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Accelerated Articles

Fabrication of Metallic Microstructures Using Exposed, Developed Silver Halide-Based Photographic Film

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This paper demonstrates that the pattern of silver particles embedded in the gelatin matrix of exposed and developed silver halide-based photographic film can serve as a template in a broadly applicable method for the microfabrication of metallic microstructures. In this method, a CAD file is reproduced in the photographic film by exposure and developing. The resulting pattern of discontinuous silver grains is augmented and made electrically continuous by electroless deposition of silver, and the electrically continuous structure is then used as the cathode for electrochemical deposition of an additional layer of the same or different metal. The overall process can be completed within 2 h, starting from a CAD file, and can generate electrically continuous structures with the smallest dimension in the plane of the film of ∼30 μm. Structures with aspect ratio of up to 5 can also be obtained by using the metallic structures as photomasks in photolithography using SU-8 photoresist on the top of the electroplated pattern and exposed from the bottom, followed by development and electroplating through the patterned photoresist. This method of fabrication uses readily available equipment and makes it possible to develop prototypes of a wide variety of metallic structures and devices. The resulting structures—either supported on the film backing or freed from it—are appropriate for use as passive, structural materials such as wire frames or meshes and can also be used in microfluidic, microanalytical, and microelectromechanical systems.

This paper describes a method of microfabrication that enables rapid prototyping of metallic microstructures with dimensions of ≥30 μm. The advantage of this procedure is that it allows laboratories with no access to sophisticated facilities for writing the masks required for photolithography to carry out microfabrication at feature sizes useful in a range of applications: microfluidic systems,[1] cell biology,[2] microanalytical systems,[3] microsensor,[4] and microelectromechanical systems (MEMS).[5,6] The fabrication process involves five steps: (i) printing of a design embedded in a CAD file on paper using a high-quality (600 dots/in., dpi) office printer; (ii) photographic reduction of this print onto silver halide-based photographic film using a commercial slide maker; (iii) development of the exposed film; (iv) electroless deposition of silver metal directly on the exposed, developed film—that is, the finished slide—to make the pattern electrically continuous; (v) electrochemical deposition of metal or other electroactive material onto the silver to form or reinforce the final pattern. We believe that this method will be especially useful in the fabrication of metallic microstructures for use in prototyping devices, and in applications—3D fabrication, fabrication with unfamiliar materials—where conventional projection photolithography is difficult to apply or inapplicable.

A multitude of techniques for shaping (such as stamping, grinding, and milling) and joining (such as welding and mechanical joining) metals are highly developed for the fabrication of macroscopic structures. Application of these techniques to the fabrication and assembly of metallic microstructures (structures having features of <100 μm) becomes increasingly difficult as the sizes become smaller. For that reason, new approaches to

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microfabrication that are not derived from fabrication techniques used at large scale have been developed.[7−11] A widely used technique for fabrication of metallic microstructures is microelectrodeposition of metals on an appropriately shaped mandrel or template. Two examples of this class of processes are through-mask electroplating and LIGA (lithographie, galvanoformung, abformung),[12] both of which are based on projection photolithography (for LIGA, commonly carried out using X-rays, although the availability of the SU-8 class of photoresist has reduced the need for X-ray exposure in making thick structures). Although these methods provide routes to metallic microstructures, they are processes with several steps and require facilities of limited availability.

Recently we described methods for the microfabrication of metallic, 2D and 3D structures based on the combination of soft lithography and microelectrodeposition, the latter both through a mask of photoresist and onto patterned, conducting surfaces.[13] The pattern-transfer step in all of the soft lithographic techniques uses an elastomeric stamp with a surface relief structure that carries the desired pattern.[14] These stamps are usually formed by molding poly(dimethylsiloxane) (PDMS) against a "master" composed of a relief pattern in photoresist and obtained by photolithography. We generate these masters using a technique based on high-resolution commercial printing[15] and high-resolution optical reduction.[16] This procedure is efficient: from design, through stamp, to initial structure typically requires no more than 24 h. Both the preparation of the mask and the generation of the master by photolithography require access to specialized devices and facilities (i.e., high-resolution image setters, clean rooms) that are more readily available than the mask-making facilities required in high-resolution photolithography, but that are still not available to every laboratory that might benefit from medium resolution microfabrication.

The method we describe here represents a further simplification of the process for microfabrication using soft lithography and a further extension of the philosophy of widening access to methods of microfabrication. It uses a readily available photographic film recorder—a commercial slide maker—that reproduces the pattern of a CAD file—printed on paper with an office printer—directly onto silver halide-based photographic film. The pattern of silver particles in the developed photographic film, after electroless deposition to make the structure electrically conductive, serves as a template for electrochemical deposition of additional metal and generates metallic microstructures. The entire procedure, from reproduction of the CAD file onto photographic film to completion of the final metallic structures, can easily be finished within 2 h and uses only readily available equipment. This procedure makes it possible for virtually all laboratories to generate a variety of useful metallic structures with feature sizes as small as 30 μm.

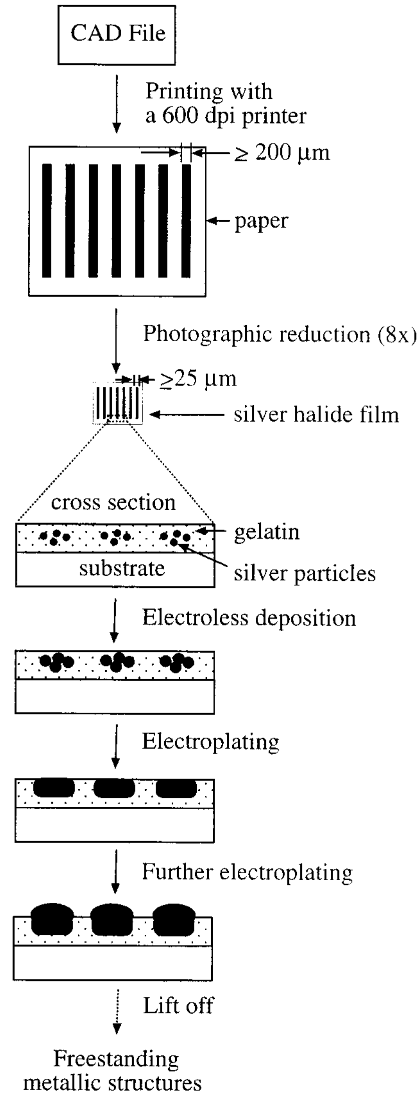

Figure 1. Schematic representation of the fabrication of metallic microstructures by exposure and development of silver halide-based photographic film, followed by electroless and electrochemical plating. A 600 dpi print of a CAD file is photographically reduced (~8×) onto a silver halide-based photographic film. After development, the resulting pattern of Ag particles is converted to a continuous structure by electroless deposition of additional silver. Subsequent electroplating with a metal of choice results in a rigid metallic microstructure that can, if desired, be lifted from its substrate by dissolution of the gelatin.

EXPERIMENTAL SECTION

Materials and Equipment. We used Polagraph 35 mm instant black and white slide film (Polaroid Corp.; Cambridge, MA). HaloChrome silver electroless plating solution (Rockland Colloid Corp; Piermont, NY), Tech 25 E gold plating solution (Technic Inc.; Providence, RI), Tech nickel plating solution (Technic Inc.), Poly(dimethylsiloxane) (Sylgard 184; Dow Corning, NY), and SU-8 photoresist (Microchem Co.; Newton, MA) were used as received. $NiSO_4 \cdot 6H_2O$ (99%), $NH_3 \cdot H_2O$ (29.8%), $Na_2H_2PO_2 \cdot H_2O$ (>99%), $Ru(NH_3)_6Cl_3$ (>99%), NaCl (>99%), HCl (1 N), $Na_2S_2O_3$ (>99%), K$_3$-

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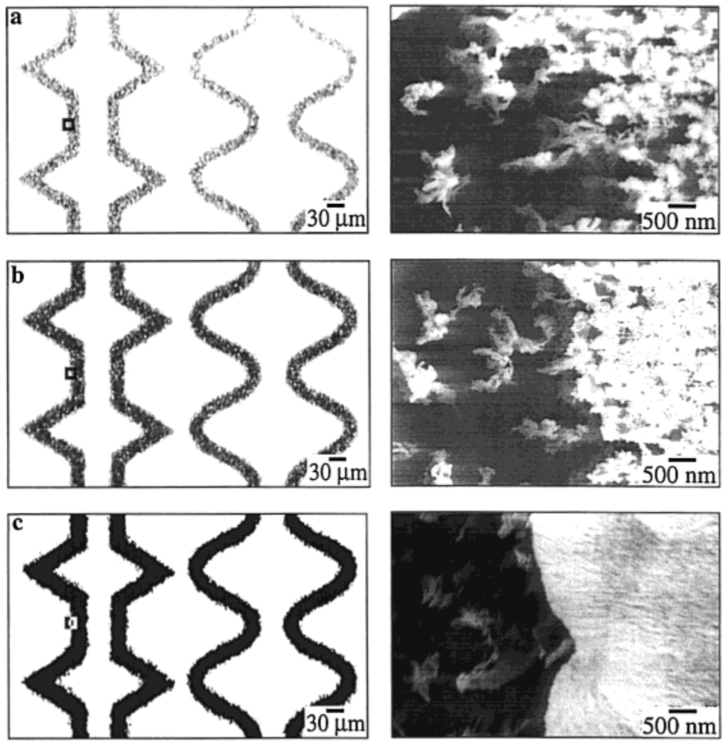

Figure 2. Optical micrographs (illumination with transmitted light) of a pattern of shaped lines generated using silver halide-based photographic film, and scanning electron micrographs of their microstructure (top view): (a) after development, (b) after electroless plating of silver, and (c) after electroplating of gold. The SEMs were taken at the edge of the lines (the highlighted areas in the optical micrographs). The gelatin protection layer was removed by RIE so we were looking at the details of the pattern of silver particles only.

$Fe(CN)_6$ (>99%), $K_4Fe(CN)_6$ (99%), and propylene glycol methyl ether acetate (PGMEA) were obtained from Aldrich. The black and white slide maker was bought from Polaroid (model IPC-2). The scanning electron micrograph (SEM) was done on a LEO digital scanning electron microscope (model 982), and the cyclic voltammetry measurements were performed on a AFCB1 Bipotentiostat (Pine Instrument Co.; Grove City, PA).

Fabrication. *Metallic Microstructures.* The test patterns were designed using Freehand and printed on paper using a 600 dpi printer. We reduced the printed images on slide films using the black and white slide maker. The contrast was set in the medium-contrast mode, and the exposure time was ~0.5 s. We developed the slide film using the developing package for Polagraph 35 mm slide film. The developed film was put in the silver electroless plating solution for ~15 min and then the desired metal was electroplated onto the patterns of silver.

Three-Electrode System for Microfluidics and Cyclic Voltammetry Measurement. The PDMS membrane was made by casting PDMS against an SU-8 master.[14] The solutions were injected into the channel using a single-use syringe connected to the inlet with a piece of polyethylene tubing. The system was treated with a 0.1 N HCl solution for ~1 min prior to the electrochemical measurements. The concentration of oxygen in all solutions was reduced by bubbling Ar gas through for at least 5 min.

High Aspect Ratio Structures. The electroplated film was put in an etching solution containing 0.1 M $Na_2S_2O_3$/0.01 M $K_3Fe(CN)_6$/0.001 M $K_4Fe(CN)_6$[17] for ~1 min to get rid of the gold particles reduced by the gelatin in the nonpatterned area. This etching step is necessary to make the film more transparent to UV during the patterning of photoresist. The film was immobilized on a glass slide using Scotch tape. We spin-coated SU-8 photoresist directly onto the film at 500 rpm for 20 s. The film was baked at 95 °C for ~10 h, followed by exposure from the bottom for 7.5 min (10 $mJ \cdot cm^{-2} \cdot S^{-1}$ at 405 nm) with a Karl Suss MJB3 contact aligner and postbaking at 90 °C for ~10 min. The photoresist was developed in PGMEA for ~4 h with magnetic stirring. Finally, through-mask electroplating of the film carrying the patterned photoresist in a nickel electroplating bath was performed for ~150 h while a current of 10 mA was maintained.

RESULTS AND DISCUSSION

Method of Fabrication. Figure 1 illustrates the procedure used to fabricate metallic microstructures using silver halide-based photographic film. The key element in this film is a polyester backing (typically ~100 μm thick) covered with a gelatin layer (typically ~2 μm thick) that contains silver halide.[18] A CAD file was first printed on paper with a 600 dpi office printer. A commercial slide maker was then used to reproduce the black and white image on the silver halide-based photographic film. The developed film leaves the silver(0) particles isolated, with no electrically continuous path connecting the pattern. Electroless deposition of additional silver, catalyzed by these silver grains, increased their size to the point at which they came into contact.[19,20] At that point, the entire image became electrically

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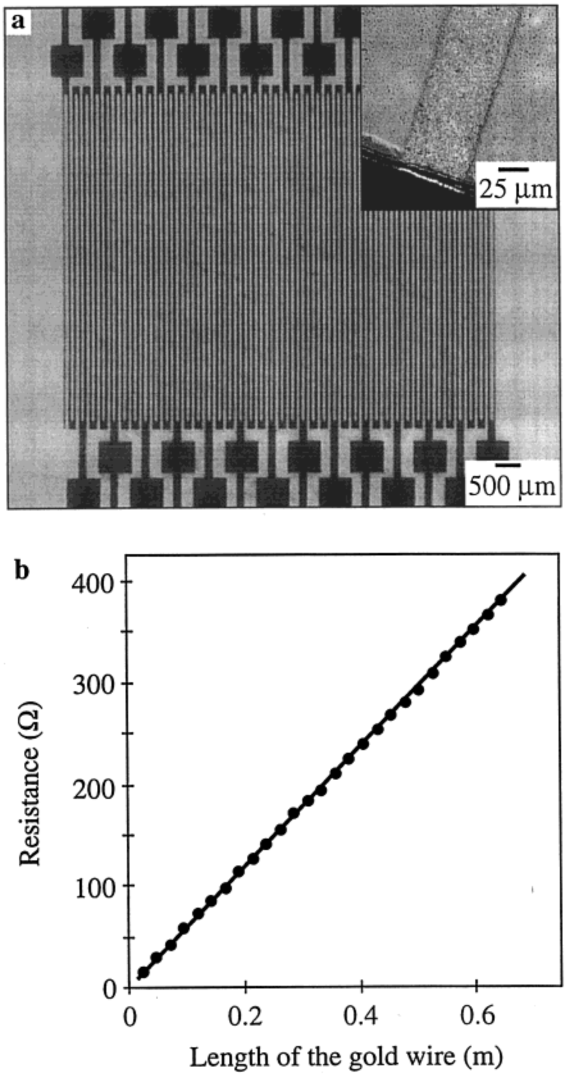

Figure 3. (a) Optical micrographs of a continuous, serpentine gold wire (∼50 μm wide, ∼2.5 μm thick, and ∼648 mm long) made on silver halide-based film. The inset is an oblique view of the edge. (b) A test of electrical continuity: the dependence of measured resistance (two-probe method) on the gold wire length.

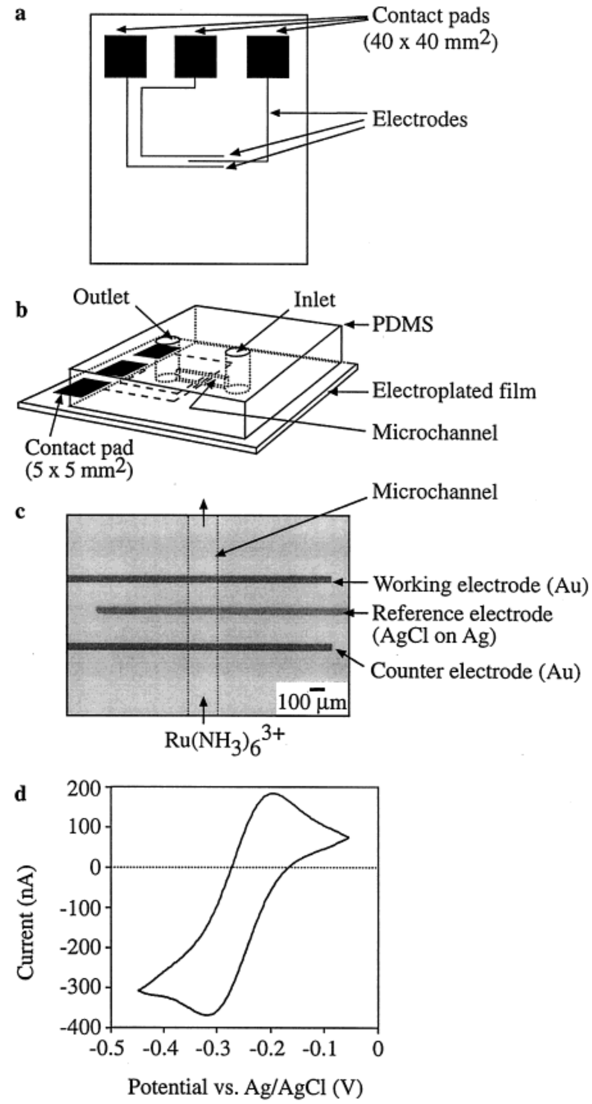

Figure 4. (a) Design, as printed on paper, used to fabricate a three-electrode system. (b) Schematic depiction of the microfluidic system with the in-channel electrode system in place: the polyester substrate carrying the three electrodes was brought into conformal contact with a PDMS membrane having a channel (200 μm wide and 50 μm high) embossed in its surface and reservoirs for adding a solution for analysis. (c) Optical micrograph of the "fingers" of the three electrodes. The width of the gold electrodes (working and counter) and the silver electrode (reference electrode) was ∼60 μm, and the spacing between the two closest electrodes was ∼190 μm. (d) Cyclic voltammogram of ∼100 nL of $Ru(NH_3)_6Cl_3$ in water (2 mM, with 0.1 M NaCl as electrolyte, pH 7) recorded with this system (scan rate 100 mV/s).

conducting (provided, of course, that the original design was continuous). Subsequent electroplating using this image as the cathode provided metal structures that had the mechanical strength or optical density required for further applications. Free-standing metallic microstructures can be obtained by dissolution of the gelatin matrix in which they are embedded. Due to the high permeability of the gelatin layer (∼2 μm thick),[19] the metal was deposited from both the side and the top on the silver structures during the initial electroplating process. Once the metal grew out of the gelatin layer, the speed of deposition on the top of the metal structure was higher than on the side due to mass transport limitations to delivering metal ions to the sides of the structures or within the gelatin film.

Quality of the Structures. Figure 2 shows optical micrographs of metallic lines (∼30 μm wide) generated by each of the steps in the fabrication process. After development of the photographic image and before electroless deposition, the primary pattern of silver halide grains had a line width of ∼25 μm and an edge roughness of ∼2 μm. After electroless plating, the line width increased to ∼26 μm and the edge roughness remained approximately the same. After electroplating, a line width of ∼30 μm and an edge roughness of ∼3 μm were observed. These lines present the smallest dimensions we can obtain at the present time. The limited optics of the slide maker resulted in distorted, incomplete reproduction of patterns with smaller features. The edge roughness of patterns printed on the paper also contributed to the resolution of the final pattern, but it was not the major factor. The smallest feature sizes of the metallic structures we obtained using a master pattern printed with a 3387 dpi high-resolution image setter were still ∼30 μm, with edge roughness of ∼3 μm. Figure 2 also shows scanning electron micrographs of the

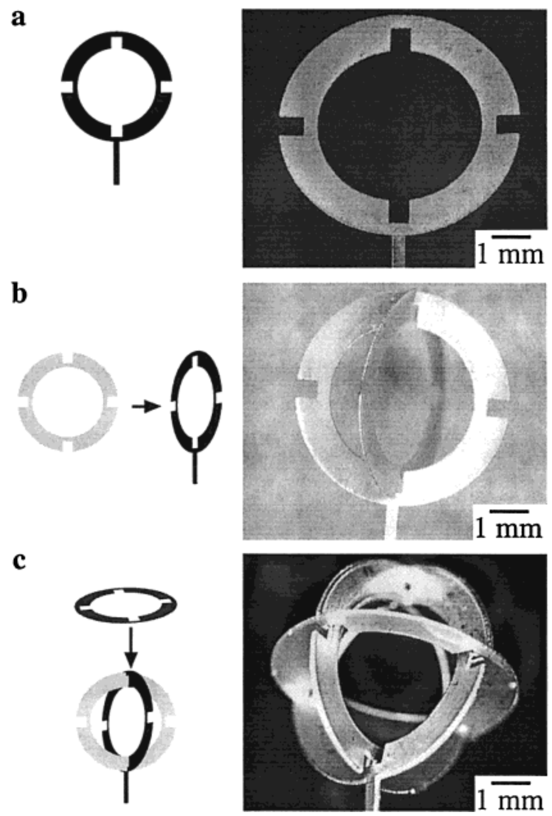

Figure 5. Optical micrographs and schematic stepwise assembly of a nickel three-circle open spherical structure from pieces fabricated by electrodepostion on silver halide-based photographic film. After deposition of the nickel (~50 μm thick) the metallic structures were released from the film by dissolving the gelatin with hot water and then were assembled by hand.

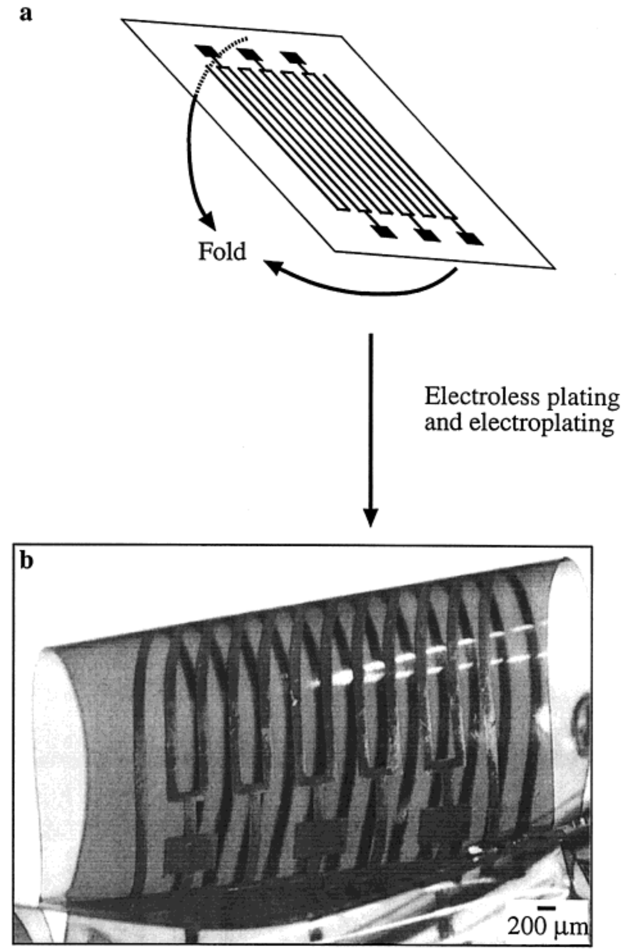

Figure 6. Making curved metallic structures by folding the silver halide film before electroless plating. The optical micrograph in (b) is a curved nickel serpentine wire made on the silver halide film. The line width of the line is ~100 μm, and the thickness is ~2 μm.

microstructure of the line patterns in the different stages of the fabrication process. The growth and fusion of silver particles upon electroless plating and electroplating are clearly visible.

Figure 3 shows a gold serpentine wire (~50 μm wide and ~2.5 μm thick; total length of ~648 mm) which we fabricated to test the electrical continuity of metallic structures made using this procedure. A uniform resistivity of ~7 × 10^{-8} Ω·m was measured over the full length of the wire, which is ~3.5 times higher than the value reported for pure bulk gold (~2 × 10^{-8} Ω·m).[21] A residual gelatin network, or a network of grain boundaries still presented inside the wires after electroplating, can explain this difference.

Fabrication of a Three-Electrode System for Microfluidics. We fabricated a three-electrode system using the procedure described in Figure 1. We differentiated the electrodes into two sets by selective electroplating: two wires and their contact pads were covered with gold (for the working and counter electrodes) and one wire and corresponding contact pad with silver (for the reference electrode). The polyester base in the film enabled us to use this three-electrode structure in a microfluidic device by placing a PDMS membrane with a channel embossed in its surface directly on this structure (Figure 4). Cyclic voltammetry of a solution containing $Ru(NH_3)_6Cl_3$ demonstrated the performance of this three-electrode system.

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Fabrication of Free-Standing, Three-Dimensional Structures. The solubility of the gelatin base in dimethylformamide or hot water allows for the fabrication of free-standing structures.[19] The conditions required for release are sufficiently gentle that even fragile structures are not damaged. Figure 5 shows a 3D structure, an open sphere, assembled from pieces that have been fabricated using this technique. The line width of each of the nickel circles was ~1 mm and the thickness was ~50 μm. We believe that this method offers an alternative approach to rapid fabrication of elements for 3D structures/MEMS.

Fabrication of Curved Structures. The flexibility of the film makes it possible to fabricate topologically complex microstructures. Figure 6 shows a nickel serpentine wire (~2 μm thick and ~100 μm wide) fabricated by electroplating on a folded silver halide film.

Fabrication of Isolated Structures Using Electroless Plating. The procedure described above works well to make continuous metallic structures. During the fabrication of discontinuous structures, there is no continuous electrical pathway joining all the elements of the pattern, and therefore, it is not possible to use electroplating. To solve this problem, we used an electroless Ni plating solution (2.6 g of $NiSO_4·6H_2O$, 5 mL of $NH_3·H_2O$, and 3.6 g of $Na_2H_2PO_2·H_2O$ in 200 mL of H_2O) that can build a thick Ni layer on the patterned silver particles (continuous or discon-

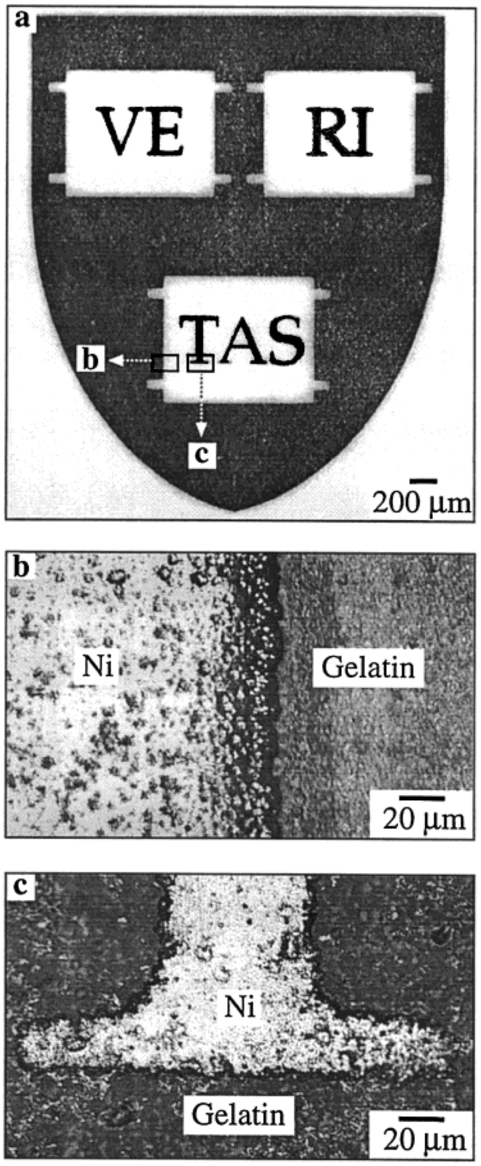

Figure 7. Optical micrographs of discontinuous metallic structure fabricated by electroless deposition on the developed silver halide film: (a) A "VERITAS" logo in nickel (∼2 μm thick). (b, c) Magnified views of the highlighted areas in (a).

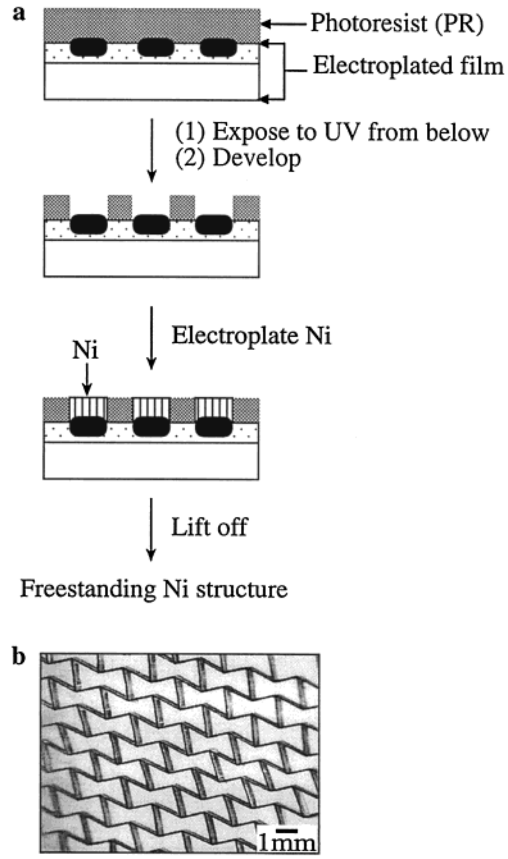

Figure 8. (a) Schematic representation of the fabrication of metallic microstructures with high aspect ratio using electroplated film as a mask in photolithography followed by electroplating through the patterned photoresist. The negative photoresist (SU-8) was spin coated on the film, and the film was exposed to UV light from below. After development and electroplating using the original, low aspect ratio metallic structures as the cathode, a high aspect ratio metallic structure formed and could be lifted off from the substrate if desired. (b) Optical micrograph of a nickel structure with an aspect ratio of 5 fabricated using the procedure described above (line width ∼80 μm, height ∼400 μm).

tinuous). Figure 7 shows a "VERITAS" logo consisting of a ∼2 μm nickel layer deposited using electroless plating alone.

Fabrication of Structures with High Aspect Ratios. The structures fabricated above all have low aspect ratios, typically less than 0.1 (height:width). Figure 8 shows the fabrication of structures with high aspect ratio. First, the film carrying the low aspect ratio structure was used both as the substrate and as the mask in a photolithographic step. Subsequent use of the photoresist pattern as the mask to direct electrodeposition of metals while using the original, low aspect ratio structure as the cathode resulted in high aspect ratio structures.

The fact that the film serves as the substrate and the fact that the metallic structures on the film not only serve as the mask in the photolithographic step but also as the cathode in the electroplating procedure reduce the number of steps significantly compared to conventional processes for the fabrication of high aspect ratio metallic structures. We obtained a negative Poisson ratio structure[22] with a maximum aspect ratio of 5 (Figure 8b). The fabrication of structures with aspect ratio higher than 5 was challenging for the following reasons: (i) The adhesion of SU-8 photoresist with gelatin was not good with increasing thickness of the SU-8. (ii) The PGMEA solution used in developing SU-8 also attacked the gelatin. (iii) Due to diffusional limitations, the electrodeposition through the SU-8 mask was slow with increasing aspect ratios.

CONCLUSIONS

The single step of the simple photographic reproduction of a CAD file onto a silver halide-based film replaces the multiple (partly photolithographic) steps in microcontact printing and LIGA for the fabrication of appropriately shaped mandrels for microelectrodeposition.[12,23] The complete procedure from CAD file to metallic structure can easily be completed within 2 h if instant film is used and if structures with ≥30 μm feature sizes are satisfactory for the application at hand. In principle, any photo

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camera or slide maker that accepts silver halide-based film will be sufficient for the reproduction of the CAD file pattern. The smallest feature sizes we obtain using a common office slide maker are ~30 μm wide ~2 μm thick. Structures with thickness smaller than 2 μm are porous due to the gelatin network. Higher resolution in the width of the structures can be obtained using more professional photographic equipment.[19] The intrinsic limit of resolution for this technique lies with the quality of the photographic equipment and is limited by aberrations of the optical elements and not by the size of the grains in the film (<100 nm). The maximum size of a structure—or an array of structures—is limited by the size of the film used, typically 35 × 22 mm^2. Larger size silver halide-based film is available (up to 300 × 400 mm^2).[18] The equipment that accepts this film size is, however, not common.

Silver halide-based film should be useful for the fabrication of a broad range of interesting structures for MEMS, microfluidics, and microanalytical systems such as the in-channel electrochemical detection system we have shown. This technique requires only routinely available equipment, facility, and materials and makes ≥30 μm-scale fabrication of metallic microstructures in laboratories of chemistry, biology, engineering, and other areas substantially more convenient than procedures based on conventional photolithography.

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