Effect of hydrogen treatment on characteristics of titanium oxide nanotube micro hydrogen gas sensors

Tsubasa Tobe, Ryota Kojima, Yasuo Kimura and Michio Niwano

Laboratory for Nanoelectronics and Spintronics, Research Institute of Electrical Communication, Tohoku University 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan phone: +81-22-217-5502, fax: +81-22-217-5503 email: ykimura@riec.tohoku.ac.jp

A gas sensor is an important device used in various fields, such as security and environmental monitoring. A metal oxide semiconductor gas sensors has useful features of simple structure and high sensitivity. It generally consists of porous materials and the change of its conductance is sensed when gas molecules adsorb on the surface. Miniaturization and integration of gas sensors give a lot of advantages such as low power consumption, improvement of portability, high reliability, and simultaneous measurement of multicomponent. A general metal oxide semiconductor gas sensor is operated at several hundred degrees Celsius and large power is consumed by heating sensors. Therefore, miniaturization of the sensors suppresses the power consumption due to reduction of the heater size. In addition, integration of sensors gives large redundancy which improves reliability by application of the majority method and simultaneous measurement of multicomponent can be applied to one-chip breath sensors. Then, we used anodization process as a bottom-up process because anodization process is compatible with photolithography and forms nanotubes with homogenous pore diameter and period. Additionally it has been reported that gas sensors using anodic titanium oxide (TiO$_2$) nanotubes have good performance [1,2]. We have reported that TiO$_2$ nanotube hydrogen gas sensors can be miniaturized by local anodization [3]. However, the response characteristic was affected by the number of measurements. The stability to target gas is an important factor because it influences accuracy and reliability. In this study, the TiO$_2$ nanotube micro gas sensors were annealed in a hydrogen atmosphere in order to improve the stability to hydrogen. We describe the effect on the response characteristics before and after hydrogen treatment.

Figure 1 illustrates the fabrication process of a TiO$_2$ nanotube micro gas sensor. A titanium (Ti) thin film of 100 nm in thickness was deposited on a glass substrate by DC magnetron sputtering, and it was patterned by photolithography to form Ti micro wires. A protective silicon dioxide layer was deposited on the Ti wire except a region which was anodized. A part of the Ti micro wire was locally anodized to form a TiO$_2$ nanotube film connecting with two Ti electrodes. An ammonium fluoride and water containing ethylene glycol solution was used as an electrolyte. The TiO$_2$ nanotube film was crystalized by annealing in an oxygen atmosphere at 450 °C. The hydrogen treatments of sensors were carried out in 10% hydrogen diluted with nitrogen at 400 °C for 2 hours. Figure 2 shows a field emission scanning electron microscope (FE-SEM) image of a TiO$_2$ nanotube film formed by local anodization. Figure 2 shows the response of TiO$_2$ nanotube micro hydrogen sensors before and after hydrogen treatment. In the case of the sensor without hydrogen treatment, a detection current continued to increase. On the other hand, in the case of the sensor with hydrogen treatment, a detection current was stable. This indicates that hydrogen treatment stabilized response characteristics of a TiO$_2$ nanotube hydrogen sensor independently of the sensitivity.

Fig. 1: The illustration of the miniaturized gas sensor fabrication process.

Fig. 2: A SEM image of an anodic titanium oxide nanotube formed by local anodization.

Fig. 3: Response characteristics of TiO$_2$ nanotube micro hydrogen gas sensors before and after hydrogen treatment.

Fig. 4: A plot showing the response of TiO$_2$ nanotube micro hydrogen sensors to 10% hydrogen before and after hydrogen treatment.

References