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Pt Nanoparticles Dispersed on SnO_2 Thin Films: A Microstructural Study

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Platinum nanoparticles (3–5 nm) dispersed on polycrystalline SnO_2 (8–25 nm) thin films were obtained by codeposition of Pt and SnO_2 from ultrahigh frequency spraying of a solution. SnO_2 grain size decreases as the platinum concentration increases (0–11%). A comparison is made with pure platinum films where Pt grain size (20–40 nm) is much greater than in Pt/SnO_2 films. A HREM study shows well crystallized nanoparticles with good interaction between Pt particles and SnO_2 grains. Contrary to other noble metal particles, no icosahedral or decahedral morphologies due to multitwinning are observed.

Introduction

SnO_2 cassiterite is a *n*-type semiconductor widely used as a transparent electrode. Although its surface conductivity is very sensible to the nature of the surrounding atmosphere, relatively little is known about most of the mechanisms controlling its behavior. In general, the gas adsorption on the material surface leads to a modification of the density of free electrons close to the surface. Such a phenomenon permits gas detection on ceramics and thin films of polycrystalline SnO_2 (*1–3*). Since this is a surface phenomenon, a very precise knowledge of the microstructural characteristics is required.

Electrical properties of this material, such as selectivity and sensibility, can be improved by dispersion of small metallic particles (Pd, Pt) on the SnO_2 grain surface (*4, 5*). Metallic aggregates such as Au, Ag, Pd, and Pt have previously been studied (*6, 7*). It is well established that isolated metallic aggregates frequently form particular microstructures due to the presence of multitwinning with a central *C5* axis (*8*). Analytical and electronic studies have also been performed on Pd clusters deposited on monocrystalline (110) SnO_2 (*9*) and polycrystalline Al_2O_3 (*10*). Moreover, some catalysts formed by Pt supported on either γ-Al_2O_3 or

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SiO_2 have been studied by electron microscopy (*11–13*).

We present, in this paper, the synthesis and microstructural characterization of the Pt/SnO_2 system which is formed by aggregates of Pt nanoparticles dispersed on the surface of SnO_2 grains. This study has been performed on thin films prepared by a modified CVD process.

Experimental

The process has been reported elsewhere in connection with thin film elaborations of several kinds of oxides (*14, 15*). It is based on the pyrolysis on a heated substrate of an aerosol produced by ultrahigh frequency spraying of a solution. Ultrafine droplets (2–4 μm) were produced from the surface of this solution by an ultrasonic beam (850 kHz) focused close to the surface. The aerosol was conveyed by purified air close to the heated substrate where both precursor decomposition and pyrolysis occur, leading to films of good quality (Fig. 1).

Pt/SnO_2 films were obtained by dissolving dibutyltin diacetate and 0–10% platinum acetylacetonate (with respect to tin acetylacetonate) in acetylacetone (0.1 *M* concentration). Pure platinum films were obtained using a solution of platinum acetylacetonate dissolved in acetylacetone (0.1 *M*). Depositions were carried out on polycrystalline Al_2O_3 and oxidized ⟨100⟩ silicon. Temperature range was 480–550°C. For TEM observations, 30–60 nm thickness films were deposited on nickel grids (3 mm diameter) covered with a very thin amorphous SiO_2 membrane (10–20 nm).

Crystallinity of the films was analyzed by X-ray diffraction (Cu $K\alpha$ radiation). Grain sizes were determined using the Scherrer formula with a standard (well crystallized SnO_2 powder). Film surface and film composition were studied by scanning electron microscopy with EDS X-ray microanalysis. Very localized X-ray microanalysis (1–2 nm) was performed on the platinum and tin oxide particles with a STEM. Transmission electron microscopy was carried out on a 200 CX (200 kV) Jeol electron microscope. Platinum particle structure was observed with HREM by using a Jeol 4000 EX electron microscope (400 kV).

Results and Discussion

1. Analytical Characterization

Thin films have been deposited on either alumina or silicium substrates at temperatures between 480 and 550°C. The film thickness varies between 1 and 2 μm. The Pt precursor concentration in the solution is in the range 1–10% (per mole). The Pt percentage obtained is 0.5–11%, depending on both the initial concentration of the solution and the temperature (Fig. 2). An increase of the temperature produces an increase of the Pt amount deposited in relation with the SnO_2 deposit.

2. X-Ray Diffraction (XRD) and Grain Size

XRD patterns (Fig. 3) can be indexed on the basis of the cassiterite unit cell (*16*). No evolution of the unit cell parameters is observed with increasing Pt amount. Moreover, no Pt-related phase is detected by XRD, indicating that platinum, either metallic or oxide, is deposited as very small particles which cannot be seen by XRD. This is confirmed by transmission electron microscopy, as described below.

The SnO_2 average grain dimension, measured by XRD, varies from 8 to 25 nm for synthesis temperatures ranging from 400 to 550°C (Fig. 4). For a given temperature such a dimension decreases, very quickly at the beginning and then more slowly, as the platinum concentration increases. An annealing at 600°C for 72 hr produces an increase of the average size, the increase becoming less

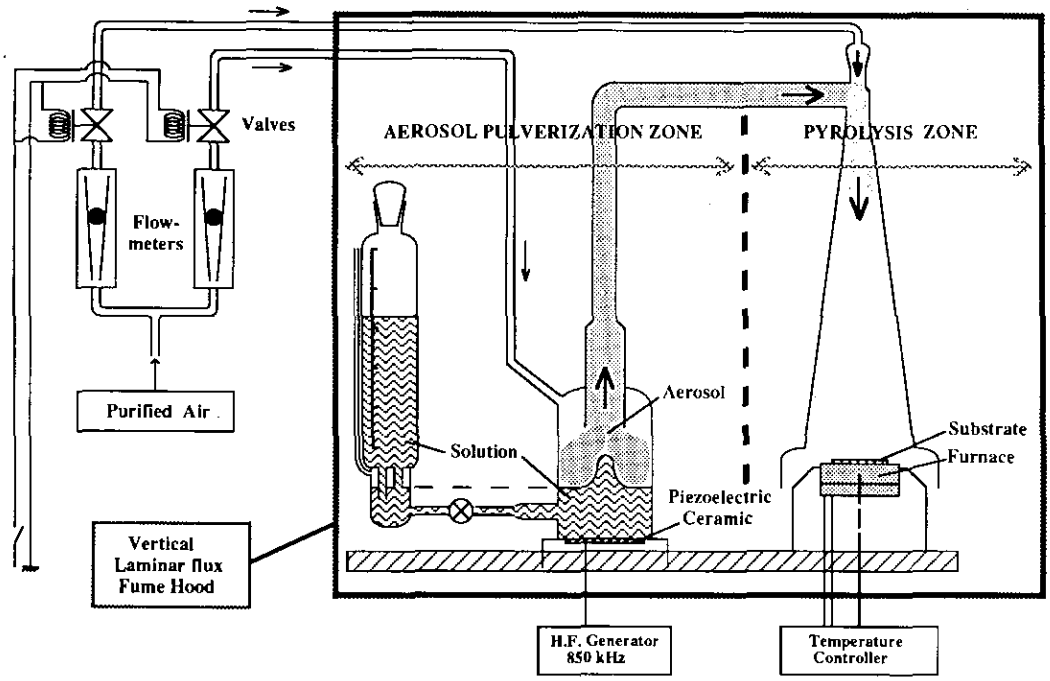

FIG. 1. Schematic representation of thin film deposition system.

pronounced as the platinum content increases.

3. *TEM and SEM Microstructural*

Electron diffraction patterns of a sample obtained at 540°C, having 11% Pt, show diffraction maxima characteristic of SnO_2 and an extra reflection corresponding to the (110) spacing of metallic Pt (Fig. 5a). The corresponding bright field micrograph (Fig. 5b) shows spherical nanometric aggregates (A) dispersed on irregular grains (B) with inhomogeneous particle size. A very localized X-ray microanalysis study performed on a STEM apparatus confirms the existence of two different phases: platinum-free tin oxide grains (B) of large dimensions, which are probably SnO_2, and platinum particles corresponding to the darkest aggregates (3–5 nm) dispersed on cassiterite grains.

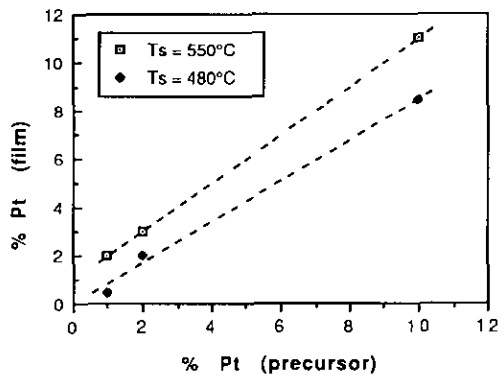

FIG. 2. The change in the platinum concentration of the films with the change in the platinum concentration of the precursor solution.

The deposit of pure Pt performed at 540°C leads to the formation of grains showing an average size of 30 nm, as measured by XRD. The bright field micrograph, shown in Fig. 5c, has been obtained on a layer of about 40 nm thickness. The existence of grains much bigger than those obtained in the Pt/SnO_2 thin films can be clearly appreciated.

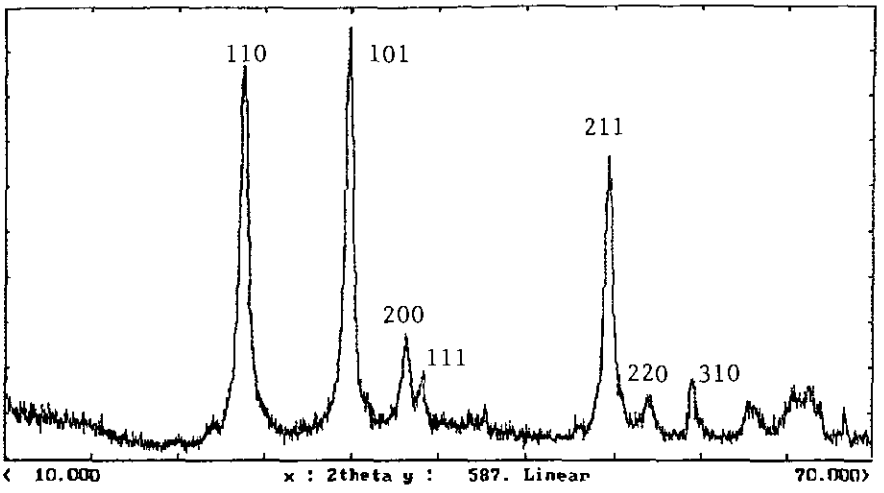

FIG. 3. X-ray diffraction pattern of Pt(11%)/SnO_2 film obtained at 540°C.

By comparing the growth of pure platinum grains with the growth of platinum grains obtained on SnO_2 (Fig. 5b), it seems that the Pt growth is decelerated by the presence of SnO_2 grains. Reciprocally, the SnO_2 grain growth is slightly affected by the presence of a small amount of Pt (11%). Accordingly, by simultaneous deposition of both Pt and SnO_2 with a small proportion of Pt, a dispersion of Pt nanoparticles on SnO_2 grains is obtained.

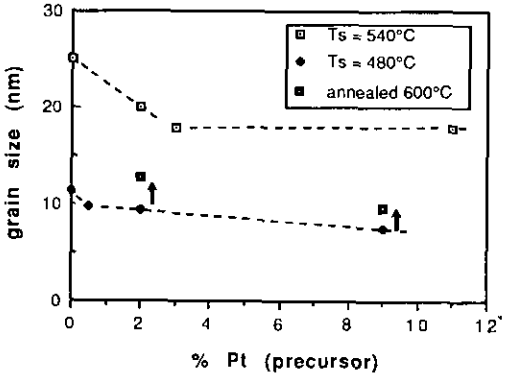

FIG. 4. The change in average grain size of SnO_2 with platinum concentration of precursor solution and with elaboration temperature. The arrows indicate the increase of grain size after an annealing at 700°C for 72 hr.

4. *HREM of Pt Particles*

Figures 6a and 6b show some high resolution electron micrographs, performed at 400 kV, corresponding to the material prepared at 540°C with 11% Pt. It can be seen that Pt particles are well crystallized showing a strong interaction with SnO_2 grains. These particles seem to grow epitaxially on the SnO_2 grains. Thus, Fig. 6a shows that the (111) crystallographic planes of Pt are parallel to the SnO_2 (101) planes. The difference between these crystallographic spacings (15%) originates a dislocation on the SnO_2 grain structure. More generally, a distortion of the SnO_2 structure is observed on the Pt–SnO_2 interface, while the Pt structure remains unalterable. Although small Pd metal particles frequently form icosahedral and decahedral morphologies due to multitwinning, HREM images of Pt/SnO_2 thin films do not show this kind of anomaly (Fig. 6b). This is in agreement with the results shown by other authors (*17, 18*) on isolated Pt aggregates obtained by other experimental procedures.

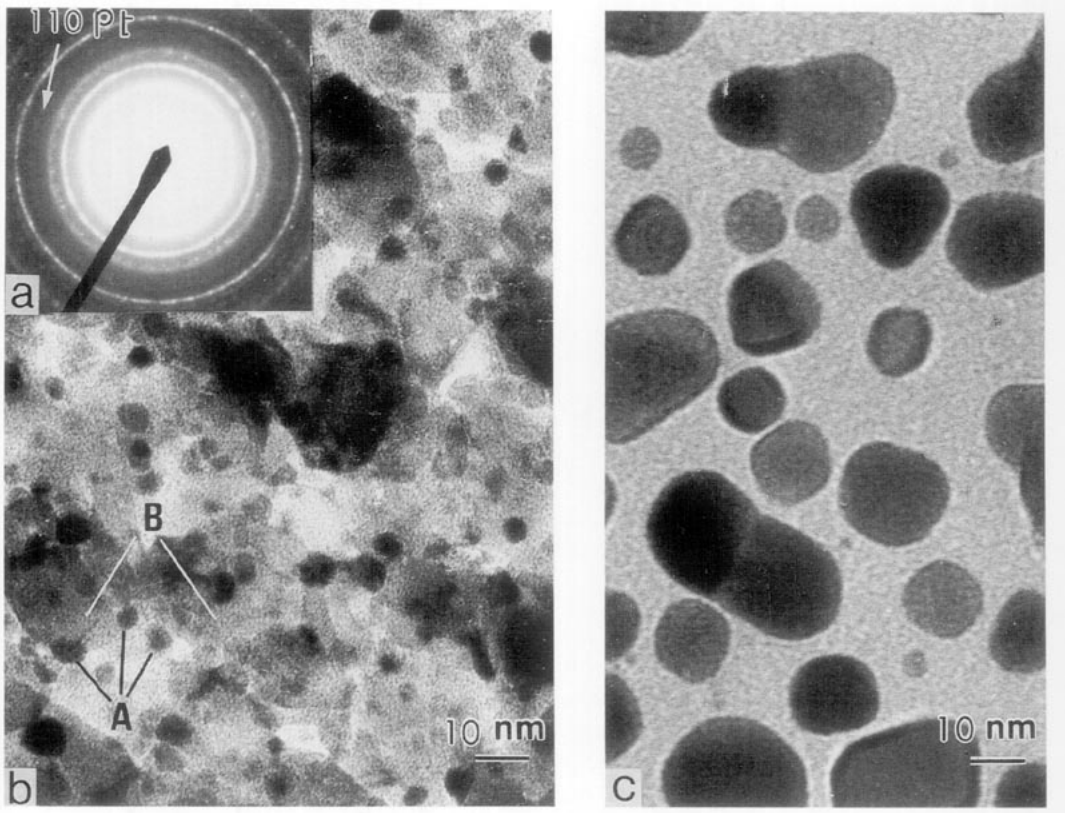

FIG. 5. Transmission electron microscopy: (a) diffraction pattern and (b) bright field image of Pt(11%)/SnO_2 film obtained at 540°C (A, quasispherical platinum particles and B, irregular SnO_2 grains); (c) bright field image of pure platinum film obtained at 540°C.

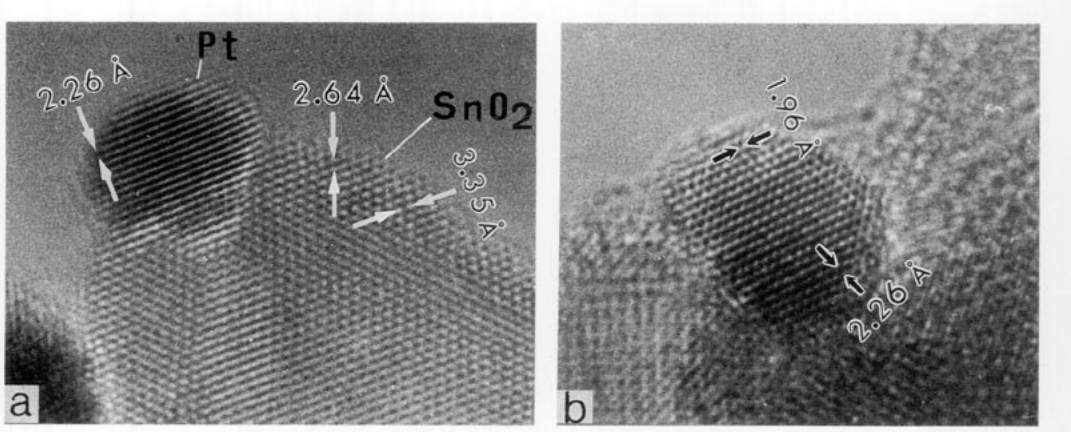

FIG. 6. HREM of Pt(11%)/SnO_2 film obtained at 540°C: (a) interaction between Pt particle and SnO_2 grain induces a distortion of SnO_2 grain; (b) no multitwinning appears in the Pt particle structure.

In order to study the influence of Pt loading on the behavior of SnO_2 as a gas sensor, electrical measurements will be performed as a function of both temperature and surrounding atmosphere.

Conclusion

By codeposition of metal and metal oxide it is possible to synthesize metallic nanoparticles dispersed on the surface of oxide grains. Codeposition with a low Pt concentration allows us to limit the grain size of metallic particles. This morphology is attractive for catalysis and gas sensor applications.

Under these experimental conditions, well crystallized and quasispherical platinum particles are obtained without anomalous morphology due to multitwinning, as previously observed either under other experimental conditions of elaboration or with other noble metals.

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