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Fabrication of micro hydrogen gas sensors by local anodization of titanium wires

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1. Introduction

Gas sensors are used in various systems such as security, in-car device, and environment monitoring systems and they are one of the most important devices. The metal oxide semiconductor gas sensor is one of gas sensors and it has useful features of simple structure and high sensitivity. It generally consists of porous metal oxide semiconductor [1, 2] and the change of the conductance or resistance 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 multi-component. The 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 [3]. The reduction of power consumption also improves the portability. 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.

Miniaturization and integration of gas sensors require position controllability and uniformity of materials. It is important to precisely control the position of a device. Photolithography is a suitable technique for precise position control. Uniformity of the material is important to control the device characteristics because the device characteristics depend on the position in the case of using inhomogeneous materials. The bottom-up process is suitable for formation of homogeneous nanomaterials. Therefore, it is important to develop a hybrid process between photolithography and bottom-up process. This requires that the bottom-up process is compatible with photolithography. Then, we used an anodization process, which is compatible with photolithography, as a bottom-up one [4]. The anodization process forms nanotubes with homogenous pore diameter and period [5-8]. It has been reported that gas sensors using anodic titanium oxide nanotubes have good performance [9-14]. In this study, we miniaturized metal oxide semiconductor gas sensors using an anodic titanium oxide nanotube film by the hybrid process.

2. Experiment

As shown in Fig. 1, a titanium film was deposited on a silica substrate by DC magnetron sputtering (Fig. 1 (a)) and

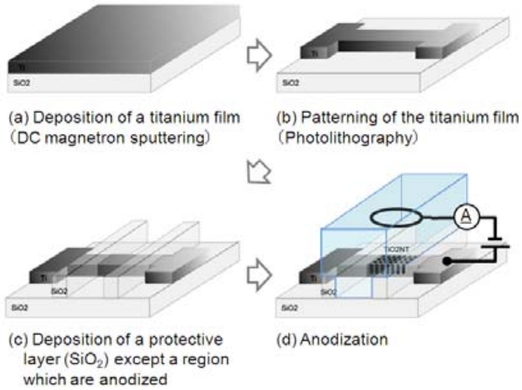

Fig. 1 Fabrication process of micro gas sensors by local anodization of titanium wires

the titanium film was patterned to form the titanium wire (Fig. 1 (b)). The width of the titanium wire was 100 µm or 3 µm. A protective silicon dioxide layer was deposited on the titanium wire except a portion of it (Fig. 1 (c)). After that the part of the titanium wire was anodized in an ammonium fluoride and water containing ethylene glycol solution (Fig. 1 (d)). The length of the anodized region was 25 µm or 3 µm. The concentrations of ammonium fluoride and water were 0.05 M and 5 vol.%, respectively. Platinum was used as a counter electrode. The applied potential was 40 V. Finally, the anodic titanium oxide nanotube layer was crystallized by annealing in the oxygen atmosphere at 400 °C for one hour, followed by 450°C for 30 min. The response of the miniaturized gas sensors to hydrogen gas were observed at 300°C.

3. Results and discussion

Figure 2 shows a cross-sectional SEM image of an anodic titanium oxide nanotube film formed by local anodization of titanium wires. We can see that a anodic titanium oxide nanotube film was formed. The inner diameter and the period of pores were about 50 nm and 100 nm, respectively. It is important for titanium oxide nanotubes to contact with each other because current flows in the horizontal direction when the titanium oxide nanotube film is applied to a gas sensor. From Fig. 2, we can see that anodic titanium oxide nanotubes contact with each other.

Figure 3 shows X-ray diffraction patterns for anodic titanium oxide nanotube films before and after annealing at 400 °C for 1 hours followed by 450 °C for 30 min. From Fig. 3, we can see that anodic titanium oxide nanotube

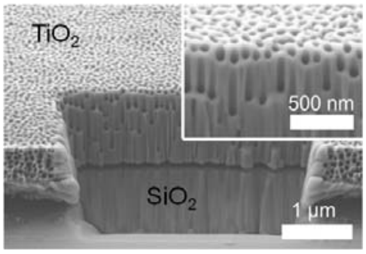

Fig. 2 A cross-sectional SEM image of an anodic titanium oxide nanotube film.

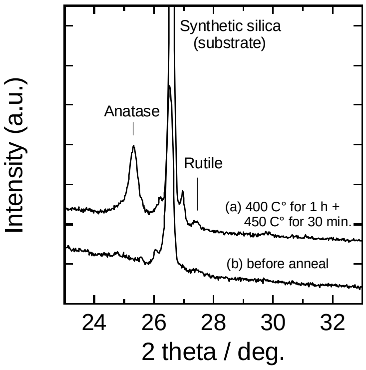

Fig. 3 X-ray diffraction patterns for anodic titanium oxide nanotube films before and after annealing in the oxygen atmosphere at 400 °C for 1 hours followed by 450 °C for 30 min.

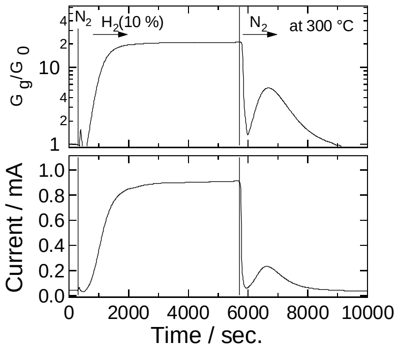

Fig. 4 The response characteristics of a miniaturized hydrogen gas sensor at 300 ºC.

films were amorphous and it was transformed to anatase by the anneal process.

Figure 4 shows the response of the miniaturized hydrogen gas sensor at 300 ºC, where an applied voltage was 10 V. From Fig. 4, we can see that the conductance of the sensor in 10 % hydrogen gas G_{H2} was 20 times as large as that in a nitrogen atmosphere G_0. This indicates that a micro gas sensor can be fabricated by the hybrid process. Furthermore, the sensed current of 1 mA indicates that the miniaturization is effective in an increase in the sensing current and that a picoammeter and formation of interdigitated electrodes are not necessary for sensing current. Furthermore, we fabricated smaller sensors. The length and width were 3 μm and 3 μm, respectively. As shown in Fig. 5, the

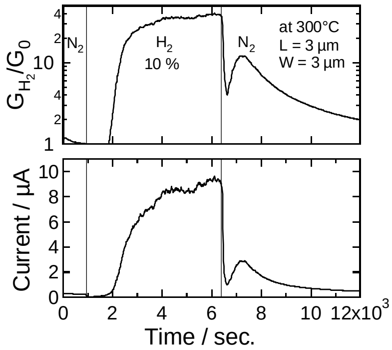

Fig. 5 The response characteristics of a miniaturized hydrogen gas sensor at 300 ºC.

miniaturized gas sensor worked as well as larger one. This indicates that the anodization process is suitable method for miniaturization of gas sensors.

3. Conclusions

We miniaturized anodic titanium oxide nanotube gas sensors by means of the local anodization process of titanium wires which was patterned by photolithography. The miniaturization was effective in an increase in the sensing current. Furthermore, we demonstrated that hydrogen gas sensors of 3×3 μm^2 can be fabricated by the local anodization process. This indicates that the anodization process is suitable method for miniaturization of gas sensors.

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