Influence of surface morphology on H_2S sensing property of Cu_2O thin film deposited by RF magnetron sputtering

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Abstract: This study introduces a simple deposition of Cu_2O thin films with surface morphologies composed of columns, submicron-rods and submicron-branches on glass substrate from metallic Cu targets by tailoring the Ar/O_2 ratios during the sputtering. The obtained samples were used to fabricate gas sensor. The H_2S sensing properties of the sensors at working temperatures from 100 °C to 300 °C were studied, in which Cu_2O submicron-branches performed the best sensing property comparing with the rest morphologies. A transformation of Cu_2O to Cu_2S and CuS was consider as a main factor to the sensing mechanism of the sensors.

1. Introduction

In recent years, there is no doubt that metal oxide micro- and nano-structures have played a vital role in the development of science and technology because of their important in many applications including catalysts, sensors, energy storage, solar cell, magnetic materials, anti-bacterial, drug delivery. A widespread interest in tailoring size and shape of metal oxide is, nowadays, a hot issue due to the dependents of optical, electronic, magnetic and catalytic properties on the dimension as well as morphology of the material. A wide variety of physical and chemical approaches have been developed and carried out to solve the problem. Sputtering is a physical deposition method that is, nowadays, frequently used not only in laboratories but also in industrial plants because this method allows operators to mass deposit highly uniform thin films. There were many efforts to synthesis of 1-D structure using direct current (DC) sputtering and radio frequency (RF) sputtering [1-2]. Most of those materials were received by tailoring the substrate temperature, the topography of the substrate and the surface mobility of the adsorbed species. To date, a precise understanding of the formation mechanism, however, of those materials by sputtering is still unclear.

Cuprous oxide (Cu_2O) is a promising p-type metal oxide semiconductor with a direct bandgap band gap of ~2.17 eV. It has been applying in many fields, such as catalysis [3], lithium-ion battery anode materials [4], photoelectrode [3], low-cost solar cells [5], etc. In addition, Cu_2O is a potential material for detecting H_2S, NO_2 and ethanol. To enhance the catalytic and sensing properties, many studies have examined the synthesis of this material with different morphologies, such as nanowires [6], nanotubes [7], and variety of nano- single crystals [8] using a range of chemical and physical methods. Cu_2O thin films were deposited by sputtering [9]. Nevertheless, controlling the surface morphology of Cu_2O using RF magnetron sputtering is still a great issue.

In this study, Cu_2O thin films with surface morphologies composed of columns, submicron-rods and submicron-branches were deposited on glass substrates by RF magnetron sputtering. Sensing properties of those morphologies toward H_2S were investigated. The sensing behaviors of those morphologies were compared and discussed in detail.

2. Main results

Sensing measurements of the Cu_2O thin films and submicron-sized rods and trees were performed at temperatures of 100 °C-300 °C under an H_2S concentration of 1-10 ppm. Figure 1 shows the responses of the sensor devices toward 10 ppm of H_2S at 200 °C (a) and 300 °C (b). At an operating temperature of 200 °C, the thinfilm sensor was not sensitive toward 10 ppm of H_2S. In contrast, the sensor consisting of submicron-sized trees showed the highest response of approximately 1800, followed by the response of the submicron-rods sensor (with a signal of just above 8). On the other hand, the sensor resistance in this measurement did not recover. At 300 °C, the submicron-rods sensor showed a response of approximately 60 against 10 ppm of H_2S, whereas the response of the submicron-tree device decreased to just above 1000. In addition, the response times of the thin films, submicron rods and submicron trees were 10 min, 5 min, and 2.5 min, respectively.

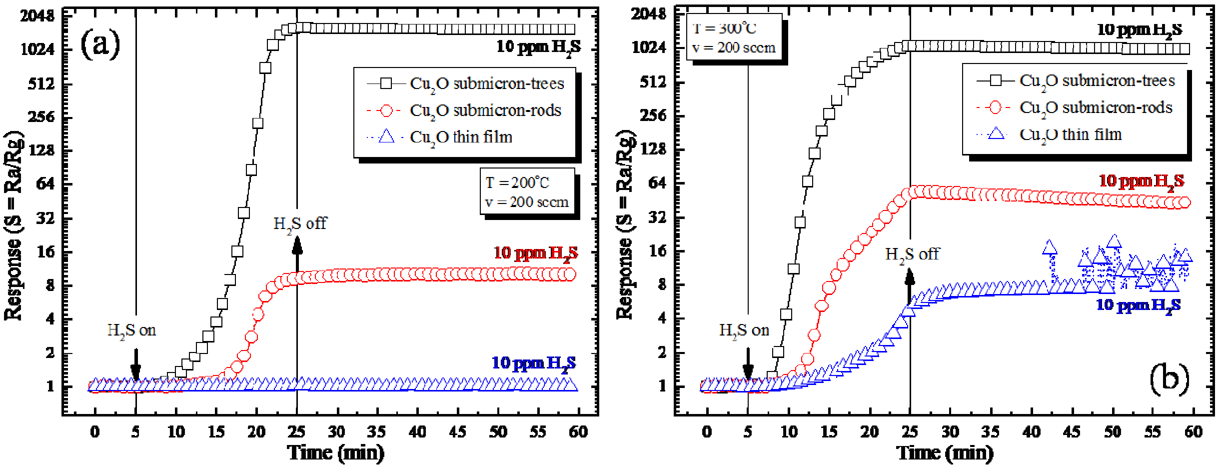

Fig. 1. H_2S responses of the thin film, submicron-rod and submicron-tree sensors at 200 °C (a) and 300 °C (b).

For the thin-film device, the sensing area was located between two electrodes and the sensor resistance is the sum of the total surface resistance, and the bulk resistance, connected in parallel. For the submicron-rod device, the sensing area is a combination of resistance of Cu_2O submicron-rods, which are connected to each other from electrode to electrode and the surface resistance. In addition, the appearance of the Cu_2O submicron-rods may lead to the formation of a discontinuous electrode layer after deposition. The electrode resistances arise from the serial connections of the Ni/Au resistance and Cu_2O grain/rod resistances, which form an extra sensing area. This explains why the submicron-rod device showed a better sensitivity toward H_2S than the thin-film device. Moreover, at an operating temperature of 200 °C, the Cu_2O submicron-sized rods or trees appeared to be the unique sensing units because the thin film surface of the thin-film device showed no response toward H_2S.

3. Conclusions

In conclusion, cuprous oxide thin films with ring-like canyons (diameter of 2-3 μm), submicron-sized rods (large head/small root with diameters of 100-700 nm and lengths of 2-8 μm), and submicron trees were synthesized by RF-magnetron sputtering. The morphologies of Cu_2O were easily tailored by modulating the ratio of Ar/O_2 during the sputtering process. For the gas-sensing measurements, the sensor based on Cu_2O submicron-trees showed the best H_2S sensing property at 200 °C among the three different morphologies investigated. Both the submicron-sized tree and rod sensors were selective toward H_2S. A discontinuous electrode composed of Ni/Au and Cu_2O rods/branches led to the formation of an extra sensing area. The appearance of sulfur at the grain boundaries was detected by XPS and TEM, revealing that the CuS and Cu_2S phases formed simultaneously during the tests above 200 °C. Therefore, the sensing mechanism of all samples involved a phase transformation from Cu_2O to CuS.

References

1. J. H. Park, H. K. Park, et al., Journal of The Electrochemical Society, Vol. 158(5), pp.K131-K135, 2011.
2. M. K. Fung, Y. C. Sun, et al., Appl Phys A, Vol.104, pp.1075-1080, 2011.
3. L. Zhang, H. Wang, ASC Nano, Vol.5, pp.3257-3267, 2011.
4. C. Q. Zhang, J. P. Tu, et al., J Alloy Compd, Vol.441, pp.52-56, 2007.
5. K. Akimoto, S. Ishizuka, et al., Sol Energy, Vol.80, pp.715-722, 2006.
6. P. Grez, F. Herrera, et al., Mater Lett, Vol.92, pp.413-416, 2013.
7. F. Luo, D. Wu, et al., J Cryst Growth, Vol.285, pp.534-540, 2005.
8. X. Liang, L. Gao, et al., Adv. Mater., Vol.21, pp.2068-2071, 2009.
9. Z. G. Yin, H. T. Zhang, et al., Appl Phys Lett, Vol.86, 061901, 2005.