Screen printed In$_2$O$_3$-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$_2$O$_3$ (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$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$ 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$_2$O$_3$ are promising candidates for the detection of low concentration of oxidizing gases like O$_3$.

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NOx.... In this work, we report on the sensing properties of screen-printed In$_2$O$_3$ (Indium Oxide) while adding a moderate quantity of SnO$_2$ (Tin Oxide). Screen printed In$_2$O$_3$-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$_2$O 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$_2$O$_3$-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$_2$O$_3$-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 tapping 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$_2$O$_3$-SnO$_2$ (10 wt% Sn), In$_2$O$_3$-SnO$_2$ (20 wt% Sn) and In$_2$O$_3$-SnO$_2$ (35 wt% Sn) nanocomposite. The XRD patterns of In$_2$O$_3$-SnO$_2$ (Fig. 1) show peaks that agree with the cubic structure of the In$_2$O$_3$ powder (JCPDS No. 89-4595). It is worth noting that only peaks corresponding to In$_2$O$_3$ appear in the XRD patterns; these peaks are less intense but finer as compared to that corresponding to In$_2$O$_3$ [3, 4, 5] indicating a possible increase of the grain size.

The In$_2$O$_3$-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$_2$O$_3$-SnO$_2$ (10 wt% Sn), $a_2 = 10,131$ Å for the In$_2$O$_3$-SnO$_2$ (20 wt% Sn) and $a_3 = 10,148$ Å for the In$_2$O$_3$-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$_2$O$_3$ lattice [3, 4, 5].
Fig. 1. XRD patterns of (a): In$_2$O$_3$ (10 wt% Sn), (b): In$_2$O$_3$-SnO$_2$ (20 wt% Sn) and (c): In$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$, respectively; hence, no evidence crystalline SnO$_2$ phase was detected. The In$_2$O$_3$ crystallites are therefore surrounded by an amorphous SnO$_2$ phase.

Thus, a part of Sn$^{2+}$ ions were inserted into the In$_2$O$_3$ 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$_2$O$_3$ and SnO$_2$ phase remained independent [4,7].

Fig. 2. (a) TEM image of the In$_2$O$_3$-SnO$_2$ nanocomposite; (b) HRTEM image for 2 different interplanar spacing patterns of In$_2$O$_3$.

While in many cases thin films have a high density and a rough surface, one may guess that of such granular and porous In$_2$O$_3$-SnO$_2$ nanocomposite increases with rms.

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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$_2$O$_3$-SnO$_2$ (10 wt% Sn) to about 18.7 nm for In$_2$O$_3$-SnO$_2$ (35 wt% Sn) nanocomposite, indicating, at a first sight, that the active surface of the In$_2$O$_3$-SnO$_2$ (10 wt% Sn) nanocomposite becomes higher than that In$_2$O$_3$-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$_2$O$_3$-SnO$_2$ (10 wt% Sn) and (b) In$_2$O$_3$-SnO$_2$ (35 wt% Sn) nanocomposite

3.3 Sensor response of the In$_2$O$_3$-SnO$_2$ nanocomposite

We begin by studying the resistance behavior of In$_2$O$_3$-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$_2$O$_3$-SnO$_2$ nanocomposites versus temperature under constant flowing air. It can be easily seen that the In$_2$O$_3$-SnO$_2$ (35 wt% Sn) nanocomposite is more resistive than the In$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$-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 $S$ (%):

$$S (%) = \frac{|(R_g - R_a)|}{R_a} \times 100$$  \hspace{1cm} (1)
Where $R_a$ is the resistance of the film in air and $R_g$ is that upon exposure to NO$_2$. Figure 5 shows the response of the In$_2$O$_3$-SnO$_2$ films as a function of the operating temperature.

![Figure 5](image_url)

**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$_2$O$_3$-SnO$_2$ (10 wt% Sn ) layer occurs at an operating temperature of about 180 °C, while the In$_2$O$_3$-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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ (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.

References