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Screen printed In_2O_3-SnO_2 nanocomposite: Structural and morphological properties and application for NO_2 detection

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Abstract. In this work, we report on the sensing properties of screen-printed In_2O_3 (Indium Oxide) while adding a moderate quantity of SnO_2. It was found that the addition of SnO_2 improves the response and decreases the operating temperature of the sensitive element for NO_2 detection. However, a non-controlled amount of SnO_2 leads to opposite result; for this reason in the present investigation we test films with different composition in order to optimize the quantity of SnO_2 to be added. The crystallinity, roughness and morphology of the obtained In_2O_3-SnO_2 nanocomposite were analyzed using X-ray Diffraction (XRD), Transmission Electronic Microscopy (TEM) and Atomic Force Microscopy (AFM). The atomic composition of the In_2O_3-SnO_2 films was determined with the energy dispersive spectroscopy (EDX) analysis during TEM observations. The effect of the composition on the cristallinity and morphological properties of the films was analyzed. Finally, the In_2O_3-SnO_2 films were tested like sensitive elements for NO_2 detection, wherein the effect of the composition was correlated with the sensor response in NO_2 ambient. It was found that the addition of a moderate quantity of SnO_2 to In_2O_3 exhibited high sensitivity at rather lower operating temperatures.

1 Introduction

Gas sensors are important in environmental monitoring, home safety and chemical controlling. Metal oxide sensors have been widely investigated because of the smallness of the dimensions, low cost and high compatibility with semiconductor processing [1]. In general, the gases that we seek to detect are carbon monoxide (CO), nitrogen oxides (NO_x) or Ozone. SnO_2 is the most popular material for gas sensing, which is due to its suitable physical-chemical properties such as natural non-stoichiometry and phase stability. Many approaches have been studied to improve the gas sensors sensitivity at low working temperature; this includes the addition of active catalysts, the reduction of the crystallite grain size and in recent years the mixing of two metal oxides. The conductivity of the metallic oxides varies according to the gas environment change. The response and the optimal operating temperature, in presence of a particular gas, are characteristics of each metallic oxide. Several works reported that gas sensors based on In_2O_3 are promising candidates for the detection of low concentration of oxidizing gases like O_3,

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NO_x,… In this work, we report on the sensing properties of screen-printed In_2O_3 (Indium Oxide) while adding a moderate quantity of SnO_2 (Tin Oxide). Screen printed In_2O_3-SnO_2 nanocomposites were prepared with different proportion of Indium and Tin. We studied the structural and the morphological properties of these semiconductors and their use as sensitive layers in our gas sensor devices.

2 Experimental

The SnO_2 gel was synthesized from a solution containing 2 ml of $SnCl_4.2H_2O$ and 40 ml of methanol and stirred for 2 hours at room temperature. The obtained mixture was aged for 72 hours, and then 40 ml of absolute ethanol was slowly dripped into the former solution while stirring at a temperature of 80 °C during 2 hours. The obtained SnO_2 was mixed in different proportion with an In_2O_3-based one [2] and deposited by the screen printing method on a glass substrate. The obtained layer is annealed in an IR furnace at a temperature of 570 °C during 45 minutes [2]. Three types of layers have been prepared: In_2O_3-SnO_2 (10 wt% Sn, 20 wt% Sn and 35 wt% Sn) nanocomposites. The Structural analyses were carried out using a Panalytical X-Pert Pro X-Ray diffractometer (λ Cu Kα=1.54060 Å) with a scanning angle (2θ) varying from 25° to 65°. The Morphological characterization was investigated with transmission electron microscopy (Tecnai ultra Twin G2-Philips) and atomic force microscopy (AFM-NanoScope 2, Digital Co. Instruments, Veeco) using normal silicon nitride tips in taping mode. The atomic composition was determined with energy dispersive spectroscopy (EDX) analysis during TEM observation. After that, the layer to be tested is placed in a gas chamber that offers several possibilities of test and measurement.

3 Results and discussion

3.1 Structural analysis

Fig. 1 shows the XRD patterns of the screen printed In_2O_3-SnO_2 (10 wt% Sn), In_2O_3-SnO_2 (20 wt% Sn) and In_2O_3-SnO_2 (35 wt% Sn) nanocomposite. The XRD patterns of In_2O_3-SnO_2 (Fig. 1) show peaks that agree with the cubic structure of the In_2O_3 powder (JCPDS No. 89-4595). It is worth noting that only peaks corresponding to In_2O_3 appear in the XRD patterns; these peaks are less intense but finer as compared to that corresponding to In_2O_3 [3, 4, 5] indicating a possible increase of the grain size.

The In_2O_3-SnO_2 nanocomposite constant lattice ‘a’ has been estimated by refining the XRD data (from the (222) peak) using the equation $d=a/(h^2+k^2+l^2)^{1/2}$, Where ‘h’, ‘k’ and ‘l’ are the interplanar indices and ‘d’ is interplanar spacing. The estimated lattice constants are a_1 = 10,122 Å for In_2O_3-SnO_2 (10 wt% Sn), a_2 = 10,131 Å for the In_2O_3-SnO_2 (20 wt% Sn) and a_3 = 10,148 Å for the In_2O_3-SnO_2 (35 wt% Sn) nanocomposite; the fact that $a_1 < a_2 < a_3$ may be explained by further substitutional dissolution of the Sn^{2+} ions in the In_2O_3 lattice [3, 4, 5].

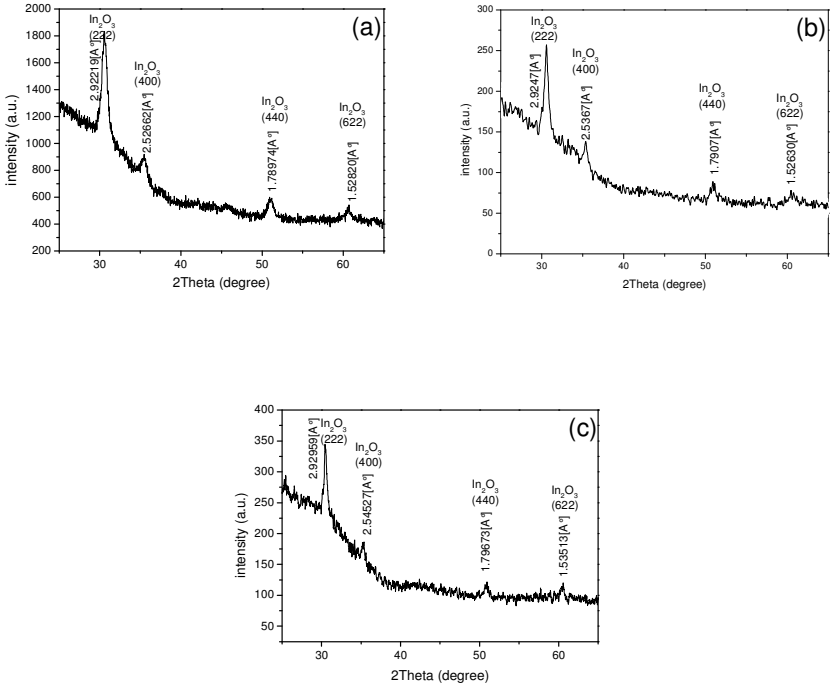

Fig. 1. XRD patterns of (a): In_2O_3 (10 wt% Sn), (b): In_2O_3-SnO_2 (20 wt% Sn) and (c): In_2O_3-SnO_2 (35 wt% Sn).

3.2 Morphological characterization

Fig. 2 shows TEM views of the samples. One may notice a non-uniform morphology and nanosized grain agglomeration (Fig. 2(a)). The In_2O_3-SnO_2 (35 wt% Sn) nanocomposite has spherical-like grains with an average size of about 14 - 18 nm (Fig. 2(b)), whereas an average size of about 12 nm was observed for In_2O_3-SnO_2 (10 wt% Sn) [6]. Inter-planar spacing of about 0.29 nm and 0.25 nm are found, which corresponds to the (222) and (400) plans of In_2O_3, respectively; hence, no evidence crystalline SnO_2 phase was detected. The In_2O_3 crystallites are therefore surrounded by an amorphous SnO_2 phase.

Thus, a part of Sn^{2+} ions were inserted into the In_2O_3 lattice and other parts (in excess) formed the SnO_2 phase which remained amorphous. This result is in agreement with that obtained from XRD analysis. In other works both In_2O_3 and SnO_2 phase remained independent [4,7].

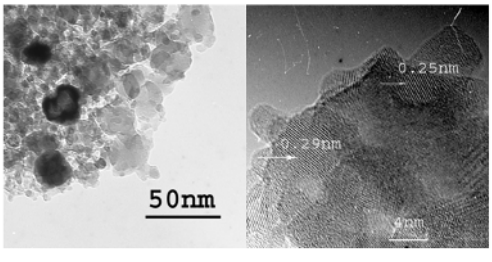

Fig. 2. (a) TEM image of the In_2O_3-SnO_2 nanocomposite; (b) HRTEM image for 2 different interplanar spacing patterns of In_2O_3

While in many cases thin films have a high density and a rough surface, one may guess that of such granular and porous In_2O_3-SnO_2 nanocomposite increases with rms.

The AFM image (Fig. 3) shows that the roughness (rms) increases with the SnO_2 content. The rms increases from 10.8 nm for In_2O_3-SnO_2 (10 wt% Sn) to about 18.7 nm for In_2O_3-SnO_2 (35 wt% Sn) nanocomposite, indicating, at a first sight, that the active surface of the In_2O_3-SnO_2 (10 wt% Sn) nanocomposite becomes higher than that In_2O_3-SnO_2 (35 wt% Sn), presuming a high electric response in presence of a reducing or an oxidizing gas.

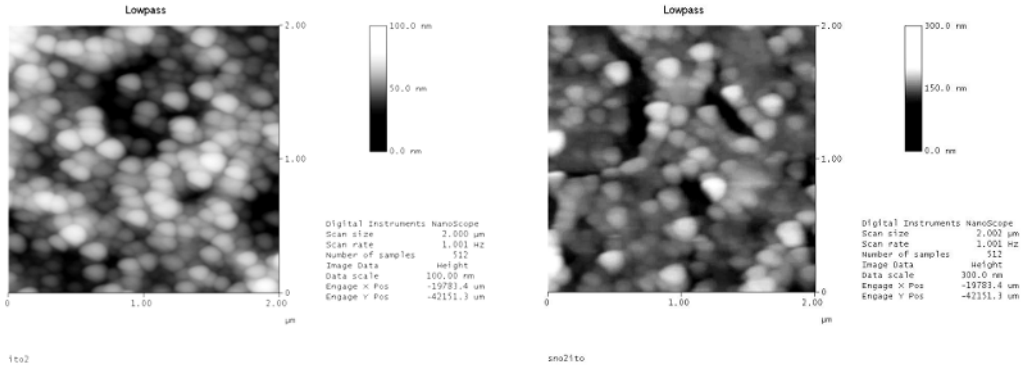

Fig. 3. AFM image of (a) In_2O_3-SnO_2 (10 wt% Sn) and (b) In_2O_3-SnO_2 (35 wt% Sn) nanocomposite

3.3 Sensor response of the In_2O_3-SnO_2 nanocomposite

We begin by studying the resistance behavior of In_2O_3-SnO_2 nanocomposites in ambient flowing air (without NO_2) versus temperature. This study is of prime importance to point out the ability of the sample to be used as a sensor. Figure 4 depicts the variation of the resistance of In_2O_3-SnO_2 nanocomposites versus temperature under constant flowing air. It can be easily seen that the In_2O_3-SnO_2 (35 wt% Sn) nanocomposite is more resistive than the In_2O_3-SnO_2 (10 wt% Sn) film; on the other hand the resistance increases while increasing Sn content, probably due to the presence of the amorphous SnO_2 phase.

It is worth noting (Figure 4) that In_2O_3-SnO_2 resistances nanocomposite decrease while varying the temperature from ambient to 230 °C. It is well known that the value of the conductivity strongly depends on the nature of the predominant defects involved in the conduction mechanism (mainly oxygen defects in semiconducting oxides). On the other hand, defects and charge carriers may be activated by increasing the temperature leading to an increase of the conductivity.

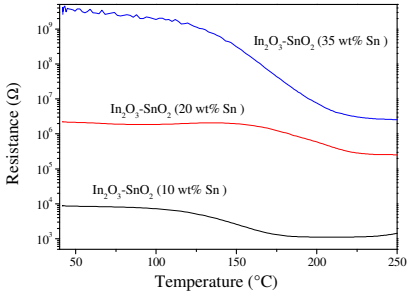

Fig. 4. Resistance of the screen printed In_2O_3-SnO_2 films measured at various operating temperatures in ambient air.

As NO_2 possesses the properties of an oxidant gas, in the present work, the sensor response of the film was represented by S (%):

$$S\ (\%) = [(Rg - Ra)/Ra] * 100 \quad (1)$$

Where Ra is the resistance of the film in air and Rg is that upon exposure to NO_2.
Figure 5 shows the response of the In_2O_3-SnO_2 films as a function of the operating temperature.

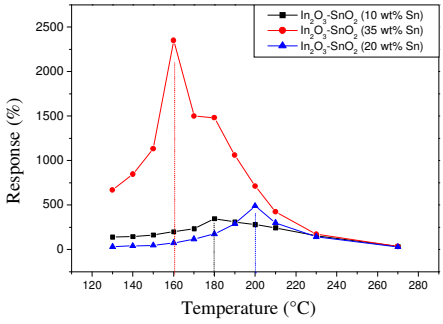

Fig. 5. Effect of working temperature on the sensor response in presence of 100 ppm of NO_2

According to Figure 5 we notice that the maximum of the response of the In_2O_3-SnO_2 (10 wt% Sn) layer occurs at an operating temperature of about 180 °C, while the In_2O_3-SnO_2 (20 wt% Sn and 35 wt%) nanocomposite exhibit a maximum at operating temperatures of about 200 °C and 160 °C, respectively. Therefore, one may note that the addition of a moderate quantity of SnO_2 to the In_2O_3 increases the response and decreases the operating temperature for NO_2 detection as already reported with similar to nanocomposites [8].

4 Conclusions

In this work, the structural and morphological properties of a nanocomposite formed by crystalline In_2O_3 and amorphous SnO_2 have been investigated. Subsequent to the increase of SnO_2 content, grain size, roughness (rms) and constant lattice 'a' increases. The nanocomposite-based sensor was found to be highly sensitive to NO_2, as SnO_2 content is optimized. It seems to be clear that the addition of a moderate quantity of amorphous SnO_2 to In_2O_3 (final Sn content = 35 wt%; final In content 65 wt %) increases the response and decreases the operating temperature of the screen-printed layer. However, it should be noted that the addition of a random quantity (non-quantified) of SnO_2 (exp: 20 wt% Sn) could degrade the NO_2 response and/or decrease the operating temperature.

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