

CHAPTER

SELF-ASSEMBLED MONOLAYERS AND LITHOGRAPHY*

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Introduction

"Small" is a word that increasingly defines a broad set of objectives in modern science and technology. Modern information technology has been built on small structures, and the demonstration that it is technologically practical to make systems of the feature size and complexity of those that constitute microprocessors and memories has opened the eyes of a broad range of technologists to the potential of small structures. There are now a very large range of recognized opportunities in technology that might be satisfied by making new types of small structures, or by reconstituting existing structures in down-sized versions; developing practical methods of fabricating these structures often remains complicated, expensive or impossible. At the same time, it is clear that there are many interesting and new phenomena that occur in small structures. One useful sub-definition of "small", when categorizing types of structures that exhibit new phenomena is "meso scale". Meso-scale structures are those that have critical dimensions that match the dimensions of the phenomena being investigated. These critical dimensions obviously vary with the application: 2-20 nm (the distance an electron travels in ballistic flight in solids at modest temperatures, before colliding with an atom and changing direction) for quantum dots; 200 - 2000 nm for interactions involving visible and infrared light, for optical structures such as in-fiber diffraction gratings; 10 - 50 μm for surface structures used in studying the biochemistry of mammalian cells attached to a surface.

Chemistry has historically been concerned with *molecules* rather than *structures*, and although some molecules can be quite large, most fall below the range of sizes of interest to the makers of small, electronically or optically functional systems. In addition, the properties of molecules are typically not those required for systems based on electronic conductivity, although they may be very useful in optical system. For a comparison of scale, benzene is less than 1 nm in its largest dimension, a typical protein has a diameter of approximately 4 nm, and a high-molecular weight polymer (for example, poly(methyl methacrylate) of 10^6 molecular weight) extended fully, might have a length of 1000 nm or 1 μm . Making well-defined structures that are more than a few nm across by conventional synthetic methods that use current chemical techniques would be a major undertaking.

Although there has not been a perfect match between molecular chemistry and the requirements of optical and electronic device physics, the need for better methods of fabrication at the lower end of the range of sizes of interest to the device community, the opportunities to build new types of mesostructures, the chance simply to build small systems to conserve space and reagents, and the need for chemistry to find new areas for exploration are now bringing a number of fields of science and technology together in unfamiliar and productive combinations. Ultimately, of course, all structures are made of atoms, and chemistry brings to these activities a specialized competence in manipulating atoms. Within the areas of microelectronic device fabrication in which microfabrication has developed most actively, however, chemistry has played an important but secondary role. The growth of silicon single crystals, photolithography, etching and doping of semiconductor devices, and device

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packaging all depend on the use of chemicals, but the intellectual leadership in microelectronics has clearly rested in electrical engineering and applied physics. As structures become increasingly small, however, they become increasingly difficult and expensive to produce by simple extensions of existing photolithographic techniques. The opportunity to extend ideas from molecular chemistry into the production of structures larger than molecules but small by comparison with those that can be routinely produced by photolithography--and especially to structures that are functional in meso-scale science and technology--is becoming more attractive as the size of these structures decreases, their complexity and variety grows, and the difficulty of fabricating them increases.

Although the opportunity to develop new, non-photolithographic methods for making small structures is a very attractive one in principle, in practice does chemistry have ideas that would enable it to contribute to the revolutions in science and technology that are accompanying the investigation of meso-scale phenomena and the construction of small devices? We believe that the answer to this question is clearly "yes", and that chemistry can contribute to the fabrication of meso-scale structures in a surprisingly broad range of areas. Among the concepts, strategies and structures from chemistry that seem to offer particular opportunity in meso-scale science and technology are these:

Non-covalent Synthesis. The most important emphasis in organic chemistry in the last 50 years has been developing a body of techniques that could be used to synthesize complex organic synthesis. This area has been enormously productive, but is not a key contributor to the generation of structures that show useful properties as materials, or electronic or optical functionality. The new area of "non-covalent synthesis"--a strategy for building large organic structures that are held together by weak interactions--hydrogen bonds, van der Waals interactions, the hydrophobic effect, charge-charge interactions¹-- offers opportunities for practical routes to new types of useful structures and functions.

Molecular Self-Assembly and Self-Assembled Structures. An important new concept in synthesis is that of molecular self-assembly.^{2,3} This concept has been extracted from the study of biological systems.²⁻⁴ In cells, enormous complexity is developed using molecules that assemble themselves into functional shapes or aggregates. Familiar examples are the formation of correctly folded, functional proteins from polymers of amino acids, the formation of functional t-RNA's from unfolded ribonucleic acids, and the formation of the cell membrane from phospholipids. This strategy for generating complexity through molecular self-assembly, if fully understood and controlled, offers a fundamentally new approach to the design and fabrication of non-biological systems.²⁻⁶

The key idea in self-assembly is that the final structure and function of the molecules or molecular aggregates are close to or at thermodynamic equilibrium, and that the individual molecules will reach these structures simply by equilibrating to their lowest-energy forms: that is, expenditure of energy, or active intervention by the experimenter, is not necessary once the molecular components of the system have been correctly designed and synthesized.^{2,3} The information that allows self-assembling systems of molecules to reach their final, functional structures is encoded in the molecular structures, and especially in molecular shapes.

Small Particles and Microstructured Solids. Chemistry has been the source of many methods of fabricating a range of structures with sizes appropriate for use in the meso-dimensional world: among these are colloids,⁷ micelles,⁸⁻¹⁰ liquid-crystalline structures,¹¹ liposomes,¹² ferrofluids,¹³ sol-gels,^{14,15} zeolites^{16,17}, phase-separated polymers,¹⁸ artificial peptide tubules,¹⁹⁻²² bubble rafts²³ and many others. Most of these structures have been developed for other reasons, but there is now an attractive opportunity to reconsider their use in meso-scale electronic, biological and optical science.

Large, Electronically-functional Molecules. An important characteristic of organic molecules is that they are typically electronically insulating. This characteristic has limited their application in microelectronic devices to applications such as insulators, adhesion promoters and thin-film dielectrics. In the last 10 years, however, a range

of organic electrical conductors have been developed, and it is increasingly practical to consider organic conductors as electrically functional components of certain types of systems (especially sensors and bioelectrical systems).

Organic materials have always been attractive for the ease with which their optical properties can be tailored, and with the recent explosion of interest in optical systems for their contribution in optical communications, there is a clear opportunity to build new types of optical systems that rely on the unique characteristics of organic materials.

Results

Self-Assembled Monolayers. Our work has focused on self-assembled monolayers (SAMs) of alkanethiolates on gold and silver.²⁴⁻²⁶ These structures are the best developed examples of non-biological, self-assembling systems that are currently available. SAMs are structures in which the constituent molecules associate with a surface and form a monomolecular layer (Figure 1). The lateral interactions between the molecules lead to ordering, and the final structures are essentially two-dimensional quasi-crystals supported by the surface.²⁷ SAMs exhibit many of the features that are most attractive about self-assembled systems: small numbers of defects (relative to what could be achieved by covalent synthesis of a structure of corresponding complexity and size); the ability to serve as the basis for the fabrication of structures with dimensions in the nm to μm range; ease of synthesis and practicality in technological applications; ability to control meso and macroscopic materials properties of the system.

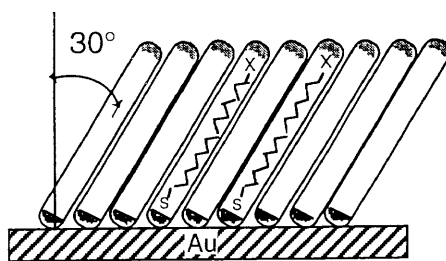


FIGURE 1

Schematic illustration of the structure at the molecular-level of a self-assembled monolayer of n-alkanethiolates on gold. The head group X (= CF₃, CH₃, OH, or, COOH, for example) can be modified to control surface properties, and the length of the alkyl chain can be varied to change the thickness of the monolayer.

This system is both the most highly developed of the model systems for self-assembled structures, and a broadly useful system in a range of applications: it thus combines intellectual content and practical application. SAMs of alkanethiolates (and to a lesser extent of alkylsiloxanes on glass or silica,^{28,29} and of alkyl phosphonates on zirconium dioxide^{30,31}) provide a high degree of control over the properties of a surface in the direction perpendicular to the surface. Two extensions of the concepts underlying SAMs provide structure in the second and third dimensions.

Microcontact Printing (μCP). Many applications of surface chemistry (and most microfabricated structures) require surfaces or thin films that are patterned in the plane of the surface. Microcontact printing³²⁻³⁴ is a versatile method for accomplishing patterning on the scale from several μm and larger to less than 200 nm, without using photolithography (Figure 2). The basis of the method is the use of an elastomeric stamp having surface relief features of the appropriate pattern, to transfer the alkanethiol to the surface of the substrate by contact. Most of our

work has been based on stamps fabricated from polydimethylsiloxane (PDMS), although other elastomers such as polyurethanes have been used as well. The stamp is usually prepared by casting the PDMS over a master prepared by photolithography, although other sorts of masters can also be used. The stamp is "inked" with a solution of the alkanethiol, and the inked stamp is then brought into contact with the surface of the gold film to be patterned, either by hand or using simple equipment for alignment.

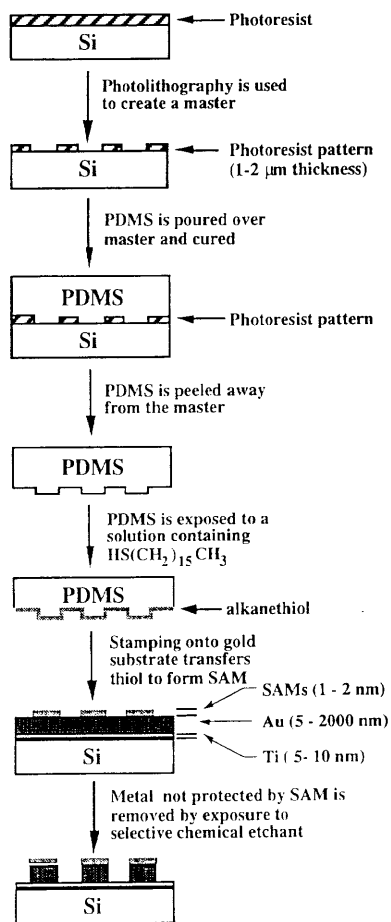


FIGURE 2

Schematic of the procedure for microcontact printing. An elastomeric stamp with three dimensional relief is formed by casting polydimethyl siloxane (PDMS, Dow-Corning Corporation, Sylgard 184) on a master. Masters are typically prepared by photolithography. The printing procedure involves several steps: i) the stamp is inked by applying a dilute solution of alkanethiol to the surface of the stamp with a cotton swab, ii) the stamp is blown dry in a stream of dry nitrogen; iii) the stamp is placed on a gold coated substrate (sometimes light pressure is applied to ensure conformal contact between the stamp and the gold); iv) SAMs are formed in regions where the stamp contacts the surface, v) the stamp is gently peeled from the surface.

It is critical that the stamp be elastomeric. If it is too rigid, it is not able to conform to the microroughness on the surface of the substrate, and pattern transfer is incomplete; if it is too pliable or soft, it is not able to maintain sufficient structural integrity to print reliably features with dimensions of $\sim 1 \mu\text{m}$. The minimum size of the features that can be prepared by μCP still has not been completely defined, and will probably depend on the degree of

perfection that is required in the final system. It is now routine to print features at the 500-nm scale,³²⁻³⁴ and 200-nm features can also be prepared³⁵⁻³⁷ (albeit with greater difficulty). It should be possible to go to structures below 100 nm, although some tailoring of the properties of the stamp may be required. The edge definition of the patterns produced by current μ CP is on the order of 50 nm.³⁸

One of the important characteristics of SAMs is that they are excellent resists for certain types of etches.^{39,40} For the system of alkanethiolates on gold and silver, the best selectivity between regions of metal covered with a C₁₆, methyl-terminated SAM and regions that are bare is accomplished with an etch of aqueous ferricyanide (Figure 3).⁴⁰ The density of defects (in terms of small holes in SAM covered regions) achieved by this system is approximately 100 per mm².⁴¹ This density is too high to be useful for high-resolution microelectronic device fabrication, but is acceptable for many other areas of application--for example, optics--where the definition of the meso-scale of sizes requires larger structures.

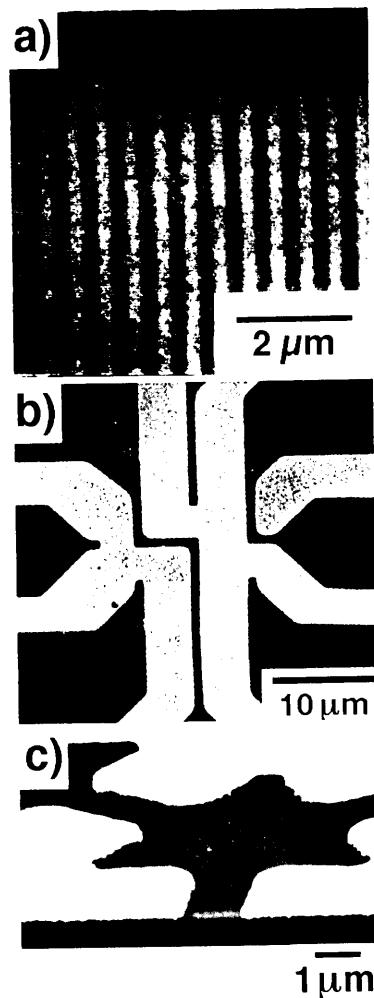


FIGURE 3

Scanning electron micrographs of metal structures on silicon fabricated by using patterned SAMs (formed by microcontact printing) as ultrathin resists against selective etchants. (a) 200 nm-wide lines of gold separated by 200 nm-wide spaces of Si/SiO₂: these are the smallest structures fabricated to date by standard μ CP. (b) Pattern in copper. (c) 200 nm-thick etched structures of silver. The edge resolution of this fabrication technique is of order 50 nm for 50 nm thick gold structures, and of order 30 nm for 50 nm thick silver structures.

*Micromolding in Capillaries (MIMIC).*⁴² Microcontact printing has provided a very useful technique for fabricating surfaces patterned with SAMs. SAMs are, typically, structures that are approximately 2 nm thick-- and thus quasi-two dimensional--and have no structural integrity independent of the support on which they rest. MIMIC is a technique that permits the fabrication of structured and mechanically stable thin-film structures with thicknesses of a few μm . In MIMIC (Figure 4), the same PDMS stamps used in μCP are brought into contact with an appropriate surface (metal, ceramic, or polymer). When in contact with a support, they form a bed of small-dimensional capillaries. If a liquid prepolymer is brought in contact with an entrance to this network, capillary forces pull the prepolymer into the bed; for suitable dimensions, the capillary network can fill completely in periods of minutes to hours. Polymerization of the prepolymer in situ to a solid, followed by removal of the PDMS stamp, results in generation of polymeric microstructures that can have substantial mechanical stability.

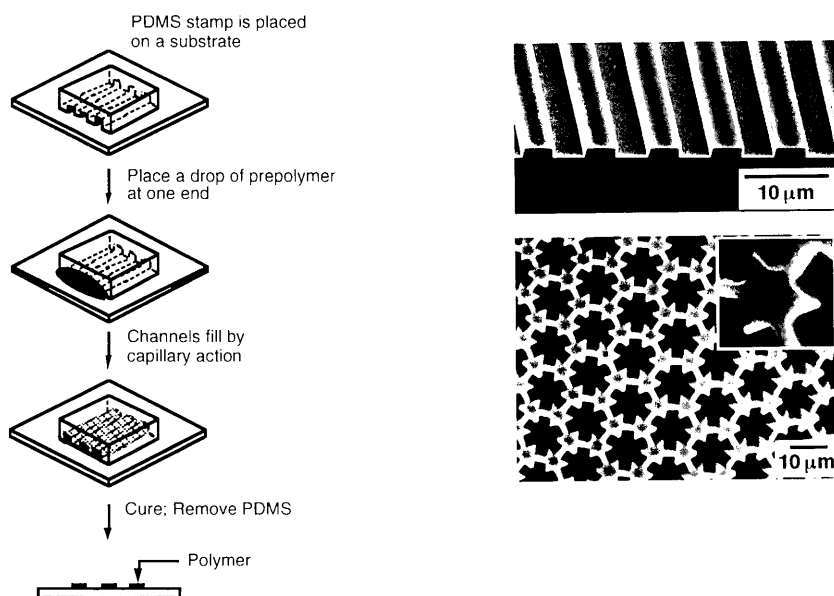


FIGURE 4

Schematic of the capillary micromolding process (MIMIC). An elastomeric stamp (similar to those used in microcontact printing) is placed in conformal contact with a substrate to form a mold that consists of a network of channels. A low-viscosity polymer precursor is placed in contact with openings to the network, and the channels fill by capillary action. After curing the polymer precursor, the elastomeric stamp is removed and can be used again. The images are scanning electron micrographs of polymeric structures fabricated by MIMIC.

Applications. SAMs, both in large-area, homogeneous form and as patterns, have now been used in a range of applications. An example of a use for a homogeneous SAM is as a surface presenting ligands that selectively interact with and adsorb proteins.⁴³ These types of surfaces are relatively easily prepared by synthesis, even when the ligand required is structurally complex, because the full power of organic synthesis can be brought to bear on the preparation of the individual molecules that are the precursors of the SAM. Investigations of the properties of these biologically functional SAMs have generated a number of types of surfaces that interact with proteins; perhaps as importantly, they have also demonstrated surfaces that do *not* adsorb proteins and are readily prepared by appropriate manipulation of the functional groups present at the termini of the alkanethiolates; these non-adsorbing surfaces are important as controls.⁴⁴ An analytical technique that is especially useful in conjunction with SAMs

that are active in biological recognition is surface plasmon resonance (SPR) spectroscopy.⁴³ In this technique, a beam of light is reflected from a thin, semitransparent gold film. The angle of minimum intensity in reflection is related to the index of refraction of the interface, and thus to the quantity of protein adsorbed at that interface (Figure 5).

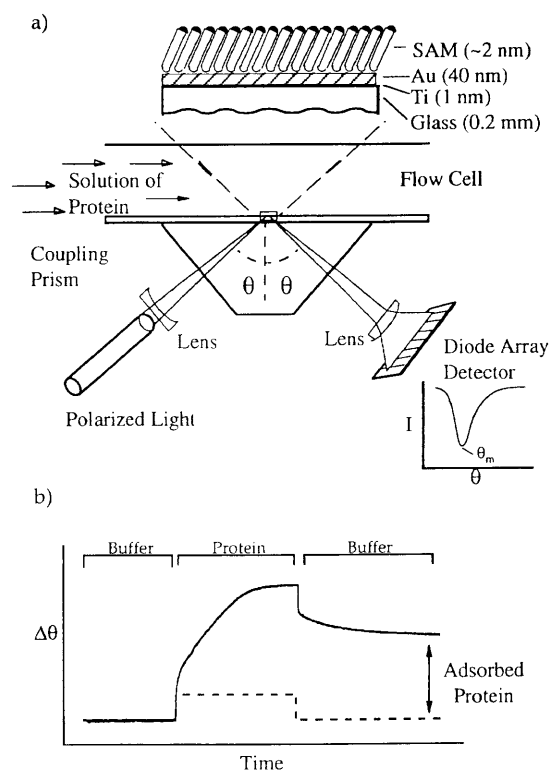


FIGURE 5

a) Schematic of the experimental set-up for using surface plasmon resonance spectroscopy (SPR) to monitor interactions between proteins and the surface of a self-assembled monolayer (SAMs). The adsorption of proteins to SAMs is measured *in situ* and in real time. p-polarized light is incident on the substrate and the angle at which the reflected light shows a minimum in intensity is recorded. This angle (Q_m) is characteristic of the optical properties of the interface and depends on the average thickness of a protein layer. b) Typical data recording Q_m versus time (solid curve). The change in the index of refraction of the protein-containing solution also causes a change in Q_m ; this contribution to the measured signal is indicated by the dashed curve. The difference between the two curves measures the amount of protein adsorbed to the SAM. The extent of protein adsorption can be controlled (0%-100% protein adsorption) by choosing an appropriately functionalized SAM; selective adsorption of specific proteins by using a SAM functionalized with a biospecific ligand is also possible. Reprinted with permission from reference 43. Copyright 1995 American Chemical Society.

The use of SAMs that are specifically functionalized to interact with proteins is valuable in examining the influence of cell morphology on cell metabolism.⁴⁵⁻⁴⁷ In one application of μ CP, a surface is partitioned into regions of SAM that are approximately 10-30 μ m in size and that interact with proteins in the medium, and

surrounding regions that do not adsorb proteins. The patterns of adsorbed proteins that result when these patterned surfaces are exposed to the medium used for tissue culture then determine the shapes of mammalian cells that attach to the surface (Figure 6). Using simple patterning, it is thus possible to dictate the shape assumed by a cell that attaches to a surface, and to examine the influence of that shape on the metabolism of the cell. The results of these types of studies are important in suggesting connections between cell morphology and cell metabolism, and may eventually shed light on complex phenomena such as contact inhibition of cell proliferation.

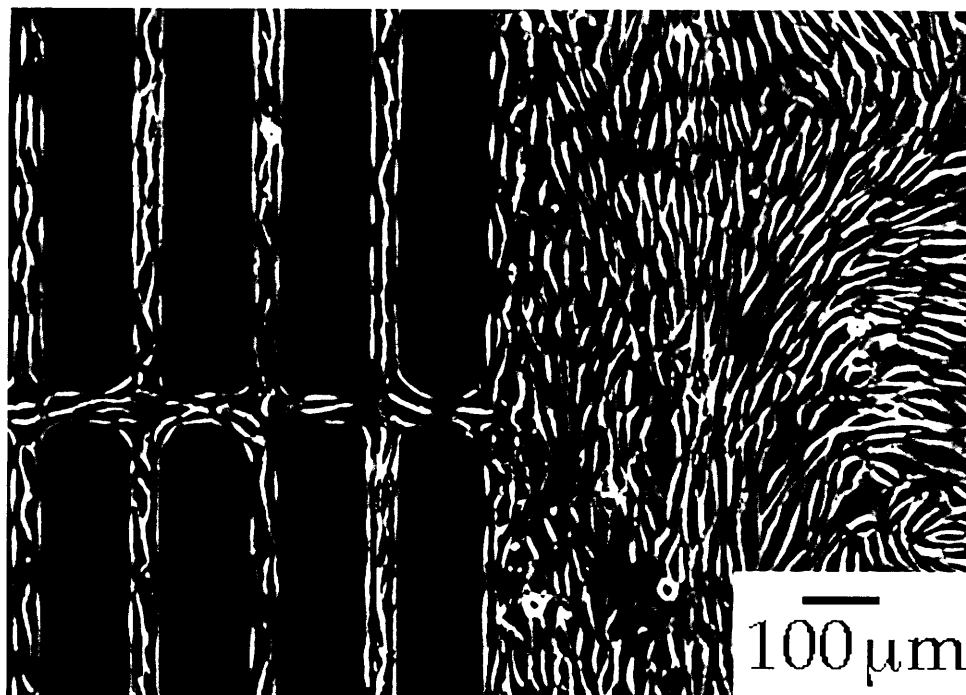


FIGURE 6

Selective attachment and spreading of bovine capillary endothelial cells on a surface covered with patterned SAMs formed by microcontact printing. The SAMs were patterned by μ CP such that certain regions of the surface were terminated by methyl groups, while others were terminated by oligo(ethylene glycol) groups. This patterned surface was exposed to a solution containing a matrix protein (fibronectin); this protein adsorbed to the methyl-terminated SAMs and did not adsorb to oligo(ethylene glycol)-terminated SAMs. Endothelial cells attached only to regions of the surface where the matrix protein was adsorbed; the pattern of cell attachment thus reflected the geometry and dimensions of the patterned SAM formed by μ CP.

In non-biological applications, μ CP have also begun to find use. One that is especially promising is formation of patterns on non-planar surfaces. Non-planar lithography is a very substantial challenge for photolithography, and even very gently curved surfaces often cannot be patterned successfully by photolithography because of limitations to depth of focus. Microcontact printing, by contrast, works as smoothly with many curved surfaces as with planar surfaces (Figure 7).⁴⁸

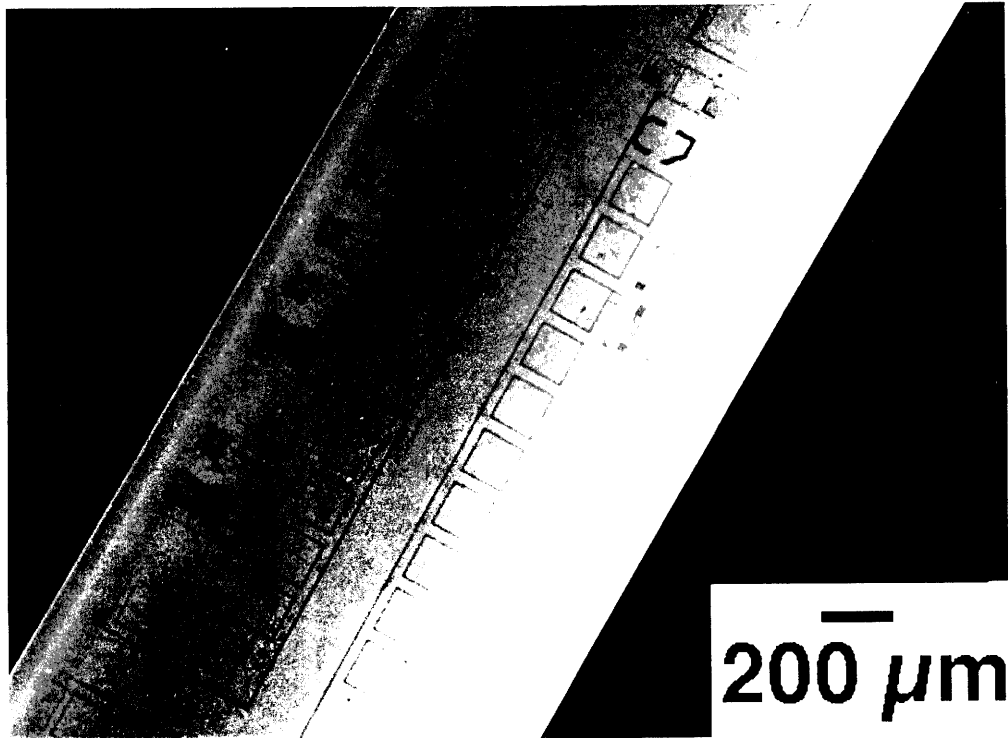


FIGURE 7

Scanning electron micrograph of gold microstructures on a glass capillary ($r=500\mu\text{m}$). The structures were fabricated by several steps: i) coating the capillary with gold; ii) rolling the gold-coated capillary across an elastomeric stamp that was inked with alkanethiol; this step formed a patterned SAM on the surface of the capillary, and iii) etching of the gold with a ferricyanide solution in regions not protected by the patterned SAMs.

Conclusions

As fabrication of small structures grows in importance in a wide range of areas--from microelectronics, through optics and microelectromechanical systems (MEMS) to cell biology--the utility of new methods of carrying out microfabrication will increase. Most structures with μm and nm dimensions are now made by photolithography. Photolithography will continue as the unquestioned dominant technology in fabrication of microelectronic devices for the foreseeable future. Photolithography has, however, important limitations for certain types of applications. It does not provide much versatility in terms of the materials properties of the polymers that can be used, nor is it easily applicable to the generation of surfaces that present complex organic functional groups of the sort needed in biochemistry and biology. It is not, in general, applicable to curved or interior surfaces. Modern photolithography is also expensive since it entails significant processing and capital costs.

Molecular self-assembly and self-assembled monolayers (SAMs), coupled with techniques for patterning such as μCP and MIMIC offer a new strategy for fabricating micro- and nanostructures. These techniques do not replace photolithography, but instead complement it. They *do* offer a high degree of control over the detailed, molecular-level structure of the interfaces. The thickness of the surface structures generated with SAMs (2 nm) is substantially thinner than those that can be prepared by photolithography. This thinness can be exploited for the development of new forms of lithography⁴⁹ or to achieve very small (<50 nm) scale features.⁵⁰⁻⁵³ They are applicable to a broader range of materials than photolithography, and may be useful in generating large-area structures. When applicable, they are probably less expensive than photolithography. SAMs have three important limitations at this time: i) There are only limited demonstrations of registration in multilevel fabrication. ii) The most highly developed systems of SAMs are combinations such as gold or silver on titanium-primed Si/SiO₂; the

presence of the heavy metals may limit their use in microelectronic device fabrication. iii) The levels of defects in etched structures that are too high to allow the yield required in fabrication of complex microelectronic systems.

Where will SAMs and other self-assembled organic structures ultimately be used, and how will they contribute to science and technology? Certain parts of the answer to this question are clear because the applications have already been demonstrated; others remain speculative. It now appears that the types of methods of fabrication used for SAMs of alkanethiolates on gold are among the best available for preparing surfaces having the complex functionality required for studying biosurface interactions. The scale of structures prepared by μ CP and MIMIC are also that required for studying and using meso-scale phenomena with light (e.g., diffraction).⁵⁴ SAMs are very well suited for fundamental studies of the physical-organic chemistry of adhesion and friction.^{38,55}

More speculative technological uses of SAMs as electrically functional components of very small devices will require learning how to manipulate and use electrical conductivity on a molecular scale. The prospects for this type of application are very attractive: in a certain sense, a well-defined molecular redox center such as ferrocene/ferrocenium are a single-electron capacitor. The practical application of this idea will, however, require the development of the speculative field of molecular electronics, and will constitute a major undertaking.

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