

Surface morphology engineering of metal-oxide films by chemical spray pyrolysis

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Abstract

Chemical Spray Pyrolysis Technique and a combination of sol-gel and spray pyrolysis techniques have been used in order to monitor the morphology of metal-oxide-based thin films to be used as functional materials. We can get from specular to rough-porous surfaces according to the physical-chemical conditions of the precursor / spraying solution. We have produced coatings of ZnO-based and NiO_x-based coatings from alcoholic and water solution. A single glass, ITO-precoated glass or alumina was used as the substrate. Porous materials of WO₃, CuWO_{4-x} and SnO₂ have been produced spraying either inorganic or metal alkoxide gels over a hot substrate. Morphology of coatings were evaluated by either SEM or optical measurements.

1 Introduction

Thin film technology is nowadays a widespread technique for materials fabrication, and numerous materials have been prepared in the form of thin films because of their technical and scientific demands. The fabrication techniques are based on different physical-chemical principles, but generally speaking most procedures can be distinguished as either vacuum-based or chemical-based techniques. Owing to their simplicity and inexpensiveness, chemical techniques have been studied extensively for the preparation of thin films; especially because they facilitate the desing of materials at the molecular level.

The chemical spray pyrolysis technique (SPT) is one of the major techniques to deposit a wide variety of thin films. It can use a variety of atomization techniques such as ultrasonic nebulisation, spray hydrolysis, corona spray pyrolysis, electrostatic spray pyrolysis, etc. Patil has recently reviewed the versatility of the chemical SPT [1].

A novel SPT procedure was developed in our laboratory [2,3,4] to deposit metal oxides (NiO_x, WO_x, ZnO, SnO₂ [3,45]) for good quality coatings. It renders, good quality thin films because the spraying solution is produced as small droplets with uniform distribution. The geometry of the chamber balances the gravitational force in such a way that large droplets can not be transported by the carrier gas and are therefore returned to the spray

chamber. This spray system has the following advantages: good size selectivity of the droplets, vorticity suppression of the spray gas in the spraying chamber and a reduced convection flow of the spraying gas in the deposition chamber.

The sol-gel process constitutes an important part of so-called "soft-chemistry". This process has many technological applications, being useful in the production of materials in thin film form [6]. It has a low cost and is rather simple [7]: a network is progressively built through inorganic polymerization reactions at room or moderate temperature. Depending on the regularity of the macromolecular structure, crystalline or amorphous materials may be prepared.

Between the starting solution and the final solid, several intermediate steps occur during which sols or gels are formed, thus giving the name of the sol-gel process. First, a sol (a colloidal suspension of solid particles in a liquid) is obtained. As the polymerization reactions proceed, the particles grow and coalesce forming clusters continuously increasing in size; finally leading to a gel which is a solid-fluid system where each phase is embedded in each other in such a way that the pores of the solid (filled with solvent) are of colloidal dimensions.

Since the ceramic is formed by reactions between molecular precursors, the homogeneity of the material is perfect at the atomic scale. This makes the sol-gel technique,

for instance, very suitable for producing optical coatings. A common process for coatings is by dipping the substrate in the colloidal solution; however one of the major drawbacks of this method is to produce films of limited thickness.

According to the kind of application, a specular or porous thin film is pursued; SPT has proved to be a very versatile technique in order to control the morphology of the coating [3,4,14,21,22]. Specular coatings are required mainly for optical applications, such as selective surfaces, mirrors, electrochromic devices, etc. Controlling the precursor solution (type of solvent and pH) and keeping fixed optimal spraying conditions such as temperature, gas pressure, etc., surface roughness can be monitored, allowing us to obtain surfaces ranging from rough to specular. In this work we shall discuss the morphology of NiO_x and ZnO films.

Porous materials are of interest in a variety of devices such as electrochromic 'smart' windows [8,9], nanocrystalline solar cells [10], batteries [11], photocatalytic reactors [12], and gas sensors [13]. Porosity can be achieved in many ways; in thin films the standard procedure relies on atomistic deposition of species under conditions giving a low ad-atom mobility so that a fine-grained crystalline or amorphous structure is built up. In this work, we take an alternative route and employ soft chemistry. When SPT and sol-gel are properly combined the resulting spray-gel technique (SGT) can be very useful for large area applications, letting the films morphology be monitored by controlling the precursors and deposition conditions. The technique basically consists in producing an aerosol from a gel, which is then sprayed over a hot substrate, where the film will grow. In this work we shall discuss the morphology of tungsten-oxide and tin-oxide-based coatings using the (SGT).

2 Morphology and related optical properties of coatings obtained by SPT

A schematic representation of an improved spray system with an optical system for an in-situ measurement of the film thickness is shown in Figure 1.

The optical system also allows the determination of the roughness of the films [14]. The morphology of the coatings was characterized by Scanning Electron Microscopy (SEM), the structure of the material by x-ray diffraction.

2.1 Pyrolytic zinc-oxide-based coatings

Zinc-oxide-based coatings are of much interest in science and technology due to their interesting potential applications [15-17], such as in thermoelectric and gas sensor devices, transparent electrodes, selective surfaces and piezo-electric devices. Using an improved system (see Fig. 1) we have grown undoped zinc oxide thin films and analyzed their growing characteristics, atomic composition, optical properties, photocatalytic response and morphology [18]. In this work the influence of spraying solution on morphology is analyzed.

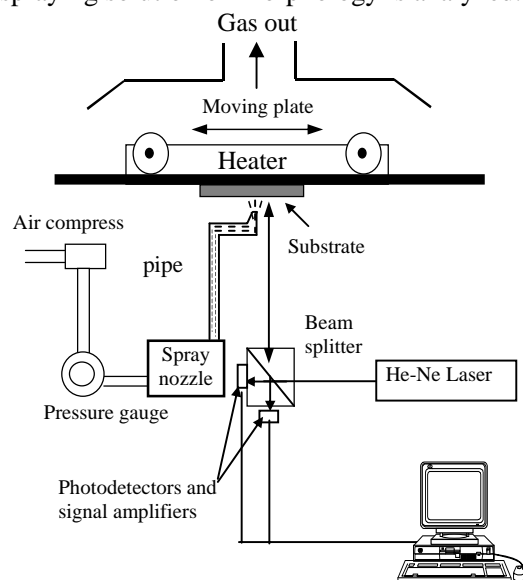


Figure 1. Spray system with an optical set-up for in-situ film thickness measurement.

Droplets of the spraying solution were obtained with a medical nebulizer and compressed air was used as gas carrier. In all experiments the gas carrier pressure was kept at 25 PSI during deposition. The fog of the spraying solution is directed to the hot substrate where the solvent evaporates taking place the pyrolytic reaction and the film starts to grow.

In order to ensure a homogeneous pyrolytic reaction on the hot substrate, the heater is moved back and forth perpendicularly to the spraying nozzle. An optical system was set up for in-situ thickness measurement during deposition; both a 632.8 nm wavelength laser beam and an array of optical sensors were used for this purpose, which also provided information on the profile of the growing film (see Fig.1).

The films were deposited onto a glass substrate pre-coated with $\text{SnO}_2\text{:F}$, which had a square resistance of 8Ω . Zinc-oxide films were deposited at 350°C and the pH of the spraying solution was kept constant at 5. The spraying was stopped when the thickness of the film reached the same number of interference fringes measured in-situ during deposition. Fig. 2 shows the in-situ normal reflectance as a function of time for different proportions of ethanol/water in the pyrolytic solution. For instance, for the ZnO film prepared at an ethanol/water ratio of 3/1, well defined interference fringes are observed to decrease in intensity as the film becomes thicker. Even more, as the amount of ethanol decreases in the precursor solution, the films become rougher as deduced of their interference fringes fast dimming; this trend is observed up to a ratio of ethanol to water of 0.2/1. For films prepared at a lower ethanol/water ratio the surface becomes smoother; then a well defined interference fringes are observed in the film prepared at a ethanol/water ratio of 0/1.

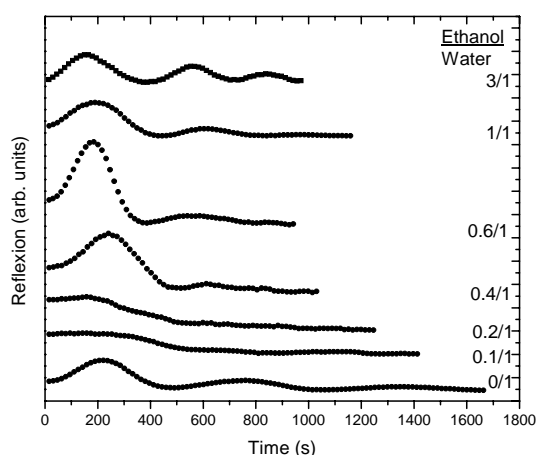


Figure 2. In-situ normal reflectance as a function of time for pyrolytic ZnO-based films. Each curve corresponds to the shown ethanol/water proportion in the precursor solution.

The SEM micrographs of the films surface for different ethanol/water ratios are shown in Fig. 3. At ratios of 0/1 and 3/1 the films morphology consists of uniform conglomerates, having a more rounded-shape in the first case. As the ethanol/water ratio increases from 0.1/1 to 0.2/1 and to 0.4/1, the conglomerates become less uniform and for ratios higher than 0.4/1 the surface gradually becomes smoother again. This behavior is

confirmed by measuring the diffuse transmittance, T_D , at a 550 nm wavelength for ZnO-based films obtained at different proportions of ethanol/water (see Fig.4). Films obtained at ratios of 0.1/1, 0.2/1 and 0.4/1 show optical diffusing surfaces, while films obtained with either pure water or pure ethanol show specular surfaces.

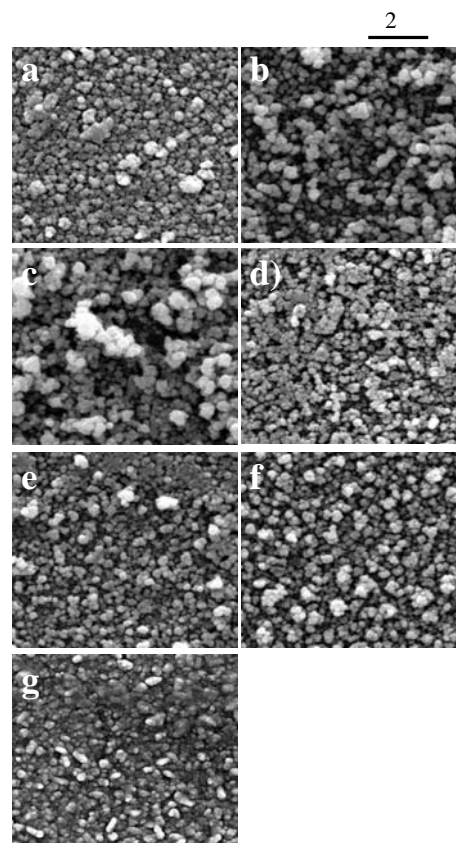


Figure 3. Morphology of ZnO-based films obtained from pyrolytic solutions at different ethanol/water proportions: (a) 0/1, (b) 0.1/1, (c) 0.2/1, (d) 0.4/1, (e) 0.6/1, (f) 1/1, and (g) 3/1.

2.2 Pyrolytic Nickel-oxide-based coatings

Nickel-oxide-based coatings have been largely studied for many kind of applications, like gas sensors, batteries, fuel cells, electrochromism, etc. They are particularly promising as electrochromic materials possessing anodic coloration [20]. Electrochromic materials are characterized by a reversible and persistent change of the optical properties under the action of an applied electric field. An electrochromic device is a multilayer system which basically comprises the electrochromic film, the counter electrode and the ionic

conductor. Optical modulation is associated with electrochemical insertion and extraction of ions to and from the electrochromic coating. Many techniques have been used to get a nickel-oxide thin film and most of them are based on vacuum processes. However, spray pyrolysis is also a good alternative for growing electrochromic-nickel-oxide-based coatings [2,21].

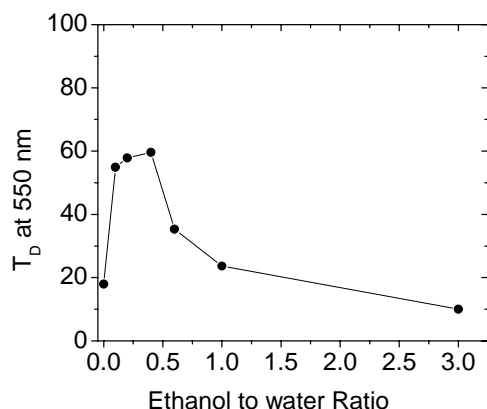


Figure 4. Diffuse transmittance, T_D , of ZnO-films obtained with different ethanol/water proportion in the spraying solution.

In this work we analyze the influence of the spraying solution in the electrochromism of NiO_x -based coatings which in turn depends on the morphology of the film.

Smooth nickel-oxide-based coatings with specular optical properties were produced in two ways: (a) using an alcoholic solution (ethanol) of $Ni(NO_3)_2 \cdot 6H_2O$ at 0.25 M, and (b) using aqueous solutions of the mixture $Ni(NO_3)_2 \cdot 6H_2O/Co(NO_3)_2 \cdot 6H_2O$ at 90/10M ratio. Those solutions were sprayed on to substrates at 300 °C during 30 minutes giving rise to coatings with 0,5-1 μm thickness. Electrochromism was studied by cyclic voltammetry using a potentiostat connected to a three electrodes cell, where a platinum foil and a saturated calomel electrode were used as counter and reference electrode, respectively. Aqueous solution of 0.1 M KOH was used as electrolyte for cation insertion/extraction. In-situ optical transmittance measurements together with electrochemical measurements were carried out using a He-Ne laser beam ($\lambda = 632.8$ nm). The transmittance measurements correspond to the cell + electrolyte + film system in which 100% transmittance corresponds to the cell + electrolyte system.

2.2.1 Films obtained from alcoholic solutions

The growth rate for coatings obtained from alcoholic solutions increases with increasing solution concentration; since the limiting dissolution of the salt was around 0.3 M, so we opted to use 0.25 M.

Figure 5 displays the cyclic voltammetric curve in 0.1M KOH electrolyte (bottom) and the in-situ associated transmittance measurements (top) for a nickel oxide. The cyclic voltammetry took place at a scan rate of 10 mV/s of the voltammogram shows the positive sweep direction, a rather extended anodic current followed by an anodic peak at around 0.6 V, whereas the negative sweep direction shows a cathodic peak at around 0.1V followed by a cathodic current region. From the in-situ transmittance measurements, it can be seen that during charge insertion (anodic reaction in the film) the transmittance of the coating decreases. Transmittance varies from 90% (bleached state) to 30% (colored state). Figure 6 shows the ex-situ spectral transmittance measurements in the visible range for the bleached and colored states. The transmittance for the bleached state reaches a maximum of about 93% at $\lambda = 540$ nm; at this wavelength the transmittance for the colored state is just 40%. This high optical transmittance in the bleached state is related to the smoothness of the film surface.

2.2.2 Films obtained from aqueous solutions

The NiO_x films were obtained spraying a 0.1 M aqueous solution of nickel nitrate on the hot substrate. X-ray diffraction analysis shows that coatings from either aqueous or alcoholic solutions produce the same structure [21]. From the in-situ measurements (see Fig. 7) one can deduce a similar electrochemical behavior for films obtained from alcoholic and water spraying solutions, even the optical contrast (transmittance variation between bleached and colored states) is noticeable for both of them. However, on the bleached state the optical transmittance of films obtained from aqueous spraying solution is only about 50%. This is ascribed to the rough surface of the pyrolytic films obtained from aqueous solution [3], which scatter the incident light.

Pyrolytic-nickel-oxide-based coatings obtained from aqueous solution can be dramatically improved in their optical transmittance at bleached state by adding in the spraying solution a small amount of cobalt nitrate [21]. Fig. 8 shows the ex-situ optical transmittance

for bleached and colored states obtained from a pyrolytic solution mixing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 10 % (molar) of cobalt nitrate. The improvement on the optical transmittance in this case is ascribed to the smoothness of the surface films [21] wherein the specular transmittance predominates.

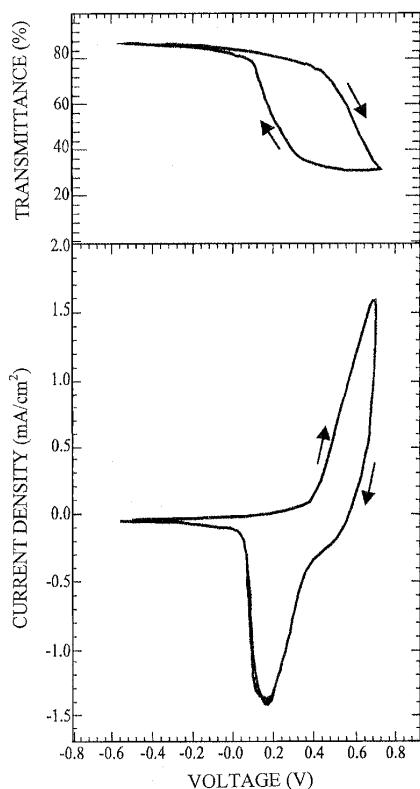


Figure 5. Cyclic voltammetric curve for a NiO_x film obtained from an alcoholic solution (bottom) and the in-situ transmittance at $\lambda = 632.8 \text{ nm}$ (top). The scan rate was 10 mV/s and the electrolyte was aqueous 0.1 M KOH .

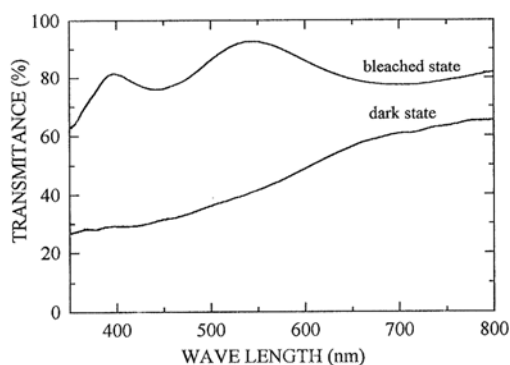


Figure 6. Optical transmittance for the bleached and colored state for the nickel oxide prepared by spray pyrolysis.

3 Morphology and related optical-electrical properties of coatings obtained by SGT

Porous materials are of interest in a variety of devices requiring a large interface between a solid and either a liquid or gas medium. Interesting applications are related to gas sensors. Semiconductor gas sensors use changes in the electrical conductance of a polycrystalline sensing ceramic to detect gas components in air. Grain contacts as well as the grain size in the oxide semiconductor microstructure, constitute key features for the transducer function [23,24]. In this work, we report highly porous WO_3 , CuWO_4 and SnO_2 coatings as gas sensing materials produced by SGT.

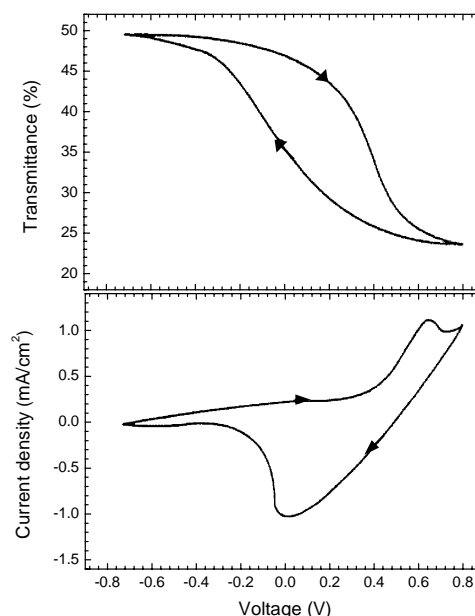


Figure 7. Cyclic voltammetric curve (bottom) and associated transmittance at 632.8 nm (top) for a pyrolytic nickel-oxide-based coating obtained from an aqueous solution of nickel nitrate. Electrolyte: 0.1 M KOH . Scan rate: 10 mV/s .

Mixed WO_3 and CuWO_4 films were prepared from a gel via acidification of 0.1 M sodium tungstate aqueous solution through a proton exchange resin. Different quantities of an aqueous solution of copper sulphate were added to the polytungsten sol to obtain a solution with a molar ratio of Cu/W from 0 to 100 %; full detail can be found in an earlier work by Damian et al. [25]. These solutions

were sprayed on to alumina substrates at 220 °C for 45 min.

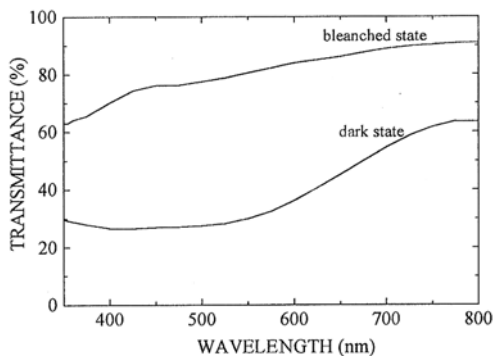


Figure 8. Optical transmittance for the bleached and colored state of the nickel-cobalt oxide film prepared by spray pyrolysis.

Nanocrystalline SnO₂ films were obtained from sols derived from either a metal alkoxide (*ter*-C₅H₁₁O)₄Sn or an inorganic (SnCl₄ 5H₂O) precursor stabilized with an ammonia aqueous solution. These obtained sols were sprayed on to glass and alumina substrates at 130 °C for 60 min. The alumina substrates were provided with preprinted gold electrodes, 0.3 mm apart, and a Pt-heating resistor on the reverse side. The samples to be tested were placed in a stainless steel chamber (4.4 L) and exposed to different butanol and ethanol vapor concentrations. The films were connected in series with both a known resistor and a 5V source. The conductance of the films was obtained by measuring the voltage drops across the resistor. Gas-sensing properties of the films were studied at 400 °C.

3.1 WO₃ and CuWO_{4-x} films

The as-deposited WO₃ film was amorphous [25]. After annealing it at a temperature higher than 300 °C, the film crystallized into the monoclinic WO₃ phase. The mixed WO₃-CuWO₄ films have similar behavior; the annealed forms have WO₃ as well as CuWO₄ phases. Fig. 9a depicts the morphology of an WO₃ film after annealing it for 3 h at 600 °C; the film was made from a solution with Cu/W molar ratio of 7%. The film's surface shows a rough topography consisting of interconnected rings and agglomerated grains. Indeed, this rough surface topography is characteristic of WO₃ films made of solutions with Cu/W molar ratio of less than 10%. The surface topography becomes smoother for WO₃ films made from

solutions with Cu/W molar ratio higher than 10% : the higher the ratio, the smoother the surface becomes.

Fig. 9b shows the typical morphology of a CuWO_{4-x} film obtained from a solution with a Cu/W molar ratio of 7%[[Has this film already been annealed?]]. The plot in Fig. 9c displays the results of a detailed study on the gas sensitivity to 5 ppm of ethanol and butanol in air of annealed CuWO_{4-x} films made from solutions with Cu/W molar ratios ranging from 0 to 100%. Clearly, films made from solutions with a 10% Cu/W-molar-ratio show the highest sensitivity to butanol, while those made from solutions with a 7% Cu/W-molar do so for ethanol. A detailed account of these is given elsewhere [25]

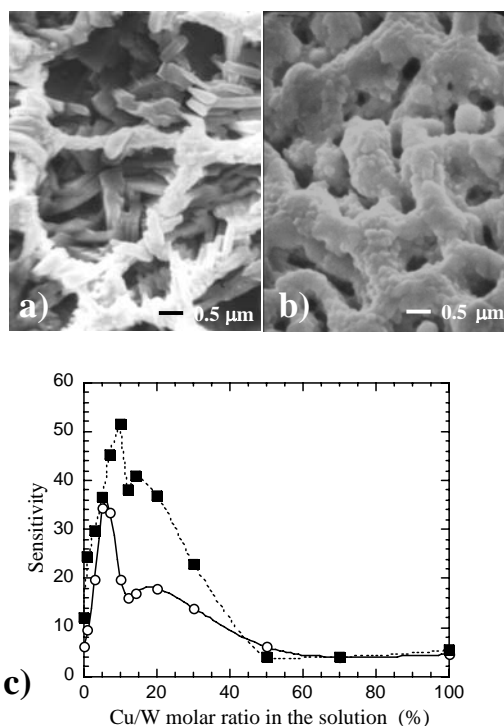


Figure 9. SEM micrograph for (a) WO₃ and (b) CuWO_{4-x} films obtained from a solution with the Cu/W molar ratio of 7%, and (c) the gas sensitivity vs molar ratio Cu/W from the solution used to obtain the films and being exposed to 5 ppm of ethanol (O) and butanol (■) in air. The operating temperature is 400 °C.

3.2 Nanocrystalline SnO₂ films

The as-deposited SnO₂ films from inorganic and metal alkoxide precursors were either

amorphous or with very small grain sizes. After annealing at a temperature of 400 °C, the samples crystallize in to SnO₂ with mean grain sizes of around 20 nm. The morphology of SnO₂ films obtained from SnCl₄·5H₂O and (C₅H₁₁O)₄Sn precursors and annealed at 500°C for 2 h are shown in Fig. 10a and Fig. 10b, respectively. The surface of the film obtained from an inorganic precursor is smooth, whereas the surface of the film obtained from a metal alkoxide is very rough, predominantly composed of interconnected rings.

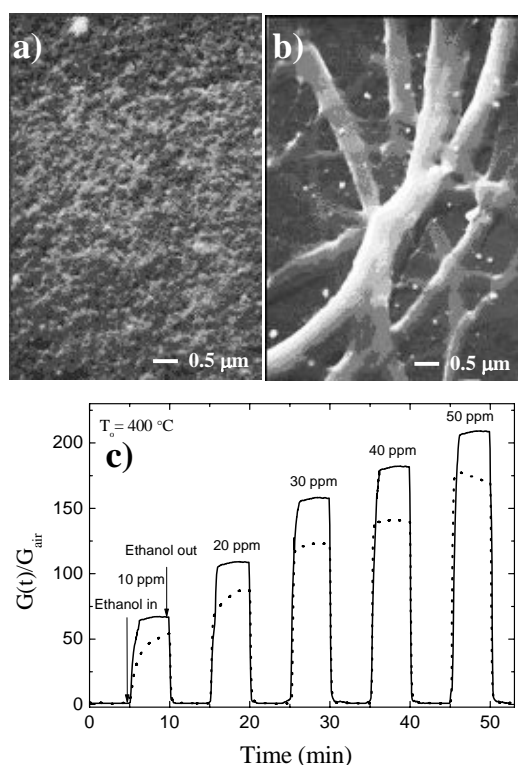


Figure 10. SEM micrographs for a nanocrystalline SnO₂ obtained from (a) an inorganic and (b) metal alkoxide precursors, and (c) their conductance response ($G(t)/G_{\text{air}}$) vs. time, to different ethanol concentrations in air. The dotted and solid line correspond for films obtained from an inorganic and metal alkoxide, respectively.

Different degrees of porosity of SnO₂ thin films were obtained using alkoxide and inorganic precursors. These annealed films were used for gas-sensing experiments. Fig. 10c shows their conductance response to different concentrations of ethanol in air. It was found that the gas sensing properties of the highly porous film obtained from metal alkoxide is

more stable and has shorter response and recover time than the compact film.

4 Conclusions

The chemical spray pyrolysis technique (SPT) offers an attractive way to prepare a wide variety of thin films materials for different kind of applications. The quality and properties of these thin film materials depend largely on the preparation conditions of particular importance for functional materials is the film's morphology, which with the SPT can be varied from specular to rough surfaces according to the spraying solution conditions. In this work we have shown the influence of water alcohol spraying solutions on the morphology of the resulting films; this characterization allow the monitoring of the films' surface morphology.

Combining the SPT with the sol-gel technique (SGT) gives the possibility to produce, under appropriate conditions very rough and highly diffuse film. under appropriate conditions. This combined technique offers new possibilities for the fabrication of highly porous films of WO₃, CuWO_{4-x} and SnO₂. The gas sensing properties of these films are excellent because of the large interface contact they present to any gas medium.

5 Acknowledgements

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