MECHANISM OF TRACE LEVEL H_2S GAS SENSING USING RF SPUTTERED SnO_2 THIN FILMS WITH CuO CATALYTIC OVERLAYER

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ABSTRACT

H_2S gas sensing response characteristics of bare SnO_2 thin films and heterostuctures with nanolayer (10 nm) of Cu and CuO are studied. Changes in resistance values, occurring with integration of Cu and CuO nanolayers on SnO_2 is acquired real-time, and compared. Rise in sensor resistance after introduction of Cu and CuO nanolayers on SnO_2 sensing layer is understood to enhance the sensing response characteristics. Formation of space charge region between p-type CuO and n-type SnO_2 and difference in work-function values between catalyst and sensing layer are shown to govern the increased value of starting resistance. Increase in starting resistance and lowering of resistance in presence of H_2S due to spill-over of dissociated H_2S gas molecule are playing crucial role in influencing the sensing response.

Keywords: Thin film, H_2S Gas Sensor, Spillover mechanism, RF Sputtering

1. INTRODUCTION

Semiconducting tin oxide (SnO_2) thin films with suitable catalysts in the form of nanoparticles, overlayers, clusters etc. [1] are known to exhibit enhanced sensitivity, better selectivity and fast response speeds to various reducing gases including H_2S. SnO_2 sensor is invariably anion deficient and oxygen vacancies are mainly responsible for making available free electrons for the conduction process [2]. In addition, the surface morphology of the sensing layer is also important for realization of sensor with enhanced response characteristics, which in turn depend on the growth kinetics.

Maekawa et. al. [3] and Chowdhuri et. al. [4] reported highly sensitive H_2S gas sensors operating at relatively low temperatures with CuO as the catalyst material. Some of the extensively investigated sensor structures for H_2S gas detection include, mixed SnO_2-CuO powders [5], Cu-SnO_2 bi-layers [6], CuO-SnO_2 hetero-structures besides others [1,7]. Processing conditions have been noted to have a significant influence on the sensing response characteristics. Introduction of CuO nanoparticles on SnO_2 thin film surface have been shown to advantageously lead to fast recovery [8]. However a systematic study exploring the influence of CuO catalyst in enhancing the H_2S gas detection capability of SnO_2 thin films is yet to be carried out. It is difficult to pin-point

the exact physical mechanism however the sensor resistance is expected to increase if oxygen is somehow adsorbed on the SnO_2 film surface. Furthermore, the presence of the catalyst is expected to introduce the spill-over phenomenon besides the creation of barrier height at catalyst-sensing layer interface leading to influencing the sensor resistance.

The present study investigates real-time measurement of step-by-step changes occurring in the sensor resistance values of CuO-SnO_2 hetero-structure as nano-scale thin (~ 10 nm) CuO overlayer is introduced on SnO_2 film (~ 90 nm) surface. The study is expected to throw light on H_2S sensing mechanism of SnO_2 based thin film sensors with CuO as the catalyst.

2. EXPERIMENTAL AND METHODS

SnO_2 thin films (90 nm) were deposited on Corning glass substrates by reactive rf sputtering process (Ar + O_2) with underlying Platinum (Pt) interdigital electrodes (IDE). An ultra thin layer of Cu (~ 10 nm) was thermally evaporated onto SnO_2 thin film surface as a continuous overlayer and the sensor structure was annealed in air at 300 ^oC for two hours to convert Cu layer to catalytic CuO. Fabrication details of the sensor are reported elsewhere [1].

The sensor response is defined as $S = R_a/R_g$, where R_a is the resistance of the sensor in the atmospheric air, and R_g the resistance in presence of reducing H_2S gas. The enhanced sensing response is expected only for those sensors that exhibit a high value of R_a and simultaneously a very low value of R_g. The in-situ monitoring of resistance values of Cu-SnO_2 sensor hetero-structure was carried out during the process of Cu film deposition using automated data acquisition and a Keithley DMM (Model: 2700) installed in the vacuum processing chamber. Sensor response of three structures: SnO_2 film (90 nm), Cu(10 nm)-SnO_2(90 nm), and CuO(10 nm)-SnO_2(90 nm), was measured as a function of temperature (60-250^oC) for a fixed 20 ppm concentration of H_2S gas in a special design test gas rig.

3. RESULTS

Tin oxide thin films deposited in the present study were transparent and strongly adherent to the substrates. The as-grown films were found to be amorphous and become polycrystalline after a post-deposition annealing treatment at 300 ^oC in air for two hours. The sensing response characteristics were studied for SnO_2 thin films (120 nm thin) deposited by rf sputtering under varying composition of processing reactive gas mixture (argon and oxygen) at a fixed sputtering pressure of 14 mTorr. The films were tested for H_2S gas (20 ppm concentration) at 170 ^oC and the results are shown in Table I. It is seen that the best results are obtained when the metallic tin target is sputtered in a reactive gas mixture having equal proportions of argon (50%) and oxygen (50%).

Table 1: Variation in Sensor Resistance in air and the response (20 ppm H_2S gas) of a SnO_2 sensor with variation in the composition of processing gas (Ar + O_2).

Ar %	O_2 %	Resistance (k ohm)	Response to 20 ppm H_2S gas at 170^oC
100	0	0.446	1.00062
90	10	3.642	1.04256
80	20	29.97	1.12047
70	30	161.35	1.42468
60	40	983	3.41786
50	50	3062	7.22063
40	60	23740	2.36145
30	70	72950	1.21461
20	80	313680	1.05623
10	90	904330	1.00842
0	100	-	-

Since film morphology with porous structure would offer effectively more surface area for the sensing gas molecules to interact, SnO_2 thin films were deposited at different sputtering pressures (10 to 18 m Torr) with the reactive gas composition fixed at Ar : O_2 = 50 : 50 and the sensor response to 20 ppm H_2S gas is shown in figure 1. The H_2S gas sensitivity increases with increasing sputtering pressure and is attributed to the expected rise in porosity of the sensing layer, which in a way increases the effective area of the surface for interaction with H_2S gas. However the SnO_2 film deposited at 18 mTorr of sputtering pressure exhibited fluctuating response characteristics especially at higher temperatures above 170 ^oC after repeated usage. In view of this problem, a sputtering pressure of 14 mTorr and a reactive gas ambient of Ar : O_2 = 50 : 50 was considered to be optimum conditions for depositing SnO_2 films for gas sensor applications.

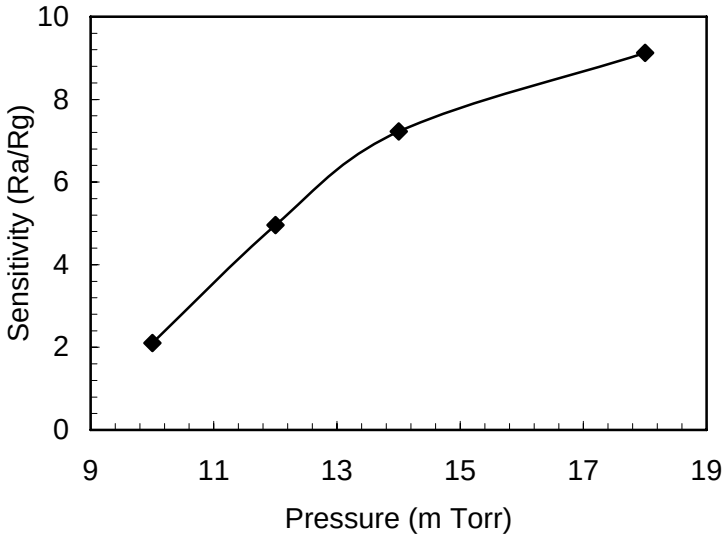

Figure 1: Response of SnO_2 thin film sensor as a function of sputtering pressure for H_2S gas

The surface morphology of 120 nm thick SnO_2 films was analysed using an Atomic Force Microscope (AFM). A Burleigh personal SPM (scanning probe microscope, KTH, Sweden), was used and images were acquired over an area 2×2 μm^2 in the contact mode. AFM studies revealed a rough surface with nano-sized round shaped grains (grain size ~ 37 nm). After the initial annealing in air at 300 °C, fine changes in the surface morphology were observed (Fig. 2a). AFM studies revealed that the spherical grains in the as grown film shown in figure 2a get transformed into smooth elongated structures after annealing as shown in image 2b with channels, and step formations, leading to an effective increase in the surface roughness of the SnO_2 film. Effect of the interaction of 20 ppm concentration of H_2S gas at a temperature of 170 ^oC on the SnO_2 film surface has been shown in figure 2c indicating the roughening of the elongated grains of SnO_2.SnO_2 thin films of varying thickness (60 to 210 nm) were investigated for their trace level (20 ppm) H_2S gas sensing characteristics. A maximum sensor response is noted at a particular temperature 170 ^oC (T_{OPT}) for all the films. Sensor response is found to increase with decreasing film thickness up to 90 nm and shows a maximum response (S ~ 14.34). However on further lowering the SnO_2 film thickness to 60 nm the response suddenly decreased to S ~ 3.17.

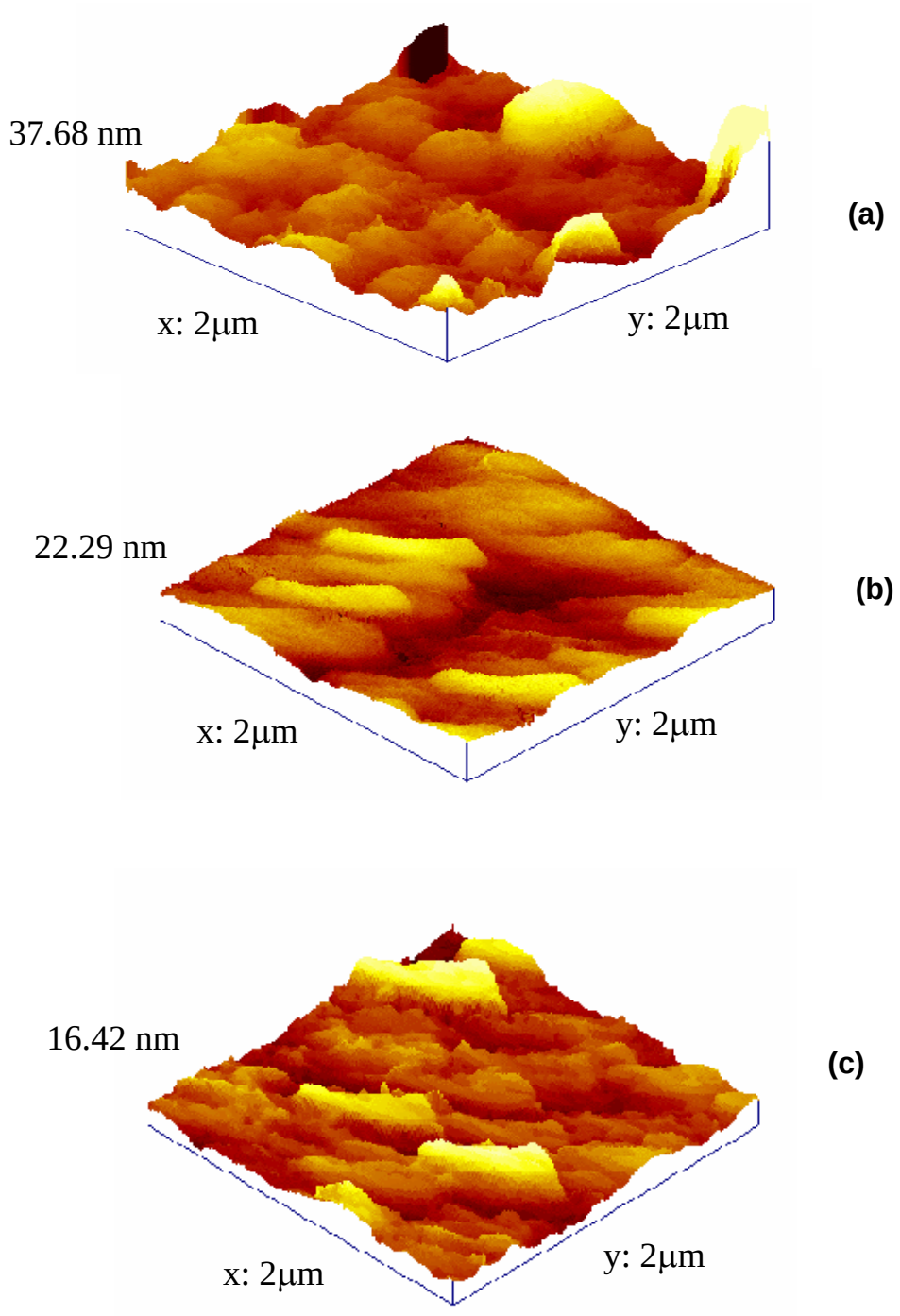

Figure 2: AFM images of 120 nm thick SnO_2 films (a) as-deposited, (b) annealed in air at 300 ^oC and (c) exposed to 20 ppm H_2S gas at 170 ^oC

The response of sensor having bare SnO_2 film (90 nm thin) is 14.3 at 170^oC, however, integration of Cu and CuO catalytic layers (10 nm) leads to the enhanced sensitivity of 23.2 and 211.3 respectively as shown in figure 3. The enhanced sensitivity observed for hetero-structure sensors was attributed to the increase in the value of R_a and a reduction in R_g. The reduction in the value of R_g is mainly due to the activation of well known spill over mechanism by the presence of ultra-thin Cu or CuO catalytic layer and modulation of space charge region at the interface of

catalyst with SnO_2 sensing layer [1]. The interaction of H_2 after decomposition of H_2S by Cu catalyst converts it into CuS at elevated temperature (~ 170^oC), and modulate the barrier height at the interface of overlayer-SnO_2 film with CuS thereby reducing the sensor resistance (Rg). The measured value of R_a at room temperature for the base SnO_2, SnO_2-Cu and SnO_2-CuO sensor structures was about 2.98 MΩ, 4.92 MΩ and 13.62 MΩ respectively. The in-situ values of resistance of the sensor structure during evaporation of Cu overlayer on SnO_2 thin film is listed in Table 2. The results help us carry out an in-depth analysis as to why resistance of the CuO-SnO_2 sensor hetero-structure increases, post-introduction of catalytic overlayer.

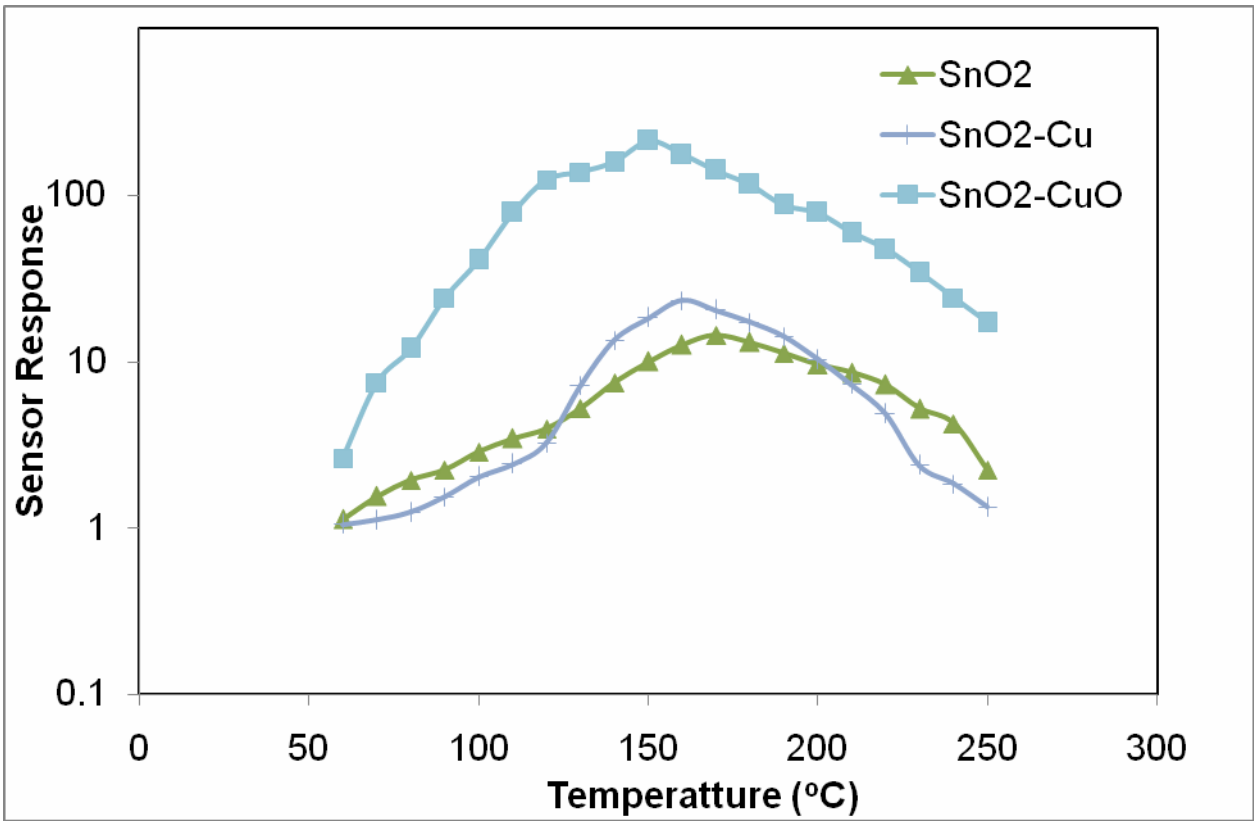

Figure 3: Sensing response characteristics of three sensor structures bare SnO_2 (SnO_2), SnO_2 with Cu overlayer (SnO_2-Cu) and SnO_2 with CuO overlayer (SnO_2-CuO).

It is interesting to note from Table 2 that the as-deposited SnO_2 thin film exhibits a lowering of its resistance value (from 2.98 MΩ to 2.42 MΩ) under low vacuum (10^{-2} mbar) and that tends to fall further (1.92 MΩ) under high vacuum (10^{-5} mbar). The expected decrease in resistance of SnO_2 is attributed to the desorption of adsorbed oxygen from SnO_2 film surface under vacuum thereby releasing the trapped electrons. An increase in the resistance (from 1.92 MΩ to 3.81 MΩ) is easily discernible (table 2) as soon as the Cu overlayer begins to deposit over the SnO_2 film surface in high vacuum (10^{-5} m bar). The observed increase in resistance with Cu metal deposition cannot be

attributed to the adsorbed oxygen on SnO_2 surface as it is unlikely because all the resistance measurements are carried out in-situ (while Cu film deposition) under vacuum. Therefore, other mechanism is responsible for the observed increase in R_a of SnO_2 sensing film after introduction of Cu metal overlayer and may be correlated with the difference in workfunctions of Cu with respect to SnO_2 layer. The workfunctions of SnO_2 and Cu are respectively 4.1 eV and 4.8 eV respectively. The integration of metal having higher workfunction is expected to transfer electrons from bulk of the SnO_2 layer towards metal due to Fermi level alignment and thereby created a space charge region at SnO_2-Cu interface giving higher resistance values. It is interesting to point out that the resistance of Cu-SnO_2 sensor hetero-structure starts increasing after introduction of air slowly and attain a saturation value of ~ 0.54 MΩ after 2 hr. The ultra-thin layer (10 nm) of Cu is expected to be discontinuous. The adsorption of oxygen (from introduced air) on the surface of sensing SnO_2 film via porous Cu overlayer is responsible for the observed behavior.

Table 2: Resistance data measured using automated data acquisition during evaporation of Cu overlayer on SnO_2 thin film in-situ:

S.No.	Activity	Pressure (m bar)	Resistance (M Ω)	Change in resistance (M Ω)
1.	SnO_2 film in atmosphere	10^3	2.98	-
2.	Film in low vacuum	10^{-2}	2.42	- 0.56
3.	Film in high vacuum	10^{-5}	1.92	- 0.50
4.	Deposition of 10 nm Cu over-layer on SnO_2	10^{-5}	3.81	+ 1.89
5.	Air introduction (2 min.)	10^3	4.92	+ 1.11
6.	After 2 hrs in atmosphere	10^3	6.54	+ 1.62
7.	Annealing in air at 300 ^oC for 2 hours	10^3	13.62	+ 7.08

Annealing the Cu-SnO_2 sensor structure in air at 300 ^oC for 2 hours is considered sufficient to transform the ultra-thin Cu layer to CuO and in agreement with earlier observations [1, 9]. Since CuO is known to be p-type semiconductor, a p-n junction is formed with n-type SnO_2 layer [1]. The formation of the p-n junction and subsequently presence of depletion region at the interface is borne out of the fact that a substantial increase in resistance (13.62 MΩ) of the CuO-SnO_2 sensor structure is obtained. Therefore, the nature of catalyst is playing a crucial role in enhanced sensitivity of SnO_2 based sensors. Besides activation of spillover mechanism for a specific gas, the difference in workfunction and the p-type of semiconducting behavior of the catalyst in comparison to the sensing layer is responsible for enhanced value of R_a thereby resulting in efficient sensor response for trace level detection of H_2S gas.

4. CONCLUSIONS

Trace-level H_2S gas (20 ppm) response characteristics of three sensor structures (bare SnO_2 film, SnO_2 film – Cu nanolayer, and SnO_2 film - CuO nanolayer) are investigated. A decrease in starting resistance of SnO_2 film was seen under vacuum due to removal of adsorbed oxygen. The integration of Cu-nanolayer having higher work-function increases the sensor resistance due to transfer of electron from conduction band of SnO_2 layer to metal nanolayer. The resistance was further increase after annealing the heterostructure sensor at 300^oC due to conversion of metal Cu layer to p-type semiconducting CuO nanolayer. The difference in work-function of catalyst and sensing layer besides the formation of space charge region at the interface of catalyst-sensing are identified for the large starting resistance. The large starting resistance of heterostructure sensor (SnO_2 film - CuO nanolayer) and the activation of the spill-over mechanism gives the improved sensing response characteristics, and pave a way to realize novel structures for trace level detection of various gases.

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