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Communications

Polymeric *Sacrificial* Layers for the Control of Microstructure and Porosity of Oxide Thin Films Deposited by Plasma-Enhanced Chemical Vapor Deposition

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Plasma-enhanced chemical vapor deposition (PECVD) is a well-known technique developed during the past decades for the deposition of thin films of oxides, polymers, metals, and so forth, and the treatment of surfaces. These films and plasma-based treatments have been successfully applied in fields such as microelectronics, the packaging industry, optical films, and biomaterials.[1−4]

A new method for the control of the porosity and microstructure of oxide thin films deposited at room temperature by remote PECVD has been developed in our laboratory. The method is based in the removal of a sacrificial polymeric layer, which is deposited in the same reactor used for the deposition of the oxide film. This novel procedure is independent of the particular organometallic precursor employed for the deposition and, therefore, of the type of oxide. A critical requisite for this polymeric layer is that it is plasma-etched with a sufficiently high rate during the deposition of the oxide. This requires that the polymeric layer is easily and fully oxidized into volatile species.

In this communication, we present some basic characteristics of these polymeric films and show several experimental results that illustrate the possibilities of their use for the preparation of porous oxide films.

The reactor employed for the PECVD synthesis of both the polymeric and oxide materials is a remote microwave reactor that has been described in previous papers.[5−7]

The polymeric films have been deposited using a plasma of toluene (5 sccm) and oxygen (20 sccm), controlling the pumping capacity of the chamber to achieve a final pressure of ~1 Torr.

The C 1s core level spectrum measured by X-ray photoelectron spectroscopy (XPS) of a polymeric film is shown in Figure 1a). The figure includes the fitting of the C 1s core level with different components that account for the different carbon functionalities of the film.[8] From the XPS analysis, the O/C ratio of the polymer thin film is 0.78 with 70% of carbon atoms in

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Table 1. Preparation Protocols of SiO_2 Thin Films

sample	deposition 1	deposition 2	substrate
(a)	SiO_2 (reference)		Si(100)
(b)	Pol.: 25 nm + SiO_2: 150 nm	Pol.: 25 nm + SiO_2: 450 nm	Si(100)
(c)	Pol.: 40 nm + SiO_2: 150 nm	Pol.: 40 nm + SiO_2: 450 nm	Si(100)
(d)	Pol.: 60 nm + SiO_2: 150 nm	Pol.: 60 nm + SiO_2: 450 nm	Si(100)
(e)	Pol.: 60 nm + SiO_2: 475 nm	Pol.: 60 nm + SiO_2: 475 nm	Si(100)
(f)	Pol.: 40 nm + SiO_2: 275 nm	Pol.: 40 nm + SiO_2: 275 nm	Al sheet
(g)	(Pol: 50 nm + SiO_2: 275 nm) × 7 (seven cycles)	Al sheet	

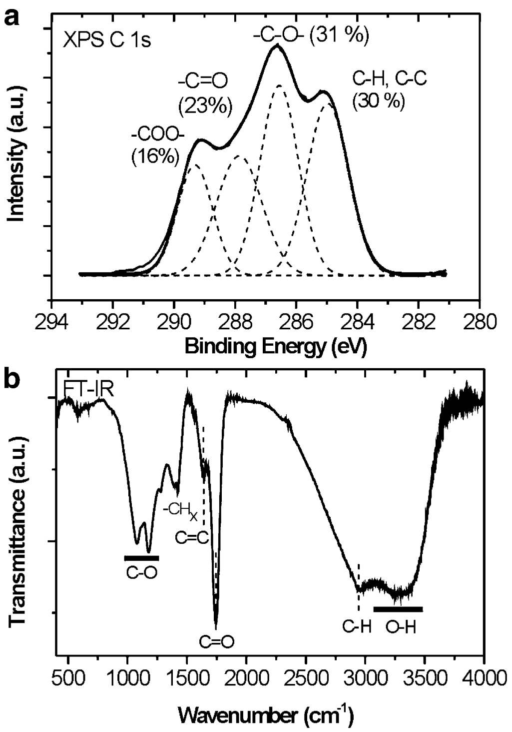

Figure 1. (a) C 1s photoelectron core level spectra of the surface of the polymeric films. The percentage of the different carbon functional groups is indicated. (b) FT-IR transmission spectrum of the polymeric thin film.

oxygenated functionalities. These results are consistent with the FT-IR spectra shown in Figure 1b, where the most intense bands are due to oxygenated functionalities as C═O, C−O, and −OH.

The bulk and surface analysis of the polymeric films points to the polycarbonate-like composition of the deposited material.[9] The highly oxygenated nature of these polymeric layers is the key factor for the high etching rates of these films (~200 nm/min at 2×10^{-2} Torr). This means that, after deposition in oxygen plasma at relatively high pressure, the films can be fully burned out at low pressure in the same plasma reactor. As a result of this oxidation, CO, CO_2, and H_2O were detected in the gas phase.

The preparation method of the porous oxide thin films is based in the etching of the polymeric films during the growth of the oxide layer. This procedure, repeated sequentially, enables very effective control of the microstructure of the oxide layer. Porosity is generated because of the removal of gases produced by oxidation of the polymer (i.e., CO_2 and H_2O) and the modification of the nucleation and growing mechanism of the oxide thin films.

As an example of the possibilities of this method, we will show several examples of silica thin films with controlled porosity. Silicon dioxide thin films have been deposited in the same reactor according to a procedure published recently.[5] For the PECVD synthesis, a $Si(CH_3)_3Cl$ precursor was employed in a plasma of oxygen at 2×10^{-2} Torr.

Figure 2 shows a series of scanning electron microscopy (SEM) images of SiO_2 thin films prepared according to different protocols, as listed in Table 1. These pictures illustrate the two most important factors that control the final microstructure of the layer: (i) the thickness of the organic sacrificial layer and (ii) the thickness of the sequentially deposited oxide thin film. Figure 2a−d shows the top views of four SiO_2 thin films of ~600-nm thickness deposited by two polymer−oxide cycles. The preparation protocols of these samples differ only in the thickness of the intermediate sacrificial layer. The first thin film, prepared without polymer intermediate layer, is compact and dense and shows no defined features (cf. Figure 2a). Meanwhile, the sequential deposition of the polymer and inorganic oxide produces a loss in the homogeneity of the film (images (b)−(d)). Moreover, pictures (b)−(d) clearly show that the porosity of the films increases as the thickness of the *sacrificial* organic phase increases. A comparison between (c) and (e) in Figure 2 reveals that by increasing the thickness of the intermediate oxide layers, it is possible to reduce the percolation degree between the pores of the films and to increase the diameter of the aggregates. All the films showed a columnar structure, independently of the thickness of the layer and the number of cycles used for the preparation. This is clearly seen in the cross-sectional images of Figure 2f,g. In the latter, it is also interesting that no boundary interfaces can be detected among the seven different individual SiO_2 deposition steps. This proves that the growth process of SiO_2 is continuous, even if it is interrupted by deposition-removal steps of the organic and inorganic layers. This type of microstructure with vertical pores and columns is characteristic of all the samples, though the pore size and type of columns depend on the actual preparation conditions used in each case. An estimation of porosity has been made by combining the values of the surface atomic densities (i.e., atoms cm^{-2}) determined by Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA) with the layer thickness measured by cross-sectional SEM analysis. Preliminary results indicate that it is possible to control the density of the silica films in the range 2.0−0.6 g/cm^3. On the other hand, although conventional methods to determine specific surface areas in powder materials are not easily extrapolated to thin films, we were able to

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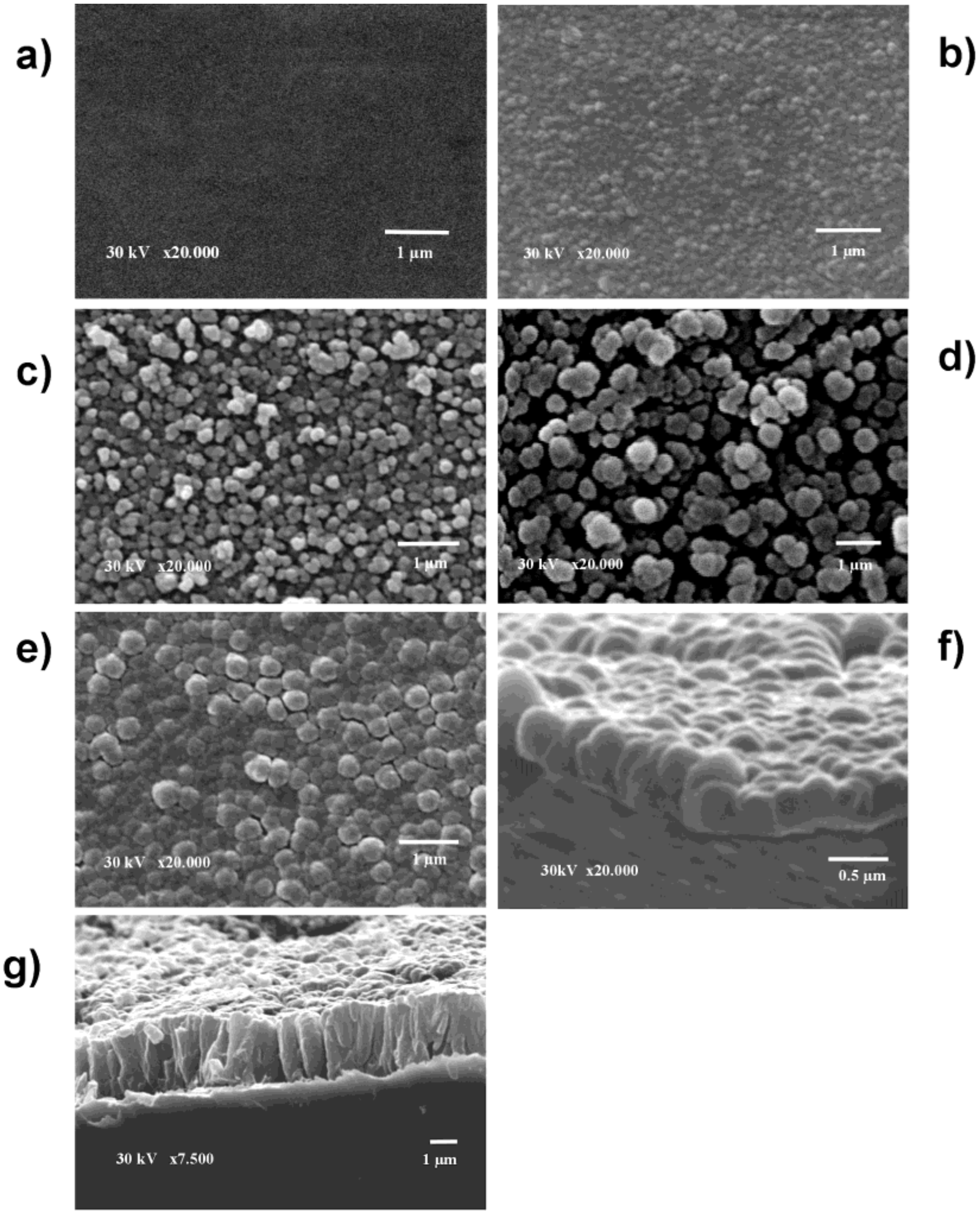

Figure 2. Scanning electron microscopy images of the films whose deposition conditions have been listed in Table 1 (see text).

measure BET surface areas for thin films grown on the two sides of a large area (i.e., 10 × 10 cm^2) aluminum foil. A value of 27 $m^2\ g^{-1}$ was determined for a sample whose SEM micrographs look very similar to that reported in Figure 2g. It is also interesting that no carbon traces were detected in the films by RBS and/or XPS after sputtering, thus proving that the polymer is completely burned off during deposition of the oxide.

Porous oxide thin films of TiO_2 and Al_2O_3 with similar microstructures have also been deposited by using $Al(CH_3)_3$ and $TiCl_4$ precursors, respectively.

Besides its general character, the reported deposition procedure enables a wide range control of the microstructure, from microporous to mesoporous films. In addition, the method allows the deposition of films with graded porosity or/and graded composition (i.e., a mixture of different oxides). This novel procedure expands the possibilities of the synthesis of oxide thin films by PECVD to the preparation of porous thin films. Its use for the fabrication of antireflective coatings, gas-filtering membranes and supports, low *k* dielectric films, or biocompatible films are under study in our laboratory. Thus, a preliminary optical characterization of porous but still transparent thin films (above a certain porosity the films scattered the light) shows as a result that they have a refractive index (*n*) as low as ~1.2 at 650 nm. This low *n* value makes these films good candidates to be used as antireflective coatings. A final remark is that this deposition method is fully compatible with the present silicon technology.

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