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Patterning Self-Assembled Monolayers on Oxide Surfaces Using a Lift-off Technique**

By Stefan Walheim, Rainer Müller, Monika Sprenger, Edgar Loser, Jürgen Mlynek, and Ullrich Steiner*

Since its discovery six years ago,^[1] microcontact printing of self-assembled monolayers (SAMs) on Au surfaces has gained remarkable popularity, mainly due to the ease of its application, compared to other lithographic techniques.^[2] The pattern formation technique of μ CP is modeled in close analogy to macroscopic relief printing. A master with a topographic pattern is used to cast an elastomeric stamp. Stamping an ink onto a surface reproduces the pattern of the master. Most commonly, the ink is a solution of thiolterminated alkane chains in ethanol, which react with the substrate surface to form a SAM. Lateral structure-sizes down to 100 nm have been reported.^[3,4] Unfortunately, the use of the thiol end-group restricts the choice of surfaces to Au, Ag, and Cu.^[2]

For many experiments in physics, chemistry, and biology, as well as for certain technological applications, the extension of μ CP to other substrate materials is desirable, in particular when transparent or non-conducting surfaces are required. Alkane molecules with various anchor groups such as alkane-silanes have been employed to generate SAMs on oxide surfaces. μ CP using these molecules has recently been reported.^[5–7] It is, however, unlikely that this technique will gain the popularity that μ CP of alkane-thiols enjoys today. The main difference between the chemisorption of thiols on gold and the silane reaction is the role of the water. H₂O is an essential ingredient in the silane reaction. The perfection of silane-based SAMs sensitively de-

[*] Prof. U. Steiner,^[+] S. Walheim, R. Müller, M. Sprenger, E. Loser, Prof. J. Mlynek Fakultät für Physik, Universität Konstanz pends on the H_2O content in the solvent and the amount of adsorbed water on the substrate. This makes the results of μ CP of silanes strongly dependent on environmental parameters such as humidity and temperature.

In this letter, we report a lift-off technique, which extends the ease and reproducibility of µCP of alkane-thiols on Au to virtually any surface onto which SAMs can be grafted. To circumvent the problems caused by the water sensitivity of the silane reaction, we make use of the more robust thiol chemistry (first row, Fig. 1). First, a 10 nm thick Au film is evaporated onto a silicon oxide surface. To guarantee sufficient adhesion of the Au to the substrate, a thin (<2 nm) Ti layer is deposited prior to the evaporation of the Au. A rubber stamp (Sylgard 184, Dow Corning) is soaked in an octadecylthiol (ODT) solution (1 mmol in ethanol) and pressed onto the Au surface. This results in a patterned SAM of ODT (Fig. 1a). The gold regions that are not protected by the SAM are etched away by a cyanide solution (1 mmol potassium thiosulfate, 0.1 mmol potassium ferricyanide, 0.01 mmol potassium hexacyanoferrate(II)trihydrate, 10 mmol potassium hydroxide in H₂O for 10 min). After cleaning the surface using a "snow-jet"^[8] (Fig. 1b), the sample is subjected for ~1 h to an octadecylsilane (OTS) solution (0.25 % in hexane), which forms a SAM on the now exposed oxide surface (Fig. 1c). In a last step, a bromine-methanol etching solution (1:80, 30 s) followed by a snow-jet treatment removes the remaining Au, revealing a laterally patterned oxide surface (Fig. 1d). In our present experiment, the contribution of the thin Ti layer is not completely understood. While it is unlikely that the Ti is removed by the two etching steps, we expect it to completely oxidize in the etching solution. For most applications, we expect the presence of a thin titanium oxide surface to be of no consequence. Future X-ray photoelectron spectroscopy (XPS) measurements should resolve this issue.

The perfect replication of a stamped ODT pattern to an inverted OTS structure is demonstrated in Figure 1. The second row in Figure 1 shows topography images taken with an atomic force microscope (AFM) in contact mode, using a silicon tip, which was rendered unpolar by an OTS layer. The third row shows images that result from a lateral variation of the friction coefficient, yielding a lateral material contrast. We have chosen a $16 \times 16 \,\mu\text{m}$ scan area which includes the edge of a stamped stripe pattern. While the stamped lines are very regular in the interior part of the stamp (Fig. 2), the irregularities at the stamp edges serve to illustrate the precision of our technique. In Figure 1a, the bright surface regions are ODT covered, leaving darker 1-2 nm deep grooves of the bare Au substrate. This is reflected in the friction image, where the ODT features a lower friction coefficient (dark) compared to the Au (bright). After the first etching step (Fig. 1b) the contrast in the topography has increased, revealing the thickness of the Au film (~10 nm). The friction image is comparable to Figure 1a, due to similar friction coefficients of the Au and oxide surfaces. After deposition of the OTS layer (Fig. 1c),

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Fig. 1. Pattern transfer by μ CP combined with a lift-off technique. The first row contains a schematic representation of the process. a) After pressing a rubber stamp onto a gold surface, a structured SAM of ODT (dark gray) is created. b) The bare Au surface regions are etched down by placing the sample into a cyanide solution. c) After incubation in an OTS solution, a SAM (black) forms on the exposed oxide surface. d) Finally, the remaining Au is removed in a second etching step and the inverse of the original ODT pattern (a) is replicated into a laterally structured OTS SAM. In the second and third row, the pattern transfer is monitored with the help of AFM topography and friction-mode images, respectively. a) The ODT pattern on Au features a height contrast of 1–2 nm and a reduced friction coefficient of ODT (dark) compared to the bare Au surface (bright). b) After the first etching step the topography contrast increases to ~10 nm, (the thickness of the Au film) while the friction contrast is similar to a). After OTS deposition (c), the topography changes only little. The contrast in the friction image is due to the increased roughness of the ODT surface. d) A second etching step completes the procedure. The 1–2 nm topography as well as the friction image are the inverse of (a).



Fig. 2. a) AFM topography and b) friction mode images of a structured OTS layer on a silicon oxide surface demonstrate the quality of the pattern transfer. In analogy to Figure 1, the 300 nm wide stripes are first stamped onto a previously deposited Au film and then transferred onto the oxide substrate. As opposed to the direct μ CP of silanes, the technique presented here is less sensitive to environmental parameters.

the topography image changes only slightly. The contrast in the friction image is due to increased roughness of the Au/ ODT surface caused by the etching step and the adsorption of OTS at defects in the ODT layer.^[9] The final pair of

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> images (Fig. 1d) demonstrates the inversion of the topography and friction contrast compared to the original ODTstamped surfaces. A comparison of (a) and (d) in Figure 1 reveals the perfect replication of the stamped pattern. Not only is the pattern with the \sim 1 µm wide stripes found in Figure 1d, but even small imperfections and details on a 100 nm length scale are reproduced. As opposed to the direct micro-contact printing of OTS, grafting a silane-based SAM from solution is readily controlled and more reproducible.

> In addition to the applicability of μ CP to a great variety of different substrate materials, our technique features some additional benefits. Due to mechanical constraints,^[10] stamps typically used for

 μCP yield macroscopically unpolar surfaces that are only locally modified by a polar pattern. This may lead to problems in further processing of the sample, for example if the surface needs to be covered by a liquid or a polymer melt.



In particular, film deposition by spin-coating onto an unpolar substrate^[11] is tricky, since the spin-coating solution does not wet the substrate and flies off the rotating surface. Since the OTS pattern after the lift-off technique is the inverse of the originally stamped ODT pattern, the sample in Figure 1d features macroscopically an oxide surface with printed OTS stripes on a micrometer lateral scale. Beyond the specific advantages of our technique, structured SAMs from OTS enjoy several advantages over their ODT analogs. The surface energy difference between OTS and silicon oxide is much larger than between ODT and Au,^[12] making patterned OTS substrates more suitable for structured wetting and demixing experiments. Potential applications for chemical and biological sensors^[13] also benefit from this increase in polarity. Furthermore, the silane bond is stronger than the chemisorbed thiols allowing experiments at higher temperatures.

In conclusion, we have combined the well-established μ CP technique of alkane-thiols on Au with a lift-off technique to transfer the stamped pattern onto a silicon-oxide surface. The main benefit of this approach compared to a direct printing technique is the improved control over environmental parameters during the deposition of the alkane-silanes, making the lift-off technique more reliable and reproducible. In addition, the lift-off technique does not depend on specific substrate materials. Therefore, extension to a wide range of surfaces and functionalized alkane chains is possible.

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Fabrication of Ordered Two-Dimensional Arrays of Micro- and Nanoparticles Using Patterned Self-Assembled Monolayers as Templates**

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This paper describes a method that uses patterned selfassembled monolayers (SAMs) of alkanethiolates on gold as templates to fabricate ordered two-dimensional (2D) arrays of solid particles, with lateral dimensions ranging from ~50 nm to ~20 μ m. A large number of methods have been developed for producing particles of various materials with sizes from nm to μ m.^[1] Most of these methods produce particles as dispersions in solvents or polymeric matrixes, and most yield a mixture of sizes. Although these dispersions are useful in many applications (for example, in paints or coatings, in imaging systems, drug formulations, or as abrasives),^[2] they have not been useful electrically or optically in functional devices.^[3]

In fabricating devices, the location of functional materials is as important as their properties. Integration of solid particles into devices usually requires placing them in specific positions. We wish to develop new, parallel methods for the fabrication of ordered arrays of small particles. The simplest model systems with which to investigate such arrays are those in which the particles form on a regular grid. Several in situ deposition techniques-for example, molecular beam epitaxy (MBE),^[4] chemical vapor deposition (CVD),^[5] reactions in Langmuir-Blodgett (LB) films,^[6] and pulsed electrochemical deposition^[7]-have been investigated for making arrays of this type. These methods are flexible and capable of generating supported planar arrays of a variety of semiconductor nanocrystallites (some of which have been used to fabricate functional devices such as arrays of quantum dot lasers^[8]), but their accuracy in controlling size distribution and spatial arrangement still needs to be improved for demanding applications. Here we report a method that uses a combination of microcontact printing of SAMs, surface-templated self-assembly, and

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