Composite Nanostructures Based on Template-Grown Boron Nitride Nanotubes

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The fabrication of boron nitride nanotubules and BN-based composite nanostructures within the pores of anodic aluminum oxide is described. Boron nitride nanotubules are produced by pyrolyzing 2,4,6-trichloroborazine over alumina templates at 750 °C. The nanotubules are polycrystalline, with crystallites exhibiting an orientational ordering such that the BN (001) planes are tilted 25° with respect to the tube axis. Nanotubules at least 20 μm long are observed, longer than what is expected for a growth mechanism that assumes a uniform substrate coating. This suggests that tubes grow in the axial direction faster than in the radial direction. As an example of a CVD-fabricated composite nanostructure, we synthesized coaxial C/BN/C nanotubules by the sequential pyrolysis of acetylene and trichloroborazine over alumina templates. BN-insulated copper nanowires were also fabricated by electrochemical deposition of copper into BN-coated templates.

Introduction

Nanostructured materials have attracted ever increasing attention over the past several years due to their unique properties and the potential to tailor these properties toward specific applications.[1] Among the multitude of applications envisioned for these materials are novel catalysts, separation media, high-sensitivity and high-speed sensors, and optical, electrooptical, and nanoelectronic devices. Template-directed synthesis is one of the major strategies used to engineer new nanomaterials.[2] This approach makes use of the nanoporous structure of media such as anodic oxide films grown on the surface of some metals, most notably aluminum, or three-dimensionally periodic assemblies of polymer or oxide nanospheres, as in opals. Electrochemical, solution-phase electroless or vapor deposition can be used to fill the pores and produce a nanostructured material. The characteristic feature size of the material is determined by the distribution of template pore sizes, while its microstructure (i.e. whether the material is amorphous or crystalline, tubular or rodlike) can be adjusted by the chemical modification of the walls of the pores within the template. A number of novel materials, including metal nanowires[3,4] and nanotubules,[5] carbon nanotubes,[6,7] and semiconductor nanowires,[8,9] have

been synthesized using this approach. Anodic aluminum oxide is particularly well suited for nanostructure fabrication because it provides a rigid matrix with well-aligned pores, whose mean diameter can be easily controlled by changing the anodization conditions. These properties can be used to nonlithographically create high-density arrays of nanodevices, such as carbon nanotube-based field emitters,[10] single-electron tunneling devices,[11] or magnetic nanowire arrays for magnetic memory.

An important direction for template-based synthesis of micro- and nanostructures is the synthesis of composite multilayered materials. A number of microstructures, such as Au/polyphenylene oxide/polypyrrole or semiconductor (TiS_2, TiO_2, ZnO)/Au, have been synthesized.[12,13] The composite nanostructures reported to date are limited to carbon/polyacrylonitrile/Au composites[12] and metal nanocluster-filled carbon nanotubes.[14,15] It is desirable to extend the range of template-synthesized nanocomposite materials. In particular, it is important to develop techniques for depositing thin metallic, semiconducting, and insulating layers within nanoporous templates. This would allow one, for example, to create high-density arrays of metal–insulator–metal, metal–semiconductor–metal, and other similar devices, which, if integrated into microelectronic circuits, would provide a new strategy for device miniaturization.

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However, to date, only nanotubules of a few metals, carbon, and polyacrylonitrile have been synthesized within nanoporous templates. In the present paper we describe the synthesis of boron nitride nanotubules within the pores of anodic aluminum oxide. Boron nitride is a wide-band-gap (5.2 eV) semiconductor widely used as a thermally stable and oxidation-resistant protective coating. While chemical vapor deposition (CVD) of binary compounds directed by templates with micron-sized features has been described,[13] our study provides the first example of CVD of a binary compound within a nanostructured template.

In the past few years interest in the preparation and properties of boron nitride nanotubes has been steadily growing. This is largely due to the fact that BN is isostructural with graphite, and a wide variety of $B_xN_yC_z$ nanomaterials with exciting properties has been envisioned.[16-18] Among the techniques used to synthesize BN nanotubes are arc vaporization of composite metal/ BN and metal/boron rods,[19,20] laser ablation of BN,[21] and the reaction of B_2O_3/N_2 mixtures with carbon nanotubes[22] or B_4C[23] at high temperatures. None of these techniques used the template-based approach employed in the present study, which allows aligned arrays of BN nanotubes of uniform size to be synthesized. Such aligned tubules are ideal for subsequent electrochemical filling or for the preparation of layered nanostructures. We also find that boron nitride nanotubes are the only synthesis product formed using our method, while the purity of nanotube-containing materials reported heretofore was often rather poor. At the same time, most of the techniques mentioned above produce crystalline nanotubes, albeit highly defective in many cases, while the nanotubules synthesized by our technique are polycrystalline. Hence, the excellent processability and purity of the template-grown BN nanotubes comes at the expense of their crystalline integrity, which may result in their somewhat poorer stability and electrical and mechanical properties.

Experimental Section

Boron nitride nanotubules were fabricated inside the pores of commercial aluminum oxide filter membranes (Anodisc, 0.1 or 0.2 μm nominal pore diameter, Whatman). The 50 μm thick membranes possess arrays of parallel pores with the pore density $\sim10^9$ cm^{-2}. BN tubes were synthesized by chemical vapor deposition. A number of boron-containing precursors have been previously used for CVD synthesis of thin boron nitride films,[24] most notably boron trichloride BCl_3 and diborane B_2H_6. However, boron trichloride is incompatible with aluminum oxide and diborane is extremely dangerous to

handle due to its pyrophoricity. Instead, 2,4,6-trichloroborazine ($B_3N_3H_3Cl_3$) was chosen as such a precursor. This compound has the advantage of being a source of both boron and nitrogen with the correct atomic ratio. It can be conveniently prepared in a one-step synthesis[25] and is known to yield stoichiometric BN films upon decomposition at 700-950 °C.[26] Trichloroborazine was synthesized from BCl_3 and NH_4Cl according to the procedure of Brown and Laubengayer[25] and purified by sublimation. A standard hot wall flow tube reactor was used for the CVD synthesis of BN nanotubes. A test tube containing several grams of trichloroborazine was connected via a plug valve to a 1 in. quartz tube placed inside a tube furnace. The quartz tube was evacuated using a turbomolecular pump fitted with a liquid nitrogen trap to prevent the corrosive reagents and products from entering the pumping system. The quartz tube was connected to the pumping system through two parallel lines, one fitted with a diaphragm valve and the other with a needle valve. The first line was used to evacuate the system prior to the deposition. During the deposition, the diaphragm valve was closed, and the system was pumped through the needle valve. The gas lines from the test tube containing trichloroborazine to the quartz tube and from the quartz tube to the valves were heated with a heating tape to prevent accumulation of the reagent. Typically, the trichloroborazine test tube was heated to 83 °C and the lines were heated to 90-95 °C. Because of the slow pumping speed through the needle valve relative to the evaporation rate of trichloroborazine, its pressure within the system during the deposition is expected to be close to its vapor pressure at the temperature of the test tube (16 Torr at 83 °C[25]). The temperature of the tube furnace during boron nitride deposition was 750 °C. A typical deposition time was 10-20 min.

The resulting boron nitride nanotubule samples were characterized by scanning electron microscopy (SEM) using a Hitachi S-4500 field emission microscope, transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using a Hitachi H-600 microscope, and electron-energy-loss spectroscopy (EELS) using a Zeiss 902 transmission electron microscope equipped with an EELS detector. The TEM samples were prepared by first dissolving the aluminum oxide templates in 0.1 M NaOH at 60-70 °C to free the encapsulated nanotubes. The nanotube-containing material was then washed with distilled water and ethanol, filtered, and suspended in ethanol by sonication. A drop of the suspension was placed on a carbon-coated TEM grid for observation.

Results

Figure 1a shows an SEM image of the surface of a 0.1 μm nominal pore diameter alumina template after boron nitride deposition. Before the imaging, the template was etched in a 60 °C 0.2 M chromic/0.5 M phosphoric acid solution for 15 min to partially dissolve the aluminum oxide and expose the structures formed within the pores. The figure shows a close-packed array of aligned tubular structures with an average diameter of approximately 280 nm and the wall thickness $\sim$100 nm. Similar structures are seen in the TEM image in Figure 1b. A typical electron diffraction pattern of an individual tube is shown in Figure 1c. It shows four reflections which correspond closely to the (002), (100), (004), and (110) reflections of a graphite-type lattice with the lattice constants $a = 2.51$ Å and $c = 6.67$ Å. These lattice constants are in an excellent agreement with those of hexagonal boron nitride ($a = 2.504$ Å, $c = 6.661$ Å). The (100) and (110) reflections are ringlike, indicating that the material is polycrystalline. However,

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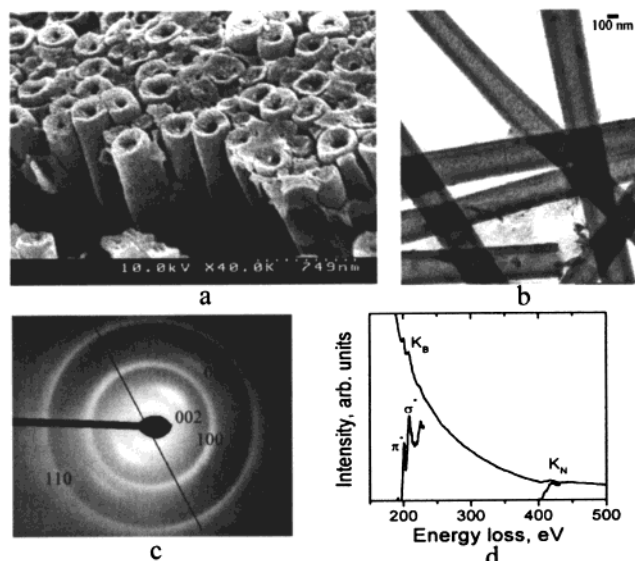(26) Stolle, R.; Wahl, G. *J. Phys. IV* **1995**, *C5*, 761.

Figure 1. (a) SEM image of template-grown boron nitride nanotubules. The alumina template has been partially dissolved to expose the tubes. The sample was sputter-coated with gold to reduce charging. (b) TEM image of BN nanotubules. (c) Selected area diffraction pattern recorded for a single BN nanotubule. The thin black line indicates the direction of the tube axis. (d) EELS spectra of an individual BN nanotubule. The upper curve is the raw spectrum; the lower curves are the background-subtracted spectra.

Figure 2. (a and c) SEM images (a side view and a top view) of template-grown C/BN/C coaxial nanotubules. The surface of the sample was ion-etched, and the alumina template was partially dissolved prior to the imaging. (b) TEM image of C/BN/C nanotubules. (d) SEM image of the sample in Figure 2c, after 10 min of oxidation at 700 °C in air. The sample was sputter-coated with gold.

the (002) and (004) reflections are arcs, indicating that the *c*-axes of the crystallites have a preferred orientation corresponding to a 25° tilt of the BN (001) planes with respect to the tube axis. The direction of the tube axis is indicated by the thin black line in Figure 1c. Other tubes show a similar orientational ordering of the BN crystallites with respect to the tube axis.

Figure 1d shows a typical EELS spectrum of an individual tube. The edges around 190 and 400 eV are the K-edges of boron and nitrogen, respectively. The relative intensity of the boron and nitrogen peaks corresponds well to that expected for stoichiometric boron nitride. The fine structure of the boron K-edge shows two sharp peaks, corresponding to π^* and σ^* preionization edges, which is characteristic of sp^2-hybridized atoms. Energy-dispersive X-ray spectra of the samples recorded on a transmission electron microscope show the absence of chlorine. Taken together, the data of Figure 1 lead to the conclusion that the structures in Figure 1a and b are nanotubes of polycrystalline hexagonal boron nitride.

The preparation of thermally stable, oxidation-resistant insulating tubes within nanosized pores of anodic aluminum oxide makes possible the fabrication of a variety of layered nanostructures using chemical vapor deposition. As an example, we fabricated C/BN/C (i.e. metal/insulator/metal) coaxial nanotubules. First, a 0.2 μm nominal pore size aluminum oxide template was coated with a layer of carbon. Carbon was deposited by flowing a mixture of 10% acetylene in nitrogen at a rate of 50 sccm through the reaction tube heated to 700 °C for 40 min. A boron nitride insulating layer was then deposited at 750 °C for 20 min, as described above. Finally, the inner carbon layer was deposited by pyrolyzing a flowing acetylene/nitrogen mixture at 615 °C for 10 h. Figure 2a and c shows SEM images of the
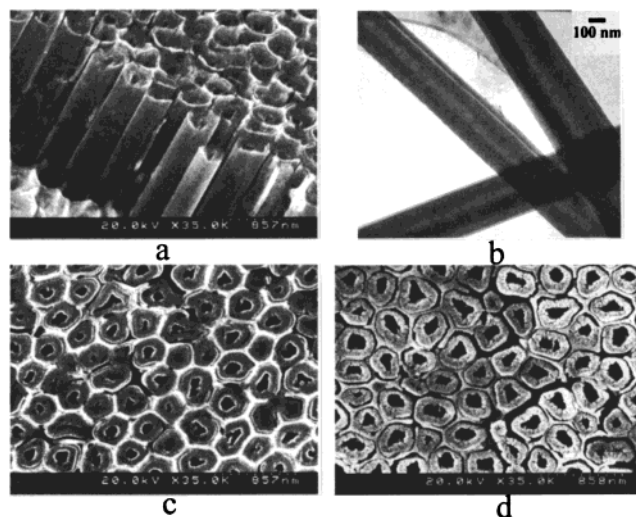
resulting nanostructures. Before the SEM imaging, the template was ion-etched for 1 h (Ar buffer gas, 3 kV dc voltage, 2 mA discharge current) to remove the surface layer and expose the tubes within the bulk of the template. After the ion-etching, the aluminum oxide template was partially dissolved in a chromic/phosphoric acid mixture, as described above. Figure 2a shows a side view of an array of tubes, while Figure 2c shows the top view. The images show tubular structures 270–360 nm in diameter with the wall thickness ~110 nm and no discernible inner structure. The TEM image of the sample (Figure 2b) shows layered tubular structures with two of the three coaxial tubes clearly discernible. The wall thickness is ~35 nm for the outer tubes and ~80 nm for the inner tubes. The inner tubes do not appear to adhere closely to the outer ones, so that a gap is formed between them. It is likely that the outer tubes correspond to the first deposited carbon layer, while BN and the second carbon layer form the inner tubes. No interface between the BN layer and the inner carbon layer was discerned in the TEM image. To reveal the position of the inner BN/C interface, we oxidized the sample at 700 °C in air for 10 min. The oxidation is expected to remove the carbon layers, leaving the boron nitride layer intact. The SEM image of the oxidized sample (a top view) is shown in Figure 2d. Comparing parts c and d of Figure 2 indicates that the average size of the tube opening increased upon oxidation. From the magnitude of this increase an estimate of 14 nm for the thickness of the inner carbon layer was obtained.

A variety of composite nanostructures can also be formed by filling template-grown boron nitride nanotubules using solution-phase techniques. As an example, we have electrochemically deposited copper inside CVD-grown BN nanotubules, thus creating insulated copper nanowires (Figure 3). A 0.7 μm thick silver electrode was evaporated on one side of a BN-coated 0.2 μm pore diameter Anodisc template. Electrical connection to the electrode was made using a silver wire attached with a conductive carbon tape. The electrode was then coated
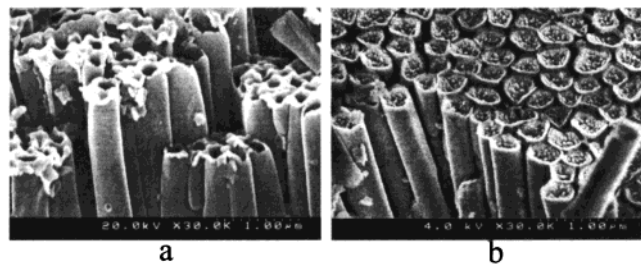
Figure 3. (a) SEM image of an array of BN nanotubes used for electrochemical copper deposition. The alumina template was partially dissolved, and the sample was sputter-coated with gold. (b) An SEM image of an array of BN-insulated electrochemically grown copper wires. The sample surface was ion-etched, and the alumina template was partially dissolved prior to the imaging.

with an insulating layer of epoxy (Torr-Seal, Varian). The template prepared in this way was used as the cathode in an electrochemical cell, with a graphite electrode as the anode. A plating solution of 125 g/L $CuSO_4 \cdot 5H_2O$ acidified with 6.25 mL/L of concentrated sulfuric acid served as the electrolyte. A dc current of 2 mA/cm^2 was passed across the cell, and the deposition was carried out for 10 h. The SEM image of the resulting sample is shown in Figure 3b. The template surface was ion-etched for 1 h, as described above, and the alumina template was partially dissolved by soaking in a 40 °C 0.05 M NaOH solution for 30 min. An SEM image of the original boron nitride nanotube sample is shown in Figure 3a for comparison. The BN tubes in Figure 3b are filled with copper which appears to be polycrystalline. Most (~99%) of the tubes were filled by this procedure, although empty BN shells were encountered occasionally.

Discussion

The fabrication of boron nitride nanotubes described above is the first example of a nanotemplate-directed CVD synthesis of a binary compound. We also demonstrated the use of CVD for fabricating layered coaxial nanostructures. Unlike the fabrication of coaxial nanostructures by laser ablation of composite targets described recently,[27] the template-directed CVD technique allows precise control of the number of layers deposited and their chemical composition and thickness. To fully realize the potential of this technique, it is important to understand the kinetics of chemical vapor deposition in nanosized pores. A successful synthesis of a nanostructure by CVD requires a sufficiently low temperature, so that the chemical reaction of the precursor compounds, rather than their diffusion into the pores of the template, is the limiting step of the process. Under BN deposition conditions in our experiment (pressure ~ 16 Torr, temperature 750 °C), the mean free path of trichloroborazine molecules is >30 μm. During carbon deposition (atmospheric pressure, temperature 615−700 °C), the mean free path of acetylene molecules is >1 μm. Therefore, the gas flow in 100−300 nm diameter pores of aluminum oxide templates proceeds in the Knudsen regime. In this regime, the mean time between collisions is given by $\tau \sim d/v$, where d is the pore

diameter and v is the mean speed of the molecules. The characteristic pore depth over which the precursor concentration becomes substantially depleted is $z = (D/k)^{1/2}$, where D is the diffusion coefficient and k is the net rate constant of the CVD reaction (i.e. the precursor depletion rate). From the Einstein−Smoluchowski equation, $D = d^2/2\tau = dv/2$. The rate constant k can be estimated from the deposition rate of boron nitride from trichloroborazine determined by Stolle and Wahl,[26] who report the rate constant $k_0 = 1.3 \times 10^5 \exp(-131$ kJ$\cdot$mol$^{-1}/RT$) m/s for BN deposition on a flat substrate. The sticking probability p (i.e. the probability that a precursor molecule impinging on the surface undergoes a decomposition reaction) is $p = k_0 n/J = 4k_0/v$, where n is the precursor concentration above the surface and J is its incident flux. The depletion rate k for molecules inside a narrow pore is then $k = p/\tau = 4k_0/d$, whence the characteristic depletion length is

$$z = d(v/8k_0)^{1/2} \quad (1)$$

For trichloroborazine at 750 °C, $k_0 = 2.6 \times 10^{-2}$ m/s and $v = 340$ m/s, so that an aspect ratio $z/d \sim 40$ can be achieved for template-grown boron nitride nanotubes without excessive thinning of the tube wall due to diffusion effects. For example, for 200 nm pores a noticeable wall thinning is expected to occur for tubes longer than 8 μm. In the TEM images, however, we observe nanotubes at least 20 μm long showing no substantial change in wall thickness along their length. Thus, it appears that the above analysis somewhat underestimates the aspect ratio CVD-grown BN nanotubes can attain before reagent transport effects become significant. At the same time, our attempts to grow boron nitride nanotubes in alumina templates with smaller (<100 nm) pores at 750 °C yielded only short tubes. Therefore, 750 °C appears to be the upper temperature limit for the growth of good-quality BN nanotubes in 100−300 nm pores of commercial Anodisc membranes.

An increase in the aspect ratio of template-grown nanotubes can, in principle, be achieved by lowering the growth temperature. However, the chemical composition of the pyrolysis product also changes with temperature. For example, pyrolysis of borazine at 475 °C was shown to yield a compound of composition $BNH_{0.3}$,[28] which can be converted into boron nitride upon heating to 900 °C. No detailed studies of trichloroborazine pyrolysis as a function of temperature have been reported, but one expects trichloroborazine to pyrolyze in a similar fashion. Thus, a compound of composition BNH_xCl_y, $x, y < 1$, is expected to form at pyrolysis temperatures in the range 500−600 °C, and further annealing would be required to convert this material into stoichiometric BN. Applying this notion, we attempted to obtain high-aspect-ratio BN nanotubes in <100 nm pores by first pyrolyzing trichloroborazine at 550 °C for 30 min and then heating the template in a vacuum at 1000 °C for 12 h. However, this approach did not produce nanotubes with good structural integrity.

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The TEM images of C/BN/C coaxial nanotubules (Figure 2b) show that in some cases there is a gap between the outer carbon sheath and the inner boron nitride tube. The presence of such a gap suggests that BN deposition occurs preferentially at the rim of a growing nanotubule rather than on its walls. In such a growth regime, the growth of a BN tube will follow the profile of the pore mouth, where the tube seed is formed. If the diameter of the pore in the bulk of the template is larger than that at its mouth (which appears to be the case for Anodisc filter membranes), the inner BN tube may detach from the carbon sheath which followed the contours of the pore wall faithfully. The presence of the preferential stacking orientation of BN crystallites suggested by the electron diffraction data (Figure 1c) is in accord with such a growth model. A relatively higher growth rate along the tube axis can also explain the fact that the aspect ratios of experimentally observed BN tubes are larger than those predicted by (1). In contrast, we did not observe any gaps between the innermost carbon tubes and the boron nitride tubes in C/BN/C layered nanostructures. This suggests that, unlike BN nanotubes, carbon nanotubes grow by isotropically coating the underlying substrate.

A number of potential applications can be envisioned for the nanostructures described in the present paper. For example, chemically inert, oxidation- and corrosion-resistant BN sheaths can provide protection for an encapsulated active medium used at elevated temperatures or in chemically aggressive environments, such as electrocatalytic metals used in fuel cells. They can serve as nanosized crucibles for carrying out high-temperature chemical reactions on the nanoscale. Also, the C/BN/C coaxial nanostructure described above is essentially a nanosized capacitor with the specific capacitance $\sim$100 pF/m. An array of such capacitors formed in an alumina template 50 μm thick should have a capacitance of $\sim$5 μF/cm^2. Such dense high-capacitance arrays may be of interest in microelectronics applications. Our preliminary measurements show that capacitances of at least 2.5 μF/cm^2 can indeed be attained using this approach.[29]

Conclusions

Boron nitride nanotubules can be conveniently prepared in the nanosized pores of commercial aluminum oxide filter membranes by the thermal decomposition of a single-source precursor, 2,4,6-trichloroborazine. Electron diffraction and EELS spectra of the nanotubules are consistent with polycrystalline hexagonal boron nitride. The growth of BN nanotubules does not appear to proceed as an isotropic coating of the underlying membrane. Rather, the deposition seems to occur preferentially at the rim of a growing tube. Such a model is corroborated by the preferential orientation of the crystallites of the BN nanotubule such that the (001) planes are inclined at a 25° angle to the tube axis. Also, the length of the tubes with uniform wall thickness is found to be greater than what is predicted by a simple kinetic growth model assuming a uniform substrate coating. The fabrication of boron nitride nanotubules is the first example of a nanopore-templated CVD synthesis of a binary compound. Using this approach, it should be possible to fabricate nanotubules made of a wide range of compounds, provided that the conditions can be established under which the deposition reaction rather than the reagent diffusion into the pores is the rate-limiting step. As an example of the usefulness and versatility of this approach, we have fabricated C/BN/C (i.e. metal/insulator/metal) coaxial nanotubules by the sequential pyrolysis of acetylene and trichloroborazine over alumina templates, and BN-insulated copper nanowires by electrochemical deposition of copper inside BN-coated templates.

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