Electron Beam and Soft X-ray Lithography
with a Monomolecular Resist

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This contribution reviews current state of electron beam and soft X-ray lithography
with a monomolecular resist. Self-assembled monolayers (SAMs) represent versatile resist
materials for such a lithography. Depending on the architecture of the SAM constituents,
they can serve as both positive and negative resists within framework of conventional
lithography, but also be used as multi-purpose templates for Chemical Lithography. The
latter technique exploits either selective modification of specific tail groups at the SAM-
ambient interface (in the case of aromatic backbone) or irradiation-promoted exchange
reaction between the primary SAM and potential molecular substituents (in the case of
aliphatic backbone). Due to the monolayer thickness of SAM resists and molecular size of
their structural building blocks, patterning down to few nanometers is in principle possible.
Currently, the lateral resolution is limited by the grain character of the SAM substrates and
parameters of the lithographic setup, with the latter being especially important in the case
of soft X-ray lithography.

Keywords: self-assembled monolayers, lithography, chemical pattern, exchange
reaction

1. Introduction
There is a significant technological demand
for further miniaturization of the patterning
technology and development of new approaches
capable to fabricate not only conventional but also
chemical lithographic patterns, which become of
particular importance in view of a clear trend
toward molecular electronics, biochips, templates
for molecular recognition, and cell receptors.
Whereas some progress can be achieved by
improvement and optimization of patterning
process, introduction of distinctly new resist
materials, as compared to currently used
photopolymers, can be more favorable, since it
not only can bring an improvement within the
current technologies, but enable development of
principally new lithographic approaches.
Perspective materials in this regard are self-
assembled monolayers (SAMs), which are well-
ordered and densely packed 2D-ensembles of
chain-like organic molecules anchored to a
substrate by a suitable headgroup [1,2]. SAMs
offer flexible molecular architecture with a broad
variety of building blocks to control and tailor
surface properties. SAMs can be modified by
electron and X-ray irradiation, UV light, and
plasma, with the character and extent of this
modification depending on the primary treatment
and molecular architecture. The tailored character
of the modification, the monolayer thickness of
the film, and the molecular size of its structural
elements make SAMs to suitable resist materials
and an ideal platform for the fabrication of micro-
and nano-structures. The patterning can be
performed either in proximity printing geometry
by irradiation of a SAM sample through a mask
[3,4], or directly by a focused primary beam, as
far the beam and the sample can be moved in a
controlled way with respect to each other [5,6], or
by an interferometric lithography, as far the

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primary beam can be diffracted onto a SAM sample [7,8]. As an exotic case of a focused primary source, one can use a scanning tunneling microscope (STM) tip and address SAM templates with an ultimate lateral resolution of this technique [9-11].

Here we review the current state of electron and X-ray lithography with SAMs as resist materials and give some examples of respective lithographic patterns. The review is mostly based on our own results, but also includes references to the relevant work by other authors. Further, we describe UV-based approach and discuss its strengths and weaknesses as compared to electron and X-ray lithography.

2. Method

The SAM resists and templates were prepared on polycrystalline Au and Ag substrates with preferential (111) texture by a standard immersion procedure; details of the sample preparation can be found elsewhere [3,12,13]. We used several thiol-based SAMs, viz. non-substituted (1-dodecanethiol) and semifluorinated aliphatic SAMs, CH₃(CH₂)₁₂SH, CF₃(CF₂)₉(CH₂)₉SH, and CF₃(CF₂)₉(CH₂)₁₁SH (abbreviated as C12, F10H2 and F10H11, respectively) and aromatic monolayers of 4'-nitro-1,1'-biphenyl-4-thiol, NO₂(C₆H₄)₂SH (abbreviated as NBPT). The patterning was performed both in proximity printing geometry, using an electron flood gun (300 eV) as the primary source and carbon Quantifoil membranes (Plano) as the masks (see ref [14] for details); by a focussed X-ray beam (387 eV), using the scanning photoelectron microscope (SPM) station at the U5 undulator beamline of NSRRC in Hsinchu, Taiwan (see refs [5,15,16] for details); and by a focused electron beam (1 keV), using an LEO 1530 scanning electron microscope (SEM) with a Raith Elphy Plus pattern generator system (see ref [17] for details).

Some of the fabricated patterns were immersed in solution of 11-aminoundecanethiol hydrochloride, HCl·NH₂(CH₂)₁₁SH (abbreviated as C11NH₂ as far as HCl is cleared) and served as templates for the growth of polymer (poly-N-isopropylacrylamide - PNIPAM) brush (see ref [17] for details). The fabricated SAM and polymer brush patterns were characterized and imaged using the SPEM setup (see refs [5,15,16] for details), X-ray photoelectron emission microscope (X-PEEM) at a microscopy branch (7.3.1.1) of the beamline 7.3.1 at the Advanced Light Source in Berkeley, USA (see ref [14] for details), and Autoprobe CP scanning probe microscope from Park Scientific Instruments, USA (see ref [17] for details).

3. Results and Discussion

Lithography with SAMs as resist and template materials relies upon the detailed knowledge of processes occurring upon exposure of SAMs to electrons, X-rays or UV light. Among these three tools, the effects of electrons and X-rays are quite similar, since not the primary X-ray photons but secondary electrons, originated from the substrate, plays the major role in the case of X-ray irradiation [18,19]. The electron/X-ray irradiation affects both hydrocarbon matrix and SAM-substrate interface [20]. There are a variety of closely interrelated irradiation-induced processes, which mostly follow a pseudo first order kinetics and level off at high irradiation doses [13,21]. All the processes can be separated in two major classes. On one hand, irradiation results in the SAM damage, including cleavage of the individual bonds, molecular fragmentation, desorption, orientational and conformational disorder, and formation of new species. On the other hand, irradiation leads to a partial cross-linking of the individual molecules within the SAM. Depending on the identity of the molecular backbone, either damage or cross-linking processes prevail. In the case of aliphatic SAMs, damage processes are the dominant ones, so that the film within the irradiated areas is disordered, contains a significant amount of defects, and has a loose grip to the substrate, since a majority of the primary headgroup-substrate bonds is destroyed [13,20,22,23]. The destroyed SAM can be etched easily by a suitable wet agent or plasma, which makes aliphatic SAMs positive resists for electron/X-ray lithography [20,24]. The patterning occurs according to the schema presented in Fig. 1a: the pattern is written by electron/X-ray irradiation and subsequently transferred to the substrate by etching, with the irradiated areas being preferentially etched. An example of such patterns can be found, e.g., in ref [4].

In contrast to aliphatic SAMs, cross-linking of the molecular backbones is the dominant process in the aromatic SAMs. Whereas C–H bonds can be easily cleaved by irradiation, oligophenyl skeletons remain mostly undamaged and can be interconnected with the neighbor species, which is
mediated by non-saturated bonds and free radicals appearing after the cleavage of C–H bonds [25]. Subsequently, the irradiated areas become quasi 2D polymer, which makes them more stable with respect to the etching agents than non-irradiated ones. Accordingly, aromatic SAMs can serve as a negative resist for lithography [25]. The patterning is performed according to the schema presented in Fig. 1b: the pattern is written by electron/X-ray irradiation and subsequently transferred to the substrate by etching, with the non-irradiated areas being preferentially etched. An example of such patterns can be found, e.g., in ref [4], where the patterns fabricated with aliphatic and aromatic SAM resists are directly compared. Since aliphatic and aromatic SAMs serve as positive and negative resists, respectively, these patterns exhibit the inverse contrasts [4].

![Schematic drawing of conventional electron/X-ray lithography with aliphatic (a) and aromatic (b) SAMs as positive and negative resist materials, respectively.](image)

Whereas the above patterns were fabricated by electron irradiation in proximity printing geometry with subsequent etching by a KCN/KOH solution, SAM-based lithographic patterns can also be fabricated by a focused electron or X-ray beam. Several examples of such patterns, written by a focused X-ray beam (provided by means of Fresnel zone plate optics) in F10H11 and F10H2 resists are given in Fig. 2. These patterns were imaged in situ with the same SPEM setup which was used for their writing. This setup allows an acquisition of a lateral distribution of photoelectrons at a selected binding energy. Both F10H11 and F10H2 SAMs exhibit three pronounced emissions in their C1s X-ray photoemission spectra (XPS), viz. the peaks at ~293.2 eV, ~290.8 eV, and ~284.6 eV related to CF3, CF2, and CH2 entities, respectively [12,26].

![In situ C1s SPEM images of lithographic patterns written by a focused X-ray beam in F10H11 (a,b) and F10H2 (c) resists. The images were acquired at the binding energy positions corresponding to CF2 (a) and CH2/C-C/C=C (b,c) moieties. The size of the letters in (a) and (b) is 50×50 μm2; the size of the image in (c) is 70×70 μm2. “TLS” is an abbreviation for the Taiwan Light Source, i.e. NSRRC.](image)

Fig. 2. In situ C1s SPEM images of lithographic patterns written by a focused X-ray beam in F10H11 (a,b) and F10H2 (c) resists. The images were acquired at the binding energy positions corresponding to CF2 (a) and CH2/C-C/C=C (b,c) moieties. The size of the letters in (a) and (b) is 50×50 μm2; the size of the image in (c) is 70×70 μm2. “TLS” is an abbreviation for the Taiwan Light Source, i.e. NSRRC.

Upon the irradiation, a predominant damage of the fluorocarbon part occurs as compared to the hydrocarbon one, so that the intensity of the peaks related to the CF3 and CF2 moieties decrease [27,28]. At the same time, the intensity of the peak at ~284.6 eV increases, since the binding energies of the C-C and C=C residuals of the fluorocarbon stem is very close to that of the CH2 entities. In agreement with this behavior, the irradiated areas in the C1s SPEM images acquired at the binding energy positions corresponding to CF2 moieties appear black as compared to the non-irradiated areas (see Fig. 2a), whereas images acquired at the binding energy positions corresponding to CH2/C-C/C=C (b,c) entities exhibit the opposite contrast (see Figs. 2b and 2c).

Generally, the use of the focussed beam allows to achieve a better lateral resolution as compared to the patterning through a mask, i.e. proximity printing. With an electron beam, a
resolution down to ~10-20 nm can be achieved; it is mostly limited by the grain size of the substrate [4,29]. The spatial resolution of the patterning with a focussed X-ray beam is about 0.5 μm, which was mostly determined by the current settings of the experimental setup and can be presumably improved by one-two orders of the magnitude [5]. So far, in the case of X-rays, much higher resolution (< 100 nm) has been achieved in proximity printing geometry [30,31].

Fig. 3. Schematic drawing of chemical electron/X-ray lithography with aromatic (a) and aliphatic (b) SAMs as template materials. A selective modification of terminal nitro groups to amino ones occurs in (a). The exchange reaction in (b) is promoted by irradiation.

Since, apart from the cleavage of C–H bonds and subsequent cross-linking, aromatic SAMs remain mostly intact upon electron or X-ray irradiation, terminal tail groups of the SAM constituents can be selectively modified. In particular, nitro (NO₂) moieties can be transformed in amino (NH₂) ones, which is the basis for Chemical Lithography with aromatic SAMs as templates, as schematically shown in Fig. 3a [3,32]. An example of this approach is given in Fig. 4a, where an X-ray absorption microscopy (XAM) image of NBPT based chemical lithographic pattern acquired at the position of the π (N*O₂) resonance is shown. Since the intensity of this resonance decreases significantly upon the nitro-amino transformation [14], the irradiated areas (dots) appear dark in the image. Note that the amino tail groups of chemical lithographic patterns can be used as selective docking sites for subsequent attachment of other moieties, resulting in fabrication of quite sophisticated chemical patterns [3,32,33].

Fig. 4. (a) XAM image of NBPT based chemical lithographic pattern acquired at the position of the π (N*O₂) resonance and (b) AFM image of a gradient polymer brush pattern (up to 300 nm height) grown on a C12/C11NH₂ template fabricated by IPER. We used electron irradiation in either proximity printing geometry (a) or by a focused electron beam provided by the SEM setup (b). The diameter of the dots in (a) is 1.2 μm; the size of the stripes in (b) is 50×10 μm². The primary irradiation dose in (b) was varied along the stripes; it is written above in mC/cm².

The above approach is not applicable to aliphatic SAMs, since, as mentioned above, the damage processes prevail in these systems, so that not individual groups but the entire molecules which constitute the SAM become damaged upon electron or X-ray irradiation. However, Chemical Lithography is possible with aliphatic SAMs as well as far as one combines the irradiation with subsequent exchange reaction. The key idea of the approach (see Schema in Fig. 3b), named irradiation-promoted exchange reaction (IPER), is a tuning of the extent and rate of the exchange reaction between the primary aliphatic SAM and a potential molecular substituent by electron or X-ray irradiation with a variable dose [34-36]. The irradiation-induces defects promote the exchange, so that, controlling their amount by a proper dose,
the extent of exchange reaction and following the composition of the resulting binary SAM can be precisely adjusted [36]. Combining IPER with electron or X-ray lithography, one can fabricate complex chemical lithographic patterns, including gradient ones [17]. An example is given in Fig. 4b, where an AFM image of a gradient polymer (PNIPAM) brush pattern grown on a C12/C11NH2 template fabricated by IPER. The maximum height of this brush is 300 nm. Until this limit, the height can be smoothly varied by irradiation dose; above this limit, a saturation of the promoting effect of irradiation occurred, due to the offset of cross-linking, which occurs for aliphatic SAMs, even though to a lesser extent than for aromatic ones [36].

![UV-irradiation](image)

![after irradiation](image)

![after exchange](image)

Fig. 5. Schematic drawing of UVPER, i.e. chemical UV lithography with aliphatic SAMs as template materials.

Note that IPER has several advantages as compared to Chemical Lithography with aromatic SAMs described above. First, one can use commercially available compounds. Second, not only nitro- amino patterns, but a broad variety of different chemical patterns based on different aliphatic compounds can be prepared. Third, IPER requires a much lower (by at least an order of magnitude) patterning dose as compared to lithography with aromatic resists (a typical dose of 30-40 mC/cm² [3,32]).

As mentioned above, the lithography with SAMs as resists and templates is possible not only with electron or X-ray irradiation, but with UV light as well. The physics is, however, completely different in the latter case, since the major effect by UV light is not the bond cleavage, but photooxidation of headgroup mediated by chemically active oxygen-derived species created by UV light [37,38]. The photooxidized SAM constituents become weakly bound to the substrate and easily substituted by other molecules capable to form a SAM on the substrate [39-41], as schematically shown in Fig. 5. A substitution within the irradiated areas can be performed either completely [39-41] or gradually [42], with the exact control over the composition of the resulting binary mixed SAM by the selection of a proper UV dose. Combining with lithography, the respective approach, UV promoted exchange reaction (UVPER) allows a creation of complex chemical patterns, including gradient ones. Major advantages of this approach as compared to IPER are a broader composition range of the resulting mixed SAMs and the possibility to perform the patterning under ambient conditions (electron and X-ray lithography require vacuum conditions) [42]. The current ultimate lateral resolution of UVPER-based lithography (20 nm [6]) is close to the values reported for the electron beam lithography with SAM resists or templates (see above) as far as near-field scanning optical microscope (NSOM) coupled to a UV laser is used for the patterning. Alternatively, high lateral resolution (and simultaneous patterning over a large area) can be achieved by using UV interferometric lithography [7,8].

4. Conclusions

We have discussed in detail different lithographic approaches involving electron, X-ray, and UV irradiation as primary tools and SAMs as resist and template materials, and presented several examples of lithographic patterns fabricated by the respective techniques. The major advantage of SAMs, except of the ultimately small thickness and molecular size of their structural elements, is their versatility, which not only allows conventional lithography with positive or negative resists, but Chemical Lithography as well. The latter possibility is especially important in view of tremendous
interest in life science, biology, and medicine, which we experience at present. There is a strong demand in creation of versatile sensors, biology inspired molecular engineered surfaces, and medical devices and implants adjusted to the human body at the molecular level. Further, there is a potential to use SAM-based lithography in printing industry and microelectronics. The current lateral resolution limit of 10-20 nm is mostly related to the substrate and can be overcome. The ultimate resolution limit is just a diameter of the SAM constituents, which is about 0.5 nm.

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References


