Fabrication of Micro-Chain Mail by Simultaneous, Patterned Electrodeposition on a Plane and Multiple Cylinders**

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Herein we describe a method for forming complex three-dimensional (3D) microstructures by decomposing them into substructures to be patterned on separate substrates, then juxtaposing the patterned substrates, and joining the substructures to form the desired structures. The broad applicability of the method is demonstrated by the fabrication of micro-chain mail, the charm of the structure of which as a target has been noted by others.[1, 2]

We decomposed the chain mail (H) shown in Figure 1 into two sets of curves and lines: one set was patterned onto a plane, and the other set was patterned onto several cylinders. The patterns on these cylinders joined the patterns on the plane, such that two neighboring lines in the center of the pattern on the plane connected to two curves on two neighboring cylinders to form an oval. This oval linked with four other ovals. The partial ovals at the sides of the pattern on the plane were completed similarly. The collection of ovals—connected in this fashion—formed the chain mail.

To fabricate this chain mail, we formed the 2D pattern (Figure 1) in photoresist on a gold-coated glass slide by photolithography, and the remainder of the patterns on cylinders as features in silver by microcontact printing (μCP).[3] The patterns on the cylinders were aligned with those on the plane so that they formed the required template. Isotropic electrodeposition of nickel metal onto areas defined by this template produced the chain mail with links that were continuous and interconnected; the electrodeposition welded the substructures together.[4] Dissolving the substrates released the metal structure; the result was a free-standing, interlinked chain mail with a wire width of about 100 μm (Figure 2).

Forming patterns on separate substrates, and joining these patterns by electrodeposition, can form 3D microstructures with complex topologies and topographies. The smoothness of the connections between the components is determined by the design of these patterns, and by the way the substrates contact each other (here, the cylinders contacted the planar substrate tangentially and the connections are smooth). Microstructures having different topologies and topographies can be generated by using the same procedure: In general, we can make any 3D wire structure that can be laid down in a plane so that all wire crossings occur on vertical lines in the plane; the number of cylinders required equals the number of vertical lines through the crossings.[5]

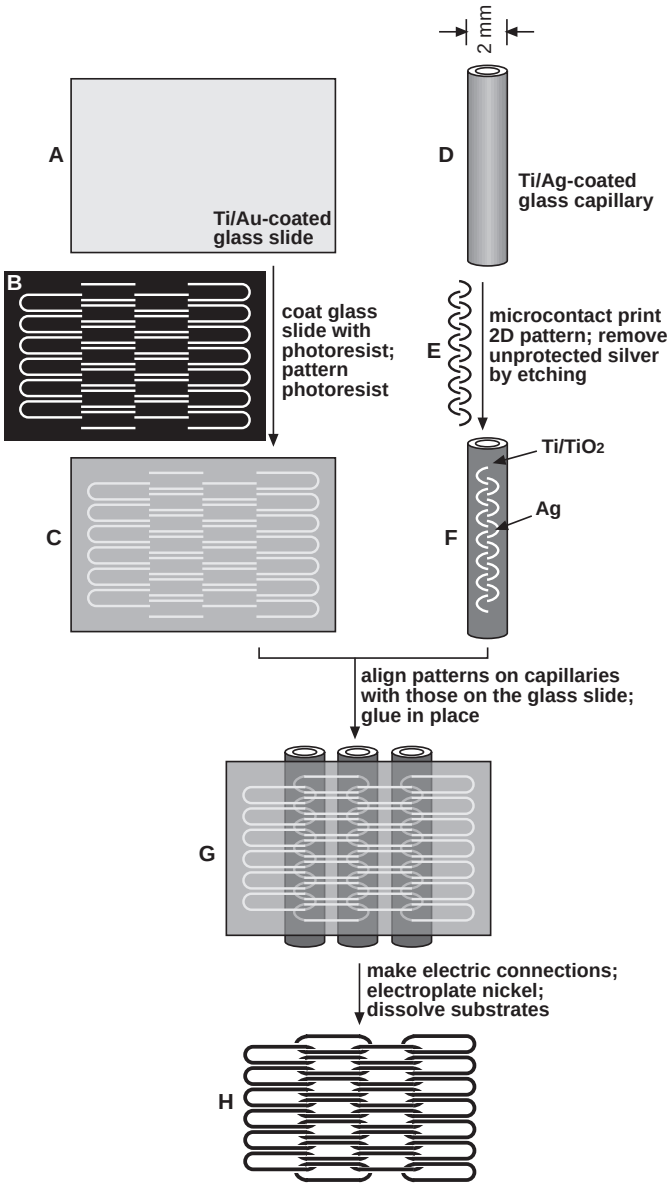

Figure 1. Schematic illustration of the fabrication of micro-chain mail using a planar substrate and multiple cylinders. The procedure begins with the deposition of a titanium adhesion layer as well as a gold layer on a glass slide. After the glass slide (A) had been coated with a positive photoresist, the pattern (B) was transferred into the photoresist by UV photolithography (C). Glass capillaries were coated in an ebeam evaporator with titanium and silver (D). Microcontact printing of hexadecanethiol with a polydimethylsiloxane stamp (with pattern E on its surface) formed a patterned, self-assembled monolayer on the capillaries (F). The surface of the titanium, when exposed to air, oxidized to a thin film, and electrodeposition did not occur on the exposed surface of the non-conductive Ti/TiO_2 film. The patterned glass slide and the capillaries were aligned so that the capillaries were in close proximity to the glass slide and their patterns matched to form a chain mail (G). Electrodeposition with nickel led to the formation of the wires of the chain mail, and the fully formed chain mail was released from the substrates (H).

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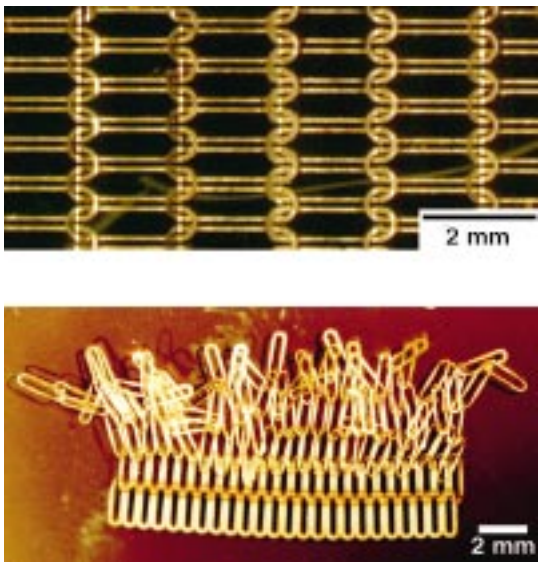

Figure 2. Top: A freely interlocked chain mail (5 × 24 ovals) fabricated by using one glass slide and five cylinders; bottom: a blow-up image of the chain mail.

Experimental Section

The masks for photolithography were produced with a rapid prototyping technique: we designed the patterns with a CAD program; the files containing these designs were sent to a commercial high-resolution printer (5010 dpi) and printed onto transparencies.[3, 6] By UV photolithography, we transferred patterns into negative photoresist (NANO XP SU-8, MicroChem Corp., Newton, MA) on silicon wafers for microcontact printing, and patterns into positive photoresist (Shipley 1813, Microlithography Chemical Corporation, Newton, MA) on a glass slide coated with a thin layer of gold by ebeam evaporation. The surface of these patterned silicon wafers was made more hydrophobic by exposing them to a vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) in a vacuum desiccator; poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184, Dow Corning, Midland, MI) was cast against the silanized silicon wafers and cured at 60 °C for about 3 h, and the elastomeric PDMS replica were peeled from the silicon wafers to be used as stamps for microcontact printing.[3] We coated the glass slide with about 1.5 nm of titanium and about 15 nm of gold by ebeam evaporation; the capillaries were mounted on a stage that rotated about two orthogonal axes during the evaporation, and coated with about 50 nm of titanium and about 70 nm of silver.[7] We used a laser-aligned arrangement of precision translation and rotation stages and hexadecanethiol (hexadecyl mercaptan, technical grade, 92%, Aldrich) as an "ink" for microcontact printing patterns onto the capillaries.[8] Subsequent wet-chemical etching was accomplished by immersing the printed substrates in an aqueous ferri-/ferrocyanide bath (0.001 M $K_4[Fe(CN)_6]$, 0.01 M $K_3[Fe(CN)_6]$, 0.1 M $Na_2S_2O_3$) for about 30 s to remove the underivatized silver. We aligned the patterns on the substrates manually under a stereoscope and immobilized them by applying 5-min epoxy at the ends of the capillaries and the glass slide. After making electrical connections to the metal with silver epoxy (SPI Supplies, West Chester, PA), we electroplated nickel onto the areas defined by the photoresist on the slide and the silver patterns on the cylinders from a nickel sulfamate-based plating bath (Techni-Nickel "S", Technic Inc., Providence, RI) at 45 °C for about 4 h at a current density of about 20 mA cm^{-2} until the matched ends on different substrates were welded. We released the fully formed chain mail from the substrates by dissolving the photoresist in acetone and dissolving the titanium and glass in concentrated HF solution. **Caution**: concentrated HF is highly corrosive to skin, tissues and bones; avoid exposure. The thin layer of gold was removed by sonication for about 1 min.

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Color-Tuned Electroluminescence from Columnar Liquid Crystalline Alkyl Arenecarboxylates**

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Columnar liquid crystals consisting of a polycyclic aromatic core surrounded by flexible side chains combine the good charge-transport properties of aromatic single crystals with the good film-forming properties of viscous liquids.[1] Thus, thin films made of large well-aligned monocrystalline domains can be obtained at room temperature after annealing the material in the liquid crystalline state at elevated temperature. The columns generally align perpendicular to the surface. Thus, the direction of maximum charge mobility, which is along the column axis due to the proximity of the aromatic cores of neighboring molecules, is normal to the plane of the film.

Such semiconducting materials may be used in light-emitting diodes,[2] where an organic film or a stack of organic layers is confined between an anode with high work function (usually formed from transparent indium–tin oxide) and a cathode with low work function (for example, Al or Mg).[3] In devices containing only a single organic layer, the fluorescent organic material needs to exhibit both sufficient hole and electron affinity to allow injection of charges of both signs into the organic layer. It is useful to prepare multilayer devices[4] in order to efficiently confine the recombination of charges in

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