FEATURE ARTICLE

Soft lithographic methods for nano-fabrication

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Soft lithography is a low-cost, non-photolithographic strategy for carrying out micro- and nano-fabrication. This unconventional approach consists of techniques based on self-assembly and replica molding of organic molecules and polymeric materials. Four such techniques, microcontact printing (µCP), replica molding, micromolding in capillaries (MIMIC), and microtransfer molding (µTM), have been demonstrated for the fabrication of patterns and structures of a variety of materials with dimension ⩾ 30 nm. This review describes these techniques and their applications in fabrication and manufacturing at the sub-100 nm scale.

The demand for fabrication techniques that are capable of forming nanometre-sized structures rapidly and economically is a major driving force in the development of nanoscience and nanotechnology.[1] A wide range of techniques have been and are being developed for nano-fabrication: e.g., deep UV (λ = 200–290 nm) and extreme UV (λ < 200 nm) photolithography.[2,3] phase-shift photolithography,[4] electron-beam writing,[5] focused ion beam (FIB) lithography,[6] X-ray lithography,[7] scanning probe lithography,[8] and others.[9] Despite the extraordinary success of these technologies, new strategies are still desired for manufacturing nanostructures; a major hurdle to cross in the development of future technologies for nano-fabrication is the enormous expense (both capital expense and operating expense) of these technologies, and of the clean rooms and specialized reagents they usually require.

This paper discusses soft lithography, a collective name for techniques based on self-assembly and molding, as a convenient and low-cost approach to micro- and nano-fabrication (Table 1). Soft lithography uses soft, organic materials (e.g., functionalized alkanes and polymeric materials) to generate patterns and structures without the use of light or other high-energy particles. Its strengths and weaknesses are very different from other microlithographic techniques. Although it is at an very early stage of development, soft lithography has been shown to be a rapid and inexpensive way of forming and transferring patterns and structures (⩾ 30 nm in dimension) onto or into other materials. This review focuses primarily on the procedures for four soft lithographic techniques, microcontact printing (µCP), replica molding, micromolding in capillaries (MIMIC), and microtransfer molding (µTM), as well as their potential applications in the fabrication of patterns and structures having at least one dimension ⩽ 100 nm.

Self-assembled monolayers and microcontact printing

Self-assembled monolayers (SAMs) are highly ordered molecular assemblies that form spontaneously by the chemisorption of functionalized alkanes onto the surfaces of appropriate substrates.[16,17] The thickness of a SAM is usually 2–3 nm, and can be tuned with an accuracy of ca. 0.1 nm by varying the number of carbon atoms in the alkyl chain. The interfacial properties of a SAM-covered substrate can be easily modified by the incorporation of organic and inorganic functional groups into and or at the end of the alkyl chain. SAMs of long-chain alkanethiolates [in particular, hexadecanethiolate, $CH_3(CH_2)_{15}S^-$] on gold represent one of the most developed and best characterized systems. They have been used as model systems for studying the properties of SAMs, such as structures,[18–20] wettabilities,[21,22] and densities of defects.[23–25]

We[10,26–35] and others[36–43] have demonstrated and developed SAMs of long-chain alkanethiolates and alkylsiloxanes as ultrathin (2–3 nm) resists in lithography at the nanometre scale (⩽ 100 nm). The formation of patterned SAMs is the key to such applications. Table 2 lists techniques that have been demonstrated for the generation of patterned SAMs with feature sizes ⩽ 100 nm. Other lithographic techniques (for example, photochemical oxidation,[44,45] cross-linking,[46] and generation of reactive groups[47–50]) are generally less convenient than µCP and have not been used with sub-µm structures, although they may still find some applications.

Microcontact printing (µCP) is perhaps the most versatile and cost-effective method for the generation of patterned SAMs with lateral dimension ⩾ 100 nm. Fig. 1 shows the schematic procedure for µCP. It uses an elastomeric stamp (usually made from polydimethylsiloxane, PDMS) with a relief

Table 2 Techniques for patterning SAMs at sub-100 nm scales

technique	smallest feature size nm	ref.
microcontact printing	ca. 100	10, 26–29
micromachining	ca. 100	30–32
neutral atom lithography	ca. 70	33–35
electron-beam writing	ca. 5–6	36–38
STM writing	ca. 10	39–42

Table 1 Four soft lithographic techniques

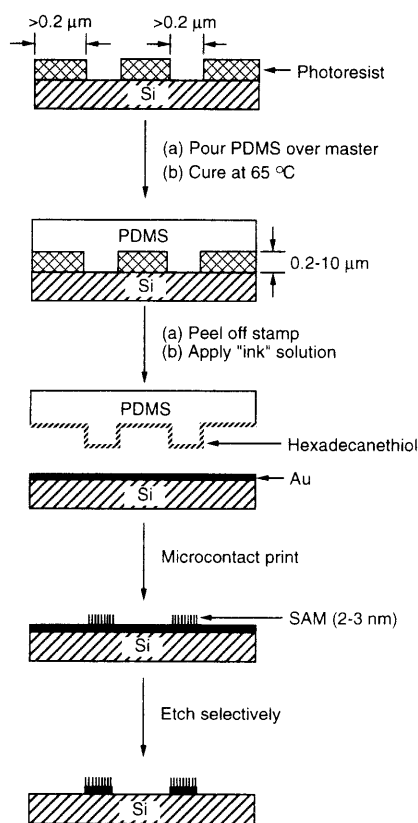| technique	smaller feature nm (lateral dimension)	largest patterned area (for this feature size)	ref.
microcontact printing (µCP)	ca. 100	ca. 50 cm² (ca. 0.5 µm)	10, 11
replica molding	ca. 30	ca. 1 cm² (ca. 0.2 µm)	12, 13
micromolding in capillaries (MIMIC)	ca. 1000	ca. 1 cm² (ca. 1 µm)	14
microtransfer molding (µTM)	ca. 700	ca. 2 cm² (ca. 1 µm)	15

Fig. 1 Schematic illustration of the procedure for μCP. An elastomeric stamp is made by casting a prepolymer of PDMS against a master that is usually made by microlithographic techniques. The stamp is inked with a solution of hexadecanethiol in ethanol, dried in a stream of N_2, and then brought into contact with the gold surface. The patterned SAMs can be used as resists in wet chemical etching to transfer patterns to the Au film.

Fig. 2 (A) Scanning electron micrograph (SEM) of an array of 2.5 μm wide lines of Au generated using the standard procedure of μCP, followed by chemical etching in a basic cyanide solution. (B) SEM of a gold pattern that was produced using μCP under water with the same PDMS stamp as in (A). The inked stamp was allowed to remain in contact with the gold surface for ca. 5 min.

structure on its surface to transfer alkanethiol molecules (the 'ink') to the surface of gold by contact.[51] It is experimentally simple and inherently parallel: it can form patterned sub-μm features over an area of ca. 50 cm² in a single impression within 30 s.[11] Microcontact printing has been used to form patterned SAMs of alkanethiolates on Au,[10,26–29] Ag,[52] Cu,[53,54] and GaAs;[55] and of alkylsiloxanes on Si/SiO₂, glass and plasma-treated polymer films.[56–60] These processes are best understood for Au and Ag substrates, where the quality of SAMs is higher relative to those on the other substrates. SAMs of long-chain alkanethiolates [$CH_3(CH_2)_nS^-$, $n \geqslant 12$] with hydrophobic terminal groups can effectively protect the underlying substrates from dissolution in certain types of aqueous etchants.[61–63] The patterns in printed SAMs can, therefore, be transferred into the underlying layers (e.g., Au, Ag and Cu) by selective chemical etching. The patterned structures of metals obtained this way can be further used as secondary masks for the etching of underlying substrates of SiO₂, Si, or GaAs.

Patterns of SAMs with dimensions >200 nm are routinely generated using μCP. Smaller features (ca. 100 nm in dimension) can also be generated using μCP by modifying the stamp and/or the printing procedure.[10,26–29] For example, mechanical compression of the stamp,[28] controlled reactive spreading of hexadecanethiol under water,[10] and casting stamps from blazed diffraction gratings[29] or masters prepared by anisotropic etching of Si(100)[27] have been used to successfully fabricate features with dimensions in the range of ca. 100 nm. Fig. 2 shows an example in which a reduction in feature size from ca. 2.5 μm to ca. 100 nm was accomplished by carrying out μCP under water, leaving the stamp in contact with the gold surface for ca. 5 min. The reduction in dimension for the underivatized regions was caused by the reactive spreading of the hexa-
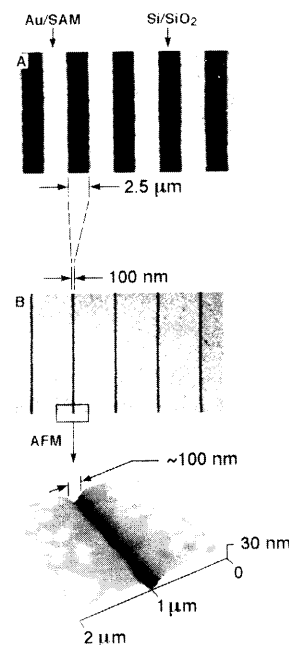
decanethiol from the edges of the pattern on the surface of the stamp. The resulting 100 nm wide lines were transferred into the thin film of gold by selective etching in an oxygen-saturated cyanide solution.

Microcontact printing followed by selective chemical etching is capable of generating arrays of micro- and nano-structures of a variety of materials with controlled shapes and dimensions. This capability has direct applications in the fabrication of custom-designed structures for studies of cell attachment,[64–66] sensors,[67] and other electrochemical and optical devices,[68–70] as well as in the fundamental studies of tribology such as wetting and adhesion.[71–74] The quality of the final products, however, has not yet met the requirements for the fabrication of microelectronic devices for several reasons. First, the best SAMs are formed on Au and Ag, and these metals are not acceptable as masks in the manufacturing of microelectronic devices. Second, even high-quality SAMs have a relatively high density (5 pits mm⁻²) of defects.[23] Third, the technology needed to register patterns in multilevel fabrication has not yet been developed. Nevertheless, the microlithographic techniques based on μCP have attracted broad attention, and their development is proceeding rapidly. We believe μCP will become an alternative method to conventional techniques for micro- and nano-fabrication in the future.

Replica molding and related techniques for nano-fabrication

Photolithography,[75] replica molding,[76–78] embossing (or imprinting),[79] and related techniques[80–82] have been demonstrated for the fabrication of micropatterns and microstructures of polymeric materials. Deep UV photolithography, electron-beam writing and X-ray lithography are the techniques commonly used in producing nano-structures (≤100 nm in dimension) with reasonably high wafer throughput. Cost of ownership issues and the requirements for fabrication space, however, have so far limited their applications, research and development.

Molding and embossing have been applied in generating

polymeric structures with feature sizes ≥ 100 nm. Functional microstructures such as diffraction gratings,[??,??] compact discs (CDs),[??,??] and microtools[??] are routinely manufactured at the mass-production scale. Fabrication in the nanometre scale using these techniques has begun to attract attention. In particular, we have introduced a range of techniques: replica molding against an elastomeric master,[??] micromolding in capillaries (MIMIC),[14,??,??] and microtransfer molding (μTM),[15,88] for forming micro- and nano-structures of polymers and sol gel materials, and Chou et al.[89,90] have demonstrated excellent results with embossing. Replica molding, MIMIC, and μTM were initially developed to make microstructures of polymers with controlled shapes on planar and or contoured surfaces; they are now being extended to the fabrication and manufacturing of nano-structures.[12]

Replica molding

The form of replica molding which we have developed differs from the conventional molding techniques in the use of an elastomeric PDMS mold. Fig. 3 illustrates the general procedure we used in the replication.[12,13] The use of an elastomeric (rather than rigid) mold simplifies the separation between the replica and the mold, and greatly reduces the possible damage to the mold and the fragile structures on the surface of the replica.

Fig. 4A and B show AFM images of a master having an array of ca. 60 nm wide and ca. 50 nm high lines, and one of its replicas of polyurethane (PU). It is evident that replica molding against an elastomeric mold faithfully replicates the original master having delicate features. We have also monitored the changes in quality of the nano-structures on the original master and the PU replicas vs. the number of replications conducted. No observable reduction in quality was found either on the original Au master or on the replicas after

making multiple (≥ 30) copies. This result demonstrates that replica molding against an elastomeric mold is capable of providing multiple copies of nano-structures from a single master; that is, it is capable of manufacturing nano-structures.

Replica molding against an elastomeric mold is an extended form of the conventional technique based on rigid molds. The use of elastomeric molds allows the sizes and shapes of the features on the final replicas to be controlled by using mechanical compression, bending, stretching, or a combination of these techniques and, thus, adds flexibility to the replica molding technique. Replica molding against a deformed elastomeric mold provides a unique new route to fabricate complex micro- and nano-structures with shapes, sizes, and periodicities that are significantly different from those on the original master. Fig. 4D gives a representative AFM image of an array of 30 nm wide lines fabricated by replica molding against a bent PDMS mold. Comparison of the nano-features on the replica (ca. 30 nm wide) to those on the original Au master (Fig. 4C) establishes that the dimensions of certain features on

A. Master

52 nm
5 μm
5 μm
2.5 μm
2.5 μm
0 → ||← 60 nm

B. Replica

49 nm
5 μm
5 μm
2.5 μm
2.5 μm
0 → ||← 60 nm

C. Master

26 nm
5 μm
5 μm
2.5 μm
2.5 μm
0 → ||← 50 nm

D. Replica

18 nm
5 μm
5 μm
2.5 μm
2.5 μm
0 → ||← 30 nm

~50 nm
SiO$_2$, Si$_3$N$_4$, metals or photoresists
Si

Pour PDMS prepolymer

PDMS
Si

Cure, peel off PDMS

~50 nm
PDMS

A   B

Mold PU   Bend PDMS, Mold PU

PU   PU
PDMS   PDMS

Cure PU, peel off   Cure PU, peel off

PU   PU
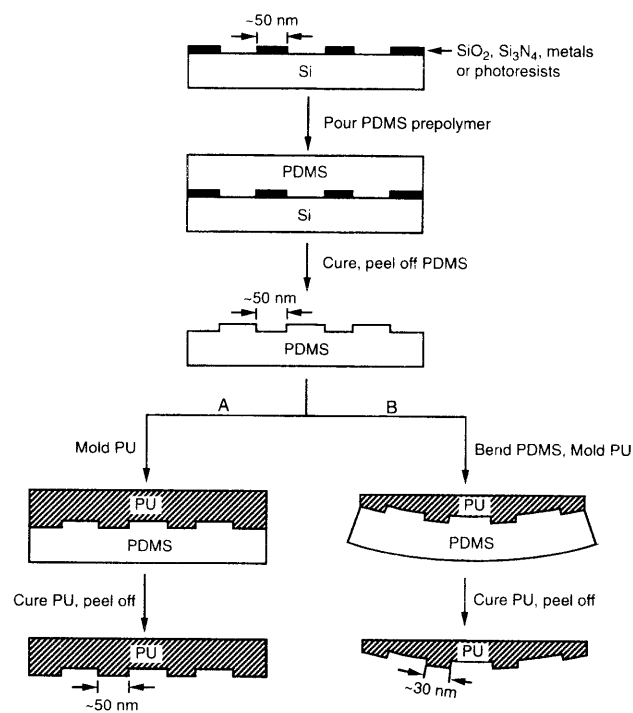~50 nm   ~30 nm

Fig. 3 Schematic procedure for carrying out replica molding against an elastomeric PDMS mold. The PDMS mold is fabricated by casting against nanometre-sized relief structures fabricated using X-ray lithography or electron-beam writing. The test pattern shown here is an array of ca. 50 nm lines. Replica molding can also be conducted while the PDMS mold is deformed, for example, by mechanical bending (B). The dimensions of the lines were reduced from ca. 50 nm to ca. 30 nm in this process while the spacings between the lines increased slightly.
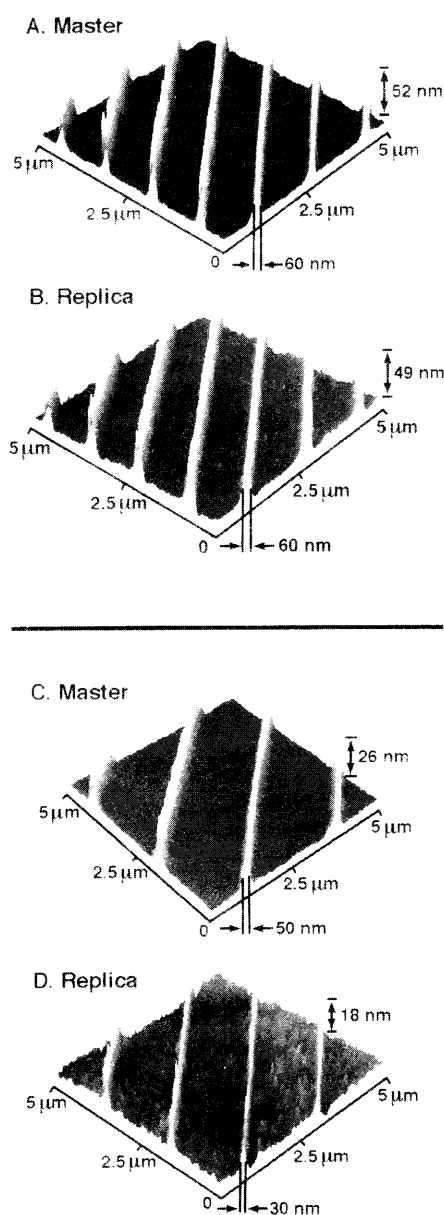
Fig. 4 (A, B) AFM images of a master with an array of 60 nm wide lines of Au on Si/SiO$_2$ and a PU replica generated from the PDMS mold cast from this Au master; (C, D) AFM images of another Au master having an array of 50 nm wide lines and a PU replica generated from a bent PDMS mold cast from this Au master

the master have been reduced significantly from *ca.* 50 nm to *ca.* 30 nm by casting against a mold deformed by mechanical bending. We have also demonstrated that replica molding against a PDMS mold is capable of generating microstructures on curved surfaces,[13] and producing functional microdevices with changing periodicities (*e.g.*, chirped diffraction gratings).[13]

Micromolding in capillaries and microtransfer molding

We recently developed a new technique, micromolding in capillaries (MIMIC), for the fabrication of microstructures of polymers and other materials (Fig. 5).[14,86–88] The PDMS master used in MIMIC is cast from an original master (for example, a photoresist master made using photolithography). Fig. 6 shows a test pattern having regions which are < 100 nm high but *ca.* 2 μm wide.[14] We have not applied MIMIC to smaller structures. Although it should, in principle, be applicable to such structures, in practice, the very slow filling of very small capillaries may limit its usefulness.

Microtransfer molding (μTM) offers a procedure, for replicating microstructures from an elastomeric mold, that is more rapid than MIMIC, and applicable to larger areas; it has been applied successfully to both planar and contoured surfaces
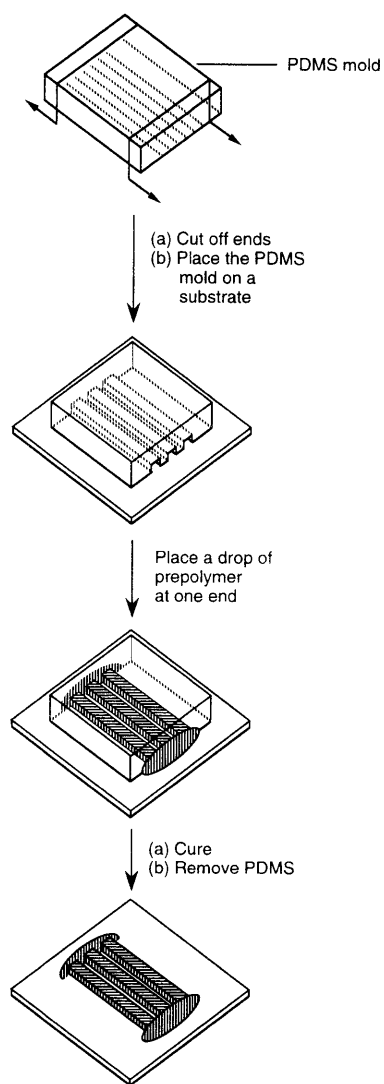

PDMS mold

(a) Cut off ends
(b) Place the PDMS
    mold on a
    substrate

Place a drop of
prepolymer
at one end

(a) Cure
(b) Remove PDMS

Fig. 5 Schematic procedure for MIMIC. This technique relies on a conformal contact formed between a support and an elastomeric (PDMS) mold with relief features on its surface to create a network of microchannels. A low-viscosity, liquid prepolymer fills these channels by capillary action. Solidification of the precursor *in situ*, followed by removal of the PDMS mold, results in the formation of polymeric structures on the surface of the support.

(Fig. 7).[15] It is also capable of generating isolated structures. Fig. 8 shows an array of submicron-wide pyramids having *ca.* 100 nm size tips made using μTM. A disadvantage of μTM is that the features that are formed usually rest on a continuous, thin (≤ 100 nm) film of the polymer.

Micromolding in capillaries and microtransfer molding are the two new techniques capable of generating microstructures of polymers, inorganic salts, and sol–gel materials on substrates of completely different materials. Fabrication of free-standing polymeric webs (using MIMIC),[86] multilayer structures (using μTM),[15] and functional devices (*e.g.*, polymeric waveguides,[15,91] waveguide couplers,[92,93] and interdigitated carbon capacitors and suspended carbon micro-resonators[94,95]) have also been demonstrated. MIMIC and μTM attract attention because of their abilities to fabricate complex topologies and structures with a broad range of materials and to accept non-planar surfaces as substrates. Until now, MIMIC and μTM have primarily been applied to the fabrication of features at micrometre scales. Their utility in forming nano-structures has begun to be explored with promising initial results (Fig. 6 and 8).

Conclusions and future work

Nano-structures (≤ 100 nm in dimension) are an important set of targets in materials science. In the past, they have been fabricated mainly using electron-beam and ion-beam writing; deep UV, X-ray, and scanning probe lithographies. Although these technologies are very capable of generating a broad range of structures, they have a number of disadvantages that may limit their applications in manufacturing: for example, they are restricted in the types of materials that can be used as resists; they are not easily applicable to curved surfaces; and most importantly, they require high capital and operating costs.

Soft lithography, in contrast, represents a class of largely unexplored, non-photolithographic techniques that offer a cost-effective strategy for fabricating and manufacturing nano-
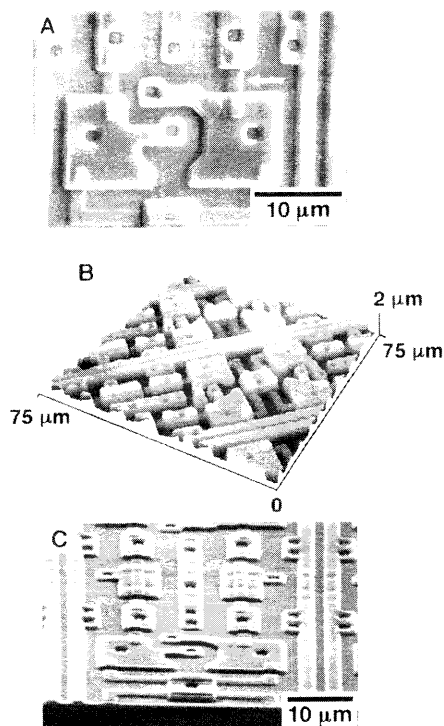

A

10 μm

B

2 μm
75 μm

75 μm

0

C

10 μm

Fig. 6 SEM (A) and AFM (B) images of patterned microstructures of PU on a Si/SiO₂ surface generated using MIMIC. The arrow in (A) indicates a line that is < 100 nm in height. (C) A cross-sectional SEM image of the fractured sample.
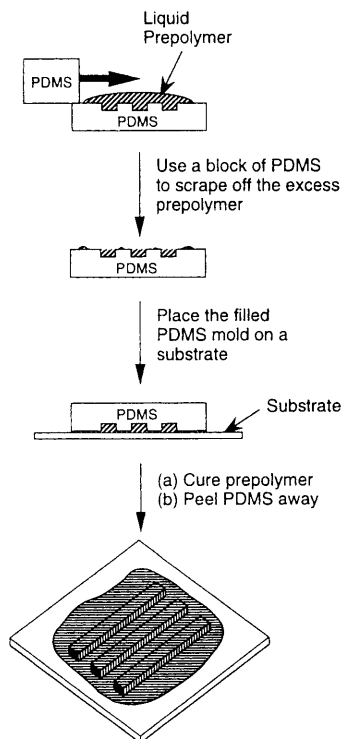
Fig. 7 Schematic diagram for μTM. A drop of prepolymer is applied on the patterned surface of a PDMS mold. The excess prepolymer is scraped away using a piece of flat PDMS, leaving a filled PDMS mold. The filled mold is then brought into contact with a substrate and the prepolymer is allowed to solidify *in situ*. Patterned microstructures are obtained after the PDMS mold is removed. The process can be repeated on a substrate whose surface has already been patterned with a layer (or layers) of relief structures to build multilayer structures layer by layer.
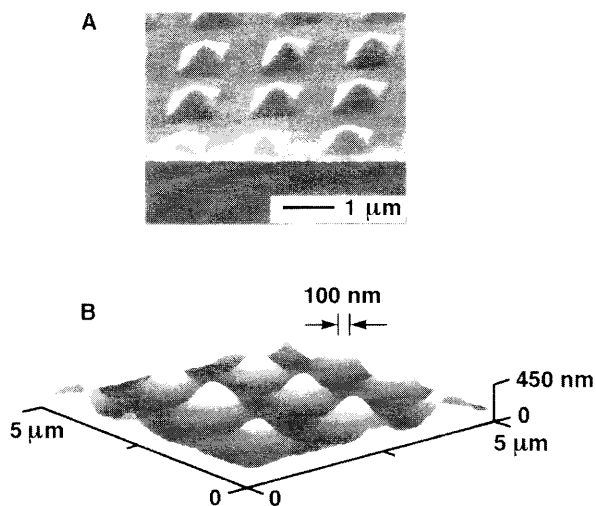

Fig. 8 SEM (A) and AFM (B) images of an array of sub-μm pyramids of PU. The tip of each pyramid, as shown in (B), is *ca*. 100 nm across. The original master was fabricated using anisotropic etching of a Si(100) substrate.

structures of metals, semiconductors and insulating materials. A number of techniques, *e.g.*, μCP, replica molding, MIMIC, and μTM, have been successfully demonstrated at the level of prototypes. As a class, they take advantage of structures and processes that use self-assembly (for example, SAMs and capillary filling). Self-assembled structures are at, or close to, thermodynamic equilibrium; they are, as a result, self-healing and defect-rejecting.[96] They should, therefore, be the basis for robust processes that are relatively insensitive to environmental

conditions, and we have, in fact, been able to generate patterned features ≥ 30 nm using a number of soft lithographic techniques, in a chemical laboratory, without using clean room facilities. Several issues remain to be solved before soft lithographic techniques find applications in the fabrication of complex, functional nano-structures. For example, the densities of defects[23] in the structures formed by chemical etching using printed SAMs as resists are still too high to be used for the fabrication of microelectronic devices. A lack of tools for registration with nanometre accuracy limits its use in multilayer fabrication. Replica molding, MIMIC, and μTM may suffer from artifacts due to deformation of the molds.[97] The levels of defects in these structures (and in structures produced using techniques such as embossing) have only begun to be characterized.

All these techniques for soft lithography are still in their early stages of development. Their opportunities and limitations in nano-fabrication and nanomanufacturing are still being defined. It is clear, however, that they offer exceptional convenience and economy in making certain kinds of structures, and the most probable strategy for their use will be to produce copies of master structures prepared by conventional but more expensive techniques (for example, X-ray lithography and electron-beam writing). The applicability of soft lithography to more complex structures will be defined as it is developed further.

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