Nano-Wire Grown Micro Thin Film Sensors and Their Gas Sensing Properties

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Abstract
SnO$_2$ nanowires were grown on the surface of SnO$_2$ thin film by heat treatment of metal Sn film under Ar gas flow at atmospheric pressure. Generally, the nanowires of metal oxide semiconductors are known to be grown at low pressure (below 0.02 Torr) and at high temperature (over 1,000 $^\circ$C). The deposited Sn metal films were annealed at temperatures of 700 ~ 900 $^\circ$C for 3 hours. The sensitivity of the thin film device on which nanowires were grown to CO gas (1,000 ppm) was 60 % at the operating temperature of 250 $^\circ$C. And it was found that the sensitivity to CO and C$_4$H$_{10}$ gases for the device annealed under Ar gas flow was much higher than those for device annealed under O$_2$ gas flow.

Keywords: Micro gas sensor, SnO$_2$ nanowire, Quartz substrate, CO gas

1 Introduction
Recently, nano technology has created a strong interest and has been studied extensively, for it can provide a device with low power consumption and enhanced properties [1-5]. In the present study, SnO$_2$ nanowires [2] were grown on the surface of SnO$_2$ thin film obtained by heat treatment of Sn metal film (2,000 Å thick) under Ar gas flow. By using the nanowires, we can enlarge the surface of the device without increasing the dimension [3].

The SnO$_2$ nanowires could be obtained by annealing at temperatures lower than 1,000 $^\circ$C (700 ~ 900 $^\circ$C) under Ar gas flow. And the sensitivities to CO and C$_4$H$_{10}$ for the nanowires grown device were much enhanced compared to those for the conventional device.

2 Experimental
Process sequences for sensor fabrication are shown in figure 1. The fabrication process is as follows. Firstly, Pt / Ti thin films as heating and sensing electrodes were sputtered on quartz substrate. Heating and sensing electrodes were formed on the same plane for simple fabrication process. And then metal Sn was thermally evaporated onto the patterned inter-digited type (IDT) Pt / Ti electrodes. Deposited metal films were annealed at the temperature range of 700 ~ 900 $^\circ$C for 3 hours at atmospheric pressure, in Ar and O$_2$ gas ambient, respectively. And to enhance the sensitivity of the thin film device to the reducing gases, about 30 Å of Pt thin films were deposited onto SnO$_2$ or nanowire grown SnO$_2$ thin films (annealed at 650 $^\circ$C for 3 hours). Photographs of fabricated sensor in front view and magnified view were shown in figure 2. The active sensing area was 1.5 x 1.5 mm$^2$.

Figure 1 : Process sequence for sensor fabrication.

Figure 2 : Photographs of fabricated sensor.
3 Results and discussions

Figure 3 shows temperature dependence of the resistance of SnO$_2$ and SnO$_2$ nanowires. SnO$_2$ and SnO$_2$ nanowires were stabilized over 300 $^\circ$C. As shown in this figure, the recommended operating temperature of the sensing materials should be chosen at above 200 $^\circ$C in terms of the device resistance variation with temperature.

Figure 4 shows SEM images of SnO$_2$ and nanowires grown by annealing SnO$_2$ thin films at various temperatures in different gas ambient. The nanowires on the SnO$_2$ thin film were formed by annealing at 900 $^\circ$C under Ar gas flow (figure 4(b)). The diameter of fabricated nanowires annealed at 900 $^\circ$C was about 70 nm. In O$_2$ gas ambient, the particles of SnO$_2$ was agglomerated and shaped in small round grains (figure 4(a)).

Figure 5 shows gas sensing characteristics for SnO$_2$, SnO$_2$ nanowires and SnO$_2$ + Pt nanowires for CO, C$_4$H$_{10}$ gas at different operating temperature. The sensitivity of SnO$_2$ nanowires (annealed in Ar gas at 900 $^\circ$C) was much higher than that of SnO$_2$ (annealed in O$_2$ gas). Sensitivity is defined by $\left[ \frac{|R_g-R_a|}{R_a} \right] \times 100 \%$. $R_g$ is the resistance in a gas environment and $R_a$ is the resistance in air. Sensitivity of SnO$_2$ thin film (annealed in O$_2$ gas) was about 20 $\%$ for CO and C$_4$H$_{10}$ 1,000 ppm at 300 $^\circ$C. And sensitivity of grown nanowires onto SnO$_2$ thin film (annealed in Ar gas at 900 $^\circ$C) was about 60 $\%$ for CO 1,000 ppm at 200 $^\circ$C. As shown in figure 5(a) and (c), optimal operating temperature of SnO$_2$ nanowire was lower than that of SnO$_2$ thin film annealed in O$_2$ gas.
Figure 5: Gas response characteristics for SnO\(_2\), SnO\(_2\) nanowires and SnO\(_2\) + Pt nanowires at various operating temperatures for CO and C\(_4\)H\(_{10}\) gas.

Also, the higher sensitivity (by 10%) was obtained for SnO\(_2\) + Pt [6-7] nanowires compared with that of SnO\(_2\) nanowires. Sensitivity of SnO\(_2\) + Pt nanowires was about 80% for CO 10,000 ppm at 250 °C and 60% for C\(_4\)H\(_{10}\) 10,000 ppm at 300 °C (figure 5(e) ~ (f)).

Figure 6 shows sensing performance for CO, C\(_4\)H\(_{10}\), CH\(_4\) gas and alcohol molecules. As shown in this figure, SnO\(_2\) nanowires exhibit the highest sensitivity to CO gas. However, the sensitivity to CH\(_4\) gas and alcohol was very low (about 10%).

Figure 7 shows time response curve of SnO\(_2\) nanowires for CO gas. The response and recovery time are 20 sec, 60 sec, respectively. And the response signals of nanowires grown SnO\(_2\) thin film showed good repeatability in 1,000 ppm CO ambient. The sensitivity was 60% for 1,000 ppm CO.

Figure 8 shows long term stability of fabricated sensor. The resistance of SnO\(_2\)+Pt nanowires was very stable for 2 months in ambient at 300 °C operating temperature.
4 Conclusions

We have studied the fabrication and gas response characteristics of SnO\textsubscript{2} nanowires. Nanowires grown SnO\textsubscript{2} thin films were prepared by heat treatment in Ar gas at comparatively low temperatures (600 ~ 900 °C) under atmospheric pressure and the gas sensing properties have been investigated. The sensitivities to CO and HC gases of the nanowires grown SnO\textsubscript{2} thin film were found to be higher than those of SnO\textsubscript{2} thin film. Especially, SnO\textsubscript{2} + Pt nanowires exhibited excellent sensitivity to CO gas (~ 70 % to 1,000 ppm CO) and high selectivity against other gases.

5 References


