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Interaction of Water Vapor with SnO_2

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Abstract

In order to observe the interaction between the water vapor and SnO_2, water vapor sensing and water vapor/solid exchange reaction using isotopic water were performed. The resistivity of SnO_2 thick film at 200-500^oC in Ar decreased by exposing water vapor + Ar. The highest sensing response was observed at 300^oC. The isotopic water (D_2O) was used as the tracer. After annealing in D_2O vapor, incorporation of deuterium (D) into solid was confirmed by the secondary ion mass spectrometry. These results indicate that hydrogen diffuse into the solid from the water vapor. Amount of the deuterium in solid seems to depend on the annealing temperature.

Key words: SnO_2, Water vapor, SIMS

Introduction

Tin dioxide (SnO_2) is a wide gap semiconductor that is widely used as the electrochemical devices, the optoelectrodevice and so on. Among them, the chmical gas sensor based on SnO_2 is one of the important applications for the safety network or the health check. SnO_2 based gas sensors are usually used for gas detection in the atomosphere or the bleath. At those conditions, water vapor (humidity) is allways contained in the target gases. Therefore, we should consider the effect of the water vapor on SnO_2, in order to design the gas sensor.

In fact, there are many reports on the effect of water vapor on the SnO_2 gas sensor [1-3]. According to those reports, water vapor mainly affects the sensor resistance at lower temperature. That is, the existence of water vapor prompts the decrease in the sensor resistance. Such behaviour is explained by the adsorption of H_2O or the formation of OH group[1, 2]. Roman et. al reported that the interaction with water vapor results in the formation of terminal hydroxyls by means of IR absorbance spectra at various temperature under dry and wet condition. On the other hand, in case of the higher temperature (more than 500^oC), water vapor affects also the stability of the sensor resistance. Kanamori et. al reported the effect of annealing in water vapor at 500^oC for ~340h on the SnO_2 thin film[3]. They mentioned that the sensor resistance is increased by the wet annealing at 500^oC, because of a catalytic activity of water vapor for the oxidation[4].

As mentioned above, the interaction between tin dioxide and water vapor is closely related to the chemisorption, formation of the hydroxyls and the oxidation of SnO_2. However, it is not clear whether hydrogen diffuse inside the solid.

It is well known that an Isotopic tracer diffusion and secondary ion mass spectrometry (SIMS) are the effective method for the evaluation of the diffusion behavior in solid. Here, in this study, we aimed to reveal the interaction between the water vapor and SnO_2. Especially, we focused on the hydrogen diffusion into solid from water vapor. The water vapor sensing and water vapor/solid exchange reaction using isotopic water were investigated.

Experimental

2.1 Gas sensing measurement:

Reagent-grade of SnO_2 powder (Kojundo chemical laboratory, Japan, 99.99%) was used as the starting material. The powder was calcined at 600^oC for 1h in air. The calcined SnO_2 was dispersed into the ethanol, to obtain the slurry for film deposition. Silica glass was used as the substrate. Au electrode (thickness: 100nm) was deposited on the silica glass by a sputtering. The SnO_2 slurry was deposited to the substrate and dried at room temperature. After annealing in the dry air at

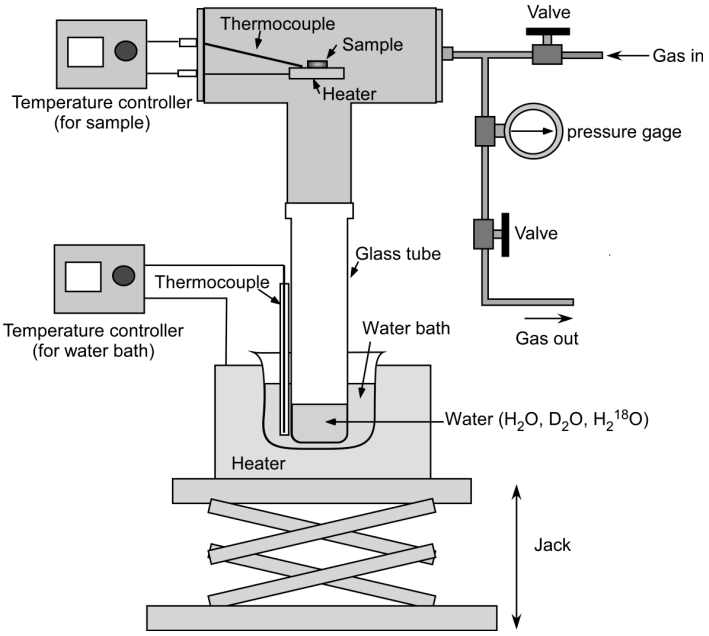

Fig. 1 Apparatus experimental set up for water vapor/solid exchange reaction

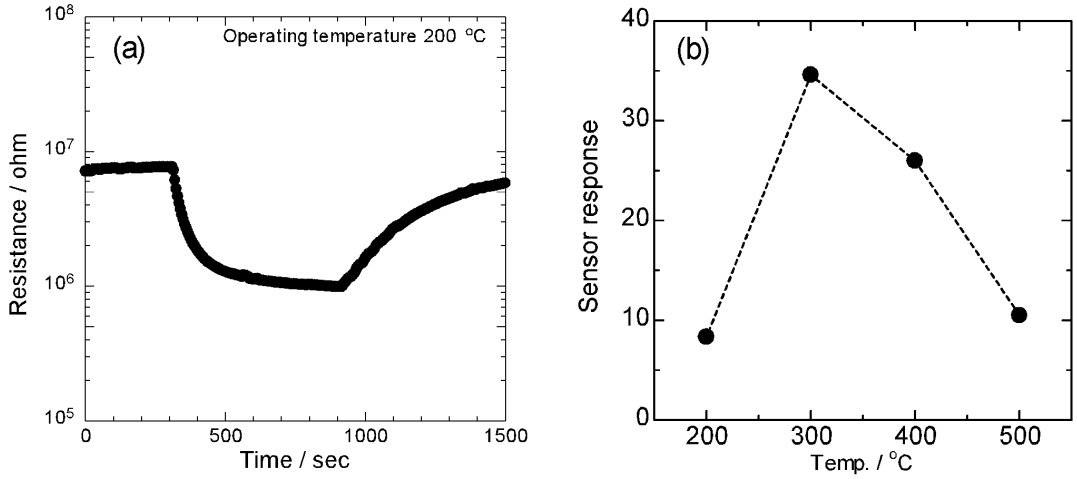

Fig. 2 (a) H_2O vapor sensing curve of SnO_2 in Ar at 200°C and (b) temperature dependence on sensor responce for wet Ar.

600°C, water vapor sensing property in Ar was tested at 200-500 °C. The humidity content of wet Ar was 61920ppm. The sensor responce is defined as $S=R_{dry}/R_{wet}$, where R_{dry} and R_{wet} are resistance in dry and wet Ar, respectively.

2.2 Water vapor/solid exchange reaction:

The isotopic D_2O (>99.8atom%, D Acros organics, Belgium) was used as the tracer. The calcined powder and the isotopic water were set to the vessel as shown in Fig. 2, respectively. The vessel was purged by dry Ar. The temperature of isotopic water was kept at 60°C and the sample was annealed at 200-400 °C for 1h. After annealing, the sample was quenched to 100°C. The obtained powder was dispersed on the Si substrate, The existence of D in the powder was evaluated by means of the secondary ion mass spectrometry (SIMS, ims-4f and NanoSIMS 50, CAMECA, France).

3 Results and discussion:

Fig. 2(a) shows the response curve of SnO_2 for the water vapor in Ar at 200°C. The sensor resistance decreased with the exposing the water vapor and the response was reversible at all operating temperatures. This tendency shows a good agreement with the reported literatures. Fig.2(b) shows the temperature dependence of water vapor sensing for SnO_2 thick film in Ar. The highest sensing responce was observed at 300 °C. Above 300°C, sensor responce was gradually

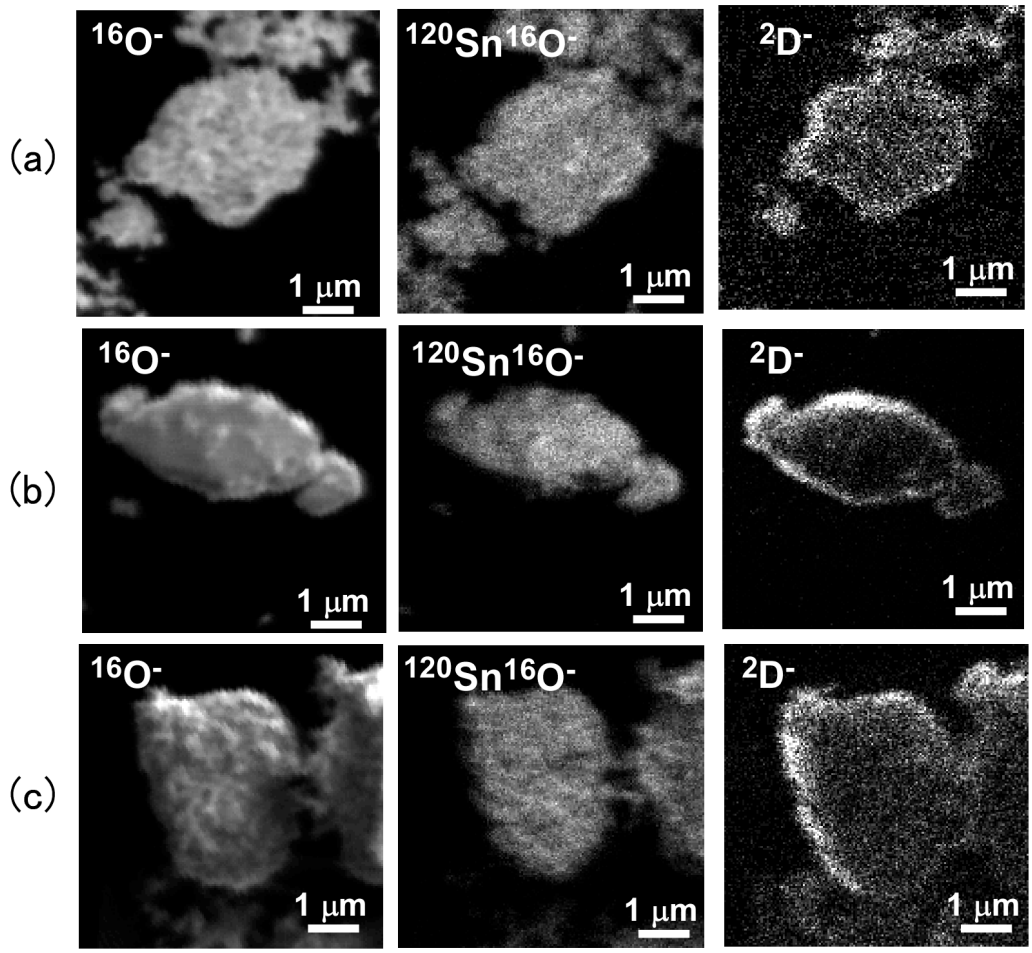

Fig.3. Secondary ion images of $^{16}O^-$, $^{120}Sn^{16}O^-$ and $^{2}D^-$ of SnO_2 powder after annealing in D_2O vapor +Ar at (a) 200, (b) 300 and (c) 400°C, respectively.

decreased as increaseing the operating temperature.

Fig. 3 shows the secondary ion images of $^{16}O^-$, SnO^- and D^- of SnO_2 powder after annealing in D_2O vapor+Ar at 200-400°C. Since the pre-sputtering was performed to remove adsorbed substance from the surface of the particles, the images of the center and the edge of the particles show the inner and outer information of the SnO_2 particles, respectively. From the $^{16}O^-$ images, the particle size of SnO_2 was estimated to be about 2-4μm. In addition, the particles which are smaller than 1 μm were also observed on the surface of particle. For all samples, the intensity of D has been observed at the same area as $^{118}SnO^-$. Moreover, it was found that the intensity of D around edge of the particles was higher than that of inside. This means that the diffusion of D into SnO_2 solid occurred as the result of the hydrogen exchange reaction between water vapor and solid.

Fig. 4 shows the relative intensity (I_D/I_{SnO}) as a function of annealing temperature.

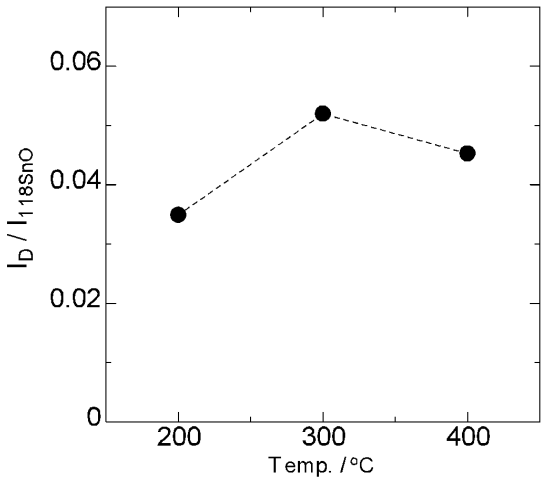

Fig.4 Temperature dependence of the relative intensity (I_D/I_{SnO}) of SnO_2 powder annealed in D_2O vapor.

The largest amount of D was overbed in the sample annealed at 300°C. In contrast, in case of annealing at 200°C, the amount of D in solid

was the smallest among the samples. This tendency shows a good agreement with the results of the sensing responce. Therefore, it indicates a possibility that the hydrogen, which diffused from water vapor affects the resistance of sensor film.

Conclusion

. The interaction between SnO_2 and water vapor was investigated, using an electric measurement and the isotopic deuterium diffusion from D_2O vapor. At all operating temperatures, the sensor resistance is decreased by exposing the wet Ar. After annealing in D_2O vapor, the existence of D in tin dioxides has been confirmed by imaging SIMS. Especially, the largest amount of D in SnO_2 after annealing in 300^oC was confirmed. From those results, it seems that hydrogen diffuse into SnO_2 solid from water vapor.

Acknowledgements

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