

### Three-Dimensional Mesoscale Self-Assembly

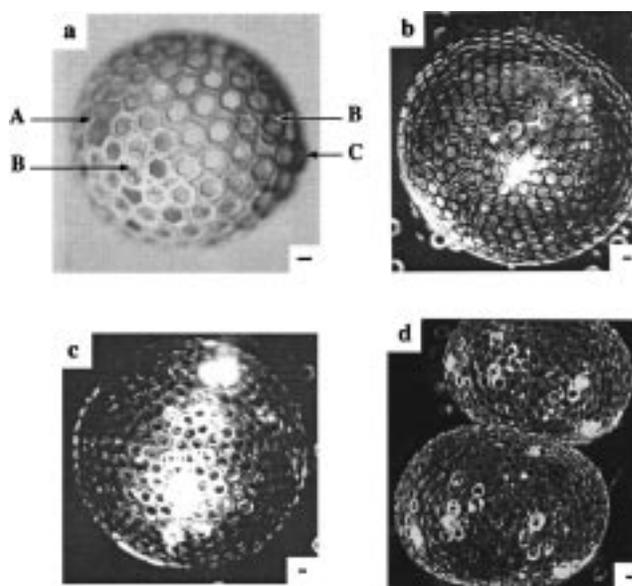
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Microfabrication, as it is now practiced, is based on photolithography and is an intrinsically two-dimensional technology.<sup>1</sup> Many important objectives in microfabrication, microelectronic devices having new architectures,<sup>2</sup> photonic band-gap crystals,<sup>3</sup> and biomimetic structures,<sup>4</sup> require 3-D fabrication. This communication describes the fabrication of a model 3-D microstructure, an open, spherical, metal lattice composed of hexagonal elements  $\sim 100 \mu\text{m}$  in size (Figure 1a).<sup>5</sup> The procedure used to fabricate this structure combined the following three elements that will, we believe, be widely applicable in 3-D microfabrication: (i) the surface of a drop of liquid to act as a template for the structure, (ii) self-assembly using capillary forces at a liquid–liquid interface<sup>6,7</sup> to order the components on the surface of the spherical drop, and (iii) microelectrodeposition of metal to form and weld together the small, regular metallic structural components.

The components on which this structure is based are open hexagons designed to support the modification of their surface properties. Using capillary forces<sup>8</sup> for self-assembly requires careful control of the wettability of the surfaces of these hexagonal rings. Hexagons **A** are designed to assemble around a drop of water suspended in heptane. All sides and one hexagonal face are hydrophobic; the other hexagonal face is hydrophilic. Hexagons **B** have all sides plus one hexagonal face hydrophilic and one hexagonal face hydrophobic; these hexagons assemble around a drop of perfluorodecalin (PFD), chloroform, or chlorobenzene suspended in water. Figure 2 outlines the preparation of hexagonal rings. An array of  $6\text{-}\mu\text{m}$  deep hexagonal molds was prepared using standard photolithographic techniques. Gold was electroplated into these molds.<sup>9</sup> To fabricate hexagons **A**, a thin layer of Si (50 nm) was evaporated on top of the wafer; this Si formed a hydrophilic layer of native  $\text{SiO}_2$ . The photoresist was removed by rinsing with acetone. The Si layer was removed simultaneously, leaving Si only on top of the hexagons. The wafers were briefly ( $< 15$  min) sonicated in ethanol to lift off the hexagons. Addition of hexadecanethiol to the suspension of hexagons rendered the gold surfaces of the hexagons hydrophobic. To fabricate hexagons **B**, the photoresist was removed prior to evaporation of Si or Ti. The Si and Ti both formed native oxide



**Figure 1.** (a) Porous sphere composed of self-assembled hexagonal rings welded by electrodeposition of Ag. The rings had approximately  $100\text{-}\mu\text{m}$  sides and were assembled on a drop of chlorobenzene in an aqueous silver-plating solution. Defects are indicated by arrows: **A**, void; **B**, double layer; **C**, point at which the electrode was attached. (b) Mesoscale self-assembly of hexagons; hexagons **A** assembled on a drop of water in heptane. (c) Hexagons **B** assembled on a drop of perfluorodecalin in water. (d) Two spheres pressed against each other do not fuse; the assemblies have substantial stability even without welding to connect the particles. Scale bar =  $100 \mu\text{m}$ .

layers and covered all sides except for the bottom; this process created hexagons with all sides and one hexagonal face hydrophilic.

We used a liquid drop as a template to direct the self-assembly of the hexagonal rings. The use of a liquid–liquid interface allowed the hexagons to adjust their positions relative to one another without frictional impediment under the influence of capillary forces.<sup>6</sup> The procedure used to assemble the spherical lattice relied on several stages of self-assembly. The hexagons were prepared and suspended in the continuous phase. On addition of a drop of the discontinuous phase, an approximately spherical liquid–liquid interface formed spontaneously. The hexagons segregated and ordered on this interface.

Hexagons **A** were suspended in heptane, and a small drop of water (diameter  $\sim 1\text{--}2$  mm,  $50 \mu\text{L}$ ) was added. The hexagons assembled on the surface of the drop (Figure 1b). In all experiments, an excess of hexagons was used, which remained suspended in heptane. These hexagons did not interfere with the assembled spheres. The inside of the sphere was pink; this pattern of coloration demonstrated that the hydrophilic Si/ $\text{SiO}_2$  sides faced the water phase. Assembly of hexagons **B** around a droplet of PFD in water gave similar spherical assemblies but with a pink exterior surface (Figure 1c). Because the hexagons had a low aspect ratio ( $\sim 1:16$ ) and a large center hole, some overlapped, giving double layers. Similar effects have been observed in other mesoscale self-assembling systems.<sup>10</sup> Other defects that can be seen in Figure 1a–c are voids that are due to poor packing of the hexagons.<sup>11</sup> When self-assembly of the hexagons at the surface of the drop was complete, the resulting structure was, of course, held together only by capillary forces.

These structures were surprisingly robust; pressing together two drops of hexane, suspended in water and covered with hexagons,

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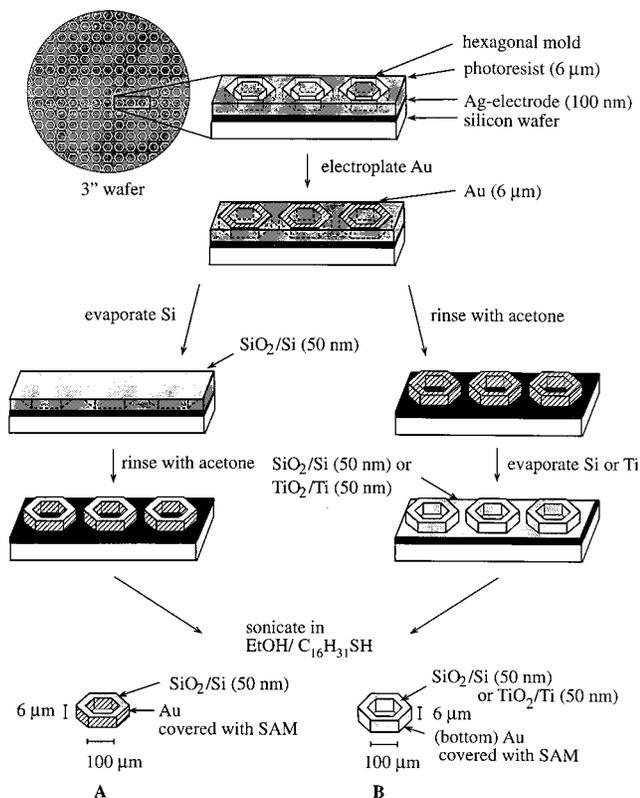
(5) Initial experiments showed that the size of the hexagons can be reduced to  $10 \mu\text{m}$  without fundamentally changing the assembly process. Hexagons with sizes smaller than  $10 \mu\text{m}$  could be fabricated, but the agitation of these particles might be difficult. The capillary forces become small (in an absolute sense), and the assemblies will be easily disturbed.

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(9) We used a commercial gold sulfite plating solution (Technigold 25 E.; Technic, Inc. Cranston, RI), with current densities of  $1\text{--}5$  mA/cm<sup>2</sup> and solution temperatures of  $45\text{--}60$  °C.



**Figure 2.** Schematic outline of the process used to fabricate the hexagonal rings.

did not result in their fusion (Figure 2d). The hexagonal rings acted as a mesoscale surfactant and prevented the contact of the liquid phases that might have led to fusion. In the absence of the two liquid phases, however, the structures had no significant structural integrity.

(11) In an attempt to improve the ordering, we fabricated 50- $\mu\text{m}$  thick hexagons made of polymer and covered at all sides but the bottom with a thin metal film. This metal layer was hydrophilic, and only the bottom hexagonal face was hydrophobic. These hexagons had a much more favorable aspect ratio and still floated at a PFD/water interface. The ordering was improved considerably. A drawback of these hexagons was that the thin metal film did not adhere well to the polymer substrate and did not allow electroplating. It has not been possible to weld these hexagons.

To weld the components, we used electrodeposition of metal. To minimize distortions due to gravitation, hexagons **B** with a Ti/TiO<sub>2</sub> layer were assembled around a drop of an approximately isodense liquid (chlorobenzene) in an aqueous silver plating solution.<sup>12</sup> An electrode was positioned at the top of the droplet, just touching the hexagons. Electroplating Ag on the hexagons resulted in the formation of a thin layer that welded them into an approximately spherical assembly. When welding was complete, addition of EtOH to the system produced a single phase system that drained from the welded sphere (Figure 1). This object, although fragile, was able to withstand the capillary forces encountered as it separated from the liquid and easily stood on its own in air.

A number of factors contributed to the success of this type of self-assembly. Capillary forces at interfaces with high surface tensions are well-suited for 3-D self-assembly. The capillary forces, for small objects suspended at the interface, are substantially larger than the force due to gravity<sup>13</sup> and are thus independent of the orientation of the interface with respect to the gravitational field of the earth. In this instance, the packing of hexagons was similar on all parts of the sphere. Microelectrodeposition provides a versatile method for forming and joining small metal objects.

The open spherical latticework generated in this procedure is composed of structural components that have no additional function; they demonstrate the effectiveness of this combination of processes for building 3-D microstructures. The next stages in the development of 3-D microstructures must include the development of individual components that, individually or collectively, have optical, electronic, or magnetic function and the development of methods of making connections between the components that are compatible with that function. These are challenging tasks, but primitive demonstrations of this type of assembly in 2-D arrays already exist.<sup>14</sup>

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