HIGHLY POROUS THIN FILMS OBTAINED BY SPRAY-GEL TECHNIQUE

Solís J.(1,2) jsolis@ipen.gob.pe; Rodríguez J. (1,2) jrodriguez@ipen.gob.pe;
Estrada W. (1,2) westrada@ipen.gob.pe

(1) Instituto Peruano de Energía Nuclear / Lima 41, Perú
(2) Facultad de Ciencias – Universidad Nacional de Ingeniería / Lima, Perú

ABSTRACT

Combining the spray pyrolysis and the sol-gel techniques (spray-gel) gives the possibility to produce very rough and highly diffuse films, under appropriate conditions. This technique is suitable for producing multifunctional metal oxides for gas-sensing, electrochromism, microbattery, and photocatalysis applications; due to the fact that it yields a large interface between a solid and a gaseous/liquid medium. The process basically consists in producing an aerosol from a gel, which is sprayed over a hot substrate, where the film is going to grow. In this work we present the results on highly porous SnO_2, WO_3, and phosphotungstic acid (PWA) thin films obtained by spray-gel.

1 INTRODUCTION

Porous materials are of interest in a variety of devices such as electrochromic 'smart' windows [1,2], nanocrystalline solar cells [3], batteries [4], photocatalytic reactors [5], and gas sensors [6]. The porosity yields a large interface between the solid and a liquid or gaseous medium. The electrochromism is the ability to attain different optical properties when a voltage is applied across them and relies on ion insertion/extraction from an electrolyte [1]. The optical properties are reversible so that the original state can be recovered by a reversal of the polarity. Semiconductor gas sensors use changes in the electrical conductance of a polycrystalline sensing ceramic to detect gas components. A chemical species on the semiconductor surface yields a signal that is transduced through the microstructure of the sintered ceramic to form a conductance change. Grain contacts, as well as the grain size in the oxide semiconductor microstructure, constitute key features for the transducer function [7].

Porosity can be achieved in many ways; with regard to thin films one normally 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 the soft chemistry. Both the spray pyrolysis and the sol-gel techniques are interesting deposition techniques for thin film fabrication (simple and low cost). When they are combined properly (spray-gel) can be very useful for large area applications and the films morphology can be easily monitored controlling the precursors and deposition conditions. The process basically consists in producing an aerosol from a gel, which is sprayed over a hot substrate, where the film will grow.

In this work, we report highly porous and diffuse phosphotungstic acid (PWA), WO_3, $CuWO_{4-x}$ and SnO_2 thin films produced by the spray-gel technique.

2 EXPERIMENTAL

The outline of the spray system used in this work is described elsewhere [8]. Combined spray pyrolysis and sol-gel techniques were used to obtain films onto either alumina substrate or glass slide. Precursor of the spraying solution for preparing the phosphotungstic acid films was an aqueous solution of 0.1M sodium tungstate ($Na_2WO_4{\cdot}2H_2O$, 99%) mixed with orthophosphoric acid (H_3PO_4, 85%) with a molar ratio P:W of 1:12; a detailed technical description was given by Medina et al. [9]. The gel was obtained via acidification of the aqueous solution through a proton exchange resin. The films were obtained by spraying the gel onto substrates at 300 °C for 60 min. 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 earlier work by Damian et al. [10]. These solutions were sprayed on to alumina substrates at 220 ºC for 45 min. Nanocrystalline SnO_2 films were obtained from a sol obtained from a metal alkoxide (*ter*-$C_5H_{11}O)_4Sn$ or an inorganic ($SnCl_4$ $5H_2O$) precursors stabilized with an ammonia aqueous solution. The obtained sols were sprayed on to glass and alumina substrates at 130 ºC for 60 min.

The microstructure of the films was analyzed by a scanning electron microscope (SEM), x-ray diffraction and infrared spectroscopy.

The electrochromism was studied with films deposited onto glass slide precoated with transparent and electrically conducting SnO_2:F. An EG&G PAR 273 potentiostat/galvanostat instrument was used for cyclic voltammetry for charge insertion/extraction. A three electrode-cell with an electrolyte of 1 M H_2SO_4 aqueous solution was set; the electrochromic film was placed as the working electrode (WE), a platinum layer as the counter electrode (CE) and a Saturated Calomel (SCE) as the reference electrode (RE). The voltage span was between –0.8 and 0.6 V vs SCE at a scan rate of 10 mV/s. Diffuse spectral normal transmittance/ reflectance were recorded in the 400 < λ < 850 nm wavelength range using a double beam Perkin-Elmer Lambda 9 spectrophotometer equipped with an integrating sphere.

For gas sensing studies the films were deposited onto alumina substrates using 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 RESULTS AND DISCUSSION

3.1 Phosphotungstic acid (PWA) films

The crystal structures of the films obtained by x ray diffraction and infrared spectroscopy correspond to phosphotungstic acid ($H_3PW_{12}O_{40}$.21 H_2O). A typical SEM micrograph of a phosphotungstic acid film is shown in Figure 1. The film showed a morphology based on fiber-shape bridges. This type of configuration was distributed uniformly through out the film surface, and behaves as highly diffusing surface in the visible range.

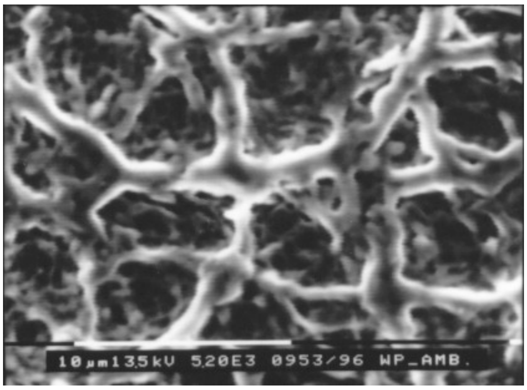

Figure 1. SEM micrograph for as-deposited PWA film.

Figure 2 displays a typical total optical transmittance and reflectance spectra for a phosphotungstic acid film for the as-deposited, colored and bleached states. The inserted charge densities during cyclic voltammetry were calculated by numerical integration of the current density with respect to time. The inserted/extracted charge density was 55.6 mC cm^{-2}.

Those results indicate that at appropriate conditions a highly porous electrochromic film can be grown using the spray-gel technique. Those films present a highly diffusing component in the transmittance and reflectance spectra.

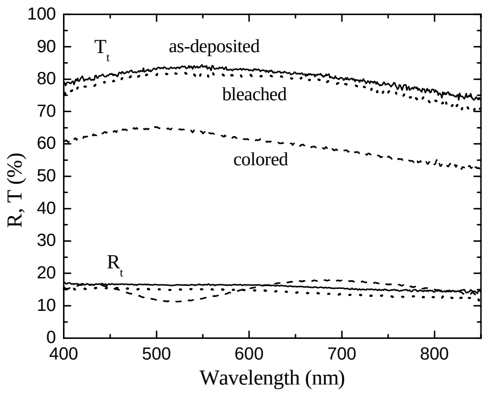

Figure 2. The total spectral transmittance and reflectance for a PWA film in as-deposited (solid line) state and after coloration (dotted line) and bleaching (dashed line) by H^+ intercalation/deintercalation.

3.2 WO_3 and $CuWO_{4-x}$ films

The as-deposited WO_3 film was amorphous. After annealing the samples at a temperature higher than 300 °C, the film crystallizes to the monoclinic WO_3 phase. The mixed WO_3-

$CuWO_4$ films have similar behaviour, the annealed films have WO_3 as well as $CuWO_4$ phases. The morphology of the post-annealed WO_3 film at 600°C for 3 h is shown in Fig. 3a. The surface of the film is very rough, with interconnecting rings and the smooth fibers turn to agglomerated grains. The films obtained from solutions of Cu/W with a molar ratio of less than 10 % present surface "irregularities" which start to decrease when films are made from a molar ratio of Cu/W higher than 10 %. Fig. 3b shows the morphology of $CuWO_{4-x}$ films obtained from a solution with the Cu/W molar ratio of 7%.

The annealed films were used for gas-sensing experiments. Figure 4 shows the results of a detailed study on the gas sensitivity of annealed $CuWO_{4-x}$ films obtained from different solutions with a molar ratio of Cu/W from 0 to 100 % to 5 ppm of ethanol and butanol in air. It was found that the optimal molar ratio of Cu/W for the solutions used to prepare the films was 10% and 7% with high gas sensitivity to butanol and ethanol, respectively.

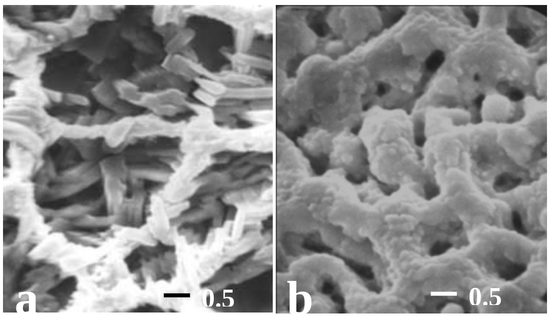

Figure 3. SEM micrograph for (a) WO_3 and (b) $CuWO_{4-x}$ films obtained from a solution with the Cu/W molar ratio of 7%.

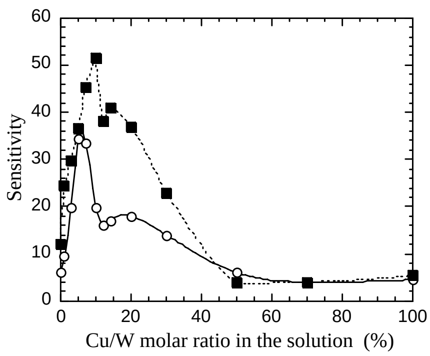

Figure 4. The gas sensitivity vs molar ratio Cu/W from the solution used to obtain the films and being exposed to 5 ppm of ethanol (○) and butanol (■) in air. The operating temperature is 400 ºC.

3.3 Nanocrystalline SnO_2 films

The as-deposited SnO_2 films from an inorganic and metal alkoxide precursors were amorphous or with a very small grain size. After annealing at a temperature of 400 °C the samples crystallize to the SnO_2 with a grain size of around 20 nm. The morphology of the post-annealed SnO_2 films obtained from $SnCl_4$ $5H_2O$ and $(C_5H_{11}O)_4Sn$ precursors at 500°C for 2 h are shown in Fig. 5a and Fig. 5b, 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, with interconnecting rings.

The annealed films at 500°C were used for gas-sensing experiments. Figure 6 shows the conductance response of both films obtained from an inorganic and metal alkoxide precursors to different concentrations of ethanol in air. It was found that the gases sensing properties of the highly porous film obtained from metal alkoxide is more stable and has a short response and recover time. The compact film is not stable and has a long response time and lower sensitivity than the porous one. Different degrees of porosity of SnO_2 thin films were obtained using metal organic or inorganic precursors.

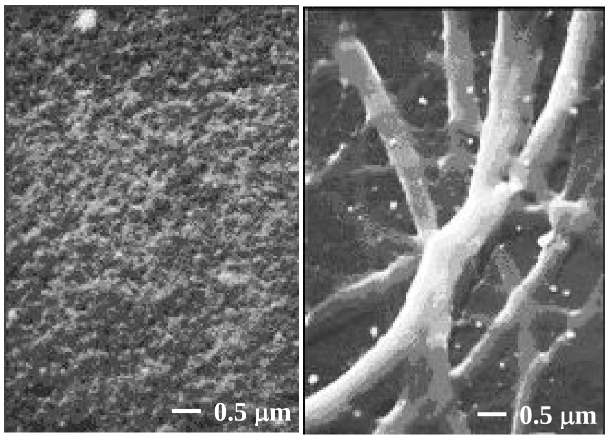

Figure 5. SEM micrographs for a nanocrystalline SnO_2 obtained from (a) a inorganic and (b) metal alkoxide precursor.

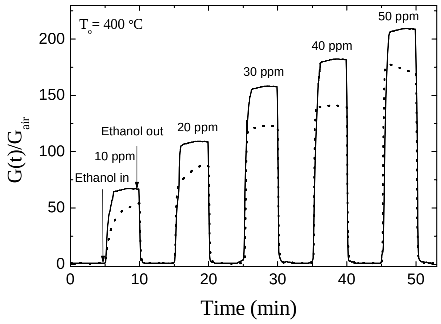

Figure 6. the conductance response vs. time, $G(t)/G_{air}$, subjected to different ethanol concentrations in air. The solid and dotted line correspond for films obtained from a metal alkoxide and inorganic precursor, respectively.

4 CONCLUSIONS

Combining the spray pyrolysis and the sol-gel techniques (spray-gel) gives the possibility to produce very rough and highly diffuse films, under appropriate conditions. This technique brings new possibilities for fabricating highly porous films of PWA, WO_3, $CuWO_{4-x}$ and SnO_2. The gas sensing and electrochromism properties are enhanced using these films due to a large interface contact with the liquid or gaseous medium.

5 ACKNOWLEDGEMENTS

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