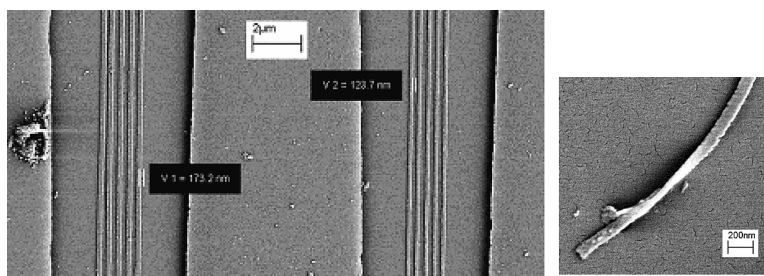


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Formation of Nanostructured Polymer Filaments in Nanochannels

Chih-Yi Peng,[†] Wook Jun Nam,[†] Stephen J. Fonash,^{*,†} Bin Gu,[‡] Ayusman Sen,^{*,‡} Kenneth Strawhecker,[§] Sudarshan Natarajan,[§] Henry C. Foley,^{*,§} and Seong H. Kim^{*,§}

Nanofabrication Facility, Department of Chemistry, and Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

Received February 6, 2003; E-mail: sfonash@psu.edu; asen@chem.psu.edu; shkim@enr.psu.edu

The realization of the full potential of nanotechnology demands the ability to accurately position a wide variety of nanomaterials to construct complex structures and devices.¹ Current lithographic techniques, including dip-pen lithography, allow precise positioning; however, the range of materials that can be synthesized is limited.² Other approaches to forming nanoscale structures involve a two-step synthesizing-and-then-positioning procedure. While a variety of materials, including nanoparticles, nanotubes, and nanorods, can be synthesized in this manner, it seriously limits the ability to control size, location, and orientation on the nanoscale.^{3–8} Herein, we describe a general procedure for the fabrication of nanodimensional channels and their use as templates for the formation of polymer filament arrays with precise dimensional and orientational control in a single integrated step. The procedure is general, allowing the synthesis of different polymeric materials through a variety of chain-growth mechanisms (e.g., radical, metal-catalyzed, and photochemical) inside nanochannels, and opens up the possibility of directed design of “just-in-place” nanoscale structures.⁹

The nanochannel templates were fabricated by the combined use of electron-beam lithography and a sacrificial metal line etching technique (Figure S-1).¹⁰ The use of electron-beam lithography allowed nanoscale control of the channel dimension, interchannel separation, and orientation, which eventually transformed into the control of the nanofilament dimension, separation, and orientation. In brief, parallel lines of desired width and length were fabricated in a resist film on silicon oxide layer grown thermally on a silicon substrate and then filled with nickel to a desired height. After resist lift-off, only nickel lines remained on the substrate. A silicon nitride capping layer was next deposited over the substrate, and finally the sacrificial nickel lines were etched away thereby creating empty nanochannels imbedded in the capping layer. In this way, we fabricated empty channels as small as 20 nm wide and 20 nm tall as shown in Figure 1a, which shows five empty, 20 nm wide by 20 nm high, channels in the cross section using a field emission scanning electron microscope (FESEM). The sample was cut in the middle of a 100 μm wide capping layer (see Figure S-1d) to create this cross section. It can be seen that the sacrificial nickel was etched away completely leaving open channels. Other channels with the same height, 20 nm, but different widths, from 30 to 200 nm, were seen to be open as well by FESEM examination (not shown).

Three kinds of polymerizations were performed in these nanochannels to demonstrate that the channels were open all the way and function as templates. Poly(methyl methacrylate) (PMMA) was polymerized in the nanochannels by introducing a solution containing the initiator AIBN (0.5 mol %) dissolved in monomer liquid. Following initiator and monomer introduction, the sample surface

was cleaned to remove the monomer, and polymerization was performed by heating at 80 °C.

To measure the dimensions of polymer filaments produced in nanochannels, the capping silicon nitride layer was removed by HF etching, and the exposed filaments were imaged with FESEM.

Figure 1b shows FESEM image of five 123 nm wide filaments of PMMA, inside nanochannels. These filaments were all 20 nm thick and equally spaced (200 nm). The continuity of polymer filaments indicates the channels were open all the way without void or collapsed region. In one instance, a twisted PMMA filament with a 170 nm width and a 20 nm height was observed by FESEM as shown in Figure 1c. These results show that the polymer filaments are formed with the same dimensions as the corresponding nanochannels. Thus, the nanochannel templates precisely define the dimension and location of polymer nanofilaments, and, most notably, nanofilaments can be released without breaking.

An oxygen plasma exposure was utilized to verify the exposed filaments seen in Figure 1b were organic polymers, because an oxygen plasma can etch only the polymer but not an inorganic dielectric or metal. Figure S-3 shows FESEM of polymer filaments before and after oxygen plasma etching. This establishes that the filaments in the channel region were polymers; clearly the silicon lines beyond the channel region were not etched by the oxygen plasma.

Solidlike behavior of PMMA fibers was confirmed by intermittent contact atomic force microscopy. Figure 1d is a scan at low force (ca. 100 nm free-oscillation amplitude, 80 nm scanning oscillation amplitude; tip force constant 0.65 N/m; resonant frequency 43.5 kHz) showing a PMMA nanofilament. The filament was then scanned at a single spot for several line scans at large force (0 nm scanning oscillation amplitude). The original fiber was then rescanned showing where it was cut by the AFM tip. The underlying silicon surface remained undamaged. Figure 1e shows line profiles of the nanofilament before and after cutting.

Fluorescence imaging was also used to verify polymer formation along entire nanochannels. Because the silicon nitride capping layer was transparent to UV–vis light, this layer was not removed. Poly(1-pyrenylmethyl methacrylate) in channels was obtained by introducing a homogeneous solution of 1-pyrenylmethyl methacrylate and AIBN in toluene into the channels and heating at 80 °C. Figure S-4 shows the fluorescence imaging of formed polymers in the nanochannels. The fluorescence from 10 different polymer line groups with designed widths ranging from 200 to 20 nm was detected by fluorescence microscope where different line width groups were separated by 10 μm as shown in Figure S-4. This picture confirms that the polymerization did take place in the channels and that the channels were open without collapsed regions. As the polymer was exposed for longer times, it bleached as shown in the rectangular area in Figure S-4.

Photopolymerization is also possible inside nanochannels because the silicon nitride capping layer is UV transparent. Figure S-5 is a

[†] Nanofabrication Facility.

[‡] Department of Chemistry.

[§] Department of Chemical Engineering.

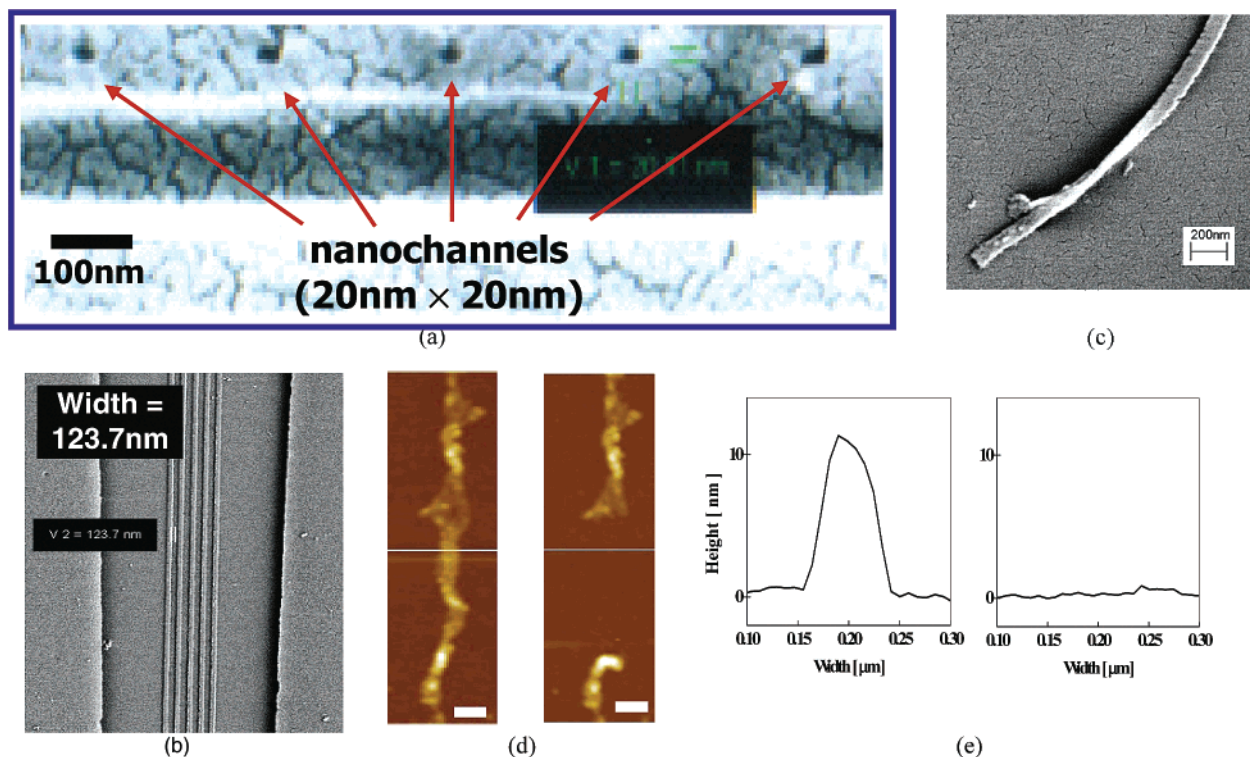


Figure 1. (a) FESEM cross-section picture showing five 20 nm wide, 20 nm high nanochannel templates, which are spaced 200 nm apart. (b) FESEM picture of a set of PMMA nanofilaments. Each filament is 120 nm wide, 20 nm thick, and separated 200 nm from others. (c) FESEM picture of a twisted polymer nanofilament having 170 nm width and 20 nm height. (d) AFM of polymer nanofilament cutting: the left picture shows scan of one PMMA nanofilament at low tapping force; the right shows the same nanofilament scanned again at low force after scanning a single line at high force; scale bar is 100 nm. (e) Line profiles of the nanofilament before and after cutting.

fluorescence microscope image showing the photoluminescence of polythiophene nanofilaments produced via photoinduced coupling of 1,4-diiodothiophene inside nanochannels upon UV irradiation with a 200 W Hg lamp.

Heterogeneous metal-catalyzed polymerization in nanochannels through diffusion of monomer vapor was demonstrated by production of poly(norbornene) filaments at 25 °C using $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ ¹¹ catalyst loaded via wet impregnation. Polymers with dimensions consistent with those of designed nanochannels were formed (Figure S-6). In the wider filaments (200 nm), some defects are observed; when the channel is narrower, the formed polymer nanofilament is more continuous.

In conclusion, we have demonstrated the use of hard etching methods to create nanoscale templates with precise dimensional and orientational control and their use in the production of polymer filaments with cross sections as small as 20 nm high by 20 nm wide. The procedure is general as illustrated by the radical, coordination, and photochemical polymerizations that were performed in these nanochannels. The polymers grown follow the dimensions of the channels, allowing the precise control of the dimension, location, and orientation of polymers. The approach opens up the possibility of “just-in-place” manufacturing and processing of patterns and devices from nanostructured polymers using well-established polymer chemistry.

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provided by Michael Rogosky and the staff of the PSU NNUN site for nanofabrication and by Simon Gilroy for fluorescence imaging.

Supporting Information Available: Nanochannel fabrication procedure, AFM of empty channels, oxygen plasma etching, fluorescence imaging, and polynorbornene nanofilaments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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