Printing technology

DOI: 10.1002/smll.200500213

Fabrication of Thin, Metallic Films along the Sidewalls of a Topographically Patterned Stamp and Their Application in Charge Printing**

*Tingbing Cao, Qiaobing Xu, Adam Winkleman, and George M. Whitesides**

This manuscript describes a method to generate thin, electrically conductive, metal films on the sidewalls of relief patterns on a poly(dimethylsiloxane) (PDMS) stamp using a combination of thin-film metal deposition and nanotransfer printing (nTP), a technique developed by Rogers and co-workers.[1,2] The PDMS stamps—with their sidewalls supporting conductive metal films—are used to generate patterns of charge in thin films of dielectrics by using electrical microcontact printing (e-μCP).[3,4] These patterned dielectrics are substrates for selective deposition of particles: submicrometer polystyrene (PS) spheres or iron oxide particles, for example, adhere specifically to the regions of charge.

The most commonly used methods for micro- and nanofabrication—photolithography and e-beam writing—have limitations: high capital and operating costs, small areas of exposure, and limitations on the sizes of features.[5] Many new techniques are being developed to circumvent the current limitations of traditional lithography.[6,7] A theme common to several of these techniques is size-reduction, that is, using "large and easy-to-fabricate" masks or templates to yield similarly shaped features, which are a fraction of the original size. Size-reduction techniques using variations on photolithography include phase-shifting photolithography,[8–10] photolithography with undercutting at lithographically defined step edges,[11] edge lithography with deposition or removal of material in regions defined by defects at the edges of topographic features,[12,13] and size-reduction photolithography.[14] Edge-spreading lithography, a combination of microcontact printing and controlled chemical diffusion, is a non-photolithographic technique that also uses mesoscopic templates to generate nanometer features.[15,16]

Precise control of the thickness of metal films deposited by electroplating or by evaporation is achievable to within a few nanometers (in 20-nm-thick films). Metallic nanowires with controllable dimensions have been fabricated by electrodepositing metals within nanoporous membranes,[17–19] evaporating and transferring from a selectively etched GaAs/AlGaAs superlattice,[20] and sectioning an embedded thin metal film with a microtome.[21] Metal evaporation onto nonplanar substrates, including microspheres[22] and microdominos,[23] results in pseudo-three-dimensional structures with critical dimensions of <15 nm.

Rogers and co-workers[1,2,24,25] and later Delamarche and co-workers[26] have developed nTP, a very useful new form of soft lithography. The process of nTP uses evaporation of thin metal films onto PDMS stamps that were generated by replica molding from photolithographically fabricated masters. These metal-coated stamps, when brought into contact with a second substrate having appropriate surface chemistry, selectively transfer the metal film from the raised features of the PDMS to the substrate. The transfer depends on weak adhesion of the metal to the original stamp, strong adhesion to the substrate to which the metal transfers, and conformal contact accomplished by the elastomeric stamp. The nTP technique has generated features with lateral dimensions of <100 nm and vertical dimensions of <20 nm.

Many techniques can embed charged particles—either electrons or ions—into dielectric materials. Most of these methods are serial: electron beams,[27] focused ion beams,[28] and scanning probe tips[29,30] are all useful in this kind of writing. One parallel technique, e-μCP, employs a topographically patterned, PDMS stamp coated with a thin metal film[3,4,31,32] and can embed charge over $\approx 1\ cm^2$ in only a few seconds. In addition to embedding charge, e-μCP bleached a poly(4-vinylphenol) film doped with phloxine B to generate optical waveguides.[33]

Patterned electrostatic potentials can act as templates for self-assembly. Stemmer et al. demonstrated the selective adhesion of nanoparticles to patterns of embedded charge written using a scanning probe.[34] Dip-pen nanolithography has achieved similar results by patterning thiols with terminal carboxylic acids and exposing these patterns to suspensions of sub-micrometer, amine-modified polystyrene spheres.[35] Parallel techniques, including microcontact printing[36,37] and the selective adsorption of polyelectrolytes,[38,39] have provided templates for the assembly of both single and multiple particle types on a substrate. Using substrates patterned by e-μCP, charged particles have selectively adsorbed from solid, gas, and solution phases.[3,4,31,32,40]

The process used in this study to fabricate thin, electrically conductive, metal films on the sidewalls of a PDMS stamp, and for using these patterned, conductive sidewalls to pattern charge in dielectric materials, is illustrated schematically in Figure 1. The process for fabricating the metal films on the sidewalls (Figure 1 A–C) is a variation of the method developed by Rogers and co-workers for nTP.[1,2] The groups of Rogers and Delemarche focused their attention on the *transferred* material and on the ability to pattern new substrates. Our interest is in the original PDMS stamp, and in the *removal* of material from it.

As originally described, this technique used collimated gold deposition normal to the PDMS stamp to ensure a discontinuous film; the sidewalls of the PDMS features were intentionally left free of deposited metal.[24] We intentionally used noncollimated metal deposition in order to form thin

[*] Dr. T. Cao, Q. Xu, A. Winkleman, Prof. G. M. Whitesides
Department of Chemistry and Chemical Biology
Harvard University, 12 Oxford Street, Cambridge, MA 02138 (USA)
Fax: (+1) 617-495-9857
E-mail: gwhitesides@gmwgroup.harvard.edu

[**] This research was supported by the Army Research Office (W911NF-04–1–0170) and used the shared Resource Facilities supported by the National Science Foundation under NSEC (PHY-0117795) and MRSEC (DMR-0213805) awards.

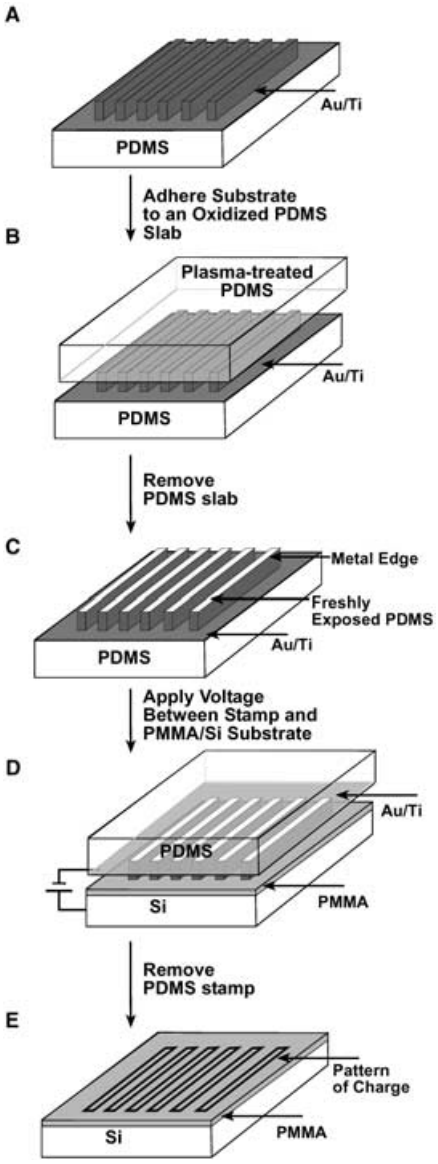

Figure 1. A schematic representation outlining each step of the procedure of fabricating a PDMS stamp with thin, metallic edges using nTP, and of performing e-μCP with this stamp. A–C) A PDMS stamp, which was fabricated by soft lithography and coated with a thin film of Au followed by a layer of Ti, conformally contacts a flat, oxidized PDMS stamp to remove the metal film from the raised features of the stamp. D–E) A voltage applied between the PDMS stamp with the remaining, conducting metal edges and a dielectric thin film embeds a pattern of charge in the thin film that corresponds to the outline of the relief features of the PDMS stamp.

films on all surfaces of the PDMS stamp. We first evaporated a thin film of Au (10–40 nm) onto the PDMS, followed by a layer of Ti (2–5 nm); the Ti layer promoted adhesion during transfer of the film. Both the metal-coated PDMS stamp and a flat slab of PDMS were oxidized using an air plasma. The two PDMS pieces were brought into conformal contact and separated; during the separation, the raised plateaus of the Au/Ti thin film are transferred to the oxidized PDMS slab. After separation, the PDMS stamp retained the metal film along its sidewalls and trenches. The metal edge along the sidewalls is thin (i.e., the thickness of the evaporated film, which is 10 to 40 nm) and sharp, and the entire metal structure remains electrically conductive and can be addressed from the ends of the stamp.

Figure 2 displays a set of SEM images of the metal-coated PDMS stamps before and after the transfer printing.

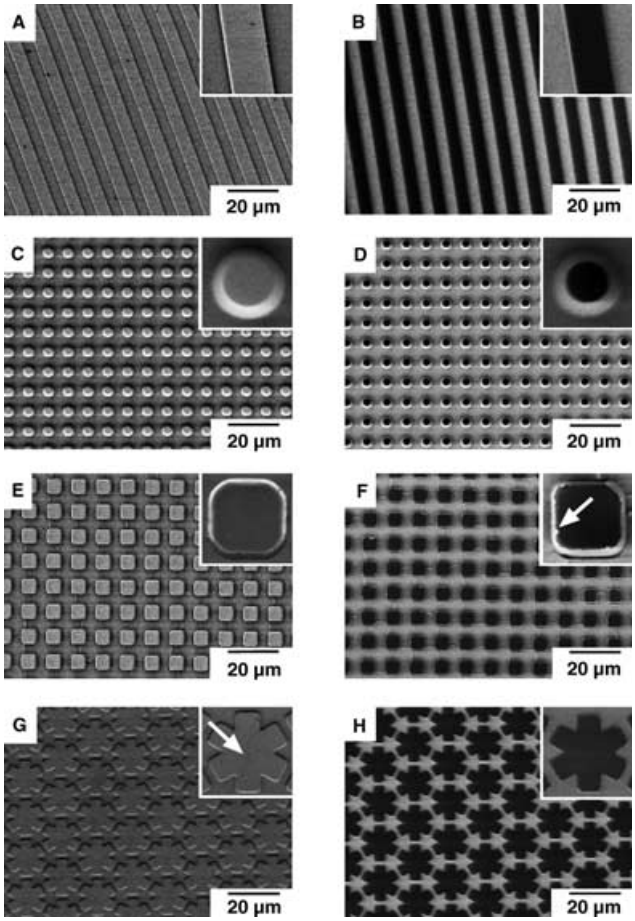

Figure 2. SEM images of the gold-coated PDMS stamps before (A, C, E, G) and after (B, D, F, H) nTP. Lines and three types of posts (circular, square, and an asterisk) demonstrate some of the possible patterns. In the SEM images, the light regions denote metal film, and the dark regions denote the PDMS from the raised lines or tops of the posts where the metal was removed by nTP. The insets represent an average post and illustrate the quality of the metal film; some buckles in the continuous metal film (G) and spots of excess metal due to incomplete transfer (F) are apparent.

Before transfer, metal film is present on all surfaces of the topographically patterned PDMS stamp. After transfer, the metal film remains on the sides and bottoms of the trenches (those not brought into conformal contact with the PDMS slab). The thickness of the metal film on the sidewalls of the PDMS can range from 10–40 nm. When films are thinner than 10 nm, we observe metal on the sidewalls by SEM, but the stamps are not completely conductive. When films are thicker than 40 nm, removing metal from the plateaus generates noticeably more defects and lower edge resolution than when they are $\approx$20 nm.

The quality of the transfer process is not perfect. The metal-edge roughness from the transfer process is about ±45 nm from the edge of the plateaus of the PDMS stamp. This edge roughness is approximately the grain size of gold from our evaporator.[41] There are two principal types of defects: those resulting from incomplete transfer of metal, and those resulting from transfer of too much metal. Incomplete transfer occurs when a small portion of the metal film on the plateau surface does not transfer to the oxidized PDMS slab. This type of defect is less common in the large flat regions than near the edges, and is generally not important in e-μCP, since the residual material is usually not electrically connected. (These defects are more problematic for our applications when they occur at the edge of the sidewalls and retain an electrical connection.) Excess metal transfer only occurs along the edges of the top surface and the sidewalls; it affects the quality of the printed charge.

Figure 1D and E illustrates the process that was used to embed charge from electrodes (prepared as described in Figure 1A–C) into dielectric materials. This process is similar to that developed by Jacobs.[3] A current density of $\approx 40\ \mu A\,mm^{-2}$ is passed between the electrodes for 20 s. Using this technique, we are able to pattern both positive and negative charge in dielectric materials supported on p-doped and n-doped silicon wafers, respectively.

Figure 3 shows Kelvin probe force micrographs (KFM) of the patterns of embedded charge generated from the corresponding PDMS stamps in Figure 2. The widths of the lines of electrostatic potential are ≈300 nm. This width does not change over the range of thicknesses of the metal film (10–40 nm). We have printed charge with a single stamp in excess of 150 times without noticing any degradation in the quality of the pattern of charge or in the appearance of the stamp. Metal transfer can often be seen in the first few cycles of charge printing. This metal is usually from the top, flat region of the stamp, not the edge, and reflects incomplete transfer in the step described in Figure 1C.

In Figure 3, the substrate for all of the images is poly(methyl methacrylate) (PMMA). We have also patterned charge in other polymeric dielectrics (including polystyrene and Teflon AF) and in inorganic dielectrics (SiO_2). All of these dielectric substrates were <500 nm thick and yielded similar charge patterns. We were unable to pattern charge in thick (>10 μm), free-standing polymeric films (i.e., Saran and poly(ethylene)). For these thick films, we could not measure any current while applying as much as 200 V.

We have used the dielectric substrates with patterns of charge, similar to Figure 3A and B, to adsorb nanospheres selectively. Using a substrate with a pattern of embedded positive charge, the substrate is dipped into an ethanol solution containing 200 nm, sulfonate-modified, polystyrene spheres. Upon withdrawal from the solution, rinsing the substrate with fresh ethanol, and evaporation of the solvent, the nanospheres selectively adhere to the charged regions. The polystyrene spheres have a negative surface potential and are attracted to the regions of positive charge. Using a PMMA film on a p-doped silicon wafer with a pattern of embedded positive charge, the substrate can be dipped into a neutral, dry powder of iron oxide (300–800 nm). Nitrogen gas is passed over the substrate to remove excess particles. The substrate is also sonicated in hexane for 3–5 s to remove the particles that adhere nonspecifically.

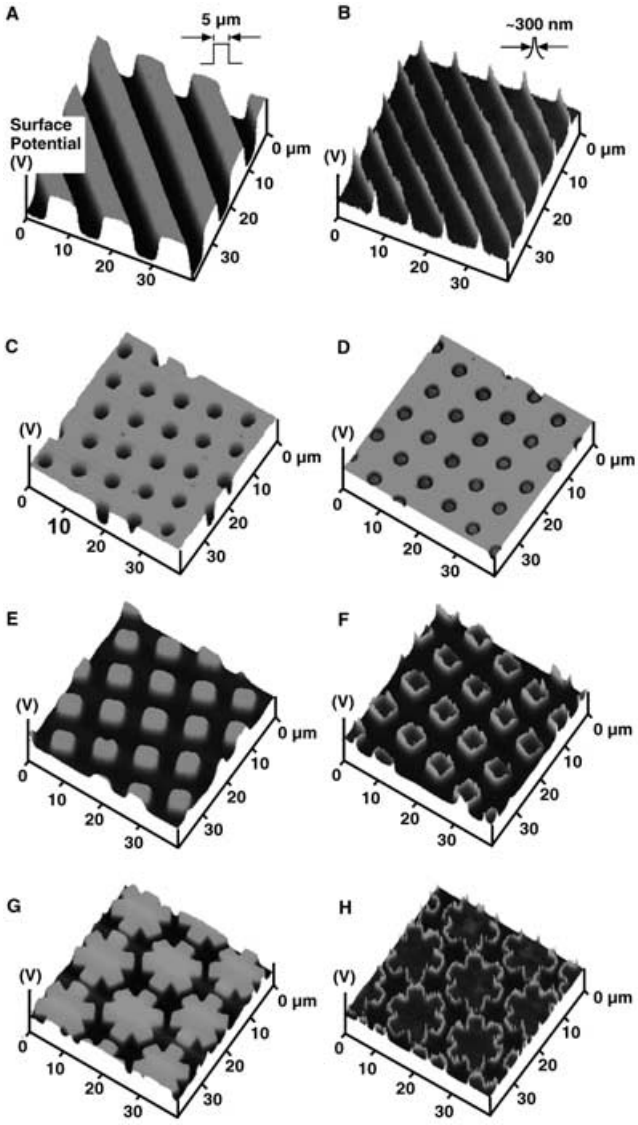

Figure 3. KFM images obtained from the e-μCP of metal-coated PDMS stamps shown in Figure 2. The images in the left column (A, C, E, G) are from stamps completely coated in a thin metal film, and the images in the right column (B, D, F, H) are generated by the corresponding stamps after removing the upper plane of metal by nTP. It is possible to pattern both positive (A, B, E, F, G, H) and negative (C and D) surface potentials using e-μCP.

Figure 4A and C are images illustrating the particle assembly and distribution over a pattern of charge using PDMS stamps before nTP and Figure 4B and D are from substrates patterned with charge from PDMS stamps after nTP.

In conclusion, we have demonstrated a new application of nanotransfer printing, namely, to fabricate electrically connected metal sidewalls on PDMS stamps. We used these metal edges in an extension of the technique for e-μCP developed by Jacobs and co-workers.[3,4] These substrates se-

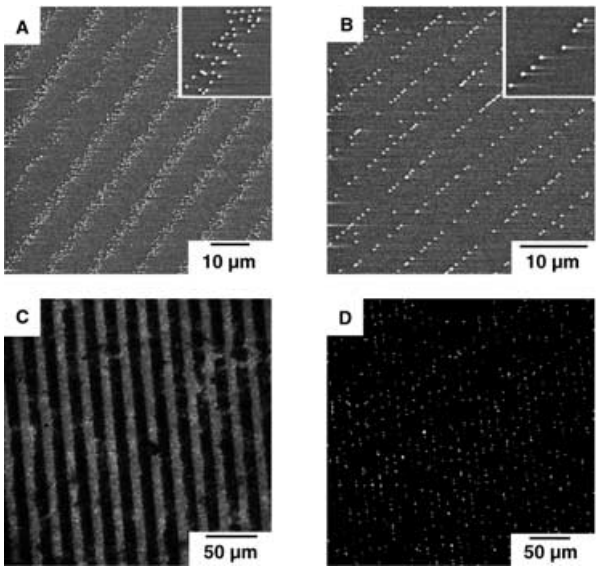

Figure 4. A, B) SEM images of nanoparticle adsorption over the pattern of charge illustrated by the alignment of 200 nm, sulfonate-modified PS spheres over the positively patterned PMMA substrate of Figure 3A and B. The insets illustrate local particle assembly; the size-reduction pattern yields structures only one particle across. C, D) Dark-field optical images of dry, neutral iron oxide nanoparticles assembled over a negatively patterned PMMA substrate.

lectively adsorbed sub-micrometer particles to the regions of the pattern of charge.

This process has three major advantages over other techniques for fabricating nanometer-wide metal structures: 1) It provides a rapid and simple way to fabricate 10–40-nm-wide, vertically patterned metallic structures; 2) it can generate a wide range of patterns: the limitations are those of soft lithography; 3) the metal edges on which it is based are supported by soft substrates; the mechanical compliance of this system enables good conformal contact with hard dielectric substrates for charge imprinting.

This method also has its limitations. First, the smallest dimension of the pattern of charge is an order of magnitude larger than the metal edge. Second, there are limitations to the patterns it can generate and apply for charge imprinting. Isolated or discrete structures of metal (e.g., wells) cannot be used for patterning charge without more complex geometries for the stamps to ensure electrical connectivity.

Experimental Section

All materials and chemicals were purchased commercially and used as received.

Fabrication of the metal on the sidewalls: Soft lithography and rapid prototyping were used to fabricate features in SU-8 (MicroChem Corp.) that were subsequently replica molded using PDMS pre-polymer to fabricate the flexible stamps. The stamps were coated with 10–40 nm of Au and 2–5 nm of Ti using an electron beam evaporator. These metal-coated stamps and a flat slab of PDMS were oxidized using an air plasma (≈2 torr, 100 W, Harrick Scientific Model PDC-32G) for 1 min. To transfer the metal film from the raised features, the PDMS stamp and slab were brought into conformal contact and separated. The images of the stamps before and after transfer were obtained by SEM (LEO 982).

Printing of charge: A thin film of polymer (typically PMMA, 100 nm thick) was spin-coated onto a silicon wafer (please refer to: www.Universitywafer.com). This dielectric was brought into conformal contact with the PDMS stamp. An electrical current density of $\approx 40\ \mu A\,mm^{-2}$ was applied for 20 s using a Keithley 2400 electrometer. The images of the patterns of the charge were obtained using an atomic force microscope (D3100, NSIV; Digital Instruments) in surface potential mode.

Particle adhesion: A solution of 200 nm sulfonate-modified polystyrene spheres (1.7% by weight; Duke Scientific Corporation) in water (1 mL) was diluted in 10 mL of ethanol. The charged wafer was placed into the solution for 1 min. Upon removal from the solution, the substrate was rinsed with fresh ethanol and the substrate was dried using a stream of nitrogen gas. Images were obtained using a scanning electron microscope (LEO 982).

A positively charged wafer was dipped into dry, neutral iron oxide particles (300–800 nm, Polysciences, Inc.). A stream of nitrogen gas blew off the excess particles. The substrate was sonicated for 3–5 s in a solution of hexanes. Images were obtained using an optical microscope (Leica) in dark-field mode.

Keywords:

electrodes · microcontact printing · nanostructures · nanotransfer printing · polymers

[1] Y. L. Loo, R. L. Willett, K. W. Baldwin, J. A. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 7654.
[2] Y. L. Loo, R. L. Willett, K. W. Baldwin, J. A. Rogers, *Appl. Phys. Lett.* **2002**, *81*, 562.
[3] H. O. Jacobs, G. M. Whitesides, *Science* **2001**, *291*, 1763.
[4] H. O. Jacobs, S. A. Campbell, M. G. Steward, *Adv. Mater.* **2002**, *14*, 1553.
[5] B. D. Gates, Q. B. Xu, J. C. Love, D. B. Wolfe, G. M. Whitesides, *Annu. Rev. Mater. Res.* **2004**, *34*, 339.
[6] B. D. Gates, Q. B. Xu, M. Stewart, D. Ryan, C. G. Willson, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1171.
[7] Y. N. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823.
[8] J. A. Rogers, K. E. Paul, R. J. Jackman, G. M. Whitesides, *Appl. Phys. Lett.* **1997**, *70*, 2658.
[9] K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, J. Albert, *Appl. Phys. Lett.* **1993**, *62*, 1035.
[10] T. W. Odom, V. R. Thalladi, J. C. Love, G. M. Whitesides, *J. Am. Chem. Soc.* **2002**, *124*, 12112.
[11] J. C. Love, K. E. Paul, G. M. Whitesides, *Adv. Mater.* **2001**, *13*, 604.
[12] J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature* **1998**, *394*, 868.
[13] H. Yang, J. C. Love, F. Arias, G. M. Whitesides, *Chem. Mater.* **2002**, *14*, 1385.
[14] Y. K. Choi, J. Zhu, J. Grunes, J. Bokor, G. A. Somorjai, *J. Phys. Chem. B* **2003**, *107*, 3340.
[15] M. Geissler, J. M. McLellan, Y. N. Xia, *Nano Lett.* **2005**, *5*, 31.

[16] J. M. McLellan, M. Geissler, Y. N. Xia, *J. Am. Chem. Soc.* **2004**, *126*, 10830.
[17] B. R. Martin, D. J. Dermody, B. D. Reiss, M. M. Fang, L. A. Lyon, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **1999**, *11*, 1021.
[18] C. R. Martin, *Science* **1994**, *266*, 1961.
[19] J. C. Love, A. R. Urbach, M. G. Prentiss, G. M. Whitesides, *J. Am. Chem. Soc.* **2003**, *125*, 12696.
[20] N. A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P. M. Petroff, J. R. Heath, *Science* **2003**, *300*, 112.
[21] Q. B. Xu, B. D. Gates, G. M. Whitesides, *J. Am. Chem. Soc.* **2004**, *126*, 1332.
[22] J. C. Love, B. D. Gates, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Nano Lett.* **2002**, *2*, 891.
[23] B. D. Gates, Q. B. Xu, V. R. Thalladi, T. B. Cao, T. Knickerbocker, G. M. Whitesides, *Angew. Chem.* **2004**, *116*, 2840; *Angew. Chem. Int. Ed.* **2004**, *43*, 2780.
[24] E. Menard, L. Bilhaut, J. Zaumseil, J. A. Rogers, *Langmuir* **2004**, *20*, 6871.
[25] J. Zaumseil, M. A. Meitl, J. W. P. Hsu, B. R. Acharya, K. W. Baldwin, Y. L. Loo, J. A. Rogers, *Nano Lett.* **2003**, *3*, 1223.
[26] H. Schmid, H. Wolf, R. Allenspach, H. Riel, S. Karg, B. Michel, E. Delamarche, *Adv. Funct. Mater.* **2003**, *13*, 145.
[27] K. Mikihiko, S. Norio, D. Takehiro, F. Hiroshi, K. Takeshi, E. Mitsuru, *Proc. SPIE-Int. Soc. Opt. Eng.* **2001**, *4334*, 263.
[28] H. Fudouzi, M. Kobayashi, N. Shinya, *Langmuir* **2002**, *18*, 7648.
[29] H. O. Jacobs, A. Stemmer, *Surf. Interface Anal.* **1999**, *27*, 361.
[30] J. E. Stern, B. D. Terris, H. J. Mamin, D. Rugar, *Appl. Phys. Lett.* **1988**, *53*, 2717.
[31] C. R. Barry, M. G. Steward, N. Z. Lwin, H. O. Jacobs, *Nanotechnology* **2003**, *14*, 1057.
[32] C. R. Barry, N. Z. Lwin, W. Zheng, H. O. Jacobs, *Appl. Phys. Lett.* **2003**, *83*, 5527.
[33] D. B. Wolfe, J. C. Love, B. D. Gates, G. M. Whitesides, R. S. Conroy, M. Prentiss, *Appl. Phys. Lett.* **2004**, *84*, 1623.
[34] P. Mesquida, A. Stemmer, *Adv. Mater.* **2001**, *13*, 1395.
[35] L. M. Demers, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 3159; *Angew. Chem. Int. Ed.* **2001**, *40*, 3069.
[36] J. Tien, A. Terfort, G. M. Whitesides, *Langmuir* **1997**, *13*, 5349.
[37] J. Aizenberg, P. V. Braun, P. Wiltzius, *Phys. Rev. Lett.* **2000**, *84*, 2997.
[38] K. M. Chen, X. P. Jiang, L. C. Kimerling, P. T. Hammond, *Langmuir* **2000**, *16*, 7825.
[39] H. P. Zheng, I. Lee, M. F. Rubner, P. T. Hammond, *Adv. Mater.* **2002**, *14*, 569.
[40] M. Kang, H. Kim, B. W. Han, J. Suh, J. Park, M. Choi, *Microelectron. Eng.* **2004**, *71*, 229.
[41] J. C. Love, D. B. Wolfe, R. Haasch, M. L. Chabinyc, K. E. Paul, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **2003**, *125*, 2597.

Received: June 29, 2005

