

Patterning Disorder in Monolayer Resists for the Fabrication of Sub-100-nm Structures in Silver, Gold, Silicon, and Aluminum

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Abstract: This paper describes the development of a new methodology, “topographically directed etching” or TODE, that relies on patterned regions of disorder in SAMs to generate features specifically at the edges of topographically patterned metal films. The features that are produced have lateral dimensions of <50 to 200 nm and are at least an order of magnitude smaller than those patterned originally in the material, when the original patterning is at the scale of μm . Several variations of this methodology are described, the results of which include the generation of 100-nm *trenches* in silver, gold, SiO₂/Si, and Al₂O₃/Al, 100-nm *lines* of silver, asymmetric structures in aluminum and silver, and 50-nm features in curved silver surfaces. Although the techniques can be combined with photolithography, the pattern transfer step is based on chemical reaction and is therefore not limited by diffraction or depth of focus. This methodology makes the fabrication of \sim 100-nm structures accessible to chemists/materials scientists without access to tools required for electron-beam writing and other procedures of nanofabrication.

Introduction

The fabrication of nanostructures¹ (structures with smallest dimension <100 nm) is interesting for its possible application in nanoelectronics,² information storage,³ and optics.⁴ Current methods for generating these structures include electron-beam (e-beam) writing⁵ and X-ray and EUV lithography,^{6,7} all methods that require specialized equipment. Each of these methods has its own intrinsic limitations; e-beam writing, although able to produce structures as small as \sim 2 nm, is a serial process, and X-ray and EUV lithography are limited by the complexity of the processes that use them.

We and others are developing new, inexpensive processes to fabricate nanostructures: soft lithography^{8,9} and embossing^{10,11} are examples. Embossing uses a rigid master to imprint relief structures into materials such as polymers, semiconductors, and metals. Micromolding has replicated features with dimensions of \sim 12 nm with a fidelity of \sim 30%.¹² Embossing with a master

of SiO₂/Si can generate features in Si with lateral dimensions of \sim 25 nm.¹⁰

Soft lithography is a collection of techniques that have in common the use of an elastomeric element in the pattern-transfer step. One of these soft lithographic techniques, microcontact printing (μ CP), uses an elastomeric stamp to transfer a pattern of alkanethiol molecules to those regions of a silver or gold substrate that contact the stamp.^{13,14} The alkanethiol assembles rapidly into an ordered monolayer on the surface. Contact printing with alkanethiols on gold can generate patterned SAMs with lateral dimensions as small as 100 nm;^{15,16} these dimensions may represent the size limit for this technique, however, because of diffusion of ink molecules in the printing stage^{16,17} and the fragility of the SAM. The pattern can be transferred into the substrate using the SAM as a resist to protect the surface against etching.^{13,16} Many of the defects encountered on etching surfaces protected by SAMs probably involve defects in the SAMs.

Recently we described a new methodology for patterning SAMs that *intentionally* generates highly localized regions of disorder in SAMs at the edges of steps in topographically patterned evaporated metal films; these regions of disorder provide sites for the nucleation of several processes such as the formation of condensation figures, patterns of crystals of CaCO₃ and etching.¹⁸ We used this methodology (which we have named “topographically directed etching” or TODE) to fabricate 50-

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nm trenches in topographically patterned films of silver supporting SAMs of alkanethiols.¹⁸

Here, we demonstrate several new capabilities of TOD: (i) patterning of materials that are technologically more relevant than silver: especially, SiO₂/Si and Al₂O₃/Al, (ii) fabricating 100-nm *lines* of silver (rather than trenches in silver) by selectively exchanging molecules that confer resistance to etching at the disordered region before etching, (iii) varying the width of the etched features by controlling the duration of etching, (iv) using corners to generate regions in the SAM with greater disorder than at edges and thus focusing etching at these points, (v) fabricating asymmetric structures in aluminum and silver by depositing the second layer of metal at an angle away from the surface normal, (vi) patterning 50-nm features on curved silver surfaces.

These experiments rely on the ability of different regions of the substrate to support SAMs with different amounts of order, and in particular, for smooth regions of the surface to support well-ordered SAMs, while nonsmooth (stepped or rough) regions support less-ordered or disordered SAMs. Each of the substrates—silicon, aluminum, and silver—forms a native oxide under ambient conditions. For aluminum, the surface oxide can prevent adhesion of subsequent layers of aluminum and is sufficiently reactive to be etched, either completely or in part, in basic solutions such as the developer we use in photolithography. With silicon, the oxide has no detrimental effect on the outcome of the procedure because the layer we deposit to generate the surface topography required by this method is SiO₂. Silver is the most sensitive of the three substrates to oxidation or contamination, both changes in the surface of the film that can prevent adhesion of a second layer of metal and also the formation of well ordered SAMs. When the surface cannot form a well-ordered SAM, the technique breaks down; etching initiates at defects (such as pinholes) in the bulk SAM in competition with (or in preference to) disordered regions.

The combination of these ideas provides a set of experiments with the capability to fabricate both *raised* outlines and *etched* outlines of an original pattern in the material of interest, with sizes ranging from 50 to 200 nm. We believe that the ability to introduce controlled disorder into SAMs will find general use for any system that requires the patterning of SAMs with features in this size range. It is particularly useful because the methods required to generate the original μm -scale pattern (the pattern whose outline becomes the features after application of this method) can use either the standard methods and masks of photolithography, appropriate methods from soft lithography, or newer methods (such as dry lift-off¹⁹). The essential requirement is that the patterning method be compatible with metal evaporation and lift-off.

This procedure is another that puts the fabrication of true nanostructures (<100-nm feature sizes) within the capability of chemical laboratories.

Results and Discussion

Preparation of Topographically Patterned Substrates. To induce the regions of disorder in the SAM, we introduce abrupt changes in the topography of the substrate by patterning one layer of a metal onto a second layer of the same metal by evaporation through a layer of patterned photoresist (Figure 1). The procedure, when applied to evaporated metal films, consists of four stages: (i) deposition of a continuous film of a metal

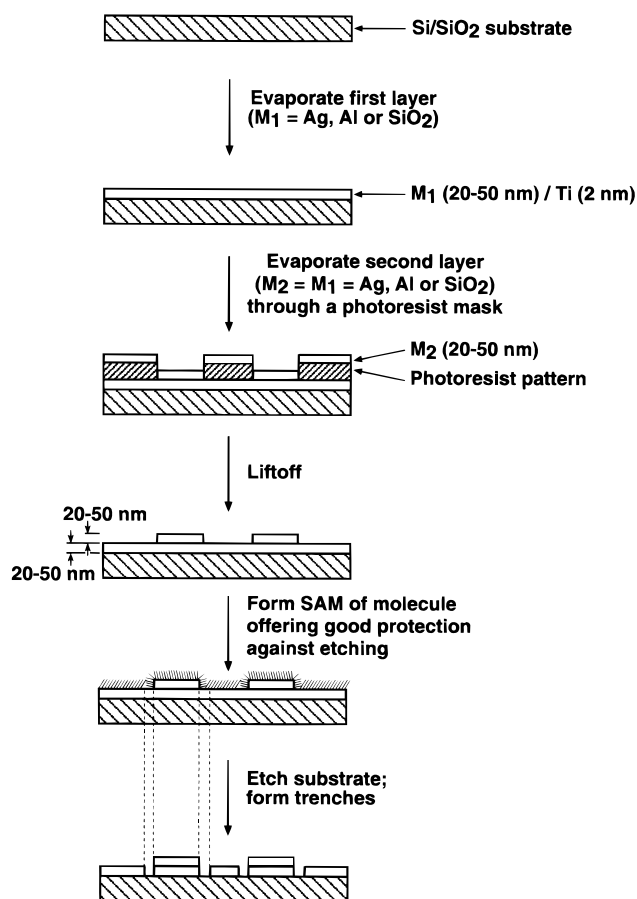


Figure 1. Outline of the procedures used for fabrication of nanostructures using topographically micropatterned materials. Trenches were formed by selective etching of regions of the substrate protected by disordered SAMs.

capable of supporting the formation of a SAM, (ii) deposition of a pattern of a second layer of the same metal, with or without an adhesion promoter, (iii) formation of a SAM on this patterned surface, (iv) completion of processes (exchange or etching) that take advantage of locally disordered regions in the SAM.

Topographically Directed Etching of Silver and Gold Films. We begin this discussion by presenting our previous results demonstrating selective etching of sub-100-nm trenches in topographically patterned silver films supporting SAMs of HS(CH₂)₁₅CH₃.¹⁸ We show these results in conjunction with analogous experiments with topographically patterned films of gold, and films of combinations of silver and gold, all supporting SAMs of HS(CH₂)₁₅CH₃ (Figure 2). Each of these films was prepared by our standard procedure and is shown before and after etching. We were able to generate 60-nm trenches in films of silver (Figure 2A), 100-nm trenches in films of gold (Figure 2B), and 70-nm trenches in films of gold-on-silver (Figure 2C).²⁰ Silver-on-gold is not a useful configuration of metals because silver, even when protected by a SAM, is almost completely etched in the gold etching solution over the same length of time we used to etch the gold-on-gold substrate; there is no preferential etching at the edges of the second layer (Figure 2D).

With each combination of silver and gold, there is a consistent difference between the etched lines and circles; during equal periods of time, the circles were etched more than lines, indicating that etching initiates more rapidly around circles than

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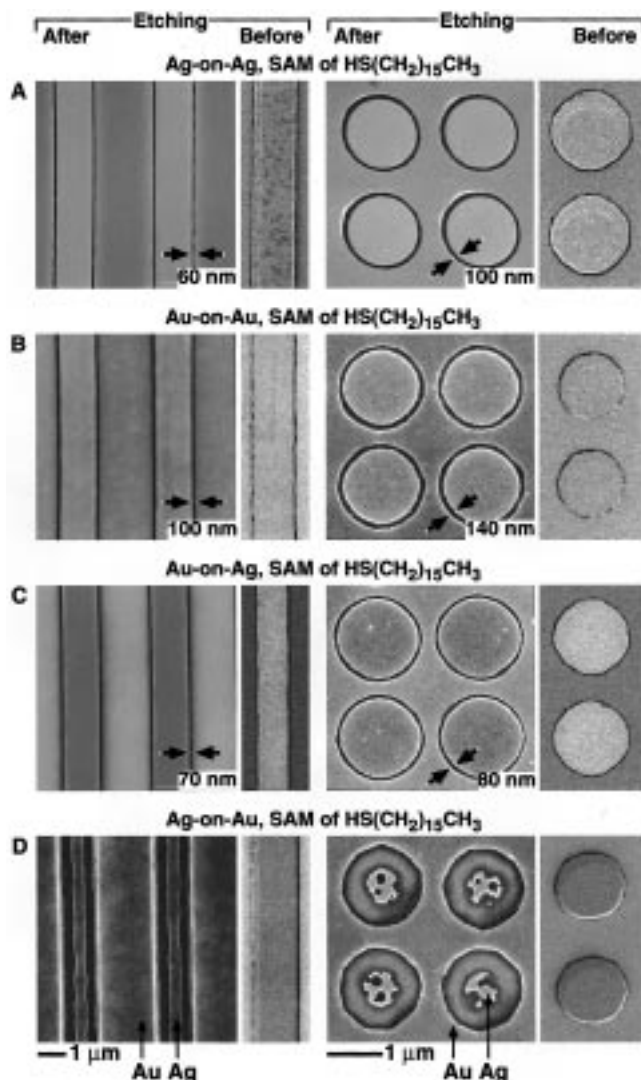


Figure 2. SEMs showing the results of TODE applied to topographically patterned films of silver and gold supporting SAMs formed from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. (A) Silver-on-silver etched in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M), and sodium thiosulfate (0.1 M) for 12 s. (B) Gold-on-gold etched in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M), sodium thiosulfate (0.1 M), and potassium hydroxide (1 M) for 40 s. (C) Gold-on-silver etched in the same etching solution as in (A) for 12 s. (D) Silver-on-gold etched in the same etching solution used in (B) for 40 s. The silver is almost completely removed in the time of the etch.

along lines. We will discuss in detail the factors that govern differences in the rate of initiation of etching later in the paper.

We are able to reproduce these standard results at least 60% of the time. There are, however, several aspects of the experimental procedure—in particular, maintenance of the quality of the metal substrates—that are particularly critical to its success.

The goals of this paper therefore are to explain the principles that define the basic method, to determine its ability to pattern materials other than silver and gold, and to explore its other capabilities.

Topographically Directed Etching Can Produce 100-nm Features in SiO_2 and $\text{Al}_2\text{O}_3/\text{Al}$. Because SAMs of alkanethiols on silver are particularly highly ordered,^{21,22} we were uncertain

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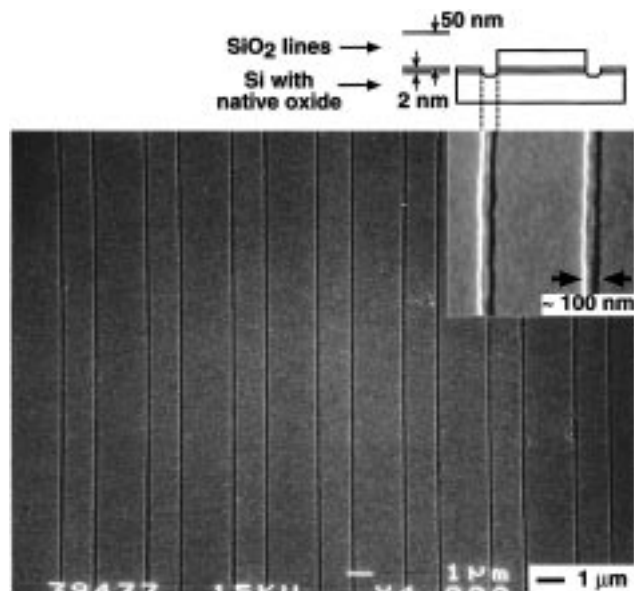


Figure 3. Scanning electron micrograph (SEM) of 100-nm trenches in SiO_2/Si formed by etching regions of the topographically patterned substrate protected by disordered SAMs. The micropatterned substrates were formed by evaporating a layer of SiO_2 (50 nm) onto the native oxide (~ 2 -nm thick) of a Si wafer through a pattern in photoresist, followed by liftoff. We exposed the SiO_2/Si substrates to a solution of $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ in anhydrous hexane (10 mmol) for 10 h and then rinsed with hexane. The substrates were etched with 1% HF for 20 s and then immediately with 3 M KOH solution (water with 25% *i*-PrOH) for 120 s to transfer the features from the SiO_2 into silicon.

whether this method could be extended to materials, other than silver, on which the structure of SAMs would be less ordered. Figure 3 shows the results of TODE applied to a film of SiO_2 . We evaporate a layer of SiO_2 onto the native oxide of silicon through a layer of patterned photoresist and liftoff the photoresist and undesired SiO_2 . We then form an alkylsiloxane SAM on the resulting topographically patterned film of SiO_2 from $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$. Figure 4 shows the results of analogous experiments involving $\text{Al}_2\text{O}_3/\text{Al}$ (fabricated as above) protected by a SAM formed from $\text{CH}_3(\text{CH}_2)_{17}\text{PO}(\text{OH})_2$. Monolayers of siloxanes on SiO_2 involve networks of Si–O linkages connecting the headgroups with silanol groups on the surface.^{23,24} We had expected, therefore, that our ability to introduce disorder into SAMs of alkylsiloxanes on SiO_2/Si would be less than with alkanethiols on silver. In fact, the discrimination between the edge regions and the planar regions is very good. Monolayers of phosphonates on Al_2O_3 do not involve covalent networks, and we presume the structure of the interface between phosphonate groups and the surface^{25,26} to be substantially less ordered than that between alkanethiols and silver.^{21,22} This system gives “messier” results, because the complication introduced by lateral etching of the Al_2O_3 layer between the evaporated aluminum layers is especially obvious, but the results of TODE with all systems of SAMs and substrates, however, are comparable—in each instance we observe the formation of ~ 100 nm trenches in silver-on-silver, gold-on-gold, gold-on-silver, SiO_2 -on- $\text{Si}(\text{SiO}_2)$, and $\text{Al}(\text{Al}_2\text{O}_3)$ -on- $\text{Al}(\text{Al}_2\text{O}_3)$.

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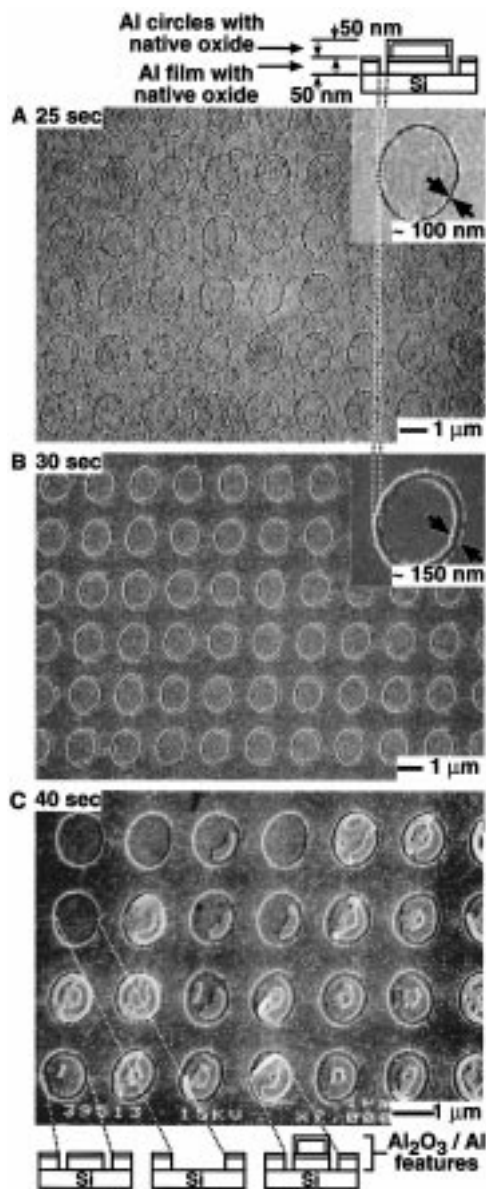


Figure 4. SEMs of 1.5- μm circular trenches in aluminum formed by preferential etching of regions of the topographically patterned substrate protected by disordered SAMs formed from $\text{CH}_3(\text{CH}_2)_{17}\text{PO}(\text{OH})_2$. The substrates are prepared by evaporating aluminum (50-nm thick), through a pattern in photoresist, onto a film of aluminum (50-nm thick) with an adventitious surface film of aluminum oxide ($\text{Al}_2\text{O}_3/\text{Al}$; this nomenclature is shorthand, and does not imply any knowledge of the hydration of the aluminum oxide layer). The intervals of time for which the sample was exposed to the etchant (phosphoric, acetic, and nitric acids and water in a ratio of 16:1:1:2 by volume) were: (A) 25, (B) 30, and (C) 40 s. The second layer of aluminum de-adheres from the surface as etching proceeds, exposing the bottom, unprotected layer of $\text{Al}_2\text{O}_3/\text{Al}$ to the etching solution; with time, the bottom layer is etched also.

The Duration of Etching Determines the Size of the Trenches that are Generated. Figure 4 shows that as the duration of etching increases, the width of the resulting features changes and, in this case, 1.5 μm circles of $\text{Al}_2\text{O}_3/\text{Al}$ on $\text{Al}_2\text{O}_3/\text{Al}$, leads to undercutting that may contribute to de-adhesion of both layers of metal. The poor adhesion is probably the result of an interlayer of Al_2O_3 between the first and second layer of aluminum during the processes that generate the pattern: spinning on photoresist, photolithography, and development of the imaged pattern. The structure in Figure 4C contains three

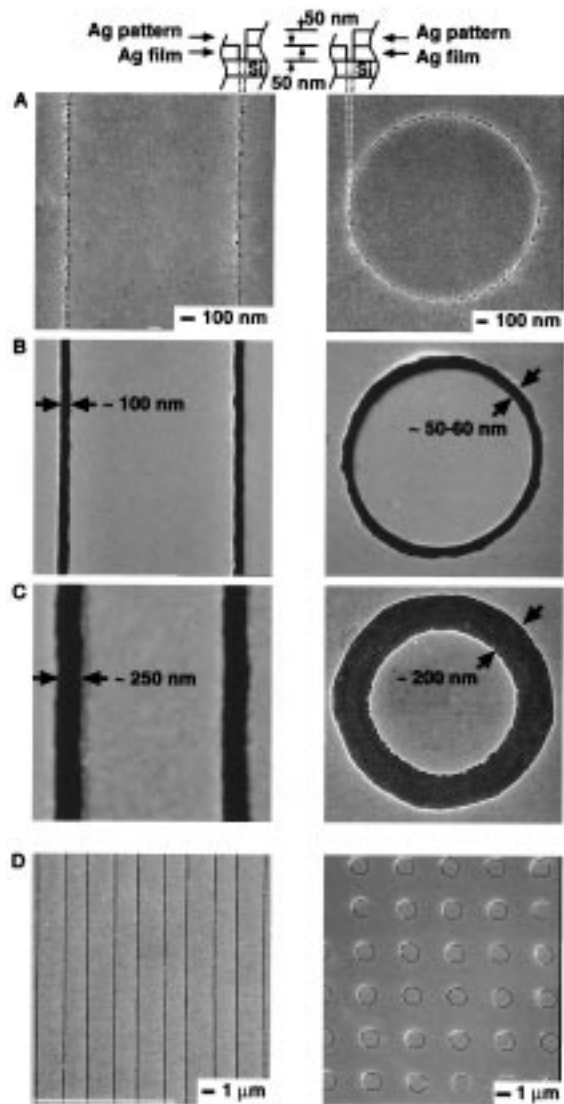


Figure 5. SEMs showing the influence of the duration of etching on the development of structure in silver substrates micropatterned with 2- μm wide lines (left) and a square array of circles with 1.5- μm diameter (right), supporting SAMs formed from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. The time of etching in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M) and sodium thiosulfate (0.1 M), was 7, 10, and 20 s in (A), (B), and (C), respectively, leading to different widths in the resulting features of the patterns. (D) Low magnification images showing that the etching is consistent over a large area.

different kinds of features: (i) trenches in the original surface, (ii) trenches in the surface with the second layer of metal removed, (iii) holes (the size of the features in the original pattern) where both layers of metal have been removed. With longer etch times, the surface would contain only the third type of structure.

To understand further the influence of the duration of etching on the development of structure in the substrate, we etched regions of disordered SAMs formed from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ on topographically patterned films of silver for different lengths of time (7, 10, and 20 s) (Figure 5); we can etch silver with greater edge resolution than aluminum. The size of the initial etch pits is ~ 10 nm—comparable to the size of individual silver grains—and with time the etching proceeds isotropically from the point of nucleation to each side of this region; the features in the substrate widen with increasing time in contact with the etch. The substrate is etched more rapidly on the side of the

interface that has only one layer of metal (the thin side of the interface), and the resulting trench has different edge resolution on each side— <10 -nm on the side with two layers and 10 – 20 -nm on the side with one layer—depending on the thickness of each layer (Figure 5B,C). This relationship between structure and duration of etching may make it possible to control the ultimate shape of the fabricated structures by carefully controlling the time of etching.

The Pattern of Protection of the Disordered Region can be Reversed to Fabricate Positive Structures in Silver and $\text{Al}_2\text{O}_3/\text{Al}$. One challenge in the development of a new method of fabrication is to ensure that it is sufficiently flexible to make both raised and etched features; the examples in this paper thus far have all been of trenches etched into the various substrates. We have shown that molecules at the disordered regions of SAMs on silver and gold are more susceptible to exchange with molecules in solution than those in ordered SAMs.¹⁸ We can use this capability for exchange to generate *raised* features in metal films. The procedure, which reverses the pattern of protection the SAM provides for the surface, is similar to that described in Figure 1. It consists of five stages (Figure 6): (i) deposition of a continuous film of a metal capable of supporting the formation of a SAM, (ii) deposition of a pattern of a second, thin layer of the same metal *without* an adhesion promoter, (iii) formation of a SAM from short molecules on this patterned surface that offers poor protection against etching, (iv) exchange of the short molecule preferentially at the disordered regions with longer molecules from solution that form a SAM that offers good protection against etching, (v) etching of the substrate. We carried out this procedure on topographically patterned silver substrates using a SAM formed from $\text{HS}(\text{CH}_2)_5\text{CO}_2\text{H}$ exchanged with $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$, and aluminum substrates using a SAM formed from $\text{HO}_2\text{C}(\text{CH}_2)_2\text{PO}(\text{OH})_2$ exchanged with $\text{CH}_3(\text{CH}_2)_{17}\text{PO}(\text{OH})_2$ to fabricate patterns of circular outlines (Figure 6A,B) and a more complex pattern (Figure 6C). It is important not to use an adhesion promoter for the second layer of silver because it will act as a resist for etching the bottom layer of silver.

The procedure depends on an even more subtle difference in the pattern of protection the SAMs afford the substrate than with TODE, where etching takes place at the disordered regions of one kind of SAM in preference to ordered regions of the same SAM. Here, etching initiates at regions of the planar surface protected by a SAM formed from a short molecule in preference to disordered SAMs formed from a longer molecule in regions of a topographical step. To help distinguish the two regions of SAM, the short molecule is terminated with a hydrophilic headgroup ($-\text{CO}_2\text{H}$); SAMs with hydrophilic headgroups do not protect surfaces against etching as well as SAMs with hydrophobic headgroups. We do not know exactly which parts of the original substrate remain protected and become the final features. The height of the features, however, is approximately the combined thickness of the two layers of metal.

Etching is Sensitive to the Conditions Used to Prepare the Topographically Patterned Surface. The success of these experiments depends primarily on the ability of the metal surface to form a well-ordered SAM and for that SAM to disorder at abrupt changes in topography. To avoid contamination (or other mechanisms of degradation) of the surfaces, and to ensure the ability of the metal films to support the formation of well-ordered SAMs, the time spent fabricating the structures—in particular, the time following the fabrication of patterns of photoresist—must be minimized.

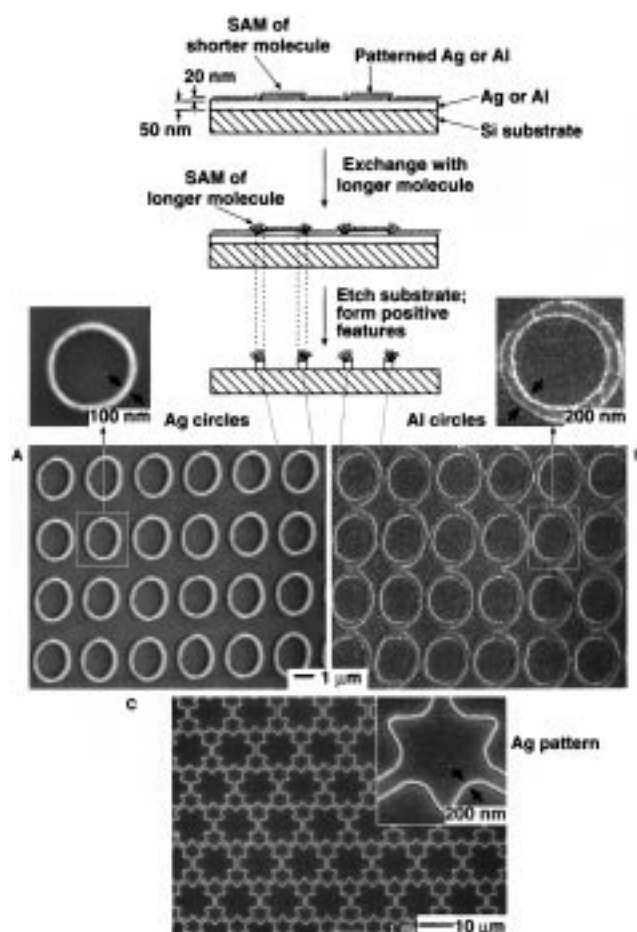


Figure 6. SEMs showing the formation of positive circular outlines (raised features) in (A) silver and (B) aluminum from topographically patterned substrates. For silver, the first layer was 50-nm thick and the second layer (without an adhesion promoter) 20-nm thick. The silver substrates were exposed to $\text{HS}(\text{CH}_2)_5\text{CO}_2\text{H}$ in EtOH (10 mmol) for 10 h, rinsed with EtOH, and then placed in a solution of $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ in EtOH (10 mmol) for 1 h to allow selective exchange of labile, short-chained molecules at the disordered regions with long-chained molecules in solution. The substrates were etched for 40 s in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M), and sodium thiosulfate (0.1 M). The aluminum substrate (first layer 50 nm, second layer 20 nm) was treated first with $\text{HO}_2\text{C}(\text{CH}_2)_2\text{PO}(\text{OH})_2$ (5 mmol in 10% aqueous EtOH) for 10 h then $\text{CH}_3(\text{CH}_2)_{17}\text{PO}(\text{OH})_2$ (5 mmol in 10% aqueous EtOH) for a further 10 h. The substrate was etched for 40 s in a combination of phosphoric, acetic, and nitric acids and water in a ratio of 16:1:1:2 by volume. (C) SEM of a more complex pattern in silver formed by the same procedure as that for the circular outlines in (A).

Two other factors that influence the outcome of the procedure are the use of an adhesion promoter between the two layers of metal, and the angle relative to the surface normal at which the second layer of metal is deposited. Without an adhesion promoter, the surface oxide that forms on both silver and aluminum prevents good adhesion of the second layer of metal (Figure 4C); this image also shows that the etching is extremely sensitive to local variations in structure across the substrate. We will discuss separately the formation of asymmetric structures by deposition at an angle.

SAMs Are More Disordered at Corners Than Edges. To test the hypothesis that different types of change in topography create different amounts of disorder in the SAM, we fabricated structures with both sharp corners and edges and compared the ability of SAMs on these structures to protect the surface against

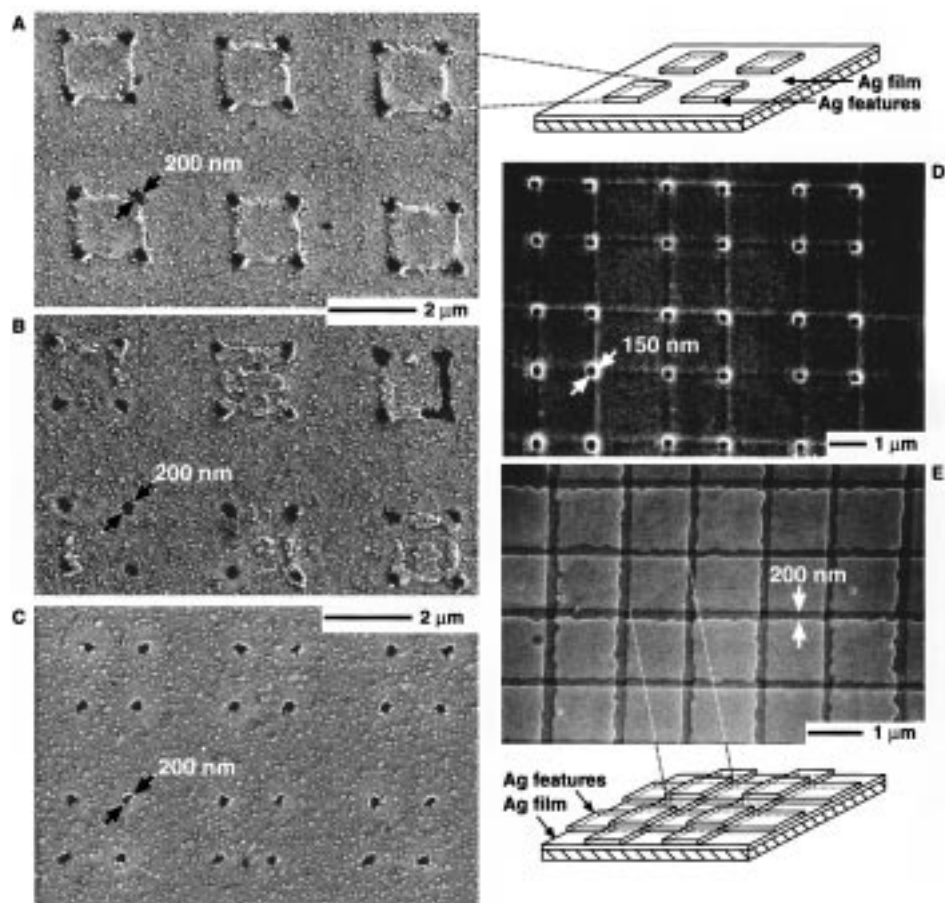


Figure 7. SEMs showing etching at corners in preference to etching at edges. (A–C) SEMs of three different regions of the same pattern of holes, fabricated by performing TODE for 10 s on a pattern of squares of silver (without titanium) on a film of silver, supporting a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. The squares are at different stages of de-adhesion from the film of silver in each of the pictures, showing that the outcome of the process is extremely sensitive to local variation in conditions across the substrate; the de-adhesion of the squares is rapid on the time scale of etching. (D) Pattern of holes made by etching for 10 s an array of crossed silver lines on a silver film supporting a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. (E) Pattern of trenches and holes made by etching a similar substrate to that in (D) for 20 s. The substrates are prepared by evaporating silver (20 nm, titanium 2 nm) through a pattern of 2- μm lines of photoresist followed by liftoff of the photoresist; the process is repeated at 90° to the first set of lines. The etching begins at the corners of the evaporated structures (D) and then proceeds at the edges (E). The edge resolution is consistent with Figure 5; edges of thin features are rougher than edges of thick features.

etching. Figure 7 shows that corners are etched in preference to edges. This observation suggests that SAMs at corners are even more disordered than those at edges (which in turn are more disordered than SAMs on planar surfaces); we can therefore create a hierarchy of disorder in the SAM. We demonstrate this effect by fabricating two different topological patterns with corners and edges—squares of silver on a silver film and orthogonal lines of silver on a silver film. The squares were formed by evaporating silver (20 nm, without titanium) through a mask of photoresist patterned with square holes, followed by liftoff of the photoresist (Figure 7A–C). The orthogonal lines were formed by evaporating silver (20 nm, with titanium 2 nm) through a mask of photoresist patterned with 2- μm lines followed by liftoff of the photoresist, then repeating the process—evaporation of lines through a mask of photoresist followed by liftoff—at 90° to the first set of lines (Figure 7D,E). Figures 7A–C show three different regions of the same pattern of squares, each showing that corners are etched preferentially to edges. The pictures, however, also show different stages of de-adhesion of the squares of silver from the film of silver due to the lack of titanium and the formation of an interlayer of Ag_2O ; the squares detach from the surface before etching along the edges can take place. Figures 7D,E show two crossed lines structures etched for 10 and 20 s, respectively. The corners are

etched first (Figure 7D), then with increased etch times the edges are also etched (Figure 7E). In agreement with Figure 5, the etched features have greater edge resolution where the silver layer is thicker, resulting in a straight edge, whereas the edges of the thinner area is more wavy. It is essential in these experiments that the corners be sharp, not rounded; when the corners are rounded, etching proceeds smoothly around the edge of the pattern. The limit of this case then is when we etch circles, but even then we see that SAMs around circular outlines are more disordered than at edges, and initiation of etching is more rapid around the circumference of circles than along the edges of lines (Figure 2).

Asymmetric Features Can Be Fabricated by Depositing the Second Layer of Metal at an Angle. We have shown previously that shadow evaporation of the second layer of metal induces asymmetry in the width of the disordered region around a given feature;¹⁸ we are effectively changing the edge structure of the evaporated film. Here, we use this method of controlling the change in topography of the surface to fabricate asymmetric features in aluminum and silver.

The pattern in Figure 8A was made by evaporating aluminum through a stencil mask (a TEM grid) onto a film of Al_2O_3 at an angle of $\sim 20^\circ$ from the surface normal—the arrow indicates the direction of deposition from the source. The side of the

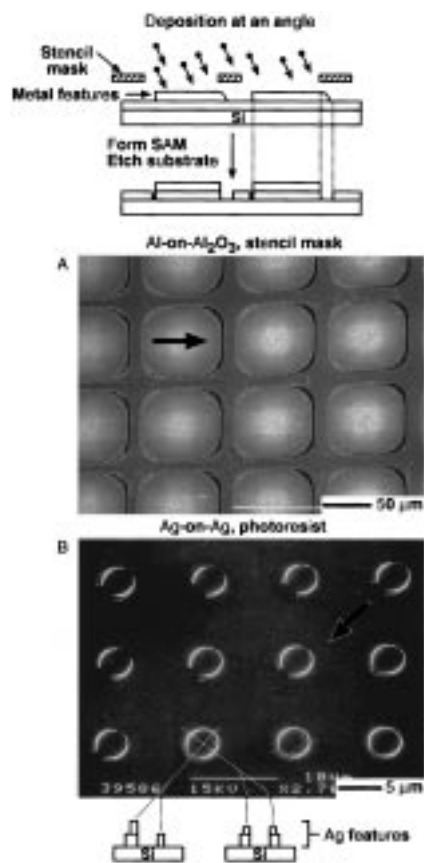


Figure 8. SEMs of patterns produced when the second layer of metal was deposited at an angle of $\sim 20^\circ$ from the surface normal. The arrows indicate the direction of deposition away from the source. (A) Aluminum was evaporated through a stencil mask onto a film of $\text{Al}_2\text{O}_3/\text{Al}$. We formed a SAM from $\text{CH}_3(\text{CH}_2)_{17}\text{PO}(\text{OH})_2$ then etched for 40 s. (B) Silver was evaporated through a pattern of photoresist onto a silver film, followed by liftoff of the photoresist. We formed a SAM from $\text{HS}(\text{CH}_2)_5\text{CO}_2\text{H}$, which exchanged preferentially at the disordered regions, with molecules of $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ from solution, as in Figure 5, and then etched the substrate for 40 s. The features are asymmetric in the direction of the deposition.

evaporated feature that supports a more disordered SAM, the side further from the source, is etched more rapidly than the other side. We can also effect shadowing by evaporating at an angle through a pattern in photoresist (Figure 8B). By exchanging the SAM in the disordered region before etching—the sample is prepared in a similar way to that in Figure 6A, aside from the shadow deposition of the second layer—we can fabricate asymmetric raised features. The circular outlines are thicker on one side, but because the thick side supports a more disordered SAM than the thin side, it is etched more rapidly; this rapid etching can result in a break in the thick region of the feature.

Topographically Directed Etching Can Be Carried Out On Curved Surfaces. The examples presented have used masks of photoresist prepared by conventional photolithography on planar substrates for the deposition of the second layer of metal. We can, however, take advantage of a soft lithographic technique such as maskless photolithography,²⁷ a technique that uses the topography on the surface of a layer of photoresist to direct UV light inside that layer, to pattern photoresist on curved surfaces.

The photoresist, dip-coated on a curved substrate that is covered with a film of silver (50 nm, titanium 2 nm), was

(27) Paul, K. E.; Breen, T. L.; Aizenberg, J.; Whitesides, G. M. *Appl. Phys. Lett.* **1998**, *73*, 2893–95.

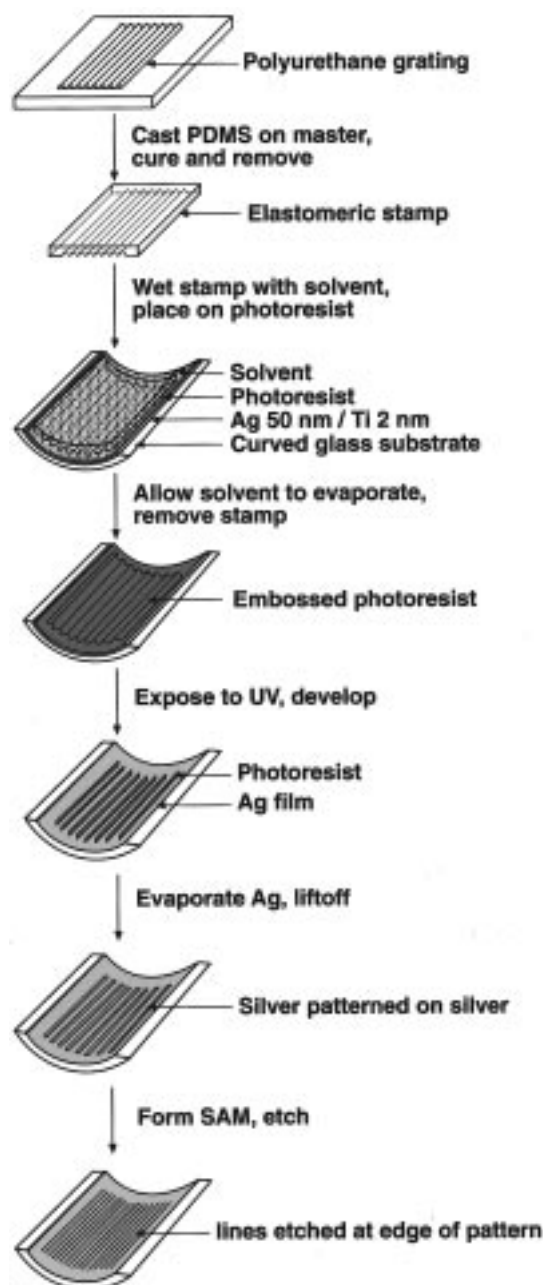


Figure 9. Scheme illustrating the use of an elastomeric mold to fabricate embossed features in photoresist on a curved glass substrate coated with a silver film. The features were then exposed to UV light and developed.

patterned by solvent assisted embossing²⁸ with a flexible, elastomeric mold, then exposed to UV light and developed (Figure 9). We evaporated a second layer of metal and lifted off the photoresist to generate topographically patterned structures on the curved substrates. The substrates were cylindrical pieces of glass with a radius of curvature of 3 cm. The procedure subsequently is the same as that used on planar substrates; we form a SAM from $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ then etch the substrate preferentially at regions of disorder in the SAM: this procedure generated features ~ 50 -nm wide separated by less than 500 nm (Figure 10).

The resolution of the features formed on the curved surfaces is equal to that of those formed on planar surfaces. The curvature

(28) Kim, E.; Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 651–654.

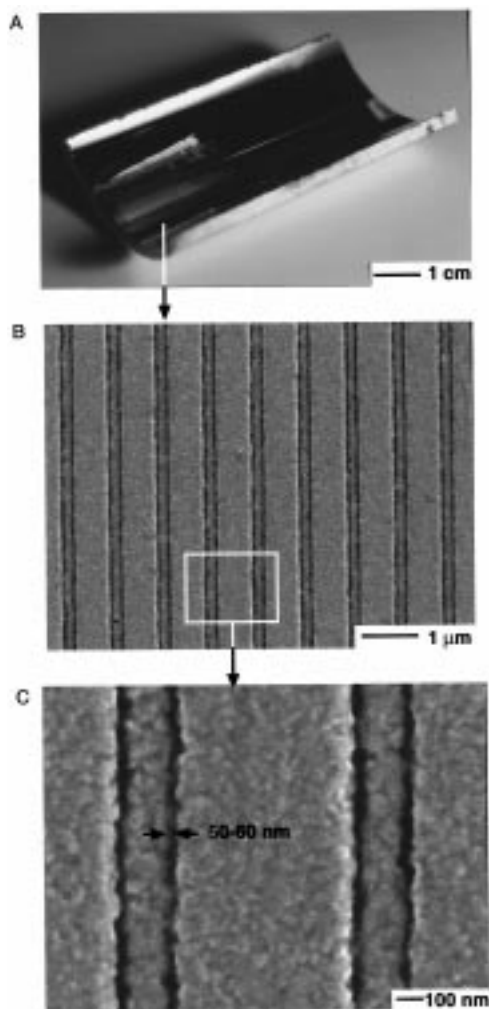


Figure 10. (A) Photograph of a topographically patterned silver film on a curved surface (radius of curvature 3 cm). (B–C) SEMs of etched features (~50-nm wide) in the silver film fabricated by etching for 20 s. Evaporation through the photoresist pattern on the curved surface is inherently shadowed and results in asymmetry in the features; only the ridge of the curved surface is orthogonal to the direction of deposition.

of the substrate, however, causes shadowing during the evaporation of the second layer; this shadowing results in asymmetry in the width of the etched features, and the side of the lines further from the source is etched more than the side close to the source (Figure 10C).

Application of Topographically Directed Etching to the Fabrication of Optical Polarizers. Figure 11A shows the transmission of polarized light (853 and 633 nm) by an array of 120-nm slits in silver on a quartz substrate. The linearly polarized beam passed through a half-wave plate (rotated mechanically) before passing through the sample to the detector where its transmitted intensity is recorded automatically by computer. The extinction ratio is ~3:1 for light at 853 nm and ~2:1 for light at 633 nm. The difference in the extinction ratio at the two wavelengths reflects the discrimination of the sample toward the two incident wavelengths.

The efficiency of polarization (Q) through an array of well-separated slits²⁹ can be predicted using eqs 1–2 ($x = ka$, where $2a$ is the width of slit, and $\log \gamma = 0.577$ is Euler's constant); Q_1 is for \mathbf{E} parallel to the length of the slit, and Q_2 is for \mathbf{E} perpendicular.³⁰

(29) Lochbihler, H.; Depine, R. *Appl. Opt.* **1993**, *32*, 3459.

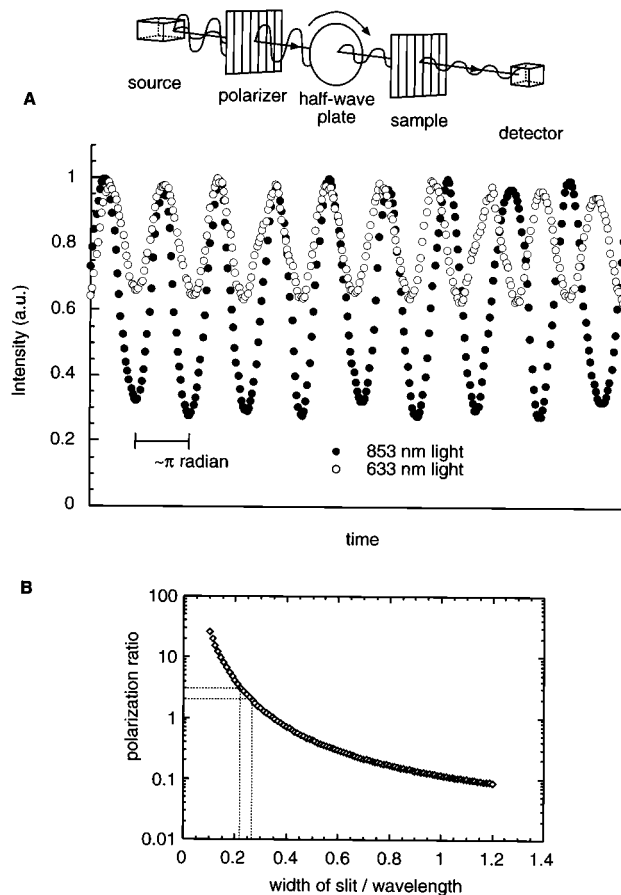


Figure 11. (A) Plot of the relative intensity of linearly polarized light (823 or 633 nm) transmitted through an array of 100-nm slits in a topographically patterned silver substrate (Figure 5D) as a function of time. Time corresponds to the rotation of a half-wave plate through which the beam passes before it reaches the sample. The intensity of the transmitted beam is detected and recorded by computer. The two curves are not in phase because the rate of rotation of the half-wave plate is not consistent, but each excursion from maximum to minimum to maximum corresponds to a rotation by π radian. The parameter of interest is the ratio of I_{\min} to I_{\max} for the two wavelengths. (B) Plot showing the relationship between the polarization ratio and the width of the slit divided by wavelength. The two selected points are the observed polarization ratios at the two different wavelengths and the widths of slits to which they correspond.

$$Q_1 = \frac{2}{x} \frac{\pi^2}{\pi^2 + \{2 \log(\gamma x/4)\}^2} [1 + 1/4 x^2 + \dots] \quad (1)$$

$$Q_2 = \frac{\pi^2 x^3}{16} [1 + 5/16 x^2 \{1 - 8/5 \log(\gamma x/4)\} + \dots] \quad (2)$$

These equations are complementary, by Babinet's principal, to those used to calculate polarization by reflection from strips. By plotting Q_1/Q_2 we are able to see the relationship between the ratio of polarization and the width of the slit divided by the wavelength (Figure 11B). By using this curve we find that our measured efficiencies require a slit width of ~170 nm, although one assumption of the theory is that the lines are perfectly conducting. It is possible, however, that silver grains at the edges of the features have oxidized and decrease the conductivity, thereby increasing the width of the slit.

As expected from a large ratio of slots to opaque metal bands in the sample, the fraction of the light that is transmitted in

(30) van de Hulst, H. C. *Light Scattering by Small Particles*; Dover: New York, 1981.

these structures is low (<5%); the percentage of the sample used here that was transparent was ~4%. The most plausible application of this type of polarizer would be one in which high-temperature performance was required but in which transmission efficiency was not an important parameter.

Conclusions

There are several advantages of TODE for producing structures with lateral dimensions <50 to 200 nm over other forms of lithography. The features that are generated specifically at the *edges* of topographically patterned metal films are at least an order of magnitude smaller than those originally patterned on the material, when the original patterning is at the scale of micrometers. Because the pattern transfer step is chemical, TODE is not limited by either diffraction or depth of focus. The method can also take advantage of conventional photolithography for the fabrication of the original patterns and to assist in processes such as registration. We can, however, use methods other than photolithography to introduce changes in the topography of the surface: for example, photoresist patterned on curved substrates by solvent-assisted embossing. The width of the features generated by TODE is, in part, determined by the structure of the substrate at the edges of the evaporated features (Figure 8) and the grain size of the material (Figure 5A); the minimum width of the etched feature is potentially as small as the width of the region of disorder.

The disadvantages of this technique are that it is dependent on edges for pattern transfer—we can only make outlines of features—and that the etching is sensitive to many experimental parameters; in particular, the quality of the metal surface and the sharpness of the edges.

With the existence of several, readily accessible methods for patterning metal films, we believe that TODE is a method that places the fabrication of a useful selection of nanostructures within the reach of chemists and others outside the microelectronics community.

Experimental Section

Materials. Ethanol (Pharmco, Brookfield, CT, 200 proof), iso-propyl alcohol (Mallinckrodt, AR grade), hexane (Mallinckrodt, Phillipsburg, NJ, anhydrous), aluminum etchant type "A" (Transene Co., Danvers, MA), poly(dimethylsiloxane) SYLGARD 184 (Dow Corning, Midland, MI), hexadecanethiol (Fluka, 95%), 2-carboxyethylphosphonic acid (Aldrich 94%), octadecyltrichlorosilane (United Chemical Technologies, Bristol, PA), potassium ferrocyanide (Aldrich), potassium ferricyanide (Mallinckrodt), sodium thiosulfate (Aldrich), potassium hydroxide (VWR), hydrofluoric acid (VWR, 49%), and photoresist (Shipley 1813, Microchem Corp., Newton, MA) were used as received. Octadecanephosphonic acid and 6-mercaptohexanoic acid were available from previous studies. Silver, aluminum, titanium, and quartz used for the e-beam evaporations were of 99.999% purity. Silicon wafers (Silicon Sense, Nashua, NH) were test grade, n- or p-type Si(100). Quartz windows (Chem Glass, Vineland, NJ) were cleaned by washing with soapy water, then water and ethanol. Curved glass substrates (radius of curvature 3 cm) were cut from glass tubing (Chem Glass) and cleaned by washing with soapy water and then water and ethanol.

Preparation of Topographically Patterned Substrates. For silver, gold, and aluminum layers, silicon wafers were coated first with a 2.5-nm thick film of titanium to promote adhesion and then with a 50-nm thick film of aluminum or silver, or a 15-nm thick film of gold, using an e-beam evaporator (it is critical, when depositing silver, that the base pressure in the evaporator be $<1 \times 10^{-6}$ Torr). We formed patterns in photoresist on these metal-coated substrates using conventional photolithographic techniques (it is important *not* to use primer before the photoresist is spun onto the substrate) and then deposited a second layer of the same material (50 nm thick for silver and aluminum, 15

nm for gold). Liftoff of the photoresist revealed the topographically patterned substrate. Micropatterned SiO₂/Si substrates were formed by evaporating a layer of SiO₂ (50 nm) through a pattern in photoresist—prepared using conventional photolithographic techniques—onto the native oxide (~2 nm thick) of a silicon wafer followed by liftoff.

Preparation of SAMs and Etching. Silver and gold substrates were treated with a solution of HS(CH₂)₁₅CH₃ (10 mM in EtOH) for 1 h, rinsed with ethanol, and etched. Substrates with M₁ = silver were etched in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M), and sodium thiosulfate (0.1 M) for 10–20 s. Substrates with M₁ = gold were etched in an aqueous solution of potassium ferrocyanide (0.01 M), potassium ferricyanide (0.001 M), sodium thiosulfate (0.1 M), and potassium hydroxide (1 M) for 40 s. Aluminum substrates were exposed to a solution of CH₃(CH₂)₁₇PO(OH)₂ (5 mmol in 10% aqueous EtOH) for 10 h and then rinsed with EtOH. The substrates were etched with a commercial etching solution (aluminum etchant, Transene Co., Danvers MA) containing phosphoric, acetic, and nitric acids and water in a ratio of 16:1:1:2 by volume, for ~30 s. We exposed SiO₂/Si substrates to a solution of CH₃(CH₂)₁₇-SiCl₃ in anhydrous hexane (10 mmol) for 10 h and then rinsed with hexane. SiO₂/Si substrates were etched with 1% HF for 20 s and then immediately with 3 M KOH solution (water with 25% *i*-PrOH) for 120 s.

Exchange Experiments. The topographically patterned silver substrates were prepared by using the method described above. The first layer was 50-nm thick, and the second layer (without an adhesion promoter) was 20-nm thick. The substrates were exposed to HS(CH₂)₅-CO₂H in EtOH (10 mmol) for 10 h, rinsed with EtOH, and then placed in a solution of HS(CH₂)₁₅CH₃ in EtOH (10 mmol) for 1 h to allow selective exchange at the disordered regions. The substrates were etched for 40 s in the silver etching solution described previously. The aluminum substrate (first layer 50 nm, second layer 20 nm) was treated first with HO₂C(CH₂)₂PO(OH)₂ (5 mmol in 10% aqueous EtOH) for 10 h then CH₃(CH₂)₁₇PO(OH)₂ (5 mmol in 10% aqueous EtOH) for a further 10 h. The substrate was etched for 40 s in the etchant already described.

Preparation and Etching of Substrates with Corners. The silver substrate in Figure 7A–C was fabricated by evaporating silver (50-nm thick) through a grid of square holes in photoresist formed on a silver film (50-nm thick with titanium, 2-nm thick) followed by liftoff of the photoresist. The substrate in Figure 7D,E was prepared by patterning one layer of 2- μ m lines in silver (using the procedure already described—photolithography to pattern 2- μ m lines in photoresist, evaporation of silver (20-nm thick with titanium, 2-nm thick) followed by liftoff) then a second layer of 2- μ m silver lines (20-nm thick with titanium, 2-nm thick) perpendicular to the first (by repeating the same procedure as the first layer of lines). Both silver substrates were exposed to a solution of HS(CH₂)₁₅CH₃ (10 mM in ethanol) for 1 h, rinsed with ethanol, and then etched by using the etchant described previously for 10 (Figure 7A–C) and 20 s (Figure 7D,E).

Deposition at an Angle. The substrates used in Figure 8 were prepared by evaporating the second layer of metal at an angle of ~20° away from the surface normal (the direction of the beam is indicated by arrows pointing away from the source). Aluminum was deposited through a TEM grid (in close contact with the surface), and silver was deposited through a patterned film of photoresist (~1- μ m thick). We formed SAMs and etched the substrates by methods described previously.

Patterning Curved Surfaces. We used solvent-assisted embossing²⁸ with a flexible, elastomeric mold to pattern photoresist that was dip-coated on a curved glass substrate. The mold was prepared by casting and curing PDMS on a commercial 1200 lines/mm holographic grating. The embossed photoresist was exposed and developed according to previously published methods.²⁷

Polarization Measurements. The substrate for this experiment (an array of 120-nm trenches in a topographically patterned silver film) was similar to that shown in Figure 5D; it was fabricated using methods already described. The attenuation of light passing through the sample was measured by passing a beam of polarized light (853 or 633 nm) through a half-wave plate that was rotated mechanically and then passed

through the sample. The intensity of the transmitted light was detected and recorded by computer at the rate of 10 data points per second.

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