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The control of thickness on aluminum oxide nanotubes by Atomic Layer Deposition using carbon nanotubes as removable templates

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ABSTRACT

Aluminum oxide (Al_2O_3) nanotubes with wall thicknesses from 2 to 20 nm were synthesized by atomic layer deposition (ALD) technique using multiwalled carbon nanotubes (MWCNTs) as templates. Al_2O_3 material was deposited on the MWCNT at 100 °C by a hot walls ALD reactor. Trimethyl-aluminum (TMA) and water were used as precursor and oxidant, respectively. Transmission Electron Microscopy (TEM) shows that the wall thickness of Al_2O_3 coatings is precisely controlled by adjusting the number of ALD-cycles of TMA/H_2O. In order to remove the carbon template by oxidation, the Al_2O_3-coated MWCNT were heated under air flow from ambient temperature up to 800 °C. The correlation between thicknesses and thermal properties of the Al_2O_3-coated MWCNTs were studied in detail by thermogravimetric analysis (TGA). It was found that the heating rate is a critical step in the removal of the carbon template, being a slower rate mandatory to avoid the spontaneous combustion of carbon at the kindling point. We recommend heating rates of 3 °C/min or less; higher rates might produce nanotubes with significant proportions of voids. TEM confirmed the production of amorphous Al_2O_3 nanotubes that retained the cylindrical shape of the parent MWCNTs template with excellent control of wall thickness, except for the very thin films with thicknesses below 2 nm (<10 ALD-cycles).

1. Introduction

The template-based growth is a versatile method to prepare free-standing nanomaterials. The majority of Physical or Chemical Vapor Deposition methods (PVD or CVD) have been tailored to create one-dimensional (1D) nanoscale materials such as nanotubes, nanorods or nanowires, using the original geometric shape of certain nanomaterials as templates or scaffolds [1]. This field is still evolving, with new fabrication methods reported in the literature for the synthesis of nanostructures with great potential for technological applications. In many of them, the carbon nanotubes (CNTs) have been used as an effective template for the fabrication of ceramic and vitreous nanotubes. Nanotubes of Al_2O_3[2][3], Fe_2O_3 [4], ZrO_2 [5], V_2O_5 [6], MoO_3 [2], SnO_2 [7][8][9], Eu_2O_3 [10], TiO_2 [11], SiO_2 [11], and other metal oxides have been synthesized by exposing CNTs to different physical or chemical process. For these studies, in order to obtain pure metal oxide nanotubes, the carbon template has been subsequently removed by a heating at high temperatures in an oxygen atmosphere [1][6][10][11]. Although great efforts have been focused on the fabrication of ceramic nanotubes by this template approach of CNTs, still remain some technical difficulties. Perhaps the biggest challenge is the control of wall thickness of the ceramic nanotubes, as it is required by some applications of nanotechnology. For this reason, the coating technique must give excellent conformality and deposition control at the nanoscale level. The atomic layer deposition (ALD) can be the answer to that problem. ALD is a versatile technique that can be used to coat and functionalize surfaces either with single or multiple components. The foremost advantage of ALD is its ability to control the coating thickness down to the atomic level as a function of number of ALD cycles. ALD do not depend on the line of view to reach secluded spots; thus it can be applied to almost any kind of high aspect ratio structures producing pinhole-free conformal coatings and chemically-bonded layers by the use of sequential self-limiting surface reactions and low temperatures [12][13]. Therefore, ALD has emerged as an important technique of nanofabrication for a variety of technological applications [14]. For example, Liang et al. [15] reported the synthesis of highly porous alumina particles with precise wall thickness control by ALD using highly porous poly(styrene–divinylbenzene) (PS–DVB) particle as sacrificial templates. These particles may find wide application in nanotechnology and catalysis.

The metal oxide nanotubes are promising as the next-generation materials for electronics and advanced catalysts applications. Al_2O_3 has excellent combination of physical and chemical properties, such as thermal stability, inertness, good electrical insulation, low density and permeability, high strength and toughness [16–18]. Therefore, Al_2O_3 nanotubes could exhibit a significant enhancement in the fabrication of nanocables, nanojacks [19], nanocapacitors [20], gate oxides in

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memory devices [21], catalyst supports and templates [22], as compared to conventional CNTs.

In this work, Al_2O_3 coatings were grown by ALD on MWCNTs at 100 °C using trimethyl-aluminum (TMA) as precursor and water as oxidant. The MWCNTs used as templates were subsequently removed by controlled heating in oxygen atmosphere. Although other authors have studied the synthesis of Al_2O_3 nanotubes or nanoparticles by ALD using TMA/H_2O and following the template-based growth method [23–26], the main contribution of this work is the synthesis of Al_2O_3 nanotubes with the precise control of thickness from 20 nm to a minimum value of 2 nm by adjusting both, the sequential self-limiting reactions (ALD-cycles) to obtain the desired coating thickness, and the conditions for thermal removal of carbon template avoiding damage to the cylindrical shape of the nanotube because of spontaneous combustion. This work also shows extrapolation of bulk properties to nanoscale objects by analysis of thermal properties of MWCNTs coated with very thin Al_2O_3 layers. Therefore, the purpose of this research is to provide a simple method to produce Al_2O_3 nanotubes with tunable thickness to 2 nm.

2. Experimental

2.1. Preparation of MWCNTs

MWCNT were synthesized by CVD using the spray pyrolysis method [27]. First, a pneumatic nebulizer was fed with 6 mL of a solution which contained toluene (Aldrich 99.8%) as a carbon source and 2.5 wt % of ferrocene (Aldrich 98%) as a catalyst precursor. Then, a Vycor tube was heated at 900 °C by a tube furnace (Thermo Scientific, Lindberg Blue M). Once furnace temperature was stabilized, argon (99.99%) was used to generate a mist through the nebulizer and to carry the aerosol into the Vycor tube during 10 min. After reaction, the furnace was cooled under argon flow. Finally, the MWCNTs film formed at inner walls of the Vycor tube was mechanically removed. The raw MWCNTs were treated in order to decrease the iron (Fe) content, as follows: 0.5 g of raw MWCNTs was added to 50 mL of a HNO_3 solution (Aldrich, 70%). The mixture was placed in an ultrasonic bath for 1 h and then stirred for 12 h while refluxed. The product was filtered under vacuum, washed with deionized water, and dried at 70 °C for 8 h. It is well know that the acid treatment implies a mild functionalization of the MWCNTs surface with carbon oxide groups [28–30].

2.2. Atomic Layer Deposition

Al_2O_3 material was deposited on MWCNTs using a hot wall stainless steel reactor; a more detailed description of the original experimental setup of our ALD reactor and its use to achieve homogeneous and conformal coatings on powders, can be found in our previous work [31]. The MWCNTs (~10 mg) were placed into the reaction chamber using a porous capsule as sample-holder (2 cm^3 capacity and 60 μm pore size). During the deposition process, TMA was kept at room temperature whereas chamber and the manifold were externally heated at 100 °C. Under these conditions, Al_2O_3 coatings were grown using alternating cycles of TMA and deionized water. These ALD-cycles, including dosing and purge, were automatically controlled by pneumatic switching valves. In all the experiments the number of ALD-cycles used was in the range between 5 and 200 cycles, and the dose-times were fixed at 50 and 100 ms for TMA and H_2O, respectively. Residence time was fixed at 5 s. Precursor excess or oxidant (in the gas phase) was purged by N_2 gas (~20 sccm flow rate) and then removed by a mechanical pump attached through a pneumatic switching valve located at the upstream end of the chamber line. Purge times for both TMA and H_2O were fixed at 30 s. The internal pressure of the reactor was between ~ 10 mTorr and ~3 Torr. After completion of the deposition process, the MWCNTs coated with Al_2O_3 at a certain number of ALD-cycles were collected and stored for their characterization analysis.

2.3. Thickness calibration

The thicknesses of the Al_2O_3 layers were obtained, in first instance, by means of spectroscopic ellipsometry (SE) using a Si-wafer as witness sample (1.0 cm^2) that was put on the reaction chamber along with the deposition capsule, taking for granted the same deposition rate in the witness sample as in the MWCNTs powders. The SE measurements were carried out with a multi-wavelength rotating analyzer instrument M-44 (J.A Woollam Co.), covering the 1.625 to 4.405 eV photon-energy range in at least three different spots in the substrate surface. Thicknesses were calculated using the software WVASE*32TM*, considering the optical constants of Al_2O_3 (refractive index and extinction coefficient) from reference [32], and a numerical model that includes as input an approximation of thickness for all individual layer of the witness sample ($Si/SiO_2/Al_2O_3$), where the thickness of the SiO_2 native oxide layer was determined previously to deposition, and was in the range of ~ 2.5 nm. For thickness fitting of the Al_2O_3 layer, the SiO_2 thickness was kept fix. Blank runs up to 200 °C verified a negligible SiO_2 growth. In second instance, the thickness of Al_2O_3 coatings were observed directly by transmission electron microscopy (TEM) using a JEOL JEM 2010 microscope, at 200 kV. There was a very good correlation between the thickness measured by TEM and those determined by ellipsometry. Ellipsometry was the preferred choice for routinely sample analysis because is an expedite technique.

2.4. Template removal and thermogravimetric analysis

The carbon template removal was performed using a Thermogravimetric Analysis (TGA) instruments, Q600 analyzer from TA Instruments. Batches of ~ 4 mg of MWCNTs coated with Al_2O_3 were loaded in the instrument. The heating was performed in dry air atmosphere (19-21 % O_2) at temperature increases from room temperature to 800 °C with heating ramp rates of 3 or 10 °C min^{-1}. The mass-loss was employed to determine thermal decomposition of MWCNTs. The residual mass (M_{res}) was quantified from TGA plots. Oxidation temperature (T_o) of MWCNTs in the presence of Al_2O_3 was estimated as the range between the weight loss onset temperatures (when oxidation just begins, T_{onset}) in the TGA plots, and the corresponding temperature of the maximum in the weight loss rate, i.e. the temperature of the maximum rate of oxidation (T_{max}) in the differential thermogravimetric analysis (DTG) plots.

3. Results

In Fig. 1 is summarized the experimental procedure to obtain inorganic nanotubes by ALD using CNTs as templates; the TEM images shows the morphological changes in each stage. In the first step, raw multiwall nanotubes are positioned in the deposition capsule of the ALD reactor. In the second step the MWCNTs are coated with *x*-ALD cycles that produce MWCNT-*x*Al_2O_3. In the third step the MWCNT-*x*Al_2O_3 sample is placed in the TGA instrument and heated up to 800 °C, this render a *x*Al_2O_3 free standing alumina nanotubes; where in *x*Al_2O_3 sample nomenclature, the *x* denotes the sample prepared with *x*-ALD cycles.

The success of the above procedure to prepare thick samples is clear in Fig. 2 by TEM micrographs. In Fig. 2a-c raw MWCNT (before Al_2O_3 deposition) at different magnifications are showed; MWCNTs encapsulated with Al_2O_3 using 200 ALD-cycles, designed as MWCNT-200Al_2O_3, are shown in Fig. 2d-f; and free standing Al_2O_3 nanotubes obtained after the removal of its carbon template, designed as 200Al_2O_3, in Fig. 2g-i. The diameter of MWCNT, determined from higher magnification TEM images (Fig. 2b-c) corresponds to ~40 nm. The presence of remnants of Fe is observed as a dark contrast in the core of the hollow tubes owing to its role as a catalyst during MWCNT synthesis. Although treatment with acid to remove the by-products from CNTs is considered to be highly efficient, the encapsulated ones are difficult to be removed by