FLUIDIC MICROASSEMBLY USING PATTERNED SELF-ASSEMBLED MONOLAYERS AND SHAPE MATCHING

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ABSTRACT

We have demonstrated a fluidic technique for the self-assembly of microfabricated silicon parts onto silicon and quartz substrates using patterned shapes of hydrophobic self-assembled monolayers (SAMs). Shape recognition is achieved by the minimization of interfacial free energy, and binding is due to the large adhesion energy between hydrophobic surfaces in water. Test parts were fabricated using deep reactive ion etching of silicon-on-insulator wafers with 15 μm silicon thickness. In order to pattern the block and substrate surfaces with hydrophobic and hydrophilic regions, gold films were evaporated onto the surfaces and patterned into the desired shapes. Then, the surfaces were exposed to an octadecanethiol SAM solution which forms a hydrophobic monolayer on gold but leaves the silicon (or quartz) areas water-wetting. Using a thin layer of lubricant on the binding sites, we have observed spontaneous alignment of test blocks to patterned hydrophobic regions on a substrate under water. Part-substrate shape matching has been demonstrated for square, rectangular, and complementary spiral shapes. Sub-micron alignment precision was achieved, as measured by comparing vernier scales located on the test blocks and substrate. Bonding to the quartz substrate was accomplished by using a UV-polymerizable liquid as the lubricant layer. The general approach described here may be applied easily to a variety of part and substrate material combinations, and thus can enable the assembly of complex hybrid systems.

INTRODUCTION

The current "microengineering tool kit" is capable of producing a great range of sensor and actuator devices [1]. This set of fabrication methods consists mainly of bulk and surface silicon micromachining, laser micro-machining, and LIGA. In the next generation of MEMS, micromechanical sensors and actuators will be integrated with electronic and optical components to give powerful and complex microsystems [2]. At present, however, this remains a significant challenge since the fabrication sequences and material requirements of the different components are often incompatible. The development of efficient wafer-scale assembly techniques can be used to overcome this hurdle and combine a diversity of materials on a single chip.

In order to be successful, a microassembly technique must be able to position a large number of components simultaneously with microscale precision. Once the parts are assembled, reliable mechanical bonds and electrical connections to the substrate may be furnished. Parallel microassembly techniques which fulfill these criteria fall into two categories—wafer-to-wafer transfer and self-assembly [2]. In the first route, microstructure transfer occurs between aligned wafers. The placement of structures is predetermined by the layout on the donor wafer, as in the work by Singh *et al.*, which employs compression bonding and cold welding between metal contacts [3]. Alternately, Holmes and Saidam have used laser-assisted release to position individual components on a target wafer in a different layout than on the donor grid by exposing the donor through a mask and moving both wafers accordingly [1].

In the self-assembly approach, a solution of microcomponents flows over a target wafer patterned with binding sites, resulting in part-substrate attachment. This technique can easily give different donor and target substrate layouts, thus reducing materials costs. In addition, since the parts may be fabricated and tested separately, this approach can reduce the yield losses associated with monolithic processes [2]. In the work of Smith and coworkers, for example, trapezoidally shaped microcomponents made of GaAs fill similarly shaped holes in a silicon substrate in a fluidic process [4]. Their process is based on the three-dimensional shape complementarity of the microcomponents and the receptor holes, and relies on gravitational forces. In a dry approach, Böhringer *et al.* have conducted feasibility experiments on the use of electrostatic traps for self-assembly in vacuum, with ultrasonic agitation to overcome friction and adhesion [2].

In this paper, we describe a fluidic self-assembly technique driven by surface interactions between matching thin-film shapes patterned on the components and the substrate, as shown in Fig. 1. Since this assembly method does not require bulk machining of the substrate or place shape constraints on the microcomponents, it is easily applicable to diverse systems of parts and substrates.

The biomimetic technique described here is driven by the minimization of interfacial free energies to achieve shape recognition; binding results from the large adhesion energy between hydrophobic surfaces in water [5]. Whitesides and coworkers first used these concepts to self-assemble millimeter-sized plastic components into three-dimensional aggregates in water [6,7]. This paper extends their work into the field of microscopic part-to-substrate assembly. Here, the surfaces of silicon microparts and

silicon and quartz substrates are patterned with hydrophobic and hydrophilic regions. Differentiation is accomplished by patterning evaporated gold shapes on the surfaces and depositing self-assembled monolayers (SAMs) on them using alkanethiol precursor molecules. This approach renders the gold regions hydrophobic while leaving the silicon or quartz areas water-wetting. Other strategies for patterning SAMs such as UV lithography [8] and microcontact printing [9] are also available in the literature.

The assembly technique described here can give sub-micron alignment precision since the positioning depends on the resolution of the patterned SAM shapes. Also, this approach may be applied to a variety of part and substrate materials, including semiconductors, metals, glass and plastics.

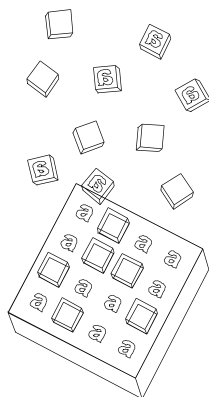


Figure 1. Self-assembly of microscopic parts to a substrate in water using patterned SAMs and shape matching.

EXPERIMENTAL

Fabrication. The silicon test blocks with gold patterns on one side are fabricated from silicon-on-insulator wafers with a Si (100) layer thickness of 15 μm (Bondtronix). The block shapes are defined using deep reactive ion etching in a Surface Technology Systems silicon etcher with photoresist as the masking layer. After photoresist removal, thin gold films (5-15 nm) with chrome as an adhesion layer (2 nm) are evaporated onto the wafers. SJR 5700 photoresist (Shipley) is used in the gold/chrome patterning step to ensure uniform coverage over the 15 μm-high features. The etching of the gold and chrome films is done using Gold Etchant Type TFA (Transene Company) and Cr-7 Chromium Photomask Etchant (Cyantek Corporation), respectively.

The alignment precision afforded by this assembly technique is measured using blocks with vernier teeth on their edges and substrates patterned with the corresponding vernier scales. To eliminate the photolithographic contribution of layer to layer misalignment, block fabrication is limited to one photolithography step to define the block shape. Gold/chrome films are evaporated onto the entire wafer, coating the top faces of the blocks as well as the exposed areas of the sacrificial oxide. The vernier scales have 0.2 μm resolution.

In order to etch the sacrificial oxide layer and release the blocks into solution, a chip is immersed in concentrated HF (49%) in a Teflon dish. Since HF etching renders the silicon surfaces of the blocks and the handle chip hydrophobic, the blocks are attracted to the handle chip when the oxide etching is complete. The chip is then transferred to a clean glass dish containing methanol, which wets the hydrophobic silicon surfaces and allows the blocks to be released into the solution. The blocks sink slowly to the bottom of the dish and are easily rinsed with methanol to remove traces of HF. The blocks are stored in clean glass vials filled with methanol. All glassware is cleaned in a 4:1 (vol.) solution of H_2SO_4:H_2O_2 for 20 min. and rinsed in deionized water prior to use. Block dimensions are given in Fig. 2.

The silicon (100) (Wacker Siltronic) and quartz (Hoya) substrates used in the assembly experiments are prepared by evaporating gold/chrome films onto the wafers, photolithographically patterning the films with the desired shapes, and etching with gold and chrome etch solutions.

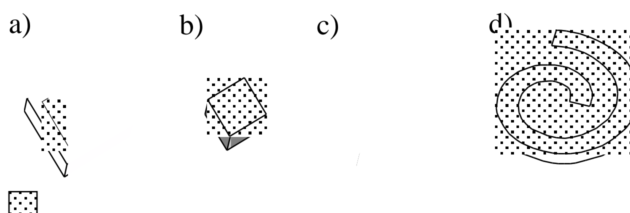


Figure 2. Assembly test blocks are fabricated from a 15 μm thick silicon (100) layer. Top face dimensions: **a)** 400 × 400 μm^2, Au/Cr: 380 × 380 μm^2 **b)** 150 × 150 μm^2 **c)** 250 × 500 μm^2 **d)** outer radius 450 μm, width 100 μm.

Formation of Monolayers. The SAM solution is 1 mM octadecanethiol ($CH_3(CH_2)_{17}SH$, Aldrich) in absolute ethanol (Aaper). The blocks stored in methanol are first rinsed with water. Then, a brief (15 s) rinse with dilute H_2O_2 (8%) is used to reoxidize the silicon surfaces and make them hydrophilic, as well as gently clean the gold regions. Next, the blocks are rinsed in pure ethanol; the ethanol is drained and the vial is filled with the SAM solution. The blocks and substrate chips are immersed in the solution overnight. Silicon (100) and gold/chrome-coated silicon chips are included to monitor the surface conditions. Once the monolayers are formed, the blocks and substrate chips are rinsed several times with ethanol and stored in methanol. Contact angle measurements on monitor chips are performed using a Ramé-Hart goniometer with water and hexadecane.

Assembly Experiments. The procedure for the assembly experiments is as follows. A substrate chip is removed from methanol and dried using nitrogen. To provide lubrication for the assembly process, a drop of an alkane (in this case, 2,2,4-trimethylpentane, anhydrous grade, Aldrich) is applied to the substrate surface before submerging the chip in water. Under water, droplets of the alkane only wet the hydrophobic SAM-coated regions. Then, the blocks stored in methanol are rinsed with water. This is done carefully to prevent the blocks from seeing

the air-water interface and floating there. The blocks are then drawn into a clean glass pipette and delivered to the submerged substrate surface. Excess blocks are removed with a stream of flowing water. Bonding to the quartz substrate is accomplished using a photopolymerizable liquid as the lubricant, as in [7]. The glue was polymerized with UV exposure to the backside of the substrate (15 mW/cm^2, 2 hours).

RESULTS AND DISCUSSION

Surface Treatment. Immersion of clean gold/chrome coated silicon test pieces in the dilute alkanethiol solution results in the formation of a close-packed monolayer, as confirmed by water and hexadecane contact angles of 104 and 40°, respectively [10]. When silicon substrates patterned with gold/chrome shapes are treated with the SAM solution, the gold regions are rendered hydrophobic while the oxide-coated silicon areas remain hydrophilic. Fig. 3a shows a water droplet selectively dewetting from a SAM-coated gold spiral as it dries. When this substrate is coated with a hydrophobic liquid such as an alkane and then immersed in water, water displaces the oil film on the hydrophilic regions, but not on the hydrophobic shapes. In Fig. 3b and c, alkane droplets are observed wetting the hydrophobic patterns under water. This results from the minimization of interfacial liquid energies, since the energetic cost of the water next to the alkane is lower than that of water bordering the more hydrophobic methyl groups of the SAM. The size of the drops is determined by the buoyancy of the alkane in water and the area of the hydrophobic region [9]**.** This thin liquid layer provides the means for lubrication in the assembly experiments [6,7].

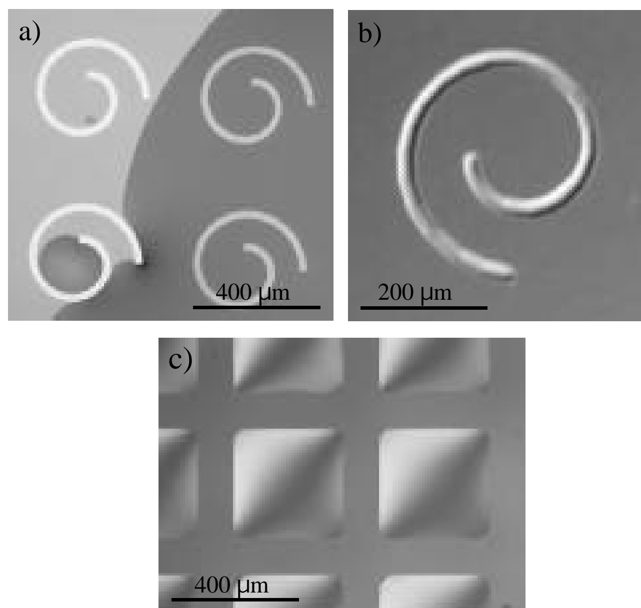
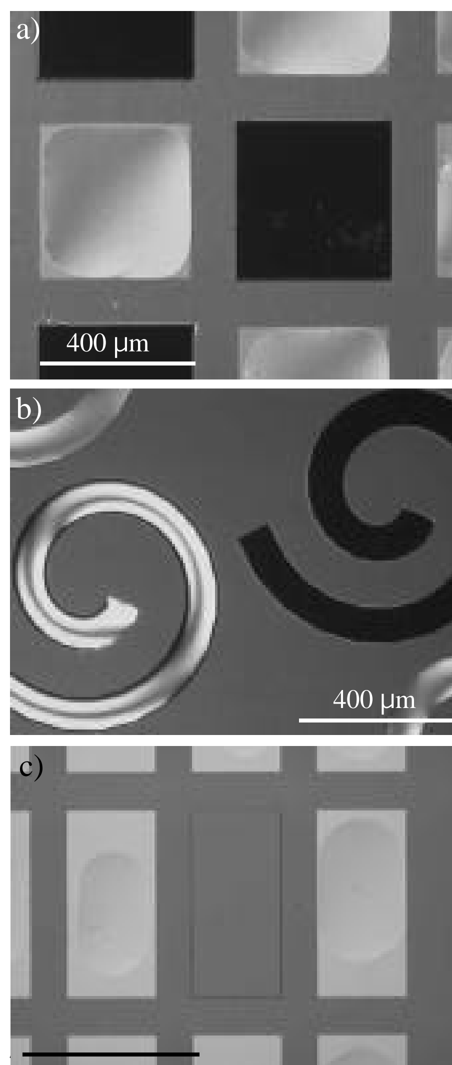


Figure 3. **a)** Water droplet selectively dewetting from a hydrophobic SAM-coated gold spiral on a silicon (100) surface. Photographs taken under water of alkane droplets wetting **b)** a hydrophobic spiral on a patterned silicon surface, and **c)** hydrophobic squares on a quartz substrate.

Assembly Experiments. In the assembly experiments, silicon test parts with hydrophobic SAM-coated gold patterns on one face are pipetted towards a submerged, lubricated substrate and unbound parts are removed using flowing water. The hydrophilic silicon side of a block does not stick to either the hydrophobic or hydrophilic regions of the substrate. In contrast, when a block lands with its hydrophobic gold side down and comes into contact with a matching, lubricated pattern on the substrate, adhesion occurs. This results from the strong adhesion energy that exists between hydrophobic surfaces in water [5]. The liquid lubricant layer facilitates movement of the test block to minimize the amount of hydrophobic surface area in contact with water, thereby minimizing the interfacial free energy of the system [6]. This spontaneous shape matching occurs within seconds and has been observed for block shapes of various symmetries— squares, rectangles and spirals (Figs. 4 and 5). Without the lubricant, the blocks cannot overcome friction to adjust their relative alignment to the substrate pattern.



500 µm

Figure square **b)** spiral and **c)** rectangle shapes onto patterned, lubricated silicon surfaces under water. Assembled parts appear black in a) and b) due to use of Nomarski interference.

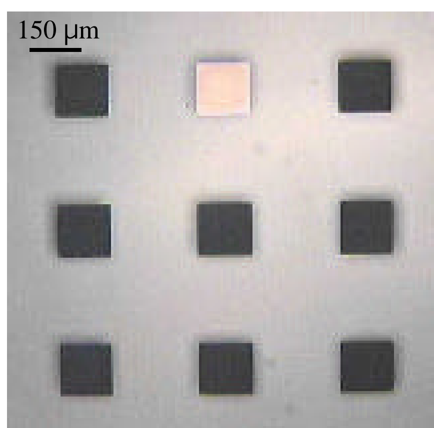


Figure 5. 3 × 3 array on quartz, with one empty site (top row, center) and eight assembled blocks.

Experiments using blocks and substrates with vernier scales indicate that this assembly technique gives sub-micron positioning precision. Fig. 6 shows photographs of the substrate pattern, a block self-assembled onto this shape, and a close-up of the block-substrate vernier scales.

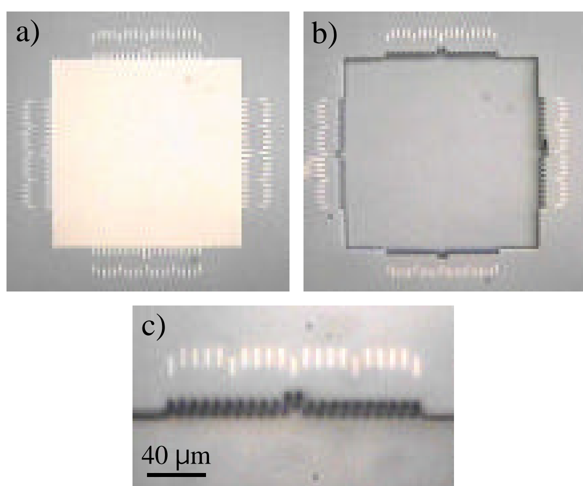


Figure 6. **a)** Hydrophobic gold pattern (400 × 400 μm^2) on a silicon substrate with vernier scale to measure alignment precision. **b)** Self-assembly of test block with corresponding vernier teeth. **c)** Close-up of block-substrate vernier alignment. Alignment precision is 0.4 μm.

Bonding using the UV-polymerizable glue was successful, and experiments with a heat-polymerizable adhesive for bonding to opaque substrates are underway.

CONCLUSIONS AND FUTURE WORK

We have used a fluidic technique based on patterned shapes of hydrophobic SAMs to assemble microfabricated silicon blocks onto silicon and quartz substrates. Here, the driving force for self-assembly is the minimization of the interfacial free energy of the system; self-alignment to a lubricated binding site occurs within seconds of contact for square, rectangular and spiral part shapes. Part-substrate bonding occurs due to hydrophobic interactions, and can be made permanent by using a polymerizable liquid as the lubricant. This assembly approach offers three main advantages over existing assembly methods— it gives submicron precision, there is a great deal of flexibility in the choice of part and substrate materials, and it does not require bulk micromachining of the substrate. Refinement of this assembly method will include designing a test block reflow system to assemble large arrays and establishing part-substrate electrical connection.

Currently, we are applying this technique to assemble Si (100) micromirrors onto surface-micromachined actuators for improved reflectivity and flatness. In future work, we will observe the self-assembly process using video microscopy to investigate the process dynamics.

Acknowledgments

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