Electroless Metallization of Dendrimer-Coated Micropatterns**

By *Alexander M. Bittner,** Xiao C. Wu*, and *Klaus Kern*

We combined microcontact printing (μCP), the chemical modification of surfaces, and the binding and reduction of metal ions to produce arrays of metal clusters and metal patterns. Pd^{2+} was bound in and at polyamine–amide (PAMAM) dendrimer molecules with potential ligands (amides and amines or carboxylate). Pd clusters formed after reduction. They provided chemically well-defined nuclei for the electroless deposition of metals. After producing a passivation pattern with μCP, deposition occurred only on those pixels or lines that were covered with Pd clusters. The method is quite general, as exemplified by two different passivation examples, alkanethiolate on gold and alkylsilane on oxidized silicon wafers.

1. Introduction

Arrays of pixels and lines that are composed of metal clusters are of great interest for new nanoscale devices and for their interconnection. For example, they can serve as anchors for the self-assembly of functional molecules such as DNA attached to gold clusters,[1,2] where the functionalities and biological activity of DNA opens the route to further modification. In addition, the electronic properties of a surface or of an adsorbate are locally modified by the presence of a metal cluster in close proximity, leading, for example, to an enhancement of radiation emission or absorption that allows nanoscale spectroscopy to be performed.[3] An important prerequisite for the application of cluster arrays in nanotechnology is their routine and cost-effective fabrication.

Here, we present a straightforward, parallel approach for the wet-chemical fabrication of metal cluster arrays. Lateral and vertical definition should ideally reach the atomic scale. For this, we have employed a combination of microcontact printing (μCP) (which is conceptually and experimentally much simpler than standard lithography), chemical modification of surfaces, and metal ion binding followed by reduction. This offers a wet-chemical, and thus simple and versatile, route towards metal clusters and functionalities. The metal cluster size can be tuned by confining the precursor—the metal ions—in and at a polyamine–amide (PAMAM) dendrimer that is comprised of potential ligands for Pd^{2+} (amides and amines or carboxylate). During or after a chemical reduction, the metal atoms in/at the dendrimer coalesce to form a cluster. The defined number of binding sites per dendrimer assures a well-defined cluster size.[4] Tunability of the cluster size is important, as the optical,[3] magnetic, and electronic properties[5] of a cluster depend very much on its size.

The combination of μCP and self-assembled mono- or multilayers (SAMs) is ideally suited for fabricating patterns and well-defined functionalities. Clusters can be introduced either via a sol of prefabricated metal clusters,[6] or via the binding of metal ions and their consecutive reduction. Some, mostly noble metal, clusters offer the possibility of further modification by the selective, electroless deposition of a second metal onto the cluster. Hence, we conducted experiments on metal-ion binding and reduction on chemically modified surfaces. The use of dendrimers enables ions to be concentrated in/at a single molecule, and this facilitates the coalescence of the atoms upon reduction.[4] Pd clusters formed in this way provide a chemically well-defined activation for the electroless deposition of metals. Furthermore, the deposition can be chosen to be selective, i.e., to occur only on the pixels or lines that are coated by Pd clusters.

2. Results and Discussion

2.1. Alkylsilane/Carboxylate-Terminated Dendrimer Patterns on Oxidized Silicon Wafers

For the fabrication of the patterns (see Figs. 1 and 2) flat stamps were coated with $C_{16}H_{33}SiCl_3$ in hexane, dried, and brought into conformal contact with a patterned PDMS stamp. This step ensured that a patterned stamp did not swell due to hexane uptake.[7] The pattern on the oxidized silicon wafer was then formed by transfer (conformal contact) and hydrolysis of the silane. We note that the surface binding depended on the direct reaction of trichlorosilane groups, as well as on the reaction of silanes that were already hydrolyzed in the solution.[8] The complex chemistry of the layer is simplified as "RSi-$(OH)_2$–O–wafer" in the following Equations 1–4 (further condensation to intermolecular Si–O–Si linkages is possible, but this simplified notation stresses that not all molecules are interconnected).

The scanning electron microscopy (SEM) images show a good contrast between the alkylsilane pattern produced and the substrate (see Fig. 3), pointing towards the formation of more than a single layer of alkylsilane.[9] The ellipsometric thickness of the printed (unpatterned) layer was ca. 4.4 nm,

[*] Dr. A. M. Bittner, X. C. Wu, Prof. K. Kern
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, D-70569 Stuttgart (Germany)
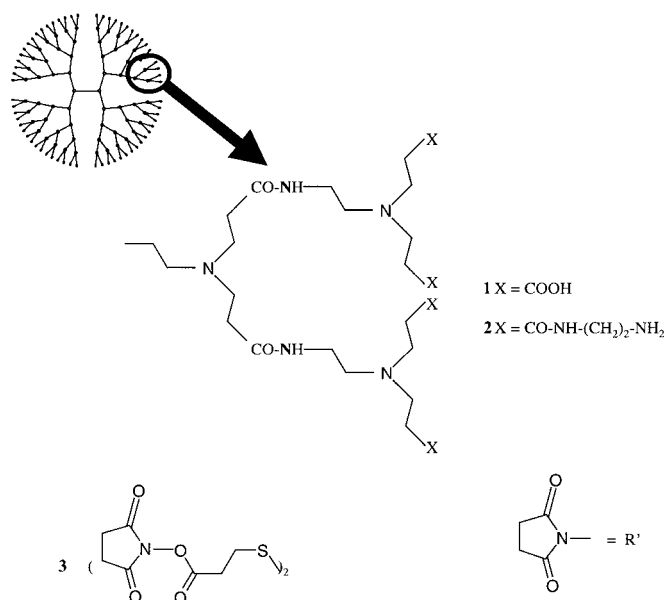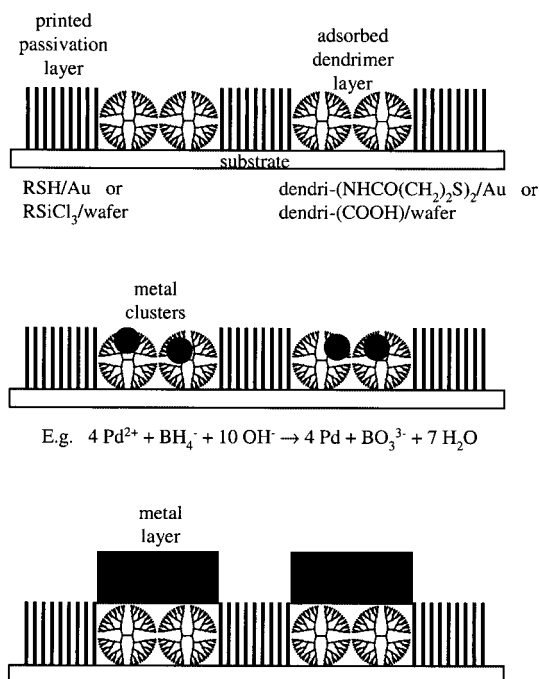E-mail: a.bittner@fkf.mpg.de

Fig. 1. The HOOC– and H_2N–terminated dendrimers **1** and **2**, employed in this study. Their true shape is nearly spherical. The "active ester", **3**, can react with **2** to yield a dendrimer with disulfide termini. R′ is the succinimidyl group.

E.g. $4 Pd^{2+} + BH_4^- + 10 OH^- \rightarrow 4 Pd + BO_3^{3-} + 7 H_2O$

E.g. $Cu(EDTA)^{2-} + 2 HCHO + 4 OH^- \rightarrow Cu + H_2 + 2 H_2O + 2 HCOO^- + EDTA^{4-}$

Fig. 2. Scheme of the metallization process. Dendrimer molecules (here simplified and drawn as disks) adsorb on the non-passivated parts of the surface. Adsorbed metal ions are reduced to clusters that act as nucleation centers for the electroless deposition of a metal layer.

Fig. 3. SEM images of an oxidized silicon wafer after μCP of $C_{16}H_{33}SiCl_3$. The silane was first transferred to a flat stamp, and from there to a patterned stamp. The pattern should contain several layers, since the SEM image shows a good contrast between alkylsilane layer and substrate.

lowing chemical modification: immersion in an aqueous solution of carboxylate-terminated dendrimer (generation 3.5) caused the binding of dendrimers at the bare surface patches. After rinsing with H_2O, the surface was placed in contact with a solution of Na_2PdCl_4 in HCl. Fresh preparation and immediate use prevented the hydrolysis of the Pd^{2+}, which would otherwise result in (unwanted) large chloro-hydroxyl polynuclear complexes.[10] Pd^{2+} bound to the carboxylate as well as the amine and amide groups, and surplus solution was rinsed off with H_2O. Aqueous $NaBH_4$ was used as the reducing agent.

---

1. Microcontact printing (flat stamp technique) of $RSiCl_3$ on oxidized silicon wafers (see text):

$$RSiCl_3 + 2H_2O + HO\text{–wafer} \rightarrow$$
$$\text{``}RSi(OH)_2\text{–O–wafer''} + 3HCl \qquad (1)$$

2. Adsorption of G3.5–dendri–COOH (see Fig. 1) on bare areas:

$$\mathbf{1} + HO\text{–wafer} \rightarrow \mathbf{1}\text{–HO–wafer} \qquad (2)$$

3. Complex formation between Pd^{2+} and G3.5–dendri–COOH (also at amine and amide groups):

$$\text{dendri–}(COOH)_2 + Pd^{2+} \rightarrow \text{dendri–}(COO)_2\text{–Pd} + 2H^+ \qquad (3)$$

4. Reduction to Pd clusters:

$$4 Pd^{2+} + BH_4^- + 10OH^- \rightarrow 4Pd + BO_3^{3-} + 7H_2O \qquad (4)$$

---

which is about twice the thickness of a single $C_{16}H_{33}SiCl_3$ layer. The static water contact angle (measured with an unpatterned stamped layer) is close to 110°, indicating the formation of a hydrophobic passivation layer. The transfer was not perfectly homogeneous, which, however, did not interfere with the fol-
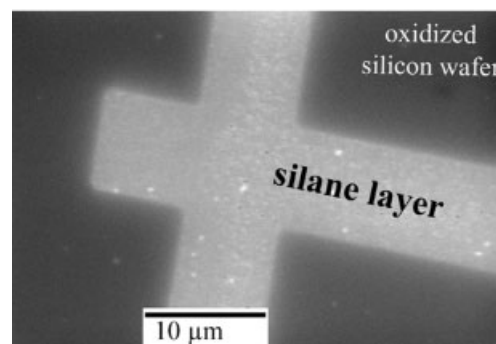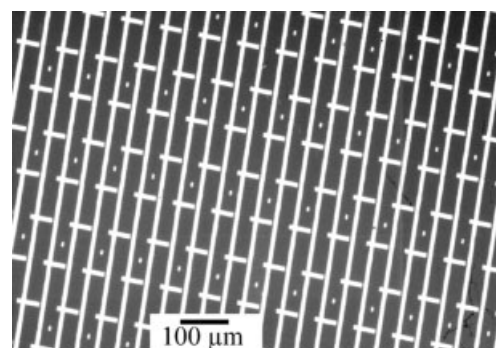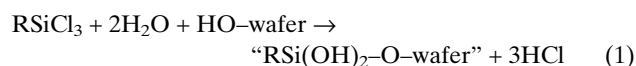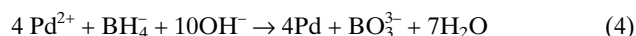
After this treatment, the dendrimer layers were filled with Pd clusters,[11] and the layers were easily imaged by atomic force microscopy (AFM). Figure 4 shows that the selectivity was close to 100 %, i.e., the layers (white, 400 nm high) formed exclusively on the bare patches of the substrate; elsewhere the
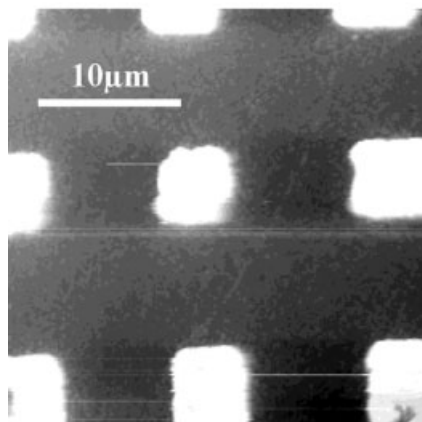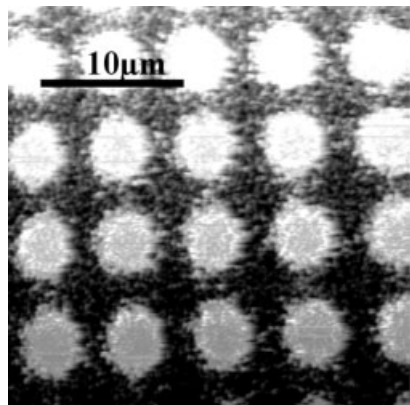

Fig. 4. Intermittent-contact AFM images of a thick Pd–dendrimer composite (white) on an oxidized silicon wafer surface that was patterned with passivating alkylsilane layers (black). The binding of Pd^{2+}, and its reduction to Pd, occurred only on the bare parts of the wafer, where a G3.5COOH dendrimer was adsorbed. The images show different areas with different patterns.

alkylsilane molecules hindered the binding of the dendrimer, and thus offered very good protection. Note that the alkylsilane layer was not (or only to a very small extent) attacked by the reducing agent. The surprisingly thick patterns resulted from a high dendrimer concentration and thus multilayer adsorption.[12] Due to the slightly acidic pH (the pKs for alkanecarboxylic acids are between 4 and 5), the wafer surface was protonated (OH groups), and the dendrimer was partially protonated: thus hydrogen bonds could form. Both protonated and deprotonated carboxylate groups can easily form hydrogen bonds to OH groups and to each other, thus interconnecting the dendrimer molecules. Due to the flexible shape of the dendrimers, amine groups could also interact with the surface, but protonated tertiary amine groups could not interact strongly with the surface OH groups. Deprotonated amines may compete with carboxylate groups: however, since the molecule has a near-spherical shape in solution, the outer carboxylate sur-

face has at least a kinetic advantage. The same is true for the multilayers. Furthermore, the fact that the multilayers can be subjected to acidic solutions without damage (see below) suggests that deprotonated amines play no major role. UV spectra of dendrimer solutions treated in the same way suggest that no Pd^{2+} remains after the reduction, although preliminary X-ray photoelectron spectroscopy (XPS) results suggest that a few percent of the Pd molecules are present as Pd^{2+} (after immersion and transfer to vacuum). Furthermore, we can conclude from the AFM results that the thus formed Pd/dendrimer composites are closely packed, otherwise their extreme height could not be explained. If the intermolecular bonds were weak (loose packing), the AFM tip would be able to move the Pd/dendrimer composite.

Average roughness analyses from non-contact AFM images suggest that the alkylsilane layers and carboxylate-terminated dendrimers on an oxidized silicon wafer demixed into tens of nanometer-wide domains (Fig. 5). We observed this phenomenon on non-patterned surfaces when they were first immersed,
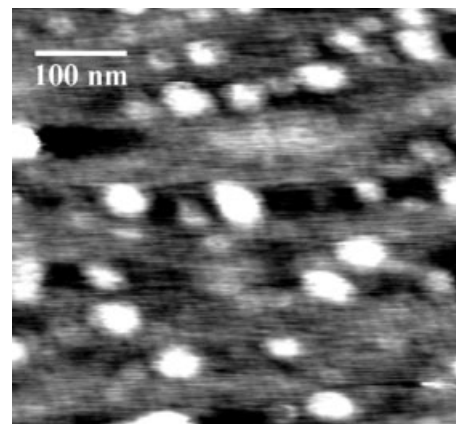

Fig. 5. Intermittent-contact AFM image of an oxidized silicon wafer surface that was first immersed in 10 mM $G4NH_2$ dendrimers for 20 h. The white spots (height lower than 5 nm) were only observed after immersion in 1 mM $C_{16}H_{33}$-$SiCl_3$, in hexane, for 2 h: a clear indication of a demixing phenomenon.

for 20 h, in a 1 μM aqueous solution of the dendrimer. A flat topography (roughness below 1 nm) suggests the adsorption of one or more well-spread layers of molecules. After 2 h contact with a 1 mM hexane solution of the silane, we detected patches several nanometers in height (Fig. 5). These can be interpreted as either a thick layer of alkylsilane formed at the defects in the dendrimer layers, or as dendrimers that were shifted from their position since $RSiCl_3$ binds more strongly to the surface's OH groups. The phenomenon can be compared with the displacement of dendrimers on gold by thiols.[13] Domains (patches) form, i.e., the adsorbates are immiscible on this surface. This result is very important when the surface density of the metal–dendrimer clusters must be reduced—a simple dilution strategy (a few dendrimer molecules in a matrix of alkylsilane) would most likely fail. A much different behavior can be expected from alkanethiolates on Au,[14–16] which leads us to a second strategy (see below).

### 2.2. Alkanethiolate/Disulfide + Amine-Terminated Dendrimer Patterns on Au

The procedure is explained in the Experimental section (see also Figs. 1 and 2, and Equations 5–10). Stamps were inked with thiol and brought into conformal contact with a gold surface. A pattern was formed by the transfer and reaction of the thiol, and was comprised of a monolayer.[17] Since the substrate in this case is conductive, the electrodeposition of Cu should produce a pattern. However, the passivating alkanethiolate layer is damaged when copper is deposited galvanically: indeed, copper readily inserts between thiolate and gold in the underpotential deposition range.[18–20] Thus, we exploited the electroless dendrimer–cluster method:[21] an amine-terminated dendrimer (generation 4) was reacted with an active ester that contains a disulfide group. According to the stoichiometric ratio of ester/dendrimer, ca. 20 % of the amine end-groups can be transformed to amides with disulfide groups. The latter form a strong bond only with the bare Au surface; it is likely that the disulfide bond is cleaved, since disulfide layers have the same properties as thiolate layers.[22] The disulfide thus binds to the bare Au, but not to the alkanethiolate layer, upon contact of the solution with the patterned surface. However, we found that this also applies when unmodified dendrimer was used. For the unmodified dendrimer as well as for the disulfide, we can expect a prolate adsorption geometry—the spherical shape was not preserved on the surface, as we proved with scanning tunneling microscopy (STM), where the apparent height of single molecules (1 nm) was far below the diameter (> 4 nm). After rinsing with ethanol, the surface was placed in contact with aqueous $CuSO_4$, and then reduced with aqueous $NaBH_4$. After this procedure, the dendrimer layer was filled with Cu clusters.[23] They are prone to oxidation, and were thus quickly modified by rinsing with H_2O and by covering the surface with a Cu electroless deposition bath.

A thick layer of copper (see Fig. 6) deposited selectively on the dendrimer–Cu layer, i.e., elsewhere the alkanethiolate hindered the binding (thiolate bonds) of the dendrimer, as well as the binding of Cu^{2+}. The deposition time was chosen so that the thickness was well above the limit of an optically visible metal layer (several tens of nanometers). That the metal layer remained confined to the pattern, even for very thick layers, is an indirect proof that we indeed produced Cu clusters that acted as catalytic nuclei for the electroless deposition process. Deposition from the same bath on pure gold, or on metal on top of an organic structure, was found to be much faster: this easily led to overgrowth of the pattern. For the slow growth on the dendrimer–Cu layer, it was even more important that the thiolate layer hindered the binding of Cu^{2+} and/or HCHO. This is also true when electroless Ni is deposited on a patterned passivated Au surface.[17] In contrast, copper was deposited electrolessly on areas activated with a Pd catalyst μCPed on a non-conductive oxide.[24]
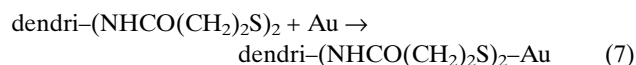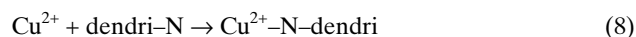
1. Microcontact printing of RSH on Au:

$$RSH + Au \rightarrow RS\text{–}Au + 1/2\ H_2 \tag{5}$$
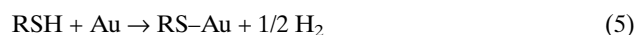
2a. Preparation of disulfide-terminated dendrimer (See Fig. 1):

$$\mathbf{2} + \mathbf{3} \rightarrow dendri\text{–}(NHCO(CH_2)_2S)_2 + 2R'\text{–}OH \tag{6}$$
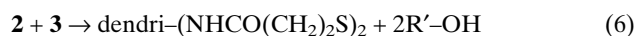
2b. Adsorption of disulfide-terminated dendrimer on bare areas:

$$dendri\text{–}(NHCO(CH_2)_2S)_2 + Au \rightarrow$$
$$dendri\text{–}(NHCO(CH_2)_2S)_2\text{–}Au \tag{7}$$

3. Binding of Cu^{2+} to dendrimer amine groups:

$$Cu^{2+} + dendri\text{–}N \rightarrow Cu^{2+}\text{–}N\text{–}dendri \tag{8}$$

4. Reduction to Cu clusters:

$$4\ Cu^{2+} + BH_4^- + 10OH^- \rightarrow 4Cu + BO_3^{3-} + 7H_2O \tag{9}$$
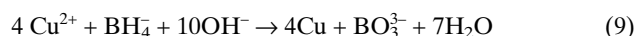
5. Electroless deposition of Cu on the Cu clusters:

$$[Cu(EDTA)]^{2-} + 2HCHO + 4OH^- \rightarrow$$
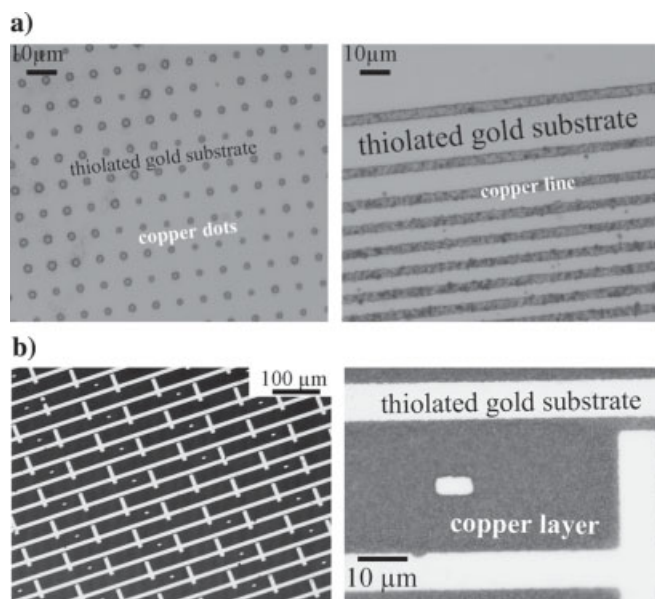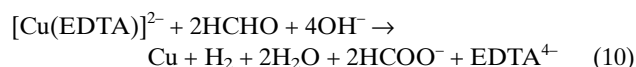$$Cu + H_2 + 2H_2O + 2HCOO^- + EDTA^{4-} \tag{10}$$

Fig. 6. a) Optical microscopy images of Cu pixels (black) produced by the electroless deposition of Cu on a Au surface modified with disulfide-terminated dendrimers. The gray parts had been passivated by μCP of an alkanethiol. b) Optical microscope images of a Cu pattern (black) produced by the electroless deposition of Cu on a dendrimer-modified Au surface. The gray parts had been passivated by μCP of an alkanethiol. Note that the Cu pattern is black. The choice of the pattern allows the production of Cu lines or pixels (a) or Cu areas separated by passivated gold lines (b), or even both, in a single step.

3. Conclusion

We have presented two simple methods for the rapid and highly parallel structuring of a surface with metal clusters and layers. Lateral dimensions reach the μm scale, and an extension into the 100–1000 nm range is straightforward. The methods are based on combining patterning and chemoselectivity. Electroless deposition (in one or two steps) is a mild method that does not attack microcontact printed passivating layers. The flexible nature is obvious from our choice of two very different substrates—metallic Au and oxidized silicon wafers.

4. Experimental

μCP stamps were molded from poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Chemicals) at 60 °C. The master was a silicon wafer treated with $C_8F_{17}(CH_2)_2SiCl_3$ (ABCR) vapor at ca. 40 mbar (water beam pump) in a desiccator. The feature size of the master ranged from 300 nm up to several μm. The pattern was etched in a 1000 or 400 nm deep oxide layer on a silicon wafer (Institute for Microelectronics Stuttgart, IMS). We also employed μCP stamps from the IBM Zürich Research Laboratory (Switzerland).

The procedure for fabricating the alkylsilane patterns with a Pd cluster/dendrimer composite was as follows (see also Figs. 1 and 2): Flat PDMS stamps were inked with 2 mM $C_{16}H_{33}SiCl_3$ (Fluka) in hexane (puriss. p.a., Fluka; dried over molecular sieves) for 25 s, then blown dry with Ar and brought into conformal contact with a patterned PDMS stamp. The stamp was placed in conformal contact with an oxidized silicon wafer (orientation (100); Crystal, Berlin). The wafer was terminated by silicon oxide with OH groups by the standard RCA procedure: 15 min immersion in a 1:1:5 mixture of 25 % NH_4OH (VLSI Selectipur, Merck)/31 % H_2O_2 (VLSI Selectipur, Merck)/H_2O (Millipore, 18 MΩ cm) at 65–75 °C; followed by 15 min immersion in a 1:1:5 mixture of 37 % HCl (Suprapur, Merck)/30 % H_2O_2/H_2O at 65–75 °C. We termed these samples "oxidized silicon wafers".

Dendrimer layers in alkylsilane patterns were produced by immersing the oxidized silicon wafer in an aqueous solution (1 μM) of carboxylate-terminated PAMAM dendrimer (generation 3.5, Aldrich) overnight. After rinsing with H_2O, the surface was placed in contact with a solution of freshly prepared 0.67 mM Na_2PdCl_4 (Aldrich) in HCl (pH 1). The reduction solution was 5 mM $NaBH_4$ (Fluka, purum p.a.) in H_2O.

Alkanethiolate patterns on gold with a Cu/dendrimer composite (see also Figs. 1 and 2) were fabricated as follows: stamps were inked with 1 mM $C_{18}H_{37}SH$ (98 %, Aldrich) in ethanol (p.a., Roth) for 25 s, then blown dry with Ar and brought into conformal contact with a gold surface (gold evaporated on mica at 300 °C, or on chromium-coated glass at 25 °C; in the latter case flame-annealed). A dendrimer with disulfide groups was synthesized as follows [21]: 883 mg of amine-terminated PAMAM dendrimer (generation 4, Aldrich) and 40 mg 3,3′-dithio-bis(propionic acid)-N-hydroxysuccinimide ester (Fluka) were dissolved in 1 mL ethanol + 1 mL tetrahydrofuran (Uvasol, Merck). The solution was left to react for 10 min, then the patterned surface was immersed in it for 15 h, rinsed with ethanol, and immediately placed in contact with an aqueous solution of 1 mM $CuSO_4$ (99.999 %, Aldrich). The reduction was accomplished using 5 mM $NaBH_4$ in H_2O. The copper electroless deposition bath consisted of: 40 mM $CuSO_4$, 140 mM Na_2SO_4 (p.a., Merck), 120 mM Na_2H_2EDTA (Aldrich), 300 mM NaHCOO (ACS, Sigma), 30 mM HCHO (puriss. p.a., Fluka), at pH 13 (NaOH). The immersion times for Cu electroless deposition (ELD) were varied from several minutes to nearly half an hour, in order to obtain different amounts of Cu.

AFM images were recorded with a M5 Autoprobe instrument (ThermoMicroscopes)—mainly in the intermittent-contact mode—and with MikroMasch Si tips. STM images were obtained with a Molecular Imaging PicoSTM and etched tungsten tips. SEM was performed with a JSM-6400 scanning microscope. Contact angles were determined with a Krüss G 10 goniometer. Ellipsometric measurements were performed in air, with an EL X-02C ellipsometer (DRE, Ratzeburg) at a 70° angle of incidence and at 633 nm wavelength. A two-layer transparent film model was used for the thickness calculations of the molecular layers (refractive index set to 1.45) on the oxidized silicon wafers.

[1] C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, *Nature* **1996**, *382*, 607.
[2] C. M. Niemeyer, M. Adler, B. Pignataro, S. Lenhert, S. Gao, L.F. Chi, H. Fuchs, D. Blohm, *Nucleic Acids Res.* **1999**, *27*, 4553.
[3] S. R. Emory, W. E. Haskins, S. Nie, *J. Am. Chem. Soc.* **1998**, *120*, 8009.
[4] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181.
[5] *Cluster and Nanostructure Interfaces* (Eds: P. Jena, S. N. Khanna, B. K. Rao), World Scientific, Singapore **2000**.
[6] H. X. He, H. Zhang, Q. G. Li, T. Zhu, S. F. Y. Li, Z. F. Liu, *Langmuir* **2000**, *16*, 3846.
[7] M. Geissler, A. Bernard, A. Bietsch, H. Schmid, B. Michel, E. Delamarche, *J. Am. Chem. Soc.* **2000**, *122*, 6303.
[8] D. Wang, S. G. Thomas, K. L. Wang, Y. Xia, G. M. Whitesides, *Appl. Phys. Lett.* **1997**, *70*, 1593.
[9] Y. Xia, M. Mrksich, E. Kim, G. M. Whitesides, *J. Am. Chem. Soc.* **1995**, *117*, 9576.
[10] H. Kind, A. M. Bittner, O. Cavalleri, K. Kern, T. Greber, *J. Phys. Chem.* **1998**, *B102*, 7582.
[11] M. Q. Zhao, R. M. Crooks, *Angew. Chem. Int. Ed.* **1999**, *38*, 364.
[12] V. V. Tsukruk, F. Rinderspacher, V. N. Bliznyuk, *Langmuir* **1997**, *13*, 2171.
[13] H. Tokuhisa, M. Q. Zhao, L. A. Baker, V. T. Phan, D. L. Dermody, M. E. Garcia, R. F. Peez, R. M. Crooks, T. M. Mayer, *J. Am. Chem. Soc.* **1998**, *120*, 4492.
[14] F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151.
[15] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **1996**, *271*, 1705.
[16] J. F. Kang, S. Liao, R. Jordan, A. Ulman, *J. Am. Chem. Soc.* **1998**, *120*, 9662.
[17] A. Kumar, H. A. Biebuyck, G. M. Whitesides, *Langmuir* **1994**, *10*, 1498.
[18] O. Cavalleri, H. Kind, A. M. Bittner, K. Kern, *Langmuir* **1998**, *14*, 7292.
[19] O. Cavalleri, A. M. Bittner, H. Kind, K. Kern, T. Greber, *Z. Phys. Chem.* **1999**, *208*, 107.
[20] M. Epple, A. M. Bittner, K. Kuhnke, K. Kern, W.-Q. Zheng, A. Tadjeddine, *Langmuir* **2002**, *18*, 773.
[21] V. Checkik, R. M. Crooks, *Langmuir* **1999**, *15*, 6364.
[22] G. Nelles, H. Schönherr, M. Jaschke, H. Wolf, M. Schaub, J. Küther, W. Tremel, E. Bamberg, H. Ringsdorf, H.-J. Butt, *Langmuir* **1998**, *14*, 808.
[23] A. W. Bosman, A. P. H. J. Schenning, R. A. J. Janssen, E. W. Meijer, *Chem. Ber./Rcl.* **1997**, *130*, 725.
[24] H. Kind, M. Geissler, H. Schmid, B. Michel, K. Kern, E. Delamarche, *Langmuir* **2000**, *16*, 6367.