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SnO_2 thin films used as ammonia sensing layers at room temperature

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Abstract. Gas sensors based on the SnO_2 thin films were prepared by dip-coating method starting from their corresponding sols. The as-elaborated thin coatings were afterwards annealed at different temperatures during various times. Their morphology, composition and microstructure were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). The results of electrical and sensing measurements indicated that the sensor annealed at 300°C for 3 hours exhibited the best sensitivity towards the detection of NH_3 at room temperature.

1. INTRODUCTION

Ammonia is a produced utilized extensively in many chemical industries, such as fertilizer factories, refrigeration systems, food processing, medical diagnosis, fire power plants, etc. It is well admitted that NH_3 is a harmful and toxic compound [1]. Therefore, it is necessary to monitor its concentration by developing corresponding efficient sensors. Efforts were performed to develop SnO_2-based gas sensors able to detect ammonia [2]. The various ammonia sensors reported, were basically sensitive to NH_3 only at higher temperature (>200°C), which is not convenient while sensing [3]. Thus, the development of room temperature sensors is necessary. The present work, aims at developing room temperature sensors with a low cost using sol-gel process. The SnO_2-sensors were first characterized and then evaluated for NH_3 detection at room temperature. The influence of the temperature and the time of annealing were investigated regarding the NH_3 gas sensing efficiency.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis

To prepare the precursor solution, 5.13 g (0.02 mol.) of anhydrous tin tetrachloride ($SnCl_4$) was dissolved under stirring in 16 mL of absolute ethanol and placed into a closed flask. 9.14 g (0.09 mol.) of triethylamine $N(C_2H_5)_3$ dissolved in 38 mL of the absolute ethanol was added dropwise over 45 minutes to the previous solution. The mixture was stirred for additional 1 hour at room temperature, thereafter 5 mL of absolute ethanol were added and the stirring was kept for additional 14 h at room temperature. The alcoholysis of tin tetrachloride in the presence of triethylamine was obtained according to the following reaction:

$$SnCl_4 + 4C_2H_5OH + 4(C_2H_5)_3N \rightarrow Sn(O - C_2H_5)_4 + 4(C_2H_5)_3NHCl \downarrow . \quad (1)$$

After phase separation, the clear supernatant was then recovered (pH ∼ 8), filtered and used as a sol to prepare SnO_2 powders or thin films.

The thin films were deposited on the substrates by dip coating at a withdrawing speed of 50 mm.min^{-1} from the beforehand mentioned sol. The substrate was constituted of a thick SiO_2 layer grown on top of a silicon substrate where a pair of interdigitated Ti/Au electrodes was deposited. Afterwards, powders and thin sensitive layers were air-annealed at various temperatures for different times.

2.2. NH_3 detection procedure

The gas sensitivity of SnO_2 to NH_3 was measured according to procedure described elsewhere [4]. Briefly, before each NH_3 detection experiment, the sensor was kept under synthetic air flow during 3h in order to obtain a stable electrical resistance. Once stabilized under dry air, the sensor was exposed to 100 ppm of ammonia for 30 minutes. Then the sensors were cleaned using synthetic dry air for baseline response recovery. The sensor's responses to NH_3 were recorded at room temperature. The response of the sensor was defined as Rg/Ra, where, Ra and Rg were the electrical resistances of the sensor respectively in the synthetic air and target gas (NH_3).

2.3. Characterizations of samples

The annealed powders were characterized by X-ray diffraction (XRD) using a Philips X pert MPD diffractometer (Cu Kα radiation ($\lambda = 0.15406$ nm)) and the morphology of the thin films was investigated using scanning electron microscope (Jeol JSM-5500) SEM.

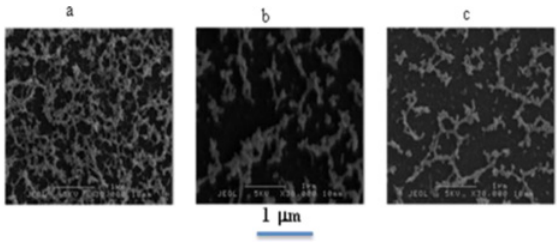

Figure 1. SEM micrographs of SnO_2 films annealed during 1h at (a) 300 °C, (b) 400 °C and (c) 500 °C.

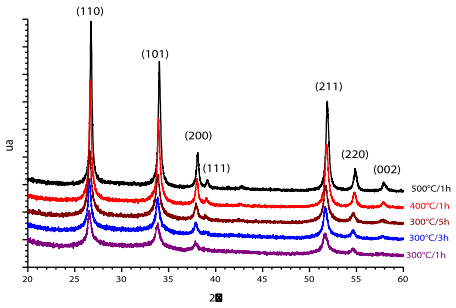

Figure 2. The XRD patterns of the synthesized SnO_2 nanostructures after heat-treating at different times and various temperatures.

3. RESULTS AND DISCUSSIONS

3.1. Samples characterizations

The morphologic analysis of the surfaces revealed relatively high porous films (Fig. 1). The inter-granular contacts of the SnO_2 decreased with the annealing temperature due likely to the removal of organic products.

Due to the very low thickness of the deposited layers (about 100 nm), no significant XRD results have been obtained by performing a direct analysis on the thin films prepared. So, XRD characterizations were only performed on SnO_2 powders. The X-ray diffraction patterns of SnO_2 under different conditions of thermal treatments are presented in Figure 2. They revealed several peaks at 26.7°, 33.9°, 38.1°, 51.8° and 54.9° which were clearly ascribed to polycrystalline tetragonal rutile SnO_2 (JCPDS file n° 41–1445).

No reflections corresponding to crystalline by products were found in the pattern, indicating that the as-prepared samples crystallized in a pure rutile structure. Besides, the peaks intensities were observed to increase with the temperature and/or the time of annealing, thus indicating the enhancement of the samples crystallinity.

3.2. Influence of annealing temperature on NH_3 gas sensing

Figure 3 shows the gas sensing response of the SnO_2 films towards 100 ppm of ammonia at room temperature. It could be seen that, the response increased upon exposure to NH3 gas and returned to the original value upon exposure to the air. The sensor annealed at 300°C for 1 hour exhibited excellent sensitivity to NH_3 at room temperature.

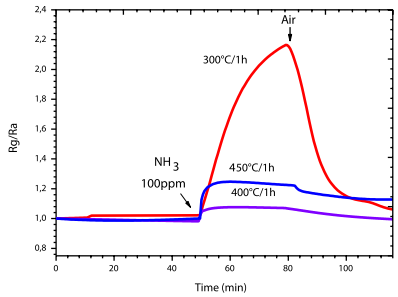

Figure 3. Response of SnO_2 films heat treated at 300, 400 and 500°C for 1h exposed to 100 ppm of NH_3 at room temperature.

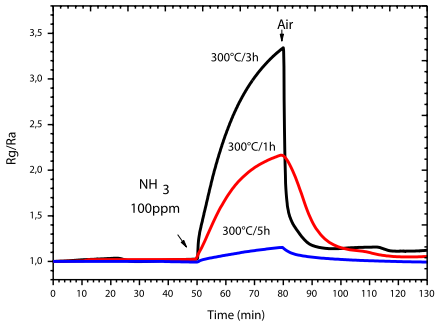

Figure 4. Response at room temperature to 100 ppm NH_3 gas of SnO_2 films heat treated at 300 for 1, 3 and 5 h.

3.3. Influence of annealing time on NH_3 gas sensing

Regarding the influence of annealing time, on the response of SnO_2 sensors to 100 ppm NH_3 at room temperature, the maximum sensitivity was observed for the sample annealed at 300°C for 3h (Fig. 4).

4. CONCLUSION

In summary, a simple and economical technique using cheap products in conjunction with dip coating were used to prepare SnO_2 films for ammonia sensing at room temperature. The control of the morphology and the composition of nanostructured SnO_2 films, by optimizing the temperature and the time of annealing, was important towards the development of efficient SnO_2 ammonia sensors able to operate at room temperature.

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