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Chemical Lithography

Electron-Beam Chemical Lithography with Aliphatic Self-Assembled Monolayers**

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Lithography is an important fabrication technique in science and industry. A variety of different approaches, including photolithography,[1] interference lithography,[2] UV and extreme UV lithography,[3,4] X-ray lithography,[5] electron-beam lithography,[6] nanoimprint lithography,[7] microcontact printing,[8] and scanning probe methods (for example, dip-pen nanolithography, "constructive" nanolithography, and near-field photolithography),[9–11] have been developed. Among these techniques, photolithography is the most widely used commercially, especially in microelectronics. At the same time, X-ray lithography and electron-beam lithography (EBL), which are capable of much higher patterning resolution (down to a few nanometers),[12] are becoming increasingly popular. In particular, EBL can be performed both in proximity printing geometry using a stencil mask and by direct writing with a focused electron beam as it scans across a resist-coated substrate, with a lateral resolution limited by the diameter of the beam only.

Increasingly popular resist materials for EBL are self-assembled monolayers (SAMs).[13,14] These resists comprise individual amphiphilic molecules, which, in their turn, consist of three essential parts: a head group that anchors the molecule to the substrate, a tail group that defines the surface properties of the entire system, and a spacer connecting the head and tail groups and mediating the self-assembly.[13,15] As a result of the well-defined structure, ultimately small thickness, and molecular character, patterning down to the molecular size (about 0.5 nm) is possible in principle with a SAM resist. A further advantage is the dependence of the changes induced by electron irradiation on the character of the SAM constituents. In particular, for aliphatic SAMs, irradiation results mostly in fragmentation and disordering of the films, which makes them a positive resist for EBL.[14] In contrast, in aromatic SAMs, an electron-induced quasi-polymerization prevails over the fragmentation, thus making these films negative resists for EBL.[14,16]

Furthermore, as aromatic SAMs remain mostly intact under electron irradiation, chemical modification of the tail group by electrons is possible, which enables the fabrication of chemical lithographic patterns and templates.[14,17,18] This approach is usually referred to as electron-beam chemical lithography (EBCL).[14,18] Despite its advantages, EBCL with aromatic SAMs as resists has several essential drawbacks. First, so far only SAMs with a nitro tail group have been used for EBCL, which utilize nitro-to-amino transformation induced by electrons.[17,19,20] Second, the respective compounds are not commercially available. Third, the efficient nitro-to-amino transformation requires a large irradiation dose of 30–40 $\mathrm{mC\,cm^{-2}}$,[17,18] which is a constraint for industrial implementation of this technique, as it means a long time for chemical patterning.

Herein, we show that all the above drawbacks can be avoided if EBCL is performed not with aromatic but with aliphatic SAMs as resists. As the first example of this new technique, we demonstrate the fabrication of different chemical patterns on the basis of commercially available SAM resists, which serve as templates for surface-initiated polymerization (SIP). The choice of SIP for the test experiments was, on the one hand, related to good visualization of the resulting polymer brushes and, on the other hand, to the possibility of comparing the results with the available data for SIP on aromatic templates. So far, different polymer brushes have been fabricated by a combination of EBCL and SIP with 4′-nitro-1,1′-biphenyl-4-thiol (NBPT) SAMs as resists.[19–21]

As a basis for the new lithographic technique, we used a recently developed approach to fabricate mixed SAMs: the irradiation-promoted exchange reaction (IPER).[22,23] The key idea of the approach is tuning the extent of the exchange reaction between a SAM covering the substrate and a potential molecular substituent by electron irradiation, which allows binary mixed SAMs of variable composition to be obtained depending on the dose. The physics behind this method is the creation of irradiation-induced chemical and structural defects in the primary SAM, which promote the exchange reaction.[23] As the irradiation can be performed by a focused electron beam, the IPER can be directly implemented in the lithographic framework and used for the fabrication of different chemical patterns on the micro- and nanometer length scales.

The whole procedure for the test experiments is shown schematically in Figure 1, and the details are described in the Experimental Section. As the first step, patterns were "prewritten" in an aliphatic resist, SAMs of 1-dodecanethiol (DDT) on Au(111), by an electron beam; the dose was kept below 5 $\mathrm{mC\,cm^{-2}}$, which is far beyond the dynamic range of the IPER (0–1 $\mathrm{mC\,cm^{-2}}$).[23] The fabricated patterns were "developed" by an exchange reaction with 11-aminoundecanethiol hydrochloride (AUDT), which resulted in the fabrication of chemical templates consisting of methyl tail groups of DDT and amino tail groups of AUDT. Note that both DDT

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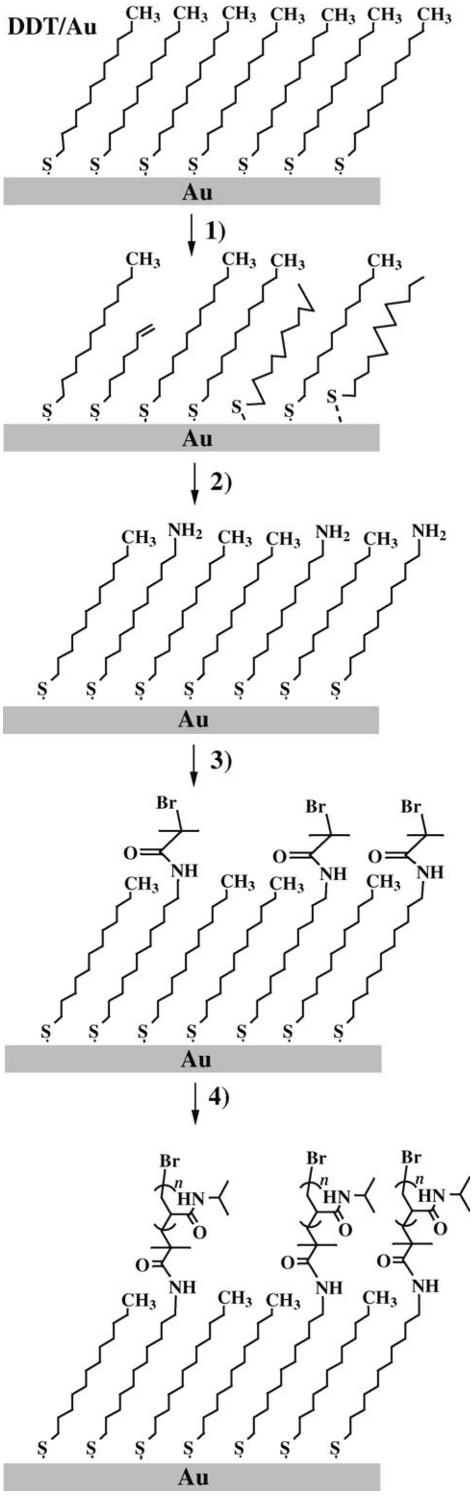

Figure 1. EBCL with aliphatic SAMs, with the subsequent fabrication of a polymer brush: 1) electron-beam writing in the primary SAM; 2) fabrication of a chemical template by exchange reaction; 3) selective anchoring of the surface initiator (BIBB) to the NH_2 sites; and 4) SI-ATRP of NIPAM in the presence of catalysts. See text for details.

and AUDT are commercially available. As the next step, a surface initiator, bromoisobutyryl bromide (BIBB), was selectively attached to the amino tail groups of AUDT, and surface-initiated atom-transfer radical polymerization (SI-ATRP) of *N*-isopropylacrylamide (NIPAM), which is the building block of the test polymer polyNIPAM (PNIPAM), was performed by following the methods of references [19] and [24]. The choice of AUDT as the second component of the chemical templates (along with DDT) was related to the fact that its amino group provides a docking site for BIBB.

Several examples of the resulting PNIPAM brushes are presented in Figure 2. The DDT–AUDT templates are clearly stable enough to allow their growth, even though aliphatic SAMs are generally believed to be less stable than aromatic ones. The maximum height of the brushes is significantly greater than that of the analogous brushes obtained by EBCL on NBPT-based templates under identical polymerization conditions.[19] Gradient stripes of different widths are shown in Figure 2a and b, with their quality being at least comparable to the analogous gradient brush obtained on an NBPT-based template.[21]

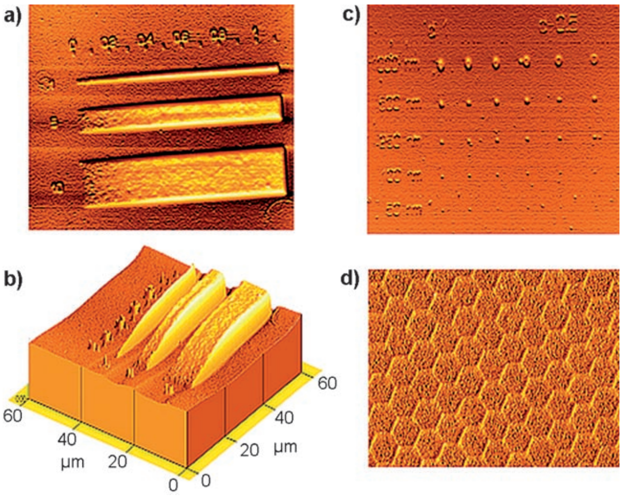

Figure 2. AFM images of PNIPAM patterns obtained by EBCL with aliphatic SAMs as resist: a) gradient stripes of width 1, 5, and 10 µm; b) 3D image of these stripes; c) dots with a variable diameter of 1000, 500, 250, 100, and 50 nm (from top to bottom) prepared with different primary irradiation doses (decreases from left to right); and d) honeycomb pattern with a wall width of 100 nm.

The respective height profiles along the stripes are depicted in Figure 3a as functions of irradiation dose. According to these profiles, the height of the brushes increases continuously with increasing dose, and becomes saturated above a dose of 2–2.5 $\mathrm{mC\,cm^{-2}}$ following the density of the AUDT molecules (that is, NH_2 anchors) governed by the IPER. As is known from previous SIP experiments on aromatic templates,[21] a larger grafting density leads to a higher polymer brush because of the straightening of the polymer chains within the feature. The observed saturation of the gradient height at high doses is related to the saturation behavior of the IPER above its dynamic range. This behavior is explained by the set-off of irradiation-induced cross-linking, which also occurs in aliphatic SAMs, and which hinders the IPER and achieves a balance with exchange-promoting defects.[23] The difference between the saturation dose from the previous work

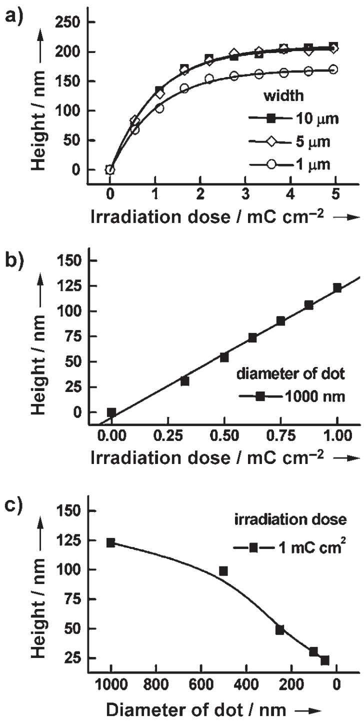

Figure 3. Height profiles of the PNIPAM brushes: a) sampled height profiles along the gradient stripes (Figure 2a and b) as functions of the primary irradiation dose; b) height of the dots with a diameter of 1000 nm (Figure 2c) as a function of the primary irradiation dose; and c) height of the dots prepared with a primary irradiation dose of 1 mCcm^{-2} (Figure 2c) as a function of dot diameter.

(1 mCcm^{-2})[23] and the 2 mCcm^{-2} in this study can be related to the different molecular substituents and different electron energies used for IPER.

The height profiles observed for the gradient stripes are reproduced by the dot brush, as revealed by Figure 3b, in which the height of the dots with a diameter of 1000 nm is plotted as a function of irradiation dose. Once more, a continuous increase of the brush height with increasing dose is observed, and the height values correlate with those from the gradient pattern (Figure 3a). This result shows that both continuous gradientlike objects and separate dotlike features can be fabricated within an extended height range up to 200 nm.

However, for small features the maximum height is related to their size, as demonstrated in Figure 3c, in which the height of the dots prepared with a primary irradiation dose of 1 mCcm^{-2} is plotted as a function of the dot diameter. It can be clearly seen that this height decreases continuously with decreasing dot diameter (a similar effect is also observed for the gradient stripes: compare the heights of the 1-, 5-, and 10-µm stripes in Figure 3a). Such behavior has been observed previously for polymer brushes on NBPT-based templates, and was related to the widening of the fabricated features as a result of the spreading of the side chains.[21] Nevertheless, extended nanometer-scale structures of sufficient height can be prepared by the presented technique, as revealed by Figure 2d, which shows an AFM image of a honeycomb pattern with a wall width of 100 nm. This is one of many imaginable examples for the fabrication of biomimetic nanopatterns that can be realized by EBCL.

In conclusion, we have presented a new EBCL technique, which utilizes not aromatic but aliphatic SAMs as resist materials. We demonstrated the feasibility of this technique by the fabrication of polymer micro- and nanobrushes in a broad height range, which have a quality at least comparable to that of the analogous patterns prepared on aromatic templates. The advantages of the technique are 1) the use of commercially available compounds; 2) the broad variety of different chemical patterns based on different aliphatic compounds; and 3) a much lower (by at least an order of magnitude) patterning dose as compared to aromatic resists. The approach is not limited to SIP, which is used here only as a test example, but can be utilized in different applications that rely on chemical patterning, for example, biomedical studies and sensor fabrication.

Experimental Section

Gold substrates were prepared by thermal evaporation of 100 nm of gold (99.99% purity) onto polished single-crystal silicon (100) wafers (Silicon Sense) primed with a 5-nm titanium adhesion layer. The resulting films had a grain size of 20–50 nm and predominantly (111) orientation.[23]

DDT, NIPAM, BIBB, triethylamine (NEt$_3$), *N*,*N*,*N*′, *N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (CuBr), ethanol, methanol, and dichloromethane (CH$_2$Cl$_2$) from Sigma–Aldrich (Germany) and AUDT from Asemblon (USA) were used without further purification.

Primary SAMs were formed by immersion of fresh gold substrates in a solution (1 mM) of DDT in ethanol for 24 h at room temperature. After immersion, the samples were carefully rinsed with pure ethanol and dried in an argon stream.[23]

Chemical lithography was performed by an LEO 1530 scanning electron microscope with a Raith Elphy Plus pattern generator system. The electron-beam energy was chosen at 1 keV; the residual gas pressure was about 5×10^{-6} mbar.[19]

Exchange reactions were carried out by immersion of irradiated DDT SAMs in a solution (1 mM) of AUDT-HCl in ethanol for 2 h at room temperature.[23] After immersion, the samples were carefully rinsed with pure ethanol and dried in an argon stream.

The fabricated DDT–AUDT patterns were placed in a flask containing dried CH$_2$Cl$_2$ (5 mL) and NEt$_3$ (0.36 mM, 50 µL). Then the surface initiator BIBB (2.02 mM, 250 µL) was added dropwise at 0°C. The mixture was kept for 1 h at this temperature and then at room temperature for 6 h. The substrates were rinsed with CH$_2$Cl$_2$, sonicated, rinsed with ethanol, and then dried in a nitrogen flow.[19,24]

In the course of SI-ATRP, all chemicals were added to the flask in steps according to the nitrogen counterflow principle.[19] Prior to use, the flask was heated under vacuum to remove moisture and oxygen, and then flushed with nitrogen after allowing it to cool to room temperature. For SI-ATRP, the fabricated samples were immersed in a degassed solution of a mixture of NIPAM (18.56 mM, 2.1 g) in Millipore water/methanol (4:1 v/v, 10 mL), CuBr (0.02 mM, 2.5 g), and PMDETA (0.05 mM, 18 µL). The polymerization was allowed to continue overnight at room temperature. Thereafter, the samples were removed from the reaction flask, rinsed with water and methanol, and finally dried in a nitrogen flow.[19,24]

AFM images were obtained in the contact mode with an Autoprobe CP scanning probe microscope from Park Scientific Instruments (USA).

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