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Nanocrystalline SnO_2 by liquid pyrolysis

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Liquid pyrolysis is presented as a new production method of SnO_2 nanocrystalline powders suitable for gas sensor devices. The method is based on a pyrolytic reaction of high tensioned stressed drops of an organic solution of $SnCl_4 \cdot 5(H_2O)$. The main advantages of the method are its capability to produce SnO_2 nanopowders with high stability, its accurate control over the grain size and other structural characteristics, its high level of repeatability and its low industrialization implementation cost.
The characterization of samples of SnO_2 nanoparticles obtained by liquid pyrolysis in the range between 200ºC and 900ºC processing temperature is carried out by X-ray diffraction, transmission electron microscopy, Raman and X-ray photoelectron spectroscopy. Results are analyzed and discussed so as to validate the advantages of the liquid pyrolysis method.

Keywords: SnO2, liquid pyrolysis, grain size, nanopowder, gas sensor.

SnO_2 nanocristalino mediante pirólisis líquida

La pirólisis líquida se presenta como un nuevo método para producir SnO_2 nanocristalino en polvo ideal para sensores de gas. El método se basa en una reacción pirolítica de gotas altamente tensionadas procedentes de una solución orgánica de $SnCl_4 \cdot 5(H_2O)$. Las principales ventajas del método son la capacidad para producir nanopartículas de SnO_2 con una gran estabilidad, el preciso control sobre el tamaño de grano y sobre otras características estructurales, el alto nivel de repetibilidad y el bajo coste en su implementación industrial.La caracterización de las muestras de las nanopartículas de SnO_2 obtenidas por pirólisis líquida en un rango de temperatura de procesado que va de 200ºC a 900ºC se ha realizado mediante difracción de rayos X, microscopía electrónica de transmisión, espectroscopía Raman y espectroscopía fotoelectrónica de rayos X. Los resultados se han analizado y discutido. Éstos validan las ventajas del método de la pirólisis líquida.

Palabras clave: SnO_2, pirólisis líquida, tamaño de grano, polvo nanométrico, sensor de gas.

1. INTRODUCTION

Since SnO_2 is a semiconductor material suitable for gas sensor devices (1), the research effort in the last years has focused on its synthesis techniques in order to obtain nanoparticles with predefined characteristics. Because gas sensor devices which involve changes in resistance are based on surface reactions, it is essential to achieve a high specific surface sensor material to improve their sensitivity (2). Thus, nanopowders of SnO_2 are required for the implementation of such devices. Up to now, several techniques have been used in order to carry out their production: sol-gel, spray-pyrolysis, CVD, sputtering, and laser ablation (3). Whereas the first two have unknown influences on some parameters, the last three are expensive and have problems with material stoichiometry.

Thereby we propose, as an alternative to previous procedures, the liquid pyrolysis technique as a new method to obtain nanometric grains of SnO_2 with a high level of stability and a great specific surface. The control on the grain size and on other structural characteristics, e.g. the strain, the stress and the grain shape, is noteworthy not only for its accuracy but for the influence on the gas sensor parameters. The repeatability and the low cost of the new method make it appropriate for industrial implementation purposes.

2. EXPERIMENTAL PROCEDURE

The technique is based on a pyrolytic reaction producing SnO_2 nanocrystalline particles by using a liquid solution. The method consists in two main steps. First an organic solution of $SnCl_4 \cdot 5(H_2O)$ in methanol is prepared. Then, high tensioned droplets micropiped from the solution are spread on a polished substrate. This enables a high surface for a posterior oxidation treatment (whithin an adequated atmosphere) which facilitates the access of oxygen to droplets.

The second step is a thermal treatment within ambient atmosphere. The substrate with the spread droplets is introduced in a muffle furnace and heated. The temperature rate has been of $20 K min^{-1}$ up to achieve the wanted value of processing temperature. Then, droplets are heated for 24 minutes at this temperature. Because the initial trial material is not stable (it has several defects and a lack of crystallinity) and gas sensors work at high temperatures a thermal impact treatment is needed in order to have stabilized material. It has been proven experimentally that 24 minutes is enough time to obtain stabilized SnO_2 by liquid pyrolysis. The going down of the temperature is free.

The samples are obtained by varying two parameters, namely, the solution concentration and the processing tempe-

rature. The working ranges are 0.1 to 5 molar for the concentration and 200ºC to 900ºC for the temperature.

The structural characterization of SnO_2 nanopowders obtained by liquid pyrolysis is made by XPS (X-Ray Photoelectron Spectroscopy), XRD (X-Ray Diffraction), TEM (Transmission Electron Microscopy) and Raman Spectroscopy.

XPS data were collected in a Physical Electronics 5500 spectrometer working at a pressure of 6E-9Torr. Aluminum K_α X-Rays were produced by a Physical Electronics X-Ray source, which produces photons with an energy of 1486.6eV and with a natural line width of 0.9eV.

X-Ray diffraction patterns have been obtained with a Inel CPS-120 X-Ray diffractometer using Cu K_α radiation (λ=1.5406Å), with an operating voltage of 40kV and a current of 30mA. Data were collected in steps of 0.03 degrees (2θ) from 0 to 120º.

The TEM (Transmission Electron Microscopy) observation of the powders was carried out by using a CM30 SuperTwin electron microscope operating at 300keV. The powders were mixed, dispersed in ethanol and deposited on a carbon membrane for observation.

Raman Spectroscopy was performed with a Jobin-Ybon T6400 instrument with a laser source of 514nm wavelength and an incident power of 2mW. Data acquisition time was 12 minutes in a range between 300 and 900cm^{-1}.

3. RESULTS AND DISCUSSION

The analyzed material obtained by liquid pyrolysis has no contaminants as XPS data show in figure 1B, though some residual Cl from the initial solution remains at 200ºC (figure 1A).

The crystallization of the nanopowder has been studied as a function of the processing temperature. Figure 2 shows the XRD patterns of the different samples obtained under various processing temperatures. It can be observed that the crystallization occurs at about 400ºC and that nanopowder increases its crystallinity with the increase of the processing temperature. A similar result is achieved by Raman spectroscopy data (figure 3) that reveal that E_g (472cm^{-1}), B_{2g} (774cm^{-1}) and A_{1g} (630cm^{-1}) peaks start to develop at 400ºC. Other vibrations which develop at higher processing temperatures are related with surface modes usually present in nanosized tin oxide (4). This feature indicates that the specific surface of our material is high, what is required for gas sensors applications where gas/material reactions take place at material surface. From 600ºC to 700ºC processing temperature a qualitative change on the shape of the peaks is noted in figures 2 and 3. This change on the intensity of the peaks involves a change on the crystallinity degree and it will have effects on the behavior of the distortion, the strain and the grain size curves. Crystallized samples exhibit the cassiterite SnO_2 structure, what is shown both by XRD and by Raman spectroscopy data.

Grain size from samples processed at different temperatures is calculated applying the Scherrer's formula (5) on XRD data

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D is the dimension of a crystal, K is a fitting constant close to 1 which is adjusted by TEM, λ is the wavelength, θ is the angle of the analyzed reflection and β is the rate between the area and the intensity of the analyzed reflection.

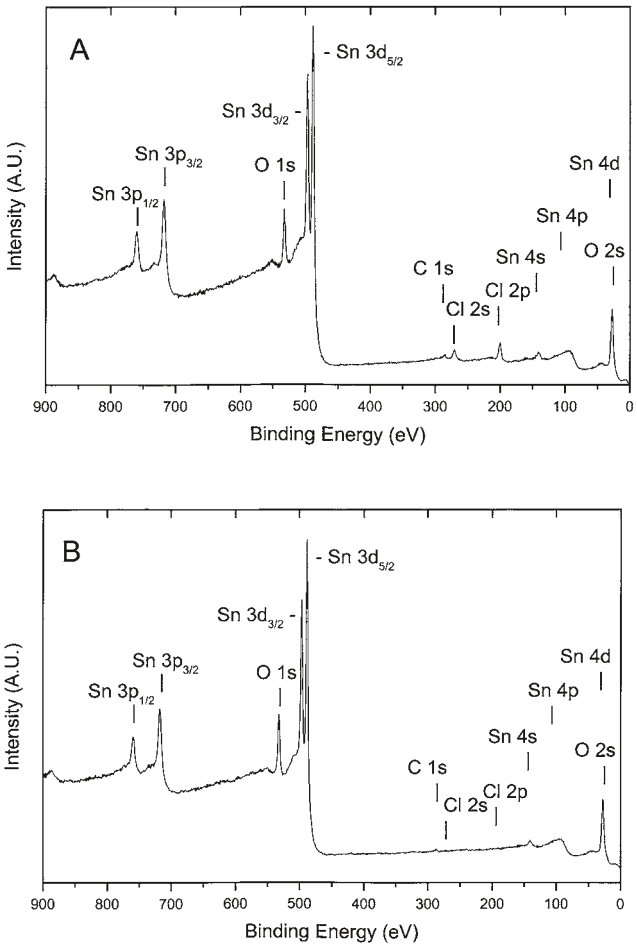

Figure 1. XPS spectrums of 5M solution concentration samples obtained at a processing temperature of (A) 200ºC and (B) 800ºC.

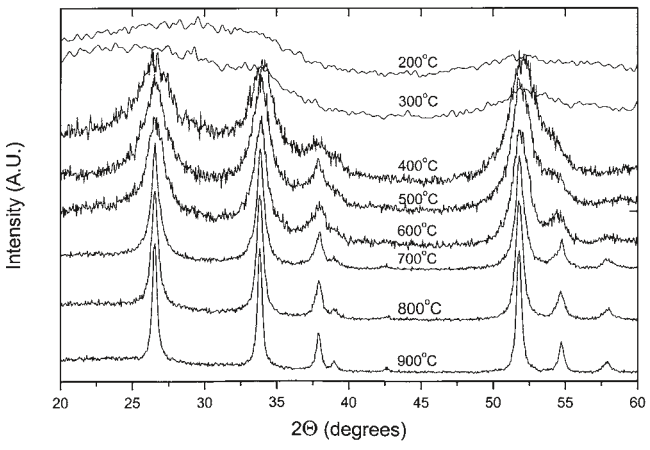

Figure 2. XRD diffractograms of 5M solution concentration samples. From top to bottom: 200, 400, 500, 600, 700, 800 and 900ºC processing temperature.

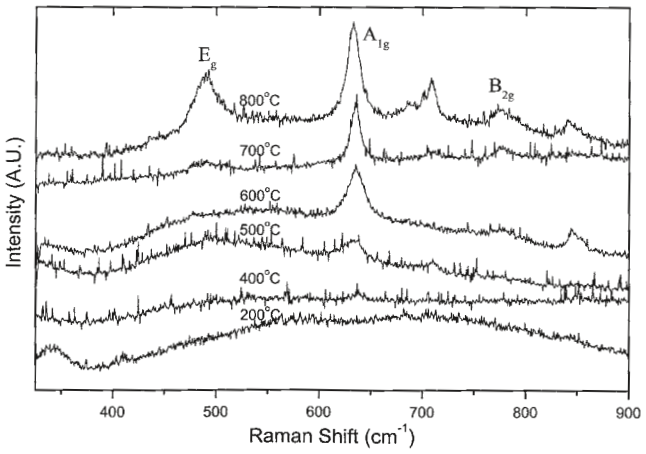

Figure 3. Raman spectrums of 5M solution concentration samples. From bottom to top: 200, 400, 500, 600, 700 and 800ºC processing temperature.

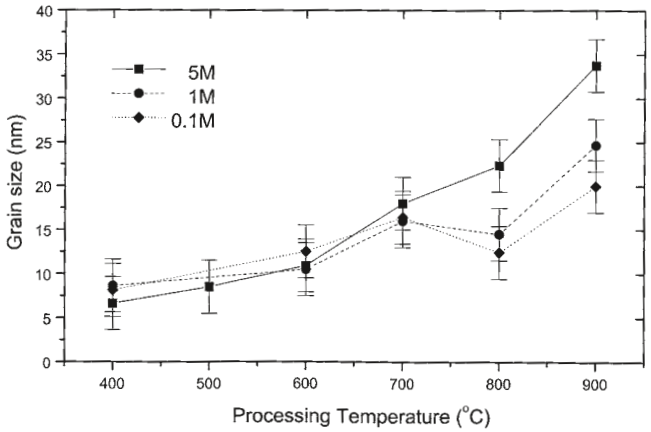

Figure 4. Grain size of samples of different solution concentration vs. processing temperature. Errors in measurements are indicated by error bars. These errors were evaluated taking into account the difference between results from Scherrer formula (see text) and TEM observations

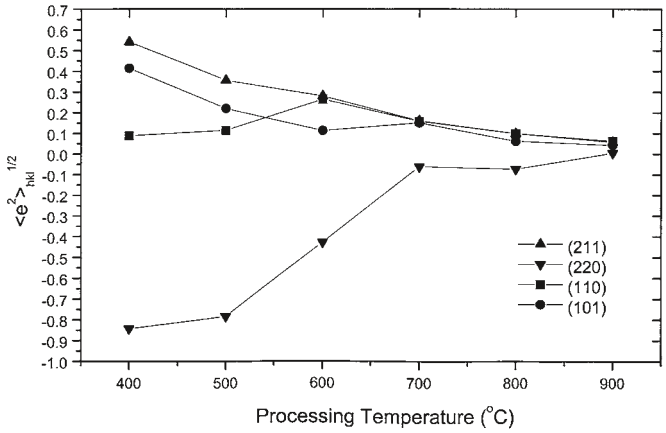

Figure 5. Strain of 5M solution concentration samples vs. growth temperature.

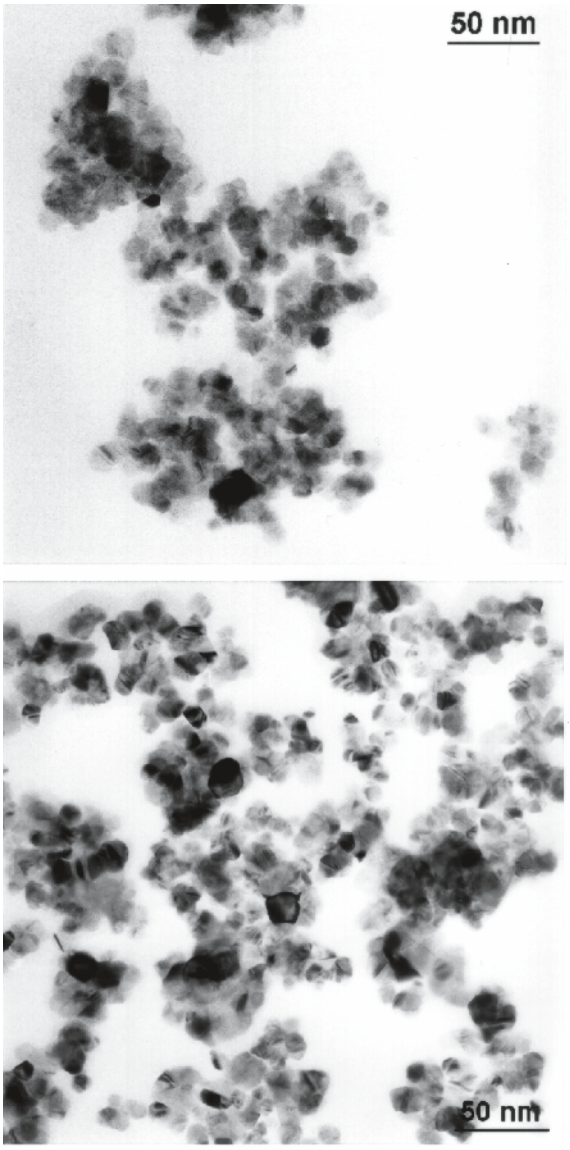

Figure 6. TEM images of the 5M solution concentration samples obtained at a processing temperature of 600ºC (top) and 800ºC (bottom).

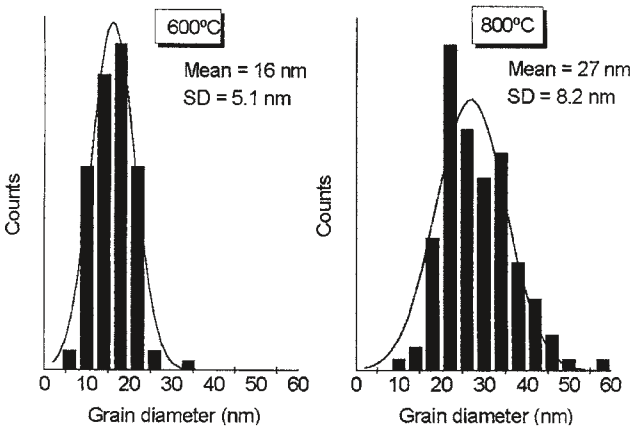

Figure 7. Histograms for the grain size of the 5M solution concentration samples obtained at a processing temperature of 600ºC and 800ºC.

Using this formula the grain size has been depicted versus the processing temperature in figure 4. From 400ºC to 600ºC, a slight growth of the grain size can be observed. The samples have a grain size between 6.0 and 33.0nm. Therefore, it is possible to control by an easy thermal process the SnO_2 grain size under accepted values in gas sensor applications of the order of 50-100nm (6).

Moreover, figure 4 shows the influence of the solution concentration on the grain size evolution. At processing temperatures below 700ºC, the grain size is almost independent on of the solution concentration taking into account the error bars. But at processing temperatures above 700ºC, the solution concentration has a major influence on the grain size evolution. The grain size evolution of the which seems to suggest an easier availability of the material to grow when molarity concentrations are higher, like it takes place in solid solutions processes. Samples with a 5M solution concentration can be fitted by an exponential function.

Using XRD data it is possible to study the strain of the nanopowders. Figure 5 shows the mean orthogonal strain of the atoms located in the (110), (101), (211) and (220) planes versus the processing temperature. There is a remarkable difference between (220) plane and the other planes. Whereas the others' strain is compressive, the (220) strain plane is tensile. Strain disappears at 700ºC. Hence, the crystalline lattice can be considered almost perfect from 700ºC.

Because TEM techniques give information of the nanoparticles structure on a more local scale, the particle size and shape study can be performed. TEM micrographs in figure 6 show that grain size is larger when the processing temperature increases. Again, a change in the behavior of the grain size and crystallinity is noted above and below the 700ºC. At 600ºC (figure 6, top) grains are stronger stucked together than at 800ºC (figure 6, bottom). Then, the lower level of agglomeration at 800ºC of processing temperature than at 600ºC means that particles are more crystalline. The shape of the nanoparticles is also processing temperature dependent as TEM images reveal. Faceted surfaces are clearly observed in the samples processed at 800ºC. Also, different grains with flat surfaces which have definite orientations are united in order to minimize the total surface or interfacial grain energy.

Direct observation of the grains by TEM agrees well with the grain sizes calculated by XRD as histograms show in figure 7 (7).

4. CONCLUSIONS

Liquid pyrolysis is a new production method of SnO_2 nanocrystalline grains suitable for gas sensor devices. The method is based on a pyrolytic reaction of high tensioned drops of an organic solution of $SnCl_4 \cdot 5(H_2O)$. Several samples are obtained by this method after a thermal treatment based on heating the samples for 24 minutes at a particular temperature (processing temperature). Two parameters have been varied, namely, the solution concentration and the processing temperature. The results of the characterization of the samples validate the advantages of the liquid pyrolysis method: its capability to produce SnO_2 nanopowders with high stability, its accurate control over the grain size and other structural characteristics, its high level of repeatability and its low industrialization implementation cost.

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