Sensors and Materials, Vol. 20, No. 8 (2008) 425–433
MYU Tokyo

S & M 0740

Effect of Depositing Tin Oxide Thin Film in Liquid Phase and Dip-Coating Cu and Au Catalysts on H_2S Gas-Sensing Performance

Jin-Chern Chiou, Sheng-Wei Tsai*, Ya-Shu Liu and Chen-Tang Huang[1]

Department of Electrical and Control Engineering, National Chiao-Tung University,
1001 University Road, Hsinchu, Taiwan 300, R.O.C.
[1]Oriental System Technology, Inc.,
No. 25, Industry E. Road 9th, Hsinchu Science Park, Hsinchu, Taiwan 308, R.O.C.

(Received July 30, 2008; accepted November 23, 2008)

Key words: LPD, tin oxide, porous, catalyst, gas sensor

In this study, unlike conventional methods used to grow gas sensor films, a liquid-phase deposition method was used to deposit fluorine-doped tin oxide as the sensing material of a gas sensor. Furthermore, silica was doped into the film as an inhibitor to prevent the grain growth of tin oxide during the calcination process. This structure can be used to improve the sensitivity of a H_2S sensor. By adding a moderate quantity of copper and gold catalysts on the surface of film, the sensitivity can be dramatically improved.

1. Introduction

There are several methods of manufacturing metal oxide sensing films; in early processes, the powder calcination method was mainly used. From the batch-processing viewpoint, screen printing is frequently used in fabrication processing to manufacture gas sensors. In recent years, there has been a tendency to combine film growth deposition technologies with semiconductor processing to simplify the complex fabrication processes. As a result, a process was developed to integrate semiconductor circuits with micro-electro-mechanical systems (MEMS) to promote miniaturization and low power consumption. Generally, thin film deposition processes have involved chemical vapor deposition (CVD), electron-beam evaporation, and sputtering, etc. However, these processes not only require expensive equipment, but also cause pollution due to their interaction with other materials. They also require special machines and materials for their use. For example, sputtering requires expensive alloy targets, and CVD requires additional piping and flow control, raising the manufacturing costs. Moreover, these processes have a serious disadvantage in terms of the difficulty of doping a catalyst into tin oxide.

To overcome the above-mentioned disadvantages of conventional semiconductor

*Corresponding author: e-mail: gavin0916.ece93g@nctu.edu.tw

fabrication processes, a liquid-phase deposition (LPD) method is used to deposit tin oxide thin film onto a substrate. The LPD method was first introduced in the fabrication process reported by Nagayama *et al.*[1] It was initially aimed at coating a glass substrate with silica film to prevent the alkali ion from passing from the glass surface into the transparent electroconductive film, which reduces the lifetime of the device. Various metal-fluoro complexes were used to produce different metal oxide thin films by LPD. The chemical reaction mechanism is given by[2]

$$MF_x^{(x-2n)-} + nH_2O \leftrightarrow MO_n + xF^- + 2nH^+. \quad (1)$$

By the law of mass action for the products, the equilibrium reaction will shift towards the right by adding H_3BO_3 or aluminum metal as a F^- scavenger, which readily reacts with F^- and forms the stable complex ions given in eqs. (2) and (3):[2]

$$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \quad (2)$$

$$Al + 6HF \leftrightarrow H_3AlF_6 + 2/3H_2. \quad (3)$$

In the current chemical process, the LPD method simply requires a chemical reactor without the need of an expensive vacuum environment. Note that for mass production, the LPD process is an attractive cost-effective deposition method for gas sensor fabrication. Furthermore, tin oxide thin film possesses a lower process temperature and higher sensitivity than other metal oxides. The purpose of this study is to improve the porosity of tin oxide thin film and to decrease the response time by investigating various deposition conditions to increase sensitivity to hydrogen sulfide using different catalysts.

2. LPD Process Steps

2.1 *LPD mechanism*

The mechanism of the deposition of SnO_2 thin film by LPD is as follows.[3]

1. SnF_2 powder was dissolved into DI water to produce $Sn(OH)_4$.

$$SnF_2 + 4H_2O \rightarrow Sn(OH)_4 + 4H^+ + 2F^- \quad (4)$$

2. $Sn(OH)_4$ molecules bond with each other to form an oligomer that can approach the substrate surface because of van der Waals' forces, as illustrated in Fig. 1(a).
3. A dehydration reaction occurs between the polymer and the Al_2O_3-OH present on the substrate surface, followed by Sn-O-Al_2O_3 bond formation (Fig. 1(b)).
4. Because HF is present in the solution, etching occurs during deposition, and $(Sn(OH)_{4-x}F_x)$ is also formed in the thin films, as shown in Fig. 1(c).
5. The deposition of LPD-oxide film on the substrate surface occurs due to the repeated absorption of the polymer described in step 2 (Fig. 1(d)).
6. H^+ and F^- are detached after high-temperature calcination to form a tin oxide thin film, as shown in Fig. 1(e).

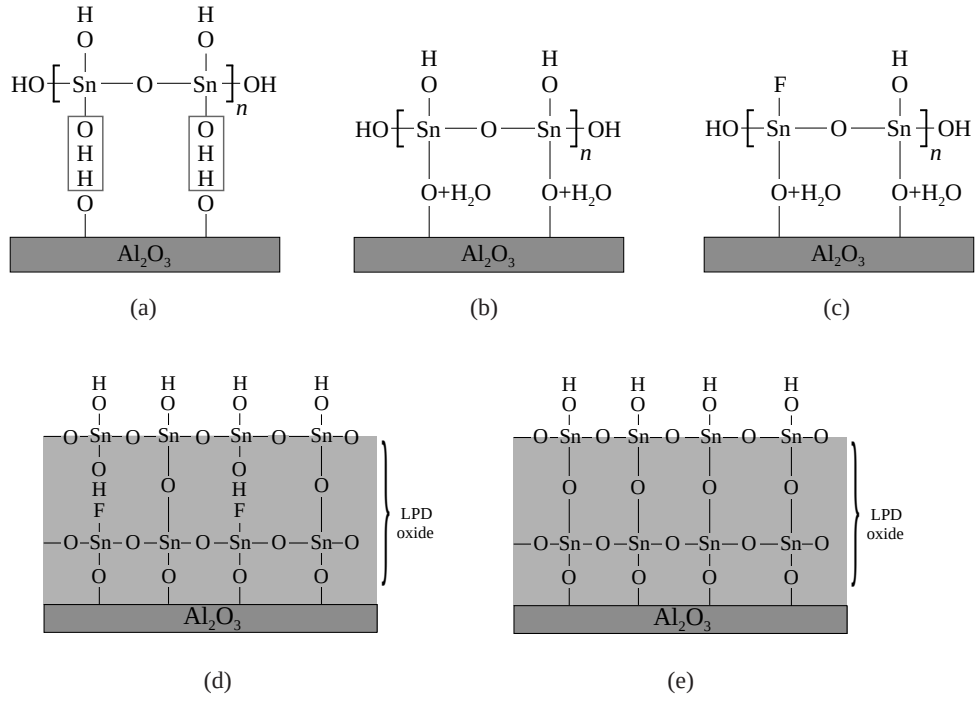


Fig. 1. Liquid-phase deposition (LPD) mechanism: (a) $Sn(OH)_4$ oligomer is formed, (b) dehydration reaction occurs between the polymer and Al_2O_3-OH present on the substrate surface, (c) ($Sn(OH)_{4-x}F_x$) is formed in the thin film, (d) LPD-oxide film is deposited on the substrate surface, (e) tin oxide thin film is formed by annealing treatment.

2.2 *Preparation of SiO_2-doped SnO_2 thin film*

LPD aqueous solutions were prepared by dissolving commercial SnF_2 powder into deionized (DI) water. The powder completely dissolved by stirring to form $Sn(OH)_{4-x}F_x$ solution.[4] Boric acid (H_3BO_3) was dissolved in DI water and used as a F^- scavenger. The $Sn(OH)_{4-x}F_x$ aqueous solution was used as a starting solution. The SiO_2-doped SnO_2 solution was prepared by adding flurosilicic acid (H_2SiF_6) to the starting solution.

An Al_2O_3 substrate was fixed on a stable platform and immersed in the $Sn(OH)_{4-x}F_x$+ H_2SiF_6 solution at 60°C for 6 h while stirring. After deposition, the Al_2O_3 substrate was removed from the solution, washed with DI water, and then dried at 60°C in air. The flow diagram of film fabrication is shown in Fig. 2.

The deposition rate of pure self-fluorinated tin oxide film can be dramatically enhanced by increasing the deposition temperature and the concentration of SnF_2 in the solution. In this study, both process parameters were kept at 60°C and 0.1 M. The average deposition rate was about 20 nm/h. However, for SiO_2-doped tin oxide, the addition of boric acid is the key factor. The concentration of boric acid is dependent on the quantity of flurosilicic acid added to the solution.

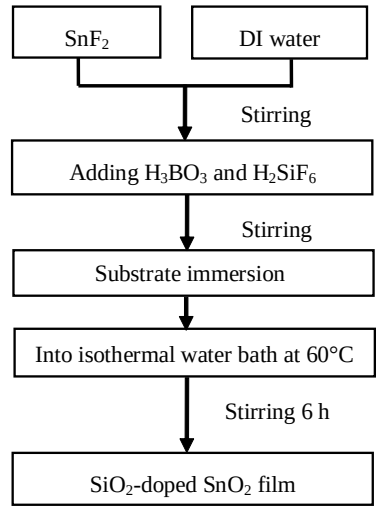


Fig. 2. Flow diagram of SiO_2-doped SnO_2 thin film.

2.3 *Methods of calcination and adding catalyst*

To avoid a rapid temperature increase that leads to the filAm cracking easily, in this study the film heat treatment was performed by increasing the temperature by 3℃/min to the maximum temperature, maintaining this temperature for 1 h, then cooling naturally to room temperature. The heating process is shown in Fig. 3, and the maximum temperature is 600°C.

The SiO_2-doped SnO_2 thin film underwent heat treatment, then was immersed in catalytic solutions of both copper and gold for several seconds. The sensor film was removed from the catalytic solution, and dried at room temperature, then placed on a heating platform immediately. The treated thin film was calcined again after doping the catalyst. This was necessary so that the doped catalyst accumulated on the SnO_2 thin film surface, thus optimizing the gas sensing performance of the thin film.

3. Results and Discussion

3.1 *Composition analysis*

The results of energy dispersive X-ray spectroscopy (EDX) analysis for SnO_2 and SiO_2-doped SnO_2 powder are shown in Table 1. Sn, O and F were detected for all samples. It is noted that the as-deposited powder contains about 23–29% fluorine. The fluorine was removed from the powder when the calcination temperature was higher than 500°C. Pure SnO_2 and SiO_2-doped SnO_2 powders are formed by heating.

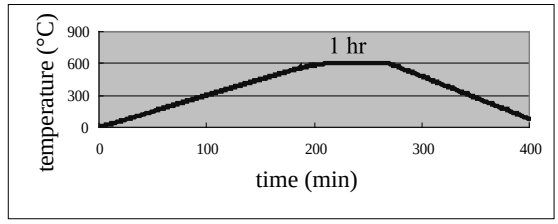


Fig. 3. Heating process after the film deposition.

Table 1
Components of the precipitates.

Composition	Calcination Temperature	Sn (%)	O (%)	F (%)	Total (%)
SnO_2 powder	As-deposited	23.66	52.61	23.73	100
	400°C	23.58	75.92	0.5	100
	500°C	26.37	73.63	0	100
	600°C	25.28	74.72	0	100
	700°C	24.45	75.55	0	100
SnO_2:SiO_2 powder	As-deposited	18.23	53.66	28.11	100
	400°C	20.70	77.42	1.88	100
	500°C	27.23	72.77	0	100
	600°C	18.42	81.58	0	100
	700°C	18.39	81.61	0	100

3.2 *Response characteristics of sensors to H_2S*

When H_2S reacted with the adsorbed oxygen on the surface of the SnO_2 thin film, electrons were released:[5]

$$H_2S_{(ads)}+3O^{2-} \rightarrow SO_{2(g)}+2H_2O+6e^-. \quad (5)$$

Figure 4 shows the response of sensors prepared by the LPD method to various H_2S concentrations. Upon exposure to H_2S, the resistance of the sensor (Rs) is reduced, and stability is not achieved until the rates of oxygen absorption and desorption are equal. Moreover, it is noted that as the concentration of H_2S increases, the resistance of the sensor significantly decreases. Therefore, the concentration of H_2S may be obtained by measuring the resistance.

We compared two types of thin films (SnO_2 and SnO_2:SiO_2) that were doped with different concentrations of Cu: 5 mM, 2.5 mM, and 1.25 mM. Figure 5 shows the response of the SnO_2 thin film with various Cu concentrations to different H_2S concentrations. As the concentration of Cu increases, sensitivity significantly increases. Note that the SnO_2 thin film doped with 2.5 mM Cu has the highest sensitivity. Under the same conditions, the characterization of Cu-doped SnO_2:SiO_2 thin film is shown in Fig. 6. In general, the working temperature of a metal oxide gas sensor is above 300°C. The performance of a sensor will degenerate with time due to the grain growth at high temperatures. That is to say, the control of the grain size and the inhibition of grain

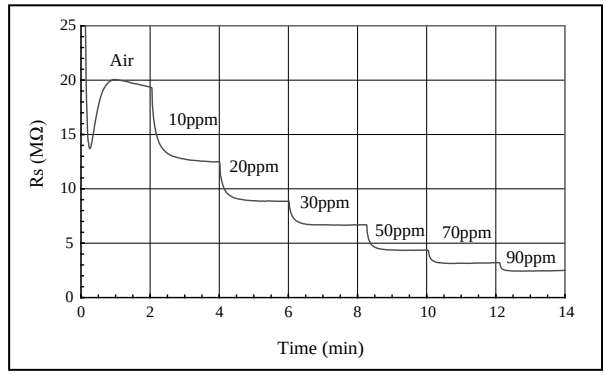


Fig. 4. Value of Rs for various concentrations of H_2S.

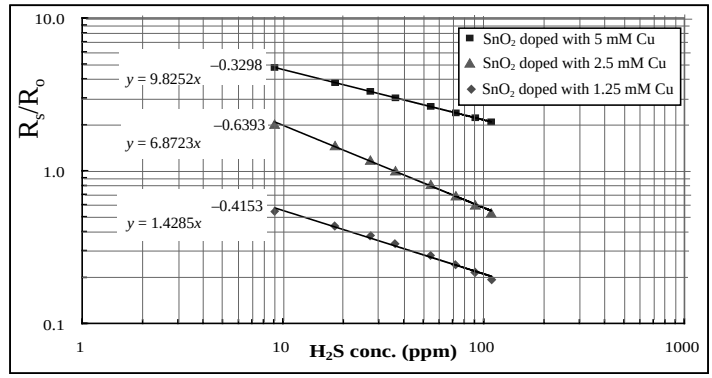


Fig. 5. Relation between resistance and H_2S concentration for SnO_2 doped with three different concentrations of Cu.

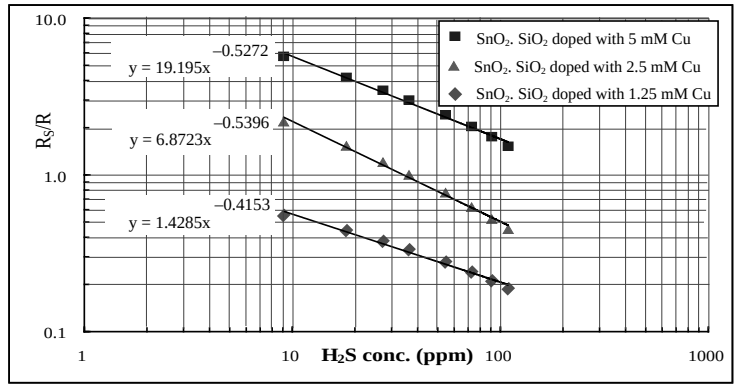
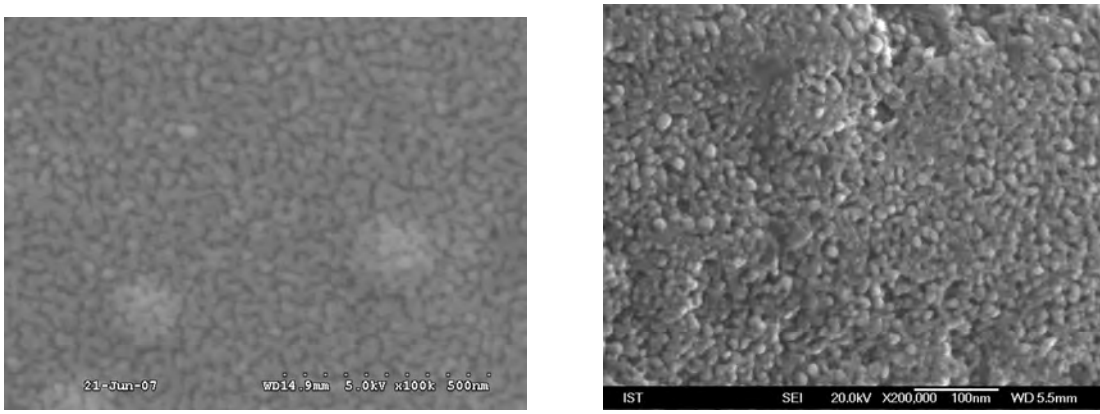


Fig. 6. Relation between resistance and H_2S concentration for SnO_2:SiO_2 doped with three different concentrations of Cu.

growth on the sensing material is very important for this type of gas sensor. In this study, the in situ doping of SiO_2 in tin oxide film deposited by the LPD method is proposed for the first time. Using SiO_2 as an inhibitor can markedly enhance the sensitivity of the sensor and prevent the degeneration of performance with time. The grain size of the thin film is about 20 nm as shown in the scanning electron microscope (SEM) images in Fig. 7. According to the measured results, the 2.5 mM Cu-doped SnO_2:SiO_2 thin film had the greatest sensitivity.

The final sensitivity can be expressed as a gas concentration characteristic by curve fitting. The sensitivity of six test samples was determined by the relationship between the relative resistance of the gas sensors and the concentration of H_2S. The slopes of the gas concentration characteristics of the six test samples are shown in Table 2. It is noted that the sensitivity of the SnO_2:SiO_2 film is higher than that of the corresponding SnO_2 film.

In 1992,[6] Chen found that SnO_2 sensor thin films with a Au catalyst could sense H_2S gas and inhibit performance degradation. Therefore, in this study, four concentrations of Au catalyst (45, 30, 15, and 7.5 mM) were doped into SnO_2:SiO_2 films with a Cu catalyst. Figure 8 shows the relation between the resistance and H_2S concentration for different concentrations of the Au catalyst. The sensitivity significantly increases when the catalytic concentration increases. However, if the catalytic concentration is higher than 30 mM, the sensitivity is reduced. This is due to the fact that the SnO_2:SiO_2 film surface is affected by metal ions, resulting in a large number of regathering reactions.



(a) (b)

Fig. 7. SEM images of (a) SnO_2 and (b) SnO_2.SiO_2 films calcined at 600°C for 1 h in air.

Table 2
Sensitivity of the six samples.

Film/Catalyst	5 mM Cu	2.5 mM Cu	1.25 mM Cu
SnO_2	0.3298	0.5396	0.4153
SnO_2:SiO_2	0.5272	0.6393	0.4341

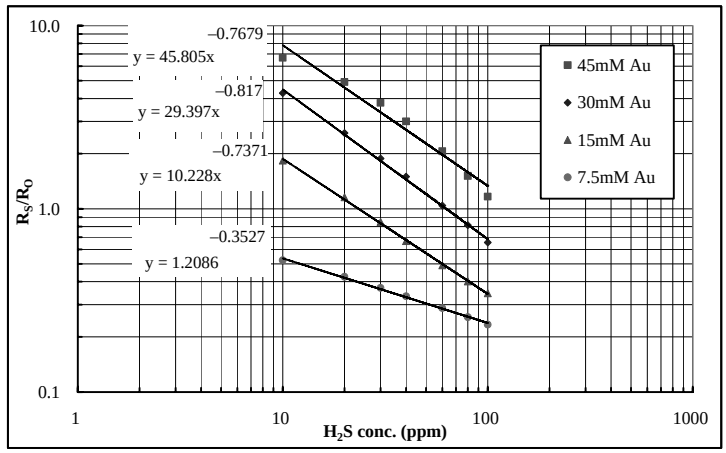


Fig. 8. Relation between resistance and H_2S concentration for $SnO_2.SiO_2$ doped with 2.5 mM Cu and various concentrations of Au.

Table 3
Sensitivity of doped and undoped SiO_2 films.

Film	Catalyst	Sensitivity without doping Au	Sensitivity after doping 30 mM Au
SnO_2	5 mM Cu	0.3298	0.5652
SnO_2	2.5 mM Cu	0.5396	0.6223
SnO_2	1.25 mM Cu	0.4153	0.6667
$SnO_2.SiO_2$	5 mM Cu	0.5272	0.6771
$SnO_2.SiO_2$	2.5 mM Cu	0.6393	0.8165
$SnO_2.SiO_2$	1.25 mM Cu	0.4341	0.9367

The value of sensitivity, given by the slope of the lines in Fig. 8 plotted on logarithmic axes, is 0.81 at the concentration of 30 mM Au. At the Au concentration of 45 mM, the sensitivity is worse than that at 30 mM. Also, the relation between the resistance rate of the sensor and the H_2S concentration is less linear than that at 30 mM. Therefore, the SnO_2:SiO_2 film doped with 2.5 mM Cu and 30 mM Au has the best performance.

On the basis of these results, 30 mM Au was doped to the six thin films listed in Table 2. Table 3 shows the response of the various films to H_2S gas.

The results show that the sensitivity of the film doped with 1.25 mM Cu+30 mM Au is greater than that of the film doped with 2.5 mM Cu+30 mM Au. However, a nonlinear characteristic was obtained as shown in Fig. 9. According to these results, the performance of the H_2S gas sensor can be optimized by tuning.

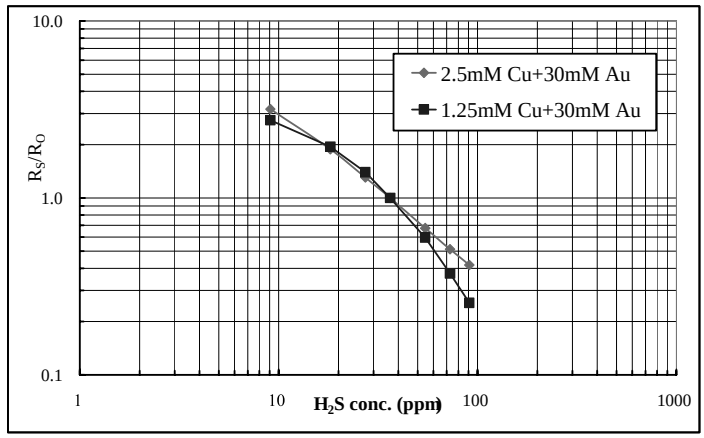


Fig. 9. Relation between resistance and H_2S concentration for SnO_2.SiO_2 films doped with 1.25 mM Cu+30 mM Au and with 2.5 mM Cu+30 mM Au.

4. Conclusions

In this study, tin oxide thin film is deposited on an Al_2O_3 substrate by LPD, and silica oxide is doped into the film to control the grain size of tin oxide, which improved the sensing properties of the film. Cu and Au can be mixed to form a new type of catalyst. Our results show that after adding this new catalyst, both SnO_2 and SnO_2:SiO_2 films have greater sensitivity and lower power consumption.

References

1 H. Nagayama, H. Honda and H. Kawahara: J. Electrochem. Soc. **135** (1988) 2013.
2 S. Yamanaka, T. Hamaguchi, H. Muta, K. Kurosaki and M. Uno: J. Alloys Compd. **373** (2004) 312.
3 C. L. Chen: Investigation and Application of Room-Temperature Liquid Phase Deposited Silicon Oxide ($SiO_{2-x}F_x$), Masters Thesis, Electronics Engineering, National Chiao Tung University, Hsinchu, Taiwan (1994).
4 K. Tsukuma, T. Akiyama and H. Imai: J. Non-Cryst. Solids **210** (1997) 48.
5 R. S. Niranjan, K. R. Patil, S. R. Sainkar and I. S. Mulla: Mater. Chem. Phys. **80** (2003) 250.
6 C. Y. Chen: Mater. Society **68** (1992) 62.