New semiconductor oxide nanocomposites obtained by aerosol-assisted chemical vapor deposition

I. Sayago[1], J.P. Santos[1*],J.L. Fontecha [1], M.J. Fernández[1], M.C. Horrillo[1], and M. Alonso[2]

[1] Instituto de Tecnologías Físicas y de la Información (ITEFI-CSIC), Madrid, Spain
[2]Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Madrid, Spain
Keywords: AACVD, nanocomposites, semiconductor oxides.
∗Presenting author email: jp.santos@csic.es

Abstract
In this work, the use of the Aerosol Assisted Chemical Vapor Deposition (AACVD) technique to obtain nanocomposites of zinc and tin oxide is investigated.
The aerosol was produced using two distinct techniques: an ultrasonic air humidifier and a Collison type atomizer. These two methods for aerosol generation produce different size distributions of droplets, which in turn resulted in very different film characteristics. The structure and surface morphology of the deposited thin film have been investigated by scanning electron microscopy (SEM). The deposition mechanism and the influence of size droplets on deposition will be considered.

Introduction
AACVD is a deposition technique that allows the growth of nanomaterials with a low cost, simplification of processes and the "in situ" growth of highly adherent films at relatively low temperatures (e.g. ≤500 °C). Unlike traditional deposition techniques (sputtering, sol-gel, CVD), the AACVD provides a flexible route to synthesize a variety of metal oxide semiconductor (MOX) for their application in gas sensing.
The aerosol droplet size depends largely on the method used to generate one. The aerosol droplet diameter is given by Lang's equation [1]. The average droplet size produced using a standard humidifier (20 kHz) and methanol as solvent is 45 μm. In contrast, the collision type atomizer generates an aerosol with a smaller droplet diameter of 0.3 μm.

Experimental and discussion
AACVD consists of an aerosol generator and a reactor. The substrates (silicon micromachined structures) are placed, in the latter. It has a heating resistor that allows reach temperatures up to 400 ºC. The carrier gas (air) transfers the generated aerosol droplets to the hot substrates, where the nanocomposite films are deposited. Two different aerosol generators have been used: the ultrasonic air humidifier (Artrom HC-130) and the Collison type atomizer (TSI 3076).
Samples have been sintered with the two aerosol dispenser types under the same conditions (temperature, time, solvent, concentration of precursor, carrier gas). The precursor solution has been obtained using zinc acetate (10 mmol) and tin (IV) chloride (10 mmol) dissolved in methanol (50:50 Zn:Sn mol% ratio).

We highlight the crucial role that the droplet size plays in the deposition process to control morphology and physical characteristics of the films as can see in SEM images (Figure 1) of the film deposited by AACVD with the two generators at 400ºC. The samples grown with the atomizer showed a surface formed by spherical nanoparticles with a typical size of 100 to 500 nm (Figure 1a). This morphology is indicative of an aerosol assisted CVD process where the extensive reaction has occurred in the gas phase. However, the samples grown by the humidifier had a complex morphology with different triangular and tetrahedral uniformly distributed structures. It was also observed the presence of regular hexagonal crystals and spearheads (Figure 1b). The EDX analysis confirmed that the first ones correspond to Zn and the last ones to Sn.

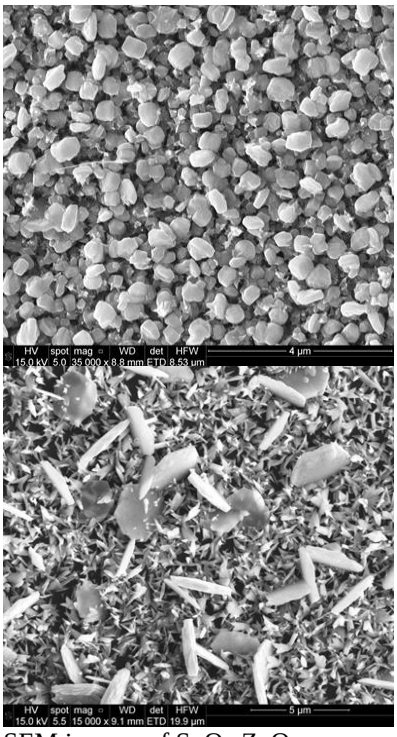

Figure 1. SEM images of SnO_2-ZnO nanocomposite as-deposited films from precursor solutions of 50:50 Zn:Sn mol% with a) atomizer and b) humidifier.

Acknowledgements
This work has been supported by the Spanish Economy and Competitiveness Ministry under the project TEC 2013-48147-C6-4-R. Authors want to thank Universidad de Extremadura for SEM and EDX analysis.