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Characterization and Gas Sensing Properties of Copper-doped Tin Oxide Thin Films Deposited by Ultrasonic Spray Pyrolysis

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Tin oxide-based thin films are deposited by ultrasonic spray pyrolysis technology, in which Cu addition is introduced to enhance the gas sensing performance by H_2S detection. The thin films are porous and comprise nano-sized crystallites. One of the Cu-containing thin film sensors demonstrates a fast and significant response to H_2S gas. The values of power law exponent *n* are calculated to discuss the sensitivity of the sensors, which is significantly promoted by Cu additive. The sensitivity of Cu-doped SnO_2 gas sensors is determined by two mechanisms. One is the normal gas sensing mechanism of SnO_2 grains, and the other is the promoted mechanism caused by the transformation between CuO and CuS in the H_2S detection.

Keywords: tin oxide thin film, gas sensor, spray pyrolysis, hydrogen sulfide, sensitivity.

1. INTRODUCTION

Tin oxide (SnO_2) has become one of the best candidates for gas detection since its first appearance in commercial fabrication in 1962 [1]. This type of gas sensor succeeded in gas leakage warnings that prevented people from harm. Meanwhile, researchers were aware of the importance of SnO_2 gas sensors, on which great effort has subsequently been exerted in both practical and theoretical aspects [2]. The known working mechanism of a SnO_2 body comprises a joint function of receptor and transducer [3, 4]. The SnO_2 grain transduces the gas presence into a change in electrical resistance, controlled by the adsorbed oxygen on the grain surface. The sensor resistance decreases when exposed to reducing gases, while it increases if oxidizing gases are detected.

In recent decades, various devices have been fabricated in the forms of thick film [5], thin film [6] and nanostructures [7]. Response, sensitivity, and selectivity are deemed as the key parameters concerning gas sensors. One of the effective methods to improve sensor performance is the doping of foreign elements, which can substantially change the sensing properties and mechanism. Usually, Cu doping has been used to enhance sensor performance in H_2S detection. The sensitivity and selectivity subsequently benefited from the heterojunction between n-type SnO_2 and p-type CuO [8]. However, there is still a lack of complete understanding about this type of sensor. For example, the sensitivity of SnO_2 gas sensors for H_2S gas detection is enhanced by Cu additive [9], but the promotion mechanism of the sensitivity is not yet understood.

To reveal the effect of Cu additive on promoted sensitivity of SnO_2 gas sensors, the present work reports the SnO_2-based thin films fabricated using ultrasonic spray pyrolysis technology. $SnCl_2 \cdot 2H_2O$ was used to prepare the precursor for deposition on alumina substrates. $CuCl_2 \cdot 2H_2O$ was introduced to enhance the gas sensing performance in the H_2S detection. The thin film characteristics were discussed on the basis of the composition, morphology, crystallite size and electrical resistance in air. The gas sensing properties were tested by exposure to H_2S gas. The relationship between sensor response and gas concentration was concluded to calculate the values of the power law exponent of the SnO_2-based thin films. The promotion mechanism of sensor sensitivity was discussed based on the effect of the Cu additive in the detection of H_2S.

2. EXPERIMENTAL DETAILS

SnO_2 thin films were deposited by ultrasonic spray pyrolysis technology on the alumina substrates with a pair of interdigital electrodes, the pattern of which has been previously described [10, 11]. $SnCl_2 \cdot 2H_2O$ was dissolved into absolute ethyl alcohol, in which the concentration of Sn^{2+} was kept to be 0.1 mol/L. The Sn solution was stirred in a magnetic stirring apparatus at 74 °C for 1 hour. $CuCl_2 \cdot 2H_2O$ was dissolved according to identical methods to prepare a Cu solution, in which the Cu^{2+} concentration was 0.1 mol/L. The alumina substrates were placed in a tube chamber, which was heated to 350 °C. A flow of 80 sccm N_2 was used as the carrier gas to send the ultrasonicaly atomized spray of the Sn compound into the chamber, where the Sn composite was deposited on the substrates. The deposition time was 2 hours. The obtained sample was tagged as “FS(Pure)”. The “FS(Sn-Cu)” sample was prepared by continuous deposition, which included Sn spray pyrolysis for 2 hours, and then Cu spray pyrolysis for 2 hours. Similarly, the “FS(Cu-Sn)” sample was acquired by a 2 hour Sn deposition after a 2 hour Cu

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deposition. The three types of samples were sintered at 550 °C for 2 hours.

X-ray diffraction (XRD) analysis was conducted by D/MAX-Ultima (Rigaku Corporation, Japan). The surface and profile morphology were observed by scanning electron microscopy (SEM; XL-30TMP, Philips, Netherlands). The resistance and gas sensing properties of the thin films were measured by a computer-controlled system, which has been previously described [11, 12]. All measurements of thin film electrical properties were conducted at the operating temperature of 100 °C and under identical relative humidity of 40 %. The toxic H_2S was used as the target gas, the concentration of which was denoted by C_{H2S}. The film response (S) was defined as the ratio of the film resistance in the air (R_a) to film resistance in the target gas (R_g), expressed as $S = R_a/R_g$. The power law exponent n was calculated by $n = \mathrm{dlg}S/\mathrm{dlg}C_{H2S}$, which also defines the sensitivity of a gas sensor.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the FS(Pure), FS(Sn-Cu) and FS(Cu-Sn) samples on the alumina substrates with Ag interdigital electrodes; the standard patterns of SnO_2, Al_2O_3 and Ag are also illustrated. Three main SnO_2 peaks of (110), (101) and (211) are observed in all samples. However, the two peaks (a) and (b) for metallic Sn are found in the FS(Sn-Cu) sample, indicating that the Cu-containing layer may prevent the oxidation of the Sn-containing layer. Another peak (c) is detected in the FS(Cu-Sn) sample for CuO-Al_2O_3 compounds, which may result from the interaction between the Cu-containing composite and the substrate.

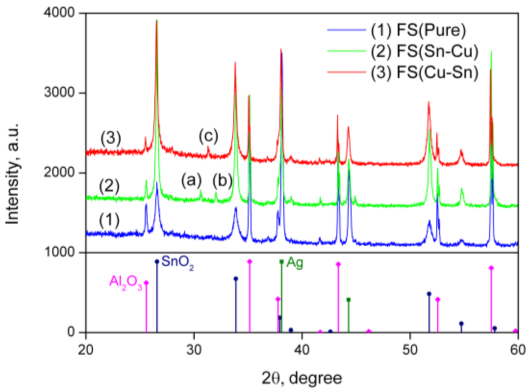

Fig. 1. XRD patterns of the FS(Pure), FS(Sn-Cu) and FS(Cu-Sn) thin film samples on the alumina substrates with Ag electrodes

Fig. 2 a, b show the morphology of the FS(Pure) thin film. The sample is porous and the grains appear spherical with varying sizes. Large grains with radii of several hundred nanometers are observed, indicating that secondary grain boundaries may exist inside such grains. Fig. 2 c, d show the profiles of FS(Sn-Cu) and FS(Cu-Sn) thin films on Al_2O_3 substrates, respectively. The porosity of the thin films is illustrated by the profile observation.

The characteristics of the three types of thin film samples are listed in Table 1. The crystallite size of the FS(Pure) thin film is as small as 26.4 nm, calculated from the XRD pattern according to Scherer's formula. Comparatively, Cu-containing samples demonstrate larger SnO_2 crystallite size. The size of SnO_2 crystallites in the FS(Sn-Cu) thin film is 80.1 nm while that of the FS(Cu-Sn) sample is 57.0 nm. The typical film thickness of the present samples is measured to be approximately 150 nm from SEM profile observation. The deposition rate of Cu compound was found to be very low, so that the film thicknesses of three samples were almost the same. The electrical resistances of the thin films are measured in the air at 100 °C. The FS(Pure) sample demonstrates the smallest resistance of 69.3 KΩ. The resistances of the thin films are significantly enhanced by the deposition of the Cu composition. This enhancement may be ascribed to the heterojunction between the n-type SnO_2 and p-type CuO grains [8]. It is known that sensor properties have a grain size effect when the grain radius approaches the width of the depletion layer. This effect, which shows a negative relationship between grain size and gas sensing properties, has been discussed in previous literature [12, 13]. For the present samples, Cu-added thin films demonstrate greater grain sizes and enhanced sensor performances. This indicates that that Cu addition effectively improves the gas sensing properties in the detection of H_2S gas.

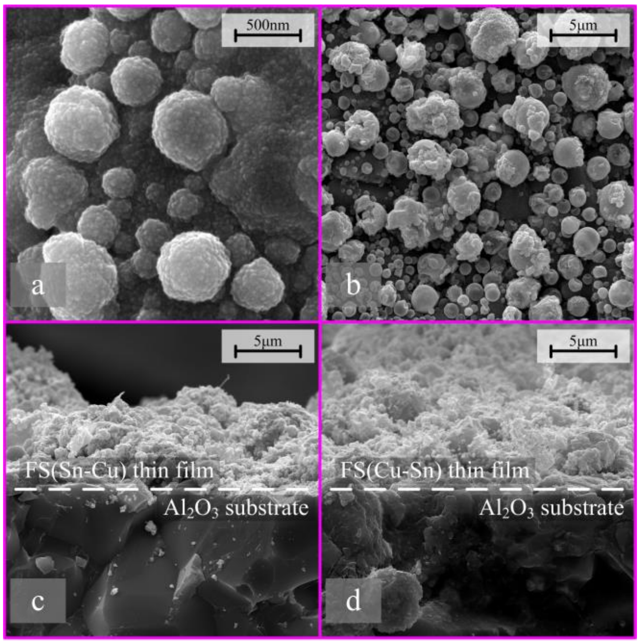

Fig. 2. Film morphology: a, b – of the FS(Pure) thin film; c – in profiles of the FS(Sn-Cu); d – FS(Cu-Sn) samples

Table 1. Characteristics of the FS(Pure), FS(Sn-Cu), and FS(Cu-Sn) thin film samples at 100 °C

Sample	SnO_2 crystallite size, nm	Resistance in air, KΩ
FS(Pure)	26.4	69.3
FS(Sn-Cu)	80.1	481.7
FS(Cu-Sn)	57.0	692.6

Fig. 3 shows the dynamic gas-sensing performances of thin films exposed to H_2S gas with the concentrations ranging from 13.7 to 95.9 ppm. The responses increase with gas concentration, the increase of which is indicated by the arrows in Fig. 3. The FS(Cu-Sn) thin film demonstrates the best response of 13709 to 95.9 ppm H_2S gas, to which the FS(Pure) sample only gives a response of 149. It is very difficult to precisely explain why the FS(Cu-Sn) thin film responds more than the FS(Sn-Cu) sample to H_2S detection. This phenomenon may be caused by several possible factors, such as film structure, number and size of p-n heterojunctions, and the possibility that CuO grains react with H_2S gas. Thus, further investigations are expected regarding those aspects.

It is known that the responses of semiconductor gas sensors follow a power law [14], the exponent of which can be obtained from the relationship between the sensor response and the gas concentration in the logarithmic coordinates. Fig. 4 shows the calculated n values (sensitivity) of the prepared thin film sensors. For FS(Pure) thin film, n is equal to 0.47 and approaching 0.5 when the adsorbed oxygen is dominated by the O^- species [15]. In another aspect, much larger n values greater than 1 are observed for the Cu-containing samples. The same result was also observed in previous work [9]. However, the promotion mechanism of sensitivity caused by the Cu additive is still unclear.

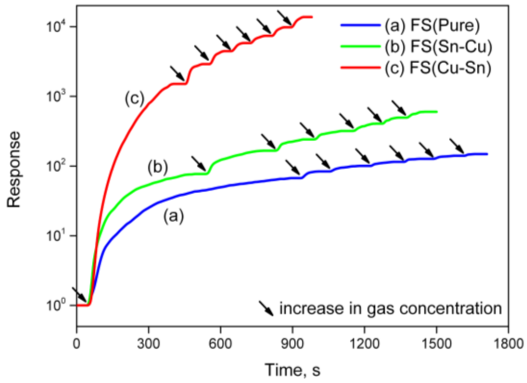

Fig. 3. Dynamic gas-sensing response to H_2S gas with the concentration from 13.7 to 95.9 ppm

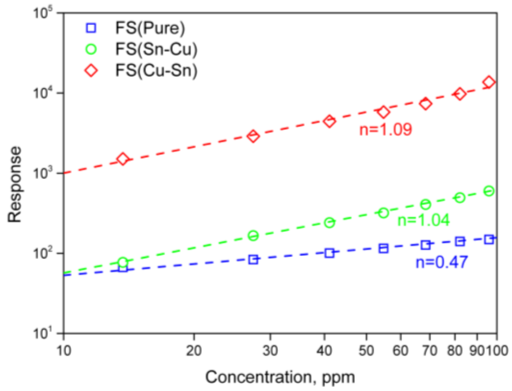

Fig. 4. The relationship between the thin film responses to the concentration of the H_2S gas and the calculated values of the power law exponent (n)

It has been proved that Cu additive in the SnO_2 system occurs in the form of p-type CuO after sintering. CuO establishes the heterojunction and the potential barrier at the grain boundary connecting to n-type SnO_2 grains. The exposure to H_2S gas causes the transformation of CuO to CuS, as expressed in Eq. 1.

$$H_2S+CuO \xrightarrow{k_1} CuS+H_2O . \quad (1)$$

The reverse transformation takes place when the Cu-doped SnO_2 gas sensor enters the aerial atmosphere, as expressed in Eq. 2.

$$2CuS+3O_2 \xrightarrow{k_2} 2CuO+2SO_2 . \quad (2)$$

Several presumptions are proposed for discussion as follows: (1) the nominal concentration of CuO and CuS grains in the SnO_2 thin films are indicated by [CuO] and [CuS], which indicates the number of CuO or CuS grains involved per unit volume of the thin film; (2) CuO grains can adsorb m H_2S gas molecules during gas detection when CuO converts to CuS; (3) each CuS resultant provides t carriers into the nearby depletion layer of the SnO_2 grain for conductance, $[CuS] = t[e^-]$. Therefore, the following equation detailing the accumulation of CuS can be obtained.

$$\frac{d[\mathrm{CuS}]}{dt} = k_1 C_{\mathrm{H_2S}}^m[\mathrm{CuO}] - k_2(t[e^-])^2 P_{O_2}^3 . \quad (3)$$

At the steady state, $d[CuS]/dt = 0$. Thus, $[e^-]$ can be formulated as Eq. 4.

$$[e^-] = \left(\frac{k_1[\mathrm{CuO}]}{k_2 t^2 P_{O_2}^3}\right)^{1/2} C_{\mathrm{H_2S}}^{m/2} . \quad (4)$$

It is known that the response of thin films is proportional to $[e^-]$ so that S is proportional to $C_{H2S}^{m/2}$. Hence, the power law exponent n is equal to $m/2$ for Cu-added SnO_2 gas sensors. The specific value of m is significant, but it cannot be known at this time. According to the definition, its value is likely to be much larger than 2, which leads to a large value of n; this could be the sensitivity promotion mechanism of the Cu-added SnO_2 elements. However, from experimental observation, the value of n remains around 1. This implies that the sensitivity of Cu-doped SnO_2 gas sensors may be controlled by two mechanisms: one is the normal gas sensing mechanism of pure SnO_2 grains, while the other is the promoted mechanism caused by the transformation between CuO and CuS in H_2S detection. Once the specific value of m is determined, the contribution of each mechanism can be separated.

4. CONCLUSIONS

SnO_2-based thin film gas sensors were fabricated on alumina substrate by ultrasonic spray pyrolysis technology. Three types of thin films were prepared and characterized by XRD, SEM, and electrical properties. The thin film samples were porous and demonstrated crystallite sizes of 26.4-80.1 nm. The gas sensing performances of the thin films were tested by exposure to toxic H_2S gas, to which the FS(Cu-Sn) sample showed a fast and high response of 13709 at 100 °C. The power law exponent n was calculated for each sample. The value of n for FS(Pure) sample was 0.47 while the values for the Cu-containing samples were greater than 1. The promotion mechanism of sensor sensitivity was discussed based on the transformation between CuO and CuS in H_2S detection by Cu-doped SnO_2 gas sensors. The sensitivity of such devices is controlled by two mechanisms, one of which is the normal gas-sensing mechanism of SnO_2 grains and the other of which is the Cu-promoted mechanism in the SnO_2 element for H_2S detection.

Acknowledgments

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