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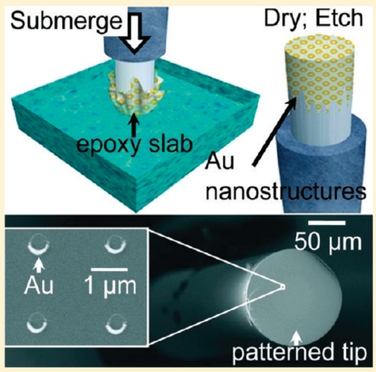
Patterning the Tips of Optical Fibers with Metallic Nanostructures Using Nanoskiving

Darren J. Lipomi,[†] Ramses V. Martinez,[†] Mikhail A. Kats,[‡] Sung H. Kang,[‡] Philseok Kim,[†,‡] Joanna Aizenberg,[†,‡] Federico Capasso,[‡] and George M. Whitesides*[,†]

[†]Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States

[‡]School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138, United States

ABSTRACT: Convenient and inexpensive methods to pattern the facets of optical fibers with metallic nanostructures would enable many applications. This communication reports a method to generate and transfer arrays of metallic nanostructures to the cleaved facets of optical fibers. The process relies on nanoskiving, in which an ultramicrotome, equipped with a diamond knife, sections epoxy nanostructures coated with thin metallic films and embedded in a block of epoxy. Sectioning produces arrays of nanostructures embedded in thin epoxy slabs, which can be transferred manually to the tips of optical fibers at a rate of approximately 2 min^{-1}, with 88% yield. Etching the epoxy matrices leaves arrays of nanostructures supported directly by the facets of the optical fibers. Examples of structures transferred include gold crescents, rings, high-aspect-ratio concentric cylinders, and gratings of parallel nanowires.



KEYWORDS: Nanoskiving, nanofabrication, fiber optics, plasmonics, SERS, ultramicrotomy

This paper describes an integrated approach for patterning two-dimensional (2D) arrays of metallic nanostructures on the cleaved facets of optical fibers. The process combines nanoskiving—here, the thin sectioning of patterned epoxy nanoposts supporting thin metallic films to produce arrays of metallic nanostructures embedded in thin epoxy slabs[1,2] (Figure 1)—with manual transfer of the slabs to the optical fibers (Figure 2). The ability to pattern the facets of optical fibers and other small substrates with nanostructures could enable several applications, which include sensing based on localized surface plasmon resonances (LSPRs),[3] label-free detection of extremely dilute chemical and biological analytes[4] using surface-enhanced Raman scattering (SERS),[5,6] optical filters,[7,8] diffraction gratings,[9] and noselike chemical sensors.[10,11] The small sizes and mechanical flexibility of these "optrodes" allow them to be inserted into the small volumes that are otherwise inaccessible (e.g., the bloodstream).[12]

It is extremely challenging to pattern optical fibers, because spin-coating them with resist is impossible, and mounting them in electron-beam writers and photolithographic exposure tools is difficult.[13] Our process takes advantage of the easily manipulated slabs of epoxy in which the nanostructures produced by nanoskiving are embedded. These slabs can be transferred to essentially any smooth (but not necessarily planar) substrate.

Background . Challenges Remaining in Nanofabrication. Nanofabrication is the collection of methods that generates and arranges structures that have at least one lateral dimension between 1 and 100 nm.[14,15] Silicon integrated circuits, which contain nanoscale components, are mastered using scanning-beam lithography and manufactured using photolithography; these methods will continue to produce less expensive and more powerful semiconductor devices for at least the next decade.[16,17] The problem of producing complex architectures on large, planar, rigid substrates is, thus, largely solved for the foreseeable future.

The ability to pattern unusual substrates—those that are nonplanar, mechanically compliant, incompatible with the conditions and instrumentation of conventional fabrication, very small, or disposable—could enable new applications in chemistry,[18] biology,[19] medicine,[20] optics,[21] and materials for energy conversion and storage.[22] Materials such as organic semiconductors,[23] carbon nanotubes,[24] and wavy silicon,[25,26] and methods such as printing[27] and molding[28] with elastomers, nanoimprint lithography,[29] nanostencil lithography,[30] and other unconventional processes,[14] are filling niches inaccessible to conventional lithography. There nonetheless remain challenges in nanofabrication for which a general solution does not yet exist.

Methods of Patterning Optical Fibers. The size and shape of an optical fiber preclude the use of ordinary lithographic processes. Producing a uniformly thick coating of resist is a particular challenge. Spin coating produces a raised region

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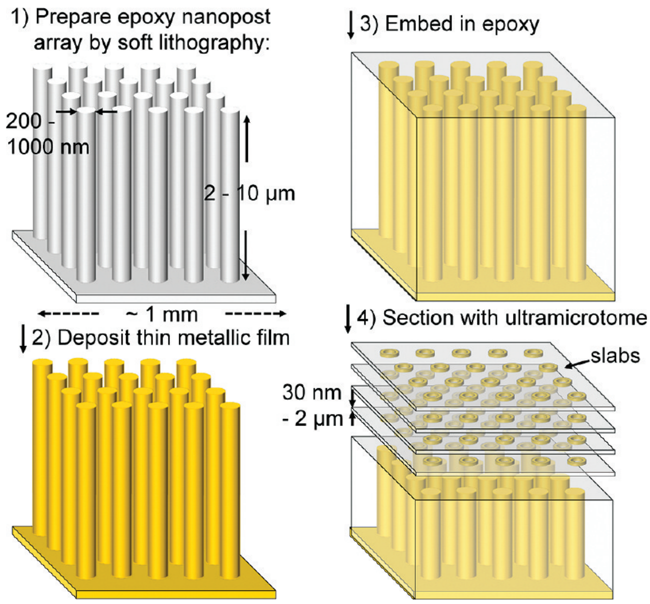

Figure 1. Example of a procedure used to fabricate arrays of metallic nanostructures by embedding and sectioning a metallized array of epoxy nanoposts using an ultramicrotome. This procedure produces manipulable slabs of epoxy containing arrays of metallic nanostructures.

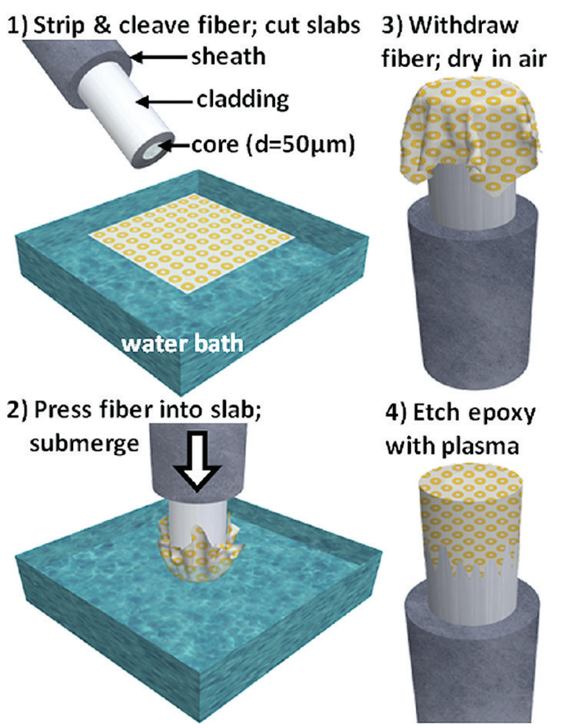

Figure 2. Summary of the procedure used to fabricate and transfer arrays of metallic nanostructures to the facets of optical fibers.

around the perimeter of a substrate (or "edge bead"), which for small substrates can be as large as the substrate itself.[13] Kelkar et al. described a resist that can be deposited by evaporation. Evaporated resists produce uniform coatings, but the process requires specialized vacuum equipment, resist, and developer.[31] Direct patterning of the optical fibers by focused-ion beam (FIB) milling is susceptible to contamination of the substrate with gallium atoms. Inadvertent implantation of gallium can interfere with optical methods of sensing.[32]

Patterning substrates with arbitrary sizes and properties cannot be accomplished with a single technique of nanofabrication. It is possible, however, to expand the range of substrates that can be patterned by dividing patterning into two independent processes: generation and transfer of structures. This division ensures that the size, shape, composition, or mechanical properties of the substrate do not affect the generation of the pattern.

Our laboratories recently described a method by which gold nanostructures defined by electron-beam lithography (EBL) could be transferred to the facets of optical fibers using a sacrificial polymeric film.[13] While this method was successful in transferring arbitrary patterns of gold nanostructures to hemispherical substrates and optical fibers and was used to produce a bidirectional optical probe for SERS,[6] the method is serial and each array must be written individually by EBL.

Fabrication and Transfer of Arrays Using Nanoskiving. Nanoskiving is a simple method of nanofabrication whose key step is sectioning a planar or topographically patterned thin film, encapsulated in epoxy, with an ultramicrotome equipped with a diamond knife (Figure 1). After sectioning, the structures remain embedded in thin epoxy slabs. The slabs are macroscopic objects that preserve the orientations of the nanostructures within the arrays and also provide physical handles by which the user can transfer the nanostructures to substrates. After being deposited on a substrate, the epoxy slab can be removed by etching with an air plasma. This action leaves free-standing nanostructures on the substrate.[1,2]

Experimental Design . Nanoskiving. There are very few methods of fabrication in which the processes of generating and transferring patterns are completely decoupled, beside decal transfer printing,[33] in which the structures must be fabricated serially and transferred to a stamp. We chose nanoskiving, because it offered an integrated approach to both the fabrication and transfer of nanostructures: we reasoned that we could capture floating slabs manually with the cleaved surfaces of optical fibers, in the same way that microtomed specimens are retrieved using TEM grids.[34]

Nanostructures. We chose five types of nanostructures to transfer to optical fibers: crescents, rings, split rings, double rings, coaxial cylinders, and a grating of nanowires. These structures are interesting for their optical and plasmonic properties. Figure 1 summarizes the procedures used to produce closed rings by coating conformally the epoxy posts with gold, but structures bearing open loops, concentric rings, or other line segments can be made as well. Open-loop structures can be fabricated by placing the substrate at an angle to a collimated source of evaporating metal. "Shadow evaporation" can thus be used to coat only the sidewalls of the epoxy features in the path of the evaporated atoms. Upon embedding and sectioning these structures, we have obtained crescents and split rings.[35] To produce parallel nanowires, Xu et al. began with an epoxy grating bearing parallel rectangular ridges. Conformal deposition of gold and subsequent embedding and sectioning yielded arrays of parallel nanowires whose geometries corresponded to the sidewalls of the epoxy ridges.[2] Concentric annular structures can be made using multiple depositions of thin films on an epoxy template. In a previous report, we made concentric rings and concentric, counterfacing split rings by (1) depositing gold on epoxy nanoposts, (2) using the gold as a working electrode for conformal electrodeposition of polypyrrole (PPy), and (3) depositing a second layer of gold.[35] Embedding and sectioning this structure produced concentric gold rings separated by a spacer of PPy. The epoxy and PPy could be etched with an air plasma.[35] We were able to obtain high-aspect-ratio structures by sectioning thick (up to 2 μm in Lipomi et al.[35]) slabs of the embedded structures. We used gold for all nanostructures because it has useful plasmonic properties, it is not oxidized in the ambient atmosphere, and it is soft enough to produce a high yield of nondefective nanostructures when sectioned.[36]

Fibers. We chose a typical multimode optical fiber with a cladding diameter of 125 μm and a core diameter of 50 μm. We chose this fiber for a potential application of SERS using 785 nm light. To prepare the fibers for the transfer of slabs, we stripped the polymeric jacket and cleaved the silica fiber manually with a diamond scribe or with a fiber cleaver.

Fabrication. Figure 1 shows a schematic drawing of the process used to generate nanostructures (gold rings, in the example shown). We used a procedure described in a previous paper.[35] Briefly, we obtained an array of epoxy nanoposts by replica molding using a procedure published by Pokroy et al. (step 1).[37] Physical vapor deposition (step 2), followed by embedding in additional epoxy (step 3), produced a block with gold-coated nanoposts. An ultramicrotome, equipped with a diamond knife whose sharp edge has a radius of curvature of 3−6 nm,[38] sectioned the block into slabs (step 4). As the knife passed through the block, the nascent slab (area ≤1 mm^2) containing gold rings floated onto the surface of a water-filled trough. We have produced as many as 60 slabs bearing arrays of nanostructures from a single embedded array of nanoposts.[35] The color of a slab, produced by the interference of white light, can be used to estimate its thickness: gray, <60 nm; silver, 60−90 nm; gold, 90−150 nm; purple, 150−190 nm; blue, 190−240 nm; green, 240−280 nm; yellow, 280−320 nm.[39] We used 80−150 nm slabs for all experiments, though our laboratory has produced slabs with thicknesses of 30 nm to 2 μm.[35,40]

Transfer. Figure 2 summarizes the procedure used to transfer the floating arrays to the facets of optical fibers. We captured a floating slab with the tip of a fiber, by holding the fiber with tweezers, and pressing down manually on the slabs, from above, with the tip of the fiber (steps 1 and 2). As we drove the slab under the surface of the water using the tip, the slab wrapped itself around the tip. When we withdrew the tip from the water bath, the slab was attached irreversibly to the tip. We allowed the water to evaporate (step 3), while we repeated the process with another fiber. Each transfer took approximately 30 s. After the water evaporated, the appearance of a slab covering the tip of a fiber resembled a tablecloth draped over the top and sides of a round table. After allowing the tip to dry in the ambient atmosphere, exposure to an air plasma using a benchtop plasma cleaner (1 Torr, 100 W, 10 min) revealed nanostructures supported by the tip of the fiber (step 4).

Results and Discussion. Figure 3a shows a low-magnification scanning electron microscope (SEM) image of an optical fiber. Figure 3b is a close-up of the facet of a fiber bearing an array of gold crescents. The pattern extends to the edge of the facet. The process can be used for any structure or array of structures that can be produced using nanoskiving. Figure 3c shows a grating of parallel gold nanowires with line widths of 50 nm.[2]

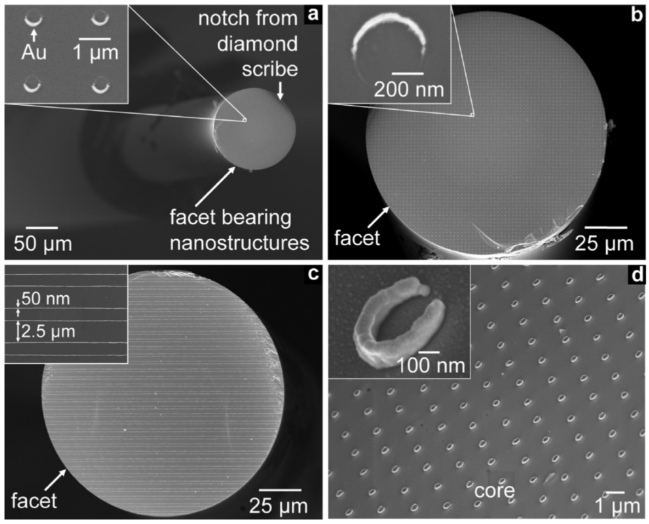

Figure 3. (a) An optical fiber bearing an array of gold crescents (shown in the inset). (b) A close-up of the facet. The inset is a single gold crescent. (c) A facet bearing a grating of gold nanowires. (d) The core of a fiber bearing an array of gold split rings.

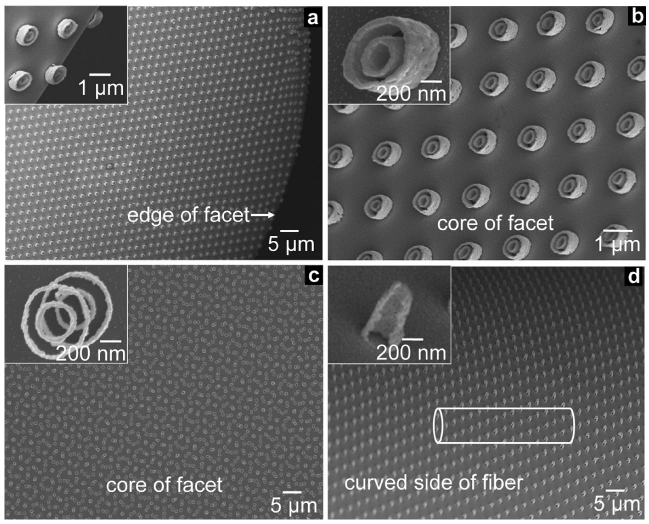

Figure 4. (a) A portion of an optical fiber bearing an array of concentric gold rings. (b) The core of the same optical fiber as shown in (a). The structures have 50 nm thick walls, and are 400 nm tall. (c) The core of an optical fiber bearing overlapping arrays of concentric gold rings. (d) An array of gold split cylinders on the curved (cylindrical) side of a stripped optical fiber. The long axis of the optical fiber is parallel to the long axis of the outline drawing of the cylinder.

The nanowires span the entire facet. Figure 3d shows the core of a fiber bearing an array of gold split rings.

A unique characteristic of nanoskiving is its ability to produce high-aspect-ratio structures. Figure 4a shows a portion of the cleaved facet of a fiber bearing concentric double rings, produced by a published procedure,[35] whose walls are 50 nm thick and whose heights are 400 nm. Figure 4b shows the core of the same fiber. Double patterning—iterative transfers of slabs—yields overlapping arrays of structures. Figure 4c shows overlapping arrays of concentric gold rings.

There are some forms of fiber-based sensing applications that require coupling light to nanostructures on the curved sides of

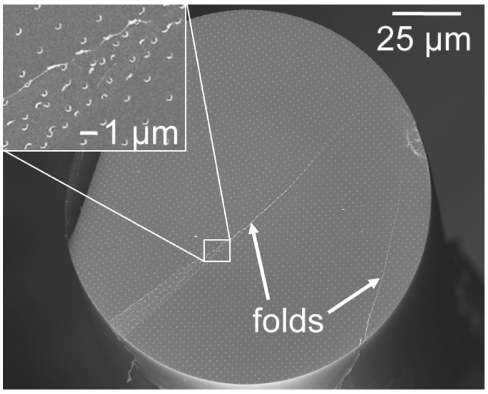

Figure 5. A facet bearing a poorly transferred array of crescents. There was a fold in the epoxy slab as it was transferred to the fiber. The inset shows a region of the fold, which contains jumbled nanostructures.

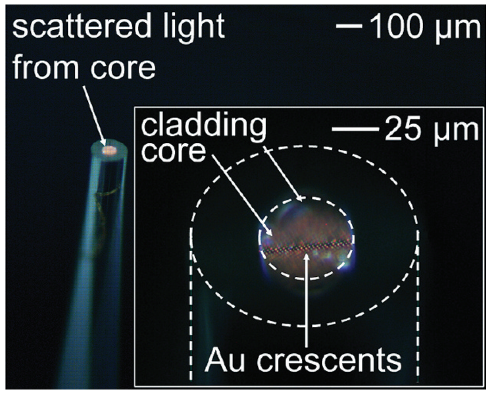

Figure 6. Optical image of a cleaved facet of an optical fiber supporting an array of gold crescents. Light from a halogen source is coupled to the core of the fiber at the opposite end of the fiber. The inset is a close-up of the facet. Light, supplied by the fiber, scatters from the gold nanostructures on the core of the optical fiber and not those on the cladding. The fiber is tilted ∼45° to isolate only the light scattered from the nanostructures (tilting prevents nonscattered light from the fiber from entering the objective of the microscope directly).

stripped fibers.[3] Figure 4d shows an array of 2 μm tall split cylinders of gold transferred to the curved side of a stripped optical fiber. In a previous report, Xu et al. demonstrated the same concept by wrapping a slab bearing an array of U-shaped structures around a glass rod.[2]

Defects. There are two classes of defects that occur during the process described. The first class comprises those that occur because of the mechanical stresses of sectioning, combined with the intrinsic brittleness of evaporated films and the compressibility of the epoxy matrix.[36] Fracture of individual structures and global compression in the direction of cutting are the two most prominent defects observed and were described in detail in an earlier report.[36] The second class of defects includes those that occur because of the transfer. Folding of the slabs, in which a crease runs across the facet of a fiber, is the most prominent type of defect due to the transfer.

In one experiment, we transferred 16 arrays of 80 nm thick slabs bearing gold crescents and examined the tips of the fibers for defects by SEM. The yield of successful transfers was 14/16 (88%). We defined a successful transfer as one in which the core of the optical fiber was completely covered by the array of nanostructures with no folds (as in Figure 3b). The two unsuccessful transfers of this group exhibited folds that ran across the core of the optical fiber. Figure 5 shows an example of one of the two defective transfers in the set of 16 from which we calculated the yield. A fold in the slab produced a boundary in the array, where the orientations of the axes of the arrays were different on either side of the fold. After etching the epoxy with an air plasma, the nanostructures were jumbled in the immediate vicinity of the fold.

The extent to which defects such as folds affect optical applications depends on whether or not there is optical interaction between the nanostructures. Jumbled nanostructures and boundaries between grains would affect applications related to diffraction and polarization and any application in which there is a resonance due to the effects of the array, that is, a resonance mediated by the exchange of photons between multiple nanostructures within the array. On the other hand, effects such as near-field enhancement in the vicinity of individual nanostructures and the "lightning rod effect",[41] would not be affected by disordered regions of structures. For applications that require consistency between devices, it would be necessary to discard arrays bearing folds. We believe, however, that the development of an automated process would reduce the occurrence of folds.

A consequence of the physical nature of the attachment of the structures to the glass facet of the optical fiber is that the structures can be rubbed off easily if touched inadvertently. While we did not explicitly test the adhesion of the structures to the fiber when immersed in different solvents (e.g., for SERS), the patterns should remain intact due to van der Waals forces. Smythe et al. found that gold structures printed on the facet of an optical fiber (without an adhesion layer) survived immersion for 12 h in a 3 mM solution of benzene thiol in methanol.[6] Resistance to delamination could be increased, if necessary, by leaving the epoxy matrix intact (if the application permitted the presence of the epoxy), employing a thiolated monolayer to promote adhesion, or sputter-coating conformally a thin layer of silicon dioxide over the patterned fiber.

In order to demonstrate that it will be possible to address the nanostructures optically, we coupled light from a halogen source into the fiber and obtained optical microscope images of the cleaved facet of the fiber. Figure 6 shows light scattering from an array of gold crescents on top of the core of the optical fiber. We tilted the fiber with respect to the focal plane, so that only the scattered light from the nanostructures entered the objective. While the crescents covered the entire facet (core and cladding), light scattered only from those on the core. Scatterers with well-defined shapes could be used to couple light of specific frequencies into and out of the fiber. Metallic nanostructures with designed plasmon resonances would enable sensing based on SERS or LSPR.[6]

Conclusions. Nanoskiving is well—perhaps uniquely—suited for fabricating and transferring patterns of nanostructures to the tips of optical fibers and other small substrates. In addition to producing arrays of metallic nanostructures that are potentially useful for plasmonic applications,[2,8] nanoskiving produces these arrays in transferrable epoxy slabs that can be placed conveniently on substrates of many compositions, sizes, and topographies. All structures produced by nanoskiving—two- and three-dimensional arrays of metallic, dielectric, and semiconducting particles, gratings of nanowires,[2] single-crystalline gold nanowires,[42] and conjugated polymers[43]—can be mounted on the facets of fibers using the same process. We also believe that this process could be extended to other delicate films (e.g., photoresist, conjugated polymers, and other materials floated on the surface of water) that would be difficult to deposit on the fibers directly.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gwhitesides@gmwgroup.harvard.edu.

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