STRUCTURAL CHARACTERIZATION OF HIGHLY ZINC DOPED SnO₂ FILMS OBTAINED BY SPRAY PYROLYSIS

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Tin oxide belongs to a group of surface-sensitive sensors, which detect gases by a change in surface conductivity (1, 2). In this work, we report the preparation and microstructural characterization of tin oxide thin films heavily doped with zinc. The structural and morphological properties were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) as a function of doped percentage.

We have used a simple and reproducible spray pyrolysis technique, tin oxide thin films doped by zinc were obtained over a glass substrate, we use a medical nebullizer, which was used as a solution atomizer, the glass was heated by hot plate. Additionally, the nebullizer was mounted onto a mobile stage, which provides oscillatory movement to obtain uniform covered thin film. The started solution was 0.05 M dilution of tin tetrachloride in methanol, zinc nitrate were used as a source of zinc. The doped atomic ratio Zn/Sn in solution was 0.1, 0.2, 0.5 and 1. The deposition temperature was 675 K.

TEM bright field images of tin oxide doped by zinc were polycrystalline and that their structure corresponded to the tetragonal Cassiterite system. Morphology were analyzed by scanning electron microscopy, it is shown that crystalline agglomerate in round shaped grains. Film thickness was obtained by reflectance measurement in F-20 fibber optic based system. Thickness varies as a function of doped percentage parameters between 300 to 700 nm.

The structural and morphological properties were studied as a function of doped percentage, the grain size change for each doped rate, for example Zn/Sn = 25.7 % at. we find nanostructure material with 3.4 x 65 nm, like show in fig. 1c. To get the composition (Zn/Sn ratio) and film stoichiometry (Sn/O ratio) we have analyzed the films by X-ray energy dispersive spectroscopy (EDS) DX-4, fig 2 show the proportion Zn/Sn in the film is less than that in the solution, nevertheless, it can be observed almost a linear correlation between both quantities. When Zn/Sn increase, we can see changes in the microstructure.

The feasibility of depositing zinc doped of tin oxide films has been demonstrated by a simple and reproducible spray pyrolysis technique. These results support the viability of the spray pyrolisis technique to obtain nanostructured materials including dopants.

References

2 Yamazoe N. Sensors Actuators 1991; 5; 7-19.
Fig 1. Bright field TEM micrographs of doped SnO₂ films deposited onto glass as a function of dopant contents in film. a) 5.8, b) 10.4 and c) 25.7 at. % Sn/Zn.

Fig. 2. Dopant concentration Zn/Sn in film (at. %) as a function of their contents in solution (at. %).