Submicron Contact Printing on Silicon Using Stamp Pads

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Received April 15, 1998. In Final Form: October 5, 1998

Submicron scale microcontact printing of silanes onto silicon wafers is studied. Silicon microstructures are used as masters to prepare silicone rubber stamps, which are found to peel off the master easily even at wedge angles of 80° if the master has been silanized before. Stripe structures with periodicities down to 200 nm were generated. At these small scales, capillary condensation in the wedges of the stamp during the stamping process is difficult to avoid. We demonstrate a novel "stamp pad" technique which allows us to overcome this problem.

Microcontact printing (μCP) has become a widely used technique for chemically structuring solid surfaces.[1−5] It uses soft stamps for transferring solutions of reactive molecules onto the surface to be structured, where they form covalently bound, self-assembled monolayers (SAMs). As the stamp, one has to use a material which is rigid enough to support a topographic microstructure at its surface, "porous" enough to incorporate a sufficient amount of active solution, and soft enough to enable a smooth contact with the solid surface onto which printing is desired. The method has originally been demonstrated with alkanethiolate solutions which were transferred with silicone rubber stamps onto gold surfaces.[4] Structures with a lateral scale down to about 1 μm could easily be obtained.

Since it has been shown that the SAMs obtained in this way can even act as lithography resists,[6] it appears tempting to investigate how far this technique can be further developed toward smaller lateral length scales. In this direction of development, one arrives soon at some limitations of the gold films usually employed in this field: their roughness is not negligible on the nanometer scale, and structuring of semiconductors may be more significant in view of the wide applications possible and the technological knowledge already at hand. Therefore, several groups are already routinely using μCP for depositing alkane silanes onto oxidized silicon wafers,[7−9] with a quality of the results close to what one usually obtains with noble metal surfaces. In the present paper, we investigate the process of μCP of silane compounds onto oxidized silicon wafers using silicone rubber stamps that have been cast from lithographically structured silicon masters. Our aim is to investigate, for this combination of materials and techniques, possible bottlenecks in lateral resolution and SAM quality and to provide potential solutions to these problems.

The masters were prepared by reactive ion etching (RIE) of ⟨100⟩ silicon wafers (25 Å of native oxide) through a holographic photoresist structure. The latter was generated by exposure of the resist to two crossed argon laser beams and consisted thus of an arrangement of parallel stripes. The spatial period of this structure is well defined by the wavelength of the light and the mutual angle of the laser beams. The RIE process resulted in grooves with a depth of 200−300 nm depending on etch duration. The angle of the side walls of these grooves (with respect to the horizontal) varied from 65 to 80° depending on the etching conditions. Figure 1 shows a scanning force microscopy (SFM) image of a typical master, which has been obtained with a special high-aspect-ratio tip (prepared by electron beam deposition of carbon) which allows us to image rather steep structures such as the steep walls of the grooves. Before stamps were cast from these masters, the latter were silanized in a hexane solution (2 mM) of octadecyltrichlorosilane (OTS).

Stamps were cast from poly(dimethylsiloxane) (PDMS).[10] Care was taken that the flow of the liquid occurred along the grooves in order to avoid air entrainment between the master and the liquid. That this was easily possible is due to the simple structure of our masters, but in principle, every structure may be cast if the PDMS is deposited onto the master in a vacuum. Cross-linking of the PDMS, which contained a suitable cross-linking agent, was achieved by baking at 60° C for several hours. Afterward, the stamps could be easily peeled off, although one might anticipate that there is some cross-linking between the PDMS and the chemically rather similar native oxide of the master. Obviously, the silanization applied before casting prevents this process sufficiently to avoid sticking even at the rather steep slopes of the master structure. Inspection of the masters by SFM after the casting process did not reveal any remainders of silicone rubber on the master surface. Without renewal of silanization, stamps could be prepared

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(1) Drelich, J.; Wilbur, J. L.; Miller, J. D.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1913.
(2) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60.
(3) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790.
(4) Drelich, J.; Millert, J. D.; Kumar, A.; Whitesides, G. M. *Colloids Surf., A* **1994**, *93*, 1.
(5) Xia, Y.; Mrksich, M.; Kim, E.: Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.
(6) Xia, Y.; Whitesides, G. M. *Langmuir* **1997**, *13*, 2059.
(7) John, P. M. S.; Craighead, H. G. *Appl. Phys. Lett.* **1996**, *68*, 1022.
(8) Wang, D.; Thomas, S.; Wang, K.; Xia, Y.; Whitesides, G. *Appl. Phys. Lett.* **1997**, *70*, 1593.
(9) Jeon, N. L.; Finnie, K.; Branshaw, K.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3382.

(10) Sylgard 184, purchased from Dow Corning. This formulation contains a cross-linking agent which is activated at elevated temperature.

10.1021/la980429s CCC: $18.00 © 1999 American Chemical Society
Published on Web 03/11/1999

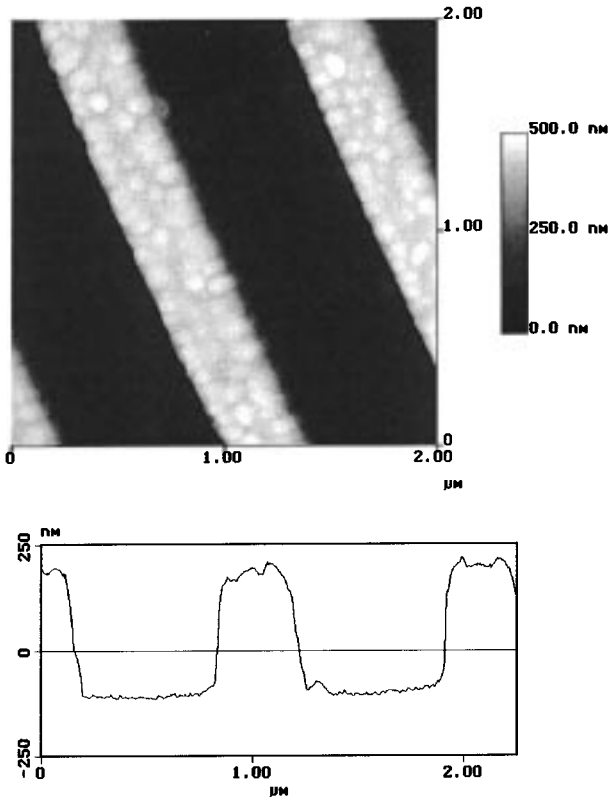

Figure 1. SFM topography image (top) of a typical silicon master. In the section cut perpendicular to the parallel grooves (bottom), the sharp and steep (incline angle is 80°) structure of the wall is clearly visible.

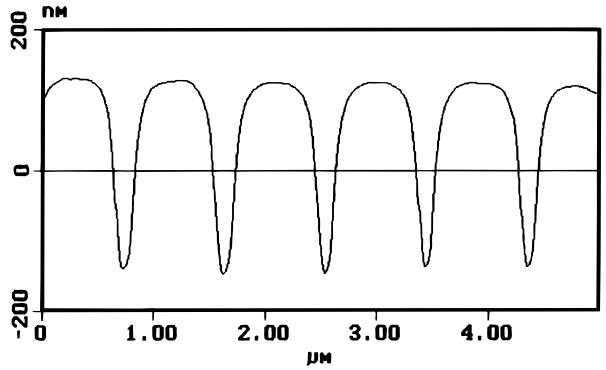

Figure 2. Section of a SFM topography image of a cross-linked PDMS stamp with 910 nm periodicity cast from a silicon master as displayed in Figure 1. Although the uniform, stripewise structure is reproduced, the shape of the stamp is quite different from the geometric "negative" of the master. The sharp edge structure of the master is significantly rounded, probably due to stress arising during the cross-linking process.

many times from the same master without noticeable loss in quality.

If the casting process was ideal, one would expect the stamp topography to be the exact inverse of the master topography. That this is not at all the case is demonstrated in Figure 2, which shows a section of a SFM image of a typical stamp. The structure is significantly rounded, and the maximum slope obtained is smaller than that observed at the master. We attribute this distortion of the structure to the relaxation of stress induced in the rubber during the cross-linking process. One should also be aware of the fact that when the stamp is inked with the solution used for stamping, swelling will further deform the stamp, which may give rise to further rounding of the structure.

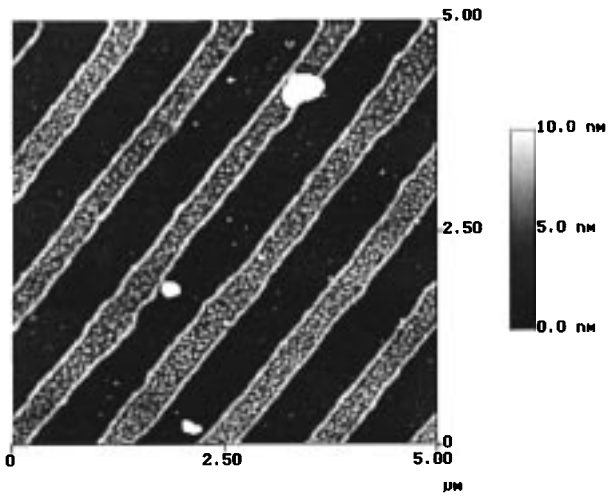

Figure 3. SFM topography image of a stamped structure with 970 nm periodicity where the stamp was inked directly with the solution (the large white spots are dust particles deposited after sample preparation).

While these effects are not expected to be very pronounced for large structures, they are obviously of great importance for the submicron structures investigated here. One cannot expect to obtain a printed structure which represents an exact geometric image of the wells in the master. On the contrary, it is to be expected that the structure of the printed film depends strongly on the pressure applied during printing, since the pressure will flatten the rounded stamp surface and thus widen the printed regions.

Silicon wafers were used as the substrate to be printed on, and as the "active" molecules of the printing "ink", we used perfluorinated monochlorosilanes ((heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane purchased from the ABCR Company, Karlsruhe, Germany) in 2 mM hexane solution. We did not use trichlorosilanes in order to prevent side effects from polymerization within the silane itself due to residual moisture (e.g., in the stamp). This allowed us to obtain good results at ambient humidity. As a solvent, hexane (dried to a water content of less than 0.005%) was used, which gave rise to some moderate swelling of the stamp material. This was not considered as a problem for the present study, since we were not interested in an exact reproduction of the spatial period of the master. Silicon wafers (courtesy of Wacker Chemitronic) were cleaned before printing by the standard RCA method.[11] Printing was performed shortly after rinsing the substrates with Millipore water and drying with argon gas.

When the stamps were directly inked, dried, and printed with, one typically obtained a result such as the one shown in Figure 3. One clearly sees that the thickness of the deposited film is considerably larger at the boundary between the regions of different silane density. Furthermore, stripewise deposition of small (height $\leq$ 5 nm) hillocks is observed. The topographic appearance of the sample was not changed if the sample was rinsed with hexane and ethanol, including ultrasonication. On the basis of the observed topography, one might be tempted to assume that the stripes with the little hillocks correspond to the stamped regions, the others corresponding to the voids in the stamp. It will be shown below, however, that the opposite is the case. Note that a typical height of the hillocks is 5 nm, and the rather homogeneous thickness between them is about 2.5 nm (with respect to

(11) Kern, W. *RCA Eng* **1983**, *28*, 99.

the topographic height of the adjacent stripes), significantly larger than the length of the molecules. In any case, it is clear that the structure displayed in Figure 3 is different from the desired stripewise deposition of a self-assembled monolayer of active molecules, in the sense that there is too much material deposited.

Any amount of ink in excess of what is really needed for building the desired SAM in the desired place is obviously disadvantageous. In the first place, it gives rise to undesirable swelling of the stamp. Second, SAMs which may initially form on the surface are masked by excess amounts of material. We have thus explored a novel way of selectively inking the stamp only in those places which are finally used in the printing process. We inked a structureless silicone rubber block which was cast from a plane silicon surface for 10 s with the solution. After having dried the rubber block with a stream of argon for 20 s, we placed the stamp atop this plane inked surface with a light pressure and waited for 3−5 s to let the ink diffuse from the plane silicone rubber (the stamp pad) into the stamp, which could occur only where the two objects were really in contact. We used this rather short interaction time in order to keep inking of the stamp to a necessary minimum. Although transport through the gas phase is possible in principle, it is expected to be much slower, in particular because the vapor pressure of the large silane molecules is small.

When the stamp was inked in this way, printing results such as the ones shown in Figure 4 were obtained. For this imaging, which was performed in tapping mode, care was taken to prevent well-known artifacts in the topography due to the tapping process on structures with varying wettability and chemical composition.[12−14] The somewhat uneven width of the printed stripes is not a surprise in view of the rounded shape of the stamp structures. The topographic height difference is found to be 0.5 nm, which is to be compared to the length of the silane molecules, 1.3 nm. This suggests a molecular tilt angle of 67°, which corresponds, assuming close packing of the molecular chains, to an area per molecule of about 2 times the cross section of the molecule. In fact, by silanization with the same molecules through the gas phase, monolayers with a thickness of 1.2 nm could be easily obtained, as revealed by standard small-angle X-ray analysis. This shows that the above-mentioned tilt angle is not due to steric interaction of the molecular headgroups close to the substrate. In contrast, the fact that the coverage achieved by printing is only about 50% of the maximum achievable coverage may be attributed to the fact that the printing procedure involves a close contact of the stamp with the substrate. The PDMS molecules may thus block a considerable fraction of the substrate on a nanometer scale and thus prevent part of the substrate from participating in the grafting process.

It should be noted that, even with the stamp pad technique presented here, structures similar to the one displayed in Figure 3 may be obtained when the stamp is in contact with the pad for too long a time. This is shown in Figure 5, where the elevated rim structures are visible, similar to the case in Figure 3. Furthermore, on some of the stripes, hillocks can be seen as well, as indicated by the arrow. These occur only on those stripes which show elsewhere a lower topography (by 0.5 nm corresponding to one monolayer) than that of their alternating counterparts, as is clearly visible in the section which is displayed in Figure 5 (bottom). This strongly suggests the following scenario. Upon successful printing, a monolayer or less is deposited where the stamp touches the substrate. If exactly one monolayer is deposited, the result may be perfect. However, a little excess solution in the stamp gives rise to capillary condensation in the wedges at the boundaries of the regions of contact. At these places, significantly more material is deposited, which gives rise to the elevated rims observed in Figures 3 and 5. If even more ink is present, capillary condensation may even fill the entire channel between the substrate and the stamp where the latter has a groove. In this case, material is excessively deposited between the regions of contact, giving

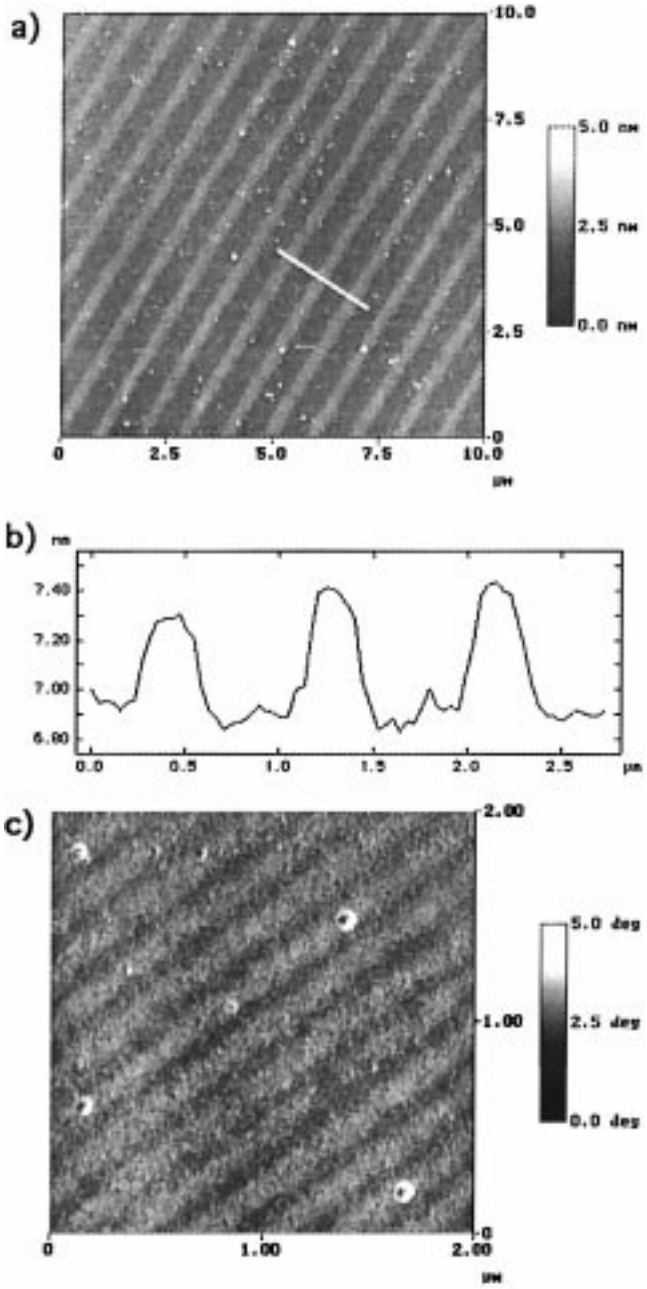

Figure 4. (a) SFM topography image of a stamped structure with 870 nm periodicity obtained with the "stamp-pad" technique. Quite uniform stripes of perfluorinated monochlorosilane with a height of 0.5 nm can be seen. The white bar indicates the cross section displayed in part b. (c) Stamped structure with 200 nm periodicity obtained with the "stamp-pad" technique (phase image), which is presently the smallest structure we could generate.

(12) Kuehle, A.; Soerensen, A. H.; Bohr, J. *J. Appl. Phys.* **1997**, *81*, 6562.
(13) Van Noort, S. J. T.; Van der Werf, K. O.; De Grooth, B. G.; Van Hulst, N. F.; Greve, J. *Ultramicroscopy* **1997**, *69*, 117.
(14) Brandsch, R.; Bar, G.; Whangbo, M.-H. *Langmuir* **1997**, *13*, 6349.

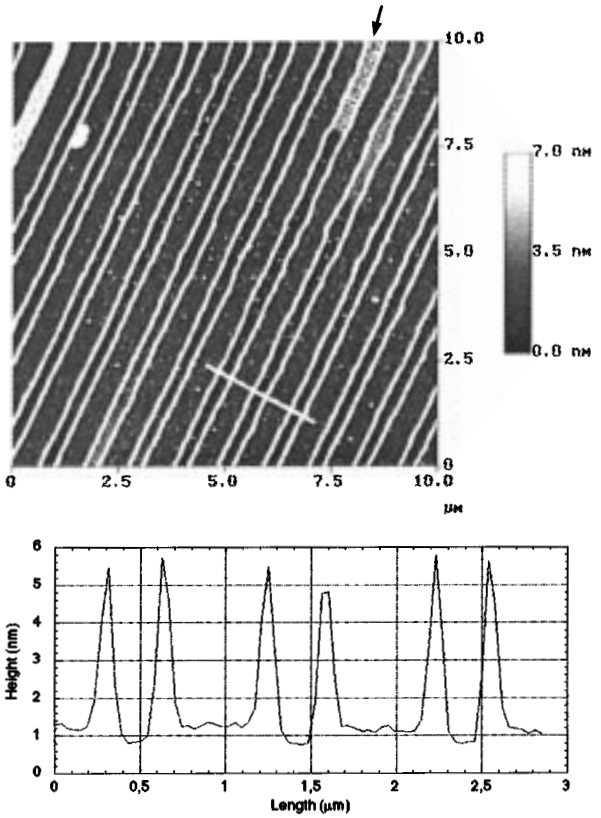

Figure 5. SFM topography image (top) of a stamped structure with 970 nm periodicity where the stamp became "too wet" even with the stamp pad technique. The broad stamped and the smaller nonstamped stripes are separated by rims about 5 nm high. This can be seen too in the section (bottom) where the height difference between stamped and nonstamped regions of 0.5 nm is also visible. The section is indicated by the white solid line in the topography image (top). The region of partial filling by capillary condensation is indicated by an arrow.

rise to the rather thick films bearing the hillock structures. In Figure 5, this becomes quite clear from the fact that one stripe is only partly filled with a hillock film (see arrow). Seemingly, the channel between the stamp and the substrate was only partly filled by capillary forces and corresponds to a stripe with a topography elsewhere *lower* than that of the adjacent stripes. It thus turns out that a "dry" stamp is essential for the stamping process at submicron scales.

On the basis of this scenario, one may interpret the hillocks in a quite straightforward manner as a consequence of dewetting of the ink left behind upon removal of the stamp. Grafting of the perfluorosilane molecules onto the substrate renders the latter hydrophobic, such that dewetting becomes very probable. Each hillock thus appears to be the remainder of perfluorosilane left behind by one of the sessile droplets formed quite typically upon dewetting.[15] It should finally be noted that neither the hillocks nor the elevated rims could be dissolved with hexane. This is not a surprise because, even at low relative humidity, these tiny structures are expected to be stabilized (and thus rendered unsoluble) by dimer formation, since they are directly exposed to atmospheric moisture.

In conclusion, we have examined the performance of submicron contact printing of silane compounds using silicon masters. We have found that the silicon rubber used as the stamp material is not easily capable of molding the shape of the master at high precision. Problems encountered comprise distortions of stamp shape due to imperfections of the molding process and unavoidable swelling by the ink solvent, as well as capillary condensation in the stamp grooves. Nevertheless, introducing the use of an unstructured stamp pad, we are able to produce submicron structured SAMs rather reliably.

Acknowledgment. Helpful discussions with Dr. Roland Wagner are gratefully acknowledged.

LA980429S

(15) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75.