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## Nanoskiving: A New Method To Produce Arrays of Nanostructures

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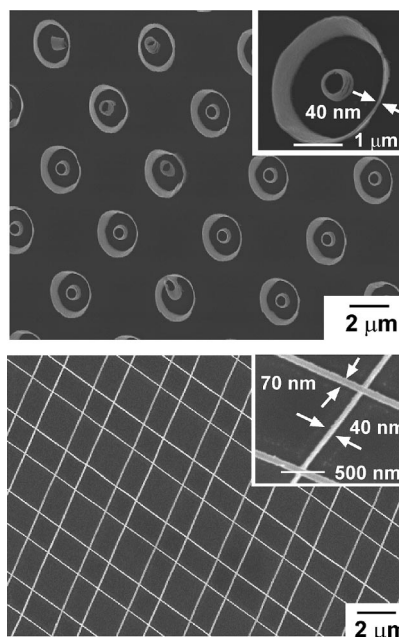
### CON SPECTUS

This Account reviews nanoskiving—a new technique that combines thin-film deposition of metal on a topographically contoured substrate with sectioning using an ultramicrotome—as a method of fabricating nanostructures that could replace conventional top-down techniques in selected applications. Photolithography and scanning beam lithography, conventional top-down techniques to generate nanoscale structures and nanostructured materials, are useful, versatile, and highly developed, but they also have limitations: high capital and operating costs, limited availability of the facilities required to use them, an inability to fabricate structures on nonplanar surfaces, and restrictions on certain classes of materials. Nanoscience and nanotechnology would benefit from new, low-cost techniques to fabricate electrically and optically functional structures with dimensions of tens of nanometers, even if (or perhaps especially if) these techniques have a different range of application than does photolithography or scanning beam lithography.

Nanoskiving provides a simple and convenient procedure to produce arrays of structures with cross-sectional dimensions in the 30-nm regime. The dimensions of the structures are determined by (i) the thickness of the deposited thin film (tens of nanometers), (ii) the topography (submicrometer, using soft lithography) of the surface onto which the thin film is deposited, and (iii) the thickness of the section cut by the microtome ( $\geq 30$  nm by ultramicrotomy). The ability to control the dimensions of nanostructures, combined with the ability to manipulate and position them, enables the fabrication of nanostructures with geometries that are difficult to prepare by other methods. The nanostructures produced by nanoskiving are embedded in a thin epoxy matrix. These epoxy slabs, although fragile, have sufficient mechanical strength to be manipulated and positioned; this mechanical integrity allows the nanostructures to be stacked in layers, draped over curved surfaces, and suspended across gaps, while retaining the in-plane geometry of the nanostructures embedded in the epoxy. After removal of the polymer matrix by plasma oxidation, these structures generate suspended and draped nanostructures and nanostructures on curved surfaces. Two classes of applications, in optics and in electronics, demonstrate the utility of nanostructures fabricated by nanoskiving.

This technique will be of primary interest to researchers who wish to generate simple nanostructures, singly or in arrays, more simply and quickly than can be accomplished in the clean-room. It is easily accessible to those not trained in top-down procedures for fabrication and those with limited or no access to the equipment and facilities needed for photolithography or scanning-beam fabrication.

This Account discusses a new fabrication method (nanoskiving) that produces arrays of metal nanostructures. The defining process in nanoskiving is cutting slabs from a polymeric matrix containing embedded, more extended metal structures.



## What is Nanoskiving?

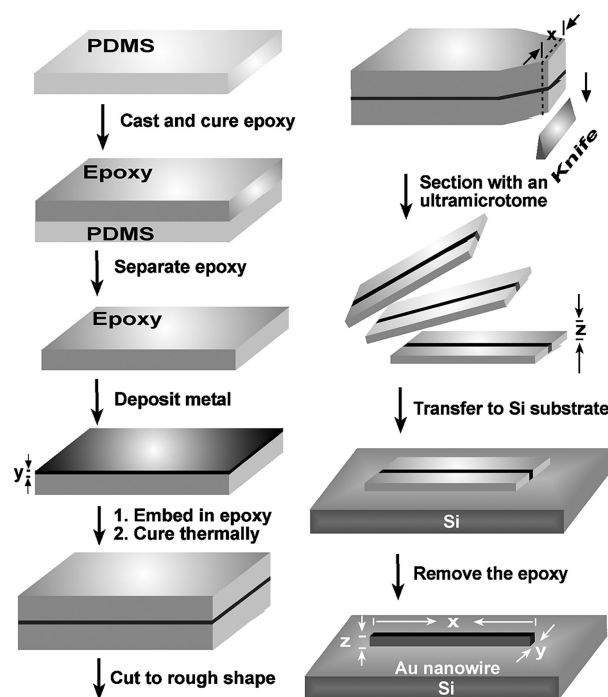
"Nanoskiving" is the name we have given to a technique for the fabrication of nanostructures that combines the deposition of thin films on flat or topographically patterned polymeric substrate using physical vapor methods with sectioning using an ultramicrotome.<sup>1</sup> Figure 1 outlines the procedure used to fabricate nanomaterials by nanoskiving. The first step utilizes an epoxy substrate obtained by curing an epoxy prepolymer (e.g., Araldite 502) against a flat or topographically patterned poly(dimethylsiloxane) (PDMS) stamp formed by soft lithography.<sup>2</sup> A number of deposition techniques make it possible to form films with nanometer thickness on the surface of this flat or topographically patterned epoxy. We embed the resulting structure in more epoxy and generate an epoxy block containing an embedded thin film. An ultramicrotome sections this block to produce slabs that are, remarkably, as thin as  $\sim 30$  nm. After sectioning, the slabs typically float on the surface of water filling the sample-collecting reservoir of the microtome. The epoxy sections can be transferred onto a solid substrate, where the removal of epoxy by oxygen plasma generates freestanding nanostructures; the dimensions of the structures (Figure 1) are determined by the topography of the substrate ( $x$ ), the thickness of the deposited film ( $y$ ), and the thickness of the epoxy slab generated by sectioning ( $z$ ).

Figure 2 is a collage of images of both simple and complex metal nanostructures fabricated by nanoskiving;<sup>3–5</sup> these images establish both the versatility of this technique and the positioning of these structures on unconventional substrates.

This Review focuses on the development and use of nanoskiving as a technique to produce nanomaterials, including a historical context, applications, advantages, and disadvantages.

## Motivation of Nanoskiving

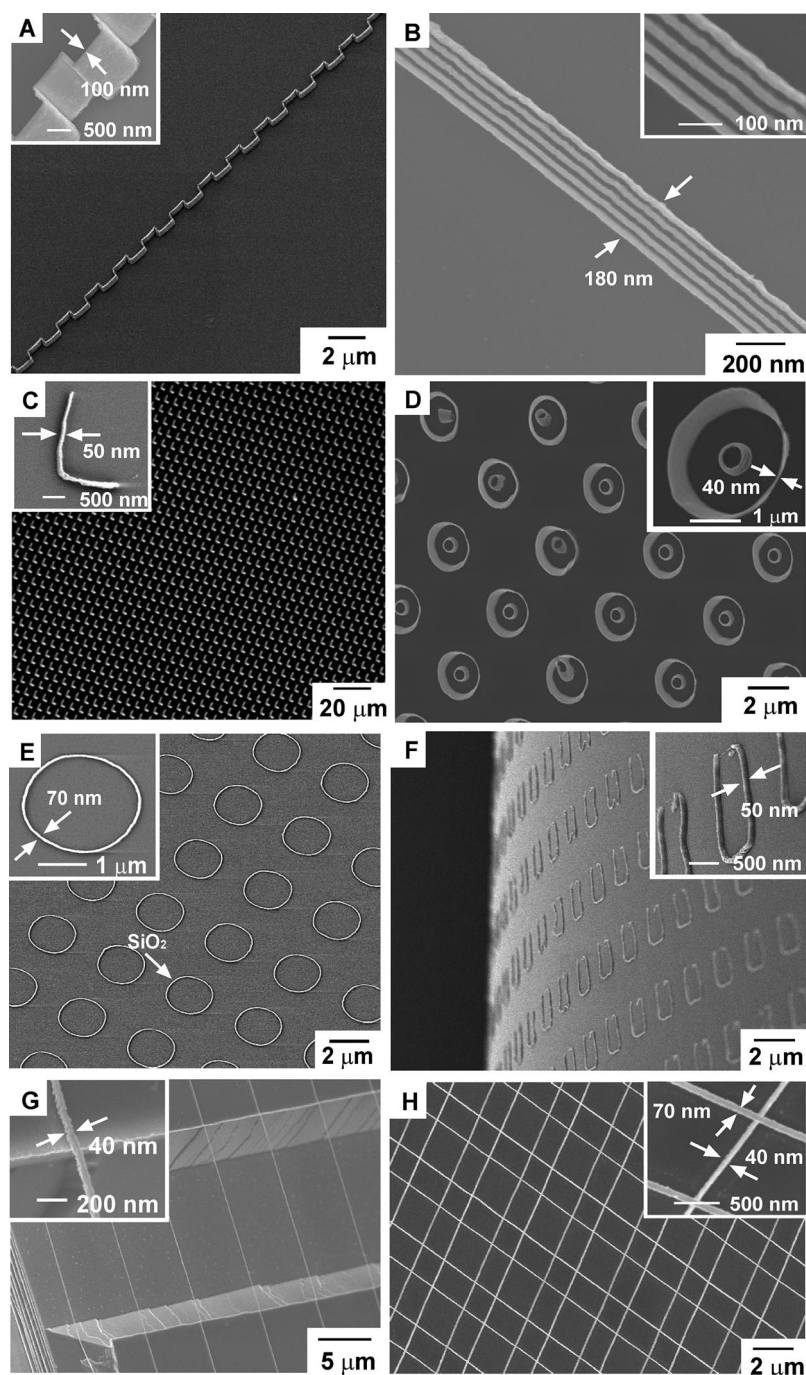
Nanoskiving is fundamentally a technique that generates structures with nanometer-scale dimensions by sectioning thin films deposited on a master structure fabricated in epoxy. It takes advantage of two techniques, deposition of the thin film on the master from the vapor phase (e.g., by e-beam evaporation or sputtering) and sectioning using a microtome, to produce nanometer-scale features in two dimensions. The third dimension is fixed by the topography of the master. The master can be prepared using conventional photolithography (which may require a clean-room for features smaller than  $\sim 0.5$ – $1\ \mu\text{m}$  but can be conducted outside a clean-room for larger features). Masters are also readily available at either low or no cost from commercial vendors or university-based



**FIGURE 1.** Fabrication of metal nanowires by nanoskiving. This procedure begins with the replication of a flat or topographically patterned PDMS surface in epoxy, followed by the deposition of a thin film of metal on the epoxy by e-beam evaporation or sputtering. The topography of the original template determines the dimension along the  $x$ -direction. The thickness of the evaporated metal film determines the dimension in the  $y$ -direction and can be as small as 20 nm for gold. After embedding the thin metallic film in more epoxy and curing, sectioning with an ultramicrotome produces sections with a thickness ( $z$ ) as small as 50 nm using a standard  $45^\circ$  diamond knife. After sectioning, transfer of the epoxy section to a silicon substrate and removal of the epoxy with an oxygen plasma leaves free-standing metal nanostructures. The  $y$ - and  $z$ -dimensions of these nanostructures throughout the paper are as defined in the figure.

foundaries.<sup>6</sup> Structures such as anodized aluminum membranes, electron microscope grids, and patterns for optical metrology are readily available commercially and can serve as masters for soft lithography (see Supporting Information, Figure S1). Some structures (e.g., straight, extended wires) require only flat surfaces. Thus, although for users with access to clean-room facilities it may be convenient to make certain custom masters using these facilities, there are numerous ways of obtaining appropriate masters that do not require access to a clean-room at all.

Nanoskiving uses an ultramicrotome to produce nanostructures embedded in sub-100 nm thick slabs of supporting matrix. We utilize this capability to produce nanostructures with compositions and geometries that are challenging to make using conventional techniques (e.g., extreme UV (EUV) or X-ray photolithography, e-beam lithography (EBL), focused



**FIGURE 2.** (A) SEM image of 100-nm wide, 1- $\mu$ m high step-shaped nanostructures fabricated by nanoskiving a metal-coated epoxy substrate prepatterned with 1- $\mu$ m wide lines with 1- $\mu$ m spacing.<sup>3</sup> (B) SEM image of parallel gold nanowires with 20-nm spacing, by nanoskiving a flat epoxy substrate coated with a multilayer, composite Au/SiO<sub>2</sub> film, followed by complete etching of the SiO<sub>2</sub> spacing layers using reactive ion etching.<sup>3</sup> (C) Dark-field optical microscopy image of “L-shaped” nanostructures patterned over a  $\sim 3$ -mm<sup>2</sup> area by nanoskiving in a direction parallel to the patterned substrate.<sup>4</sup> (D) SEM image of double loop-shaped gold nanostructures.<sup>5</sup> (E) SEM image of loop-shaped SiO<sub>2</sub> nanostructures on a SiO<sub>2</sub>/Si(100) substrate by using gold loop-shaped nanostructures as a physical mask during reactive ion etching with CF<sub>4</sub>. (F) SEM image of an array of “U-shaped” gold nanostructures positioned on the curved surface of a glass rod.<sup>3</sup> (G) SEM image of parallel gold nanowires draped over 20- $\mu$ m wide “truncated-V”-shaped trenches, etched in a Si(100) surface.<sup>3</sup> (H) Cross-bar nanostructures fabricated by the orthogonal stacking of two epoxy slabs containing arrays of gold nanowires on top of each other. The insets are high-magnification SEM images of the nanostructures.

ion-beam (FIB)).<sup>7–9</sup> Ultramicrotomes are generally much more accessible and less expensive than clean-rooms, e-beam writ-

ers, and related equipment. Furthermore, many materials (especially organics that are amenable to nanoskiving) are for-



bidden in semiconductor facilities. The slabs produced by nanoskiving enable the structures to be manipulated and positioned on arbitrary substrates, including curved surfaces and over gaps, and while retaining the relative in-plane positions of arrays of structures.

## Nanoskiving: Description of the Procedure

Ultramicrotomy, which enables the reproducible generation of sections with a thickness of  $<100$  nm, allows biologists to examine details of cellular or tissue ultrastructure.<sup>10</sup> Materials scientists adapted ultramicrotomy to study the details of nanometer-thick (10–100 nm) sections of inorganic and organic materials.<sup>11</sup> In nanoskiving, the “sample block”, which is ultimately sectioned by the ultramicrotome to produce nanomaterials, is typically fabricated by embedding one or multiple structures (e.g., a film on a flat surface or a conformal film over a topologically patterned surface) within an embedding matrix; this embedding matrix, in our work a cross-linked epoxy resin, sections well because of its mechanical properties.

**Embedding Matrices: Selection of Materials.** The mechanical properties of the embedding material must be appropriate for microtome sectioning at room temperature: this material must have a relatively large elastic (Young’s) modulus ( $E > 1500$  MPa).<sup>12</sup> Materials with a value of Young’s modulus of this magnitude are considered “brittle” and include such common polymers as poly(methylmethacrylate) (3100 MPa), polystyrene (3050 MPa), polycarbonate (3000 MPa), and epoxy-based resins such as Epon (3030 MPa) and Durcupan (3000 MPa).<sup>12</sup> Softer resins ( $E < 1500$  MPa) including materials such as low-density polyethylene (230 MPa) and PDMS (0.5 MPa) do not allow cutting of thin sections at room temperature, although they may when colder.

The embedding material must have some flexibility because the sections bend at an angle of  $\sim 90^\circ$  as they move from the sample block to the surface of the water in the trough used for collecting the samples.<sup>12</sup> The embedding material must provide support for the nanostructures formed upon sectioning in order for the structures to be manipulated. The embedding matrix must be removed easily and quickly by etching if desired. The adhesion of the embedding matrix to the surface of the embedded material must be sufficient to prevent delamination during sectioning.

**Choices of Materials for Thin-Film Formation.** There are a number of methods for the deposition of thin films of metals with nanometer accuracy; for metals, these include physical vapor deposition, chemical vapor deposition, and atomic layer deposition.<sup>13</sup> The best method to form thin films

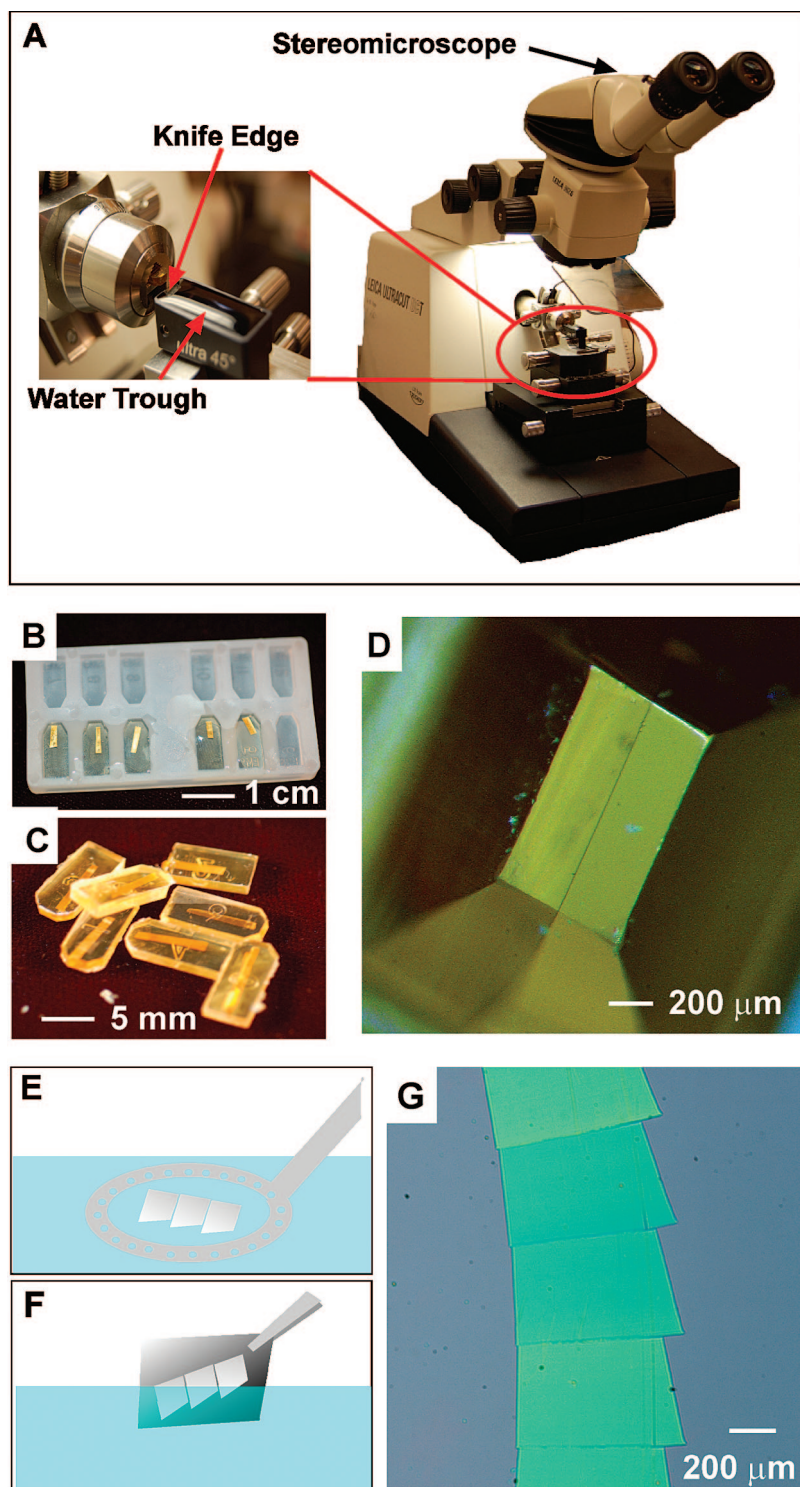
of organic materials, including conducting and electroactive polymers, is spin-coating.

The mechanical properties of the embedded material influence the outcome of the final structures that result from sectioning. Structures of malleable materials (e.g., gold and silver) can be cut without significant catastrophic damage to the nanostructures. Brittle materials, such as chromium and silicon, usually crack or break during sectioning. This limitation can be mitigated by using an ultrasonic knife or a diamond knife with a small wedge angle ( $35^\circ$ ) and by proper selection of the embedding matrix.<sup>14</sup>

**Knife Options.** Knives are commonly made either from glass or from high-quality, natural diamond. The formation of high-quality sections requires the use of diamond knives whose sharp edge has a radius of curvature of 3–6 nm.<sup>15</sup> These knives are considerably more expensive than glass knives. (Diamond knives range from \$1700–3500, depending on the knife angle and the width of the cutting edge; the cost of disposable glass knives is  $\sim \$0.50/\text{knife}$ ) Glass knives are used typically one time because these knives dull quickly. Diamond knives have significantly longer service life than glass knives; they require resharpener only every 1–2 years. The cost of resharpener ranges from \$800–2200, depending on the knife specifications (knife angle and the width of the cutting edge), and the resharpener process takes 2–3 weeks.<sup>16</sup> In some cases, knives may dull very quickly if they are not suited for the material to be sectioned. For example, we found that sectioning gold thin films embedded in Araldite epoxy with a diamond knife with a wedge angle of  $25^\circ$  resulted in rapid damage of the knife edge.

**Operation of the Ultramicrotome.** The ultramicrotome, pictured in Figure 3A, has a “sample arm” that holds the sample to be sectioned securely. The samples can be prepared by casting the embedding material in a mold of appropriate dimensions (Figure 3B). In preparation for sectioning, a face of the block of epoxy containing the embedded thin film (Figure 3C) must be manually trimmed to a trapezoid with a cross-sectional area of  $\sim 0.5$  mm (height)  $\times$   $\sim 0.5$  mm (width) (Figure 3D). The alignment of the face of the block with the knife requires several steps; we include an abbreviated procedure for the correct alignment of the knife with the sample block face in Supporting Information.

The ultramicrotome mechanically advances the sample arm toward the stationary knife in controlled steps.<sup>17</sup> The mechanism that advances the sample comprises a stepping motor and spindle, and a lever transforms micrometer-increment steps of the sample arm into nanometer-increment steps. The lever and its bearing assembly ensures high stability and



**FIGURE 3.** (A) Photograph of an ultramicrotome and close-up photograph of the sample and diamond knife mount. (B) Photograph of the flat-embedding mold in which the Au-coated epoxy film (planar or patterned) is placed. (C) After curing, the epoxy blocks are pressed out of the mold. (D) A photograph of the face of the sample block trimmed with a razor blade into the shape of a trapezoid. The surface created with the razor blade is smoothed using a glass knife before final sectioning with a diamond knife. (E, F) Schematic illustration of the two methods used for the collection of slabs after microtoming and for the further manipulation of these sections (e.g., positioning on a substrate). Epoxy sections floating on the surface of water are collected either with a loop which supports a thin film of water and holds the sample by capillarity or by the “direct-capture” of the epoxy film onto a substrate (piece of silicon wafer shown in Figure 3F). (G) Bright-field optical microscopy image of self-assembled multiple sections on the surface of a  $\text{SiO}_2/\text{Si}(100)$  substrate.

step increments as small as approximately 1 nm. After each incremental advance of the sample, the sample arm moves through a down stroke (total displacement  $\sim 1$  cm) and then returns to its starting position before advancing again. During the downstroke of the sample arm, the sample is forced against the edge of the knife to section the sample. The sections are generated at rate of 1 Hz; this rate allows for the production of 200 slabs in 10 min.

It is not entirely clear how the microtome produces nanometer-thick sections. There are two mechanisms postulated for sectioning:<sup>1,2</sup> (i) During direct-sectioning (or “true-sectioning”), the edge of the knife remains in contact with the epoxy block through the entire process of section removal. This mechanism is believed to be the primary mechanism for soft, plastic materials. (ii) In cleavage-fracture, the edge of the knife initiates a crack that propagates in the sample block. This mechanism is believed to be responsible for sectioning hard, brittle materials. Both mechanisms could operate during the sectioning of heterogeneous materials (e.g., heterostructures and interfacial materials).

**Collecting and Transferring the Sections.** “Wet sectioning” is the most commonly used sectioning technique because of its convenience; the sections float onto the surface of water (which fills the trough on the back side of the knife) as they come off of the edge of the knife. The water reduces damage (e.g., compression) to the sample by reducing the friction between the back edge of the knife and the epoxy section. The sections (i.e., the epoxy slabs with embedded metal nanostructures) floating in the trough can be collected and transferred by several techniques to solid substrates. The slabs can be removed from the trough using a collection loop (2-mm diameter) (Figure 3E),<sup>10</sup> in which a meniscus of water that spans the loop supports the sample. The sample can be transferred to a substrate (e.g., silicon wafer or TEM grid) by touching the loop to the substrate (by capillary action). Alternatively, the samples can be collected by submerging the substrate directly below the floating epoxy section(s) and pulling the substrate toward the section(s) in such a way that it (or they) settle on the substrate (Figure 3F). Figure 3G is an example of the direct deposition of a series of epoxy sections on a piece of silicon wafer.

**Removing the Embedding Matrix.** After transfer of the section to a substrate, the embedding matrix can be removed to produce free-standing nanomaterials. To remove the embedding matrix (Araldite 502), we expose it to an oxygen plasma. The time necessary to remove the embedding matrix completely is dependent upon the thickness of the section

removed with the ultramicrotome and the character of the plasma (i.e., oxygen partial pressure, power, and time).

## Fabrication of Complex Nanostructures Using Topographically Patterned Substrates

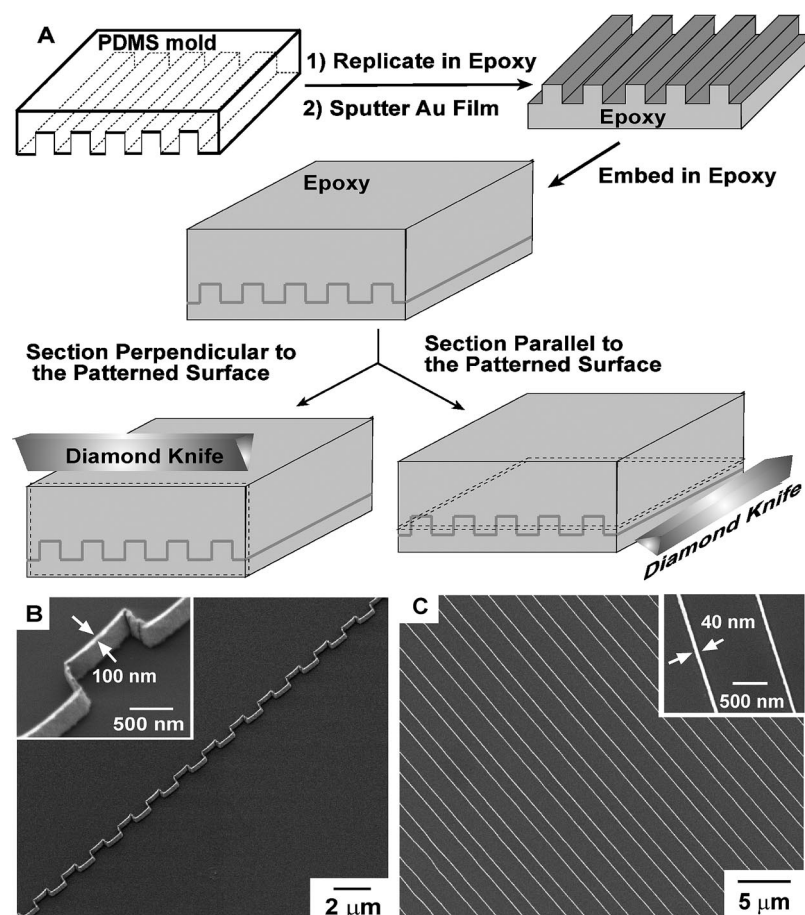
Figure 1 illustrates the simplest possible application of nanoskiving: sectioning a flat epoxy substrate coated with a thin film of metal to produce wires. We are able to fabricate more complex nanostructures by choosing the topography of the substrate and by rationally selecting the orientation used to section the substrate (Figure 4A). Figure 4B shows a free-standing, step-shaped nanostructure fabricated by nanoskiving epoxy replicas of photolithographically patterned 1- $\mu\text{m}$  wide lines with 1- $\mu\text{m}$  separation in a direction perpendicular to the plane of the patterned substrate.<sup>4</sup> One advantage of perpendicular sectioning is that a single block can be sectioned to form multiple samples, (e.g., a 2-D metal film embedded in an epoxy matrix (1-cm long) can generate  $\sim 10^5$  sections with 50-nm thickness); nanoskiving is, thus, in principle, a “nanomanufacturing” process.

Figure 4C shows an array of gold nanowires fabricated by sectioning epoxy replicas in the plane *parallel* to the patterned substrate.<sup>5</sup> Photolithography (or another type of patterning method) defines one dimension; this dimension thus can be varied and controlled within the limits of the patterning technique. Parallel-sectioning generates large arrays of metallic nanostructures in a single section. The number of elements defined in the patterning step determines the number of nanostructures in the section. A shortcoming of the parallel-sectioning approach in some applications is that only a limited number of individual sections can be generated from a single sample because of the limited aspect ratio (height:width) of features fabricated by photolithography. For example, a circular post with a 2- $\mu\text{m}$  diameter and 2- $\mu\text{m}$  height defined by photolithography can generate a maximum of approximately forty 50-nm thick sections when sectioned in the plane where the top of the circle resides. This limitation, however, could be overcome through the use of a high-aspect-ratio fabrication technique,<sup>18,19</sup> such as LIGA, deep RIE, and surface micromachining.

## Applications of Nanostructures and Arrays of Nanostructures Fabricated by Nanoskiving

The following examples demonstrate the utility of nanoskiving:





**FIGURE 4.** (A) Schematic illustration of the procedure used to fabricate complex nanostructures by sectioning a topographically patterned substrate ( $1\text{-}\mu\text{m}$  lines with  $1\text{-}\mu\text{m}$  separation) positioned in different orientations (relative to edge of the knife). (B, C) The difference in the shape of the nanostructures obtained from the same sample with different orientation of the sample and knife: (B) perpendicular-sectioning to the substrate patterned with rectangular ridges leads to the formation of continuous stepped structures and (C) parallel-sectioning leads to parallel  $1\text{-}\mu\text{m}$  lines with  $1\text{-}\mu\text{m}$  separation. Both (B) and (C) are SEM images of gold nanostructures supported on a  $\text{SiO}_2/\text{Si}(100)$  substrate.

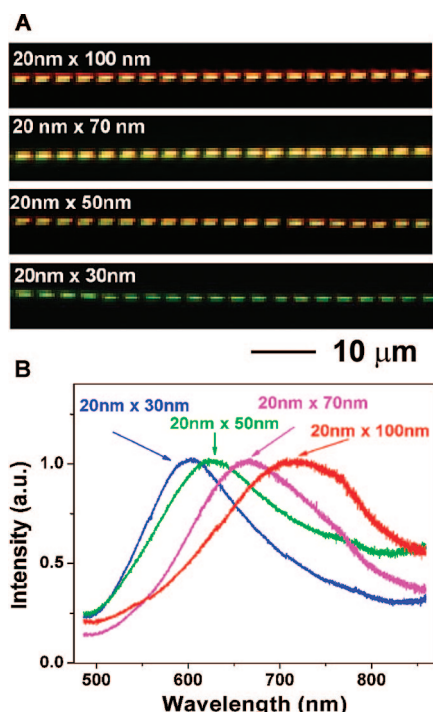
### Frequency-Selective Surface-Plasmonic Nanowires.

Localized surface plasmon resonance occurs when incident light resonates with the collective excitation of the conduction electrons on the surface of metallic nanostructures.<sup>20</sup> Local electromagnetic fields near the structure can be many orders of magnitude higher than the incident fields; these strong, oscillating fields generate intense scattered light around the wavelength of the resonant peak. The enhancement in local field and strong scattering is useful for a number of applications, including surface-enhanced Raman scattering,<sup>21</sup> subwavelength optical waveguides,<sup>22</sup> biolabeling, and biosensing.<sup>23</sup> The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance of a nanostructure depend on the size, shape, material of fabrication, and local environment (i.e., dielectric properties) of the particle.<sup>24</sup> Nanoskiving provides a simple route to uniform metallic nanowires of well-defined cross-sectional dimensions.

Figure 5A and B show color, dark-field optical images (and corresponding scattering spectra at visible wavelengths) of a series of gold nanowires with the same dimensions in length ( $x = 2\text{ }\mu\text{m}$ ) and width ( $y = 20\text{ nm}$ ), but different in height (the  $z$ -dimension ranges from 30 to 100 nm), which is the thickness of the epoxy sections formed by nanoskiving. The resonant wavelength of the surface plasmons on gold nanowires depends on the aspect ratio of the cross-section of the nanowires. The spectrum shifts to longer wavelength as the aspect ratio ( $z/y$ ) of the cross-section of the nanowire increases. A similar shift in the resonant wavelength of the surface plasmons is observed when the aspect ratio of the cross-section of the nanowire increases on changing the thickness of the evaporated metal film ( $y$ ) while holding the thickness ( $z$ ) of the section constant.<sup>25</sup>

**Nanostructures as Templates for the Fabrication of an Array of Nanoslits.** Nanoskiving has the ability to generate certain types of “master” structures; that is, it does not

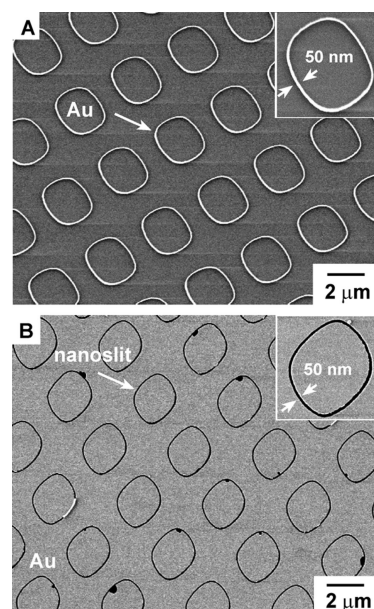




**FIGURE 5.** Surface plasmon resonance of gold nanowires with different cross-sectional dimensions. (A) Dark-field optical microscopy images of 2- $\mu\text{m}$  (x) long gold nanowires with different cross-sectional dimensions. The dimensions of the cross-section are the thickness of the gold film (y) and the thickness of the epoxy section (z) (respectively). (B) The scattering spectra in the visible regime of the gold nanowires with the dimensions corresponding to the gold nanowires in (A). As the aspect ratio (z/y) of the cross-section of the nanowire increases, the resonance of the surface plasmons shifts to higher energy.

require the nanostructures to be written in a separate step using a technique such as e-beam writing or FIB.<sup>8</sup> We demonstrated the fabrication of large-area arrays ( $\sim\text{mm}^2$ ) of nanostructures by sectioning in a plane parallel to the patterned substrate containing structures with different shapes (e.g., closed-loop and open nanostructures), defined by photolithography and selective metal deposition using shadow evaporation.<sup>4</sup> We are able to transfer these arrays of nanostructures into PDMS and other polymers by soft lithography.<sup>2</sup> The nanostructures from nanoskiving can be the physical master for the transfer of the nanostructures into other materials, such as a layer of  $\text{SiO}_2$ , through reactive ion etching (Figure 2E).

Arrays of nanostructures can also be used as shadow masks to generate an inverse replica of the structures onto the substrate (e.g., a gold film). Figure 6A shows the arrays of square-loop-shaped gold nanostructures (50-nm wide and 150-nm tall) fabricated by nanoskiving<sup>4,5</sup> and subsequently coated with a 5-nm thick Ti adhesion layer, followed by a 50-nm thick Au film, both by electron beam evaporation. The adhesion between the substrate and the loop-shaped nano-

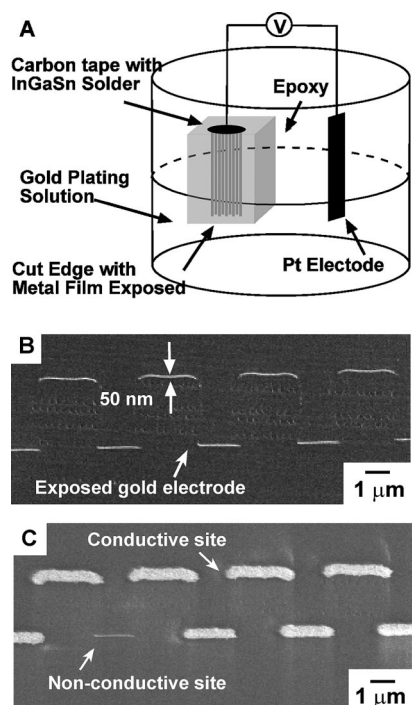


**FIGURE 6.** (A) SEM image of an array of gold nanorings on a  $\text{SiO}_2/\text{Si}(100)$  substrate. (B) SEM image of the same surface after coating the substrate with an adhesion layer (5 nm Ti) and a 50-nm thick Au layer, and removal of the original gold nanorings by sonication, generating inverse replicas of the gold nanorings in the thin-film of gold.

structures is much poorer than the adhesion between the substrate and the titanium adhesion layer of the additional evaporated gold film. The loop-shaped nanostructures on the substrate can be removed using adhesive tape or sonication to generate roughly loop-shaped nanoslits in a Au/Ti film (Figure 6B).

**Fabrication of Addressable Nanoelectrode Embedded in a Polymer Matrix.** One of the challenges for nanoscience is fanout, making connections between the nanostructures and external electrical circuits.<sup>26</sup> The most common technique to connect nanowires to electrical circuits uses a combination of e-beam lithography and photolithography,<sup>27</sup> nanoscience would benefit from new techniques.<sup>8,28–30</sup>

We have used nanoskiving to fabricate an array of nanoelectrodes that can be addressed from the back face of the slab of epoxy resin. We deposited a 50-nm thick gold film by electron-beam evaporation on an epoxy substrate patterned with parallel lines. The collimated metal deposition prevents metal coating on the sidewall of the line. We embedded the resulting structure in more epoxy, generating an epoxy block containing isolated metal wires. We exposed the cross-section of the block by cutting the sample perpendicular to the plane of the metal wire using an ultramicrotome at  $-120^\circ\text{C}$ .<sup>31</sup> The low-temperature sectioning minimizes the delamination between the polymer and metal film. Sectioning of the sample block exposes a cross-section of the embedded metal



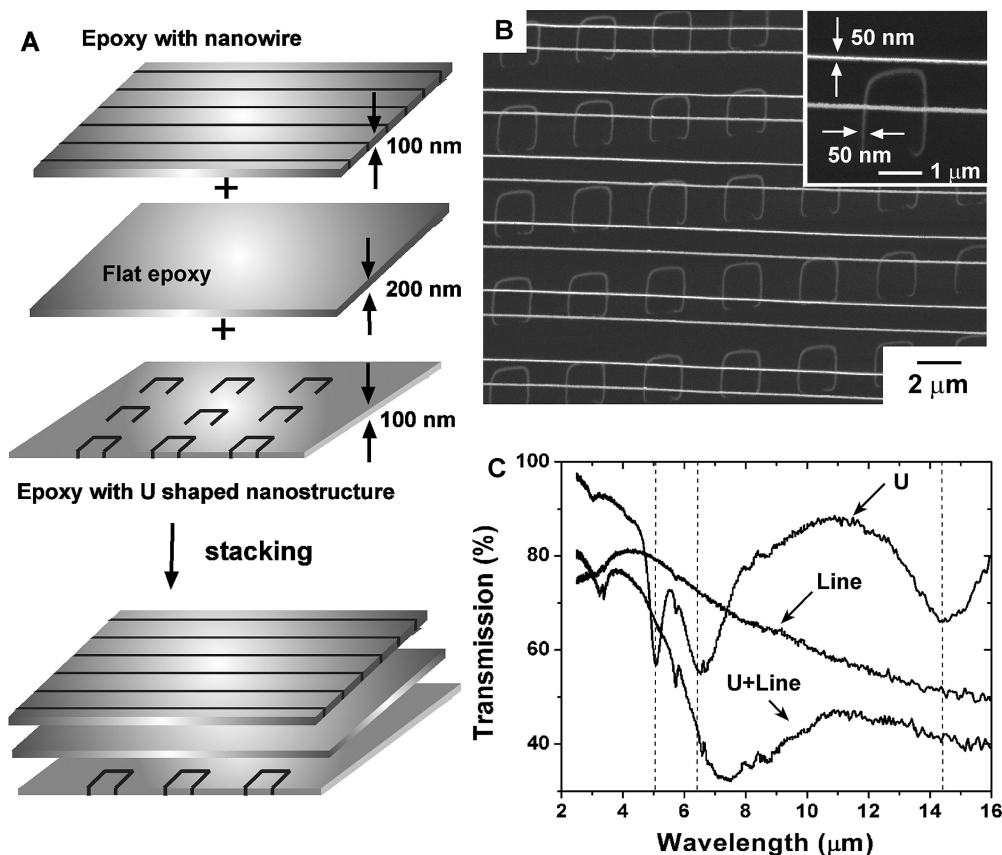
**FIGURE 7.** (A) Schematic illustration of the experimental setup used to demonstrate the electrical connectivity of the exposed edge of gold wires embedded in an epoxy matrix. Electrodeposition of gold onto the exposed gold edge of embedded wires was accomplished by connecting a wire to one face of the slab with InGaSn solder and conductive carbon tape. The electrodeposition of gold occurs on the opposite exposed face. (B) The SEM image of the embedded 50-nm wide gold film within a continuous epoxy matrix. (C) The exposed metal edge (opposite to the electrical connection) is the cathode for the electrodeposition of additional gold onto the conductive exposed edge of the nanowires embedded in the insulating matrix. Some edges are not conductive; evidenced by the lack of gold deposition during electrodeposition.

wires. The thickness of the metal film (50 nm) determines the width of the exposed metal. The exposed metal has the useful feature that it can be addressed electrically on the side of the polymer slab opposite the exposed metal edges (Figure 7A). The electrodeposition of more gold on the metal edge exposed at the surface of the epoxy slab (Figure 7B) demonstrated the electrical conductivity of the embedded nanostructures (Figure 7C). This method thus provides a route to a kind of addressable nanoelectrodes that cannot be easily achieved with conventional nanofabrication techniques (which put connections in the plane of the electrodes). This fabrication technique does not circumvent the common problem of addressing each electrode individually; in fact, this was not the intention of this demonstration. We believe that a current approach in our laboratory based on shadow deposition and nanoskiving may enable individually addressable electrodes.

**Stacking Multilayer Structures to Make Functional Quasi-3D Materials.** These thin polymer slabs containing the embedded nanostructures have sufficient mechanical strength to be manipulated to fabricate certain types of arrays of nanostructures that are otherwise difficult to prepare. For example, we positioned (by hand) nanometer-sized features by manipulating the epoxy sections ( $\sim 1 \text{ mm}^2$ ) onto curved surfaces (Figure 2D) and across gaps (Figure 2E).<sup>3</sup> Stacking the epoxy films on top of each other formed quasi-3D nanostructures (e.g., cross-bar nanostructures in Figure 2F).

Figure 8A outlines a procedure to construct multilayer structures for applications in frequency-selective surfaces at mid-IR wavelengths by stacking sections on top of each other.<sup>3</sup> The bottom layer of epoxy contained an array of U-shaped gold nanostructures, with dimensions 50 nm ( $y$ )  $\times$  100 nm ( $z$ ). We stacked a second section of epoxy (200-nm thick with no embedded nanostructures) on top of the epoxy slab containing the U-shaped nanostructures, followed by a third layer containing parallel gold nanowires with dimensions 50 nm ( $y$ )  $\times$  100 nm ( $z$ ) on top of the stack (Figure 8B).

These large-area, highly ordered arrays of nanostructures have the right dimensions required to test many of the properties of nanostructures acting as true plasmonic oscillators in the IR regions of the electromagnetic spectrum. We demonstrated the ability of single layers of arrays of square loop and open (L- and U-shaped) nanostructures to serve as mid-infrared band-stop optical filters.<sup>4</sup> Figure 8C shows the transmission spectra of the stacked multilayer nanostructures and the individual films of epoxy-embedded nanostructures. The mid-IR transmission spectrum had three resonant peaks (5.1, 6.5, and 14.5  $\mu\text{m}$ ) for the array of U-shaped nanostructures; we attribute these resonances to first-order and harmonic resonant plasmon modes induced by the unpolarized incident infrared light.<sup>4</sup> The transmission spectrum of a single epoxy slab (100-nm thick) containing periodic parallel lines had no resonant peaks, and the transmission decreased continuously in the 4- to 16- $\mu\text{m}$  region. The transmission spectrum of the stacked multilayer assembly has a significantly more asymmetric line shape than the transmission spectra of the array of U-shaped nanostructures, with a single resonant peak at  $\sim 7 \mu\text{m}$ , which is red-shifted from the 6.5- $\mu\text{m}$  peak observed with the U-shaped nanostructures. The slab containing arrays of nanowires acts as a mid-IR wire grid polarizer<sup>3</sup> and attenuates the two resonant peaks excited by the incident p-polarized light from arrays of U-shaped nanostructures.<sup>4</sup>



**FIGURE 8.** (A) Schematic illustration of the procedure for constructing multilayer structures by the stacking of multiple sections. (B) SEM image of the stacked, epoxy-embedded multilayer structure. The inset is a high-magnification SEM image of the stacked structure. (C) Mid-IR transmission spectra of the individual elements and multilayer structure embedded in epoxy.

## Comparison with Other Techniques

Nanoskiving is a simple and inexpensive route for the production of nanomaterials (ranging from simple, single nanostructures to large-area arrays of more complex nanostructures) with minimal facilities. There are examples of nanostructures (Figures 2A,C–H, and 4–8) in which we used clean-room facilities to fabricate the template (defines x-dimension), but the nanoscale features come from a combination of evaporation/deposition and sectioning with the ultramicrotome, not from photolithography. The smallest x-dimension demonstrated in this Review is 1–2 μm and does not necessarily require a clean-room for its fabrication, just access to a contact aligner. The fabrication of the array of parallel nanowires (Figure 2B) required no access to a clean-room. We demonstrated in a previous publication that commonly available masters (i.e., diffraction grating) can be used to fabricate nanostructures without the need of a clean-room.<sup>3</sup>

Nanoskiving can generate patterns of nanostructures with relatively large areas (~mm<sup>2</sup>) (Figure 4). Self-assembly of the epoxy sections containing the nanostructures (Figure 3G) allows tiling of patterned arrays of nanostructures over areas

of cm<sup>2</sup>; this area of patterning is still not comparable with the areas (~500 cm<sup>2</sup>) of patterning achieved with photolithography and nanoimprint lithography.<sup>32</sup> Nanostructures with high-aspect-ratio structures that are difficult or impossible to fabricate by other methods can be generated easily with nanoskiving (Figure 2A). Nanoskiving allows for the positioning and assembly of nanomaterials because the slices can be physically manipulated. The slices can be positioned over non-planar topologies including curved surfaces and gaps or stacked on another slab of epoxy containing embedded nanostructures to form multilayer, quasi-3D structures (Figure 2D–F).

Nanoskiving substitutes “sectioning by microtome” for the “exposure” in photolithography, “writing” in e-beam lithography and scanning probe lithography, and “printing/molding” in soft and imprint lithography. Nanoskiving can serve as a method for *both* mastering *and* replicating arrays of nanostructures. In the role of a mastering technology, it is related, albeit distantly, to electron-beam or scanning probe lithography; in the role of a replicating technology, it has some analogy to photolithography or soft lithography. The versatility of



nanoskiving as a technique for both mastering and replicating is not found in any of the other methods used for nanofabrication.

Nanoskiving also has, of course, limitations. Nanoskiving is currently restricted to generating unconnected line structures. The inability to fabricate connected structures limits the application of these nanostructures in applications such as making integrated circuits. It also does not currently have the stability in the pattern necessary to generate sections that can be registered precisely.

## Outlook

**Potential Applications of Nanoskiving.** Nanoskiving is not competitive with photolithography or scanning beam methods for making the multilayer, registered structures required for integrated circuits. Instead, this technique will be of primary interest to researchers who wish to generate simple nanostructures, singly or in arrays, more simply and quickly than can be accomplished in the clean-room. It is easily accessible to those not trained in top-down procedures for fabrication and those with limited or no access to the equipment and facilities needed for photolithography or scanning-beam fabrication.

**Challenges Associated with Nanoskiving As a Tool for Research and Manufacturing.** Many of the procedures important in nanoskiving, especially sample mounting and aligning, are presently done exclusively by hand, and the generation of high-quality sections requires an experienced microtome user. The development of an automated microtome instrument would be required to reduce or eliminate the influence of the user on the quality of the section. Nanoskiving would also benefit from advances in the ultramicrotome setup, such as (i) ease of alignment of the knife edge with the face of the sample, (ii) ease of manipulation and positioning of thin polymer sections, and (iii) methods for the integration of nanostructures produced by nanoskiving into other systems, such as optical fibers or microfabricated devices.

The sectioning procedure can lead to artifacts and defects in the nanostructures. Brittle materials, such as SiO<sub>2</sub>, tend to crack and form small segments during sectioning. The sample can compress during sectioning, causing deformation of the nanostructures and also causing the true thickness of the individual nanostructures or individual elements in the array of nanostructures to be greater than the nominal thickness.<sup>33</sup> The compression in the sectioning process can be minimized with the use of ultrasonic knives<sup>14</sup> and by the choice of an embedding material that decreases the amount of compression.<sup>34</sup>

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**Supporting Information Available.** A collection of images of potential masters for soft lithography that can be purchased commercially and/or fabricated outside of a clean-room facility and the procedure for correct alignment of the microtome is given. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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## BIOGRAPHICAL INFORMATION

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## FOOTNOTES

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