Structured polymer surfaces have gained increased attention in various research fields during the past few years. By structuring of polymer surfaces, in particular of polymer brushes, functional surfaces with defined properties, for example for the study of cell adhesion\cite{1,2} and of cell alignment,\cite{3,4} have been prepared. Moreover, patterning of polymer brushes allows the alteration and control of their wetting properties.\cite{5} Patterned polymer brushes can be obtained by different methods including top–down approaches such as electron beam chemical lithography (EBCL),\cite{6–8} photolithography,\cite{9} dip-pen lithography,\cite{10} and microcontact printing (μCP)\cite{11,12} and bottom–up methods such as Langmuir–Blodgett (LB) lithography.\cite{13} These methods mainly rely on a “grafting from” approach in which lithography is used to site-selectively initiate a polymerization process or to site-selectively install a polymerization initiator. In the latter case, subsequent polymerization eventually leads to structured polymer brushes. In addition, studies on the mechanical manipulation (nanoscratching/nanoshaving) of polymer films prepared by spin-coating,\cite{14} as well as self-assembled monolayers (SAMs)\cite{15–17} and the nanowear of different polymer film architectures,\cite{18} have been performed, and even heated atomic force microscopy (AFM) tips have been used for lithographic processes on polymer films.\cite{19}

Herein, we present an alternative approach to obtain structured polymer brushes by mechanical nanoscratching with AFM lithography. We will show that this method works very well for structuring polymer brushes, whereas moderate results are obtained by nanoscratching of spin-coated polymer films. To the best of our knowledge, intentional scratching of polymer brushes by an AFM tip has not been reported to date, whereas AFM lithography on spin-coated films is known.\cite{14} Furthermore, we will demonstrate that site-selective immobilization of functionalized materials such as dyes (lissamine rhodamine B derivatives and boron-dipyrromethene (BODIPY) derivatives) into these structured polymer brushes can be achieved.

Various controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP)\cite{20} reversible addition–fragmentation chain transfer (RAFT)\cite{21} and nitroxide-mediated polymerization (NMP)\cite{22} have been successfully applied for the preparation of polymer brushes by surface-initiated radical polymerization (SIP). The thin films of brush polymers in the present studies were prepared by using NMP on oxidized Si wafers containing a 300-nm oxide layer (Figure 1).

Immobilization of the polymerization initiators 1–3 was achieved by transsilyletherification on the oxidized Si wafer. SIP was performed by placing the initiator-covered wafer into neat styrene (125 °C, polystyrene (PS) brushes) or neat n-butyl acrylate (105 °C, poly(n-butyl acrylate) (PNBA) brushes) in the presence of sacrificial alkoxyamine 4 or 5, respectively. Poly(N-isopropylacrylamide) (PNIPAM) brushes were obtained by SIP in a solution of NIPAM in C6D6 (125 °C).

For control experiments, polymers synthesized under standard NMP conditions were used for spin coating. For a better comparison, the polymers used in the spin-coating process had about the same molecular weight as the polymers of the brushes, which are covalently bound to the wafer (for details on sample preparation see Supporting Information).

Figure 1. Immobilization of alkoxyamine initiators and SIP by using NMP.
AFM lithography experiments were performed on a Dimension 3000 AFM equipped with silicon tapping mode cantilevers \((k \approx 42 \text{ N m}^{-1})\) operating in contact mode and, if not stated otherwise, at a set point of 5 V yielding a loading force of about 22 \text{ mN}. The lithographic pattern, as shown in Figure 2, consists of six single scan lines, the first on the left of the field, written from top to bottom, consecutively followed by lines with decreasing distances in-between (2.0 \text{ mm}, 1.5 \text{ mm}, 1.0 \text{ mm}, 500 \text{ nm}, 200 \text{ nm}) and a 1 \text{ mm} \times 1 \text{ mm} square that is written by 20 overlapping scan lines (line distance 50 nm, deviations are due to the drift of the microscope during lithography). After AFM lithography the structured wafers were washed with chloroform by using ultrasonication to remove the scratched-out polymer. Results of such a lithographic procedure on different polymer brushes and in comparison on spin-coated films are shown in Figure 2.

The comparison of lithography on spin-coated films and polymer brushes reveals obvious qualitative differences (Figure 2a). The polymers investigated in this work can be categorized into two groups: the more crystalline PS and PNIPAM and the comparatively soft and viscous PNBA. Evidently the lithography results reflect these differences. The PS and PNIPAM systems show similar results in lithography. The single scan lines broaden in scan-direction by more than four times by going from polymer brushes to spin-coated wafers (from 100 to 450 nm) due to the dragging of polymer by the tip. The excavated material is clearly visible at the end of the grooves (Figure 2a, upper and middle image on the left). Overall, the scratch borders are not well-defined and some material is also piled on the rim of the scratch on spin-coated films. No broadening of scan lines is observed on scratched PS and PNIPAM brushes although the scratched-out material is clearly visible at the end and to a smaller extent at the rims of the groove. This implies a smaller adhesive force of the spin-coated films to the substrate than of the cohesive force within the polymer film, so that further material is dragged along with the moving tip. In the case of the polymer brushes, the cohesive forces cannot overcome the binding of the brushes to the substrate, hence leaving the vicinity of the scratched areas intact. Another considerable advantage of the polymer brushes is the feasibility of cleaning the sample after lithography by sonication. While spin-coated films were washed away completely, only the material scratched out gets removed from the polymer brushes. The images in the right column of Figure 2a show the polymer brushes after sonication in chloroform for 20 s. The excavated material is removed completely at the end of the scan lines, as well as at the rims, leaving the clean lithographic pattern. In the case of PNBA-covered wafers, the difference between AFM lithography on spin-coated films and on polymer brushes is even more pronounced. Here, lithography by AFM on the spin-coated film is impossible because the resulting scratches are immediately filled up again by the reflow of the previously scratched polymer (curing of the scratches, lower left image in Figure 2a). The lithographic pattern is, however, recognizable on the PNBA brush, although the pattern is partially filled with reflowing material (lower middle image in Figure 2a). After sonication this reflowing material is removed and the pattern becomes clearly visible (lower right image in Figure 2a).

The section analysis of the pattern on a PS brush shows that the square area, as well as the single scan lines, was written down to the substrate (silicon oxide layer), and the footprint of
the single scan lines is about 100 nm (Figure 2b). To demonstrate the stability and resolution of the lithographic process on polymer brushes, we used an altered pattern design consisting of multiple single scan lines as shown in Figure 3a. Line structures of 200-nm periodicity were achieved. All lines are well-defined showing no broadening. Due to the stability of the structure, even a second writing over the existing scratched lines (perpendicular to the first scratch direction) is possible, resulting in the pillar structures shown in Figure 3b. The lithography process is highly reproducible and does not seem to depend crucially on the exact loading force or polymer film thickness as long as a certain threshold force is overcome. The threshold force needed for reproducible pattern writing was found to be about 7.9 µN, although some hysteresis effect was observed, allowing for lower loading forces down to 4.0 µN in consecutive lithography after writing with the higher threshold force once. The hysteresis can be explained by taking into account tip modification at higher loading forces. The size of the flattened area at the tip apex was found to be about 0.16 µm² on electron micrographs, yielding estimated contact pressures of 49 GPa at the threshold force (7.9 µN) and 25 GPa at 4.0 µN. Even for the high loading force of 22 µN (≈138 GPa) used in the regular lithographic procedures no substantial modification of naked silicon oxide surfaces was observed (for detailed description and images of threshold force determination and tips after lithography see Supporting Information). Overall the range of needed loading forces is comparable to preliminary studies of the removal of an alkyl silane monolayer by AFM lithography. [23,24]

The stability of the polymer brush toward solvents allows us to further process the scratched brushes in solution (scheme depicted in Figure 4). This would not be possible on spin-coated polymer films. As an example we used the pink dye lissamine rhodamine B sulfonyl chloride (6) and alkyl-chain-conjugated derivatives thereof (7–9) to target the brushes or the scratched areas for selective deposition (structures given in Figure 5, for synthesis of the modified dyes 7–9 see Supporting Information). Dye immobilization was performed by placing the structured wafer into a CH₂Cl₂ solution containing the dye for 3 days. After removal of the dye solution the wafer was cleaned by sonication with CH₂Cl₂ and water. An AFM image of the lithographic pattern and fluorescent microscopy images of the resulting dye distribution on a patterned PS brush are shown in Figures 5a and b.

Interestingly, the polar dye 6 does not enter the polymer brushes. It selectively adsorbs to the scratched areas (Figure 5b, left image). However, when a C4 hydrocarbon chain is covalently bound to the dye (→ 7) the interaction of the dye with the polymeric material becomes stronger, but 7 still adsorbs more in the scratched areas (stronger fluorescence). Attachment of a C7 hydrocarbon chain (→ 8) further shifts the dye distribution toward the brush regime, but in the scratched areas dye is still clearly visible. Pleasingly, the dye with a hydrocarbon chain of ten carbon atoms (→ 9) selectively adsorbs on the polymer-covered regions. In this case, at the scratched areas of the wafer, which are free of polymer brushes, no dye adsorption was observed. Hence,
depending on the length of the alkyl chain attached to the polar chromophore, the immobilization of the dye molecules either at the brush polymer regime or in the scratched areas can be controlled and adjusted. The site-specific dye immobilization is probably caused by intermolecular interactions of the alkyl chain of the dye with the polymer brushes (for 9) or by hydrogen bonding of the Si–OH groups of the scratched areas with 6.

Furthermore, we studied the immobilization of BODIPY dyes (hydrophobic dyes) 10 and 11 and found that both adsorb to the brush region (Figure 5c). Thus, for hydrophobic dyes long alkyl chains are obviously not necessary for immobilization into the brush area. Combining the two types of adsorption behaviors of the dye molecules we further achieved the selective deposition of two different dyes (BODIPY derivative 11 and lissamine rhodamine B sulfonyl chloride 6) into the polymer brushes and on the scratched areas on the same sample by exposing the wafer to a CH2Cl2 solution containing both dyes (Figure 5d). The hydrophobic BODIPY 11 adsorbs to the brush region and 6 is site-specifically immobilized into the scratched area. We believe that this approach is highly promising for selective immobilization of chemical compounds into specific areas of structured brushes.

In conclusion, we demonstrated substantial differences between spin-coated polymers and polymer brushes during high-loading-force AFM lithography. Polymer brushes with a thickness of 20–30 nm can be reproducibly structured and scratched down to the substrate (silicon oxide layer of the wafer) even with single scan lines without dragging of material in the vicinity. Equidistance line structures with 100-nm resolution were achieved in such a simple lithography process. Higher resolution is expected by further parameter optimization (polymer brush system, AFM tip, loading force, etc.). Parallel-pattern writing by cantilever arrays is considered for future experiments to enable patterning of larger surface areas in shorter times. The possibility of cleaning the structured polymer brushes by sonication and removing the excavated material without altering non-scratched areas results in lithographic patterns with well-defined rims. Furthermore, the stability against solvents allows us to further process the structured wafers in solution. As first examples, dye molecules were site-selectively immobilized into the structured brushes either in the polymeric region or on the scratched part of the structured wafer. The two different regions of the wafer can be selectively addressed by tuning the chemical structure of the dye. By choosing suitable pairs and modifications, different dyes can be immobilized in separate areas (i.e., one in the polymeric and the other in the scratched areas) on the same sample.

**Experimental Section**

*Immobilization of polymerization initiators 1, 2, and 3:* Si wafers were cleaned by ultrasonication in solvents of increasing polarity (pentane, CH2Cl2, acetone, methanol, ultrapure water) for 5 min. The clean surfaces were oxidized with freshly prepared piranha solution (conc. H2SO4/H2O2 (30%) 7:3) for 45 min. The surfaces were rinsed again with ultrapure water and blown dry with argon. The oxidized wafers were placed into a sealed tube and a solution of 1 (or 2 or 3) was added (1.5 mL, 10 mM in absolute toluene). The mixture was allowed to stand at 60 °C (1) or room temperature (r.t.) (2 or 3) for 3 days. The surfaces were rinsed again with ultrapure water and blown dry with argon. The oxidized wafers were placed into a sealed tube and a solution of 1 (or 2 or 3) was added (1.5 mL, 10 mM in absolute toluene). The mixture was allowed to stand at 60 °C (1) or room temperature (r.t.) (2 or 3) for 3 days. The surfaces were rinsed again with ultrapure water and blown dry with argon. The oxidized wafers were placed into a sealed tube and a solution of 1 (or 2 or 3) was added (1.5 mL, 10 mM in absolute toluene). The mixture was allowed to stand at 60 °C (1) or room temperature (r.t.) (2 or 3) for 3 days. The surfaces were rinsed again with ultrapure water and blown dry with argon.

Typical procedure for the surface-initiated polymerization of styrene: A Schlenk tube was charged with 2,2,6,6-tetramethyl-1-(1-phenyl-ethoxy)-piperidine (4) (3.7 mg, 14 μmol, 0.1 mol%) and styrene (1.63 mL, 14.2 mmol, 1.00 equivalent) in CH2Cl2. The tube was subjected to three freeze/thaw cycles, a Si wafer containing immobilized alkoxyamine initiator 1 was added and the tube was sealed off under argon. The polymerization was carried out under argon at 125 °C for 24 h. The resulting mixture was cooled to r.t. and dissolved in CH2Cl2. The wafer was taken out of the solution,
continuously extracted with CH₂Cl₂ for at least 14 h, and AFM experiments were carried out. CH₂Cl₂ was removed from the styrene/PS solution under reduced pressure and residual monomer was removed in vacuo at 60 °C for 12 h. Conversion was evaluated gravimetrically. Molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography. Conversion: 84%; \( M_n = 54 \text{ 900} \text{ g mol}^{-1} \); PDI = 1.26; thickness of PS brushes: ≈ 20 nm.

**AFM lithography:** All lithographic patterns were written with silicon tapping-mode cantilevers (k≈42 N m⁻¹) on a commercial AFM (DI Dimension 3000 with Nanoscope IIIa controller) in contact mode. The loading force is about 22 μN (set-point of 5 V) for all experiments if not noted otherwise. The polymer brush samples were sonicated in chloroform for 20 s after lithography to remove scratched-out material.

**Immobilization of dyes:** A Si wafer with grafted PS brushes was placed into a sealed tube and a solution of 6, 7, 8, 9, 10, or 11 in dry CH₂Cl₂ (0.1 mM) was added. The mixture was allowed to stand at r.t. for 3 days. The surface was ultrasonicated in CH₂Cl₂ three times for 5 min and in ultrapure water once for 5 min. The surface was dried in an argon stream prior to analysis by fluorescent microscopy.

**Keywords:**
- lithography
- patterning
- polymer brushes
- scanning probe microscopy


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