Spatially Selective Electroless Deposition of Cobalt on Oxide Surfaces Directed by Microcontact Printing of Dendrimers

X. C. Wu, A. M. Bittner,* and K. Kern

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1,
D-70569 Stuttgart, Germany*

We describe a simple method for the fabrication of arbitrary submicrometer patterns of cobalt on a nonconducting surface with wet chemical methods and microcontact printing (μCP). A hydroxyl-terminated dendrimer is transferred from a stamp to the surface. The thickness of the dendrimer layer can be tuned by varying the concentration of the dendrimer ink solution. These dendrimer molecules act as host molecules. The guests, palladium ions, sorb into the layer and act as nucleation centers for electroless cobalt plating. We produced cobalt structures down to several hundred nanometers lateral size and up to several tens of nanometer thickness with high spatial selectivity. The printed dendrimers are cage-like molecules with well-defined chemical groups; hence, they can selectively bind guest molecules (here palladium complexes) when the latter possess chemical groups that favor a host–guest interaction. Printing dendrimers therefore points toward a more general method to create patterns with chemical functionality.

Introduction

The formation of (sub)micrometer patterns is usually based on lithographic techniques. Whenever chemical functionalities come into play, these techniques reach their limitations; for example, in most cases patterns are formed by gas phase deposition or by etching. Of these techniques only the deposition can create a new species on a substrate. However, the chemical functionality is limited by the number of deposited compounds. Microcontact printing (μCP) can offer an interesting alternative.[1] Its strength is that either a passivation layer can be printed, followed by steps that are similar to those used in lithography, e.g. etching, or that an "active" layer can be formed, i.e., molecules with functional groups can be directly deposited. The latter strategy, albeit requiring compatible stamp–molecule–surface systems, does in principle not depend on the nature of the substrate and is hence generally applicable. In addition, purely wet chemical methods can be applied and significantly simplify the patterning process. The method has been used to print a variety of molecules on surfaces. Recently Bernard et al. further extended the μCP technique to biological systems. They succeeded in printing proteins onto surfaces while preserving the biological activity.[2]

In the case of printing passivation layers, μCP of self-assembled monolayers (SAMs), such as alkyl-terminated thiols and chlorosilanes, has gained remarkable popularity. Up to now, the best system for μCP is printing thiols on gold substrates since the substrate is a well-defined surface (a single crystal can be employed) and since the printed layer is monomolecular and well-characterized. Lateral structures of 100 nm and less have been achieved.[3,4] However, the use of the thiols restricts the choice of surfaces to several metals such as gold or copper.

For many experiments, the extension of μCP to other substrates is desirable, especially when nonconducting surfaces such as oxide surfaces are required. One simple way to pattern oxide surfaces is via direct μCP of chlorosilanes.[5–8] However, this method has limitations: (1) Due to the sensitivity of chlorosilanes to environmental parameters such as humidity and temperature, the quality of chlorosilane-based printed SAMs is difficult to control and guarantee. (2) The solvents for chlorosilanes are hydrocarbons; they can easily swell the poly(dimethylsiloxane) (PDMS) stamps. This will lead to a distortion of the printed pattern, especially for small feature sizes. An alternative method to pattern oxide surfaces is the so-called lift-off technique:[9] it is based on printing thiols on Au/Ti/Si substrates, followed by several passivation and etching steps. In this way, an inverse of the original pattern is obtained on oxide surfaces. Although this method avoids the disadvantages of direct printing of chlorosilanes, many steps are involved in obtaining a patterned surface. Note that for the above-mentioned three methods the ink molecules are *nonfunctional* molecules. They act either as a resist layer for further etching or as a passivation layer for preventing the functional molecules from entering the patterned regions.[10,11]

For the case of printing specific chemical functions, the inks normally contain the corresponding functional molecules.[2,12–14] They can be printed either as functional

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molecules or as catalysts for the formation of other functional materials. Although a direct μCP of various functional materials is desirable, the printing is not straightforward due to different surface−material−stamp interactions for each functional material. More important, printing is not always successful.[15] Therefore, the patterning of functional molecules is usually based on *indirect* processes, i.e., the direct μCP of SAMs forms patterns, but the unpatterned regions are used to assemble functional molecules.[16,17]

Electroless deposition (ELD) of metals is a process widely used for the production of fine metal patterns in printed circuits.[18] ELD occurs by an autocatalytic redox process, which generally takes place only on surfaces capable of catalyzing it. Noncatalytic surfaces first have to be "activated" with a metal catalyst before the metallization can occur. Selective deposition can be achieved either by selective deactivation of a catalytic substrate[19] or by selective activation of a nonreactive surface by a catalyst.[20] Oxide surfaces are good examples for the latter case. Apart from widely used photolithographic techniques for the production of patterned catalysts, the above-mentioned direct μCP of functional materials has also been used to pattern specific catalysts. For example, Hidber et al. printed palladium nanoparticles onto nonreactive surfaces and then used them as catalysts for the ELD of copper.[21] Similarly, Kind et al. reported the direct printing of a special Pd^{2+} complex on Si wafer with a Ti layer as a catalyst for the reduction of Pd^{2+}. Copper layers were obtained by immersion of the sample in an ELD bath.[22]

Here we show a simple way to pattern oxide surfaces by the combination of μCP of a functional host molecule with ELD. The host is a dendrimer. The dendrimer molecules employed possess amine, amide and hydroxyl groups that act as binding sites of palladium ions, which in turn can be reduced to palladium metal. Cobalt is a metal that can be plated without external current source; the deposits reach several tens of nanometer thickness. Upon immersion of a patterned substrate in a cobalt ELD bath, a selective deposition of cobalt films on the patterned regions is realized. We chose cobalt patterns as an example since we aim at showing that μCP can also produce conducting and even magnetic patterns on oxidized silicon wafers; such patterns usually have to be fabricated by lithographic techniques. Our method allows to fabricate lines, pixels etc. on any surface that contains a sufficient amount of hydroxyl groups.

2. Experimental Part

2.1. Substrates and Stamps. The substrates were silicon wafers (orientation (100), Crystal, Berlin). The wafers were terminated by silicon oxide with OH groups by the standard RCA procedure: 15 min immersion into a 340−350 K hot 1:1:5

mixture of 25% NH_4OH (VLSI Selectipur, Merck), 31% H_2O_2 (VLSI Selectipur, Merck) and water (Millipore, 18 MΩcm); 15 min immersion into a 340−350 K hot 1:1:5 mixture of 37% HCl (Suprapur, Merck), 31% H_2O_2 and water. We term these samples "oxidized silicon wafers". Poly(dimethylsiloxane) (PDMS) stamps (Sylgard 184, Dow Corning) were formed on flat polystyrene dishes or patterned silicon wafer masters (IBM Zürich and IMS Stuttgart; before first use, each master was rendered hydrophobic with fluoroalkyl-trichlorosilane vapor). The stamp was activated in a 1 mbar oxygen plasma before inking.

2.2. Inking, Printing, and Loading of Pd^{2+} Catalyst. Polyamidoamine (PAMAM) starburst dendrimer (generation 4) terminated with hydroxyl (Aldrich), here referred to as G4OH, was dissolved in 99.8% ethanol (Roth) with concentrations from 2 μM to 0.2 mM as ink solutions. Freshly activated stamps were covered with one drop (20 μL) of ink solution for 25s, and then blown dry with argon. The stamp was brought in conformal contact with a freshly cleaned silicon wafer for 10−120 s and peeled off from the substrate. One drop of an aqueous solution containing 0.36 mM Na_2PdCl_4, 0.1 M NaCl and 0.01 M 2-morpholinoethanesulfonic acid (MES, pH = 4.9) as a buffer[23] was put on the substrate for 5 to 15 min, then the substrate was rinsed with water several times.

2.3. Electroless Cobalt Deposition. The metallization solution was prepared immediately prior to use by mixing three parts of cobalt stock solution, two parts of reductant, and five parts of water. The stock solution was prepared by adjusting a 100 mL aqueous solution of 1 g NH_4Cl, 0.6 g $CoCl_2$, and 0.8 g of Na_2EDTA to pH = 7 with 2 M NaOH. The reductant consisted of a solution of 1.7 g of dimethylamineborane (DMAB) in 50 mL water.[24] The patterned substrate was put in an argon-bubbled cobalt bath at 310 K for 1 to 3 min to obtain a metallic film.

2.4. Instrumentation. Ellipsometric measurements were performed in air with an EL X-02C ellipsometer (DRE, Ratzeburg) at 70° angle of incidence and 633 nm wavelength. The ellipticity of the HeNe laser beam was minimized with a λ/4 plate. Measurements were made at >4 points randomly picked across the sample and averaged. A two-layer transparent film model was used for the thickness calculations of dendrimer layers on oxidized silicon wafers. The refractive index of dendrimers was fixed at 1.45. Atomic force microscopy images of patterns were obtained in intermittent contact mode with a Thermo-microscopes Autoprobe M5. We used a JSM-6400 scanning electron microscope (SEM).

3. Results and Discussion

Dendrimers are highly branched, nearly spherically shaped molecules, often with multiple chemical groups.[25] G4OH dendrimers with amine, amide, and hydroxyl functional groups have been used as templates for the direct synthesis of metal nanoparticles such as Cu, Pt and Pd within the dendrimer.[26,27] Due to the fixed number of binding sites, thus prepared metal nanoparticles show narrow size distributions and keep their catalytic activities. Dendrimers with hydrophilic end groups also form SAMs on oxidized silicon wafer surfaces (SiO_2/Si) via hydrogen bonds since the surfaces contain hydroxyl groups. Different from long chain linear molecules, dendrimers of a generation higher than 4 exhibit nearly spherical shapes in solution. When they adsorb on a hydrophilic surface, they become oblate and thus form a film (as shown in Figure 1). It is important to note that, although dendrimer SAMs are closely packed, they are not as dense as those from long chain thiols and silanes. For example, $G4NH_2$ layers on Au substrates can slow the rate for the ELD of Cu on Au, but they cannot prevent

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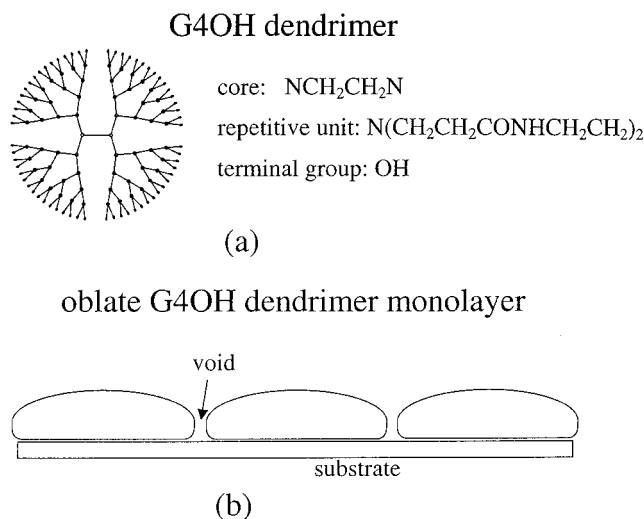(27) Zhao, M. Q.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 364.

G4OH dendrimer

core: NCH_2CH_2N

repetitive unit: $N(CH_2CH_2CONHCH_2CH_2)_2$

terminal group: OH

(a)

oblate G4OH dendrimer monolayer

(b)

Figure 1. Schematic images of a single G4OH dendrimer and of a dendrimer monolayer.

Figure 2. (a) Ellipsometrically determined thickness of G4OH films on oxidized silicon wafers. The films were formed by printing or immersion in ethanolic dendrimer solution. For printing with the ink concentrations of 2 μM (solid squares), 17.6 μM (solid circles), and 176 μM (solid triangles) an inking time of 25 s was used. For the adsorption 2 μM (empty squares) and 176 μM (empty triangles) solutions were employed. (b) Relation between the layer thickness and the ink concentration (inking time 25 s, printing time 25 s).

it, while long chain thiol SAMs on Au will suppress Cu ELD completely.[19] Dendrimer SAMs are therefore "active" by both their own functional groups and by allowing other molecules to access the substrate.

Optical ellipsometry is a convenient technique for measuring the thickness of very thin layers and has been used extensively to study the nature of SAMs. The exact calculation of the thickness of dendrimer layers needs to consider the voids unoccupied by dendrimers as discussed by Tokuhisa et al.[28] (see Figure 1). Since our main concern is the nominal *coverage* of dendrimers (not the actual thickness of the SAM or the molecules), we use the simple two-layer model (dendrimer/SiO$_2$) to obtain the thickness of a dendrimer layer. Although this model is not exact, the thus measured thickness of a G4OH monolayer—prepared by adsorption from solution—shows a good agreement with the thickness obtained by X-ray reflectivity and atomic force microscopy measurements.[29] This indicates that our simple model still is a good approximation. Figure 2a shows the relation between the average (nominal) layer thickness and the printing (or immersion) time. In the case of μCP, we employed flat stamps instead of patterned ones in order to avoid measuring uncovered regions of the wafer. For the solution adsorption process, the concentrations of G4OH have no obvious effect on the thickness of the layers. The layers rapidly reach the thickness of G4 dendrimer monolayers, (1.4 ± 0.4) nm.[29] In contrast, the concentrations of the G4OH *ink* have a large effect on the thickness of printed layers. It increases from 0.25 nm for 2 μM ink concentration to 2.8 nm for 0.18 mM. On the other hand, the printing time has no obvious effect. This is different from printing thiols and chlorosilanes, which show an obvious increase of printed SAM thickness with contact time.[4,10] Thus we can shorten printing times to decrease the lateral diffusion in the case of very small pattern sizes.

Figure 2b further details the change of the thickness with increasing ink concentration. It shows a linear correlation with the ink concentration. This indicates that the coverage of dendrimers can be tuned through the control of dendrimer concentration. This dependence of the printed thickness on ink concentration exists for thiol
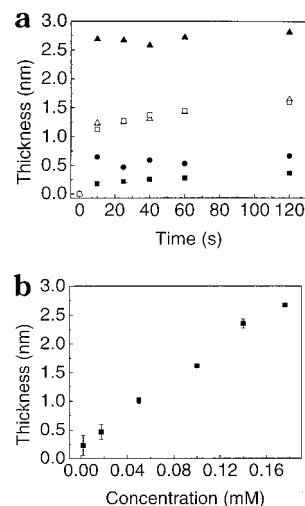
and chlorosilane systems as well, but a nonlinear increase of SAM thickness with ink concentration was observed for these two systems.[4,10] For printing thiols, normally a monolayer is obtained,[4] while in the case of chlorosilanes multilayers are easily produced.[30] Since the assembly process of chlorosilane molecules is based on hydrolysis and condensation reactions, they can easily form three-dimensional networks via self-condensation. Such networks have been used as resist layers for etching processes since printed monolayers of octadecyltrichlorosilane cannot protect a silicon wafer effectively.[6,7] G4OH dendrimers have 64 terminal hydroxyl groups. They self-assemble on hydrophilic oxide surfaces via hydrogen bonds, i.e., without a chemical reaction. They can also adsorb onto a thus formed monolayer. Therefore it is not surprising that we printed multilayers at high ink concentrations.

Figure 3 presents SEM micrographs of patterned G4OH layers at three different concentrations. With increasing concentration the printed pattern size will gradually increase. This undesired concentration "widening" of lines and pixels exists also for thiols and chlorosilanes.[4,10] Therefore an optimization of the ink concentration is required. In our case, the best ink concentration is in the range of several μM of G4OH. Figure 4 is an atomic force microscopy image of 600 nm wide linear patterns, printed with 2 μM G4OH in ethanol. It indicates that pattern sizes can easily be reduced down to several hundred nanometers. We did not expect this result; indeed, many other inks cannot be printed, diffuse too rapidly or aggregate/show dewetting.

Pd^{2+} ions in buffered fresh solutions of pH = 5 (see Experimental Section) can easily bind to the thus obtained G4OH dendrimer patterns. After washing and immersion of the palladium-treated sample in a cobalt ELD bath (see Experimental Section), a cobalt pattern will form selectively on the printed dendrimer layer. Figure 5 shows an atomic force microscopy image of a 700 nm wide cobalt line pattern produced in this way. The average height of the Co pattern is ca. 80 nm. A zoom-in (see inset of Figure

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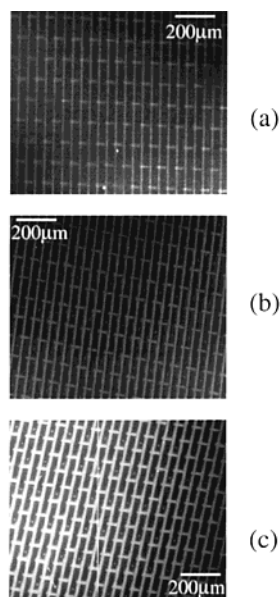
Figure 3. Electron microscopy micrographs of printed G4OH patterns on oxidized silicon wafers. Printing ink concentrations: 2 μM (a), 50 μM (b), and 100 μM (c) G4OH in ethanol. The patterns are 15 μm wide structures separated by 50 μm spaces.
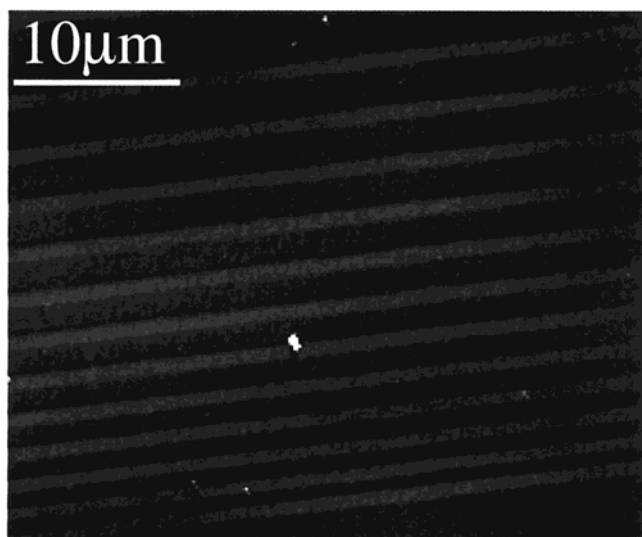

Figure 4. Topographic atomic force microscopy image of 600 nm linear dendrimer patterns on an oxidized silicon wafer, obtained in intermittent contact mode (ink concentration, 2μM G4OH in ethanol; inking time, 25 s; printing time, 25 s).

5) provides details of the Co structure, presumably grains and grain boundaries. We found that the inked stamp could be used several times without reinking. In addition to being highly relevant to applications, this leaves space for a further decrease of the ink concentration for even smaller pattern sizes.

Apart from the optimization of the G4OH ink concentration, another vital factor for the successful fabrication of the cobalt pattern is the effective binding between G4OH and Pd^{2+} ions. Each G4OH molecule has 62 tertiary amine and 124 amide groups which both can bind Pd^{2+} ions, while the 64 hydroxyl groups are relatively weak ligands. The ability of G4OH dendrimers to complex Pd^{2+} from solution requires that the amine groups are available to the solution species and that Pd^{2+} possesses at least one sufficiently labile coordination site.

Cl$^-$ is a labile coordination site in Pd^{2+} halogen complexes, thus the chemistry of Pd^{2+} halogen complexes
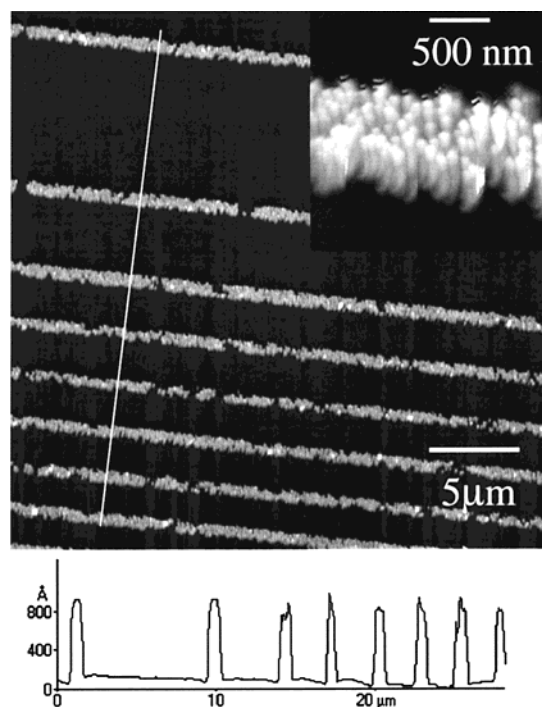

Figure 5. Topographic atomic force microscopy image of cobalt metal patterns. A cobalt ion−borane electroless deposition bath was applied to a chloropalladate-treated dendrimer pattern (ink concentration 2 μM in ethanol, inking time 25 s, printing time 25 s) on an oxidized silicon wafer surface (inset: zoom-in scan).

in aqueous solution is dominated by hydrolysis above pH $\sim$ 2. However, at pH = 1 and high chloride concentrations (0.7 M), PdCl$_4^{2-}$ solutions contain >80% of PdCl$_4^{2-}$ (sufficient labile coordination sites for amines), which is now stable against hydrolysis; palladium particles produced from these solutions on amine-terminated monolayers are catalysts for the growth of small cobalt islands.[24] However, in our case no growth of cobalt layers was observed when we treated dendrimer patterns with this solution and tried to deposit cobalt from the cobalt ELD bath. A possible reason is the partial protonation of the amine groups in the dendrimer. Protonated amines can still complex Pd^{2+} (amine complexes can be synthesized in good yield at low pH), but (de)protonation of a macromolecule leads to multiple interconnected equilibria. This could result in binding very few Pd^{2+} ions to G4OH molecules. Pd particles formed after reduction may be too small to catalyze the formation of complete cobalt layers.

A fresh Pd^{2+} solution with 0.1 M Cl$^-$ and pH = 5, prepared according to the recipe of Dressick et al.,[23] has a rather low PdCl$_4^{2-}$ concentration (<20%) compared with the above-mentioned 80%. But still the overall amount of chloropalladate species PdCl$_n$(H$_2$O)$_{4-n}^{2-n}$ (n > 0) is over 90% since the hydrolysis—finally yielding Pd(H$_2$O)$_4^{2+}$—is slow. More important, amine groups in dendrimers are deprotonated at pH = 5. Employing this solution led to cobalt growth from the ELD bath, indicating a successful complexation of Pd^{2+} ions within the dendrimer. Since amide groups are neither protonated nor deprotonated in the investigated pH range, we can speculate that only the tertiary amine groups bind substantial amounts of Pd^{2+}.

As mentioned in the Introduction, oxide surfaces can be patterned with a combination of μCP of functional molecules or particles with ELD,[21,22] but the necessary methods rely on rather complex steps (surface modification, preparation of Pd complexes) compared with the simple method we present here. In our case, all surfaces

with hydroxyl groups, such as glass, mica, and other oxide surfaces, should be suitable: generally speaking, all surfaces that can form hydrogen bonds with dendrimers. In contrast to printing catalysts, printing dendrimers means patterning a surface with a functional host molecule. Therefore, other functional molecules and particles that can bind to dendrimers can easily be connected to the patterned regions.

4. Conclusions

Compared with printing other functional molecules, the dendrimer printing method that we present here has the following advantages. (1) The requirement of special conditions such as absence of water and oxygen during microcontact printing is not as stringent as in the case of chlorosilanes. Even more important, the solvents for dendrimers are alcohols that cause only a negligible swell of the polymeric stamps. Therefore, dendrimers can be a good replacement for chlorosilanes in small pattern sizes (e.g., <1 μm). (2) Many dendrimers are commercially available and quite stable. A range of metals can be synthesized inside (or at) dendrimers via either direct adsorption/reduction synthesis or via displacement with other metals.[31] Even semiconductors and dyes can be combined with dendrimers.[32-33] Although our technique relies on the printing of molecules with only three rather simple chemical functionalities, many molecules with more complex chemical groups and even nanoparticles can easily be trapped inside or bound at dendrimers. The wide chemical and structural variability of dendrimers makes these cage-like molecules good carriers or hosts for other functional materials. We infer that the simple procedure of μCP of dendrimers will allow the patterning of surfaces with such materials. (3) We showed that arbitrary submicrometric metallic patterns can be formed with high spatial selectivity on nonconducting surfaces, based on very simple wet chemical processes.

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