1st International Conference on Sensing Technology
November 21-23, 2005 Palmerston North, New Zealand

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 ℃). The deposited Sn metal films were annealed at temperatures of 700 ~ 900 ℃ 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 ℃. And it was found that the sensitivity to CO and C_4H_{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 ℃ (700 ~ 900 ℃) under Ar gas flow. And the sensitivities to CO and C_4H_{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 ℃ 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 ℃ 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 × 1.5 mm^2.

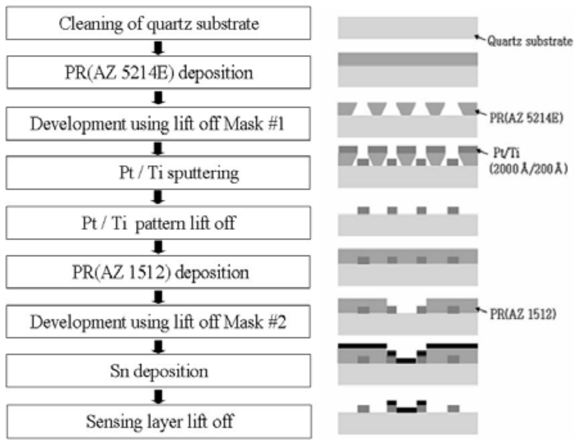
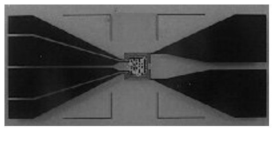
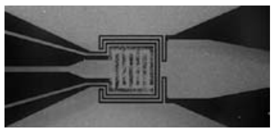


Figure 1 : Process sequence for sensor fabrication.



(a) Front view of sensor device



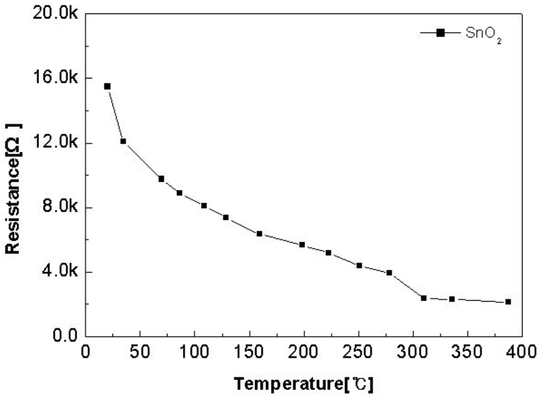
(b) Magnified view of sensing area

Figure 2 : Photographs of fabricated sensor.

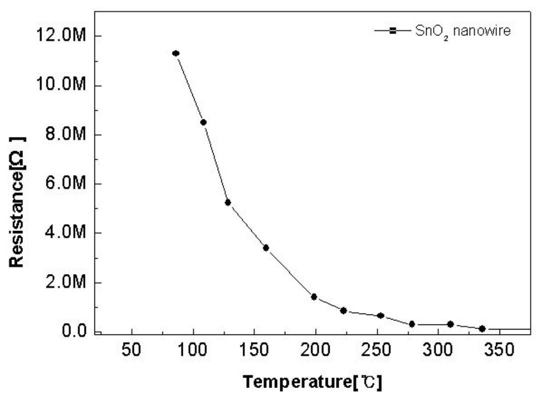
3 Results and discussions

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 ℃. As shown in this figure, the recommended operating temperature of the sensing materials should be chosen at above 200 ℃ 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 ℃ under Ar gas flow (figure 4(b)). The diameter of fabricated nanowires annealed at 900 ℃ 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)).

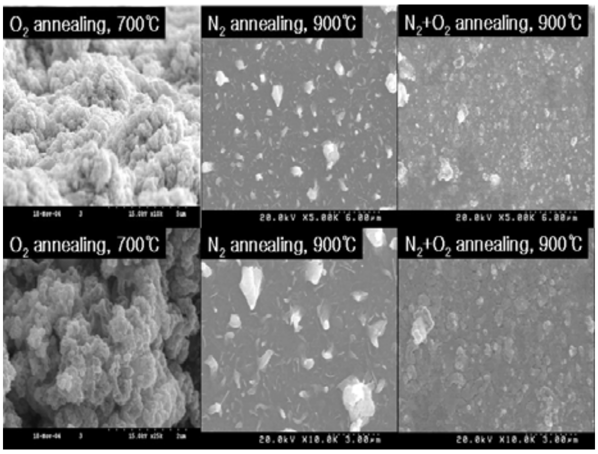


(a) SnO_2 annealed in O_2 gas

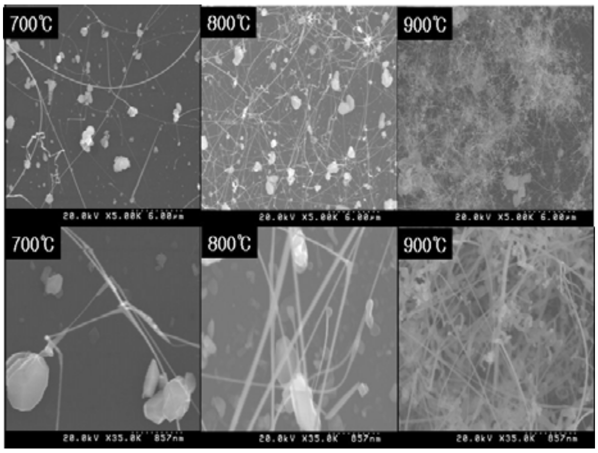


(b) SnO_2 nanowires annealed in Ar gas

Figure 3 : Temperature dependence of SnO_2 and SnO_2 nanowires.



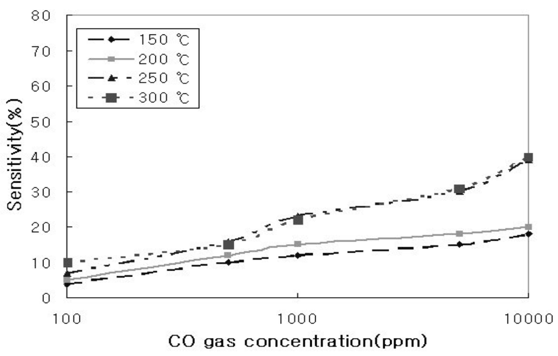
(a) SnO_2 annealed in N_2 and O_2 gases



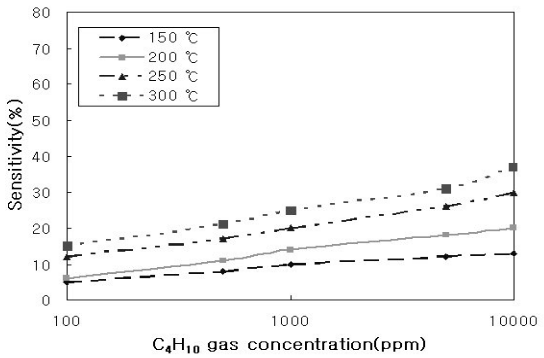
(b) SnO_2 annealed in Ar gas

Figure 4 : SEM images of SnO_2 and SnO_2 nanowires for various annealing temperatures and ambient gases.

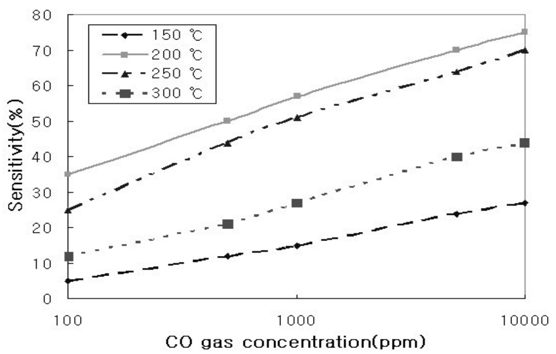
Figure 5 shows gas sensing characteristics for SnO_2, SnO_2 nanowires and SnO_2 + Pt nanowires for CO, C_4H_{10} gas at different operating temperature. The sensitivity of SnO_2 nanowires (annealed in Ar gas at 900 ℃) was much higher than that of SnO_2 (annealed in O_2 gas). Sensitivity is defined by $[\ |R_g-R_a| / R_a] \times 100$ %. 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_4H_{10} 1,000 ppm at 300 ℃. And sensitivity of grown nanowires onto SnO_2 thin film (annealed in Ar gas at 900 ℃) was about 60 % for CO 1,000 ppm at 200 ℃. 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.



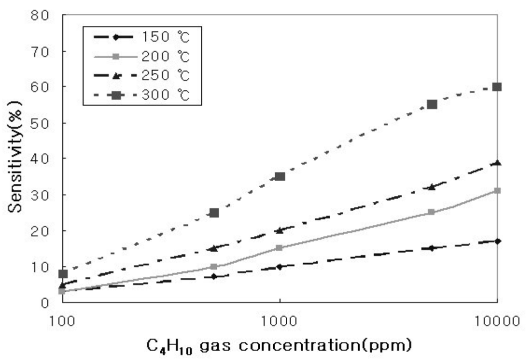
(a) SnO_2 for CO gas



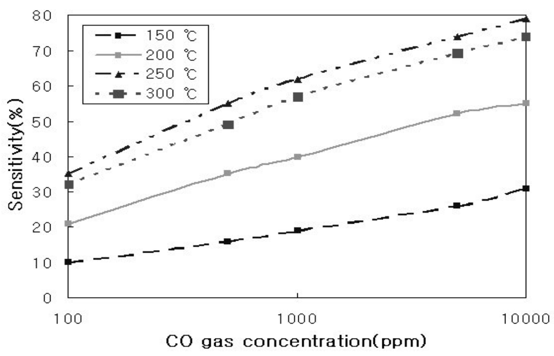
(b) SnO_2 for C_4H_{10} gas



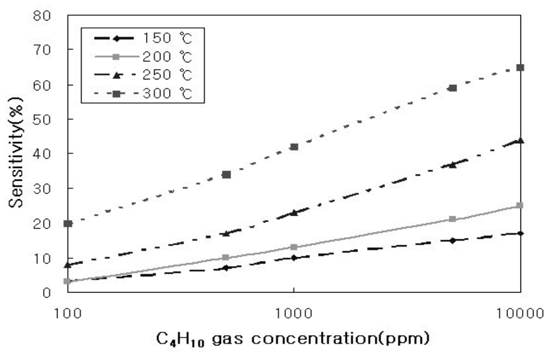
(c) SnO_2 nanowires for CO gas



(d) SnO_2 nanowires for C_4H_{10} gas



(e) SnO_2 + Pt nanowires for CO gas



(f) SnO_2 + Pt nanowires for C_4H_{10} 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_4H_{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 ℃ and 60 % for C_4H_{10} 10,000 ppm at 300 ℃ (figure 5(e) ~ (f)).

Figure 6 shows sensing performance for CO, C_4H_{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 ℃ operating temperature.

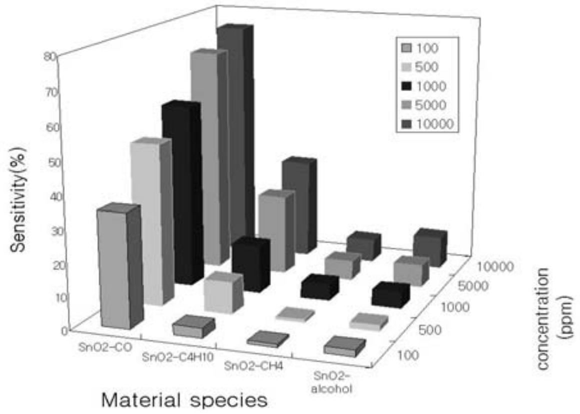


Figure 6 : Gas response characteristics for various gases.

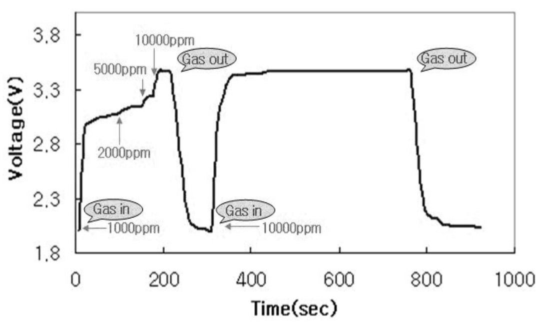


Figure 7 : Dynamic response curve for CO gas of SnO_2 nanowires.

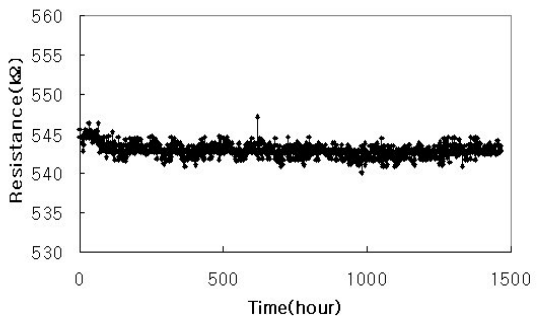


Figure 8 : Long term stability of SnO_2 + Pt nanowires.

4 Conclusions

We have studied the fabrication and gas response characteristics of SnO_2 nanowires. Nanowires grown SnO_2 thin films were prepared by heat treatment in Ar gas at comparatively low temperatures (600 ~ 900 ℃) under atmospheric pressure and the gas sensing properties have been investigated. The sensitivities to CO and HC gases of the nanowires grown SnO_2 thin film were found to be higher than those of SnO_2 thin film. Especially, SnO_2 + Pt nanowires exhibited excellent sensitivity to CO gas (~ 70 % to 1,000 ppm CO) and high selectivity against other gases.

5 References

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