
SnO₂/ZnO double layer thin films: a novel economical preparation and investigation of sensitivity and stability of double layer gas sensors

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Abstract: A double-layer SnO₂/ZnO gas sensor was produced by utilisation of SnO₂ and ZnO thin films. Top layer consisted of SnO₂ produced by a sol-gel-controlled annealing technique. Bottom coating consisted of ZnO thin film precipitated by Two-Stage Chemical Deposition (TSCD) from an aqueous zinc-containing solution. Both top and bottom coatings were analysed by SEM, XRD, EDAX and AAS. Gas sensitivity of the SnO₂/ZnO double layer was determined by electrical resistance measurements. Although sensitivity was slightly reduced by double-layer formation, selectivity and stability were considerably improved by combination of the two thin layers. The existence of an interfacial transition layer between SnO₂ and ZnO and stabilisation mechanism of the SnO₂/ZnO double layer were rigorously investigated in this research.

Keywords: 1- double-layer thin film; 2- gas sensor; 3- sol gel; 4- two-stage chemical deposition.

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1 Introduction

Efforts towards the development of simple, inexpensive and reliable devices have recently been increased with the aim to control air pollution and to detect toxic or smelling gases at low levels in the air and in the field of domestic and industry applications. Semiconductor oxides are widely used as sensing materials due to their surface properties involved in the reaction mechanism with the gas to be detected (Maosong et al., 2001; Leo et al., 1999; Ahmad et al., 2003; Mandayo et al., 2003;

Comini et al., 2001). Thin film-type gas sensors have drawn much interest because of their potential applications for sensors (Becker et al., 2000; Lee et al., 2003; Suda et al., 2003). But truly thin film gas sensors, deposited by conventional thin film methods, have generally shown poor gas selectivity and poor long-term stability (Atashbar et al., 1998). Double-layer thin film gas sensors were investigated to improve the gas-sensitive properties of thin film gas sensors (Jiao and Zhang, 1998). In the present work, the SnO₂-ZnO double-layer thin film sensor was used. The aim of the work is to show selectivity and stability improvements obtained by double-layer SnO₂-ZnO thin film production.

2 Experimental procedure

2.1 Specimen preparation

The gas-sensing materials, tin oxide (SnO₂) and zinc oxide (ZnO) were prepared by using sol-gel and two-stage chemical deposition (TSCD) techniques, respectively.

High Purity Alumina (HPA) plates were used as the solid substrate for film growth. After degreasing, the plates were washed with deionised water and dried in a steam of hot air. The final solution composition and the bath conditions used to produce ZnO layer are shown in Table 1. The complex solution of (NH₄)₂ZnO₂ having the composition shown in Table 1 was prepared in the following way. Concentrated NH₄OH was poured into 100 cm³ of 0.5 M ZnCl₂ until a white precipitate of Zn(OH)₂ was formed. Further addition of NH₄OH resulted in dissolving of the precipitate. The solution was diluted to 500 cm³ to obtain a 0.1 M solution of the Zn⁺² complex, which was found to be the most convenient concentration for production of a good quality film on the substrate. Cleaned substrates were immersed first in a cold solution of the complex and then in boiling water for 2 s. In this way the substrate was covered with a thin layer of the complex solution that decomposed to ZnO when placed in boiling water.

The technique of dipping of the substrate into separate chemicals (a cold solution of the Zn⁺² complex first and hot water second) affected a constant increase in the thickness for each immersion, so that the final thickness of the film was determined by the number of immersions. After a required number of dipping (40 times of dipping), the substrate with the deposited ZnO film was annealed at 350°C in a tube furnace for 1 h.

Table 1 Bath conditions and chemical deposition parameters with their various ranges for ZnO deposition

<i>Variable</i>	<i>Range</i>
ZnCl ₂ (g.l ⁻¹)	20–100
NH ₄ OH (ml)	10–50
Additive (Tiron)*	1 drop per litre
PH	8–11
Temperature of complex solution (°C)	10–20
Temperature of hot water (°C)	90–105

*A compound based on the benzene molecule.

SnO₂ thin film was prepared from starting precursor via the sol–gel route in the following way: 12.37 g SnCl₄ (99.99%, Aldrich) was first stirred vigorously with 15 g isopropanol. A partially alkoxy-substituted tin compound of the type SnCl_x(OC₃H₇)_y is formed in the solution with evolution of heat, as reported in other papers (Rella et al., 1997; Chatelon et al., 1994). The solution was cooled down to room temperature and a 3.42 g water–10 g propanol mixture was added for hydrolysis reaction, without using a catalyst. The hydrolysis rate and the start of the reactions occurring in sol–gel technique are not exactly known and difficult to study (Rella et al., 1997), therefore the preparation route was optimised by evaluating the feature of the film. In order to get reliable results, the preparation procedure was kept constant and reproducible. Figures 1 and 2 outline the steps for preparation of zinc oxide and tin oxide, respectively.

Figure 1 Flowchart of the process used for production of zinc oxide thin film

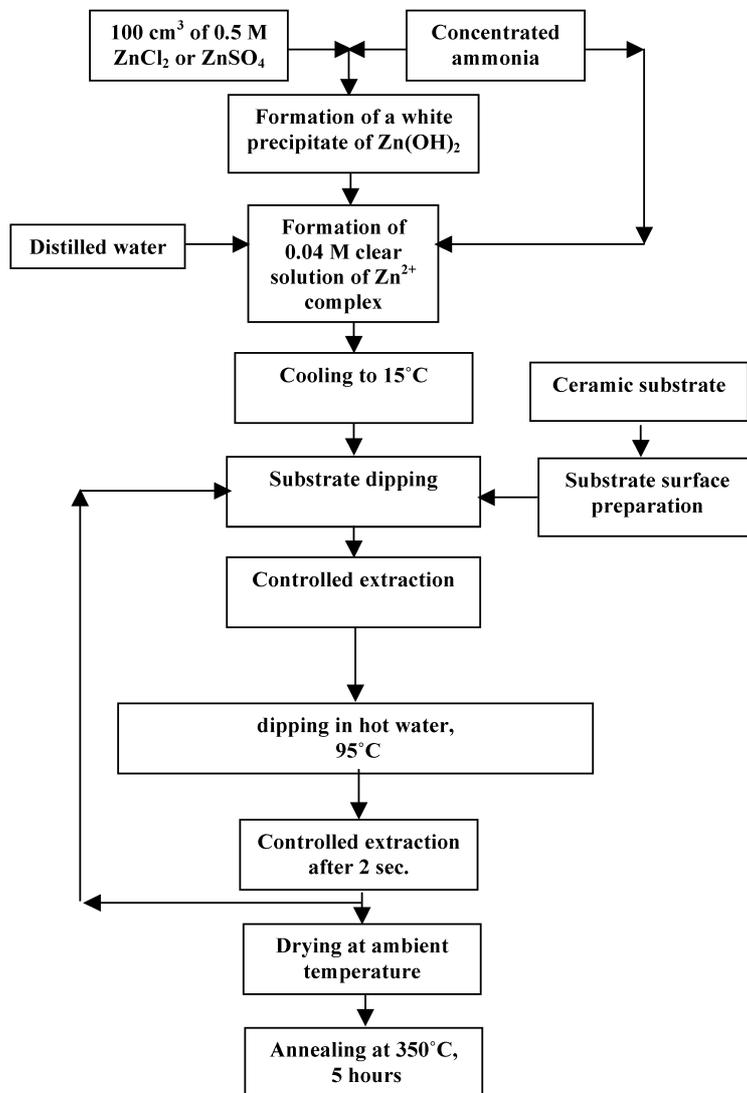
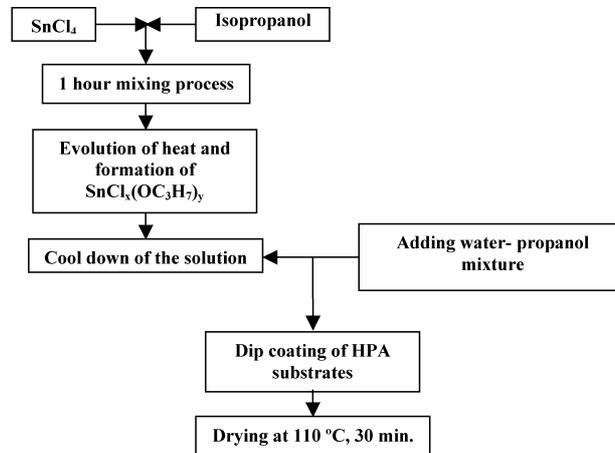
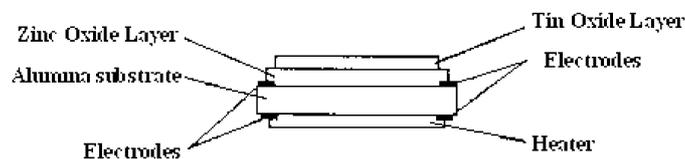


Figure 2 Flowchart of the process used for production of tin oxide thin film

Tin oxide thin films prepared after 20 times of dipping were deposited on the zinc oxide layer by using dip-coating technique. The SnO₂-ZnO double layer was first dried at 110°C for 30 min followed by the controlled annealing at a rate of 5°C/min to 600°C and held for 30 min. It is necessary to note that the total thickness of the SnO₂-ZnO double-layer thin film is 0.55 μm.

The structure of the SnO₂-ZnO double-layer thin film is shown in Figure 3. The electrodes and heater had already been affixed to the HPA substrate.

Figure 3 The structure of SnO₂-ZnO double-layer thin film

2.2 Characterisation and gas-sensing tests

ZnO and SnO₂ films produced in the present work were characterised for their surface morphology, chemical composition, phases present and preferred orientation. The surface morphology was studied by SEM using a Philips model MV2300 operated at 25 kV. The chemical composition of the deposits was determined using the Kevex model Energy Dispersive X-ray Spectroscopy (EDS) system attached to the SEM. All chemical composition values are quoted in weight per cent and represent the average of at least five measurements. In order to verify the accuracy of the EDS analysis, one deposit was also analysed by wet chemistry using Atomic Absorption Spectroscopy (AAS).

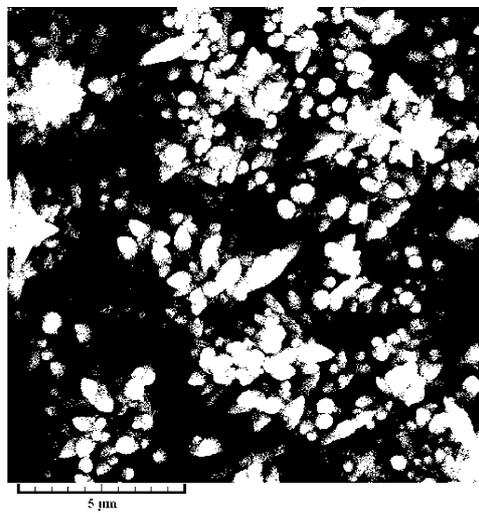
XRD was used to determine the phase present and the preferred orientation of the deposits. A Philips Xpert- Pro X-ray diffractometer with a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was employed to obtain XRD spectra using standard θ - 2θ geometry. A computer-based search and match was used for phase identification.

The resistance of the SnO₂-ZnO film in air (R_a) and in detecting gases (R_g) was measured. Gas sensitivity, S , is defined as $S = R_a/R_g$.

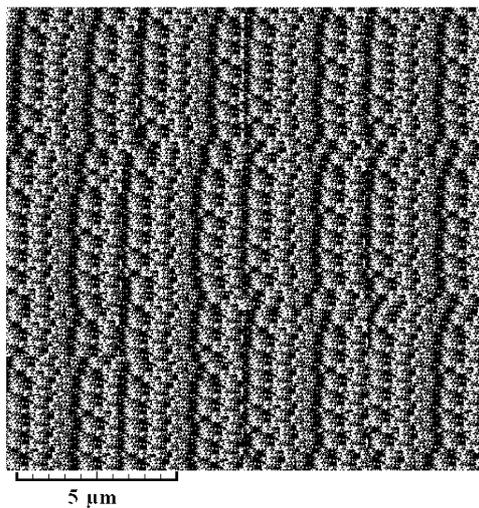
3 Results and discussion

Figure 4 shows the surface morphologies of zinc oxide and tin oxide thin films produced after 40 and 20 times of dipping, respectively. As is shown in the figure, HPA substrate causes clustering of the ZnO crystallites. Figure 4(a) clearly indicates that the zinc oxide layer deposited on HPA substrate is composed of oval-shaped crystallites preferably oriented perpendicular to the surface of the substrate. The surface of tin oxide shown in Figure 4(b) is compact and no crack or microcrack is observed in its morphology.

Figure 4 SEM micrographs showing the morphology of zinc oxide: (a) and tin oxide (b) deposits on HPA substrate



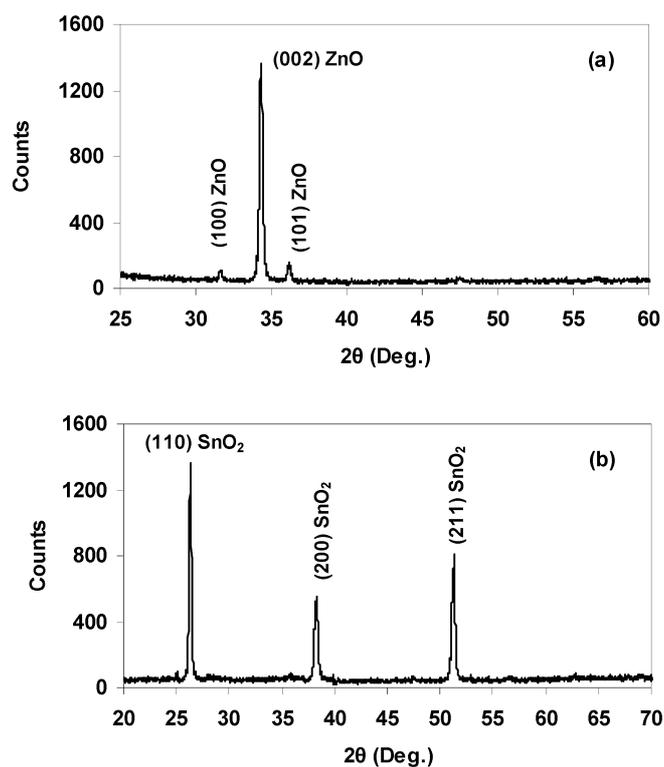
(a)



(b)

XRD patterns for ZnO and SnO₂ films are shown in Figure 5. In the ZnO XRD spectrum, the peaks at $2\theta = 31.3, 34.6, 36.2$ and 47.6 corresponds to the planes (100), (002), (101) and (102) of the hexagonal wurzite, ZnO, respectively. The preferred orientation peak occurred at $2\theta = 34.6$. These spectra indicate a good crystalline character for the deposited layer showing a preferential orientation with the *c* axis perpendicular to the substrate. Incidentally, all the obtained spectra showed in Figure 5(b) present the typical tetragonal tin oxide crystalline features.

Figure 5 XRD patterns for ZnO (a) and SnO₂ (b) thin films

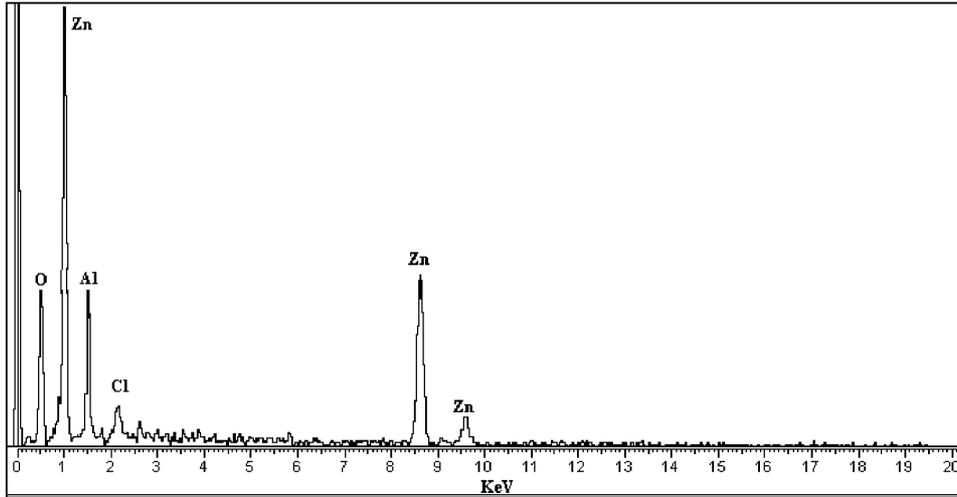


Electron dispersive elemental analysis (EDAX) spectra of the ZnO and SnO₂ films shows the presence of Zn, Sn, O, Al and a trace amount of Cl. The source of Al is the substrate (Figure 6). The Cl species may have come from the solution. As a typical example, one of the samples was also analysed by wet chemistry using AAS. AAS analysis of ZnO and SnO₂ films showed minor differences with EDAX analysis. The difference is within the acceptable range of the experimental errors.

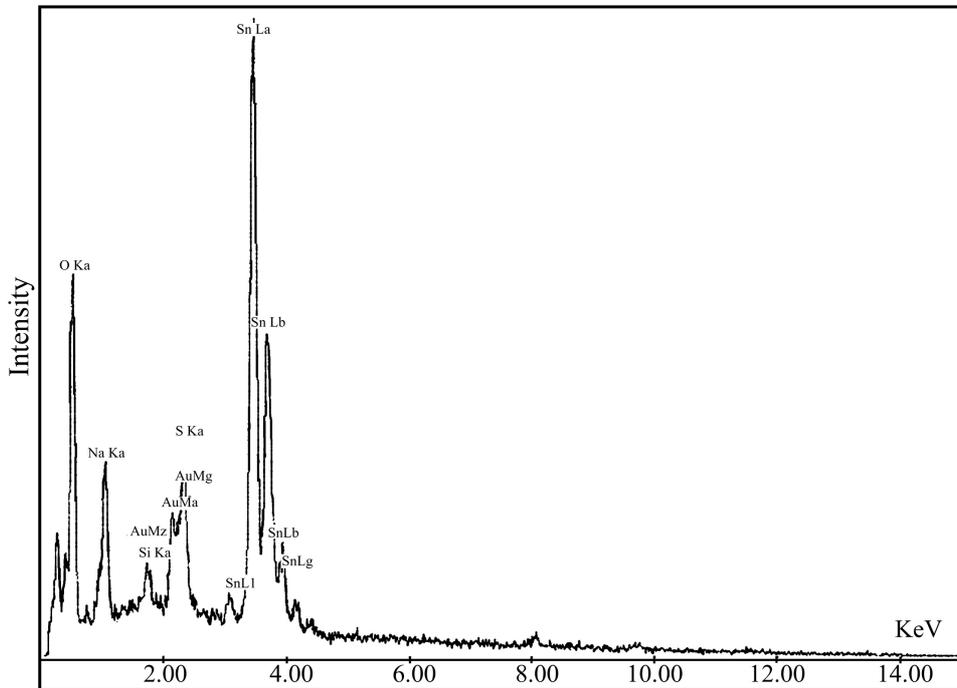
The sensitivities of the SnO₂-ZnO double-layer thin film to C₂H₅OH, CO and H₂ are shown in Figure 7. The SnO₂-ZnO double-layer thin film shows a high sensitivity to C₂H₅OH ($S = 24$), but a very low response to CO and H₂ (<3). This situation suggests that the SnO₂-ZnO double-layer thin film is a good sensor material to alcoholic gases. It is necessary to note that the selectivity of this sensor is much better than that of SnO₂ or ZnO thin film, although its sensitivity is lower (Lee et al., 2003; Maosong et al., 2001).

In Table 2, the resistance change of SnO₂-ZnO double-layer thin film in air is compared with that of SnO₂ film. The resistance of the SnO₂-ZnO double-layer thin film was stable after about 48 h, while the resistance of the SnO₂ film continued to change even after 84 h. In other words, the stability of the SnO₂-ZnO double-layer thin film was better than that of the SnO₂ film.

Figure 6 EDAX result of ZnO (a) and SnO₂ (b) thin films



(a)



(b)

Figure 7 The sensitivity of SnO₂-ZnO double-layer thin film to various gases as a function of concentration at 300°C

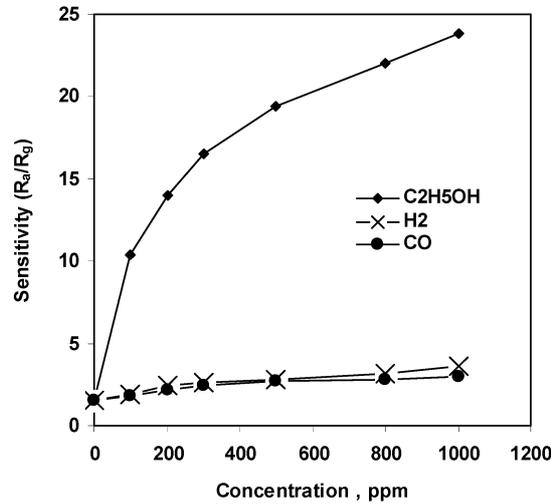


Table 2 The resistance change of SnO₂-ZnO double layer and SnO₂ film in air

Duration (h)	0	12	24	36	48	60	72	84	96	108
Resistance of SnO ₂ - ZnO film (MΩ)	65.4	70.3	72.2	76.3	82.2	82.3	82.4	82.3	82.2	82.3
Resistance of SnO ₂ film (MΩ)	40.8	43.2	45.1	48.4	52.1	53.6	56.9	56.4	55.9	56.3

The surface and interface of the SnO₂-ZnO double-layer thin film were investigated by AES. The distribution of Sn, O and Zn atoms along the vertical section was observed. It was found that Zn diffused into the SnO₂ layer and Zn diffused into the ZnO layer. Thus, an interfacial transition layer was formed between the SnO₂ layer and the ZnO layer (Figure 8). With the top layer removed, the electronic and gas-sensitive properties of the interfacial transition layer were investigated by AES. It was found that the interfacial transition layer has high resistance and low sensitivity to gases.

The SnO₂-ZnO double-layer thin film can be viewed as a parallel collection of two equivalent resistances, R_s and R_z , which refer to the resistances of the SnO₂ layer and the ZnO layer, respectively (Figure 9).

Figure 8 Schematic of interfacial transition layer in SnO₂-ZnO double-layer thin film

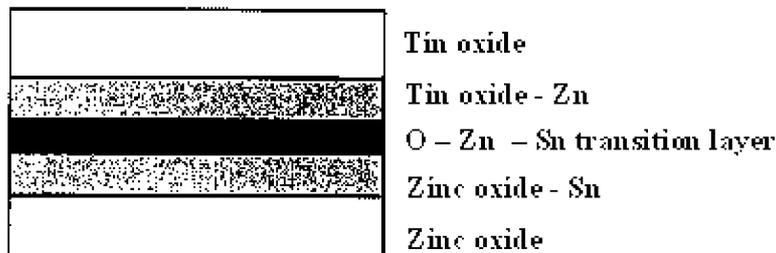
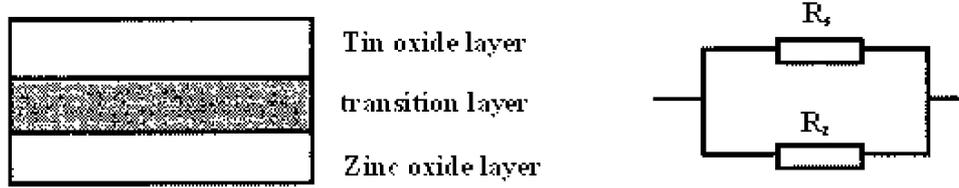


Figure 9 The equivalent circuit of SnO₂–ZnO double-layer thin film

A double-layer thin film gas sensor is characterised by the separation of the current conduction part and the gas-sensitive part (top layer). The current conduction part needs not only to be controllable in the fabrication process, but also to be stable for a long time. Zinc oxide is suitable for this purpose because of its stable condition.

The sensitivity, S , can be expressed as $S = R_{sa}/R_{sg}$; thus, the sensitivity of SnO₂–ZnO double-layer thin film, S' , can be expressed as:

$$S' = \left(\frac{R_{sa} \cdot R_z}{R_{sa} + R_z} \right) \bigg/ \left(\frac{R_{sg} \cdot R_z}{R_{sg} + R_z} \right) = \left(\frac{R_{sa}}{R_{sg}} \right) \bigg/ \left(\frac{R_{sa} + R_z}{R_{sg} + R_z} \right) = S \cdot \frac{R_{sg} + R_z}{R_{sa} + R_z}. \quad (1)$$

$R_{sg} < R_{sa}$, thus $S' < S$, i.e., the sensitivity of the double-layer film decreases slightly. This coincides with the experimental results. Because of the high sensitivity of SnO₂ film, the slight decrease in sensitivity is not a serious problem.

The expression of stability is resistance change with time. If R_{sa} resistance percentage change is δ , then

$$\frac{(1 + \delta)R_{sa} \cdot R_z}{(1 + \delta)R_{sa} + R_z} \bigg/ \frac{R_{sa} \cdot R_z}{R_{sa} + R_z} = (1 + \delta) \frac{(R_{sa} + R_z)}{(1 + \delta)R_{sa} + R_z}. \quad (2)$$

The result of equation (2) is always smaller than $1 + \delta$, thus the double-layer film has a decreased resistance change and an increased stability. The smaller the R_z , the smaller the result of equation (2), the better the stability.

4 Conclusions

With the precursors of zinc–ammonia complex, uniform and continuous ZnO and SnO₂ films were deposited on HPA substrate, respectively. SEM and EDAX techniques were used to evaluate the microstructure and chemical composition of chemically deposited ZnO and SnO₂ layers. The SnO₂–ZnO double-layer thin film exhibited improved selectivity and stability, but slightly reduced sensitivity. Existence of an interfacial transition layer between the SnO₂ and ZnO thin layers was also approved.

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