

Gas Sensing Properties of Porous Insulator/Oxide Semiconductor Multi-layered Films

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Porous insulator film, SiO_2 , Al_2O_3 or ZrO_2 , was coated on the SnO_2 or NiO film via dip-coating method. After firing at 600°C , the SnO_2 film was about 500nm in thickness and 20-30 nm in grain size. The ZrO_2 and Al_2O_3 layer exhibited contrast due to crystalline particles, though SiO_2 layer was amorphous. The resistivity of the resultant multi-layered films in dry-air and flammable gas, 1% H_2 , CH_4 , or 0.2% 2methyl-2butene, was examined. The difference in resistivity between in air and in the flammable gas of the multilayered film based on SnO_2 films was larger than that of the monolithic SnO_2 film. The multilayered films tended to have sensitivity against 1% CH_4 , though the monolithic SnO_2 film did not. The increase in gas sensitivity was mainly due to the increment of resistivity in air. This phenomenon is in conflict with the reported mechanism based on a difference in the permeability of flammable gas through the insulating layer. The multilayered film based on NiO sensing layer showed low gas sensitivity and low resistivity than the monolithic NiO film. These experimental results suggested the coated porous insulator layer enhanced the amount of the adsorbed oxygen onto the semiconductor oxide films.

Key words: SnO_2 , NiO , gas sensor, thin film, multi-layered film

1. INTRODUCTION

Gas sensing devices based on oxide semiconductors were studied extensively¹⁻⁴ and were practically applied to monitor an environmental atmosphere. The sensing mechanism of the flammable gases, such as hydrogen, propane, etc., is a detection of changes in electrical resistivity of the devices due to an adsorption of oxygen from air and a desorption of the oxygen by contact with flammable gases. The adsorbed oxygen molecules contract electrons from the oxide semiconductors to form a space charge layer on the surface of the semiconductors. The resistivity of the space charge layer depends on the type of the semiconductor. Although the n-type semiconductor, such as SnO_2 ⁵⁻⁶ and ZnO ⁷, and resultant high resistivity layer, *i.e.*, depletion layer, is usually used as a sensing semiconductor, a p-type semiconductor, such as NiO ⁸, and low resistivity layer, *i.e.*, accumulation layer, can also act as the gas sensing semiconductor.

To prepare the sensors with high sensitivity and high selectivity to gasses, multi-layered SnO_2 ⁹ film or sintered SnO_2 with coating layer¹⁰ have been investigated. The multi-layered sensor usually consisted of SnO_2 sensing layer covered with metal oxide layers. The roles of the cover layer were attributed to the catalyst and/or filtering of the sensing gases⁹⁻¹⁰. Among the cover coating oxides, SiO_2 was expected to be inert and to act only as a filter. The other oxides such as Al_2O_3 and ZrO_2 are also expected to act as filtering cover layer, if the filtering mechanism increased the gas sensitivity of SnO_2 gas sensor.

We have already reported the improved gas sensing properties of very thin¹¹ and porous SnO_2 films¹² as well as NiO thin films⁸. Here we report the results of gas sensing properties of the multi-layered gas sensors composed of SnO_2 or NiO layer as gas sensing semiconductors, and insulating oxide cover layers of SiO_2 , Al_2O_3 and ZrO_2 .

2. EXPERIMENTAL

All films were deposited by a dip-coating procedure with solutions prepared using ethanolamine as a sol modifier¹³⁻¹⁵. The reagents used were $\text{Sn}(\text{O}^i\text{Pr})_4$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zr}(\text{O}^i\text{Bu})_4$, $\text{Al}(\text{O}^i\text{Pr})_3$, and $\text{Si}(\text{OEt})_4$. The solvent was $^i\text{PrOH}$ except SiO_2 . The used ethanolamines were diethanolamine for $\text{Ni}(\text{OAc})_2$ and $\text{Zr}(\text{O}^i\text{Bu})_4$, and triethanolamine for $\text{Sn}(\text{O}^i\text{Pr})_4$ and $\text{Al}(\text{O}^i\text{Pr})_3$. The coating solution of SiO_2 was prepared by mixture of $\text{Si}(\text{OEt})_4$, EtOH , H_2O , and HCl with molar ratio of 1: 6: 6: 0.01, and used after aging for 96h. First the semiconductor layer of SnO_2 or NiO was coated on a glass substrate (Corning, #7059), then gold electrode was printed and baked. The insulating film was coated to cover the whole area of semiconductor layer. Each deposition was conducted by the dip-coating, drying at 110°C , and firing at 600°C . The deposition was repeated two and five times for NiO and SnO_2 layers, respectively, and one to four times for insulating layer to obtain the desired stacking structures.

The multilayered films were characterized by means of an X-ray diffractometer (XRD, Rigaku, RAD-2R), a transmission electron microscope (TEM, Hitachi, H-8100), and a spectrometer (Hitachi, U-3500). The gas sensing properties were measured by comparing the electrical resistivity in flammable gas atmosphere to that in dry air. In the present study, 1% hydrogen, 0.2% 2-methyl-2-butene, and 1% methane were used as flammable gases. The gas sensitivity was measured at 250° to 450°C .

3. RESULTS

3.1 Characterization of the films

The heating at 600°C crystallized SnO_2 , NiO , and ZrO_2 as rutile-type, rock salt-type, and cubic fluorite-type modifications, respectively. Al_2O_3 and SiO_2 were remained as amorphous phases. The crystalline phases of the multilayered films could be considered as simple stackings of the individual layer. Figure 1 shows TEM micrographs of three multilayered films. The SnO_2 film

with five depositions was about 450-500 nm in thickness. The cover layers, SiO_2 , Al_2O_3 and ZrO_2 , were deposited two, four, and two times, and resultant thickness were about 120, 100, and 100 nm, respectively. The grain size of SnO_2 was about 20-30 nm in diameter. The sizes of the ZrO_2 and Al_2O_3 were less than that of SnO_2 . Although the XRD measurement of Al_2O_3 film suggested the amorphous of the phase, the contrast in TEM observation revealed very fine crystalline phase in the layer, it would be γ -alumina. The SiO_2 film was very uniform and no contrast was observed. The boundary between SnO_2 and the covered oxide was very clear and no reaction between them was suggested. The SnO_2 layers had clear boundaries corresponding to the five deposition events, and also in the Al_2O_3 and ZrO_2 layers. The pore size was not recognized in the photos. Since the pore size is closely related to the grain size, the pore size of ZrO_2 film was larger than that in Al_2O_3 layer and the pore size of SiO_2 was the smallest among the three cover films. The thickness of the NiO film with two depositions was about 50 nm and grain size was about 20-50 nm in diameter.

3.2 Gas sensing properties of SnO_2 multilayered films

The examples of changes in resistivity on exposure to the flammable gases are shown in Fig. 2. The data were taken at 400°C for SnO_2 monolithic film and the film covered with ZrO_2 coating, the same films as shown in Fig. 1. The resistivity quickly decreased by an introduction of 1% H_2 and returned to the original resistivity by introducing the air again. The changes for 2methyl-2butene were also the same but less magnitude than that for H_2 . This tendency of change in resistivity is the same as expected for n-type semiconductors, i.e., the adsorbed oxygen formed a depletion, high resistivity, layer on the surface and the flammable gases removed the adsorbed oxygen to decrease the resistivity of the film. The ratio in resistivity between in air and in gas represents a gas sensitivity. The sensitivity of ZrO_2

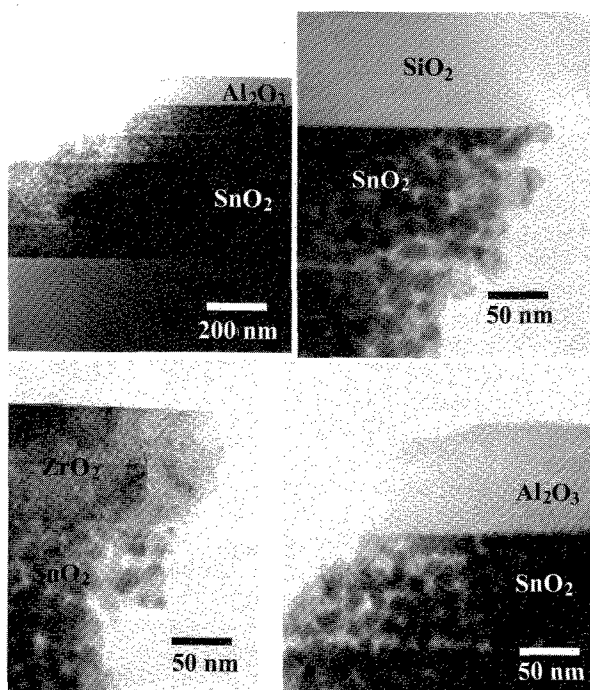


Fig. 1 TEM micrographs of cross-sections of multilayered films, $\text{Al}_2\text{O}_3/\text{SnO}_2$, $\text{SiO}_2/\text{SnO}_2$ and $\text{ZrO}_2/\text{SnO}_2$.

covered film was about 10^3 for H_2 and $10^{2.5}$ for 2methyl-2butene, whereas those of the monolithic SnO_2 film were about $10^{1.5}$ and 10, respectively. The change in sensitivity was mainly due to an increment in resistivity in air and not in the flammable gas. The resistivity of SnO_2 films covered with ZrO_2 film was $\sim 2 \times 10 \Omega\text{cm}$ in air, which is about 100 times larger than that of monolithic SnO_2 film. In 1% H_2 atmosphere, resistivities of monolithic and covered SnO_2 were not so different. Further, the SnO_2 film covered with ZrO_2 showed the sensitivity to CH_4 gas which could not change the resistivity of the present monolithic SnO_2 film. As lowering of the measuring temperature, the changing speed slowed down in both the monolithic and the ZrO_2 covered films, though the tendency, i.e., the resistivity of ZrO_2 covered film in air was larger than that of the monolithic SnO_2 film, still is maintained. At 250°C the sensitivity for 2methyl-2butene became larger than that for H_2 in both films.

The results of the other multilayered films were summarized and shown in Fig. 3. The resistivities in the flammable gasses of the multilayered films except the film with SiO_2 coating were almost the same as that of the monolithic SnO_2 film. The high resistivity of SiO_2 coated film in the gases of large molecular size, 2methyl-2butene and methane, may be caused by the low diffusivity of these gasses through the SiO_2 layer. The resistivities of the multilayered films in air were larger than that of the monolithic film and depended on the oxide films covered on SnO_2 . The resistivity of Al_2O_3 coated film was relatively low in air. This was due to the very slow change in resistivity at the introduction of air. It would become higher resistivity after sufficiently long time soaking.

Since the difference in resistivity between in air and

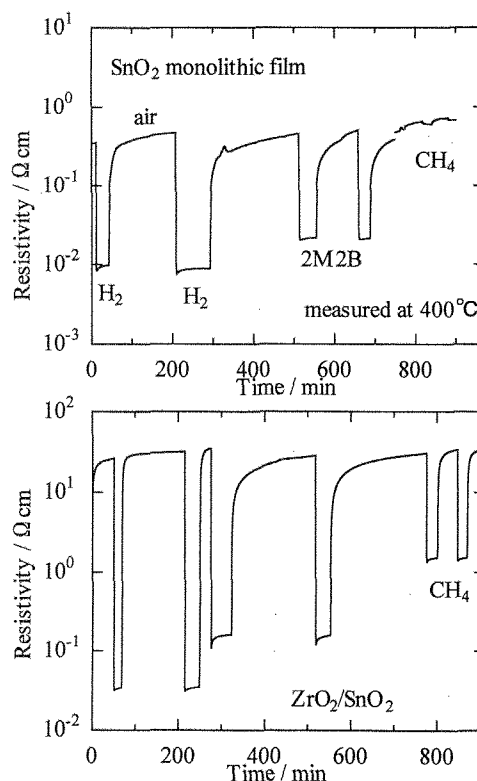


Fig. 2 Change in resistivity of $\text{ZrO}_2/\text{SnO}_2$ multilayered films on exposures to flammable gasses.

in gas corresponds to the sensitivity of the gas sensor, the multilayered film of ZrO_2/SnO_2 had good sensing characteristics for reducing gasses, including methane.

3.3 Effect of thickness of ZrO_2 overcoat

As shown in Fig.3, coating of ZrO_2 film increased the sensitivity for all gasses. The effect of thickness of ZrO_2 film was investigated. On the SnO_2 semiconductor layer, ZrO_2 films with the thickness from 6 to 100nm were deposited by varying the concentration of the solution and number of the deposition events. The thickness of the thinner ZrO_2 was estimated based on an assumption that the thickness is proportional to the concentration of the solution and the number of deposition events. The result was shown in Fig.4. The resistivity of the multilayered film in air increased with increasing the thickness of ZrO_2 up to the thickness of about 50nm and the resistivity in H_2 started to increase slightly from the same thickness, about 50nm. These changes in resistivity led the tendency that the sensitivity first increased and then became almost constant. These data suggested that the increment in resistivity was not attributed to the existence of an interface between SnO_2 and ZrO_2 , but the thickness of ZrO_2 layer influenced the resistivity. The increasing resistivity in air played a significant role to the sensitivity.

The tendency of the changes in resistivity for 2methyl-2butene was the same as the case of H_2 . For

methane, the multilayered sensor tended to have sensitivity when the thickness of ZrO_2 layer exceeded 20nm and the films became to be the higher resistivity than several Ωcm in air.

3.4 Gas sensing properties of NiO multilayered films

The gas sensing properties of NiO and SiO_2/NiO multilayered films were shown in Fig.5. In both films, two introductions were conducted for each gas, H_2 , 2methyl-2butene, or methane. When the monolithic and multilayered NiO films exposed to H_2 gas, the resistivity increased suddenly, which is an opposite change to n-type semiconductors and a typical characteristics of p-type semiconductors. Though the monolithic NiO film exhibited the sensitivity to 2methyl-2butane, the multilayered film did not. The resistivity of multilayered film lowered to about 1/100 of the monolithic film. Since the adsorbed oxygen molecule on p-type semiconductor forms low resistance layer on the surface, the experimental results suggest the coated porous insulator layer enhanced the adsorption of the oxygen onto the semiconductor oxide films. In the present study, the improvement of gas sensitivity by the over-coat of porous insulating oxide films was limited only for n-type semiconductor, SnO_2 , and was not applied for p-type semiconductor, NiO.

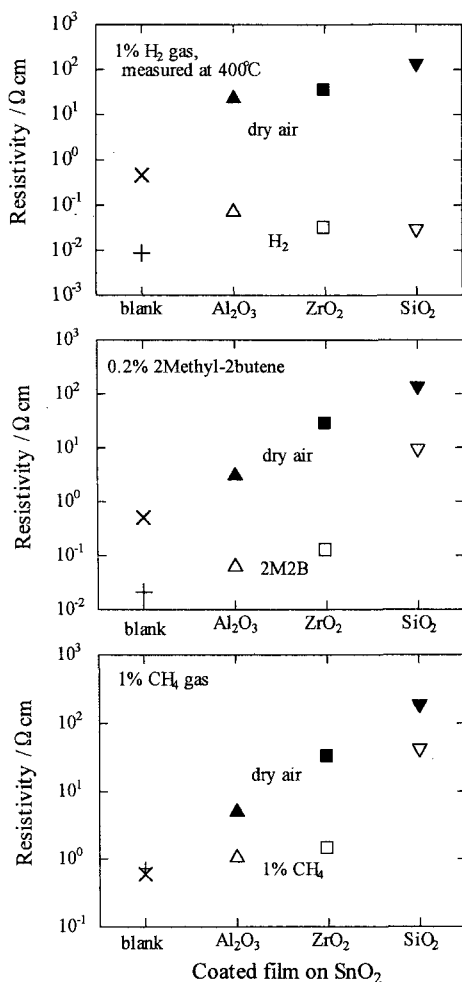


Fig. 3 Resistivity of multilayered films in air and in the flammable gases.

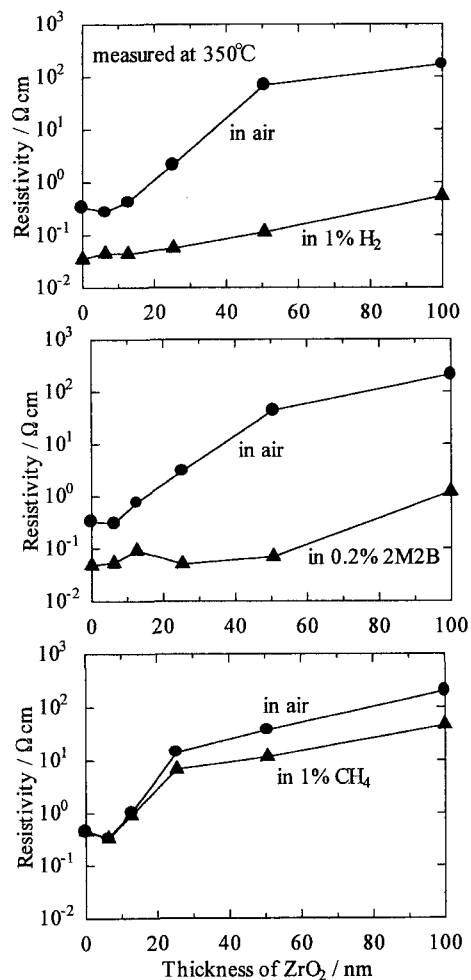


Fig. 4 Thickness of ZrO_2 film and resistivity of the films.

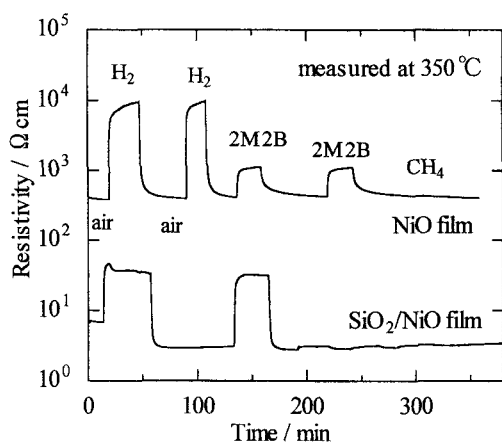


Fig. 5 Gas sensing properties of NiO and SiO₂/NiO films.

4. DISCUSSION

Egashira and co-worker⁹⁻¹⁰ developed the improved multilayered oxide semiconductor sensors with SiO₂ coating on SnO₂. They proposed the mechanism of increasing the gas sensing properties as follows; the SiO₂ layer selectively filters gases depending on the size of the gas molecules and small gasses such as H₂ concentrate on the semiconductor surface to give the low resistivity and high gas sensitivity. The mechanism was, however, not successfully applicable to our present study by following facts. First, the gas sensitivity of n-type semiconductor increased due to the increment in resistivity in air. If the insulating layer on SnO₂ acts as the filter of gas and selectively passes small molecules such as H₂, the resistivity in the gas atmosphere should be smaller comparing the monolithic SnO₂ sensor. We obtained the opposite data. Second, the SiO₂ layer decreased the resistivity of NiO semiconductor in air. This is not explainable using the gas filtering concept. And third, the sensitivity against the large molecular gasses, such as 2methyl-2butane and methane, also increased in case of SnO₂ film.

Now we can explain the present study based on an assumption of an enrichment of oxygen by the covered porous insulating layer. The porous covering layer in our experiments resulted in the increasing in resistivity of SnO₂ multilayered films in air and, in contrast, decreasing in resistivity of the NiO films. These changes suggested the increasing amount of adsorbed and negatively charged oxygen. The insulating layer may act as a filter not for flammable gasses but for oxygen in ambient.

Although the mechanism of the enrichment was under investigation, the porous body with very small pore size sometimes causes a large amount of adsorption of gasses, which led a capillary condensation in the extreme case. The degree of adsorption, or diffusion of gas, is closely related with the ratio between a mean free path of the gas molecule and the pore size¹⁶. If the both lengths become almost the same order of magnitude, the Knudsen region, in which the diffusion of molecule interacts with the surface of pore wall, tends to be dominant and the molecule is instantaneously adsorbed during diffusion. The smaller the pore size becomes, the more of the gas is adsorbed and the diffusion becomes

surface diffusion. The Knudsen diffusion is slightly dependent on temperature, and the mean free path of oxygen molecule in 1 atom is about 70 nm¹⁷. Consequently the pore sizes of the present multilayered films were smaller than the length and much larger amount of molecules tend to be adsorbed on the SnO₂ surface than that on the monolithic SnO₂. The covered insulating and porous layers with smaller pore size, ZrO₂, Al₂O₃ and SiO₂, may act as a 'cap' of the oxygen, and perhaps nitrogen, molecules and prevent the adsorbed oxygen diffusing outside the films.

5. CONCLUSION

The SnO₂ gas sensors covered with insulating oxide films of SiO₂, Al₂O₃ and ZrO₂ exhibited an excellent gas sensitivity, whereas the multilayered sensor of NiO semiconductor did not. The increment in gas sensitivity is owing to the increasing resistivity in air and the resistivity of the NiO multilayered decreased. These changes in resistivity were explained by the enhanced amount of adsorbed oxygen molecules by the covered insulating and porous layer. The mechanism of enrichment of adsorbed oxygen may closely related with the smaller pore size of the covered film than a mean free path of the oxygen.

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