

THICKNESS DEPENDENCE EFFECTS OF CuO ISLANDS ON SnO₂ IN THE NANO-SCALE RANGE FOR H₂S GAS SENSING APPLICATIONS

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Abstract. Ultra-thin CuO islands on the surface of SnO₂ thin films, exhibit a high sensitivity and a fast response speed for trace level (20 ppm) detection of H₂S gas as compared to other sensor structures. Thickness of the CuO islands in the nano-scale range yields a significant improvement in the sensor characteristics and studies on ultra-thin CuO islands in the range (2.5 to 20 nm) are reported. Optimized performance is observed with 8 nm thick CuO islands showing a high sensitivity of $8.065 \cdot 10^3$ at a low operating temperature of 150 °C. The response speed is 12 seconds and a recovery time of 366 seconds is observed under static air conditions (106 seconds in flowing air). Response time of the sensors is found to be proportional to the CuO thickness, however recovery time and sensitivity show a maximum at 8 nm CuO thickness. Modulation of the depletion regions formed between the p-type CuO and n-type SnO₂ are found to govern the sensitivity values along-with spill over of hydrogen available from the dissociated H₂S gas molecule. Thickness of the CuO islands is shown to influence the amount of adsorbed oxygen present on the uncovered SnO₂ surface and plays an important role in determining the sensitivity values of the sensors.

1. INTRODUCTION

Selective detection of reducing gases is known to be feasible with semi-conducting tin oxide (SnO₂) loaded with suitable metal additives [1]. CuO is used as the preferred catalyst material with SnO₂ for H₂S gas detection because high sensitivity [2] can be achieved as a result of the electronic interaction between p-type CuO and the n-type polycrystalline SnO₂. Reducing H₂S gas reacts with CuO catalyst in SnO₂ and modulates the depletion region at the interface by reducing its barrier height, and leads to a decrease in the resistance of the sensor. Catalytic action is governed by two mechanisms of Fermi-level energy control and Spill over, as put forward by Morrison [3]. In the spill over mechanism, the catalyst on the semiconductor surface dissociates the gas molecule (H₂S) and the dissociated species then spills over onto the semiconductor surface and influences its conductivity. H₂S detection has been extensively investigated in the recent

past using sintered pastes [4], thick [5] and thin Cu-SnO₂ bi-layers [6], CuO-SnO₂ hetero-contacts [7], and chemically fixed CuO on SnO₂ [8].

Our previous study [9] established the critical distribution of the CuO catalyst. The response characteristics of three sensors namely, pure SnO₂ films, SnO₂ films with CuO over-layer and SnO₂ films with CuO islands on surface were compared for trace level (20 ppm) H₂S gas detection. It was found that SnO₂ sensor with CuO (10 nm) islands showed a high sensitivity of $7.3 \cdot 10^3$ at a low operating temperature of 150 °C as compared to other sensors. A fast response time of 14 seconds and a recovery time of 118 seconds in flowing air were noted.

Besides the dispersion of CuO catalyst it was of interest to understand the performance of the sensor with varying CuO island thickness especially in the nano-scale range, because quantity of CuO may influence the amount of oxygen adsorption and the extent of depletion region at the SnO₂-CuO inter-

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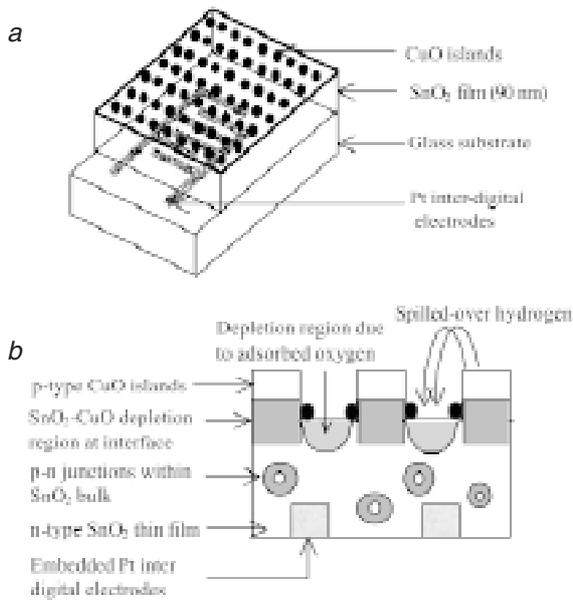


Fig. 1. (a) Schematic diagram of SnO_2 sensor dotted with CuO islands; and (b) Schematic of the sensor showing the formation of depletion regions.

face. In the present study the effect of CuO island thickness on the sensitivity and the response speed is reported.

2. EXPERIMENT

In the present work comb-shaped Platinum electrodes, lying under the SnO_2 layer, have been used to measure the changes occurring in the SnO_2 layer as a result of H_2S -CuO interaction on the surface of the sensor. Thick SnO_2 film (~ 90 nm) were deposited by reactive sputtering in $\text{Ar} + \text{O}_2$ using a metallic tin target. Cu was thermally evaporated through a mesh (pore size 600 nm) to obtain SnO_2 -Cu-dot structure. The Cu thickness has been varied in the range of 2.5 to 20 nm and after Cu deposition the structure is slowly heated in air at 300°C for 20 minutes to transform the ultra-thin Cu layer to CuO [10]. Layout of a typical sensor is shown schematically in Fig. 1(a). The sensitivity factor, S , is defined as;

$$S = R_a/R_g, \quad (1)$$

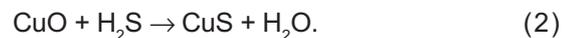
where R_a is the resistance of the sensor in atmospheric air, and R_g is the resistance in the presence of reducing gas (H_2S in the present case).

3. RESULTS AND DISCUSSION

In the SnO_2 -CuO-dot sensor after the initial heat treatment at 300°C when the Cu converts to CuO, a

hetero-junction formation takes place between the p-type CuO and the n-type SnO_2 . Formation of a depletion region at the CuO- SnO_2 interface tends to reduce the effective thickness of the underlying SnO_2 layer through which the charge carriers flow. Since copper is known to diffuse extensively, possibility for the diffusion of copper into the SnO_2 bulk leading to the formation of inter-granular barriers could not be ruled out. During the transformation of Cu islands to CuO, it is possible that Cu not only takes in oxygen from the atmosphere but also from the underlying SnO_2 support. Removal of the bulk oxygen from the SnO_2 support leaves it more oxygen deficient and increases its n-type semi-conducting nature. However such an unstable condition is expected to be counter balanced by re-adsorption of more oxygen from the atmospheric air on the uncovered SnO_2 surface. When exposed to H_2S gas both, the CuO islands on SnO_2 surface and the uncovered SnO_2 surface begin to interact simultaneously with H_2S , and the mechanism of sensing action can be described as follows.

(a) First the CuO converts to CuS, which is reported to be more metallic [11] in nature. As a result the CuO region becomes less p-type and the depletion region shifts upwards resulting in greater SnO_2 volume for the free charge carriers, and the conductivity of the sensor increases as governed by the following equation:



(b) Secondly, at the operating temperature of 150°C the depletion regions formed at the inter-granular regions in the SnO_2 bulk, can be affected by the penetrating H_2S through the grain-boundaries of the polycrystalline SnO_2 layer.

(c) Finally, Cu present in the form of CuO is known to initiate hydrogen spillover because it chemisorbs hydrogen rather weakly and the hydrogen species on its surface are highly mobile [12]. The hydrogen after spillover interacts with the adsorbed oxygen present on the uncovered SnO_2 surface and quickly removes the adsorbed oxygen. Removal of the adsorbed oxygen leaves behind excess free electrons in the SnO_2 that are available for conduction. A high sensitivity is obtained with SnO_2 -CuO-dot sensor as a result of the combined effects described above and the changes are shown in Fig. 1 (b).

Fig. 2 shows the variation in the sensitivity at a constant H_2S gas concentration (20 ppm) as a function of temperature for the SnO_2 -CuO-dot sensor with 2.5 nm, 8 nm and 20 nm thick CuO islands. A high

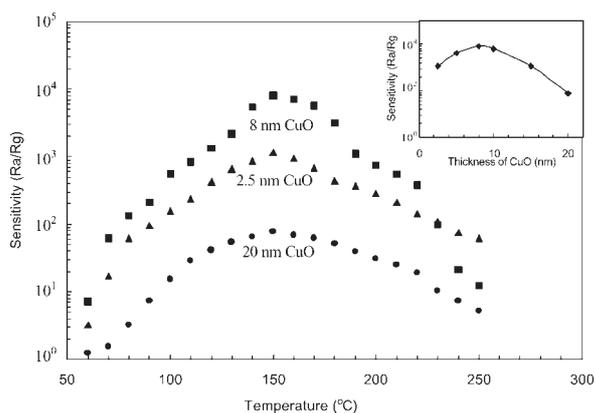


Fig. 2. Variation of sensitivity as a function of temperature for 20 ppm H₂S gas; and (Inset) Sensitivity variation with increasing CuO island thickness.

sensitivity of $8.065 \cdot 10^3$ for the 8 nm thick CuO is obtained at a low operating temperature of 150 °C. The increase in the sensitivity can be attributed to the accelerating rate of irreversible chemisorption reaction due to interaction with the H₂S gas that tends to reach an equilibrium at a critical temperature ($T_{\max} = 150$ °C). Beyond the critical temperature the chemisorption phenomenon slows down and we observe a fall in sensitivity. Variation of sensitivity of SnO₂-CuO-dot sensor with 20 ppm H₂S gas as a function of CuO island thickness is shown in inset of Fig. 2. As the thickness of the CuO islands increased from 2.5 nm to 20 nm, the variation in sensitivity clearly exhibited a maximum with 8 nm thick CuO and thereafter it decreased. It was therefore of interest to understand why the sensitivity first increased, reached a peak value and then decreased. Another important observation is the insignificant change in the temperature (T_{\max}) at which the maximum sensitivity is observed.

Fig. 3a shows the variation in resistance of the sensors with increasing CuO thickness in air (R_a), as a function of temperature (60–250 °C). The resistance R_a in air for all the sensors shows a continuous decrease with increasing temperature. This is expected, due to the semi-conducting nature where more charge carriers are able to move to the conduction band from the valence band and become available for conduction as the temperature is increased. However an interesting feature is noted specifically in the temperature range of 130–170 °C, the resistance R_a shows a small rise and becomes more pronounced with increasing thickness of the CuO islands. This observed rise in R_a may be attributed to the adsorption of oxygen on the uncov-

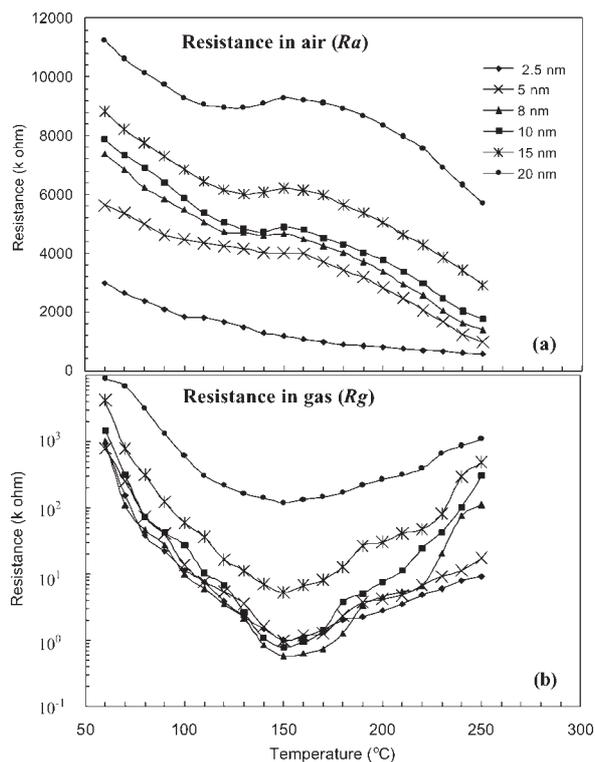


Fig. 3. (a) Variation of resistance in air (R_a) of the sensors with temperature for different CuO island thickness; and (b) Sensor resistance variation in the presence of 20 ppm H₂S gas (R_g) with temperature for different CuO island thickness.

ered region of the SnO₂ surface. Presence of this oxygen takes away free electrons from the SnO₂ bulk thus leading to an increase in the resistance. This means that CuO not only promotes hydrogen spillover upon interaction with H₂S but also enhances the adsorbed oxygen presence on the SnO₂ surface particularly in the temperature range 130–170 °C. The variations in resistance (R_g) with temperature in the presence of 20 ppm H₂S gas, as shown in Fig. 3b, indicates that the resistance R_g of all the sensors decreases to a minimum at the operating temperature, and thereafter it begins to increase. It clearly suggests that initially the process of chemisorption is irreversible and after temperature (T_{\max}) the reaction becomes reversible.

Fig. 4a depicts the response times obtained for SnO₂ films with 2.5, 8 and 20 nm thick CuO islands for 20 ppm H₂S gas. It is noted that response times increase as the CuO island thickness increases. Fig. 4b shows the recovery characteristics as a function of the aforementioned CuO thickness. The recovery time first increases to a peak value before showing a drop. However the important point is that,

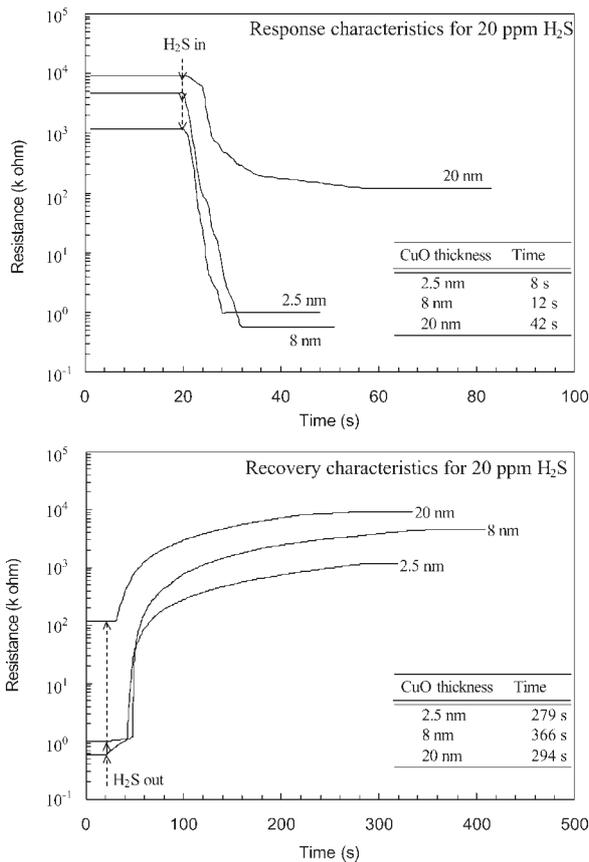


Fig. 4. (a) Response speeds of the sensors as a function of time for 20 ppm H₂S; and (b) Recovery times for the sensors after refluxing with fresh air.

higher the sensitivity of a particular configuration, slower is its recovery.

A plausible explanation for the enhanced sensitivity observed with 8 nm thick CuO islands can be as follows. Spill-over of hydrogen from the CuO surface is necessarily a surface phenomenon and since the diameter of the CuO islands remains the same in all the cases (only the thickness is different), the sensing action of the sensor seems to be governed mainly by the amount of adsorbed oxygen present on the SnO₂ surface. The amount of adsorbed oxygen on the surface of SnO₂ is directly proportional to the CuO island thickness [Fig. 3a]. Thus the sensor with 8 nm thick CuO islands offers optimum sensitivity at a low temperature of 150 °C.

4. CONCLUSIONS

The enhanced sensitivity obtained with the 8 nm thick CuO islands on SnO₂ for H₂S detection reveals the critical importance of the catalyst layer thickness in the nano-scale range. At a lower thickness (less than 8 nm) there is a lack of adsorbed oxygen on

the SnO₂ surface leading to a lower value of R_a and hence a lower sensitivity. At a higher thickness (greater than 8 nm) there is excess leftover adsorbed oxygen after the interaction of spilled over hydrogen, and as a result the resistance (R_g) does not fall to a low enough value. Besides at the higher thickness of CuO the narrowing of the depletion region is limited in the presence of H₂S gas. A critical thickness of 8 nm for the CuO islands allows the spillover mechanism to be more effective besides the fermi-level type of interaction in the SnO₂-CuO-dot sensors for H₂S detection.

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