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A study on the microstructure and gas sensing properties of ITO nanocrystals

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Abstract

The effect of different SnO_2 loading (0–25 wt.%) on the microstructural, electrical and gas sensing properties of ITO (indium tin oxide) nanocrystals synthesized by a non-aqueous sol–gel technique was evaluated. TEM, HRTEM and XRD characterization has shown that all samples have a uniform grain morphology and narrow particle size distribution, while a remarkable size reduction was observed with the increase of tin loading in the mixed oxide formulation. Redox properties of the samples were also characterized by H_2–TPR. The gas sensing properties of ITO films towards CO (100–1000 ppm) and ethanol (50–400 ppm) have been investigated. On the basis of the characterization data, explanations of the observed sensing behaviour of ITO films are given.

Keywords: ITO; Indium tin oxide; Sol–gel routes; Gas sensing

1. Introduction

Indium tin oxide (ITO) is a class of materials containing Sn^{4+} ions hosted in the In_2O_3 structure with variable load up to 12–15%, offering the best available performance in terms of conductivity and transparency combined with excellent thermal stability [1]. ITO films, synthesized by physical or chemical deposition methods are used in many applications including flat panel display technology, functional glass and solar cells [2–4]. With respect to cost effectiveness and substrate structure and geometry liquid phase processing based on nanoparticle dispersions represents an advantageous technique, however making highest demands on the electrical conductivity, crystallinity, compositional homogeneity, and morphology of the nanocrystals. Particle sizes below 50 nm are a prerequisite to lower the sintering temperatures and to prevent the scattering of light, so that high visible transparency is guaranteed.

In this paper we focused our attention on the sensing properties of ITO nanocrystals prepared by a non-aqueous sol–gel route. In comparison to reaction in aqueous media, the synthesis of metal oxides nanoparticles in organic solvent provides better control over particles size, crystallinity and surface properties [5–7]. The absence of water, in fact, drastically reduces the reaction rates allowing a more controlled crystallization. The precipitates obtained are always well crystalline right after synthesis and never need an annealing process after synthesis. In almost all the cases the particles are single crystalline with no or very few bulk defects and by avoiding nasty surfactants and other heavy organic molecules the reaction leads to clean nanopowders which are close to 100% inorganic [5]. Moreover, the synthesized nanocrystals are suitable for making gas sensors because mesoporous thin/thick film with good interconnection between particles can be easily obtained.

Various In_2O_3-based materials were investigated for sensing applications in the monitoring of both reducing (H_2, CO, alcohols) and oxidizing gases, such as O_3 and NO_x [8–11], but little is reported about the sensing properties and mechanism of ITO materials [12,13]. Aim of this work is to find correlations between the observed sensing properties and the morphological,

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Table 1
Main characteristics of the sensors investigated

Code	SnO_2content (wt.%)	<D> [a] (nm)	Resistance [b] (Ω)	Sensor response	
				C_2H_5OH [c]	CO [d]
ITO-00	0	25	5408	109	10.9
ITO-08	8	10.9	209	3.6	3.4
ITO-15	15	8.9	83	2.5	3.2
ITO-25	25	8.3	134	2.4	2.5

[a] By XRD.
[b] Measured in dry air at 250 °C.
[c] 100 ppm.
[d] 1000 ppm.

structural and electrical characteristics of ITO materials with tin loading in the 0–25 wt.% range.

2. Experimental

2.1. Samples preparation and characterization

The ITO nanopowders (2–25 wt.% SnO_2) were prepared by the non-aqueous sol–gel technique as described elsewhere [14]. Briefly, the starting precursors indium(III) acetylacetonate and tin (IV) tert-butoxide were stirred with anhydrous benzyl alcohol, transferred to an autoclave and heated at 200 °C for 48 h. The obtained powders were washed with chloroform and dried in air at 60 °C. Pure In_2O_3 was prepared according to ref. [15].

XRD analysis was carried out on a Italstructure diffractometer mod. APD 2000 in the 2θ range from 10 to 90°. The mean particle diameter was calculated from line broadening analysis of the diffraction peaks. The average crystallite size, <D>, was estimated using the Scherrer equation as follows: $<D> = 0.9\lambda / B\cos\theta$ where λ, B, and θ are the X-ray wavelength of the radiation used ($CuK_{\alpha 1}$ = 1,54056 Å), the full width at half maximum (FWHM) of the diffraction peak, and the Bragg diffraction angle respectively.

TEM and HRTEM analyses were carried out on JEOL microscopes (mod. JEM2010 and JEM2100F), both equipped with Oxford Instrument INCA-200-TEM systems that allowed elemental analysis using energy-dispersive X-ray spectroscopy (EDXS) and on a Philips CM200 FEG equipped with a filed emission gun.

Temperature-programmed reduction experiments (TPR) were performed using H_2/N_2 (5%) gas mixture. Before the experiments, the samples were treated in air for 2 h at 400 °C, cooled at room temperature and held at this temperature in a flow of helium. The temperature was then increased, fluxing the H_2/N_2 (5%) gas mixture, at a rate of 10 °C/min up to 800 °C, and held at this temperature for 0.5 h. The hydrogen consumption was determined by means of a TCD detector.

2.2. Electrical and sensing test

In order to fabricate the sensor devices, the nanopowders were mixed with water to obtain a paste and then screen printed on alumina substrates (3 mm × 6 mm) supplied with interdigitated Pt electrodes and heating elements. Before sensing tests, the sensor was conditioned in air for 2 h at 400 °C. Electrical measurements were carried out in the working temperature range from 200 to 350 °C, with steps of 50 °C. The concentrations of target gases were varied from 100 to 1000 ppm for CO and from 50 to 400 ppm for ethanol. Measurements were performed under a dry air total stream of 200 sccm, collecting the sensors resistance data in the four point mode by means of an Agilent 34970 A multimeter.

The gas response, S, is defined as the ratio R_{air}/R_g, where R_{air} is the electrical resistance of the sensor in dry air and R_g its electrical resistance at different reducing gas concentrations.

3. Result and Discussion

3.1. ITO powders synthesis and characterization

The attractive features of the non-aqueous sol–gel route have been described in detail elsewhere [[5–7], and references therein]. This process enables the controlled preparation of ITO nanoparticles with varying tin oxide content over the range of 2–25 wt.% (Table 1). The samples are named according to the starting concentrations; for example, ITO-08 corresponds to 8 wt.% SnO_2 doping in In_2O_3. Fig. 1 shows the typical morphology of ITO nanoparticles. TEM micrographs reveal a relatively homogeneous size distribution of nearly spherical particles in the range from 5–10 nm. At higher magnification, well-developed and randomly

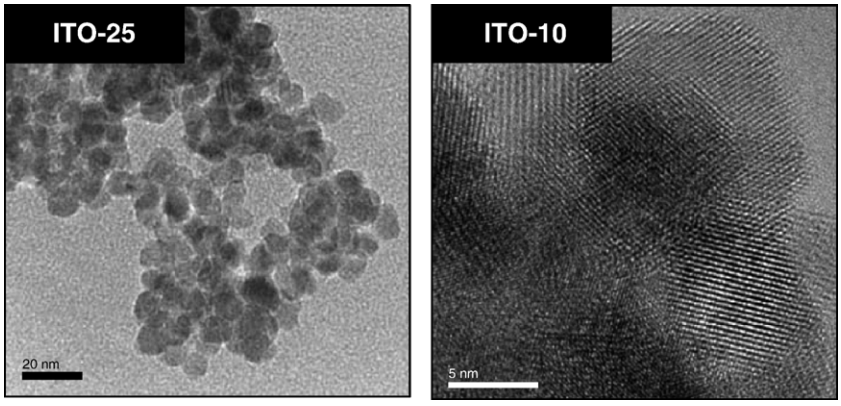

Fig. 1. TEM and HRTEM micrographs showing the uniform morphology, narrow size distributions and high crystallinity of ITO nanocrystals.