

Direct Laser Writing on Electrolessly Deposited Thin Metal Films for Applications in Micro- and Nanofluidics

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This paper presents a method that uses a tightly focused laser beam to write features on thin metal films with a resolution of several hundred nanometers to a few micrometers. Owing to the ease of fabricating electrolessly and electrolytically deposited Ni layers, we also evaluated with scanning electron microscopy the suitability of such thin Ni films as a substrate for laser writing and subsequently as an etch resist in HF etching and as a photomask in contact photolithography. Using atomic force microscopy, we characterized the feature sizes that can be obtained from three commonly used lasers: the 488 nm of a continuous wave (CW) Ar⁺ laser, the 1064 nm of a CW Nd:YAG laser, and the 337 nm of a pulsed (3 ns pulse width) N₂ laser. The smallest feature sizes that we can generate routinely are approximately 0.5 μm for the Ar⁺ laser, 1.3 μm for the YAG laser, and 2.3 μm for the N₂ laser. Using the laser-patterned Ni film as an etch mask, we have produced HF-etched channels (1.5 μm in width) in glass. In addition to Ni films, we demonstrate the flexibility of this strategy to create photomasks by writing directly on sputtered gold films and on commercially available chrome blanks.

Introduction

Fabrication processes used for producing semiconductor devices, such as electron-beam lithography, photolithography, and wet and dry etching, have inspired and been exploited by chemists and engineers in such diverse ways as the construction of microelectromechanical systems (MEMS),¹ the fabrication of photonic materials,² the patterning of surfaces for biological studies,³ and the production of microfluidic devices.^{4,5} The inaccessibility of many of the necessary instruments to chemists together with the costly and tedious nature of these processes have motivated the adaptations and modifications of these conventional methods in microfabrication and micromachining. Examples of such efforts can be seen in the numerous techniques in rapid prototyping for producing microfluidic systems, including the use of transparency masks and replica molding for prototyping microchannels in polydimethyl siloxane (PDMS),^{6–18} the use of 3D

printers,¹⁹ projection photolithography,²⁰ or composite PDMS masks²¹ to fabricate complex structures or small features, the application of hot embossing to create channels in polymethyl methacrylate (PMMA),^{22–26} and the development of methods for in-channel fabrication.^{27–32}

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Although these methods reduce both the time and cost of microfabrication, they suffer one common limitation: these methods are mostly restricted to the fabrication of microchannels in the tens of micrometers or hundreds of micrometers range. The recent availability of high-resolution photoplotting has significantly improved the resolution of these techniques of rapid prototyping, but the accessible feature sizes are still restricted to around $8\ \mu\text{m}$.¹⁰ The fabrication of channels in the few micrometer to submicrometer dimensions requires the use of electron-beam lithography for the generation of high-definition masks followed by pattern transfer using photolithography. Consequently, applications that require features in the few micrometer to submicrometer range, such as the integration of micro/nanofluidics with ultrasensitive laser-based detection schemes that often involves the use of submicrometer to a few micrometer detection focal spots^{33,34} or the patterning of the surface chemistry and topologies of substrates for single cell/molecule studies,^{3,35–37} have been constrained on one hand by the low resolution of existing rapid prototyping techniques and on the other hand by the expensive and tedious nature of traditional e-beam lithography.

To overcome the inability of existing rapid prototyping techniques to fabricate small features and microchannels, we have developed an approach that utilizes direct laser writing on electroless and electrolytically deposited thin metal films for the fabrication of structures and channels having submicrometer to several micrometers in width. This technique is also easily applied to the fabrication of large microchannels with dimensions of tens or hundreds of micrometers. The use of laser ablation in microfabrication is an intensely active area, but most of these techniques use either expensive pulsed deep UV light sources^{38–42} to create small features or are applied toward the ablation of polymer structures.^{43,44} Instead of using deep UV lasers to produce small structures and pulsed systems to generate sufficient power density for ablation, this paper exploits the inherently small spot size and high power density present at the tight submicrometer-diameter focus offered by a high numerical aperture objective, which is available with most commercially available light microscopes. By developing and characterizing an electroless and electrolytic deposition procedure that is suitable both for direct laser ablation and as a chemical resistant mask for subsequent etching (e.g., HF etch), this technique offers a simple and flexible route to generate small features in a number of substrates.

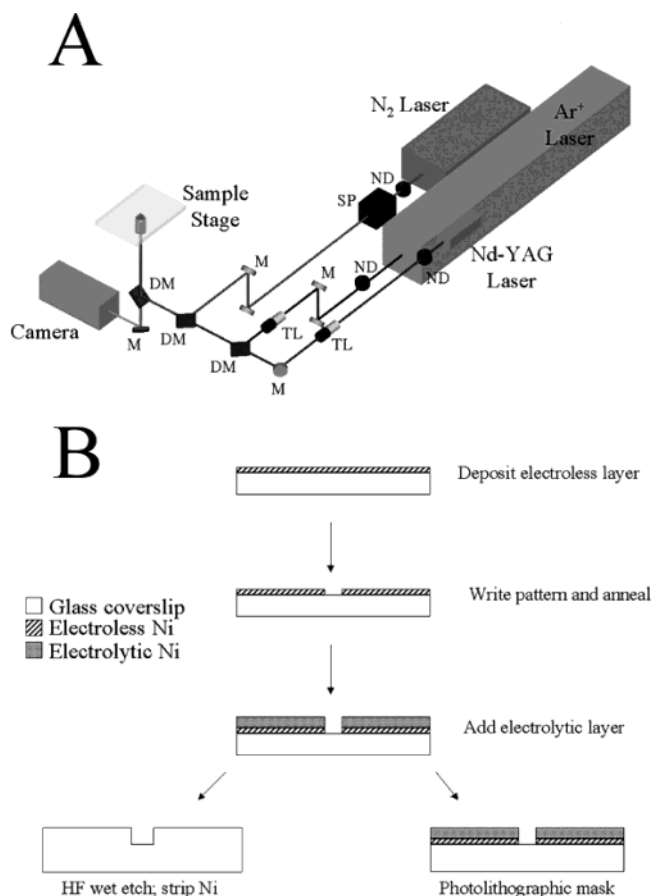


Figure 1. (A) Schematic showing the experimental setup used for characterizing the direct laser writing on metal masks. The lasers used were Ar^+ at 488 nm, Nd:YAG at 1064 nm, and N_2 at 337 nm. Abbreviations: ND, neutral density filter; M, mirror; DM, dichroic mirror; TL, telescopes; SP, spatial filter. (B) An illustration of the procedure used in which the electrolessly deposited Ni layer was patterned and then used either as an etch mask in wet etching or as a photomask in photolithography.

Experimental Section

Optical Setup. We tested three different lasers (Ar^+ at 488 nm, Nd:YAG at 1064 nm, and N_2 at 337 nm) for writing patterns on metal films (Figure 1A). Briefly, the emissions from the three different lasers were directed into a high numerical aperture (NA) objective (NA = 1.3, oil immersion) placed on an inverted microscope (Nikon TE 300) using dichroic and reflective mirrors. The output of the N_2 laser was sent through a spatial filter prior to entering the objective. All three laser beams were collimated to slightly overfill the back aperture of the objective so as to form a tight laser focus on the metal film. We adjusted the power of the laser beams with neutral density (ND) filters and by varying the current supplied to the lasers. We wrote the desired patterns onto the metal film by translating the stage of the microscope manually.

Electroless Deposition of Ni. We first cleaned the surface of the glass coverslip onto which Ni was to be plated by sonicating the coverslip in acetone for 10 min followed by boiling in a solution of 3:2:1 deionized (DI) water, ammonium hydroxide, and 30% hydrogen peroxide for 1 h. Next the cleaned coverslip was rinsed with DI water and dried with a stream of N_2 gas. A PDMS stamp was then sealed conformally around the edges of the coverslip to define a border for ease of solution exchange.

The surface of the coverslip was sensitized with a solution of SnCl_2 (0.1 g/L SnCl_2 and 0.1 mL/L HCl in DI water), where the solution was replaced every 3 min for a total of 15 min. After sensitization, the surface was activated using a solution of PdCl_2 (0.1 g/L PdCl_2 and 0.1 mL/L HCl in DI water), where again the solution was replaced every 3 min for a total of 15 min. With removal of the final aliquot of PdCl_2 , the PDMS stamp was removed and the coverslip was immersed in an electroless Ni

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plating solution (20 g/L sodium hypophosphite monohydrate, 40 g/L nickel(II) sulfate hexahydrate, 100 g/L sodium citrate dihydrate, and 50 g/L ammonium chloride in DI water) at 70 °C for approximately 20 s, after which the coverslip was rinsed with DI water and dried in a stream of N₂ gas. The higher the temperature of the electroless Ni bath, the faster the deposition occurred and the shorter the time required for immersion to deposit an adequate layer of electroless Ni. A well-deposited layer of Ni was characterized by a dark gray semitransparent/reflective appearance.

Laser Writing of Electrolessly Deposited Ni Mask, Annealing, and Electrolytic Plating of Ni. We used a tightly focused laser beam to ablate the electrolessly plated Ni film. After laser writing, the Ni film was annealed in a stainless steel box at 400 °C for 1 h under a N₂ atmosphere. Before using the annealed Ni mask as an etch resist to HF or as a photomask in photolithography, the annealed Ni layer was thickened by electrolytic plating in a solution of 240 g/L nickel(II) sulfate hexahydrate, 45 g/L nickel(II) chloride, and 30 g/L boric acid in DI water. The layer of Ni was deposited at a constant voltage of 2.0 V for ~5 min, after which a "mirrorlike" film of Ni was obtained.

Photolithography. Negative photoresist (SU-8 10) was spin-coated on a silicon wafer at 3000 rpm for 30 s and then soft baked for 1 min at 65 °C and ramped to 105 °C for 3 min. The laser-written metal film was used as a photomask for contact photolithography. After exposure (185–200 mJ/cm²), the resist was baked for 2 min at 65 °C and ramped to 105 °C for 6 min. The exposed photoresist was developed by gently washing the wafer under a stream of 1:1 propylene glycol methyl ether acetate (PGMEA) and isopropyl alcohol.

Wet Etching of Patterned Glass Coverslip. We etched the exposed glass with a 5% HF solution (diluted in DI water). After etching for the desired amount of time, the HF was removed, and the glass slide was rinsed with DI water. Next, the Ni layer was stripped by placing the glass slide in a 3 M nitric acid bath at 70 °C for ~10 min. The glass slide was then removed, rinsed with DI water, and dried under a stream of N₂ gas. Under these conditions, the etch rate for glass was ~0.4 μm/min.⁴⁵

Sputter Coating of Gold on Glass. Sputter coating was carried out using a Technics Hummer II dc sputter coater. Glass coverslips were placed in the sputtering chamber, and gold was sputtered under a 100 mTorr Ar atmosphere with a 20 mA and 2.2 kV dc bias between the sputter target and shield for 5–10 min. Upon removal from the sputter coater, the gold-coated coverslips were ready for use in direct laser writing.

Materials and Chemicals. The SnCl₂ and PdCl₂ were purchased from EM Science (Gibbstown, NJ); sodium citrate dihydrate, ammonium chloride, ammonium hydroxide, hydrofluoric acid, boric acid, and nickel(II) chloride were bought from Fisher (Fairlawn, NJ). Nickel(II) sulfate hexahydrate was obtained from Aldrich (Milwaukee, WI), hydrogen peroxide 30% from J.T. Baker (Phillipsburg, NJ), and sodium hypophosphite monohydrate from Sigma (St. Louis, MO). Glass coverslips (48 × 65 mm, no. 1 thickness) were from Gold Seal (Erie Scientific; Portsmouth, NH). Silicon wafers were obtained from Montco Silicon Technologies Inc. (Spring City, PA), chrome blanks (5 × 5 in. and 0.090 in. thick) from Nanofilm (Westlake Village, CA), SU-8 photoresist from Microchem Corp. (Newton, MA), and PDMS (Sylgard 184) from Dow Corning Co. (Midland, MI).

Results and Discussion

Laser Writing. Figure 1 shows the setup and outlines the procedure we used for the direct laser writing of features on an electrolessly deposited thin Ni layer; it requires less time and laser power to ablate the electroless film than the electrolytic film. To obtain small feature sizes, we used the diffraction-limited focus of the TEM₀₀ output of a laser, which is the lowest transverse electromagnetic mode possible and has a radial Gaussian intensity profile across the beam, to ablate the deposited metal film. In addition to small feature size, the advantage to using a highly focused laser beam is the resultant high power density at the focus (~MW/cm²) that can be achieved

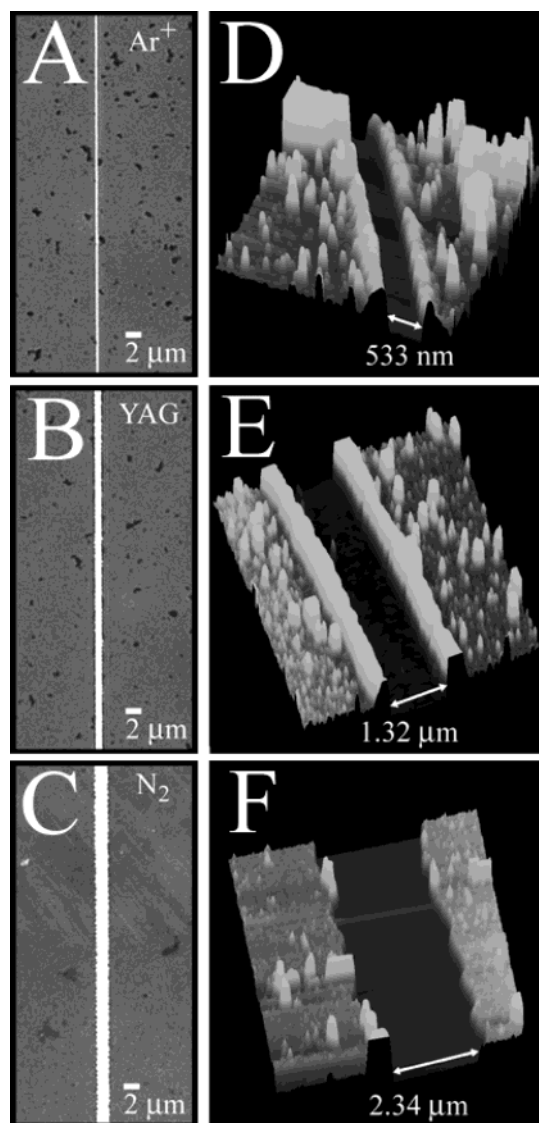


Figure 2. Bright-field and AFM images of lines written in electrolessly plated Ni by the Ar⁺ laser (A,D), the Nd:YAG laser (B,E), and the N₂ laser (C,F). The power of the Ar⁺ and the YAG lasers prior to entering the objective was 20 and 50 mW, respectively. The energy of the N₂ laser prior to the objective was 35 nJ. The z-scale height for the micrographs is 100 nm for the features written by the Ar⁺ and N₂ lasers (D,F) and 80 nm for the image by the Nd:YAG laser (E).

with a low or moderately powered laser having an output in the range of tens of milliwatts. An economical optical setup that is dedicated to the laser writing of submicron features can be readily constructed with a high NA objective, a high-resolution and high-stability translation stage, and a solid-state diode laser. In addition, setups currently used in microfluidics for sensitive laser-induced fluorescence detection that require tight focusing may be easily adapted for carrying out direct laser writing. By sustaining constant writing conditions (i.e., laser power, thickness of metal film and substrate, and plane of focus), the line widths are quite reproducible. In the event there is variation in film thickness, the plane of focus and laser power can both be easily adjusted to compensate and to maintain the desired line width. After laser writing, the metal mask can be used either as an etch mask for the subtractive pattern transfer onto the underlying substrate or as a photomask in photolithography (Figure 1B).

Feature Size. We characterized the suitability of three commonly used lasers, a continuous wave (CW) Ar⁺ laser at 488 nm, a CW YAG laser at 1064 nm, and a pulsed N₂

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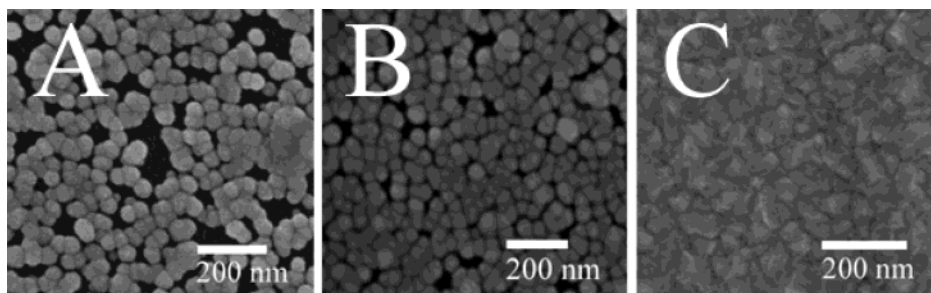


Figure 3. SEM of (A) electrolessly deposited Ni on Si before annealing, (B) after annealing, and (C) after electrolytic plating of Ni.

laser at 337 nm, for the writing of electrolessly plated Ni layers (Figure 2). The use of CW lasers with high-quality TEM₀₀ mode output produced feature sizes commensurate with the size of the diffraction-limited focal spot: the 488 nm of the Ar⁺ laser wrote a 533 nm wide line on the Ni mask, while the 1064 nm of the YAG laser produced a 1320 nm wide line. The edge roughness was ~50 nm on average for lines drawn with the Ar⁺ and YAG lasers (Figure 2). In contrast, the feature size that could be obtained with a pulsed N₂ laser (337 nm) was significantly larger at a line width of 2.34 μm, with an edge roughness of ~150 nm. The cause for this larger feature size is twofold: (1) Although the N₂ laser has an output at a shorter wavelength, it has poor spatial coherence and contains higher order modes, which makes tight focusing difficult, and (2) we used a pulse energy (35 nJ) that is significantly greater than the threshold power required for the ablation of the Ni film. At a lower pulse energy of 3.5 nJ, we have been able to write lines that are ~800 nm in width, but at this power level the ablation process was not very reproducible and lines tended to be broken. Care also should be exercised with the speed of translation of the stage. If the translation speed is faster than the product of the pulse frequency and spot size of the N₂ laser, unnecessarily rough edges or even broken lines may arise because of the poor overlap of the laser spots during the ablation process.

Characteristics of Deposited Ni Layer. Electroless deposition permits the plating of nonconducting surfaces, such as plastics, ceramics, and glass, and enables the ensuing electrolytic deposition by imparting conductivity to the nonconductive surface. In comparison with gas-phase deposition processes, this approach is economical and does not require specialized equipment. A number of metals may be deposited electrolessly, but we initially chose electroless plating^{46–51} of Ni over other metals because of the excellent chemical resistance and mechanical durability of the deposited Ni layer, which are important characteristics if the Ni layer is to be used as an etch resist. In addition, electroless Ni solution is inexpensive in comparison with other common plating solutions, such as silver and gold. As a medium for laser writing, it is desirable to achieve both strong adhesion of Ni to glass and a sufficiently thick layer of Ni to absorb efficiently the incident laser light. Although the thickness of the plated Ni increases with the time for which the

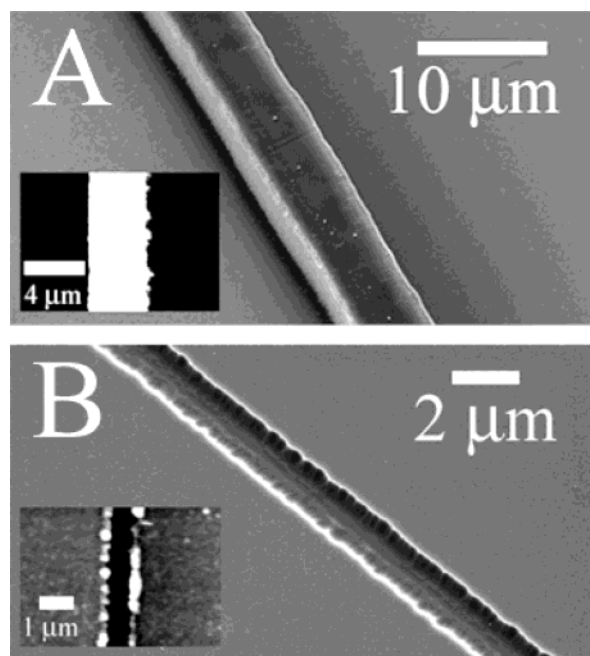


Figure 4. (A) SEM image of the SU-8 10 negative photoresist patterned on Si with contact photolithography; the inset is a bright-field image of the corresponding Ni mask. (B) SEM of an etched channel in glass using the patterned Ni layer as an etch mask; the inset is an AFM image of the corresponding Ni mask on glass prior to HF etching.

glass is immersed in the electroless plating solution, an immersion period that is too long (>25 s at 80 °C) tends to result in poor adhesion and cause the plated Ni film to flake away in subsequent rinsing steps.

The electrolessly deposited thin Ni film is roughly 30 nm in thickness and is uniform under examination with scanning electron microscopy (SEM), but this layer contains many nanometer-sized “holes” or spaces among the Ni grains (Figure 3A), which make it unsuitable to use either as an etch mask or as a photomask. To overcome this drawback, we first annealed the electrolessly plated Ni layer under a N₂ atmosphere at ~400 °C for an hour. This annealing step decreases significantly the number and size of the holes, but most importantly, it increases dramatically the adhesion strength of the Ni layer to the underlying glass surface. When compared with the electrolessly plated Ni, the annealed Ni is visually distinct under SEM (Figure 3A,B) and is characterized by a much reduced (by ~80%) electrical resistivity.

This enhanced conductivity of the electrolessly deposited Ni expedites the addition of an electrolytically plated layer of Ni, upon the addition of which the Ni layer becomes tightly packed (~200–300 nm thick) (Figure 3C) and is suitable for use as a protective layer in HF etching and as a photomask. Caution must be exercised, however, so as not to overplate the electrolytic layer, as overplating

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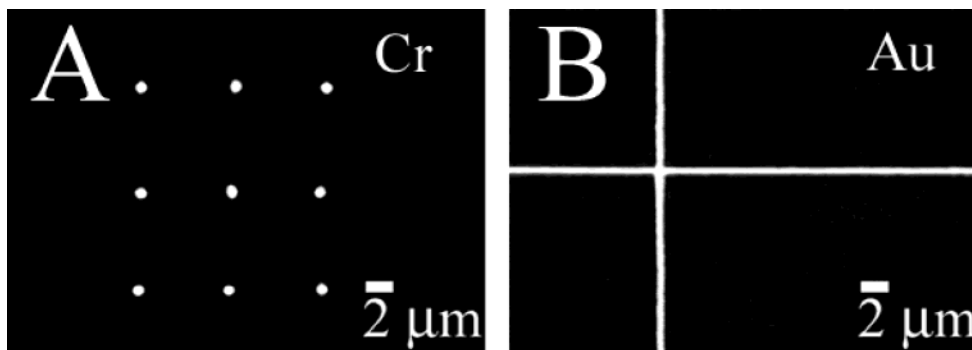


Figure 5. (A) Bright-field image of an array of 3×3 circles written in a commercially available chrome blank with the pulsed N_2 laser (35 nJ immediately prior to objective). (B) Bright-field image of a T-channel written with an Ar^+ laser (550 mW immediately prior to the objective) on gold deposited by sputtering.

can cause closure of the written features and may generate sufficient stress to lift off the Ni film.⁵² The strength of this electroless deposition procedure is the low cost and ease with which Ni masks can be generated in the laboratory environment without access to clean rooms and expensive gas-phase deposition equipment, such as evaporators and sputters.

Pattern Transfer. We used the patterned electrolytic Ni film as a photomask for the fabrication of bas-relief structures on silicon with a negative photoresist, SU-8 10. The inset in Figure 4A shows a $4 \mu\text{m}$ line we wrote with a YAG laser. For smaller feature sizes ($<4 \mu\text{m}$), the adhesion of SU-8 to silicon becomes problematic as the contact area between SU-8 and the underlying surface is reduced. Figure 4A also shows broadening of the feature size (from 4 to $6 \mu\text{m}$) in the transfer of the pattern from photomask to resist. This broadening occurred mostly during the UV exposure and subsequent baking of the resist. Despite the limitations of SU-8 photoresist, we believe this demonstration and characterization are important because of the wide-spread usage of SU-8 in rapid prototyping and in the fabrication of polymer-based microfluidic devices.

Smaller features were obtained when we used the electrolytically plated Ni directly as an etch mask for the patterned etching of glass with HF (Figure 4B). Broadening can also be observed in this pattern transfer, in which the $0.9 \mu\text{m}$ feature in the Ni mask led to a $1.5 \mu\text{m}$ etched feature in glass. This broadening originates from the isotropic nature of HF etching and the resultant undercutting of the Ni mask. This drawback of HF etching may be overcome with methods of dry etching, such as regular or deep reactive ion etching.

The feature sizes obtained with direct laser writing are significantly smaller than can be obtained with the transparency masks commonly used in rapid prototyping. While pattern transfer is carried out in parallel, the feature in the Ni mask has to be written in a serial fashion, similar to e-beam writing. As is the case for both techniques, this serial nature of the writing process means complex patterns will require proportionally more time to be produced. Here we demonstrated the writing of simple patterns with manual translation of the microscope stage, but for complex patterns, a computer-driven, high-resolution translation stage will be required. In these cases, the resolution and fidelity of the written features will also depend on the precision and stability of the translation stage.

Laser Writing of Chrome Blanks and Sputtered Gold Film. In addition to the use of Ni mask, we explored the possibility of writing directly to commercially available

blank metal masks. Figure 5A shows a 3×3 array of submicrometer holes written in 800 nm thick chrome, a pattern that may be used for creating patterned surface chemistry in the study of cell adhesion and growth.³ Figure 5B shows a T-channel written in sputtered Au film, a common geometry used for electrokinetic injection of analytes followed by capillary electrophoresis separations. While the chrome blank was purchased, we prepared the Au blank by sputtering Au on a cleaned glass surface for 10 min. Both metal masks can be used as-is in direct laser writing without further preparation. Because this method only requires a laser and a high NA objective, equipment that is available in most microscopy and optics labs, it is particularly useful for producing simple patterns with small feature sizes. Despite the convenience of using commercially available metal-coated substrates for producing photomasks, they may not be a suitable substrate for the final microdevice because of their available dimensions and cost. Commercially purchased chrome blanks, for example, tend to be thick and may not be compatible with optical applications that require short working distances. In such cases, the use of electroless and electrolytic deposition of thin metal films (which is a simple procedure to implement in a chemistry lab) as an etch mask for creating directly the final microdevice may prove to be more suitable and flexible.

Conclusion

We believe this technique provides a facile, rapid, and economical alternative to e-beam lithography for the fabrication of small microchannels or other features ($<5 \mu\text{m}$), a size range that is inaccessible to most current methods of rapid prototyping. Although we used our existing laser and optical systems to implement this technique, which utilizes moderate-cost lasers and optics, low-cost diode lasers and objectives can be easily constructed and would offer comparable performance. Unlike many rapid prototyping methods, this approach can be applied equally well to glass and other "hard" substrates when the patterned metal mask is used directly for etching, as well as to polymeric and "soft" materials when the patterned metal layer is used as a photomask for lithography. The flexibility offered by this approach should provide a versatile platform for the fabrication of integrated micro- and nanofluidic systems and MEMS devices.

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