Nano-gap Effects in Semiconductor Gas Sensors

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Keywords: Semiconductor gas sensor, Nano-gap effect, WO₃, In₂O₃, SnO₂

These days, high sensitivity gas sensors are increasingly demanded for the detection of air pollutants, VOCs (volatile organic compounds), bad-smelling gases, and so on. The semiconductor gas sensor using conductivity change of oxide semiconductor is one of promising candidates for these purposes because of its high sensitivity, compact size, simple structure and low cost. Recently, we have found that the sensitivity to dilute NO₂ was increased with decreasing gap size for the WO₃ thin film nanosensor having nano gap electrode less than 1 µm. The similar nano-gap effect was also observed for Cl₂ gas sensing using the In₂O₃ thin film nanosensor. But, the nano-gap effect was different from each other in NO₂-WO₃ system and Cl₂-In₂O₃ system. In this paper, the reasons for the difference in nano-gap effect was described with new data of nano-gap effect in the H₂S-SnO₂ system.

The nano-gap electrode was fabricated by means of MEMS techniques (photolithography and FIB). The nano-gap electrode was obtained with gap size of 0.1-1.3 µm and line width of 20 µm. The oxide thin films (WO₃, In₂O₃, and SnO₂) were deposited on the nano-gap electrode by using precursor sol solutions to be nanosensors. Figure 1 shows the schematic drawing of oxide thin film nanosensor. The objective gases were dilute NO₂ for WO₃ nanosensor, dilute Cl₂ gas for In₂O₃ nanosensor and dilute H₂S for SnO₂ nanosensor. The sensitivity (S) was defined as Rg/Ra in all cases. S>1 means the response with resistance increase, while S<1 is resistance decrease. The larger deviation of S from 1 means the higher sensitivity.

The gas sensitivities of various oxide thin film nanosensors were shown in Fig. 2 as a function of gap size. In all cases, the sensitivity tended to be increased with decreasing gap size. However, the effect of gap size was different from each other, i.e., the marked nano gap effect was obtained for the Cl₂-In₂O₃ and the NO₂-WO₃ systems, while the effect was weak for the H₂S-SnO₂ system.

In order to explain the nano-gap effect, from the simple model where a few grains were packed in the nano-gap electrode, the sensitivity was expressed by using the sensitivity at oxide-electrode interface (Sᵢ) and at grain boundary (Sₓ). Compared with the Sᵢ/Sₓ ratio for each system, it was 32 at 0.5 ppm NO₂ of WO₃ sensor, 43 at 1 ppm Cl₂ of In₂O₃ sensor, 9.7 at 1 ppm H₂S and 3.4 at 0.1 ppm H₂S of SnO₂ sensor. It is noted that in the case of NO₂ and Cl₂ detection, the marked nano-gap effect was observed due to the large Sᵢ/Sₓ ratio. On the other hand, as observed in H₂S detection, the nano-gap effect was weak due to the small Sᵢ/Sₓ ratio, especially in the case of 0.1 ppm H₂S. In the objective gas-semiconductor sensor system with the larger Sᵢ/Sₓ ratio, the oxide-electrode interface plays an important role in gas sensing, and the nano design of electrode structure like nano-gap electrode is significant for the high sensitivity gas sensor.

Fig. 1. Schematic drawing of oxide thin film nanosensor equipped with nano-gap electrode

Fig. 2. Sensitivities in various systems as a function of gap size. a) Cl₂-In₂O₃ at 250 °C, b) NO₂-WO₃ at 200 °C, c) H₂S-SnO₂ at 300 °C.
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The effect of gap size on the gas sensitivity of semiconductor gas sensor was evaluated in the NO₂ sensing using WO₃ nanosensor, the Cl₂ sensing using In₂O₃ nanosensor and the H₂S sensing using SnO₂ nanosensor. The nano-gap effect was markedly observed in the NO₂-WO₃ system and the Cl₂-In₂O₃ system (resistance increase), while the H₂S-SnO₂ system showed the weak nano-gap effect. This difference resulted from the ratio (Sᵢ/Sₕb) of sensitivity at semiconductor oxide-electrode interface (Sᵢ) to at grain boundary (Sₕb). The NO₂-WO₃ and the Cl₂-In₂O₃ systems showed the large Sᵢ/Sₕb ratio (32-43), while the small ratio (9.7) was obtained in the H₂S-SnO₂ system at the gas concentration of 0.5-1 ppm. It was found that the clearer nano-gap effect was obtained for the system having the larger Sᵢ/Sₕb ratio. In the system having large Sᵢ/Sₕb ratio, the nano-design of electrode structure like nano-gap electrode was important for high sensitivity gas sensors.

Keywords: Semiconductor gas sensor, Nano-gap effect, WO₃, In₂O₃, SnO₂

1. Introduction

These days, high sensitivity gas sensors are increasingly demanded for the detection of air pollutants, VOCs (volatile organic compounds), bad-smelling gases, and so on (1). The semiconductor gas sensor using conductivity change of oxide semiconductor is one of promising candidates for these purposes because of its high sensitivity, compact size, simple structure and low cost. Recently, we have proposed that the electrode design was important to enhance the sensitivity of semiconductor gas sensor. Namely, it was demonstrated that the sensitivity to dilute NO₂ was increased with decreasing gap size for the WO₃ thin film nanosensor having nano gap electrode less than 1 µm (2). In the nano gap electrode, the number of oxide grains is dramatically decreased and thus the contribution of oxide-electrode interface is increased in the total sensor resistance. The nano-design of electrode structure to increase the contribution of interface would enhance the sensitivity of semiconductor gas sensor. The similar nano-gap effect was also observed for Cl₂ gas sensing using the In₂O₃ thin film nanosensor (3). But, the nano-gap effect was different from each other in the NO₂-WO₃ system and the Cl₂-In₂O₃ system.

In this paper, the reasons for the difference in nano-gap effect was described with new data of nano-gap effect in the H₂S-SnO₂ system. SnO₂ was chosen as H₂S sensing material since SnO₂ was the most popular sensing material and since the SnO₂ sensor showed fairly good sensing properties to dilute H₂S in plenty of papers (4)-(7). The nano-gap effects were summarized in these three systems on the basis of the relationship between the sensitivity at interface between oxide and electrode (Sᵢ) and that at grain boundary (Sₕb).

2. Experimental

The nano-gap electrode was fabricated by means of MEMS techniques (photolithography and FIB). First, the Au line of 20 µm in width was designed on SiO₂ substrate by using a conventional lift-off method. Second, the Au line was etched with various width of 0.1-1.3 µm by using FIB technique (Focused Ion Beam, Hitachi FB-2100) to be nano-gap electrode with gap size of 0.1-1.3 µm and line width of 20 µm. The thickness of Au electrode was 300 nm.

Three kinds of sol solutions were used here for the preparation of oxide thin films, H₂WO₄ sol for WO₃ film, In(OH)₃ sol for In₂O₃ film, and SnO₂ sol for SnO₂ film. The micro-drop of the sol solution was dropped on the nano-gap electrode by using micromanipulator (Eppendorf InjectMan N12 and FemtJet), dried, and calcined at 400-650 °C for 3h in air to be oxide thin film nanosensor. The detailed procedure of nanosensor fabrication was described in our previous papers (28). The SnO₂ sol solution was donated from Nissan Chemical Ind. Co. Ltd. Figure 1 shows

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the schematic drawing of oxide thin film nanosensor. The resistance of oxide thin film was measured between two electrodes with nano-gap. The structure and the surface morphology of nanosensor were observed by means of FE-SEM (Hitachi S-4800). Figure 2 shows the typical SEM images of the nano-gap electrode and the oxide thin film on nano-gap electrode. It is seen that the nano-gap electrode has a simple structure and that the oxide thin film has ca. 100 µm in diameter.

The sensing properties to various dilute gases were measured in the flow apparatus. The objective gases were dilute NO₂ (0.05-0.5 ppm) for WO₃ nanosensor, dilute Cl₂ gas (0.05-1 ppm) for In₂O₃ nanosensor and dilute H₂S (0.1-3 ppm) for SnO₂ nanosensor. The sensor resistance was measured in air (Ra) and in these objective gases (Rg) at optimal temperatures (NO₂-WO₃: 200 ℃, Cl₂-In₂O₃: 250 ℃, H₂S-SnO₂: 300 ℃). The sensitivity (S) was defined as Rg/Ra in all cases. S > 1 means the response with resistance increase, while S < 1 is resistance decrease. The larger deviation of S from 1 means the higher sensitivity.

3. Results and Discussion

3.1 Nano-gap effect in various gas sensors Figure 3 shows the SEM images of oxide grains in WO₃, In₂O₃, and SnO₂ thin films. Each oxide grain had different shape. The WO₃ grain had disk-like shape (20 nm in thickness and 130-170 nm in diameter), the In₂O₃ grain had spherical shape (15 nm in diameter) and the grains were aggregated to form the cubic particle, and the SnO₂ grain also had spherical shape of 15 nm in diameter without aggregation. The SnO₂ thin film deposited just on the nano-gap resulted in the cracks at the edge of Au electrode. In all cases, these grains were packed in the nano-gap electrode. The number of grains in the gap ranged from a few to few tens for 0.1-1.3 µm gap.

The gas sensitivities of various oxide thin film nanosensors were shown in Fig. 4 as a function of gap size. In the case of NO₂ detection using the WO₃ sensor (Fig. 4-a), NO₂ molecules were negatively adsorbed on the WO₃ surface to increase electrical resistance of sensor. For all NO₂ concentrations, the sensitivity tended to be increased with decreasing gap size. Particularly, the sensitivity was steeply increased with decreasing gap size less than 0.8 µm.

Fig. 4-b depicts the case of Cl₂ gas detection using the In₂O₃ sensor. In this case, there were two kinds of responses, resistance increase to Cl₂ gas higher than 1 ppm and resistance decrease to Cl₂ gas less than 0.5 ppm. These responses are explained using following equations

1/2 Cl₂ + e⁻ → Cl_ads

O_ads²⁻ + 1/2 Cl₂ → Cl_ads⁻ + 1/2 O₂ + e⁻

O₂⁰²⁻ + 1/2 Cl₂ → Cl_ads⁻ + 1/2 O₂ + e⁻

In eq. (1), Cl₂ molecule is directly and dissociatively adsorbed on the In₂O₃ surface to increase the resistance. On the other hand, in eqs. (2) and (3), Cl₂ molecule is substituted with adsorbed oxygen (O_ads⁻) or lattice oxygen (O₂⁰²⁻) to decrease the resistance. When the In₂O₃ sensor is exposed to Cl₂ gas, it is considered that the sensor resistance is decreased at first due to eqs. (2) and (3), then the resistance is increased due to eq. (1) if the Cl₂ concentration is high. Thus, the In₂O₃ sensor remains the response of resistance decrease to low concentration of Cl₂, while the sensor response changes to resistance increase to high concentration of Cl₂. As shown in Fig. 4-b, in both resistance increase and decrease, the
sensitivity was increased with decreasing gap size. However, the gap size where the sensitivity began to be steeply increased was different, 0.8 μm for resistance increase and 0.5 μm for resistance decrease.

Fig. 4-c shows the case of H₂S detection using SnO₂ sensor. In this case, H₂S molecule was oxidized to consume adsorbed oxygen on SnO₂ surface to decrease the resistance (eq. 4).

\[ \text{H}_2\text{S} + 3 \text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 6\text{e}^- \]  

Compared with above-mentioned two cases, the sensitivity increase due to the decrease in gap size was small. It was found that the nano-gap effect was different from each other depending on the gas sensing system. The marked effect was obtained for the NO₂-WO₃ and the Cl₂-In₂O₃ systems, while the weak effect for the H₂S-SnO₂ system.

### 3.2 Model of nano-gap sensor
In order to explain the nano-gap effect, the model where a few grains are packed in the nano-gap electrode is considered as shown in Fig. 5. There are three kinds of resistances between electrodes, i.e., oxide-electrode interface, grain bulk, and grain boundary. Since the resistance at grain bulk is constant irrespective of gas exposure, the bulk resistance change upon exposure to objective gas is ignored for the sensitivity calculation. Thus the sensor resistance is expressed as the sum of resistances at interfaces and grain boundaries. The sensor resistance in air (Ra) is expressed as follows.

\[ Ra = 2R_{ai} + (N-1)R_{a\text{gb}} \]  

where \( R_{ai} \) and \( R_{a\text{gb}} \) are the resistance in air at interface and grain boundary, respectively, and \( N \) is the number of grains in the gap. The sensor resistance in objective gas (Rg) is expressed similarly and the sensitivity (\( S = R_g/R_a \)) is expressed as

\[ S = \frac{2R_g + (N-1)R_{g\text{gb}}}{2R_a + (N-1)R_{a\text{gb}}} \]  

where \( R_{g\text{gb}} \) and \( R_{a\text{gb}} \) are the resistance in objective gas at interface and grain boundary, respectively. From eq. 5, it is seen that Ra is proportional to \( N \). Thus, \( R_{ai} \) and \( R_{a\text{gb}} \) were calculated from the intercept and the slope in linear Ra-N relation in the range of \( N \) from 5 to 90. Further the sensitivity equation (eq. 6) was transformed by using \( S_i = R_{gi}/R_{ai} \) and \( S_{gb} = R_{g\text{gb}}/R_{a\text{gb}} \) and \( R_a-R_{a\text{gb}} \) correlation. Table 1 summarizes the results of calculation for the \( R_a-R_{a\text{gb}} \) correlations and the sensitivity equations using \( S_i \) and \( S_{gb} \). The \( R_a-R_{a\text{gb}} \) correlation was different from each other in three sensors and thus the sensitivity equation was also different from each other.

When the gap size is decreased, the number of grains in the gap is decreased and thus the number of grain boundary is decreased. This induces the increasing contribution of interface to total sensor sensitivity.
resistance. If $S_i$ is much larger than $S_{gb}$, the sensitivity is increased with decreasing gap size.

### 3.3 Sensitivity at interface and grain boundary

$S_i$ and $S_{gb}$ could be calculated from various data sets of $S$ and $N$ in Fig. 4 and by using the sensitivity equations in Table 1. The resulting $S_i$ and $S_{gb}$ were depicted in Fig. 6 as a function of gas concentration for NO$_2$-WO$_3$, Cl$_2$-In$_2$O$_3$, and H$_2$S-SnO$_2$ systems. The linear relations between sensitivity and gas concentration were obtained in log-log plot for NO$_2$-WO$_3$, Cl$_2$ (less than 0.5 ppm)-In$_2$O$_3$, and H$_2$S-SnO$_2$ systems. Further, it was found that $S_i$ was larger than $S_{gb}$ in all cases, supporting the abovementioned assumption. However, the $S_i/S_{gb}$ ratio was different from each other depending on the system. Compared with the $S_i/S_{gb}$ ratio for each system, it was 32 at 0.5 ppm NO$_2$ of WO$_3$ sensor, 43 at 1 ppm Cl$_2$ (resistance increase) and 20 at 0.5 ppm Cl$_2$ (resistance decrease) of In$_2$O$_3$ sensor, 9.7 at 1 ppm H$_2$S and 3.4 at 0.1 ppm H$_2$S of SnO$_2$ sensor. It is noted that in the case of NO$_2$ and Cl$_2$ (higher than 1 ppm) detection, the marked nano-gap effect was observed due to the large $S_i/S_{gb}$ ratio. On the other hand, as observed in H$_2$S detection, the nano-gap effect was weak due to the small $S_i/S_{gb}$ ratio, especially in the case of 0.1 ppm H$_2$S. This was confirmed by using model case. Using the sensitivity equation for NO$_2$ detection, $S$ was calculated for various $S_i$ values (= 400, 100, and 20) and the fixed $S_{gb}$ value (=10). The result is shown in Fig. 7. It is seen that the larger the $S_i/S_{gb}$ ratio is, the stronger nano-gap effect is observed. Depending on the kind of

![Fig. 6. $S_i$ and $S_{gb}$ as a function of gas concentration in various systems. (a) NO$_2$-WO$_3$, (b) Cl$_2$-In$_2$O$_3$, (c) H$_2$S-SnO$_2$.](image)

![Table 1. Relationship between $R_{a_i}$ and $R_{a_{gb}}$ and sensitivity equations in various systems.](table)

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{a_i}$</th>
<th>$R_{a_{gb}}$</th>
<th>Sensitivity $(R_g/R_a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$-WO$_3$</td>
<td>$R_{a_i} = 2.0 R_{a_{gb}}$</td>
<td>$S = \frac{4.0}{N + 3.0} S_i + \frac{N - 1.0}{N + 3.0} S_{gb}$</td>
<td></td>
</tr>
<tr>
<td>Cl$_2$-In$_2$O$_3$</td>
<td>$R_{a_i} = 2.7 R_{a_{gb}}$</td>
<td>$S = \frac{2.0}{0.37 N + 1.65} S_i + \frac{N - 1.0}{N + 4.4} S_{gb}$</td>
<td></td>
</tr>
<tr>
<td>H$_2$S-SnO$_2$</td>
<td>$R_{a_i} = 5.0 R_{a_{gb}}$</td>
<td>$S = \frac{10}{N + 9.0} S_i + \frac{N - 1.0}{N + 9.0} S_{gb}$</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 7. Calculated sensitivities for various $S_i/S_{gb}$ ratios as a function of gap size.](image)
objective gas and semiconductor sensor, the different $S_i/S_{gb}$ ratio is obtained and thus the different nano-gap effect is observed. When the gap size is decreased, the larger sensitivity increase is expected for semiconductor sensor with the higher $S_i/S_{gb}$ ratio.

In the NO$_2$ and the Cl$_2$ higher than 1 ppm) detection, these molecules are negatively adsorbed on oxide semiconductor surface to increase the thickness of electron depleted layer. It is assumed that the molecules are also adsorbed on the electrode metal (Au) to change the work function of Au, inducing the large increase in the interface resistance, i.e., the large $S_i$. On the other hand, in the H$_2$S detection, the consumption of adsorbed oxygen on oxide semiconductor surface decreases the thickness of electron depleted layer. Oxygen is also adsorbed on Au electrode. It is assumed that the work function change due to oxygen consumption is small, resulting in the small $S_i/S_{gb}$ ratio.

4. Conclusions

The nano-gap electrode is fabricated by means of MEMS techniques (photolithography and FIB). The WO$_3$, In$_2$O$_3$, and SnO$_2$ thin films are deposited on the nano-gap electrode to be thin film nanosensors. These sensors with various gap sizes are adopted for the detection of dilute gases of NO$_2$, Cl$_2$, and H$_2$S, respectively, and the nano-gap effect is evaluated for these systems. When the gap size is decreased, the large sensitivity increase is obtained for the NO$_2$-WO$_3$ system and the Cl$_2$-In$_2$O$_3$ system (Cl$_2$ higher than 1 ppm), while the small sensitivity increase is observed for the H$_2$S-SnO$_2$ system. The sensitivity is divided into the sensitivity at oxide-electrode interface ($S_i$) and at grain boundary ($S_{gb}$). The large $S_i/S_{gb}$ ratio is obtained for the NO$_2$-WO$_3$ system and the Cl$_2$-In$_2$O$_3$ system (Cl$_2$ higher than 1 ppm), while the small one for the H$_2$S-SnO$_2$ system. In the objective gas-semiconductor sensor system with the larger $S_i/S_{gb}$ ratio, the stronger nano-gap effect is observed. In such a system, the oxide-electrode interface plays an important role in gas sensing, and the nano design of electrode structure like nano-gap electrode is significant for the high sensitivity gas sensor.

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References


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