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Pattern transfer: Self-assembled monolayers as ultrathin resists

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Abstract

This review includes three sections: (i) preparation, structure, and properties of self-assembled monolayers (SAMs); (ii) techniques for patterning SAMs, including microcontact printing (μCP), UV-photolithography, and e-beam writing; and (iii) use of patterned SAMs as ultrathin resists (2–3 nm thick) in processes for pattern transfer based on selective chemical etching and selective deposition. Microcontact printing is a non-lithographic technique for forming patterned features with dimensions ≥100 nm; the initial product of patterning is organized monolayers of alkanethiolates on Au, Ag, Cu and GaAs, and of alkylsiloxanes on Si/SiO_2 and glass. In this technique, an elastomeric stamp having a surface patterned with a relief structure is used to generate patterned SAMs on the surfaces of solid materials. These patterned SAMs are resists that protect the underlying substrates from dissolution in selective etchants (for example, for evaporated thin films of Au and Ag, aqueous solutions of $K_2S_2O_3$, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$). Patterned structures of gold or silver that are produced by the combination of μCP and selective etching can be used as the secondary masks for subsequent processes such as isotropic etching of SiO_2, isotropic or anisotropic etching of Si, anisotropic etching of GaAs, and reactive ion etching (RIE) of Si. Patterned SAMs can also be used as templates for selective deposition of metals by chemical vapor deposition (CVD), electroplating, or electroless deposition.

Keywords: Self-assembled monolayers (SAMs); Pattern transfer; Ultrathin resists

1. Introduction

Lithography at nanometer scales (<100 nm) requires resists thin enough that they give features with reasonable aspect ratios between the horizontal and vertical dimensions. Traditional photoresists have been used as very thin films [1]. More recently, self-assembled monolayers (SAMs) [2–4] have begun to be explored for applications in micro/nanofabrication [5,6].

Self-assembled monolayers are highly ordered molecular assemblies that form spontaneously by chemisorption of functionalized long-chain alkanes on the surfaces of appropriate solid materials (Fig. 1(a)); their structures are effectively 2-D organic crystals or quasicrystals [2]. Self-assembled monolayers have, in the past, been extensively studied as model systems for wetting, adhesion, lubrication, corrosion, protein adsorption, and cell attachment [2–4]. Well-established systems of

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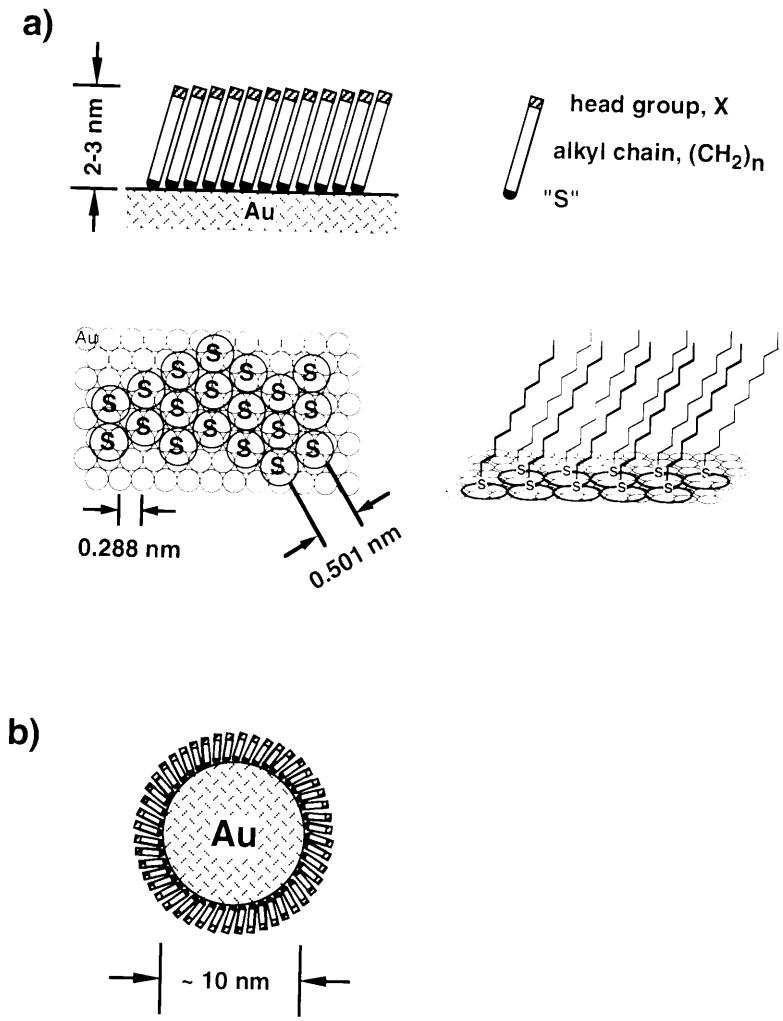

Fig. 1. (a) Representation of a highly-ordered monolayer of alkanethiolate, $(X(CH_2)_nS^-)$, on the surface of Au(111). The head group, X, allows the surface properties of the monolayer to be controlled; its thickness can be changed by changing the number, n, of methylene groups in the polymethylene chain. The alkyl chains are, on the average, tilted approximately 30° from the normal to the surface of Au. (b) Representation of a densely-packed SAM of alkanethiolate on the surface of a colloidal particle of gold with a diameter of ~10 nm.

SAMs include alkanethiolates on Au, Ag, and Cu [2–4]; and alkylsiloxanes on hydroxyl-terminated surfaces (for example, Si/SiO_2, Al/Al_2O_3, glass, mica, and plasma-treated polymers) [4,7]. Less-characterized systems of SAMs include: alkanethiolates on GaAs and InP [8,9]. Less-characterized systems of SAMs include: alkanethiolates on GaAs and InP [8,9]; alkanesulfinates on Au [10]; alkylphosphines on Au [11]; alkyl groups directly bound to Si [12]; alcohols, amines and isonitriles on Pt [4,13]; carboxylic and hydroxamic acids on Ag_2O or Al_2O_3 [4,14]; alkylphosphates on ZiO_2 [15,16]; and alkylphosphonic acids on ITO [17]. New systems are still being developed.

Self-assembled monolayers as ultrathin resists provide several potential advantages. (i) Self-assembly leads to equilibrium structures that are at, or close to, thermodynamic minimum. As a result,

self-assembling structures tend to be self-healing and defect-rejecting. (ii) The relatively low solid-vapor interfacial free energies of methyl- and fluoroalkyl-terminated SAMs allow them to be handled outside clean-room facilities without irreversible contamination. (iii) SAMs can be used as very thin passivating or insulating films for controlling adsorption of impurities on surfaces; they may be useful in fabricating capacitors and molecular electronic devices [18–20]. A typical SAM of hexadecanethiolate ($CH_3(CH_2)_{15}S^-$) on Au is ~2.5 nm thick, and the thickness of the SAM can be controlled to within 0.1 nm in most cases by controlling the number of carbon atoms in the alkyl chain (Fig. 1(a)). (iv) SAMs can act as ultrathin resists in lithographic processes. Because SAMs are so thin, some concerns (for example, depth of focus; optical transparency in UV and VUV regions, shadowing and undercutting) that currently influence the performance of photoresists in high-resolution imaging processes are not important in SAMs. The availability of nanometer thick resists also opens the door to new lithographic techniques. For example, in a process that has been suggested that uses metastable argon as the pattern-generating species, the thickness of the resist must be less than ~3 nm, since the damage in the resist by contact with the metastable atom is limited to a surface layer of $\leqslant$0.5 nm thick [21]. (v) Fabrications involving SAMs are relatively low-cost compared with conventional lithographic methods.

2. Preparation, structure, and stability of SAMs

SAMs are usually prepared by immersion of solid substrates in solutions containing species reactive toward the surface, or by exposure of the solid to vapors of reactive species [2–4]. For example, highly-ordered SAMs of hexadecanethiolate on gold can be prepared by immersing a gold substrate in a ~2 mM solution of hexadecanethiol in ethanol for several minutes. Ordered SAMs have also been formed on the surfaces of colloidal particles with diameters of $\geqslant$150 nm (Fig. 1(b)) [22,23]. The process of spontaneous formation of an ordered structure that occurs as adsorption and reaction of a thiol on gold is an example of molecular self-assembly [24].

The structure of SAMs has been characterized by transmission electron diffraction [25], polarized infrared external reflectance spectroscopy (PIERS) [3], low-angle X-ray scattering [26], low-energy helium diffraction [27], and scanning probe microscopy [28]. It is generally accepted that long-chain alkanethiolates have a $\sqrt{3} \times \sqrt{3}R30$ overlayer structure on the surface of Au(111) (Fig. 1(a)).

Different types of SAMs have different stabilities towards heating and chemicals. SAMs of alkanethiolates on Au become disordered and/or decompose at elevated temperatures (~100°C); oxidation of alkanethiolates to alkanesulfonates in the presence of UV light and ozone also reduces their stabilities [3,29,30]. In contrast, some SAMs of alkylsiloxanes on Si/SiO_2 are stable up to ~450°C [18].

3. Formation of patterned SAMs

Lateral control of SAMs has been achieved by a variety of patterning techniques. Classical techniques such as UV-photolithography [6,31–33] and e-beam writing [34–36] have been used for producing patterns in SAMs of alkanethiolates on Au, Ag and GaAs, and of alkylsiloxanes on Si/SiO_2; new techniques, such as microcontact printing (μCP) [37–40], atomlithography [21],

microwriting [41], micromachining (using an STM tip [42] or sharp stylus [43]) and micromolding in capillaries (MIMIC) [44] have also been developed for generating patterned SAMs. Patterned SAMs can be imaged and visualized using a number of techniques, such as SEM [38], AFM [45], SIMS and condensation figures (CFs) [46].

Among these techniques for generating patterned SAMs, microcontact printing is the one that seems to offer the most interesting combination of convenience and new capability (Fig. 2). Microcontact printing involves direct pattern formation by contact of an elastomeric stamp with a surface: this technique forms SAMs when used with appropriate reactants and surfaces [37–40]. It provides superior control over the surface chemistry. It is a parallel process – that is, it forms the

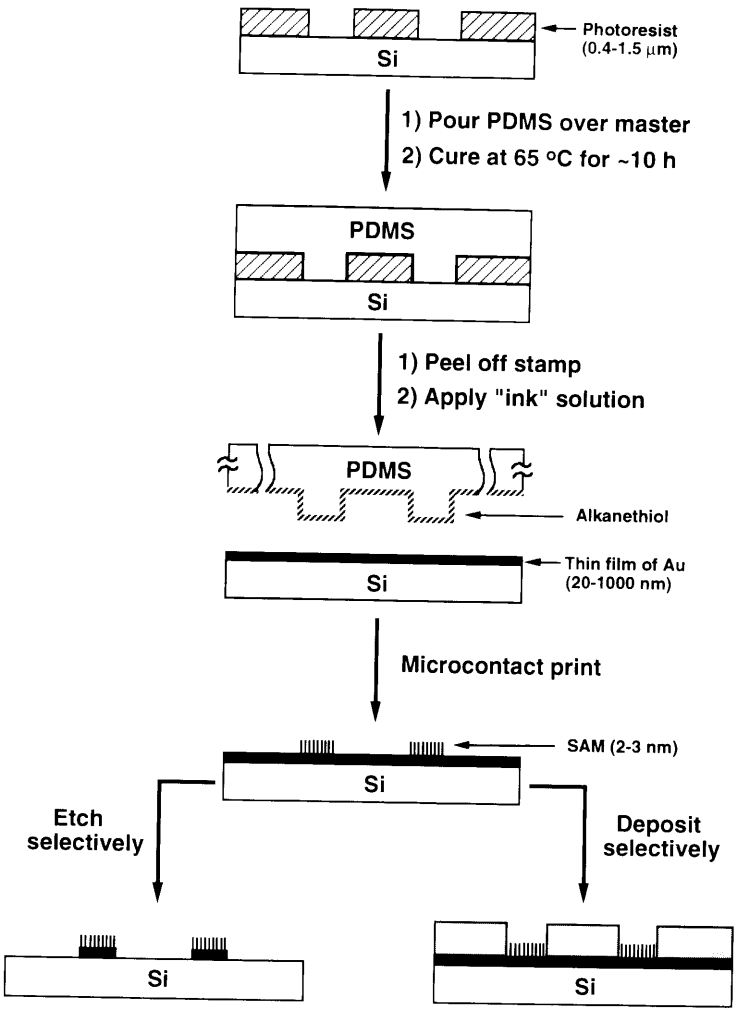

Fig. 2. Schematic procedure for carrying out μCP of alkanethiols on Au. An elastomeric stamp was fabricated by casting poly(dimethylsiloxane) (PDMS) against certain relief structure that was made by photolithography or micromachining. After applying hexadecanethiol solution in ethanol, the stamp was dried in a stream of N_2, and brought into contact with the surface of gold for 5–10 s. A patterned SAM of hexadecanethiolate was formed on the parts of the gold surface that were in contact with the stamp.

pattern over the entire area of the substrate in contact with the stamp at the same time – and thus is suitable for patterning of areas of several cm^2 on a single contact. At present, μCP has been used to pattern SAMs of alkanethiolates on Au [37–40], Ag [47], Cu [48] and GaAs [49] and of alkylsiloxanes on Si/SiO_2 and glass [50]. Features with dimensions larger than 0.3 μm can be routinely produced by μCP; smaller features (~100 nm) have also been fabricated with greater difficulty and lower reliability [51–53]. The lower limit for the resolution in this technique, the upper limit of the area that can be patterned on one contact, and the degree to which multiple impressions can be brought into registration, have yet to be established.

4. Pattern transfer from SAMs to the underlying substrates

Patterns in SAMs can be transferred to the underlying substrates either by selective etching or by selective deposition (for example, CVD, electroplating and electroless deposition).

4.1. Pattern transfer by selective etching

Table 1 summarizes selective etchants that have been studied for use with patterned SAMs generated by μCP. The most extensively studied systems are patterned SAMs of hexadecanethiolate on evaporated films of Au [37–40] and Ag [47]. Our original work focused on the system of hexadecanethiolate on Au, but hexadecanethiolate on Ag is also attractive. Etching protocols for silver are more convenient to use than those for gold – silver is chemically more reactive than gold, and thus silver dissolves more rapidly than gold in most etchants; the level of defects in SAMs on Ag seems to be lower than that on Au; silver is an excellent electrical and thermal conductor with useful properties [54]. Fig. 3(a) shows scanning electron micrographs (SEM) of a test pattern of silver (50 nm thick) that was fabricated by μCP with hexadecanethiol, followed by selective chemical etching [47]. The edge resolution of these silver features is ≤20 nm (Fig. 3(b)). The nanometer thick SAMs probably

Table 1
Selective etchants (all in H_2O) that have been used with patterned SAMs

Surface	SAM	Etchant (approximate pH)	Ref.
Au	RS	$K_2S_2O_3/K_3Fe(CN)_6/K_4Fe(CN)_6$ (14)	38, 60
		KCN/O_2 (14)	37–41
		$CS(NH_2)_2/H_2O_2$ (1)	60
Ag	RS	$Fe(NO_3)_3$ (7)	47
		$K_2S_2O_3/K_3Fe(CN)_6/K_4Fe(CN)_6$ (7)	47, 60
		$NH_4OH/K_3Fe(CN)_6/K_4Fe(CN)_6$ (12)	47
		NH_4OH/H_2O_2 (12)	47
		NH_4OH/O_2 (12)	47
		KCN/O_2 (14)	47
Cu	RS	$FeCl_3/HCl$ (1)	48
GaAs	RS	NH_4OH	34, 49
Si/SiO_2	$RSiO_{3/2}$[a]	NF/NH_4F (partially selective)	34, 50
glass	$RSiO_{3/2}$[a]	HF/NH_4F (partially selective)	50

[a] These SAMs are formed by contact of $RSiCl_3$ or $RSi(OCH_3)_3$ with the substrates.

protects the underlying substrates from dissolution by blocking the diffusional access of etchants. Fig. 3(c) is a cross-sectional SEM of silver microstructure (0.2 μm thick) that was generated by the combination of μCP and selective chemical etching. Large silver lines (~50 μm wide, ~0.2 μm thick, and separated by ~50 μm) on Si/SiO_2 produced by this method have the metallic conductivity expected for bulk metal (5.56×10^5 S/cm); and parallel lines of silver are electrically isolated from each other.

The ability to generate arrays of microstructures of coinage metals with controlled shapes and dimensions is directly useful in fabricating arrays of microelectrodes for sensors and other electrochemical devices. These patterned films of Au and Ag can also be used as the secondary masks for the etching of underlying layers of SiO_2 and Si [47,55] (Fig. 3(d)). The features shown in Fig. 3 were generated in the open laboratory, without access to clean room facilities. Because processes for formation of SAMs rely on molecular self-assembly, they resist defects and contamination. Microcontact printing can, in principle, be used for many micro/nanofabrication tasks in low-cost processes. The quality of the patterns produced are not yet compatible with that required for microfabrication of complex electronic devices, but the technology is still in an early stage of

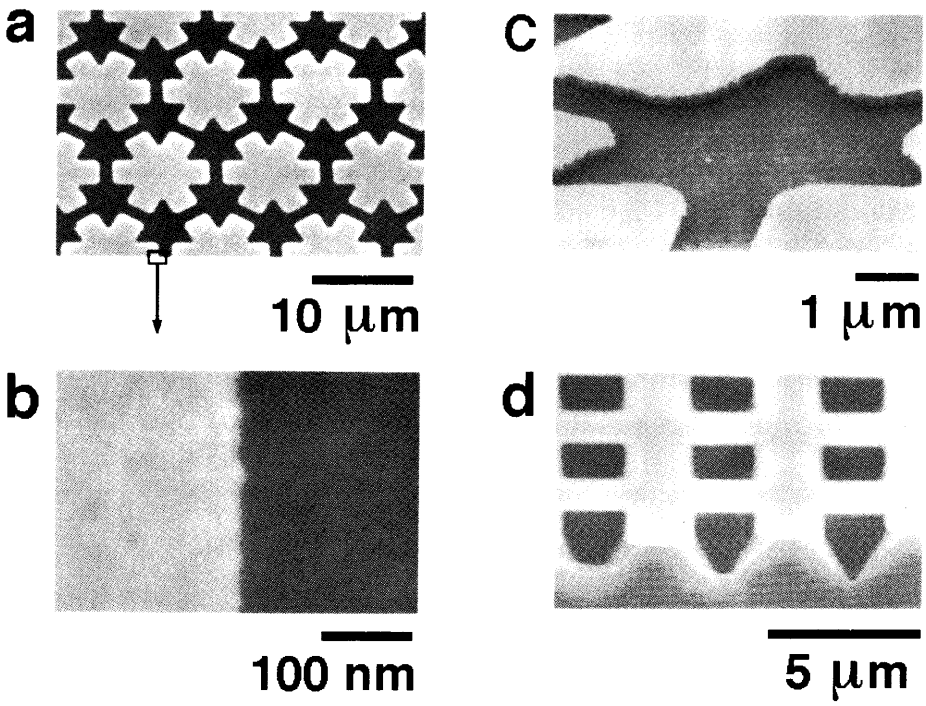

Fig. 3. (a, b) SEMs of a test pattern of Ag (50 nm thick) that was reduced by selective etching for ~15 s in an aqueous solution containing $K_2S_2O_3$ (0.1 M), $K_3Fe(CN)_6$ (0.01 M) and $K_4Fe(CN)_6$ (0.001 M), using a patterned SAM of hexadecanthiolate as the resist. The bright regions are silver, the dark regions are Si/SiO_2 where the underivatized silver has been removed by etching. (c) A cross-sectional SEM of a test pattern that was fabricated in Ag films (0.2 μm thick) using the combination of μCP and selective wet etching in the above etchant for ~45 s. (d) SEM of a silicon pattern that was formed by anisotropic etching of silicon in KOH/*i*-propanol at 65°C for ~10 min using a patterned silver film as mask. The silver mask that was formed by μCP and selective etching remained on the surface of the Si substrate.

development. It is directly applicable to many problems in fabricating sensors and optical devices, where the requirements for continuity, isolation, and uniformity in the final patterns are less serious.

A potential advantage of μCP over photolithography is that μCP can generate features with a range of different sizes using a single chrome-mask. PDMS is an elastomer, and conforms to the surface of the substrate during μCP. This characteristic of PDMS provides an opportunity to generate features with reduced sizes by physically manipulating the stamps. Fig. 4(b) shows an example in which a reduction of features from ~2 μm to ~0.2 μm was achieved simply by compressing the PDMS stamp while conducting μCP [51]. In a second example (Fig. 4(c)) manipulation of the chemistry of formation of the SAM provides another strategy for reduction in feature size: here a reduction from ~2 μm to ~0.1 μm was accomplished by using controlled reactive spreading of the hexadecanethiol on gold [52].

Photolithography cannot be easily applied to curved surfaces for a number of reasons. Because μCP

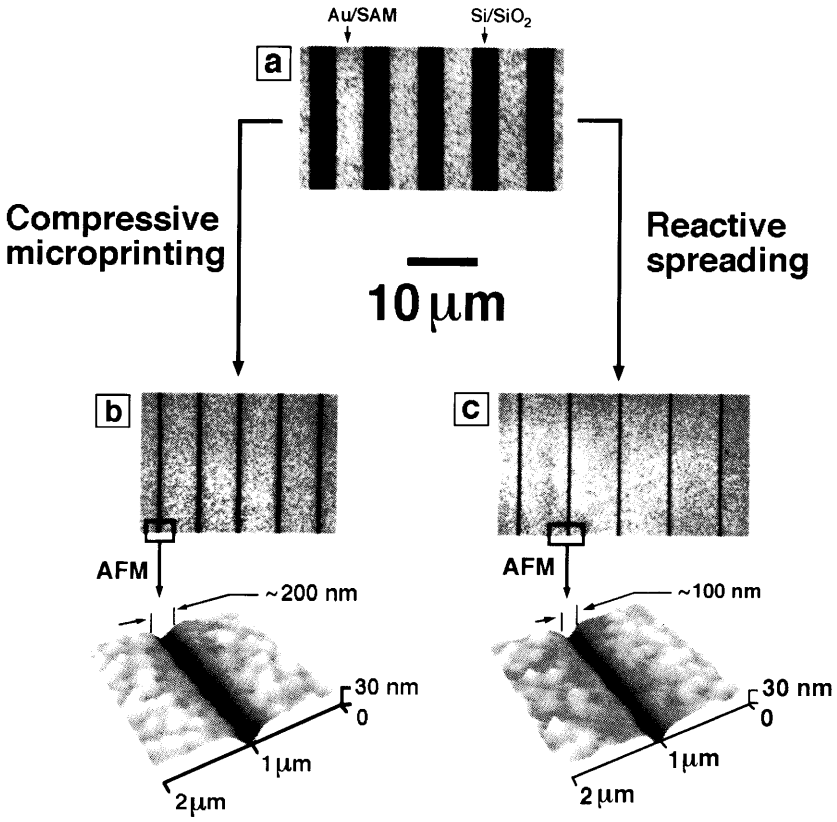

Fig. 4. (a) SEM of a test pattern of gold that was produced by the standard procedure of μCP and selective etching in oxygen-saturated cyanide solutions. (b) SEM of a test pattern of gold that was produced with the same PDMS stamp as in (a), but under mechanical compression. Size reduction from ~2 μm to ~0.2 μm was achieved in the one-dimensional compression. Two-dimensional compression was also possible. (c) SEM of a test pattern of gold that was produced with the same PDMS stamp as in (a), but printing was carried under water and the stamp was allowed to remain in contact with the gold surface for ~5 min. The reactive spreading of hexadecanthiols from the edges of the stamp caused a reduction in dimension for the bare regions from ~2 μm to ~0.1 μm.

involves conformal contact using an elastomer stamp, it can be used to print patterns on even sharply curved surfaces [56]. Fig. 5 shows SEM image of gold microstructures (Fig. 5(a)) and patterned SAMs (Fig. 5(c)) on curved surfaces. Microcontact printing generated patterns on planar and curved substrates with similar resolution (Figs. 5(b) and (c)).

4.2. Pattern transfer by selective deposition

In addition to selective etching, selective depositions of metals using CVD [57–59], electroplating [36], and electroless deposition [6,38] have also been accomplished with patterned SAMs as templates. Fig. 6(a) shows an SEM image of Cu lines that had been deposited on a Si/SiO_2 surface by CVD using (hexafluoroacetylacetonato)copper(I)(vinyltrimethylsilane) as the source gas; the pattern on the surface was defined and directed by a patterned SAM of octadecylsiloxane generated by μCP [58]. Figs. 6(b) and (c) show SEM micrographs of microstructures of copper that were produced by selective CVD; the top surfaces of the substrates had been derivatized by SAMs of octadecylsiloxane using contact printing. Copper deposited only in the recessed regions underivatized by SAMs. Procedures based on surface-selective CVD may be useful in microfabrication. For example, the

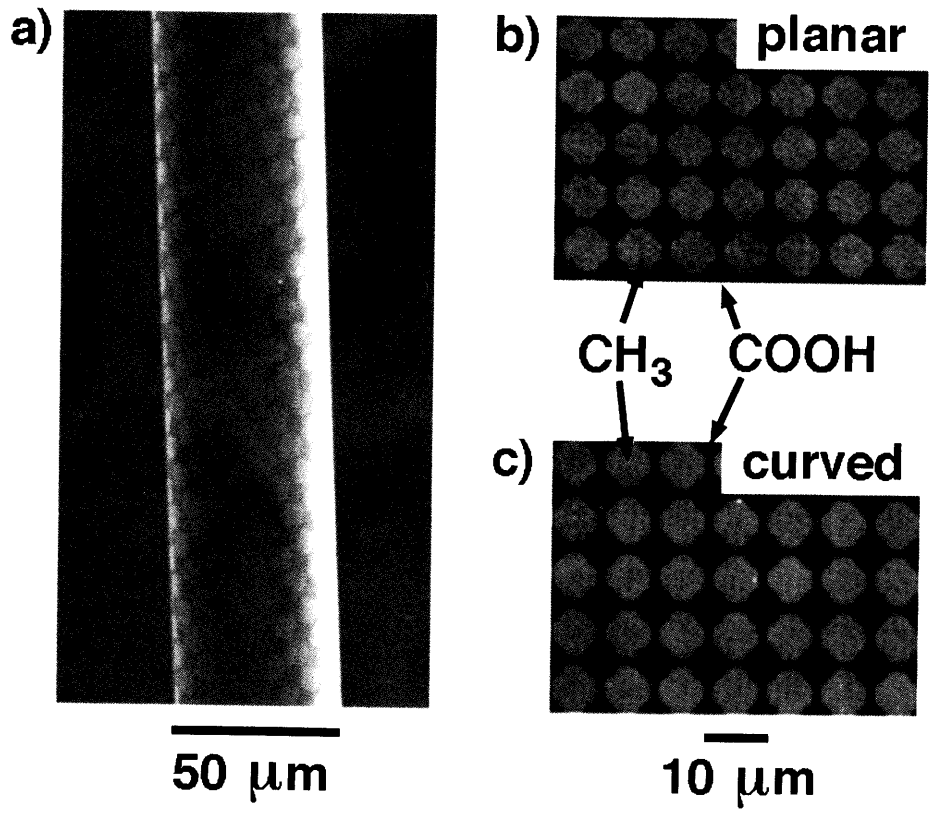

Fig. 5. (a) SEM image of a gold pattern on a curved surface. The pattern was formed on a gold-coated glass fiber by μCP with hexadecanethiol and selective etching of gold. (b, c) SEM images of patterned SAMs formed by μCP on a planar and a curved surfaces. Light regions are covered with CH_3-terminated thiolate ($CH_3(CH_2)_{15}S^-$); dark regions are derivatized with COOH-terminated thiolate ($HOOC(CH_2)_{15}S^-$).

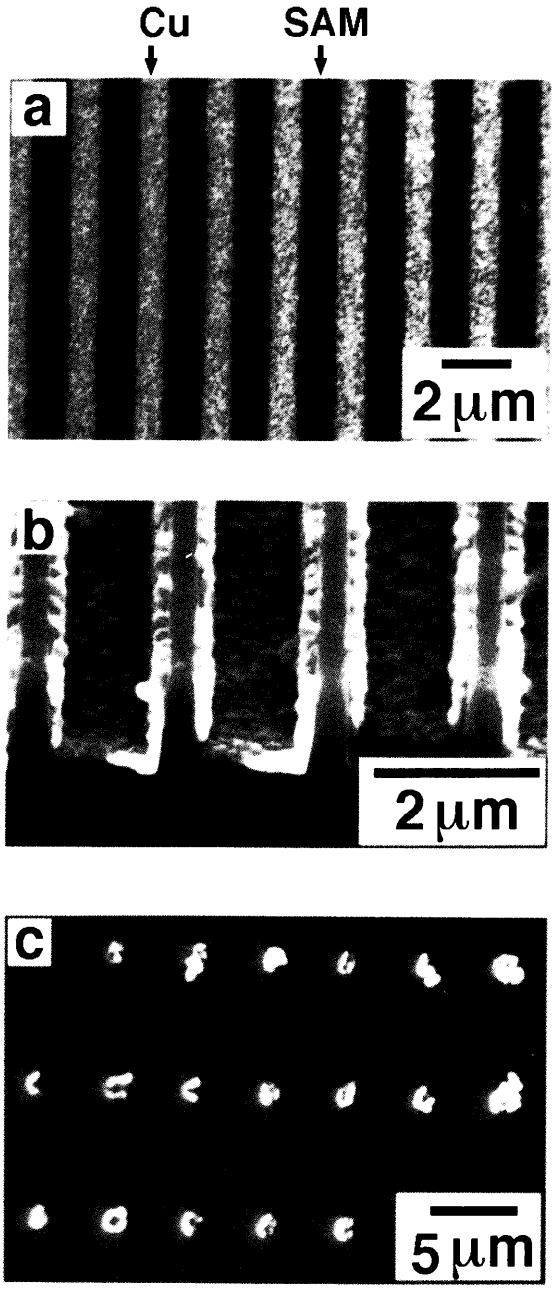

Fig. 6. (a) SEM image of copper lines produced by selective CVD on Si/SiO_2 surface that had been patterned with SAMs of octadecylsiloxane using μCP. (b, c) SEM images of copper microstructures that were fabricated on textured Si/SiO_2 surfaces; the top surface of the substrates were covered by SAMs of octadecysiloxane delivered by a flat PDMS stamp. The side walls of the ridges in (b) and the 0.7 μm drilled holes in (c) were free from the SAMs. Copper nucleated and deposited only on those regions that were not derivatized by the SAM.

topology of the substrates (especially that in (c)) is directly related to feed-throughs and related structures in many microelectronic devices.

5. Conclusions and future work

Self-assembled monolayers provide an effective and low-cost strategy for pattern transfer in micro- and nanofabrication. A variety of techniques have been developed for the formation of patterned SAMs. These patterned SAMs serve directly as nanometer-thick resists in protecting the underlying substrates from dissolution in wet etchant [37–40,47,60]. Several issues remain to be solved, however, before these patterning techniques based on SAMs find real applications in microelectronics. First, the smallest feature that can be produced by these patterning techniques has yet to be established. Currently, using SAMs as resists, the smallest feature that has been generated by UV-photolithography is ~0.4 μm [6], ~25 nm for e-beam writing [34], and ~100 nm for microcontact printing [52]. Second, the formation and distribution of defects in SAMs, especially under the conditions of chemical etching, must be understood. Using the combination of μCP with hexadecanethiol and selective wet etching, we have been able to generate patterned, defect-free, silver structures (50 nm thick) with an area of ~0.4 mm^2 [47,61]. Third, the compatibility of these patterning techniques with the production of microelectronic circuitry must be explored. The coinage metals (Au, Ag and Cu) that are widely used as substrates for the formation of SAMs of alkanethiolates cannot be used in the production of microelectronic devices based on silicon, because these atoms diffuse into the silicon and act as traps [62]. Systems that form SAMs directly on semiconductors still must be developed [12].

In more general terms, however, SAMs and patterning by μCP illustrate a new approach to microfabrication. SAMs are representative self-assembling systems, and demonstrate the attractiveness of self-assembly as a strategy for forming small, high-quality structures with remarkably little of the investment required by the more familiar clean-room technologies used in microfabrication. In particular, the fact that self-assembling systems are thermodynamic minimum structures, and therefore tend to reject defects, means that problems such as particulate contamination (with is a constant problem in photolithography and other line-of-sight techniques) will be less serious problems with SAMs (in which the SAM-forming component can spread spontaneously under the particle) than in photolithography (where particles cost shadows).

Microcontact printing illustrates the largely unexplored potential of non-photolithographic patterning techniques. This technique is capable, in a research setting, of generating 100–200 nm features; its limitations after serious development remain to be defined. The elastomeric character of the master provides both problems and opportunities in registration. The capability for large-area patterning by μCP is substantial, but still remains to be developed.

Acknowledgments

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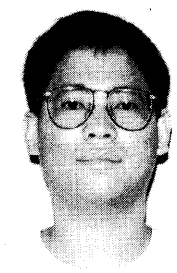

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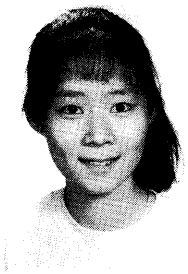

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