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Nanolithography Using Hierarchically Assembled Nanowire Masks

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ABSTRACT

A general and scalable method has been developed for patterning nanometer scale lines hierarchically over large areas using nanowires as masks for etching and deposition. Core–shell nanowires with controlled diameter and shell dimensions were aligned with nanometer to micrometer scale pitches using a Langmuir–Blodgett approach and then transferred *en mass* to planar substrates. Transferred nanowires were used as deposition masks to define metal lines with pitches from the nanometer to micrometer scale over centimeter square areas. Hierarchical parallel nanowire arrays were also prepared and used as masks to define nanometer pitch lines in 10 × 10 μm^2 arrays repeated with a 25 μm array pitch over centimeter square areas. This nanolithography method represents a highly scalable and flexible pathway for defining nanometer scale lines on multiple length scales and thus has substantial potential for enabling the fabrication of integrated nanosystems.

The development of novel methods for patterning structures on nanometer length scales can make possible fundamental investigations of new devices and could help to enable applications in nanoelectronics, photonics, and nanobiotechnology. Today, top-down approaches based on photo- and electron beam lithography are widely used methodologies for patterning structures, although these approaches become increasingly costly and/or slow as feature sizes move deeper and deeper into the nanometer regime.[1,2] Considerable effort has also been placed on developing alternative top-down patterning methods. For example, scanning probe microscopies are versatile tools for nanoscale pattern formation,[3] including the transfer of materials by dip-pen nanolithography,[4] although the throughput of these methods is inherently low due to the serial nature of scanning probe techniques. Nanoimprint lithography[5] and transfer lithography[6,7] can also pattern substrates down to the nanoscale and, in contrast to probe microscopy methods, are more parallel and potentially scalable.

Nanoscale patterning does not necessarily require top-down approaches. To the contrary, examples abound in nature where regular patterns are formed on massive scales from the bottom-up through self-assembly.[8] For instance, close-packed monolayers of submicron diameter monodisperse polymer spheres have been used as shadow masks to generate a variety of two-dimensional metal nanoparticle arrays.[9] Similarly, ordered thin films of diblock copolymers have been used as masks to fabricate periodic arrays of holes and dots with nanometer dimensions.[10] Both of these methods are attractive since they allow for (i) control of the size and spacing of structures at the nanometer scale and (ii) patterning of these features over large areas. However, other structures such as nanoscale wires are also needed, for example, to create interconnected nanodevice arrays that are central to many nanoelectronic and photonic schemes. Herein we address the issue of fabricating nanoscale wires with the development of a general and scalable method that exploits bottom-up assembly of nanowires (NWs) as masks for patterning lines with nanometer to micrometer scale pitches hierarchically over large areas.

Our overall approach is illustrated schematically in Figure 1. Surfactant-stabilized NWs are uniaxially compressed on a Langmuir−Blodgett (LB) trough to produce aligned nanowires with a pitch (the center-to-center NW−NW separation) controlled by the compression process (Figure 1a).[11,12] The aligned NWs are then horizontally transferred *en mass* onto hydrophobic substrates to form uniformly ordered parallel arrays (Figure 1b). Because compression of NWs below a pitch of ca. 100−200 nm leads to increasing aggregation due to strong inter-NW attractive forces, we use core−shell NWs[13] in which the core diameter and shell thickness are independently varied to enable control of pitch at the nanometer scale. Following transfer, selective anisotropic etching is used to remove the oxide shell of core−shell NWs and, if desired, transfer the line-pattern to the underlying substrate surfaces (Figure 1c). In addition, other materials, such as metals, can be deposited using the aligned

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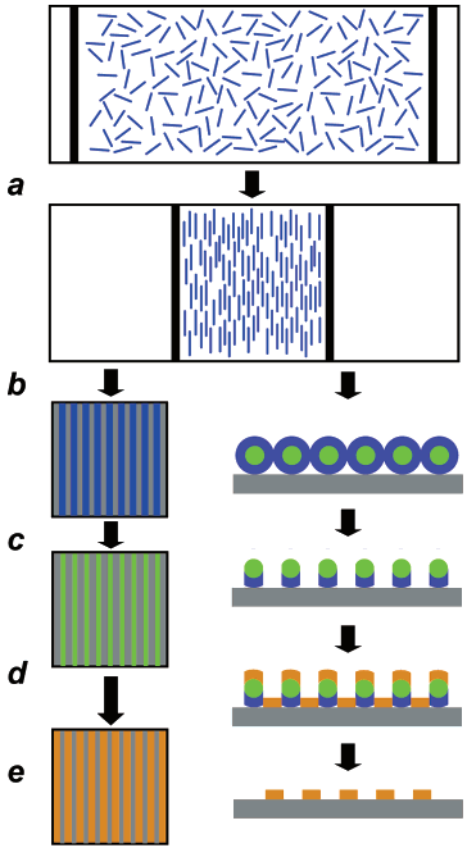

Figure 1. (a) Alignment of NWs (blue) on the water surface of a Langmuir−Blodgett trough. (b) Transfer of aligned NWs onto substrates. The top view (left) illustrates NWs compressed to finite pitch. The cross-sectional view (right) shows the case of NWs compressed to close-packed where the NWs have a core (green)-shell (blue) structure. (c) Selective anisotropic etching of the oxide shell of core−shell NWs. (d) Deposition of metal or other materials. (e) Removal of the NW mask to yield parallel lines over the entire substrate surface.

NWs as shadow masks to create arrays of nanoscale wires (Figure 1d). Finally, the NW masks are removed by isotropic wet etching and sonication to expose the etched or deposited parallel line features (Figure 1e).

We first demonstrate this overall approach with the fabrication of high density parallel metal lines. The NWs used in these studies were core−shell Si−SiO_2 NWs prepared with nearly monodisperse diameters and aspect ratios of at least 500−1000:1 using nanocluster catalyzed chemical vapor deposition.[13,14] Stable NW suspensions in isooctane-2-propanol mixed solvents were spread on the surface of the aqueous phase in a LB trough, uniaxially compressed to close-packed structures, and then transferred to silicon substrates.[11,12] Field-emission scanning electron microscopy (SEM) images show that the transferred NWs exhibit good alignment over many microns and are in a close-packed configuration (Figure 2A,B). The average NW pitch, ca. 90 nm, is consistent with the overall diameter of the core−shell nanowire (50 nm Si core and 20 nm thick SiO_2 shell) used in these experiments. Reactive ion etching (RIE) with CHF_3 was used to remove the SiO_2 on the sides and tops of the core−shell NWs,[15,16] SEM images demonstrate that RIE

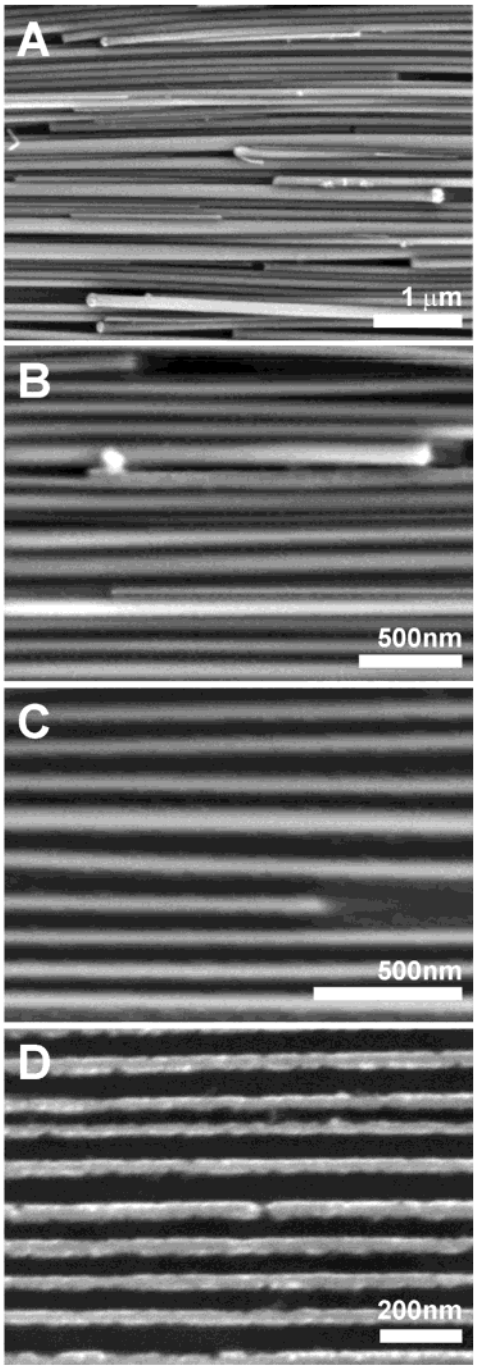

Figure 2. Typical SEM images of (A, B) close-packed parallel Si−SiO_2 core−shell NWs on silicon substrate surface; (C) parallel NWs after selective, anisotropic etching of the SiO_2 shell by RIE; and (D) 15 nm thick Cr metal lines following removal of the NW mask.

produces an increase in the average spacing between NWs to ca. 40 nm, although the NW pitch remains unchanged (Figure 2C). These results are consistent with selective and anisotropic etching of the SiO_2 shell. Last, chromium metal was deposited by thermal evaporation, and the NW shadow masks were removed by sequential 40% NH_4F aqueous solution etching followed by sonication in deionized water. Significantly, the SEM image of the resulting sample shows well-defined parallel metal lines with an average pitch, 90

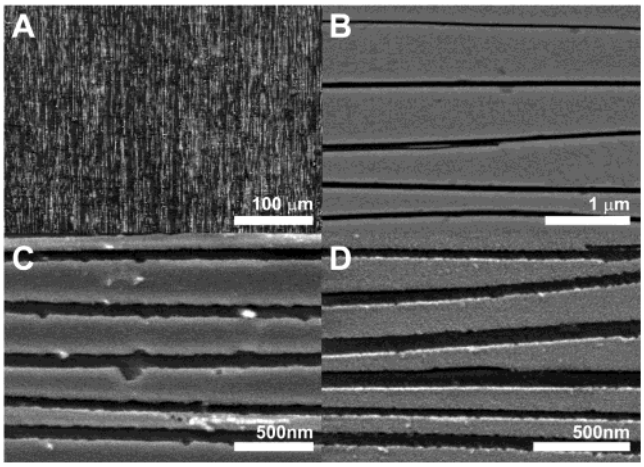

Figure 3. (A) Large-area SEM image of NWs aligned and transferred by the LB method; the NW pitch is ca. 0.8 μm. (C−D) SEM images of Cr-metal stripes with pitches of ca. 0.6, 0.3, and 0.2 μm, respectively. Brighter areas in the images correspond to the metal, while the darker lines are SiO_2 substrate surface remaining after removal of the NW masks.

nm, and line width, 40 nm, consistent with the overall process (Figure 2D).

These results demonstrate several important characteristics of our NW-based lithography approach. First, the line width and pitch can be well-controlled via the synthesis of core−shell NWs prior to assembly and subsequent processing steps. This offers the potential for rapidly and independently changing the line width and pitch on the nanometer scale. Second, the feature sizes defined by our method are comparable to state-of-art extreme UV lithography[2] and approach the limit of electron-beam lithography[1] and very recent transfer lithography[7] studies. Third, we can currently assemble nanowires in one step over areas of 20 cm^2, which exceeds most other unconventional lithography methods, and, moreover, could extend the coverage to much larger areas using modified LB instrumentation.[17] Fourth, the lengths of continuous metal lines, which are limited by the NWs used as masks, place constraints on the sizes of arrays (see below).

Our method is also quite flexible and can be used to fabricate much larger width and pitch lines. Specifically, the pitch of aligned NWs can be readily controlled from the micron to submicron scale during uniaxial compression in the LB trough,[11] and then the NWs can be transferred *en mass* to substrates as shown in Figure 3A. NWs transferred at larger separations were used directly as masks for the fabrication of metal lines without the RIE etching step described above. Specifically, chromium metal was deposited by thermal evaporation onto substrates with transferred parallel NW masks having average pitches of 0.6, 0.3 and 0.2 μm, and then the NWs were removed by sequential 40% NH_4F aqueous etching and sonication in deionized water. SEM images of the resulting structures show well-defined metal lines with average pitches of ca. 0.6, 0.3, and 0.2 μm (Figures 3B, 3C, and 3D, respectively). The spacing between metal lines (i.e., the dark lines in the images) is determined largely by the diameter of the NW used as masks, while the much larger pitch was set by NW−NW separation during the LB compression. The ability to control independently the separation and width of the metal lines during the assembly process contrasts previous examples from nanosphere lithography, where only close-packed monolayers of polymer spheres have been used for patterning.[9]

Last, we have used our NW lithography approach to prepare discrete line arrays that are tiled in a regular and definable pattern over large substrate areas. Our approach for this hierarchical patterning of lines is outlined in Figure 4A. Briefly, aligned, controlled-pitch NWs are transferred uniformly to a substrate, a pattern is defined using photolithography, and then NWs outside the pattern are removed by sonication.[12] The tiled NW arrays are then used as etch or deposition masks to fabricate line structures on the substrate as described above. To demonstrate this approach for hierarchical patterning of parallel lines, we have transferred the line pattern defined by 10 μm × 10 μm square NW arrays tiled with a 25 μm pitch into a SiO_2 substrate surface by RIE.[16] Large area SEM images show clearly that the tiled square pattern is transferred to the substrate surface

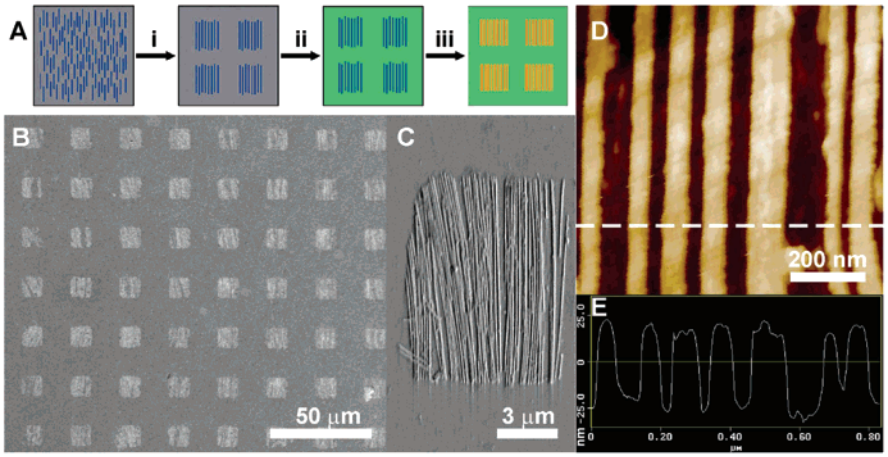

Figure 4. (A) Schematic illustration of the approach for hierarchical patterning of nanowire lithographically defined structures. (B) SEM image showing the massive square arrays of parallel lines. (C) SEM image of an expanded view of one square array. (D) AFM image of seven line features recorded from one array. The *z*-range of the image is 80 nm. (E) Plot of the height variation recorded along the cross section indicated by the dashed line in (D).

(Figure 4B), and higher resolution images further demonstrate that each square consists of a parallel array of SiO_2 lines with widths smaller than 100 nm (Figure 4C). The shapes of the lines were further characterized by atomic force microscopy (AFM). These measurements show that the etched lines have a very regular height, ca. 50 nm, which is consistent with RIE etch time and rate (Figure 4D,E).

This method should be applicable for transferring line patterns to other substrates, for example, substrates with electronically and/or optically active surface layers, as long as selective etching conditions for the substrate versus NW mask can be established. Our approach can also be used for hierarchical patterning of metal lines using the procedures describe above. Overall, this work demonstrates that the combination of conventional photolithography and our new NW lithography provides rapid and scalable access to arrays of parallel lines with well-defined order on length scales from sub-100 nm, which is defined by nanowire diameter and LB compression, to micron scale of square arrays, which is set by the photolithography pattern, to centimeter and much larger areas defined by the LB transfer method. Significantly, the order and length scales can be varied at each level in a facile and independent manner.[18]

In summary, a general and scalable method has been developed for patterning nanometer scale lines hierarchically over large areas using NWs as masks for etching and deposition. Core−shell NWs with controlled diameter and shell dimensions were aligned with nanometer to micrometer scale pitches using the LB technique and then transferred *en mass* to planar substrates over areas up to 20 cm^2. Transferred NWs were used as deposition masks to define metal lines with pitches from the nanometer to micrometer scale over centimeter square areas. Hierarchical parallel nanowire arrays were also prepared and used as masks to define nanometer pitch lines in $10 \times 10\ \mu m^2$ arrays repeated with a 25 μm pitch over centimeter square areas. This nanolithography method represents a highly scalable and flexible approach for defining nanometer scale lines on multiple length scales and thus has substantial potential for enabling the fabrication of many types of periodic nanostructures and integrated nanosystems.

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(11) Silicon NWs were dispersed in a solution of isooctane and 2-propanol (3:1 v/v ratio) containing 50 μL of 5mM 1-octadecylamine in hexane per 1 mL of suspension. The NW suspension with surfactant (about 2.4 mL) was added dropwise to the center of the water surface of a Langmuir−Blodgett trough (KSV 5000 system, KSV Instruments Ltd), and then compressed to a surface pressure between 55 and 60 mN/m. Constant surface pressure was then maintained as the 1-octadecylamine slowly dissolves into the water subphase by reducing the surface area between the L−B barriers. The compression process was stopped when the desired surface area was reached, and then parallel SiNWs were horizontally transferred using the Langmuir−Schaefer method onto Si substrates.
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(16) RIE was carried out with a South Bay Technology reactive ion etcher (RIE2000) using trifluoromethane at a flow rate of 50 sccm and a pressure of 30 mTorr. Under the power of 75 W and DC bias of −820 V, the etching rate of silica is about 60 nm/min. Etching selectivity of silica over silicon is not optimized but is sufficient for the current study.
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(18) The length of the NWs sets a natural length scale for continuous line features produced by our method, and structures much larger than this length will naturally have "broken line" defects. In this regard, our hierarchical patterning represents a good method for controlling the defects; that is, using arrays comparable to or smaller than the average length of the NWs.

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