor was prone to breakage when heated to the operating temperature. Resistance of the sensor typically increased to more than 100 MΩ after a few hundred thousand heat cycles.

In this study, we have developed a novel cold-wall MOCVD method of fabricating films to solve the problem of easy breakage of the sensor film. The method and the sensor characteristics are described in detail in the following.

2. Materials and Methods

2.1 *The novel cold-wall MOCVD method*

A microheater is used in the novel method. The process of fabricating the microheater shown in Fig. 1 is as follows. (a) SiO_2 as an insulator between the substrate and the heater and polycrystalline silicon (poly-Si) as the heater material are deposited on the silicon substrate by atmospheric-pressure CVD (APCVD) and low-pressure CVD (LPCVD), respectively. The poly-Si and the SiO_2 are annealed after phosphorus is doped into the poly-Si. (b) The poly-Si is patterned by photolithography and etching to be the heater. (c) SiO_2 and platinum are deposited using APCVD and sputtering, respectively. The SiO_2 acts as an insulator between the heater and the SnO_2 film. The platinum acts as an electrode to measure the resistance of the SnO_2 film. (d) The platinum deposits are patterned by photolithography and etching to be the electrodes for SnO_2. (e) Contact holes to the poly-Si heater are made through the SiO_2. After that, chrome and gold are deposited by sputtering and patterned as the bonding pads where electric wires are connected. (f) A cavity is formed under the heater to construct a bridge by anisotropic etching using 25% tetramethylammonium hydroxide (TMAH) solution. The temperature of TMAH is kept at 70°C during etching. The etching time is about 27 h for a 280-μm-thick Si(110) substrate. The microheater thus fabricated is shown in Fig. 2.

A schematic diagram of the novel MOCVD system is shown in Fig. 3. Tetramethyltin (TMT) is put in an isothermal bath and used as the source. Argon is used as the carrier gas, which flows into the reactor with the vaporized source. The source is oxidized by oxygen in the reactor. The flow rate of each gas is controlled by a mass flow controller (MFC). The resistance and temperature of the heater in ambient are calibrated before deposition. The microheater is put into the reactor and heated electrically. The temperature of the heater is

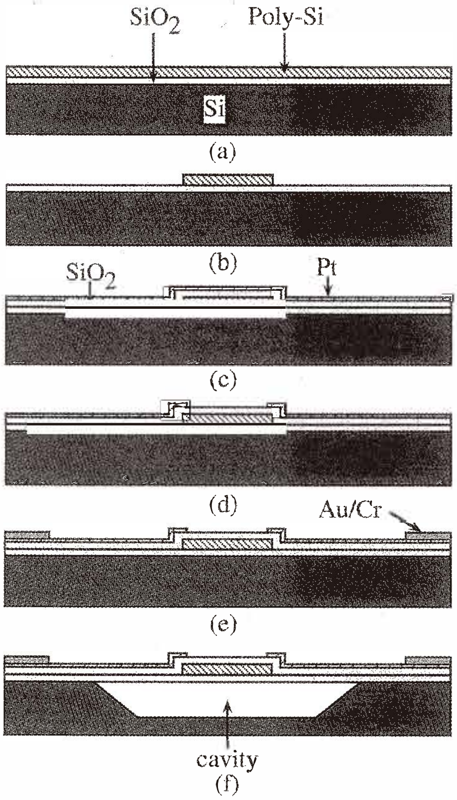

Fig. 1. Fabrication of the microheater.

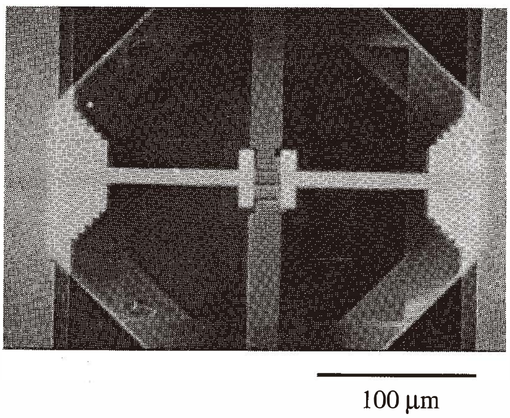

Fig. 2. An SEM image of the microheater.

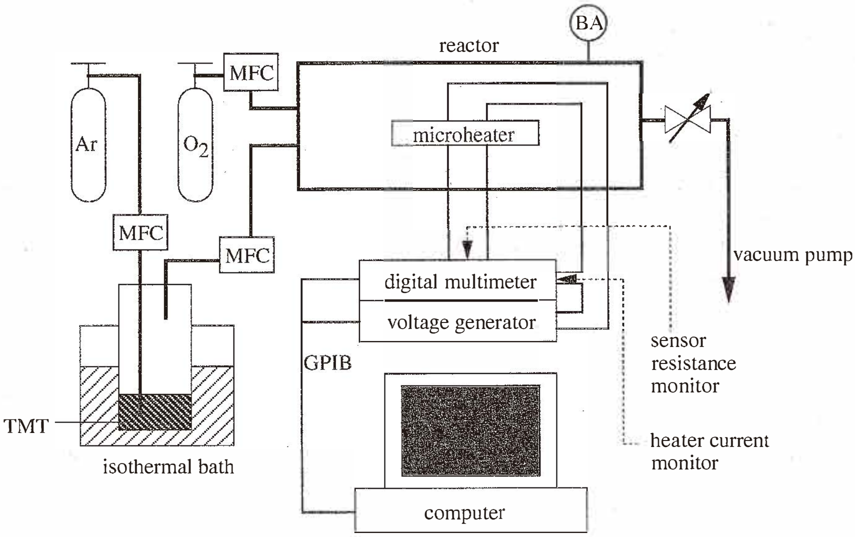

Fig. 3. A schematic diagram of the novel MOCVD system.

regulated by keeping the heater at an even resistance with a computer controlled power supply. A digital multimeter controlled by the computer is used to measure the current through the heater and the resistance of the SnO_2 film during deposition. In this experiment, temperature of TMT, and flow rates of argon and oxygen were 40°C, and 50 cc/min and 100 cc/min, respectively.

The relationship between growth rate and substrate temperature was investigated in the conventional hot-wall MOCVD by depositing SnO_2 on silicon wafers and the result is shown in Fig. 4. The substrate temperature was calibrated in advance as a function of the temperature of the heater around the reactor. Deposition occurs above about 400°C, and the rate radically increases with increasing temperature, following an Arrhenius dependence. This result is consistent with that from previous studies.[4,5] Figures 5(a) and 5(b) are images of temperature distribution on the microheater when heated electrically. The temperature was measured using a radiation thermometer. The temperature at the center of the heater is set at 500°C and 600°C. The high-temperature area is limited to the proximity of the heater. It is expected from the results shown in Figs. 4 and 5 that the SnO_2 film is selectively deposited only on and near the heater when the microheater is put into the reactor and heated electrically. A schematic diagram of the deposition using the novel method is shown in Fig. 6.

It is reported that oxidation of methane occurs above 450°C on SnO_2.[6] Practically, the operating temperature for SnO_2 to detect methane is around 500°C. When SnO_2 is deposited at the same temperature at which it operates, the SnO_2 experiences less stress during operation than when it is deposited at a different temperature. Therefore, the temperature of the heater should be around the operating temperature during the deposi-

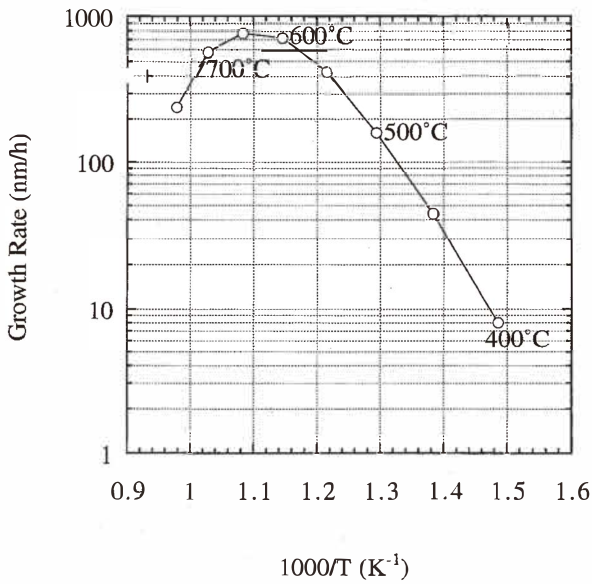

Fig. 4. Dependence of the growth rate of SnO_2 film on substrate temperature. Films were deposited using the hot-wall MOCVD method.

tion. In this experiment, two deposition temperatures were evaluated to control the area of deposition. If the deposition occurs on the area corresponding to the temperature distributions shown in Figs. 5(a) and 5(b), the area of deposition should be larger at 600°C than at 500°C, because deposition occurs above 400°C as already mentioned.

2.2 *Characteristics of the sensor*

Durability against and sensitivity to methane and humidity were investigated. The experiments were carried out in synthesized air (80% N_2 and 20% O_2) with no humidity. The heater was intermittently operated. One heat cycle consisted of 500°C for 100 ms followed by room temperature for 100 ms. Sampling of the resistance of the sensor was carried out after 10 ms of increasing temperature. Ten ms is the time required for the sensor to be heated to 500°C, because rise and fall of the temperature takes place in two ms as shown in Fig. 7.

The time dependence of the resistance of two sensors (the N-sensor and the C-sensor) was examined as a test of durability. Gas sensitivity to 1% methane was also investigated during the durability test. The sensor has to survive at least five million heat cycles for our application.

Gas sensitivities of the N-sensor to various concentrations of methane ranging from 0.01 to 1% were measured. Gas sensitivity is defined as Ra/Rg, where Ra and Rg are the resistance of the sensor in air and in the given concentration of methane, respectively. Response of the sensor to 75% humidity was also investigated.

(a)

(b)

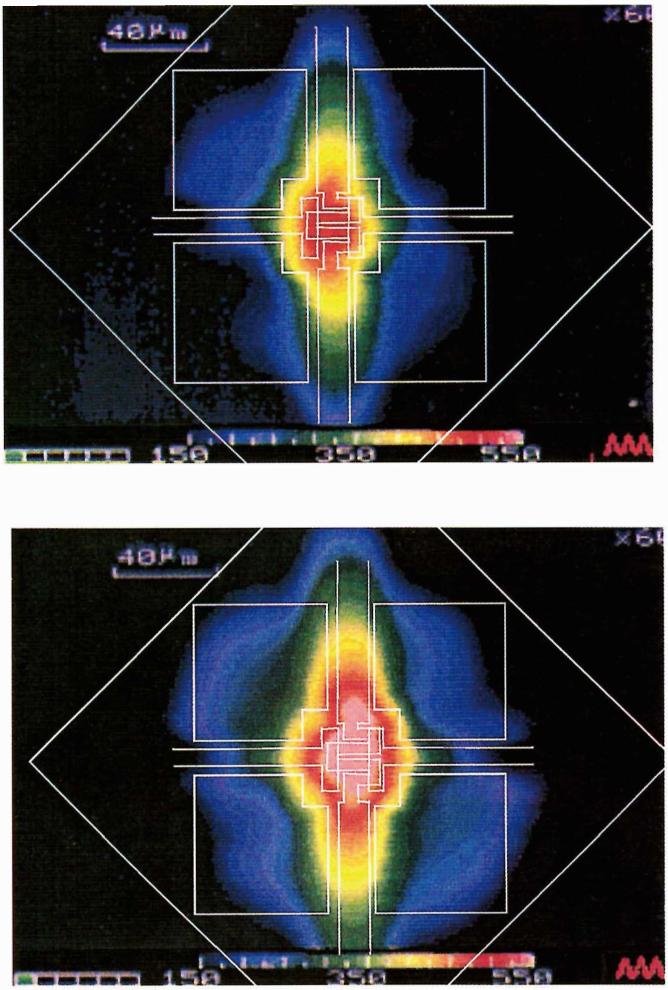

Fig. 5. Temperature distribution on the microheater. The temperatures at the center of the heater are (a) 500°C and (b) 600°C.

3. Results

3.1 *The novel cold-wall MOCVD method*

Figures 8(a) and 8(b) are scanning electron microscope (SEM) images of the N-sensor after deposition of the SnO_2 film. The temperature of the heater during deposition was 500°C in Fig. 8(a) and 600°C in Fig. 8(b). As expected, the sensor film was selectively

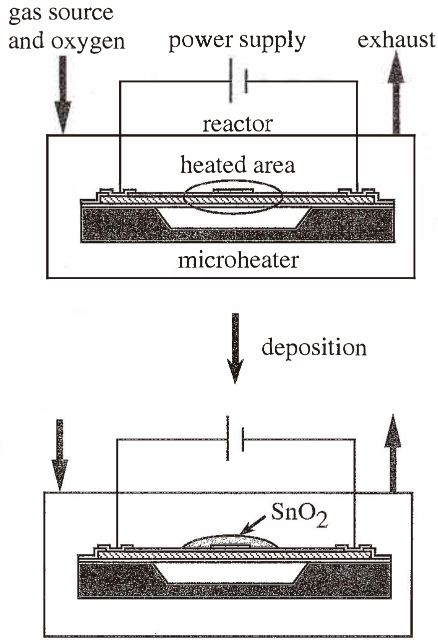

Fig. 6. Selective deposition by the novel MOCVD method.

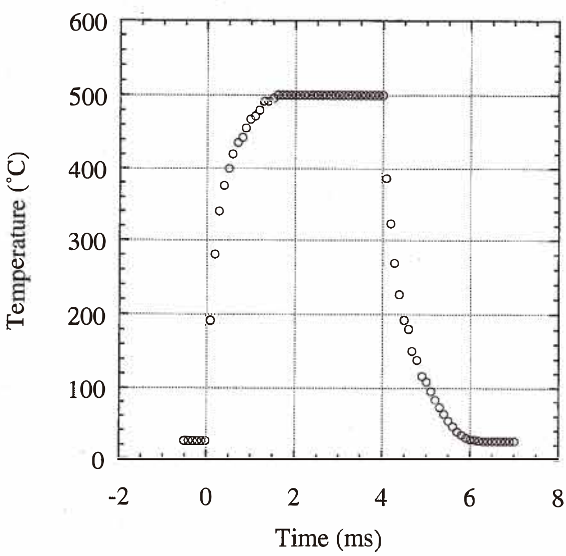

Fig. 7. Thermal response of the N-sensor when heated to 500°C and cooled to room temperature.

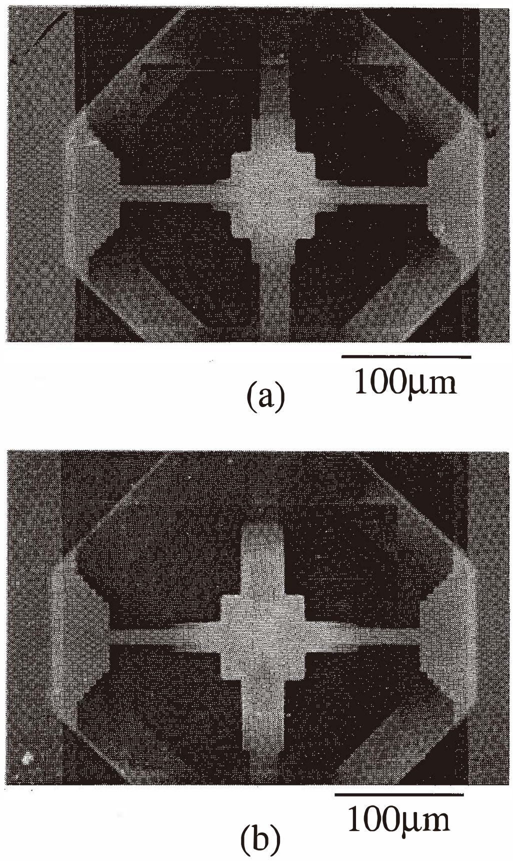

Fig. 8. SEM images of two sensors after deposition of SnO_2 using the novel method. The temperatures of the heater are (a) 500°C and (b) 600°C.

deposited on the microheater and the thickness of the film decreased with increasing distance from the center of the heater. The deposited areas on the two sensors are almost within each contour line of 400°C shown in Figs. 5(a) and 5(b). It is concluded that the area of deposition can be controlled by the temperature of the heater.

The fabrication of the micro-gas sensor is simplified by this novel method because selective deposition eliminates the need for further patterning processes of the sensor film. Furthermore, since the characteristics of the sensor are very sensitive to the fine structure of the surface, the elimination of processes that may affect the structure is an additional advantage of this method.

3.2 *Sensor characteristics*

The durability of the N-sensor was considerably improved in comparison with the C-sensor. Figure 9 shows the results of a durability test. The N-sensor used in this experiment was that shown in Fig. 8(a). The resistance of the N-sensor was quite stable over seven million heat cycles, while the C-sensor was easily broken after only a few hundred thousand heat cycles. The durability of the N-sensor was improved by more than a factor of 50 over that of the C-sensor. The dependence of gas sensitivity to 1% methane on the number of heat cycles is shown in Fig. 10. The sensitivity was found to be stable during the experiment. The resistance in Fig. 9 changes by about ± 30% from the initial value during the experiment, but it changes more for 1% methane. It is enough for our application to detect the concentration of methane. Therefore, the drift of the resistance is not a serious problem. Since our goal is to develop a gas sensor that endures five million heat cycles, the N-sensor fully satisfies our demand.

The relationship between gas sensitivity and methane concentration is shown in Fig. 11. The Japanese regulation for city gas leak detectors requires them to detect 1.25% methane. The N-sensor satisfies this regulation because it detects 1% methane. Figure 12 shows the response of the sensor to 75% humidity. The data were obtained every 10 s. The graph does not show the actual response time of the sensor because it takes about 10 min for the atmosphere to be replaced completely. Sensitivity to humidity as evaluated from the result is 1.6, which is lower than that to 1% methane. This means that the sensor can detect 1% methane even in the presence of humidity. For use in an actual environment, however, further improvement in the sensitivity to methane is required, and the sensor should be equipped with a filter to reduce the effect of humidity.

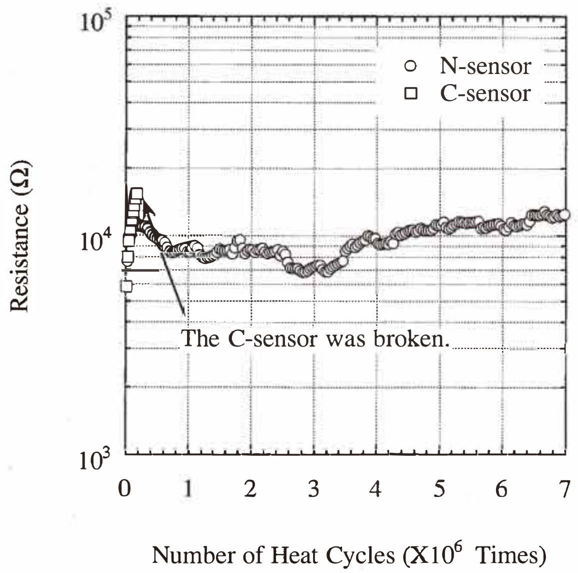

Fig. 9. Time dependence of the resistance of two sensors. The heaters were intermittently operated. One heat cycle consisted of 500°C for 100 ms followed by room temperature for 100 ms.

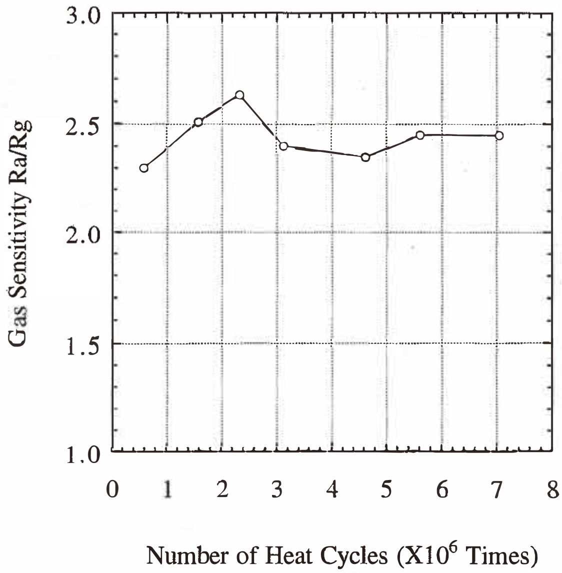

Fig. 10. Time dependence of the gas sensitivity of the N-sensor to 1% methane.

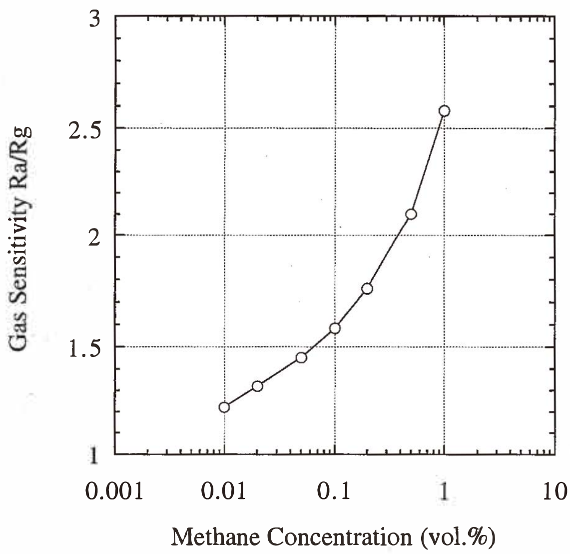

Fig. 11. Relationship between gas sensitivity and methane concentration. The heater was operated under the same conditions as in Fig. 9.

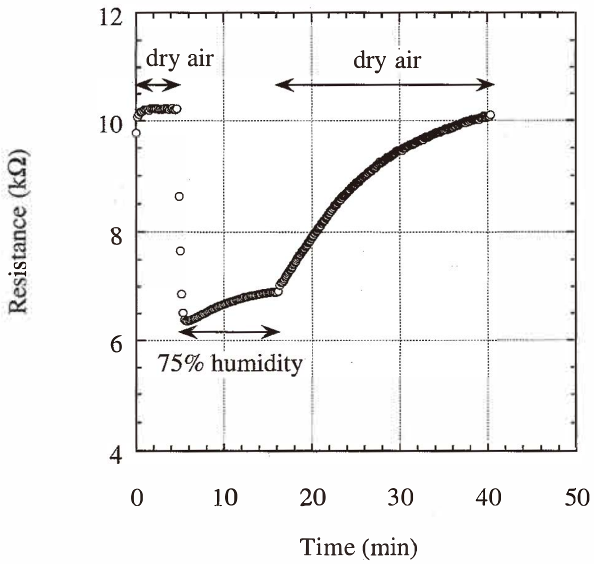

Fig. 12. Response of the N-sensor to 75% humidity.

4. Discussion

4.1 *Improvement in durability*

When the temperature of the sensor was raised, it was observed with an optical microscope that the bridge bowed up due to thermal expansion of the heater. Table 1 shows vertical displacements at the center of the heater for three types of sensors electrically heated to 500°C. Each value is the average of four measurements. Displacements were measured with an optical microscope that measure distance in the vertical direction. These displacements correspond to about a 0.05% distortion of the sensor film. A large tensile force due to distortion may cause the failure of the sensor when heated, as shown in Fig. 13(a). At first, we assumed that the improvement in durability was due to a decrease in the displacement. However, there was no noticeable difference among the three types of sensors; the values were almost the same within the error of measurement. Therefore, there must be another reason for the improvement in durability.

We consider the following reason as depicted schematically in Fig. 13(b). When a SnO_2 film is deposited using the novel method, the bridge of the microheater is in the same thermal condition as when the sensor is actually used, namely the bridge bows up because of thermal expansion of the heater. Therefore, there is essentially no stress in the SnO_2 film during heating. Although there is some stress in the film when the temperature is decreased to room temperature, the stress is insignificant. The stress is expected to be compressive, and the film is more durable under compressive stress than under tensile stress. We assume

Table 1
Vertical displacements of the bridge when electrically heated to 500°C, measured with an optical microscope.

Type of sensor	Displacement of the bridge (μm)
Microheater without SnO_2	1.6 ± 0.5
C-sensor	1.5 ± 0.6
N-sensor	1.8 ± 0.5

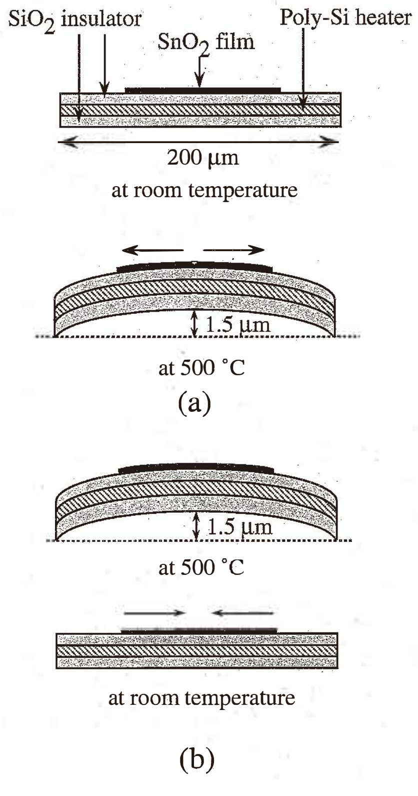

Fig. 13. Schematic cross-sectional views of two sensors at 500°C and at room temperature. (a) is the C-sensor and (b) is the N-sensor.

that this is the reason why the durability of the N-sensor was improved; however, this assumption has not been substantiated yet, because there is no available instrument that can evaluate stress of μm-order thin films.

There are other approaches to the control of the stress: 1. Use of another film with less stress than SiO_2, such as oxynitride, is effective.(2) 2. Deposition of a third film is also effective to eliminate stress.(7) For example, when the stress in the film is compressive, a third film that has tensile stress is used to cancel the compressive stress. However, it is difficult to adjust the conditions of deposition properly for these approaches. Our method is very simple because tedious parameter optimization is not required.

4.2 *Gas sensitivity*

As mentioned in 3.2, sensitivity better than that indicated in Fig. 11 is required for actual use. The morphology of SnO_2 in the N-sensor used in the experiments is shown in Fig. 14(a). Smaller grain size may be required for higher sensitivity. It is necessary to optimize the conditions for deposition to improve gas sensitivity. However, there is one serious problem with the conventional method. If we vary the conditions in conventional hot-wall MOCVD, film uniformity degrades. Since uniform deposition is indispensable to the micro-machining process, there are not many conditions possible for the process. Therefore, optimization of the deposition process is very complex and unrealistic in conventional hot-wall MOCVD. The novel method solves this problem. Uniform deposition is not essential since the method does not require any further processing of the sensor film because the film is selectively deposited on the microheater. Therefore, various conditions become possible for the deposition of the sensor film. Improvement in sensitivity by controlling conditions for deposition is thus conceivable.

We first varied deposition time to control grain size. Figures 14(a) to 14(d) are SEM images of SnO_2 with different deposition times of (a) 180 s, (b) 140 s, (c) 100 s and (d) 60 s. Depositions were performed at 500°C. Grain size decreases with decreasing deposition time, and gas sensitivity increases with decreasing grain size, as shown in Fig. 15. Optimization of other deposition conditions may also be effective for improving sensitivity.

5. Conclusion

A novel cold-wall MOCVD method for an SnO_2 micro-gas sensor has been developed. The SnO_2 micro-gas sensor fabricated using this method exhibited excellent performance in terms of durability; the resistance and the sensitivity of the sensor were quite stable over seven million heat cycles, while the sensor fabricated using a conventional hot-wall MOCVD method was broken after only a few hundred thousand heat cycles. The reason why the durability was improved may be that the stress in the sensor film deposited using the new method was significantly reduced during heating and became compressive at room temperature. Moreover, no further patterning process is necessary for the sensor film because deposition occurs selectively on the microheater. This fact makes it possible to simplify the fabrication process. Gas sensitivity of the sensor to 1% methane was about 2.9

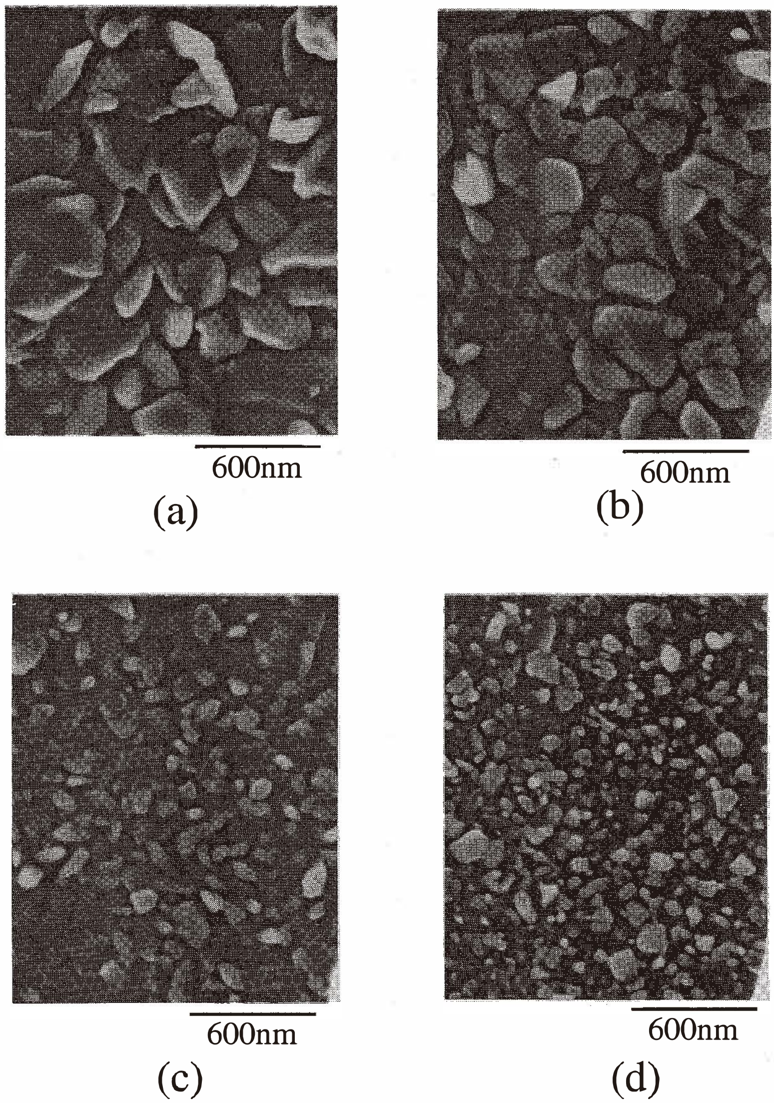

Fig. 14. SEM images of SnO_2 films with different deposition times of (a) 180 s, (b) 140 s, (c) 100 s and (d) 60 s.

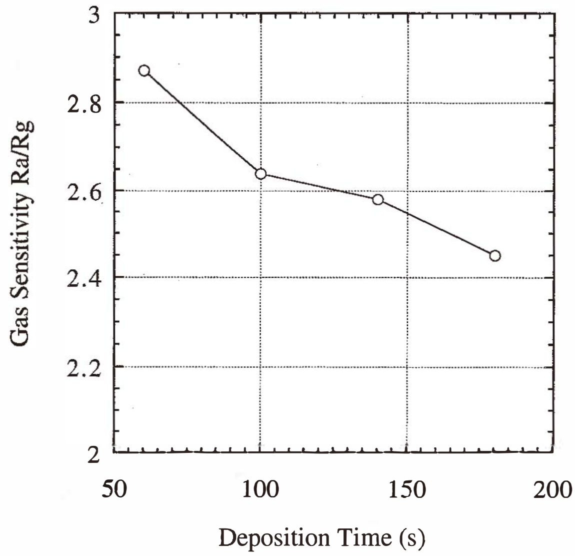

Fig. 15. Dependence of gas sensitivity to 1% methane on deposition time. The heater was operated under the same conditions as in Fig. 9.

at the maximum. Although the sensitivity was low, the novel method may improve sensitivity by optimizing film quality, because the sensor film can be deposited under various conditions using this method.

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