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Prototyping of Masks, Masters, and Stamps/Molds for Soft Lithography Using an Office Printer and Photographic Reduction

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This paper describes a practical method for the fabrication of photomasks, masters, and stamps/molds used in soft lithography that minimizes the need for specialized equipment. In this method, CAD files are first printed onto paper using an office printer with resolution of 600 dots/in. Photographic reduction of these printed patterns transfers the images onto 35-mm film or microfiche. These photographic films can be used, after development, as photomasks in 1:1 contact photolithography. With the resulting photoresist masters, it is straightforward to fabricate poly(dimethylsiloxane) (PDMS) stamps/molds for soft lithography. This process can generate microstructures as small as 15 μm; the overall time to go from CAD file to PDMS stamp is 4−24 h. Although access to equipment—spin coater and ultraviolet exposure tool—normally found in the clean room is still required, the cost of the photomask itself is small, and the time required to go from concept to device is short. A comparison between this method and all other methods that generate film-type photomasks has been performed using test patterns of lines, squares, and circles. Three microstructures have also been fabricated to demonstrate the utility of this method in practical applications.

This paper describes a method for patterning photoresist that uses desktop printing and photographic reduction to make photomasks that can be used in 1:1 contact photolithography to fabricate the masters and stamps/molds used in soft lithography. This method allows the generation of features with lateral dimensions as small as 15 μm, and with an edge roughness[1] of ∼1.5 μm. It offers a route to microstructures having dimensions useful in microfluidics,[2] microelectromechanical systems (MEMS),[3,4] and microanalytical systems.[5] It is especially appropriate for use in chemical and biochemical laboratories that do not have access to the facilities used to make photomasks to the standard of microelectronics,[6] because it bypasses the requirement for chrome masks. It also obviates the need for more readily available but still specialized devices such as high-resolution printers.[7] The work reported here does not represent new science: it intentionally focused on the exploitation of the simplest and most broadly available techniques that we could identify for forming patterns with features useful in functional microstructures. These straightforward methods, when combined with soft lithography,[8] extend the capability for microfabrication of laboratories that have no (or limited) access to the facilities required to fabricate chrome masks or to carry out high-resolution printing.

The objective of this work is to develop and compare methods for generating microstructures using facilities readily and inexpensively available to chemistry and biology laboratories. We focused on conventional 35-mm cameras and commercial microfiche makers, with the objective of defining the minimum feature sizes that could be demonstrated by combining images generated using these systems with soft lithography. The conventional method for making photomasks for microfabrication is to design the pattern of interest using a CAD system, use this design to generate a chrome mask using specialized photolithographic or e-beam tools, and then proceed with photolithography.[6] This procedure works well and is the basis for the microelectronics industry. Its drawback is that the generation of chrome masks requires special facilities and is generally slow and expensive. We and others have demonstrated that a high-resolution printer (3387 dots/in. (dpi); Linotype-Hell Co.) can quickly and inexpensively generate 20-μm patterns with tolerable edge roughness and 50-μm patterns with good quality.[7,9] Although this capability is adequate for many applications, there are circumstances in which even this high-resolution printing, while readily accessible commercially, may be unavailable or inconvenient or in which the ability to fabricate features smaller than 50 μm would be useful.

We have shown that the combination of high-resolution printing and photographic reduction onto microfiche can generate masks, masters, and stamps/molds for soft lithography with feature sizes as small as 10 μm.[10] In this work, we started with routine desktop printing, instead of high-resolution printing, to

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(1) The edge roughness of the lines is defined as the maximal variation of the lateral dimensions of the lines.

(2) Kopp, M. U.; Mello, A. J. D.; Manz, A. *Science* **1998**, *280*, 1046.
(3) Kovacs, G.; Petersen, K.; Albin, M. *Anal. Chem.* **1996**, *68*, 407.
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(6) Elliott, D. J. *Integrated Circuit Mask Technology*; McGraw-Hill: New York, 1985.
(7) Qin, D.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 917.
(8) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.

(9) We have also tried printers with 5000 dpi resolution, but the resolution we obtained was indistinguishable from that generated using a 3387 dpi printer.

(10) Deng, T.; Tien, J.; Xu, B.; Whitesides, G. M. *Langmuir* **1999**, *15*, 6575.

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generate patterns, and then reduced these patterns photographically using 35-mm cameras or microfiche makers. The resulting, reduced, patterns in black and white photographic film were used as photomasks in the fabrication of poly(dimethylsiloxane) (PDMS) stamps/molds for soft lithography. Here, we first compared this method—desktop printing combined with photographic reduction—with other methods that produce film-type photomasks. We then fabricated several microstructures to demonstrate the practical application of this method. By combining CAD, printing using an office printer, size reduction by photography, and 1:1 contact photolithography, we demonstrate a practical method for the generation of master structures for soft lithography with features down to 15 μm. The area of the pattern that can be generated by this procedure is usually limited by the format of the camera and film to 35 $\times$ 22 mm^2; larger film formats are, of course, available, but we have not explored them. Further reduction in feature size will be possible but will require better optics in the camera, slower films, and greater care in the photography than we have used.[11]

EXPERIMENTAL SECTION

Materials. Silver (>99.99%), chromium (>99.99%), titanium (>99.99%), sodium thiosulfate (>99.5%), potassium ferrocyanide (>99.9%), potassium ferricyanide (>99.9%), hexadecanethiol (>99%), trichloroethylene (TCE), acetone, methanol, ethanol, propylene glycol methyl ether acetate (PGMEA), and hexamethyldisilazane (HMDS) were obtained from Aldrich. Poly(dimethylsiloxane) (Sylgard 184) was ordered from Dow Corning. Microposit 1813 photoresist (Shipley Co., Inc., Malborough, MA), and Microposit 351 developer (Shipley Co., Inc.) were used as received. Thin films of Ag (~150 nm) were prepared by e-beam evaporation onto silicon/glass primed with Ti (~5 nm).

Fabrication of Patterns onto 35-mm Film and Microfiche. The test patterns were designed in Freehand files. An office printer with resolution of 600 dpi printed the images onto paper. We used a Nickon N800s camera or a Polaroid black and white slide maker (model IPC-2) to reduce the printed images photographically onto 35-mm film. The films we used were Kodak technical pan film and Polaroid black and white instant film. To transfer patterns onto microfiche, we sent the printed images to New England Micrographics[12] and they optically reduced the images onto microfiche (Fuji Super HR, ~70 μm thick) with 25$\times$ reduction.

Use of 35-mm Film and Microfiche as Photomasks. Substrates were cleaned in TCE, acetone, and methanol using sonication, followed by drying in an oven at 180 °C for 10 min. We primed the substrates with HMDS and then spin-coated[13] the substrates with 1813 photoresist at 4000 rpm for 40 s. The photoresist-coated substrates were baked for 3.5 min on a 105 °C hot plate and exposed with a Karl Suss MJB3 contact aligner for 20 s (10 mJ$\cdot$cm$^{-2}\cdot$s^{-1} at 405 nm) for a 35-mm film photomask and 15 s for a microfiche photomask. The photoresist was developed for 1 min in dilute Microposit 351 developer (351 developer: H_2O = 1:5 v/v).

Use of Patterns Generated from 35-mm Film and Microfiche in Soft Lithography. Photoresist patterns fabricated using 35-mm film and microfiche as photomasks were used as masters

(11) Keller, K. *Science and Technology of Photography*; VCH: Weinheim, Germany, 1993.
(12) New England Micrographics, Manchester, NH.
(13) Headway Spinner, model PWM 101; Headway Research, Inc., Garland, TX.

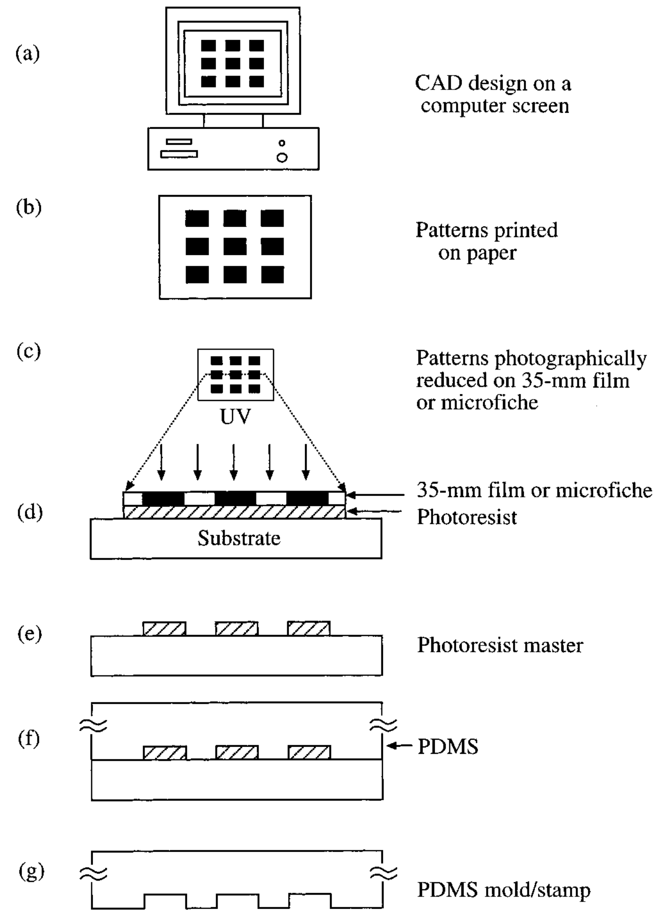

Figure 1. Outline of the processes used to fabricate photographically reduced photomasks and PDMS molds/stamps. (a) Patterns are designed using Freehand software; (b) these patterns are printed on paper using a 600 dpi office printer; (c) the printed image is reduced onto 35-mm film or microfiche using photographic reduction (~8$\times$ reduction for 35-mm film; ~25$\times$ reduction for microfiche); (d) the reduced photographic image serves as the photomask in 1:1 contact photolithography using positive photoresist (PR); (e) the exposed PR is developed; (f) PDMS is cast onto the bas-relief pattern in PR to make the PDMS mold/stamp; (g) PDMS mold/stamp is cured, and separated from the PR master.

to generate PDMS molds/stamps for soft lithography.[14] To carry out microcontact printing, substrates (thin Ag films evaporated on Ti-primed Si/SiO_2 wafers) and PDMS stamps were rinsed with ethanol and dried in a stream of N_2. We then applied a solution of hexadecanethiol (~2 mM in ethanol) with cotton Q-Tips to the surface of the PDMS stamp, dried the stamp in a stream of N_2 for ~30 s, and brought the stamp into contact with the surface of Ag for 5−10 s. Films of Ag that were patterned with SAMs were etched in an aqueous solution containing 0.1 M $Na_2S_2O_3$ /0.01 M $K_3Fe(CN)_6$/0.001 M $K_4Fe(CN)_6$.

Fabrication of Microcoils on Glass Capillaries Using Microcontact Printing. Glass capillaries with diameter of ~2 mm were coated with Ag (~50 nm)/Ti (~5 nm) using two rotation stages in e-beam evaporation.[15] During microcontact printing, we brought the glass capillaries into contact with the surface of the PDMS stamp and rolled the capillaries across the surface of the

(14) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(15) Jackman, R.; Wilbur, J.; Whitesides, G. M. *Science* **1995**, *269*, 664.

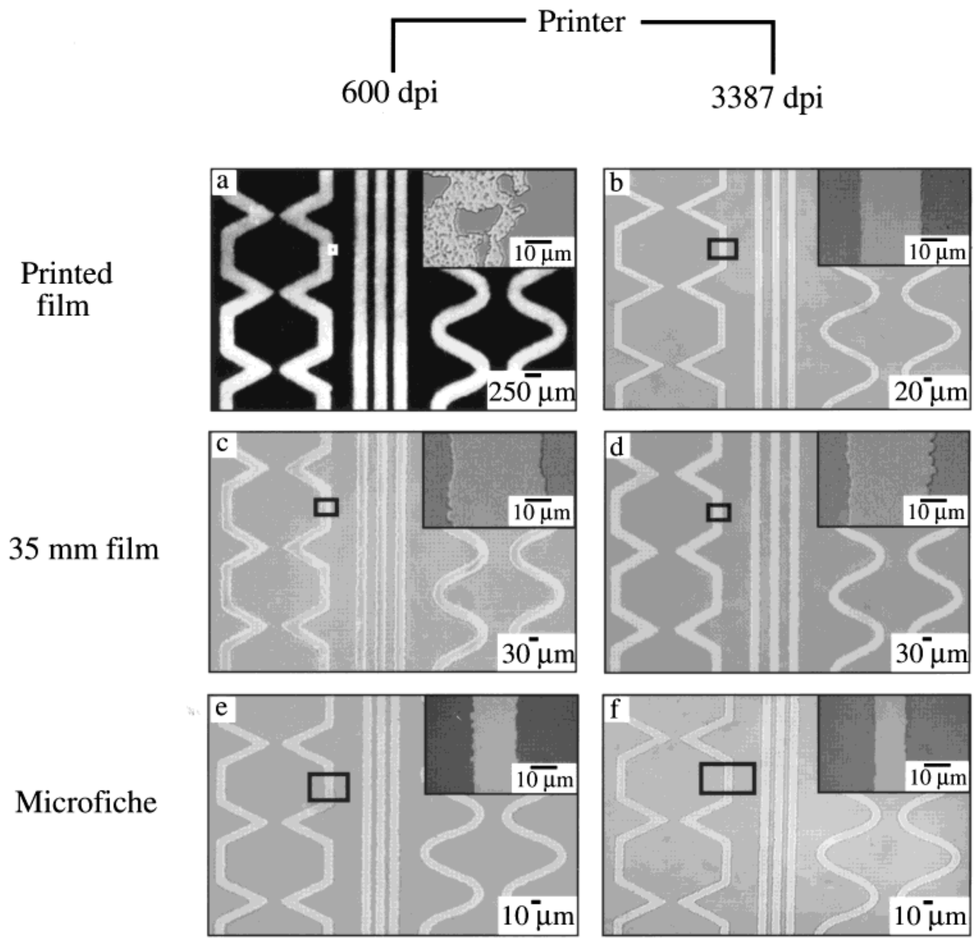

Figure 2. Thinnest silver lines (~150 nm thick) fabricated using microcontact printing, etching, and PDMS stamps prepared using different types of photomasks. The insets show magnified views of sections of lines at a common scale. Photomasks used to generate the silver patterns: (a) polymeric film printed by a 600 dpi office printer (the difference of the contrast between (a) and (b−f) was due to the different microscopes we used during the collection of the images); (b) polymeric film printed by a 3387 dpi high-resolution printer; (c) 35-mm film made by photographically reducing patterns printed with the 600 dpi office printer (the line width of the lines in the printed pattern was ~240 μm); (d) 35-mm film made by photographically reducing patterns printed with the 3387 dpi printer (the line width of the lines in the printed pattern was ~240 μm); (e) microfiche made by photographically reducing patterns printed with the 600 dpi office printer (the line width of the lines in the printed pattern was ~375 μm); (f) microfiche made by photographically reducing patterns printed with the 3387 dpi printer (the line width of the lines in the printed pattern was ~250 μm).

stamp.[15] The nonpatterned area of Ag film was etched away in an aqueous solution containing 0.1 M $Na_2S_2O_3$/0.01 M $K_3Fe(CN)_6$/0.001 M $K_4Fe(CN)_6$. The continuity of the patterned microcoil was examined by passing a current through the microcoil.

RESULTS AND DISCUSSION

Methods. Figure 1 illustrates the procedure for making the 35-mm film or microfiche images used as photomasks, and the PDMS molds/stamps. Parts a−c of Figure 1 outline the procedure for making 35-mm film or microfiche photomasks. It includes one step of computer design, one step of desktop printing, and one step of photographic reduction. Parts d−f of Figure 1 describe the fabrication of the PDMS mold/stamp using the 35-mm film or microfiche as the photomask; this mold/stamp can be used in soft lithographic techniques—micromolding in capillaries (MIMIC),[16] microtransfer molding (μTM),[17] and microcontact printing (μCP).[18]

(16) Kim, E.; Xia, Y.; Whitesides, G. M. *Nature* **1995**, *376*, 581.
(17) Zhao, X.-M.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 837.
(18) Tien, J.; Xia, Y.; Whitesides, G. M. In *Microcontact Printing of SAMs*; Ulman, A., Ed.; Academic Press: London, U.K., 1998; Vol. 24.

Comparisons of Methods Used To Make Film-Type Photomasks. We have compared six different procedures that generate film-type photomasks: (i) desktop printing (600 dpi); (ii) high-resolution printing (3387 dpi); (iii) desktop printing combined with photographic reduction onto 35-mm film; (iv) desktop printing combined with photographic reduction onto microfiche; (v) high-resolution printing combined with photographic reduction onto 35-mm film; (vi) high-resolution printing combined with photographic reduction onto microfiche. Figure 2 shows one test pattern that we used to evaluate the quality of the patterns produced by the different methods. For each, a PDMS stamp was produced using the procedure in Figure 1. This stamp was used in μCP, and the nonpatterned area was removed by chemical etching. The figure shows the thinnest silver lines[19] generated using each procedure on a Si/SiO_2 wafer. The difference of the contrast between (a) and (b−f) was due to the different

(19) The thinnest lines are continuous and have line widths that vary no more than 10% from the designed line widths.

Table 1. Dimensions and Edge Roughness (All μM) of the Smallest Features Generated Using Each Procedure

	office printer(600 dpi)			high-resolution printer (3387 dpi)		
	none[a]	35-mm film[b]	microfiche[c]	none	35-mm film	microfiche
smallest lines[d]	250	30	15	20	30	10
edge roughness[d]	40	3	1.5	1	3	1
smallest squares[d]	320	67	20	80	33	20
smallest circles[d]	320	67	20	80	33	20

[a] The designed pattern was printed onto polymeric film and the polymeric film was used as the photomask. There is no photographic reduction of the printed pattern. [b]The printed pattern was photographically reduced onto 35-mm film, and the 35-mm film was used as the photomask. [c]The printed pattern was photographically reduced onto microfiche, and the microfiche was used as the photomask. [d]See text for the definitions.

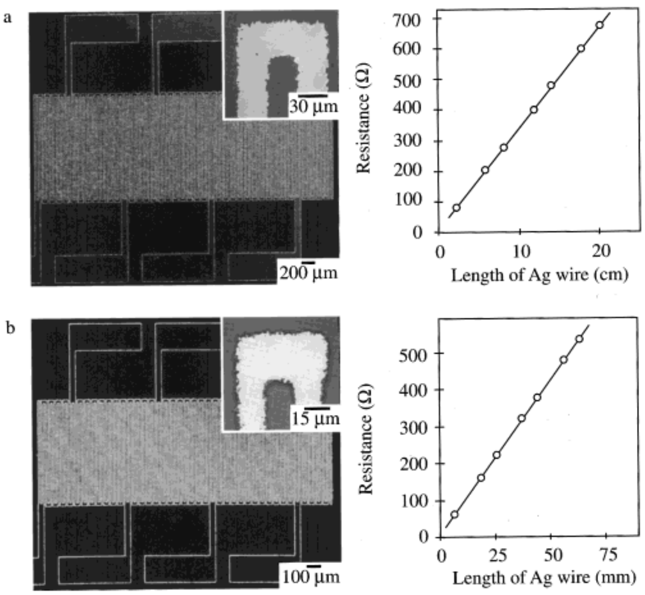

Figure 3. Serpentine silver wires generated using microcontact printing and etching and the resistance−length data measured for these wires. The photomasks used in the fabrication of PDMS stamp were (a) 35-mm film and (b) microfiche. Both were generated by photographically reducing the patterns printed with the 600 dpi office printer. The silver wire in (a) was ~30 μm wide, in (b) ~15 μm wide, and both were ~150 nm thick. The resistivities for both wires were ~2 × 10^{-8} Ω·m.

microscopes we used during the collection of the images.[20] The line width and the edge roughness[1] of the thinnest silver lines are summarized in Table 1. The thinnest lines that can be generated by printers are mainly limited by the discrete step and pixel sizes of the printers, and those generated on 35-mm film and microfiche are limited by the optical lenses used in the photographic reduction processes.

In fabricating devices, patterns more complicated than simple lines are needed. We also tested the performance of the photomasks generated using these procedures and a test pattern of squares and circles. The smallest dimensions[21] achieved by each method were summarized in Table 1. The results show that the failure of printing methods was mainly due to the digitization of the images set by the step sizes of the printers. The photographic reduction process is an analog process, and smaller dimensions were produced using it than using the printing methods.

(20) Because of the different scales of the patterns, we had to use different microscopes.

(21) The lateral dimensions of the smallest squares and circles vary no more than 10% from the designed dimensions.

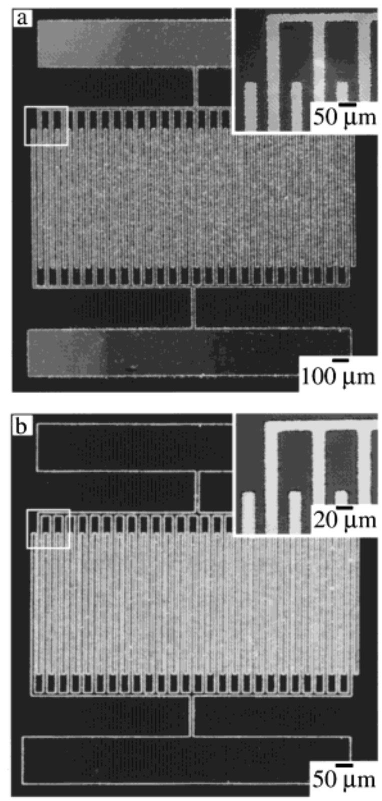

Figure 4. Interdigitated electrodes fabricated using microcontact printing. The photomasks used in the fabrication of PDMS stamp were (a) 35-mm film and (b) microfiche. Both were generated by photographically reducing the patterns printed with the 600 dpi office printer. The finger of the electrodes in (a) was ~30 μm wide, 2.5 mm long, and 150 nm thick. The finger in (b) was ~15 μm wide, 0.8 mm long, and 150 nm thick.

Fabrication of Microstructures Using Desktop Printing and Photographic Reduction. We fabricated several test microstructures to demonstrate the performance of photomasks generated by photographically reducing patterns printed with a 600 dpi office printer.

Serpentine Wires. Figure 3 shows optical micrographs of serpentine wires generated using microcontact printing and etching; conductivities measured with these wires demonstrate their electrical continuity. We combined desktop printing and photographic reduction onto 35-mm film for (a) and onto microfiche for (b), to make photomasks and PDMS stamps. The silver wire in (a) was ~30 μm wide, in (b) ~15 μm wide, and both were ~150 nm thick. The resistivities for both wires were ~2 × 10^{-8} Ω·m (the value for bulk silver is 1.6 × 10^{-8} Ω·m[22]).

Table 2. Comparison of Methods of Making Chrome Masks and Methods Using an Office Printer and a High-Resolution Printer

	chrome masks	office printer (600 dpi): none	office printer (600 dpi): 35 mm	office printer (600 dpi): μfiche	high-resolution printer (3387 dpi): none	high-resolution printer (3387 dpi): 35 mm	high-resolution printer (3387 dpi): μfiche
thinnest lines (μm)	<1[a]	250	30	15	20	30	10
edge roughness (μm)	<0.1[a]	40	3	1.5	1	3	1
advantages	high resolution	inexpensive (<\$1/in.^{2}), easy access, and short turnaround time (~4 h[b] or 1 day[c])			inexpensive (<\$1/in.^{2}), and short turnaround time (~1 day)		
disadvantages	expensive (>\$100/in.^{2}) and long turn-around time (in the order of weeks)[a]	medium resolution			medium resolution; less accessible than office printer		
applications	microelectronics	biological and chemical patterning and fabrication			biological and chemical patterning and fabrication		

[a] The exact values depend on the processes (using light or electron beam) used.[24] [b]Using 35-mm film. [c]Using microfiche.

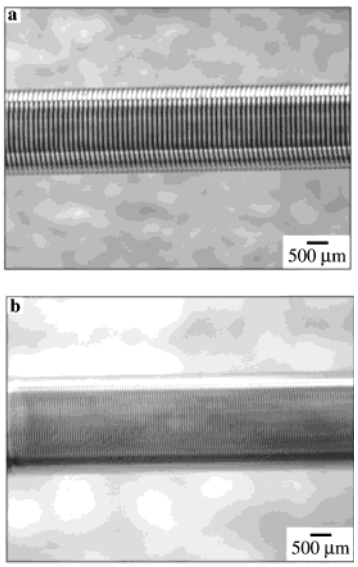

Figure 5. Continuous silver microcoils (~50 nm thick) fabricated using μCP on glass capillaries with diameter of ~2 mm. The line width of the microcoil and the space between two neighboring turns in (a) were both ~30 μm and in (b) were both ~15 μm. The photomask used in the generation of PDMS stamp was 35-mm film for (a) and microfiche for (b).

Interdigitated Electrodes. Using the same procedures, we also fabricated interdigitated electrodes of types that are representative of those used in microanalytical chemistry, cell biology, and MEMS (Figure 4).

Microcoils. Figure 5 shows continuous silver (~50 nm thick) microcoils patterned on glass capillaries. Using the procedure developed by Jackman et al.,[15] we transferred patterns onto glass capillaries covered with a silver film from a PDMS stamp using μCP; the printed pattern was converted to a coil by etching. The line width of the microcoil and the space between two neighboring turns in (a) were both ~30 μm and in (b) were both ~15 μm. The photomask used in the fabrication of the PDMS stamp for (a) was 35-mm film and for (b) was microfiche.

CONCLUSIONS

In summary, we have demonstrated a practical strategy—photographically reducing the patterns printed by an office printer (600 dpi)—for generating photomasks to be used in fabrication of masters and stamps/molds for soft lithography. This method uses only routinely available facilities—office printers and cameras—and generates photomasks having dimensions of ≥15 μm; this approach is accessible in virtually every laboratory. To make the masters and stamps/molds required for soft lithography, we have continued to use the photoresist spinners and UV exposure tools normally used in photolithographic microfabrications. We have thus not yet demonstrated a procedure to prepare PDMS stamps/molds with no access to cleanroom or specialized facilities, but the work here demonstrates a simple method of making photomasks that should be very widely accessible.[23]

Table 2 compares this method with the conventional methods of making chrome masks, and with methods using high-resolution printing. This method generates microstructures with medium resolution quickly (less than 24 h) and inexpensively. It does not have the resolution to be suitable for the fabrication of complex microelectronic devices, but it should be well suited for many applications in biology and chemistry for laboratories that have greater tolerance of edge roughness than does fabrication of microelectronic devices.

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(22) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: New York, 1999.

(23) We are continuing to develop procedures that minimize the equipment used in making stamps/molds.

(24) Advance Reproductions Corp.,North Andover, MA; http://www.advancere-pro.com.