

MOLECULAR SELF-ASSEMBLY AND MICROMACHINING

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ABSTRACT. We are developing molecular self-assembly as a strategy for the fabrication of nanostructures. We have used self-assembled monolayer films formed by the chemisorption of organic molecules onto gold substrates, in combination with micromachining, (i) to pattern gold surfaces with well-defined regions of SAMs with contrasting properties, (ii) to transfer these patterns to the underlying gold film using SAMs as nanometer-thick chemical resists for wet etching, (iii) to construct microelectrodes by taking advantage of the dielectric barrier properties of SAMs, and (iv) to create contamination-resistant films on the surfaces of metals that are otherwise highly susceptible to contamination by adventitious molecular adsorbates and particles.

1. Introduction

Molecular self-assembly is the spontaneous self-organization of molecules into equilibrium supramolecular structures (1-3). Although molecular self-assembly is ubiquitous in nature (for example, biological lipid membranes and crystallization), it is a new strategy in materials science for the fabrication of nanometer-scale structures. Using nature to provide the "existence theorem", we have designed and synthesized a range of organic molecules that spontaneously organize themselves into highly structured two-dimensional supramolecular arrays and we are currently developing applications of these new nanostructures.

Several characteristics of molecular self-assembly make it an attractive strategy for making nanostructures. First, molecular self-assembly is characterized by the spontaneous evolution to an equilibrium structure; intervention by the technologist, concurrent with the process of self-organization, is not necessary. Furthermore, because these structures exist at their thermodynamic minima, they are inherently self-repairing; a transient perturbation to the structure will be followed by a tendency to reorganize back to the equilibrium condition. Second, the process of molecular self-assembly can be remarkably free of errors; organization of as many as 10^{12} molecules can be routinely achieved with few defects in the resulting superstructures. Third, as demonstrated by the remarkably complex self-assembled structures found in nature, the use of clean room facilities is not a prerequisite for the self-assembly of molecules into structures with Angstrom-scale precision. Finally, when organic molecules are used, the properties of these molecules, and therefore, the functions of the

resulting supramolecular assemblies, can be manipulated using well-known techniques of organic and biological synthesis. Recognition of these characteristics of self-assembly has prompted us to explore molecular self-assembly as a strategy for nanofabrication, using self-assembled monolayers of organic molecules as a model system (4).

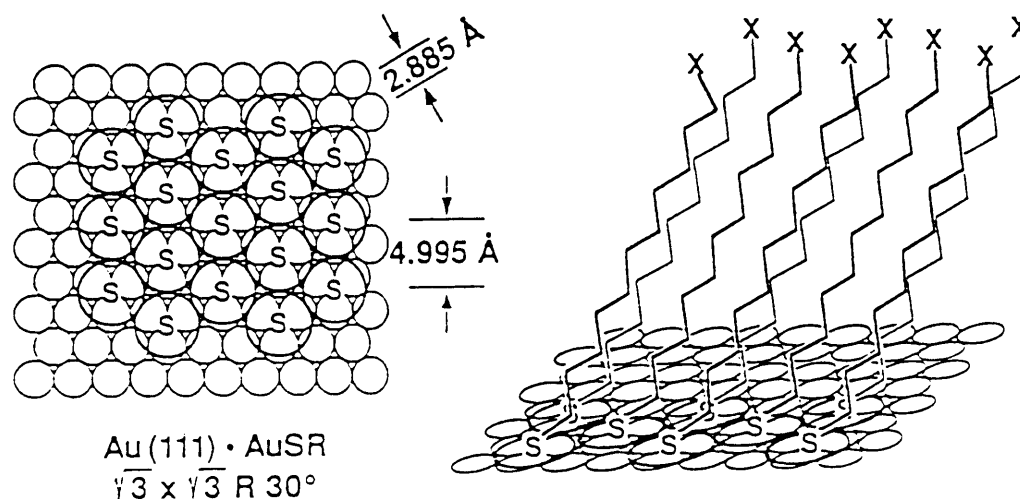


Figure 1. Schematic structure of a self-assembled monolayer formed by exposing a Au(111) surface to $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$.

Self-assembled monolayers (SAMs) are quasi-two-dimensional crystals formed by the chemisorption of organic molecules on the surfaces of metals (e.g. organic thiols on Au, Ag, Cu), metal oxides (e.g. alkane carboxylic acids onto Al_2O_3), and semiconductor oxides (e.g. organic trichlorosilanes on SiO_2) (4). Exposure of the solid substrate to the organic molecules, either in solution or in the vapor phase, results in the spontaneous ordering of the organic molecules at the solid-solution or solid-vapor interface (Figure 1). Because these monolayer films are highly ordered and because the terminal moieties (X in Figure 1) of the organic molecules can be varied using techniques in synthetic organic chemistry, these systems offer a remarkable level of control over the properties of interfaces. As a result, SAMs have served extensively as model systems for the study of interfacial phenomena (wetting, adhesion, reactivity) in organic systems.

The best characterized SAMs are probably the organic thiolates on gold substrates (4). Using this system we have explored four themes relevant to nanofabrication, including

the development of self-assembly as a technique to complement existing methods of microfabrication, as well as a future technique for making nanostructures that could potentially serve as memory and logic devices.

2. Applications

2.1. CONTAMINATION-RESISTANT SURFACES

How molecular self-assembly can complement the already existing technologies used for making electronic devices can be illustrated with the idea of developing surfaces that are resistant to contamination. Current processes for microfabrication demand stringent clean room environments to reduce contamination (by particulates and vapors) of high free energy surfaces of electronic materials such as bare metals and silicon. Because the rate of contamination of a surface depends on the free energy of its surface (materials with high free energy surfaces adsorb and stick to contaminants more quickly and tenaciously than do low free energy surfaces), and because it is well established that nanometer-thick organic films formed from SAMs can be used to create low-energy interfaces on high energy substrates (4), one promising application of molecular self-assembly is to passivate the exposed surfaces of materials during (and after) fabrication with appropriately chosen SAMs. For example, the surface free energy of bare gold, which is approximately 400 dynes/cm^2 , can be reduced to 20 dynes/cm by forming a SAM that exposes methyl groups at the surface. Using scanning electron microscopy (SEM) to image films formed from molecular adsorbates, we have demonstrated that SAMs can be used to reduce the degree of contamination of a surface from airborne and solution-borne contaminants (5). We have also observed that the electron beam-induced processes of contamination and desorption of carbonaceous films in the SEM can be influenced by the presence and type of SAM that is exposed to the electron beam (5). Self-assembled monolayers formed from fluorocarbons (nanometer-thick "Teflon" films) appear to be the most effective in reducing the contamination of surfaces. We expect that issues such as the control of surface contamination and "stickiness" will become increasingly important with the development of contact lithography.

2.2. MICROMACHINING AND MOLECULAR SELF-ASSEMBLY TO PATTERN SURFACES

We have been developing a range of methods that combine molecular self-assembly with micromachining (6), microwriting (7) and masking (8) to pattern surfaces with regions of SAMs with contrasting properties. The principle of region-specific deposition (or removal) of materials from a substrate broadly defines current microfabrication practices. Our approach, however, takes advantage of existing capabilities in organic chemistry to design and synthesize molecules with a variety of properties and to transfer these properties, using molecular self-assembly, to well-defined regions of a surface. We have combined molecular

self-assembly with micromachining, microwriting and masking to pattern surfaces with features (a region of a surface with a property that is distinguishable from its surroundings) that range in size from centimeters to 100 nanometers and which, in principle, could extend down to the scale of molecular dimensions (nanometers) using AFM and STM. The potential ability to control structure with nanometer-scale precision contrasts with optical lithography which is limited using far field optics (by diffraction effects) to linewidths greater than 0.3 to 0.5 μm .

We have developed a process of patterning a surface by combining micromachining and molecular self-assembly in three steps (Figure 2): (i) formation of an initial SAM of an organic thiolate on gold; (ii) generation of regions of bare gold in the SAM by micromachining; and (iii) formation of a second SAM on these micromachined regions (6). With simple micromachining techniques, using either a surgical scalpel blade or the end of a carbon fiber, we have patterned a surface with micrometer and submicrometer (100 nm) resolution, respectively. We have demonstrated the control of surface properties by using this new type of microfabrication to generate well-defined regions of SAMs with contrasting wettabilities on gold and silver substrates. The way in which liquids wet these surfaces can be used as a convenient technique to image the patterns generated on such surfaces (these systems also act as important models for studying the fundamental properties of wetting and adhesion at organic interfaces: Figure 3). Although we have demonstrated the patterning of surfaces with regions of contrasting wettabilities, we believe that this principle can be generalized, for example, using organic molecules that have contrasting electroactive properties, rather than contrasting wetting properties. Indeed, SAMs formed from molecules containing electroactive moieties (for example, ferrocene) have been prepared (9).

In these examples of micromachining, we have used simple techniques in order to demonstrate the result of combining micromachining and molecular self-assembly. More recently, we have begun extending our use of micromachining techniques to include atomic force microscopy (AFM) and scanning tunneling microscopy (STM). Using STM with high bias voltages (2-10 V) we have removed well-defined regions of a SAM formed from hexadecanethiol on a gold substrate (10). We believe that the combination of AFM/STM and molecular self-assembly can be used to make patterns in SAMs that are (much) smaller than 100 nm. The ultimate limit to the resolution of this technique will probably be determined by the lateral mobility of the chemical species on the surfaces.

2.3. DIELECTRIC BARRIERS

Dielectric barriers are essential components of electronic devices. We, and others, have shown (with cyclic voltammetry) that a SAM formed from hexadecanethiol on a gold substrate can reduce the rate of transport of electrons between the gold surface and contacting electrolyte (0.1M H_2SO_4) by a factor about 10,000. Although there are many unanswered questions

Figure 2. Schematic illustration of the formation of 0.1 to 1 μm scale lines with property Y (for example, Y = COOH for a hydrophilic surface) in a surface of X (for example, X = CH₃ for a hydrophobic surface) with micromachining and SAMs. Au = evaporated film of gold; Ti = evaporated film of Ti used to promote adhesion of the Au to the silicon wafer (Si).

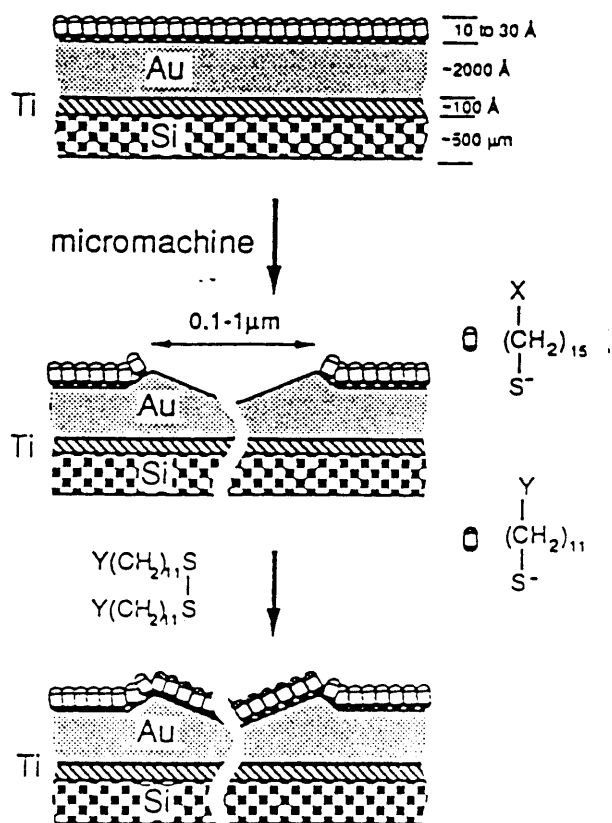


Figure 3. Drops of water on a hydrophilic SAM formed from HS(CH₂)₁₅COOH are pinned by micrometer-wide hydrophobic lines formed from [CH₂(CH₂)₁₁S]₂. The gold substrate was patterned with SAMs by combining micromachining and molecular self-assembly (see Figure 2).

surrounding the mechanism of electron transport across a surface covered with a SAM (e.g. pinhole defects, electron tunneling, thin spots), the ability of a SAM to serve as nanometer-thick dielectric barrier is a promising one. For example, the electrical function of metal oxides to act as barriers to electrons in tunneling junctions may also be achieved using SAMs. We have used the dielectric barrier properties of SAM to construct band microelectrodes, created by micromachining bare gold grooves in the surface of a gold substrate covered by a SAM. We have demonstrated microelectrode behavior (the absence of mass transport limitation during cyclic voltammetry) for an aqueous ferricyanide system (Figure 4). Because they have micrometer-widths, these microelectrodes are less prone to mass transport limitations than are macroscopic electrodes. The rapid response times of these electrodes and their ease of fabrication suggests that SAMs may serve as useful dielectric barriers for sensor systems.

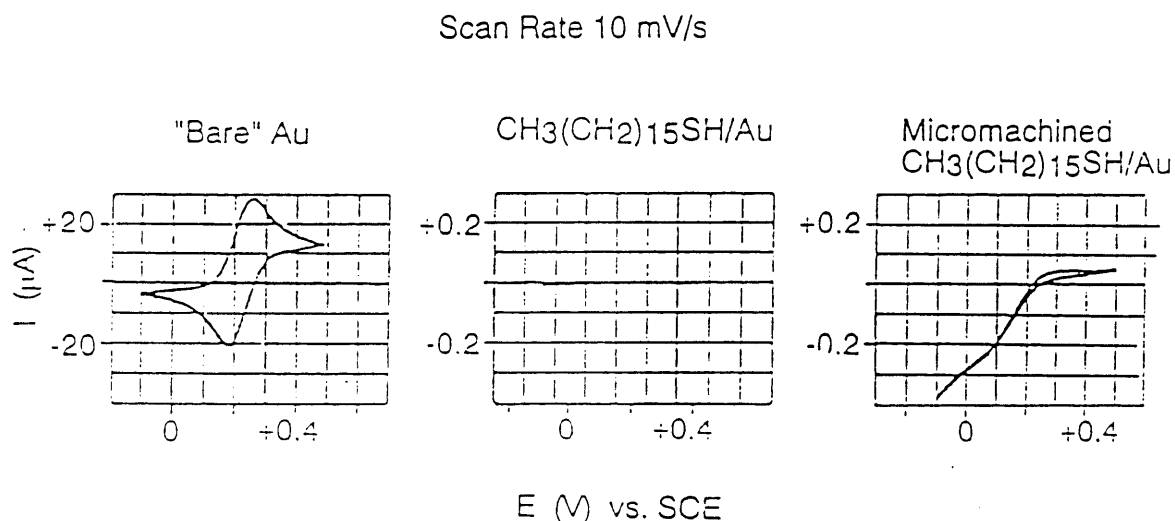


Figure 4. Rate of electron transfer to an aqueous solution of 1 mM $\text{Fe}(\text{CN})_6^{3-}$ (0.1M NaClO_4 , pH 7) using (a) a macroscopic bare gold surface, (b) a gold film covered by a SAM formed from $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, and (c) micrometer-wide band-shaped microelectrodes of bare gold formed by micromachining the surface from (b).

2.4. CHEMICAL RESISTS

SAMs can serve as nanometer-thick resists. In addition to being good dielectric barriers, SAMs can also be good barriers to certain ions in aqueous solution, including ionic species

that act as wet chemical etchants (11). We have demonstrated that SAMs formed from hexadecanethiol on a gold film (200 nm thick) can protect the gold film from an aqueous solution of alkaline potassium cyanide (a well known etchant of gold) for a sufficient time that unprotected gold areas can be etched to the silicon substrate (11). The ability of a SAM to act as a barrier to etchants of metals has allowed us to develop simple techniques to transfer patterns created in SAMs on a gold substrate into the underlying gold film. For example, using micromachining to expose a bare gold line in a SAM formed from hexadecanethiol and then immersing the entire sample in an etching solution of 0.1M KCN (in 1M KOH), we have created micrometer wide trenches in a gold film (Figure 4). With an alternative procedure, we have used neat liquid hexadecanethiol as an "ink" to write (using micropens) micrometer-wide lines of hexadecanethiol onto a gold film. By etching the entire film we have formed conducting microwires of gold from the regions protected by the SAM (Figure 4).

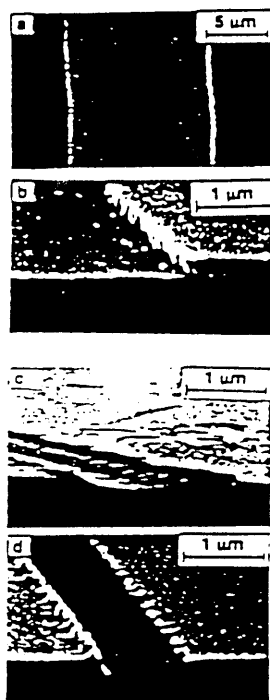


Figure 4. Scanning electron micrographs of a 10 μm gold wire (a and b) and a 1 μm trench (c and d) in a gold film. Both microstructures were made using a SAM of $\text{CH}_2(\text{CH}_2)_{15}\text{S}^-$ as a resist to an etching solution of 0.1M KCN and 1M KOH (see text and (11) for details).

3. Future Prospects and Conclusions

If molecular self-assembly is to serve as a useful strategy for nanofabrication, we believe that some of the important, and yet unanswered questions, are (i) what degree of perfection is required of a self-assembling technique?; (ii) how do we measure the degree of imperfection in a SAM?; and (iii) how far are we from what is required? To address these types of questions, we are developing assays for the detection of defects in SAMs. In one approach we use wet etching to detect the defects because etch pits (which can be observed by SEM) form at defects sites. The results of this assay indicate that (in a wet chemistry laboratory) we are able to produce SAMs on gold with fewer than 1 defect per mm^2 (or 1 defect per 10^{12} molecules)(12).

Many other interesting challenges will be faced before molecular self-assembly becomes a routine tool for nanofabrication. For example, our current forms of micromachining and microwriting are serial processes, and therefore, these techniques may be too slow for industrial processes. It is possible, however, that these techniques can be made to be parallel, for example, by stamping-type processes. Finally, we note that our recent demonstrations of forming SAMs on colloidal gold suggest exciting possibilities for nanofabrication (13). For example, colloids covered with SAMs (dielectric barriers) and assembled onto a patterned surface could form the basis of single electron transistors.

Molecular self-assembly as a principle for the fabrication of small-scale structures is a new strategy that is at the stage of "concept" rather than "development". Using SAMs as model systems, we are exploring the potential of molecular self-assembly to serve both as a supplement to existing technologies and, perhaps, further in the future, as the foundation of new types of electronics devices.

ACKNOWLEDGMENTS

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