

H₂S Detection Sensing Characteristic of CuO/SnO₂ Sensor

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Abstract: Among the various metal oxide additives tested, the complex of CuO is outstanding in promoting the sensing properties of an SnO₂ sensor for H₂S in air. The SnO₂ sensors loaded with 5 wt.% CuO is extremely sensitive to H₂S at 200°C and below, while it is almost insensitive to many other gases. The response to H₂S is rather slow but the recovery is very rapid. The added CuO particles interact electronically with the surface of SnO₂ (p-n junctions) to make the sensor highly resistive, while the interaction is disconnected when CuO is sulfurized to CuS in the H₂S containing atmosphere, leading to a drastic decrease in electrical resistance. The H₂S sensing properties, particularly the rate of response, of CuO/SnO₂ sensors are influenced by the CuO loadings and operating temperature as well as the thickness of CuO loading film.

Keywords: Tin oxide, copper oxide, sensing properties, H₂S

Introduction

The detection of H₂S, a bad-smelling and toxic gas, is very important in environmental monitoring. Therefore, much attention has been paid to the search for H₂S gas sensitive materials. The sensing properties of various semiconductor oxides, especially the SnO₂-based materials, have been extensively studied. It has been claimed that the sensitivity and selectivity to H₂S are improved by adopting a quickly cooling method ^[1] or by adding hydrophobic silica ^[2], ZrO₂ ^[3], CeO₂ ^[4], or basic

oxides^[5] to the sensor element. It was also found that the addition as noble metal Ag to SnO₂ makes the materials very sensitive to H₂S^[6,7].

We have tried to improve the H₂S sensitivity by modifying the surface of SnO₂ with various metal oxides, and found that CuO is a unique excellent promoter of the SnO₂ gas sensor for the sensitive and selective detection of H₂S. This paper deals with the H₂S sensing properties of SnO₂ sensors loaded with various metal oxides, especially CuO. The sensing mechanism of CuO/SnO₂ sensor as well as the effects of CuO loading conditions and H₂S gas concentration on the sensing characteristics are also described.

Experimental

The SnO₂ powder was prepared from SnCl₄. An aqueous solution of SnCl₄ was neutralized with an aqueous solution of ammonia (28%). The precipitate obtained (stannic acid) was thoroughly washed with deionized water, dried at 100°C and calcined at 600°C for 5h in air. To be loaded with metal oxides, the SnO₂ powder was impregnated with an aqueous solution of each metal salt (typically acetates for Ca, Sr, Ni, Cu, Zn, Cd, Ag, Zr and Ce and ammonium salts for V, Mo, W and P), followed by drying and calcining at 600°C for 5h. SnO₂ was impregnated with a solution of Cu acetate to a fixed CuO loading of 5 wt.%. The elements having various CuO loadings (1, 4, 6, 10 wt.%) were prepared in the same way.

The thickness of CuO was evaluated from multiplication of the deposition rate by the deposition time, because clusters or islands form thin films during the earliest stages of film formation. The gas sensitivity was defined : $S = (R_a - R_g) / R_a = \Delta R / R_a$, where R_a and R_g are the resistance of sensor in air and the test gas respectively.

Results and Discussion

Effects of Additives on H₂S Sensitivity

The gas sensitivity to 50 ppm was examined for the SnO₂ elements loaded with various metal oxides at 200°C. Fig.1 shows the H₂S sensitivity as a function of the electronegativity (X_i) of the loaded metal cations, we can clearly see that the sensitivity is promoted extensively by metal cation ($X_i < 2$), such as Cu²⁺, Cd²⁺, Ce⁴⁺, Zr⁴⁺ and so on, while others show no or very modest effects. This tendency is fairly consistent with the proposal of Nakahara et al^[5] that, since H₂S is an acidic gas, the H₂S sensitivity increases when the surface of SnO₂ is loaded with basic additives. Among the examined metal oxides, CuO is singularly outstanding in promoting the sensitivity. This suggests a possibility that its promoting effect results from factors other than acid-based properties of the SnO₂ surface.

Effects of CuO Film Thickness on H₂S Sensitivity

Sintered gas sensors are composed of a mixture of CuO and SnO₂, and thus, CuO is dispersed here and there in a sensor, in the thin film of this study, catalytic layer, CuO, was formed only atop the

SnO₂ film. Fig.2 shows the effects of doping layer thickness on the sensitivity of the film. It is apparent that the sensitivity of the CuO/SnO₂ film is strongly dependent on the thickness of the doping layer. Considering that CuO resistance is attributed to formation of p-n junction between CuO layer and SnO₂ film, by which electrons of n-type semiconductor SnO₂ is depleted and the sensor resistance is raised. For a sensor with a thickness of 7.5 nm, however, the sensor resistance decreased remarkably. This fact can be explained from the following: numbers and sizes of CuO islands atop SnO₂ increase, and then the distance between each pair of islands is closer, and finally electrical conduction by tunneling lowers the sensor resistance. If the thickness of the film is too thick, we consider the reason is that a certain amount of CuO cannot interact with H₂S and transformed CuS, that is to say, there are some p-n junctions. In case of a thickness of less than 7.5 nm, it is assumed that since the quantity of doped CuO is so small, p-n junction depth is so small that it could not extend to the bottom of the SnO₂ film.

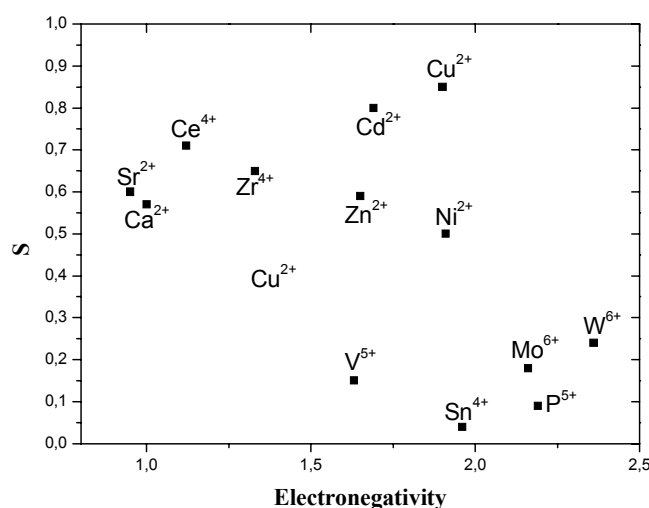


Figure 1. The sensitivity of various metal oxides-loaded SnO₂ element to 50 ppm at 200°C as a function of the electronegativity (χ_i) of the metal cations.

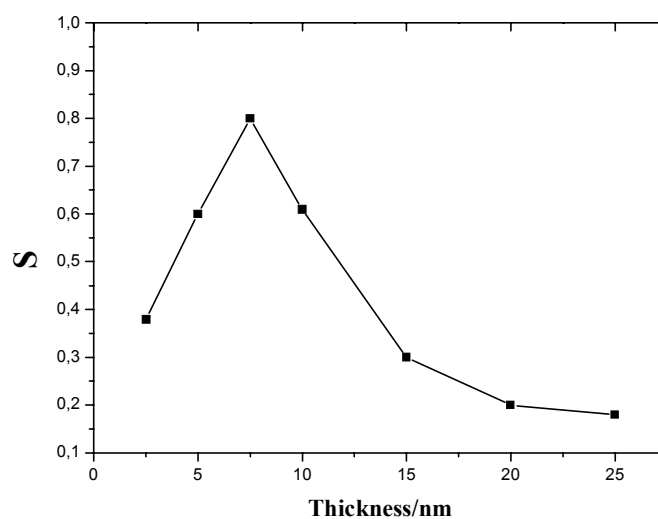


Figure 2. The dependence of sensitivity on the thickness of doping layer (1 ppm H₂S, 180°C).

Effects of H₂S Gas Concentration

Fig.3 is a plot of the sensitivity of the element as a function of H₂S gas concentration in air at different operation temperatures. The sensor exhibits a significant increase in sensitivity upon exposure to a very low concentration of H₂S (5ppm) in air, at around 100 ppm the sensitivity reaches a saturation value, and therefore we can infer that the active region of the element to be between 0 and 100 ppm.

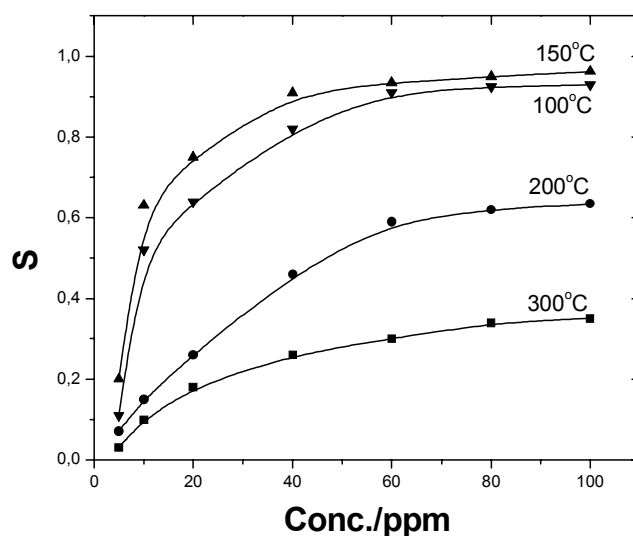


Figure 3. The sensitivity of the sensor element as a function of H₂S gas concentration at different operation temperature.

Effects of CuO Loadings and Operation Temperature

Plots of the sensitivity to 100 ppm H₂S in air as a function of operating temperature for five different elements prepared from SnO₂ with 1.0, 4, 5, 6 and 10 wt.% CuO are shown in Fig.4. In order to explain the effect of CuO loadings clearly, sensitivity of an element made from pure SnO₂ to H₂S is also plotted at the bottom of the Figure. It is evident that to a good approximation pure SnO₂ is not at all or much less sensitive to H₂S. Only on addition of CuO does it becomes sensitive to H₂S; the sensitivity to H₂S (100 ppm in air) tends to increase with increasing CuO loading up 5 wt.%. The response and recovery time of different CuO loadings for SnO₂ sensor are reported in Fig.5. At the same time, we also indicate the sensitivity curve clearly in the Figure. The response time defines the time taken for the sensor to reach 90% of the saturation value after contact by the test gas with the surface of the sensor, the recovery time is the time of the resistance recovery to the initial level after the removal of the test gas from the environment. We may see that, at CuO loadings of 10%, the response was too slow to attain a steady state during the test period of 80 min. The resistance of the pure SnO₂ element decreased very slowly from the air level on switching on the H₂S flow to reach a steady state about 40 min , after exposure to 100 ppm H₂S when the air flow was resumed, the recovery was also slow. However, the CuO (5 wt.%)/ SnO₂ element showed an extremely high

sensitivity to 100 ppm H₂S. A prominent feature of the CuO/SnO₂ element was its very fast recovery rate on turning off the H₂S. As seen from the Figure, the resistance could completely recover to the initial level in 1 min, but the response time was about 7 min. The influence of CuO loadings on the sensing characteristics are generalized as follows. If the CuO loadings are too small, CuO particles cannot cover the whole SnO₂ surface to make a sufficient number of p-n junctions (low H₂S sensitivity) . If the CuO loadings are too large, the conversion from CuO to CuS in the H₂S-containing atmosphere takes too long (slow response) . From the viewpoint of high H₂S sensitivity and switching-like recovery, an optimum CuO loading seems to be 5 wt.%. The Figure also shows that all the five elements have a maximum sensitivity at an operating temperature of 150 °C.

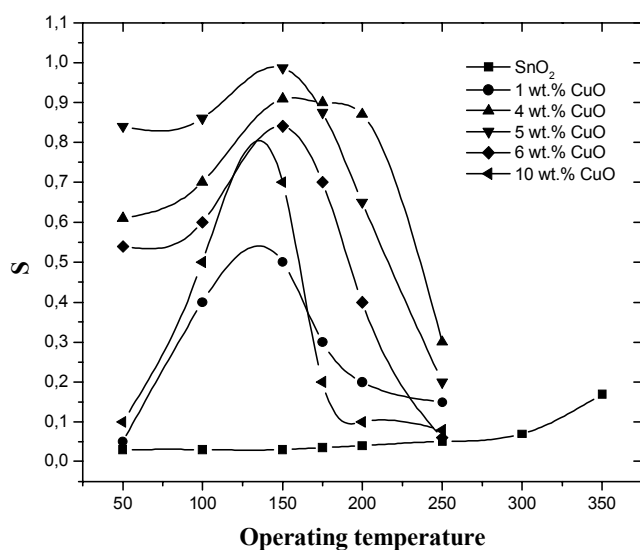


Figure 4. Gas sensitivity of pure and CuO-doped SnO₂ elements at different operating temperatures.

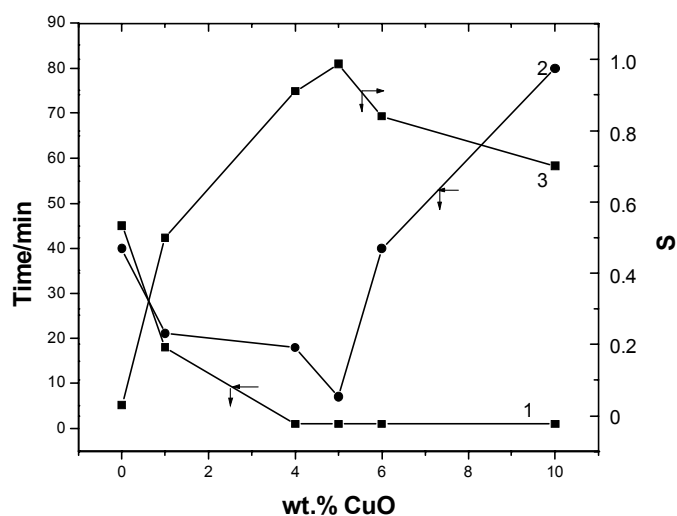
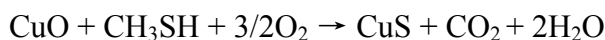


Figure 5. The effect of CuO loadings on response and recovery time and sensitivity.
1 recovery curve 2 response curve 3 sensitivity curve (150 °C)

The Selectivity of CuO/SnO₂ Element

The CuO (5wt.%) / SnO₂ element was also tested for their sensitivity to other gases such as CO, i-C₄H₁₀, CH₃SH, (CH₃)₂S, C₂H₅OH, H₂, etc. Fig.6 shows the sensitivity value for these gases (100%, i.e., without dilution) together with 100 ppm H₂S . It shows very clearly that even for such a high concentration of these gases, the CuO (5wt.%) / SnO₂ element shows very small or negligible sensitivity compared to H₂S at an operating temperature of 100 °C, except for CH₃SH. The CuO/SnO₂ element was also rather sensitive to CH₃SH at 100 °C. This is probably because CuO is sulfurized:



In the case of (CH₃)₂S, to which the element was almost insensitive, however, the sulfurization does not seem to take place. Such a gas sensing mechanism is consistent with the fact that the element was almost insensitive to all the sulfure- free gases tested.

These elements have been tested repeatedly and each time , they return to their original resistance of 9.5 MΩ ± 0.1 MΩ .These sensor elements were kept in operation continuously for 15 days and the resistance variation was monitored each day. It was found to vary from 9.5 to 9.46 MΩ.

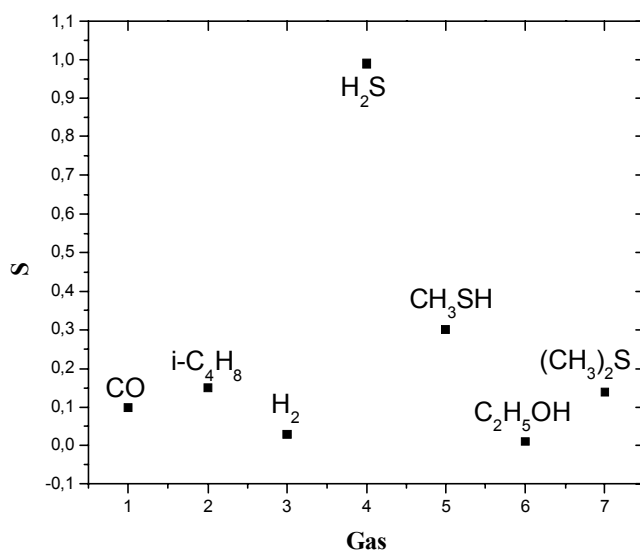


Figure 6. Cross sensitivity of CuO/SnO₂ sensor element to different gases at an operating temperature of 100°C.

CuO/SnO₂ Sensing Mechanism

The mechanism to explain the observed excellent behavior of increase in sensitivity of the CuO/SnO₂ film exposed to H₂S gas can be explained as follows. We consider that sensing reaction of hydrogen sulfide occurs only on the surface of the film and diffusion of chemical species into the inner part of the film is negligible, and p-n junction is formed only at the interface between CuO and SnO₂. While oxygen-deficient SnO₂ shows n-type conductivity by electrons, oxygen-excess CuO

shows p-type conductivity by holes. Sintered gas sensors are composed of a mixture of CuO and SnO₂, and thus, CuO is dispersed here and there in a sensor. In this case, in an oxidizing atmosphere a thick charge depletion layer is formed near the grain surface of SnO₂ as a p-n junction, as shown in Fig.7 (1). The electrons associated with these charged species are drawn from the conduction band of the bulk material, leading to an increase in resistance. As a result a potential barrier appears at the boundary forming a continuous chain of n-p-n-p junctions. The schematic band diagram of the typical n-p-n-p is a SnO₂-CuO-SnO₂-CuO and band structure in the vicinity of the CuO/SnO₂ interface can be drawn as shown in Fig. 7(2) (3). However, if the above CuO layer is exposed to H₂S or other sulfur compound gases, the CuO is converted to CuS which is a good electronic conductor in the following equations.

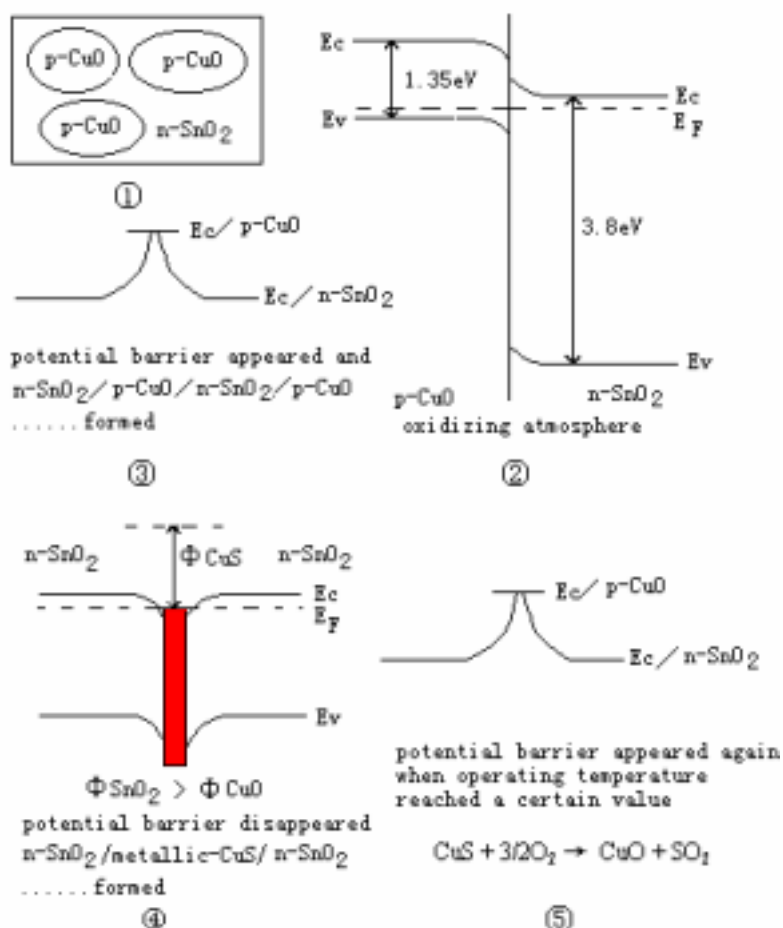
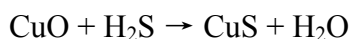
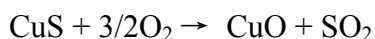


Figure 7. Schematic diagram of CuO/SnO₂ sensing mechanism.

1. SnO₂ particles surrounded by CuO 2. band structure for CuO-SnO₂ contact 3. potential barrier diagram of n-SnO₂/p-CuO/n-SnO₂/p-CuO 4. potential barrier diagram of n-SnO₂/metallic-CuS/n-SnO₂ 3. potential barrier appeared again

This CuS is known to be metallic in nature and thus the n-p-n heterostructure as well as charge depletion layer will be destroyed and transformed to a metal-n-type semiconductor configuration. A

typical metal-n-semiconductor band picture can be drawn in Fig.7 (4). Since the work function of CuS is lower than that of SnO₂ the band bending is as shown. This particular situation arises because at equilibrium there is a flow of electrons from the lower work function species, i.e., CuS, to higher work function species, i.e., SnO₂. This results in the band bending downwards which facilitates the easy flow of electrons from CuS to SnO₂ and vice versa, since there is no barrier between them as shown in Fig.7 (4). This flow of electrons results in a decrease in electrical resistance. This configuration is similar to a metal-semiconductor contact for an ohmic junction where there is an unimpeded conduction of electrons in either direction. This theory explains quite convincingly the decrease in resistance on exposure of CuO/SnO₂ sensor element to reducing gases like H₂S and the increase in resistance back to the original value once this H₂S atmosphere ceases to exist. This is because CuS converts back to CuO when heated in air at the operating temperature of about 200 °C and returns to its normal state, which is shown as follows,



So, the potential barrier appears again, as seen in Fig.7(5).

Conclusion

Among various metal oxides. CuO is a unique promoter of SnO₂ based elements for the detection of H₂S in air. Typical features of CuO/SnO₂ sensors are extremely high sensitivity to H₂S, high selectivity and very rapid recovery on switching off H₂S. The active range of a CuO/SnO₂ sensor is between 0 and 100 ppm. The optimum thickness of the CuO layer for the CuO/SnO₂ is about 7.5 nm and the optimum CuO loading seems to be 5 wt.%. The CuO (5wt.%) / SnO₂ sensor is extremely sensitive to H₂S at 150°C.

The CuO particles dispersed on the SnO₂ surface exert a strong electronic interaction with SnO₂, which makes the sensor element highly resistive. Exposure to H₂S converts CuO to CuS, resulting in the disruption of the electronic interaction and hence in a drastic decrease of the electrical resistance of the element. In this way, the unique H₂S sensing properties of CuO/SnO₂ sensors benefit from both the chemical affinity of CuO to H₂S and the strong electronic interaction taking place only between CuO and SnO₂. The dispersion state of CuO particles, such as particle size and population, is very important for the H₂S sensing characteristics, as illustrated from the significant influence of CuO loadings.

Acknowledge

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Sample Availability: Available from the authors.

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