H$_2$S Gas Sensing Properties of SnO$_2$:CuO Thin Film Sensors Prepared by E-beam Evaporation

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H$_2$S micro-gas sensors have been developed employing SnO$_2$:CuO composite thin films. The films were prepared by e-beam evaporation of Sn and Cu metals on silicon substrates, followed by oxidation at high temperatures. Results of various studies, such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) reveal that SnO$_2$ and CuO are mutually non-reactive. The CuO grains, which in turn reside in the inter-granular regions of SnO$_2$, inhibit grain growth of SnO$_2$ as well as forming a network of p-n junctions. The film showed more than a 90% relative resistance change when exposed to H$_2$S gas at 1 ppm in air at an operating temperature of 350°C and had a short response time of 8 sec.

Keywords: Gas sensor, Micromachining, Hydrogen sulphide (H$_2$S), Tin oxide (SnO$_2$)

1. INTRODUCTION

The monitoring and control of toxic H$_2$S gas is important in laboratories and industrial areas where it is used as a process gas or generated as a byproduct. Semiconductor SnO$_2$-based gas sensors are widely reported in the literature [1-13]. These sensors work on the principle of a change in electrical conductance on exposure to the gas which is to be detected. Desirable characteristics of a gas sensor are high sensitivity, fast response time, fast recovery time, selectivity and long-term stability. Sensors based on pure SnO$_2$ show good sensitivity but the selectivity has been reported to be poor as the sensors respond to all reducing gases in similar manner. In order to obtain selectivity and to improve sensitivity, SnO$_2$ has been doped with different elements like Pt, Pd, Ag, Cu, etc.

The CuO-doped SnO$_2$ thick films are found to exhibit extraordinary sensing characteristics for H$_2$S. However, the response time is found to be in the range of 5~15 min[3,5-7], which appears to be large from the applications point of view. The microstructure of these thick films consists of fine CuO particles dispersed on the surface of SnO$_2$ particles. Since the response time depends on the diffusion of gas into the sensor film, one would expect thin film-based sensors to have better response times. Furthermore, for simultaneous detection of many gases, it is desirable to prepare sensor arrays with on-chip processing electronics[8] and thick film processes are not suitable for fabrication of such integrated gas sensors. The technique of CuO dispersion on SnO$_2$ grains used to prepare thick film sensors for H$_2$S detection cannot be utilized for thin films. Therefore, the possibility of fabricating SnO$_2$:CuO sensors in thin film form with a high sensitivity to H$_2$S needs to be investigated. In a recent study, ultrathin over-layers of Cu were deposited on sputter deposited SnO$_2$ thin films and the sensitivity of the films to CO, H$_2$ and Cl$_2$ was studied[12]. It was found that the selectivity of response to different gases is improved on addition of Cu. The amount of copper

deposited in this case is reported to be insufficient to cover the SnO$_2$ grains and the improvement in selectivity of response has been attributed to changes in Fermi level of in the SnO$_2$. Lee[14] has studied the effect of Pt addition on SnO$_2$ thin film sensors prepared by reactive beam evaporation. These sensors are highly sensitive to many reducing gases including H$_2$ and CO in contrast to CuO doped sensors that show high selectivity[12]. Tamaki et al.[6] have reported pure SnO$_2$ and SnO$_2$:CuO thin film sensors prepared by low pressure evaporation followed by calcinations in air. The films were found to have a porous structure and the addition of CuO improved sensitivity to H$_2$S, yielding sensors that could detect 0.02 ppm of H$_2$S in air. In other studies[15], H$_2$S sensing properties of CuO/SnO$_2$ heterostructures have been reported and the diffusion of Cu in SnO$_2$ has been studied. Cu is seen to significantly diffuse in SnO$_2$ at a temperature of 573 K. It is observed that the transition layer formed by inter-diffusion of CuO and SnO$_2$ is responsible for the high sensitivity to H$_2$S. Rumyantseva et al.[16] have also compared the H$_2$S sensing properties of pure and Cu doped SnO$_2$ thin films. They report that CuO addition significantly improves the response to H$_2$S while reducing that to CO and C$_2$H$_5$OH. They did not find any CuO phase in the SnO$_2$:CuO films.

To summarize, both pure and doped SnO$_2$-based sensors using thin/thick films and bulk materials have been reported. Pure SnO$_2$ sensors are reported to have high sensitivity but poor selectivity to H$_2$S and therefore preparation of CuO doped sensors with high selectivity is desirable. In earlier reports, most of the studies (on SnO$_2$:CuO) have been carried out on thick films prepared by impregnation technique where CuO is dispersed on prepared SnO$_2$ particles and thereby CuO and SnO$_2$ particles remain separate in the preparation technique. In the case of thin films, the microstructure is expected to be different (and may depend on the preparation technique) as the possibility of interaction between SnO$_2$ and CuO leading to a homogeneous phase exists[15,16] and one may not expect CuO to be dispersed around SnO$_2$ grains. This may also result in a different mechanism of H$_2$S detection. Therefore, a study of microstructure in thin films is desirable.

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In this paper, bridged silicon membranes with varying thickness were designed and fabricated by combining silicon processes and MEMS technologies. A CuO-SnO₂ composite thin film was prepared by thermal oxidation of a Cu/Sn double layer on the oxidized silicon substrate with a heater and sensing electrode[17]. The sensing characteristics of the CuO-SnO₂ composite thin film with respect to H_2S gas were measured with an injective-type measurement system. The sensitivity and selectivity to H_2S of the sensing film were tested and the results were compared with its sensitivity to other gases (CO, NH_3, SO_2, H_2). Moreover, the microstructures and physical properties of the sensing film were investigated with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffractometer (XRD).

2. EXPERIMENTS

Silicon bridge type integrated micro-gas sensors were fabricated by employment of a 2-in. p-type (100) wafer with a resistivity of 3 ~ 5 Ωcm and a thickness of 300 μm. Figure 1 shows a cross-sectional view of the silicon bridge type micro-gas sensor array element. Firstly, silicon was oxidized at the temperature of 1100°C for 4 h in ambient steam. The resulting oxide film showed a thickness of 1.2 μm and was used as a protective layer during the silicon back-side etching in KOH solution. After the opening of the oxide etching window by photolithography, KOH etching was carried out. The back side oxide etching was carried out in a BHF (6:1 = NH₄F:HF) solution for 13 min and silicon was anisotropically etched in a KOH solution of 25 wt.% at 80°C. Etching time was monitored through the designed etch stop of bulk silicon. It took about 175 min for the 10 μm membrane with an etch rate of 1.65 μm/min.

An AZ 5214 photo-resist was used for the patterning of heater and sensing electrodes, and then Ti(100 Å)/Pt(2000 Å) were subsequently deposited by e-beam evaporation in a high vacuum of 5×10⁻⁵ Torr. The formation of heater and sensing electrodes was achieved by the lift-off process. After the formation of heater and sensing electrodes, the sample was annealed for one hour at 600°C in ambient N₂. The Ti/Pt heater showed good electrical properties and mechanical stability through the annealing process, as reported in other studies[18].

SnO₂:CuO sensing double layers were prepared by the following processes; the active region was defined by lift-off. The sensing materials, which consist of an Sn/Cu double layer (100/20 nm, respectively), were deposited in a high vacuum of 9×10⁻⁶ Torr by an e-beam evaporation method. The sensing film was also formed by lifting off the
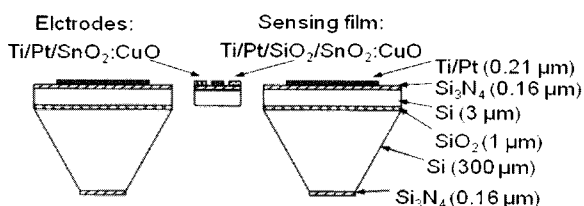
photoresistor by dipping the sample in acetone. Through the same lift-off process, a Sn/Cu double layer (100/20 nm, respectively) was formed on the predefined active region.

In order to fabricate a silicon bridge type membrane, a silicon reactive ion etching (RIE) window was opened by photolithography. Then, RIE using SF₆/Ar (25/25 sccm) plasma in a vacuum of 100 mTorr was carried out with an rf power of 100 W for 7 min.

Finally, the sample was oxidized at 700°C for 5h in ambient O₂. The samples with proposed SnO₂:CuO sensing films were realized through a series of simple process steps such as subsequent deposition and simultaneous oxidation of Sn/Cu double layers[19].

The active area, which is a suspended membrane with a thickness of 10 μm and a size of 85 μm × 75 μm, was isolated by micro-machining technology. A SnO₂:CuO sensing area was defined by a 77 μm × 23 μm region on the suspended active area.

After the final fabrication step, the sample was attached on the packaging holder using silver paste and mounted on standard TO-5 packages to carry out the electrical characterization. The characteristics of packaged samples were tested in an injection type reaction chamber with a 3,040 cm³ volume (Fig. 2). Before the beginning of test, each sensor was maintained for about 1 h for the stabilization of the sensor in the chamber.

The magnitude of the response was defined as the change in resistance of the sample on exposure to gas. It was expressed by the following relation[1,8]:

$$S = (R_g - R_a) / R_a$$

where R_a is the resistance of the sensing element in fresh air, R_g is the resistance of the sensing element in a given target gas. The result of the response measurement was automatically monitored by the use of DAQ Board.

The microstructures, binding energies and crystal structures of the sensing film were investigated using SEM, XPS, and XRD, respectively.

3. RESULTS AND DISCUSSION

3.1 H₂S sensing properties

In order to determine the optimum operating temperature of sensor films, the response of a 100 nm film was measured at different temperatures. The response curves
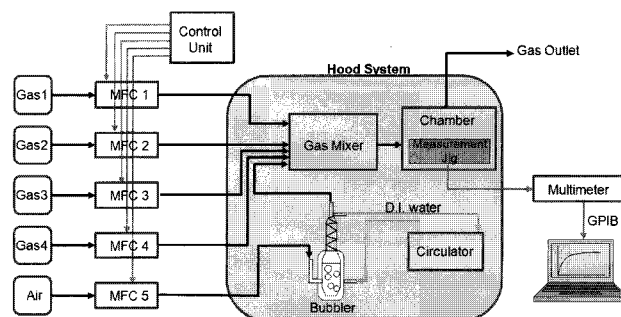

Fig. 1. Cross-sectional view of micro-gas sensor element.

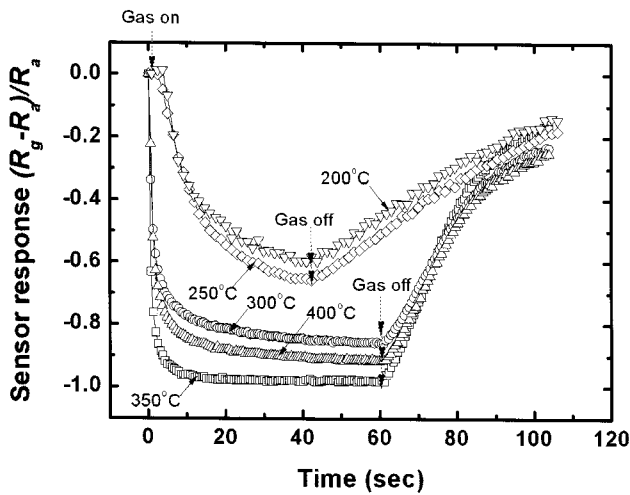Fig. 2. Block diagram of apparatus for sensing properties.

Fig. 3. Normalized response of a 100 nm film on exposure to 1 ppm of H_2S gas at temperatures of 200, 250, 300, 350, and 400°C.
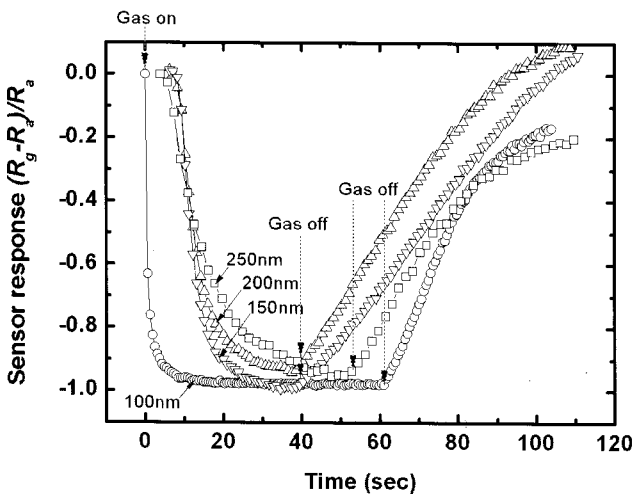

Fig. 5. Response of a 100 nm thick SnO_2:CuO sensor to 1 ppm H_2S, 1,000 ppm H_2, 100 ppm SO_2, 100 ppm CO, and 100 ppm NH_3.

Fig. 4. Response curve for 100, 150, 200, and 250 nm thick SnO_2:CuO films exposed on 1 ppm H_2S gas and then exposed to air.

Fig. 6. Sensing characteristics of the SnO_2:CuO film to H_2S gas at 350°C.

plotted as normalized resistance (maximum value of steady-state resistance obtained in air) versus time are shown in Fig. 3. It is seen that the film has a maximum sensitivity in the temperature range of 300 ~ 400°C and a minimum response time for operation at 350 ~ 400°C. The optimum operating temperature was determined to be as 350°C.

Typical response curves, recorded for 100 and 250 nm thin films on exposure to 1 ppm H_2S are shown in Fig. 4. The response time of the sensors was seen to increase with film thickness. For 100 nm film, the absolute values of resistances in air and in 1 ppm H_2S were 250 MΩ and 10 KΩ, respectively, yielding an absolute value of sensitivity of 0.99996. The high sensitivity of the films is similar to that reported for thick film-based SnO_2:CuO sensors[4,5]. The sensitivity was found to be independent of film thickness. The response times for 100 and 250 nm thick films were found to be 8 and 50 s, respectively. However, the recovery times were observed to be nearly same for both films, i.e. 40 and 50 s, respectively. The response times in this study are faster than those reported for thick films.
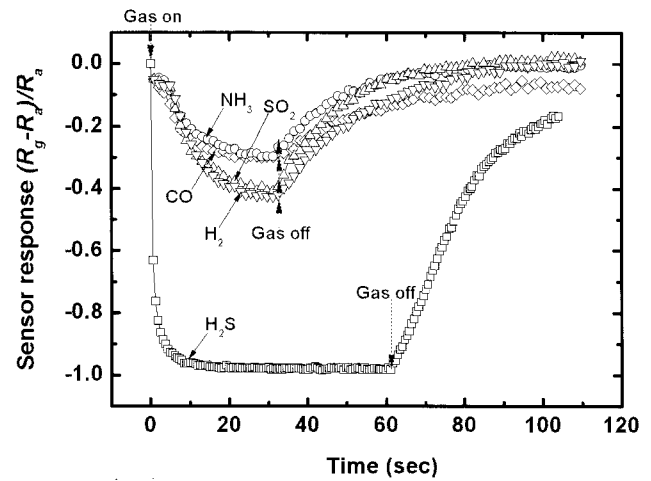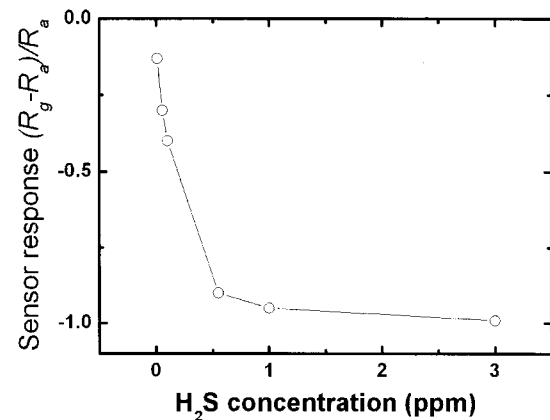
In order to check the selectivity toward H_2S, the sensors were exposed to other gases like CO, NH_3, SO_2 and H_2 and the response was recorded as a function of time. Figure 5 shows the response of a typical sensor operating at 350°C, to 1,000 ppm H_2, 100 ppm SO_2, 100 ppm CO and 100 ppm NH_3. High selectivity of SnO_2:CuO thin film sensors to H_2S is evident from this figure. The sensors did not show a significant response to NH_3 and CO either.

Figure 6 shows the sensor response measured for different H_2S concentrations in the 0.1 ~ 3 ppm range. The steady-state resistance plotted as a function of concentration for a 100 nm thick SnO_2:CuO film has been found to have a non-linear dependence on H_2S concentration, which was seen to saturate at concentrations higher than 0.6 ppm. It is noticeable that the film is highly sensitive to H_2S even at a low concentration level.

3.2 Microstructure of the thin film sensors

As shown in Fig. 7, an SEM micrograph of the SnO_2:CuO composite thin film taken at different magnifications showed the polycrystalline nature of the film with an average grain size of < 0.5 μm. The small particle
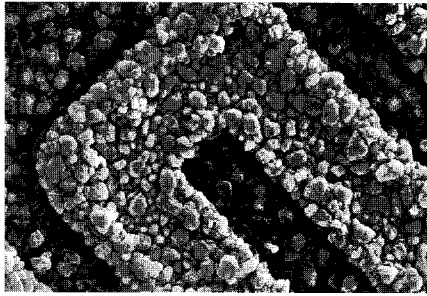
Fig. 7. SEM photographs of the CuO-SnO₂ thin films deposited on micro-heater.

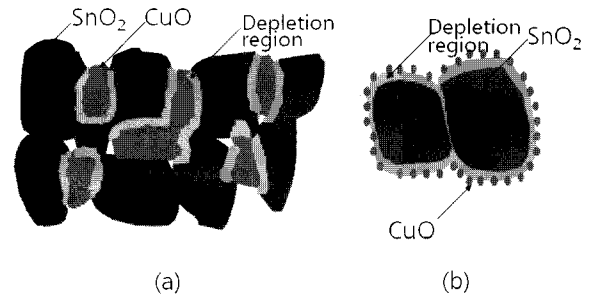(a)   (b)

Fig. 9. Schematic representation of the microstructure of: (a) SnO₂:CuO thin films employed in the present studies; (b) thick films prepared by impregnation or chemical fixation techniques as reported other groups.

Fig. 8. XRD patterns of the SnO₂:CuO thin films oxidized at 700°C for 5h in O₂ ambient.

For comparison, the reported microstructure of thick films consisting of SnO_2 grains covered with thin CuO layer is also shown here. The granular nature of films in the present case is supported by SEM of Fig. 7. Lalande et al.[21] have also reported segregation of CuO to the grain boundaries of SnO_2 grains in SnO_2:CuO system. The difference in microstructure of thin and thick films, i.e. independent grain structures compared to CuO covered SnO_2 grains is expected to arise from the difference in preparation technique. Existence of such a difference in microstructure is independently shown by results of an XPS study.

As shown in Fig. 10(a) and (b), the Cu 2p and Sn 3d spectrum of as-prepared films show peak positions at binding energies of 940.069 and 495.545 eV that almost
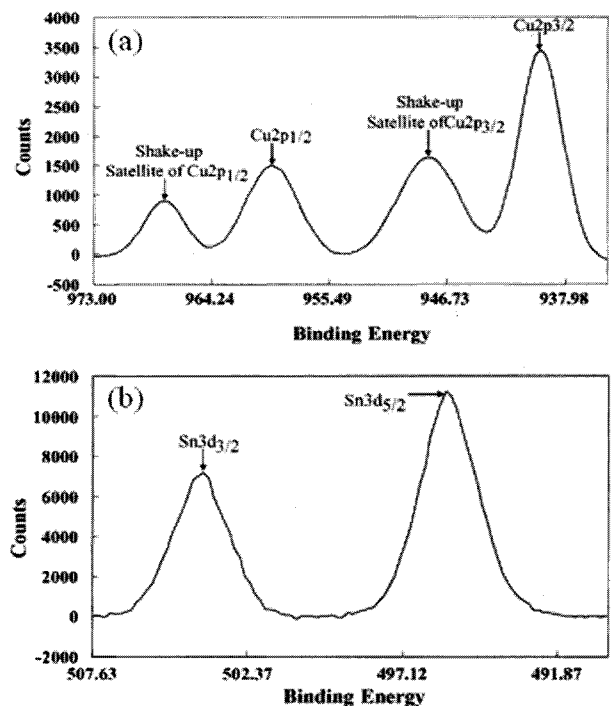
sizes like these are very desirable for high sensitivity because they give rise to a surface area for exposure to gas[20].

The XRD pattern of the CuO-SnO₂ thin film oxidized at 700°C for 5 h in ambient O₂ is shown in Fig. 8. The sample was identified to be a polycrystalline SnO_2 film with tetragonal symmetry.

No shift in the SnO_2 peak positions was observed, which indicated that CuO does not react with SnO_2. Considering the results above, it can be concluded that the deposition of a very thin Cu layer on a Sn film has a negligible influence on the crystalline structure. Due to an absence of interaction between SnO_2 and CuO, during the high temperature oxidation of SnO_2:CuO films, CuO is precipitated out of the SnO_2 grains. The CuO grains residing between SnO_2 grains, inhibits the growth of SnO_2 as well as forming a network of p-n junctions. Since CuO and SnO_2 are p- and n-type semiconductors, respectively, a p-n junction forms at each interface between CuO and SnO_2 grains, which induces an electron depleted space charge layer at the surface of SnO_2. This leads to a high resistance of the film in air. On exposure to H_2S, the CuO is converted into CuS via the reaction $CuO+H_2S \rightarrow CuS+H_2O$[4,5]. CuS, being metallic in character, destroys the p-n junctions and brings about a large drop in resistance. When the H_2S supply is turned off, CuS gets quickly oxidized to CuO by the reaction $2CuS+3O_2 \rightarrow 2CuO+2SO_2$, and the p-n junctions are restored[4,5]. The evolved microstructure of SnO_2:CuO films consisting of a network of SnO_2 and CuO grains is shown schematically in Fig. 9.

Fig. 10. XPS spectra of SnO₂:CuO: (a) Cu 2p XPS spectra and (b) Sn 3d XPS spectra.

correspond to pure CuO and SnO_2[22], respectively. It seems that the oxidation at 700°C for 5 h is enough to oxidize the surface of the metallic Cu/Sn double layer in $CuO:SnO_2$ composite thin film. This XPS measurement result may be compared to the data reported by Tamaki et al.[5], and Yamazoe et al.[3], on $SnO_2:CuO$ thick films where a little shift in BE was found. The difference in BE for thin and thick films may be explained on the basis of different microstructures (Fig. 9). It is noted that the photo-electrons detected in XPS studies originate within ~ 5 nm of the top surface. Consequently, photo-electrons from SnO_2 in the case of thick films (Fig. 9(b)) originate predominantly from the depletion region (that completely covers all SnO_2 grains). As discussed by Tamaki et al.[5], bands of SnO_2 are bent upwards in the depletion region, so that the observed BE is reduced. In the case of the thin films in the present study (Fig. 9(a)), photo-electrons originate predominantly from the bulk SnO_2, so that no shift in BE is expected as observed experimentally.

4. CONCLUSIONS

The present study demonstrates the development of H_2S sensors based on $SnO_2:CuO$ thin films, which were prepared by photolithography, bulk micromachining and E-beam evaporation techniques. These sensors exhibited very high sensitivity and fast response and recovery times. The film thickness is found to be a controlling parameter in achieving faster response and recovery times. The non-reacting character of SnO_2 and CuO, which was unambiguously confirmed by XRD and XPS measurements, allows formation of a microstructure in which SnO_2 and CuO forms an array of p-n junctions. The film showed high selectivity to H_2S gas compared with other gases like CO, NH_3, SO_2 and H_2. The high performance of the thin film seems to result not only from the unique receptor action of CuO but also from the unique microstructure which is characterized by a large surface area available for exposure to gas due to small average particle sizes. In addition, the difference in operating temperature also seems to contribute to the high sensitivity. This method for preparing CuO-SnO_2 composite thin films is thought to be of low cost and capable of achieving reproducible and sensitive thin film gas sensors for detecting H_2S gas.

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