NANO LETTERS

2007
Vol. 7, No. 3
719−722

Atomic Layer Deposition on Electrospun Polymer Fibers as a Direct Route to Al_2O_3 Microtubes with Precise Wall Thickness Control

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Received December 14, 2006; Revised Manuscript Received January 16, 2007

ABSTRACT

Atomic layer deposition (ALD) of Al_2O_3 on electrospun poly(vinyl alcohol) microfiber templates is demonstrated as an effective and robust strategy by which to fabricate long and uniform metal-oxide microtubes. The wall thickness is shown to be precisely controlled within a molecular layer or so by adjusting the number of ALD cycles utilized. By judicious selection of the electrospinning and ALD parameters, designer tubes of various sizes and inorganic materials can be synthesized.

Inorganic microtubes with precisely defined nanoscale walls have attracted considerable attention due to their potential application in technologies related, but not limited, to electronics, photonics, nanofluidics, medicine, sensing, catalysis, and controlled release.[1] A variety of different processes have been developed to fabricate such tubes from a wide range of materials. Among those processes, the template-directed approach represents a straightforward and facile route to the fabrication of nano-/microscale structures with hollow interiors. Nanorods,[2] carbon nanotubes,[3,4] and porous media[5,6] have all been successfully used as templates in this vein. Such templates are, however, expensive and difficult to produce in large volume. Natural materials including cotton and paper[7,8] have also been used as templates, but the resultant nano-/microscale structures are not easily controlled. In this work, we employ atomic layer deposition (ALD) on electrospun polymer fibers as a direct means by which to construct inorganic microtubes with well-defined nanoscale walls composed of Al_2O_3 after the templating polymer is removed. The results reported here indicate that this strategy provides an attractive, high-fidelity, and low-cost route to inorganic microtubes, as well as nanoscale tubes and other complex shapes.

Electrospinning has become a valuable and versatile route by which to obtain exceptionally long polymer nano-/microscale fibers possessing uniform diameter and good composition control.[9−14] Electrospun fibers are produced from polymer solutions as the electric field between a spinneret and a target is increased until the electrostatic force at the tip of the spinneret exceeds the surface tension of the solution drop. The resulting Taylor cone that forms is transformed into a continuous jet that forms solid fibers as the solvent evaporates. In combination with various surface modification tactics including physical vapor deposition (PVD),[15,16] chemical vapor deposition (CVD),[15] sol−gel processing,[7] and spin-on glass (SOG) incorporation,[16,17] electrospun templates have been used to fabricate metal,[15] metal oxide,[7,16] and polymer[15,18] nanotubes. However each of these deposition methods is hindered by significant process limitations. For example, sol−gel chemistry has been successfully performed on electrospun fibers to generate TiO_2 nanotubes,[7] but uniform wetting of the huge surface area of the fiber matrix presents a significant and ongoing challenge for this method. On the other hand, PVD is a line-of-sight deposition technique that does not permit conformal deposition on fibers throughout the matrix. In CVD processes, depletion of precursor frequently limits uniform coating on large surface areas. Due to the limitations of these traditional deposition techniques, it is difficult to produce long nano-/microtubes with smooth outer surfaces and uniform walls of controlled thickness at nanometer length scales.

In this work, ALD[19−22] has been applied to matrices of electrospun polymer fibers to fabricate Al_2O_3 microtubes with

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10.1021/nl062948i CCC: $37.00
Published on Web 02/06/2007

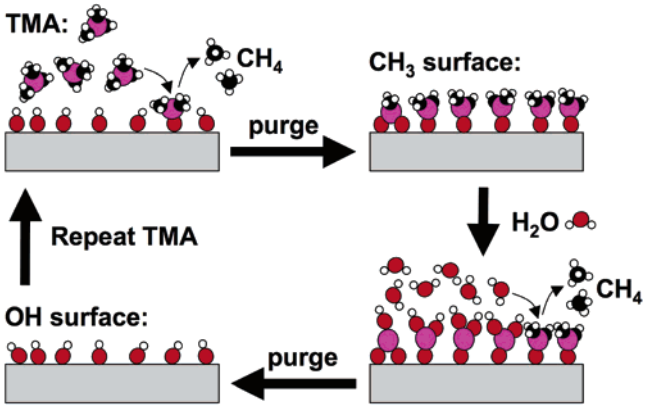

Figure 1. Schematic diagram of vapor-phase, self-limiting atomic layer deposition (ALD) illustrating the cyclic process by which an Al_2O_3 surface coating is controllably constructed layer-by-layer from TMA and H_2O precursors.

smooth wall surfaces and precisely controlled wall thickness. This strategy exploits a sequential, self-limiting deposition process that operates on the principle of alternating saturating surface reactions. During ALD, a specimen is exposed to a precursor vapor that forms a (sub)monolayer of the precursor on the substrate. After excess precursor is removed from the vapor phase by a purge gas (e.g., Ar), the reactant gas is subsequently pulsed onto the substrate, where it reacts with the adsorbed precursor layer to form a layer of the target-film-forming material. Since no gas-phase reaction occurs, the target film is grown layer-by-layer on the substrate, in which case the thickness of the deposited film can be accurately controlled by the number of cycles the process is repeated, as illustrated in Figure 1. Because of its unique process characteristics and controllability, ALD can be used to deposit conformal, uniformly thin films with precise thickness and composition control over large scales and onto substrates with complex topologies (including for example, fibers).[8,22,23] Moreover, ALD is chemically versatile and has been used to fabricate layers of metals,[24−26] metal oxides,[27] metal nitrides,[22,24] and other materials. An additional benefit of ALD is that the deposition of Al_2O_3,[21,22] TiO_2,[8] and TiN[24] can be conducted at relatively low temperatures (<150 °C), thereby reducing, if not altogether eliminating, thermal damage to temperature-sensitive substrates such as organic media.

Poly(vinyl alcohol) (PVA) with a molecular weight of 127 kDa and a degree of hydrolysis of 88% was purchased from Aldrich and used without further purification. A 7 wt % PVA aqueous solution was prepared by dissolving PVA in deionized water (DI H_2O) at 60 °C and stirring gently for 2 h. Electrospinning was performed using the parallel-plate setup described elsewhere.[14] A stable jet was formed at a flow rate of 7 μL/min and an electric field of 1 kV/cm. Representative electrospun PVA fibers were sputter-coated with Au/Pd prior to field-emission scanning electron microscopy (FESEM) analysis performed on a JEOL 6400F microscope operated at 5 kV. Coated fiber composites were fabricated by depositing thin Al_2O_3 films on the electrospun PVA fibers by ALD at 45 °C and a pressure of ~0.5 Torr. The aluminum precursor and oxygen reactant sources were

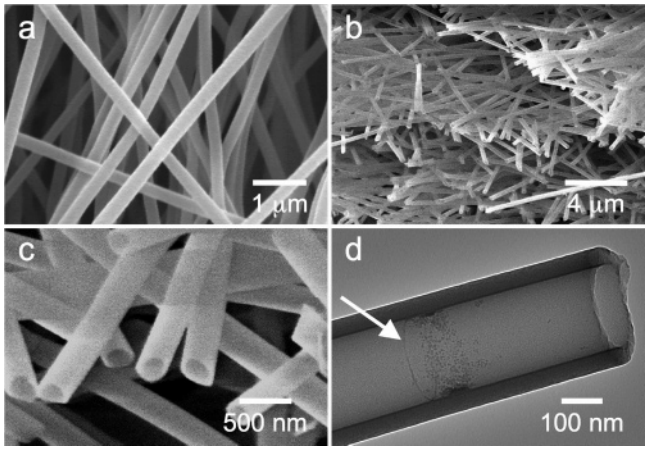

Figure 2. (a) FESEM image of electrospun PVA fibers. (b, c) FESEM images of Al_2O_3 microtube replicas prepared by ALD wherein the Al_2O_3 coating was deposited for 475 cycles at 45 °C. (d) TEM image of a corresponding Al_2O_3 microtube. The arrow in (d) identifies a peripheral circle formed inside the microtube near an apparent neck in the fiber template.

$Al(CH_3)_3$ (TMA, 95%) and DI H_2O, respectively, and were delivered to the reactor as ambient-temperature vapors. During cycling, the TMA and DI H_2O were alternately introduced into the ALD chamber (base pressure ~10^{-6} Torr) in pulses of 5 and 0.5 s, respectively. Purge times were 20 s for TMA and 60 s for DI H_2O. In conjunction with each ALD on PVA fibers, a piece of native oxide Si wafer (measuring ~1 cm × 1.5 cm, treated by JTB Baker Clean, rinsed in DI water and then N_2 blown-dry) was used as a reference substrate for growth rate measurements on a planar surface under identical deposition conditions. To remove the organic constituent after ALD, the Al_2O_3-coated PVA fibers were heated in air at 400 °C for 24 h. After the PVA was removed by calcination, the resultant microtubes were likewise characterized by FESEM under the same conditions listed earlier. Transmission electron microscopy (TEM) was conducted by sonicating Al_2O_3 microtubes in ethanol for 1 min. Several drops of the suspension were pipetted onto carbon-coated TEM grids, which were allowed to dry at ambient temperature and then imaged with a Hitachi HF-2000 microscope operated at 200 kV. Complementary energy-dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments Inca Energy 100 system to ascertain the chemical composition of the microtubes under different ALD conditions.

A representative FESEM image of individual as-electrospun PVA fibers is presented in Figure 2a. Depending on the duration of electrospinning, these fibers typically connect to form a self-supporting web. The diameters of most of the PVA fibers used in this study range from 200 to 400 nm. To reflect this size scale, we hereafter refer to the fibers as *microfibers*. In comparison with poly(L-lactide) (PLA) electrospun fibers, which have been traditionally used as templates by which to generate tubes by PVD and CVD,[15,28] PVA with surface hydroxyl groups capable of reacting with deposited precursor species is much less expensive and likewise amenable to electrospinning from aqueous solution. These considerations are ultimately important in the mass

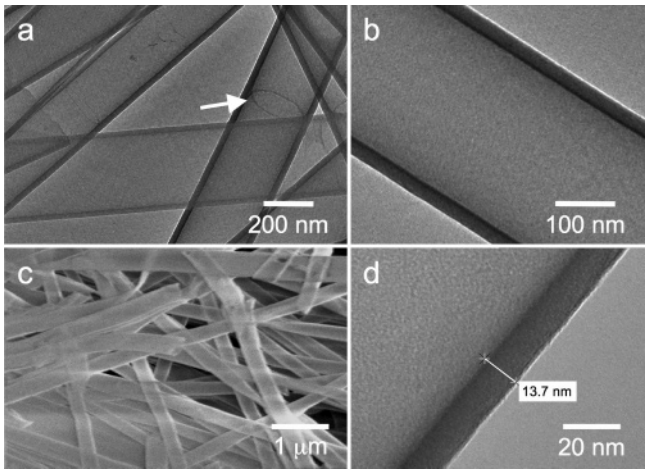

Figure 3. (a) TEM image of an Al_2O_3 microtube formed when ALD was performed on electrospun PVA fibers for 300 cycles at 45 °C. The arrow indicates a circle on the inside wall of the resultant microtube. (b) TEM image of the corresponding Al_2O_3 microtube illustrating the wall thickness. (c) FESEM and (d) TEM images of Al_2O_3 microtubes fabricated by ALD for 150 cycles at 45 °C. A wall thickness measurement is included in (d). In all cases, the electrospun PVA fiber templates were removed by heating in air at 400 °C for 24 h.

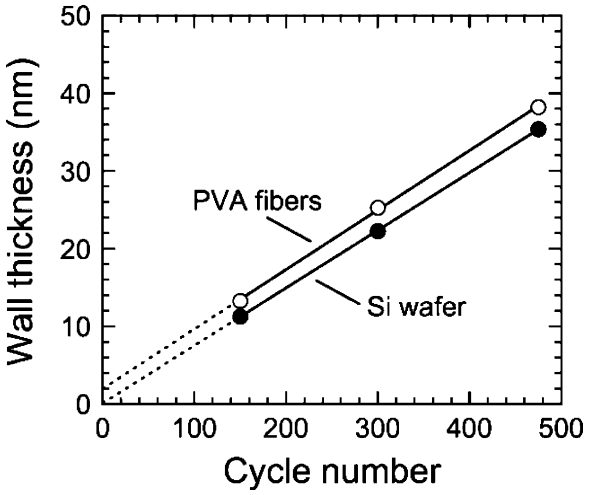

Figure 4. Wall thickness of Al_2O_3 microtubes prepared on electrospun PVA fibers (○) and measured by TEM as a function of ALD cycle number. Included for comparison is the Al_2O_3 film thickness on a planar Si substrate (●) measured by ellipsometry. The lines denote linear regressions of the data points. The corresponding average growth rates of Al_2O_3 are about 0.08 nm/cycle on the electrospun fibers and 0.07 nm/cycle on the Si substrate. Error bars (±1 standard deviation) deduced from analysis of 25 thickness measurements from each specimen are smaller than the symbols shown. Note that for deposition on the PVA fibers, extrapolation of the linear regression to zero cycle number (denoted by the dashed line) results in a small positive intercept, indicating a slight enhancement to the growth per cycle during the initial deposition period.

production of high-quality templated microtubes. The resulting conformal deposition of Al_2O_3 on PVA fibers is shown in the FESEM images displayed in parts b and c of Figure 2, as well as in the TEM image included in Figure 2d. Figure 2b indicates that the Al_2O_3 microtubes are connected together in a web, thereby preserving the original arrangement of the PVA electrospun fiber templates. This figure, which shows a large number of Al_2O_3 microtubes as only a very small part of the specimen investigated, also confirms that the ALD process yields uniform coverage over a relatively large area despite the apparent topological complexity. Most of the Al_2O_3 microtubes are observed to measure tens of micrometers in length, with many observed to extend into the millimeter range. The close-up FESEM image provided in Figure 2c reveals the structure of the hollow Al_2O_3 microtubes formed after removal of the PVA core. It is apparent from this and related images that the outer surface of the microtubes after 475 ALD cycles is relatively smooth. In this case, the wall thickness of these Al_2O_3 nanometer tubes is estimated to be about 38 nm on the basis of TEM images such as the one displayed in Figure 2d. As indicated by the arrow in this figure, the microtube replicates nanoscale features from the surface of the electrospun fiber. Attention is drawn here to a small neck in the PVA fiber, along with some small surface blemishes and a peripheral circular feature. A similar circular feature is likewise evident on the interior of a microtube produced after 300 cycles of ALD (cf. Figure 3a).

Figure 3a is a TEM image of an Al_2O_3 replica of a PVA electrospun fiber template that was first exposed to Al_2O_3 ALD for 300 cycles prior to thermal treatment in air at 400 °C for 24 h. Despite their diameter (in excess of 200 nm), these microtubes appear electron transparent when observed by TEM. The high-magnification TEM image provided in Figure 3a demonstrates that the wall thickness of the microtubes is ∼25 nm and is remarkably uniform along the length of a single tube. This observation extends to different tubes throughout the entire web. For comparison, Al_2O_3 microtubes formed after 150 ALD cycles are shown in the FESEM image in Figure 3c. In this case, the wall thickness is only ∼14 nm, according to TEM (cf. Figure 3d). An EDS analysis performed on Al_2O_3 microtubes after 150, 300, and 475 ALD cycles and subsequent heating in air at 400 °C for 24 h shows an Al:O ratio of 0.68:1 with 5% variation, thereby confirming that the elemental composition of the microtube walls is consistent with Al_2O_3. Carbonaceous residue has not been observed within the sensitivity of the EDS analysis (i.e., <0.5 atom%), as evidenced by the spectra provided in the Supporting Information. Corresponding analysis of the ALD wall thickness under these conditions is displayed in Figure 4. In this figure, the dependence of Al_2O_3 layer thickness on cycle number is discerned for (i) microtube walls on PVA fibers by TEM and (ii) planar films on Si wafers by ellipsometry. The average growth rate of Al_2O_3 on PVA fibers is ∼0.08 nm/cycle, which is, within experimental uncertainty, virtually identical to the deposition rate (∼0.07 nm/cycle) measured on the planar substrates under identical ALD conditions. A larger population of water molecules residing in the electrospun PVA fibers than on the Si substrate may explain the marginally higher growth rate on PVA.[21] The results shown in Figure 4 indicate that the wall thickness of the Al_2O_3 microtubes generated here by ALD may be precisely (within a molecular layer or so) controlled by simply altering the number of deposition cycles.

For microfluidic applications, the porosity and permeability of fabricated microtubes constitute important design concerns. Previous reports[29,30] of Al_2O_3 ALD performed on planar polymer substrates indicate that films measuring tens of nanometers thick (similar to those fabricated here) perform as high-quality gas barriers. Although the TEM images in Figures 2 and 3 show evidence of breakage (presumably during calcination and/or sonication), the Al_2O_3 microtubes appear predominantly compact and smooth without discernible nanometer-size holes, suggesting that intact microtubes are most likely impermeable to liquids (e.g., water and organic solvents), while affording low permeability to gases. Even without process optimization, the results of this study unequivocally establish that ALD is an effective and robust strategy by which to fabricate long and uniform Al_2O_3 microtubes with precise control of wall thickness from electrospun PVA microfiber templates. By judiciously adjusting the electrospinning parameters, the diameter, alignment, and structure of the templates can be further tuned as desired.[9−14] In similar fashion, the ALD process can be appropriately extended to synthesize designer microtubes of other inorganic materials such as TiO_2[8] and TiN.[24] Because ALD is a self-limiting vapor-phase process, it can be easily adapted to construct, via reactive layering, large numbers of tube structures with nanoscale-precision dimensions and controlled composition, thereby providing an attractive complement to physical self-assembly.[31]

Acknowledgment. This work was supported by the STC Program of the National Science Foundation under Agreement No. CHE-9876674 (G.N.P.) and the Department of Commerce through the National Textiles Center (R.J.S.). G.N.P. also acknowledges support from NSF under Grant CTS-0626256.

Note Added after ASAP Publication. This paper was published ASAP on February 6, 2007. Text in Figure 3 caption was revised. The paper was reposted on February 8, 2007.

Supporting Information Available: Representative EDS spectra have been acquired from the Al_2O_3 microtubes generated by ALD on electrospun polymer fibers after different cycle numbers. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL062948I