Investigation of the properties of Sb doping on tin oxide SNO₂ materials for technological applications

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Abstract: The conductivities of the oxide SnO₂ is dependent on the nature of the surrounding gas. This property stems from the adsorption or desorption on the surface of oxide grains. These phenomena are usually accompanied by electronic transfer between the adsorbed molecule and the semiconductor material, changing its conductivity. Tin oxidation and Sb doping were realized without and with heating process. The XPS technique and the TEM microscopy showed the synthesized nanocrystals. Simulated Monte Carlo program Casino is used for a scanning its profile. The surface characteristics are highlighted in the aim to be used as spatial gas sensors.

1. Introduction

Tin oxide SnO₂ is a semiconductor with a band gap of 3.6 eV. The oxygen vacancies, formed by the transfer of an oxygen atom of a normal site in the tin gaseous state, are used to obtain an n-type semiconductor. In fact, the released electrons can bind to tin atoms Sn⁴⁺, they become Sn²⁺ and behave as electron donors [1]. The adsorption is generally reversible for many gases at temperatures of the order of 400 to 500°C. For this, SnO₂ material is usually used in the field of monitoring air pollution and toxic gas detection. Furthermore, SnO₂ films stem others applications as solar cells, optoelectronic devices, thin film resistors, antireflection coatings, photochemical devices and electrically conductive glass. Tin oxide is also known for its catalytic properties, it facilitates the detailed breakdown of many hydrocarbons above 350°C. These properties are attracted the attention of scientists who have attempted to improve electrical performance by different experimental and simulated methods (microstructural stabilization, doping). [2,3] The doping of SnO₂ by antimony Sb is our goal in order to perform its conductivity to be better in detection of poisonous gas.

2. Experimental

The samples Sb: SnO₂ thin films were prepared using several techniques as reactive radio frequency (RF), sputtering process, spray pyrolysis technique, hydrothermal method from initial material SnCl₂.H₂O, polymeric precursor method by polymerization of a metallic citrate with ethylene glycol. An attempt has been made in our study to prepare Sb:SnO₂ films by the simple method of alternating electro-deposition in the Sn and Sb coatings electrolytes on SiO₂ substrate. The reaction mixture of SnO₂ and Sb powders was in 10% weight ratio. The performance of the growth sample film was largely influenced by the substrate material, its position and its temperature. In this case the electrical...
properties and the texture of the film are affected. We confirm that SnO$_2$ becomes Sb-doped using this technique and when the substrate is submitted to an heated effect. [4]

3. Results and discussion

3.1. XPS analysis and binding energies of the chemical elements in Tin oxide

The relative atomic concentrations of Sn and O were analyzed semi-quantitatively based on XPS spectra (Fig. 1). In the as-prepared sample, broad Sn3d5/2, Sn3d3/2, and O1s peaks exist around 486, 495 and 532.4 eV, and the concentrations of Sn and O are respectively about 38 and 52%, exhibiting evidence of non-stoichiometry. When the sample was annealed above 500°C for 8 h and more, Sn concentration decreases to 34% and O concentration increases to 66%, which corresponds to stoichiometric SnO$_2$. Fig.1a and fig.1b show respectively the binding energy in electron volt of the two elements oxygen with its O1s scan and the tin element with Sn d3/2 scan which corresponds to a good oxidation process giving rise to the SnO$_2$ compound. [5]

![Figure 1a. Binding energy of the element Oxygen O1s scan](image1)

![Figure 1b. Binding energy of the element tin Sn3d scan](image2)

3.2. Electron diffraction EDAX study and TEM spectroscopy

The EDX analysis shows the chemical composition of the Sb-SnO$_2$ sample. The concentration of Sb in the SnO$_2$ crystal is 10% as described as and confirmed by the same analysis. The corresponding EDAX spectrum shown in Fig.2 is in agreement with the electron diffraction micrography results. The peak broadening pattern clearly indicates that very small nanocrystals are present in the samples. The surface morphology of the SnO$_2$ sample is followed by Transmitted Electron Microscopy (TEM) apparatus which indicates a nanostructures grew onto the surface. In fig.3 a, b, c and d the electronic microscopy give us a good map of the surface of SnO$_2$-Sb doped and heated at the temperature above 500°C. The grains are so small, the morphology of the surface is uniform giving rise to crystallographic structure of Sb-SnO$_2$ with a good stoichiometric surface distribution. Increase of annealing time leads to further change of microstructure closed-packed crystallites with sharp boundary [6].
Figure 2. Energy Dispersive (EDX) showing the chemical elements inside the compounds with their energy position lines for Sb-SnO$_2$.

Figure 3a. Heated Sb doped SnO$_2$: TEM analysis showing the SnO$_2$ (grey color) and SnO island (white color).

Figure 3b. Heated Sb doped SnO$_2$: TEM analysis showing tin element distribution on the surface of the sample.

Figure 3c. Heated Sb doped SnO$_2$: TEM analysis showing the antimony element distribution on the surface of the sample.

Figure 3d. Heated Sb doped SnO$_2$: TEM analysis showing the oxygen element distribution on the surface of the sample.
4. SEM Casino program
The simulated program Casino was used as scanning electron microscopy to analysis the compounds Sb-SnO$_2$ on the substrate SiO$_2$. We give in fig.5a the electron X Ray absorbed by the matrice SnO$_2$ red color and the X-Ray diffused into the compound (blue color). In fig.5b the absorbed X-ray by the oxygen element present in the chemical formula of Sb SnO$_2$ showing the disposition of the grains on surface compounds.

![Figure 4a](image1.png)

![Figure 4b](image2.png)

**Figure 4a.** Casino ray dispatching into the crystal SnO$_2$ / SiO$_2$

**Figure 4b.** Electron scanning microscopy SEM of SnO$_2$ on SiO$_2$ substrate by Casino

5. Conclusion
Our work was based on the characterization of the SnO$_2$ oxide using spectroscopic methods. The EDS technique recorded spectra of as grown SnO$_2$ film showed that no metal phase was detected. The TEM microscopy images of SnO$_2$ films give us a good ideas on the films microstructures as grown and after annealing at 500°C for more than two hours and for one day. Increase of annealing time leads to further change of microstructure closed-packed crystallites with sharp boundary formed agglomerates of considerably smaller size (80-150 nm) with orientation parallel to the substrate.

6. References
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