Microfabrication of two layer structures of electrically isolated wires using self-assembly to guide the deposition of insulating organic polymer

Andrew J. Black [a], Paul F. Nealey [b], Joseph H. Thywissen [c], Mandar Deshpande [d], Nada El-Zein [d], George N. Maracas [d], Mara Prentiss [c], George M. Whitesides [a,*]

[a] *Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street Cambridge, MA 02138-2902, USA*
[b] *Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706, USA*
[c] *Department of Physics, Harvard University, Cambridge, MA 02138, USA*
[d] *Motorola Inc. PCRL, 2100 E. Elliot Road, Tempe, AZ 85284, USA*

Abstract

The fabrication of two layer structures of electrically isolated wire — crossed wire structures and a surface coil inductor — is described. The fabrication process utilizes the tools of soft lithography and incorporates two levels of self-assembly. The use of microcontact printing and patterned self-assembly of liquid polymers removes the need for registration of the insulating layer with the underlying layer as required in conventional lithography techniques. The performance characteristics of the surface coil inductor are measured and closely resemble those predicted by theory. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Soft lithography; Self-assembly; μCP; Surface coil inductor

1. Introduction

The ability to fabricate multilevel structures of electrically isolated wires is essential to most micro systems that use electricity to compute, store information, actuate, or sense [1–5]. The fabrication of such systems requires several different layers of pattern transfer, with each of these layers correctly registered or aligned. The requirement for registration adds to the complexity of the fabrication process. Precise optical alignment of patterns becomes increasingly more difficult as the smallest aligned features become on the order of nanometers.

We have been interested in developing non-photolithographic processes for the fabrication of structures with feature sizes between 1 and 100 μm. These processes

(which we call, collectively, "soft lithography" [6]) have in common an elastomeric element that serves to transfer the pattern. Soft lithography is useful for rapid prototyping [7] of simple microstructures, non-planar microstructures, and microstructures containing materials not commonly used in microelectronics; examples include MEMS [8], optical waveguides [9], stents [10], microcoils [11] and microtransformers [12], and simple microelectronic devices [13].

This paper describes the combination of microcontact printing (μCP) [14] with patterned self-assembly of liquid polymers [15–17] to create crossed wire structures with electrically isolated wires 10–100 μm in width, and a functional device — a surface coil inductor — with wires 100 μm in width. Because the patterned SAM directs the formation of the insulating layer — the polymer — by thermodynamic control, the combination of techniques eliminates two steps of registration that would be required to deposit/pattern an insulating layer and vias in conventional semiconductor lithography. This method extends the general capabilities of μCP to make accessible multilayer

* Corresponding author. Tel.: +1-617-495-9430; Fax: +1-617-495-9857.
E-mail address: gwhitesides@gmwgroup.harvard.edu
(G.M. Whitesides).

structures, which are necessary for fabricating complex microsystems.

The strategy for multilevel fabrication is founded on two types of self-assembly: (i) formation of patterned SAMs by μCP (using molecular scale self-assembly), followed by (ii) preferential wetting of a prepolymer on the hydrophilic regions of the monolayer (using meso- or macroscopic self-assembly). After curing, the patterned polymer initially acts as a resist for etching the underlying metal layer and subsequently serves as the electrically insulating material between the crossing lines. Potentially, the polymer could perform additional useful functions — e.g., dielectrics for arrays of capacitors.

2. Experimental

Hexadecanethiol (HDT) and 1,3-phenylenediamine were obtained from Aldrich and distilled prior to use. A diepoxide — m-bisphenol diglycidyl ether — (DER 332) was a research sample from Dow Chemical and used without further purification. $HS(CH_2)_{15}CO_2H$ was prepared by the procedure reported elsewhere [18]. Glass optical flats (1 in. diameter) (Edmund Scientific) were cleaned with piranha solution (7:3 mixture of concentrated sulfuric acid/30% H_2O_2) for 15 min at 70°C, and washed with deionized water and absolute ethanol.

CAUTION: *Piranha solution should be handled with care. It should not be allowed to contact significant quantities of oxidizable organic materials.*

The freshly cleaned flats were coated with 5 nm of Cr (1 Å/s), to promote adhesion, and then with 250 nm of Au (2 Å/s) using an electron beam evaporator (base pressure of 1×10^{-7} Torr). Stamps were prepared from poly(dimethylsiloxane) (PDMS, Sylgard 184 Elastomer, Dow Corning) as described previously [14] using patterns of 10-μm-thick positive photoresist (Shipley 1822) as masters. The masters were made using photomasks prepared by rapid prototyping [7].

In a typical procedure, a stamp was inked with $HS(CH_2)_{15}CO_2H$ by applying a 10 mM solution of the thiol in ethanol to the surface of the stamp with a cotton swab. The stamp was dried in a stream of nitrogen for 20–30 s, and placed by hand on the gold-coated flat. After 10 s, the stamp was removed, and the window washed with a 10 mM solution of HDT in ethanol until dewetting occurred (a few seconds), then washed with ethanol and blown dry in a stream of nitrogen.

2.1. Assembly of polymer by preferential wetting

Polymers were assembled either by dip-coating or spin-coating. For dip-coating, the substrates were immersed in a pre-polymer — either a UV-curable prepolymer of a polyurethane (NOA 81, Norland Products, New Brunswick, NJ), a thermally cured epoxy (equimolar quantities of 1,3-phenylenediamine and m-bisphenol diglycidyl ether mixed together at 60°C) or photoresist (SU-8 5, Microlithography Chemical, Newton, MA.) — and withdrawn from the polymer at a rate of 2.5 mm/min with the aid of a syringe pump. Polyurethane was cured under long-wavelength UV light for 5 min, and the epoxy was cured at 60°C for 20 h. Spin-coating was performed with either polyurethane (10% by volume in acetone) or SU-8 5 photoresist (50% by volume in propylene glycol methyl ether acetate) at 2000 rpm for 60 s. The polyurethane was heated at 60°C for 30 min to allow the polymer to fully dewet from the hydrophobic regions of the pattern, then cured as described previously. The SU-8 5 is cured at 60° for 15 min, then at 110° for 15 min.

Unprotected gold was removed in an iodine-based gold etch (Transene, Rowley MA) after 2 min, but etching was continued for a total time of 10 min to underetch the Au. After rinsing with water, the substrate was immersed in a Cr etch consisting of cerric ammonium nitrate and nitric acid (Cr etchant 1020, Transene, Rowley, MA) for 40 s to remove the uncovered regions of the Cr adhesion layer from the substrates.

The surface coil inductor was made by fabricating the lead first. Before the second layer of fabrication, however, the polymer was removed from the end of the lead with chromic acid so that the inside pad of the spiral would connect to the lead.

2.2. Assembly of second layer of features

Replicating the previous series of steps, chromium (5 nm) and gold (250 nm) were evaporated over the top of the first layer of features. The gold surface was stamped with finger pressure with $HS(CH_2)_{15}CO_2H$ until wetting of the pattern was observed, then washed with HDT (10 mM in ethanol) and rinsed with pure ethanol. For the crossed lines, the second layer was stamped orthogonally to the underlying lines, and for the surface coil inductor, the second layer (typically the spiral) was printed such that the pad in the center of the spiral covered the exposed end of the lead. Gold and chromium were etched as previously for 120 s and 40 s, respectively.

The polymer film covering the contact pads on the ends of wires was dissolved in chromic acid. Excess acid was washed away with water and the samples blown dry. An HP4145A semiconductor parameter analyzer was used to measure current–voltage characteristics of these structures. Lines were addressed using micromanipulators and tungsten probes. An HP4263A LCR meter was used to measure the impedance of the surface coil inductor.

3. Results and discussion

Fig. 1 describes the steps used to fabricate arrays of crossed lines (Fig. 1a) and surface coil inductors (Fig. 1b).
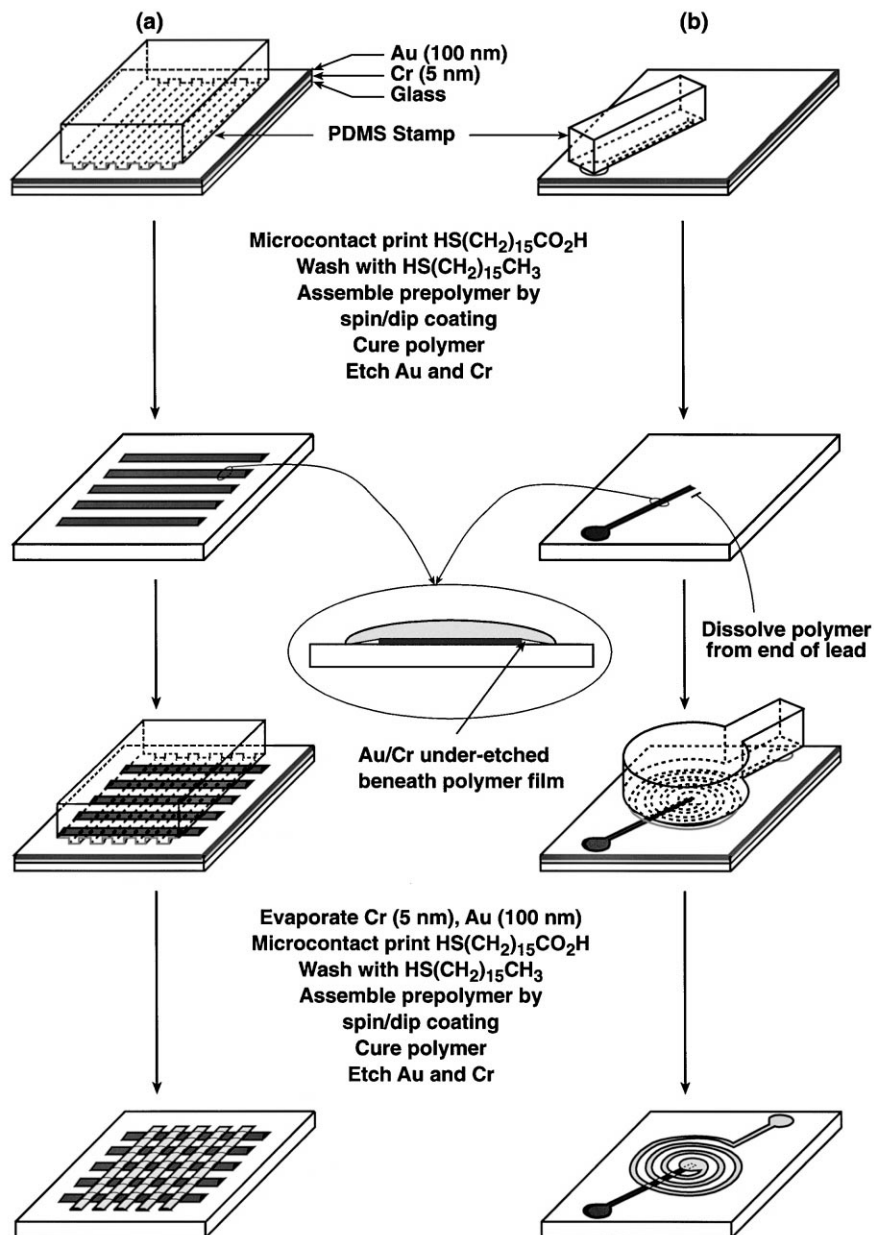
Fig. 1. Schematic representation of the procedure used to fabricate arrays of (a) crossed wires and (b) surface coil inductors. The procedures are based on two kinds of self-assembly; the formation of patterned SAMs using μCP, followed by the selective deposition of liquid pre-polymer on the hydrophilic regions of the SAM either by dip-coating or spin-coating.

We patterned SAMs by μCP of $HS(CH_2)_{15}CO_2H$ on a Au film coated on glass, then washing with $HS(CH_2)_{15}CH_3$ (HDT). Polymer was deposited selectively on the hydrophilic regions of the patterns (carboxylic acid-terminated SAMs) either by dip-coating or spin-coating.

After curing, the polymer acted as the resist that protected the underlying gold from chemical etching; it was sufficiently stable to the etch that the gold was etched underneath the polymer line without damaging the polymer. The gold line was uniformly 5–10 μm less wide than the polymer coating it; this difference in width ensured that the features in the first level of fabrication were

completely covered by the polymer and were isolated electrically from the second layer of the pattern. Chromium and gold were then evaporated on top of the polymer structure and the sequence of printing, self-assembly and curing of the polymer and etching was repeated to fabricate the second, overlaying set of features. It is important to note that we fabricated these structures on a benchtop in an open air environment.

During the second μCP step, we applied light finger pressure to cause the elastomeric stamp to conform to the contours of the first set of features (1–2 μm thick). Qualitatively, we press on the stamp until we see it wet the

substrate between the raised features in order to give a sufficiently continuous pattern of SAM across the uneven topography of the polymer layer. Inadequate pressure did not allow the pattern of the stamp to conform to the topographically patterned substrate and resulted in discontinuous features. Extreme finger pressure compressed the stamp too much, and caused the recessed regions of the stamp, in addition to the raised regions, to contact the substrate, resulting in distorted and extraneous features. Experiments with a tared balance to quantify the force applied over the area of the stamp indicated that adequate pressures are in the range of 100–150 Pa.

Under the application of light pressure, the elastomeric stamp conformed to the surface because the surface topography of the polymer layer changed smoothly. Fabricating continuous features over structures with sharp edges or abrupt changes in topography are not possible because the stamp in the printing step cannot conform properly to the surface; poor contact between the stamp and the surface results in discontinuous deposition of the polymer. Sharp edges themselves also make continuous dewetting unfavorable. The experiments suggest that the height limit at which the stamp can conform to the topography of the substrate to produce a continuous SAM pattern is ~ 3 μm.

Fig. 2 shows an array of crossed lines fabricated using the procedure in Fig. 1a. The polymer in this structure was assembled either by spin-coating or dip-coating. For the first set of lines, the prepolymer was a thermally cured epoxy and for the second set, a UV-curable polyurethane. The epoxy adhered better to the SAM/gold surface than the polyurethane with less delamination. Stronger hydrophilic interactions with the carboxylic acid-terminated SAM may account for the stronger adhesion of the epoxy. The epoxy also provided a thinner film. The polyurethane, however, is easier to work with because it cures on UV exposure rather than on heating. The polymers maintained good adhesion without delaminating from the metal layers before and after curing. Thin polymer films (< 1 μm) are difficult to form evenly because partial dewetting at the edges occurs due to surface tension.

Fig. 2a and b show that the contour of the polymer on the upper and lower lines is curved, and that the thickness of the polymer layer changes across the width of the line. In addition to the choice of polymer, the rate at which the substrate is withdrawn from the polymer has an effect on the thickness of the film — the faster it is withdrawn, the thicker the film. The second, perpendicular metal line is also not planar, but follows the contour of the polymer covering the underlying metal line. The interference fringes at the edges of the polymer lines in the inset in Fig. 2a reflect the varying distances among surfaces in these structures.

We tested the array of crossed wires to determine the extent of electrical isolation between adjacent and crossed wires. The polymer on the contact pads at the end of the wires was dissolved in freshly prepared chromic acid. The
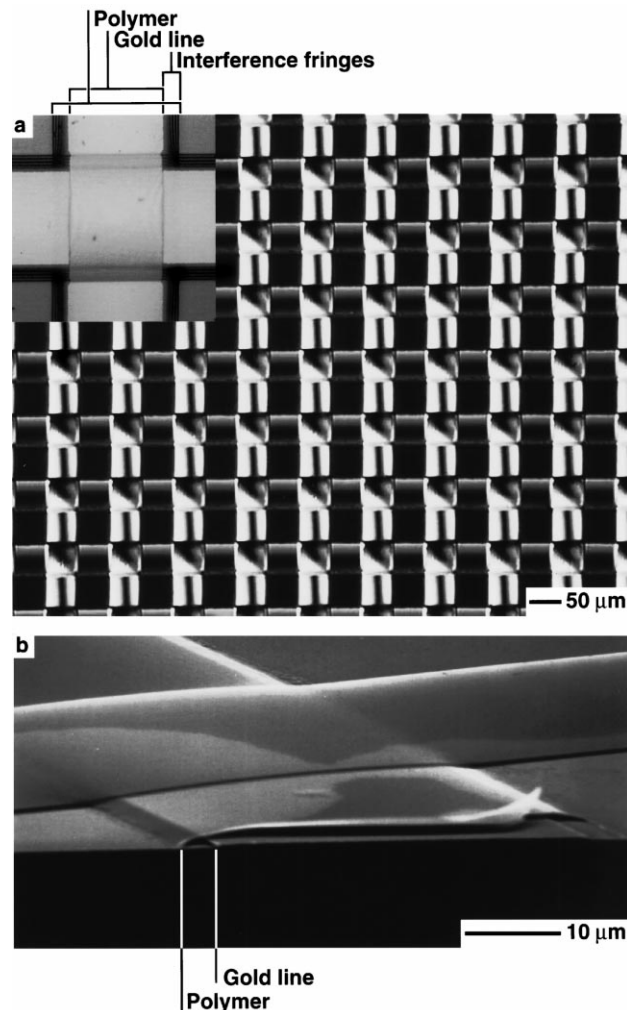

Fig. 2. (a) An optical micrograph of an array of crossed lines prepared using the scheme in Fig. 1a. The horizontal lines run underneath the vertical lines. The inset is a higher magnification picture of a crossing point of two polymer-coated gold lines. The interference fringes at the edges of the polymer are caused by the varying distances between surfaces. (b) A scanning electron micrograph of a cross-section of one of the bottom gold lines on a cleaved glass substrate. The epoxy coating extends beyond the width of the metal line, and then bends down to the substrate. The extension of the edge of the epoxy lines beyond the edge of the gold line indicates that both top and bottom lines are underetched. The polymer is peeling back slightly where the gold contact on the lower wire is exposed as a result of the cleaving. The mottled appearance of the surface is an artifact of the etching process.

exposed gold pads on each wire were then probed to determine a leakage current value for individual crossing points having dimensions of 50×50 μm^2 and 100×100 μm^2. It is important to note that the polymer chosen was not optimized during these experiments for specific electrical properties such as its dielectric constant. The leakage current between crossed wires was $\sim 10^{-10}$ A at 100 V; this value corresponds to a current density of $\sim 3 \times 10^{-6}$ A/cm^2 at 100 V. By way of comparison, the leakage current densities across 1-μm-thick Al$_2$O$_3$ and SiO$_2$ at 25°C are 1×10^{-8} A/cm^2 and 5×10^{-11} A/cm^2, respectively [4,19].

Randomly probed crossings in the same array showed a 50% variation in leakage current, although the breakdown voltage of all nodes was above 100 V. The variation is most likely due to variations in the thickness of the polymer insulating layer or to poor adhesion of the polymer to the metal lines. While the electrical properties of the individual junctions did vary, 95% of the total number of crossing junctions in the structure showed electrical isolation. Individual gold lines were continuous and had resistances between 100 and 200 Ω depending on their length. The resistance between parallel metal lines was greater than the measuring capability of the instrument, indicating excellent electrical isolation between parallel lines.

In order to demonstrate the capability of our technique to construct a functional device, we used the procedure described in Fig. 1a to fabricate a two-level structure consisting of a spiral overlaying a single lead — a surface coil inductor (Fig. 3). The lead is isolated from the rings of the spiral, but connects a pad in the center of the spiral to a contact pad outside the spiral. This surface coil inductor was made with polyurethane as the insulating layer, assembled by spin-coating. In this system, any of several polymers (including photoresist and epoxy) may be used because neither adhesion nor thickness of the polymer film is important to the function of the device. The polymer simply isolates the conductive layers after the etching.

By measuring the impedance of the device, we deduced the series resistance and inductance of the spiral. The DC resistance of the spiral was 450 Ω, and the inductance was 2.61 μH at 100 kHz, 2.83 μH at 10 kHz, and 2.85 μH at 1 kHz (avg. is 2.8 ± 0.2 μH). These values are 10–20% larger than the calculated inductance of 2.4 μH (a spiral with 20 concentric rings and an outer radius of 0.6 cm), and correspond to a magnetic field at the center of the coil of 40 G/A. The simple theory understates the inductance of the coil because it includes neither the inductance of the leads into and out of the coil nor the metal disk at the center of the spiral. These features add to the inductance of the structure and would increase the theoretical value if the theory properly accounted for them. The important result is that the measured inductance is not lower than the theoretical prediction, which would imply that some of the rings on the spiral were connected electrically. Such connections would indicate that the polymer did not completely dewet from the hydrophobic regions of the SAM during coating.

We found that the two techniques for applying the polymer resist, spin-coating and dip-coating, have different advantages and disadvantages that make each more suitable for certain types of features and types of polymers. The polymer can be deposited on straight lines either by spin-coating or dip-coating, but the spirals require spin-coating. Large, extended features perpendicular to the direction of the withdrawal motion in dip-coating dewet poorly. The polymer tends to bead on the edge of the feature and is stabilized by surface tension. For dip-coating the crossed wires, the lines are withdrawn from the polymer oriented parallel to the direction of motion in order to avoid poor dewetting of the polymer. Spin-coating is the more general technique and works for all geometries of patterns while leaving the backside surface of the sample free of polymer. On the other hand, dip-coating is capable of patterning with more viscous polymers and leaves the background regions of the patterned surface cleaner than spin-coating. In Fig. 3, there are drops of polymer remaining on the unpatterned regions of the substrate after spin-coating. The dip-coating technique, however, is slow. Withdrawing the sample from the polymer at a rate of 2.5 mm/min, it requires approximately 30 min to coat an entire 3″ wafer.

The polymer plays three roles in the overall process and is chosen therefore to meet these empirical criteria: (i) it assembles on the patterned SAM by preferentially wetting the hydrophilic regions of the SAM; (ii) it is a resist for etching; (iii) it becomes the insulating or dielectric material between the crossed lines. To self-assemble on the hydrophilic regions of the patterned SAM selectively, the polymer must have a viscosity less than ~ 500 cP s (for example, the polyurethane has a viscosity of 300 cP s). The surface tension of the polymer also must be low
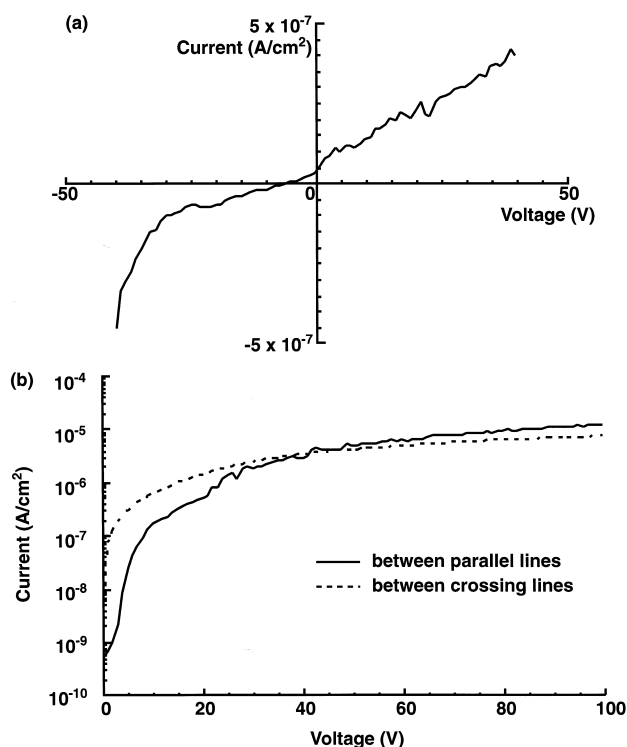

Fig. 3. Optical micrographs of a surface coil inductor prepared by the method described in Fig. 1b. The lead, coated with polymer, runs underneath the spiral, but the two features are in electrical contact at the center of the spiral — the polymer was removed from the end of the lead before the second layer of gold was evaporated. The regions of gold around the outside of the spiral are a result of the edge of the stamp contacting the substrate during printing. These regions do not interfere with the performance of the inductor.
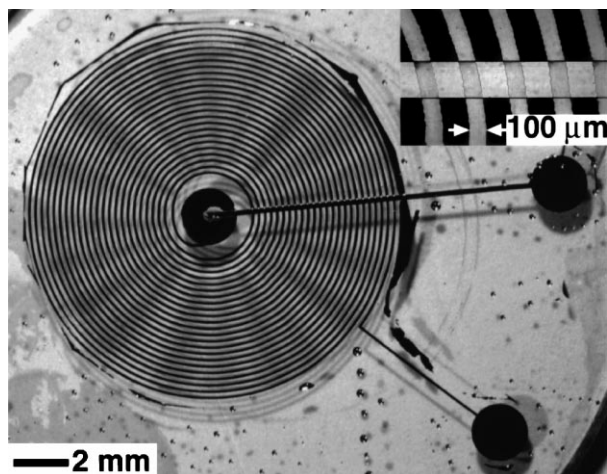
Fig. 4. Schematic representation of the procedure.

enough that the polymer spreads as a film over the pattern rather than beading. To act as a resist, the polymer must be stable under the etching conditions. We use an iodine-based etch at neutral pH [20]. It is an order of magnitude faster in etching than aqua regia, and does not damage the polymer (as does a basic ferri/ferrocyanide etch at pH = 14). The iodine etch also gives smoother underetching than either aqua regia or ferri/ferrocyanide. To be a good insulator, the polymer should form a defect-free film, without pinholes, over the surface, and have good adhesion to both the top and bottom gold lines. Reducing the number of defects in the insulating layer requires a suitable compromise between the adhesive force and the surface tension of the polymer. To function as a dielectric, for applications as capacitors, the polymer also needs to be thin (< 1 μm) and/or have a high dielectric constant.

4. Conclusions

We show that the combination of soft lithography and self-assembly is capable of fabricating simple structures — crossed lines (10×10 to 50×50 arrays of lines, 10–100 μm wide) and surface coil inductors (20 turns, 100 μm wide) — in two level arrays with a high degree of perfection. The surface coil inductor is functional and has device characteristics that closely resemble those predicted by theory, indicating the coils of the spiral are sufficiently isolated electrically (Fig. 4).

There are several advantages of this method that make it potentially useful for fabricating functional, multilevel structures that require the isolation of wires: (i) the fabrication is guided by the principles of self-assembly, first at the molecular scale by self-assembly of thiols on gold and then at the micron scale by controlling surface wetting properties, (ii) the formation of the insulating layer is self-registering and is done without a mask aligner, (iii) dewetting of the polymer works on all geometries of

features — straight lines, curved lines and corners, (iv) we can use microcontact printing to pattern surfaces with non-planar topography, providing the changes in topography are smooth and not greater than 1–3 μm, and (v) the fabrication is performed on an open air benchtop, does not require a clean room, and requires very low capital investment.

Some disadvantages of this method are that: (i) the choice of polymers is confined by the functions they must perform, (ii) it is extremely difficult to fabricate thin (< 1 μm) films of polymer for use as dielectrics, and (iii) we are unable to print continuous features over structures with sharp edges or abrupt changes in topography greater than approximately 3 μm.

Acknowledgements

References

[1] S.A. Campbell, The Science and Engineering of Microelectronic Fabrication, Oxford Univ. Press, New York, NY, 1996.

[2] W.M. Moreau, Semiconductor Lithography: Principles, Practices, and Materials, Plenum, New York, NY, 1989.

[3] S. Nonogaki, T. Ueno, T. Ito, Microlithography Fundamentals in Semiconductor Devices and Fabrication Technology, Marcel Dekker, New York, NY, 1998.

[4] M. Madou, Fundamentals of Microfabrication, CRC Press, Boca Raton, FL, 1997.

[5] W.S. Trimmer (Ed.), Micromechanics and MEMS, IEEE Press, New York, NY, 1997.

[6] Y. Xia, G.M. Whitesides, Soft lithography, Angew. Chem. Int. Ed. Engl. 37 (1998) 550.

[7] D. Qin, Y. Xia, G.M. Whitesides, Rapid prototyping of complex structures with feature sizes larger than 20 μm, Adv. Mater. 8 (1996) 917.

[8] O.J.A. Schueller, S.T. Brittain, C. Marzolin, G.M. Whitesides, Fabrication and characterization of glassy carbon MEMS, Chem. Mater. 9 (1997) 1399.

[9] X.-M. Zhao, A. Stoddart, S.P. Smith, E. Kim, Y. Xia, M. Prentiss, G.M. Whitesides, Fabrication of single-mode polymeric waveguides using micromolding in capillaries, Adv. Mater. 8 (1996) 420.

[10] J.A. Rogers, R.J. Jackman, G.M. Whitesides, Microcontact printing and electroplating on curved substrates: a means for producing free-standing three-dimensional microstructures with possible applications ranging from micro-coil springs to coronary stents, Adv. Mater. 9 (1997) 475.

[11] J.A. Rogers, R.J. Jackman, G.M. Whitesides, Constructing single- and multiple-helical microcoils and characterizing their performance as components of microinductors and microelectromagnets, J. MEMS 6 (1997) 184.

[12] R.J. Jackman, J.A. Rogers, G.M. Whitesides, Fabrication and characterization of a concentric, cylindrical microtransformer, IEEE Trans. Magn. 33 (1997) 2501.

[13] J. Hu, R.G. Beck, T. Deng, R.M. Westervelt, K.D. Maranowski, A.C. Gossard, G.M. Whitesides, Using soft lithography to fabricate GaAs/AlGaAs heterostructure field effect transistors, Appl. Phys. Lett. 71 (1997) 2020.

[14] A. Kumar, H.A. Biebuyck, G.M. Whitesides, Patterning self-assembled monolayers: applications in material science, Langmuir 10 (1994) 1498.

[15] H.A. Biebuyck, G.M. Whitesides, Self-organization of organic liquids on patterned self-assembled monolayers of alkanethiolates on gold, Langmuir 10 (1994) 2790.

[16] E. Kim, G.M. Whitesides, L.K. Lee, S.P. Smith, M. Prentiss, Fabrication of arrays of channel waveguides by three-dimensional self-assembly using patterned organic monolayers as templates, Adv. Mater. 8 (1996) 139.

[17] A. Kumar, N.A. Abbott, E. Kim, H.A. Biebuyck, G.M. Whitesides, Patterned self-assembled monolayers and meso-scale phenomena, Acc. Chem. Res. 28 (1995) 219.

[18] C.D. Bain, E.B. Troughton, Y.-T. Tao, J. Evall, G.M. Whitesides, R.G. Nuzzo, Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold, J. Am. Chem. Soc. 111 (1989) 321.

[19] K. Kukli, M. Ritala, M. Leskela, J. Jokinen, Atomic layer epitaxy growth of aluminum oxide thin films from a novel $Al(CH_3)_2Cl$ precursor and H_2O, J. Vac. Sci. Technol., A 15 (1997) 2214.

[20] Type TFA gold etch (pH 7) from Transene, Rowley, MA.