

## Ultraviolet lithography of self-assembled monolayers for submicron patterned deposition

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We report on a lithographic technique that uses self-assembled monolayers (SAMs) as a resist to fabricate patterned, chemically functionalized surfaces. Large area line, square, and triangular patterns with a periodicity of 532 nm were generated exposing SAMs of hydrophobic or hydrophilic alkanethiolates to an ultraviolet laser interference pattern at 193 nm for only a few minutes (corresponding to  $\sim 16 \text{ J/cm}^2$ ) followed by the immersion into an alternating thiol. Patterned films of  $\text{CaCO}_3$ ,  $\text{Zn(OH)}_2$ , and polymers were directly deposited on these templates. Using substrates patterned with oppositely charged SAMs, large periodic arrays of charged colloids were fabricated.

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The ability to control the growth of complex materials with submicron feature sizes is of tremendous interest for the fabrication of structured thin films, biologically active substrates, and photonic materials.<sup>1-3</sup> Those might find important applications in optical and electronic devices such as optical filters, switches, and sensors.<sup>4</sup> Depositing patterns directly is a straightforward method to create geometrically organized structures without using a complicated etching process and could prove extremely useful for microcircuit fabrication.<sup>5</sup>

Self-assembled monolayers (SAMs) provide a particularly versatile tool for controlling surface structures and properties at the molecular level.<sup>6</sup> Chemical and physical surface properties such as charge, wettability, and adhesion can be chosen simply by varying the terminal functional groups. A variety of techniques to pattern SAMs has been described. Ion and molecular beam etching<sup>7</sup> both allow patterning on a nanoscale, but are extremely slow and complicated. Microcontact printing of SAMs<sup>8</sup> emerged recently as a fast and simple alternative patterning technique. However, structures with features below  $0.5 \mu\text{m}$  cannot be made routinely using this technique. Micropatterned SAMs were shown to provide substrates for direct patterned deposition of colloids, inorganic, and organic materials.<sup>1,2,5,9-12</sup> Photopatterning of self-assembled alkanethiolate monolayers has been also demonstrated previously, but only on a  $10 \mu\text{m}$  scale, using extremely long exposure times (1-4 h),<sup>12</sup> thus limiting the applicability of the technique and further miniaturization of the structures.

In this letter we report on a lithographic technique that uses SAMs as a resist to provide patterned, chemically functionalized surfaces on a submicron scale by exposure with an ultraviolet (UV)-laser interference pattern. The fabrication consists of three steps: SAM-coated substrates are prepared, exposed to an UV-light pattern and subsequently chemically processed. Figure 1 outlines the experimental procedure. The

exposure of a SAM-coated surface with an UV-interference pattern results locally in laser-induced oxidation of the molecules. The oxidized regions are derivatized with monolayers of different chemical functionality (e.g., oppositely charged or hydrophilic/hydrophobic). We demonstrate the application of these templates for deposition of minerals, polymers and colloids to fabricate two-dimensional (2D) structures. The samples are then analyzed using scanning electron (SEM) and light microscopy. All experiments are carried out in air.

The substrate was a thin film of gold supported on a titanium-primed silicon wafer. Silicon wafers were cleaned by sonicating them for 10 min in trichloroethylene and 10 min in acetone. The wafers were coated with 2 nm of Ti, to promote adhesion, and then with 50 nm of Au. The substrate was inserted into a 10 mM solution of thiols [ $\text{HS(CH}_2\text{)}_{15}\text{CO}_2\text{H}$  (hydrophilic) or  $\text{HS(CH}_2\text{)}_{15}\text{CH}_3$  (hydrophobic)] in ethanol for at least 24 h, removed from this so-

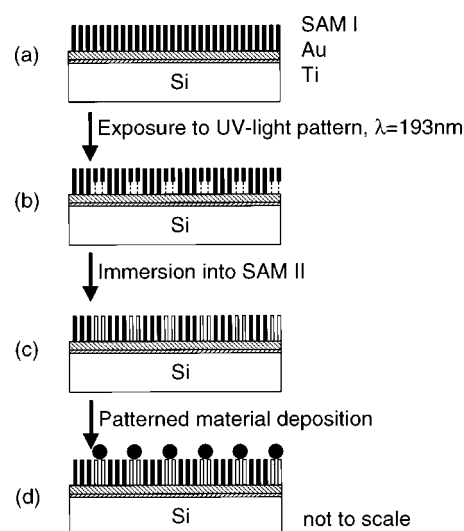


FIG. 1. Schematic of the experimental procedure: (a) SAM-coated substrate; (b) exposure to UV light ( $\lambda = 193 \text{ nm}$ ) locally oxidizes the SAM; (c) immersion into a solution displaces the oxidized SAM and derivativizes those regions with a second monolayer resulting in a chemically tailored surface with different chemical functionality; and (d) minerals, polymers, and colloids can be directly attached to the specifically functionalized regions.

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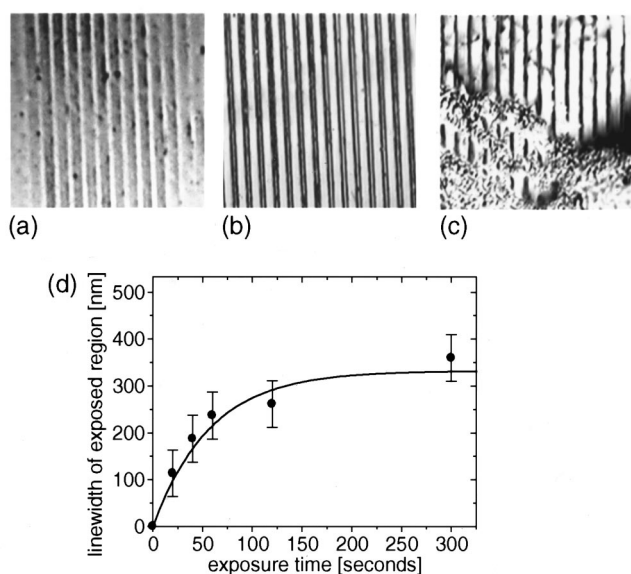


FIG. 2. (a)–(c) Light micrographs of sample surfaces exposed for different times [(a) 20 s, (b) 1 min, (c) 5 min] decorated with polystyrene (dark regions). Here the bright regions represent the exposed regions. The periodicity of the lines is 532 nm; and (d) dependence of the linewidth on the exposure time revealing a time constant of about 1 min.

lution, rinsed with absolute ethanol, and blown dry. The sample was mounted on a rotatable holder and exposed to UV light using an excimer laser (Lambdaphysik, COMPex 150 T) at  $\lambda = 193$  nm wavelength. The length of a pulse from the laser was 15–20 ns. The total pulse energy was about 55 mJ. A phasemask was used to generate the interference pattern. The phasemask had a periodicity of  $1.064 \mu\text{m}$  and was optimized for diffraction into first order. The sample was mounted directly behind the phasemask. The size of the interference pattern on the sample was about  $1 \text{ cm}^2$  and had a periodicity of 532 nm. The energy per pulse directly behind the phasemask was measured to be  $8.9 \pm 1.4 \text{ mJ/cm}^2$ . The samples were exposed for 30 s up to a few minutes at a pulse repetition rate of 30 Hz. Exposure of the SAM in air to UV light induces local oxidation of the alkanethiolates into the corresponding alkanesulfonates.<sup>13</sup> The sample was rinsed in de-ionized water to remove the molecules from the oxidized regions of the monolayer and then immersed into a 10 mM solution of either  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  or  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  in ethanol for a minute resulting in a SAM patterned with hydrophobic and hydrophilic regions.

To visualize the pattern, ultrathin polymer films of polystyrene and polybutadiene were deposited on the template.<sup>9</sup> Light micrographs of well-resolved line patterns with a periodicity of 532 nm are shown in Figs. 2(a)–2(c). The sample was originally coated with hydrophobic monolayers, the exposed parts being replaced by hydrophilic monolayers. The deposition is restricted specifically to the hydrophobic regions of SAMs (dark lines). The dependence of the generated pattern on the exposure time is analyzed in Figs. 2(a)–2(d). One clearly recognizes the increasing linewidth of the exposed regions (where no deposition took place) with increasing exposure time until damage occurs [Figs. 2(a)–2(c)]. The data [Fig. 2(d)] yield a time constant of 1 min, corresponding to a dose of  $16 \text{ mJ/cm}^2$  or  $\sim 32\,000$  photons per molecule.

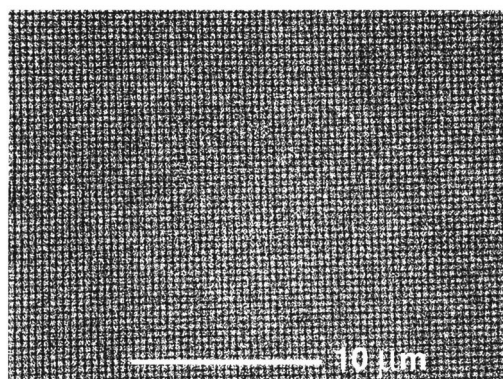


FIG. 3. SEM of a square pattern with 532 nm periodicity realized by double exposure. The sample was rotated by  $90^\circ$  between the two exposures. Minerals were selectively deposited on the hydrophilic regions (bright regions).

This seems to be a very inefficient process, but the use of high flux sources reduces the exposure time by at least one order of magnitude compared to other experiments.<sup>13</sup> The described time dependence of the process can be used as a tool to control the linewidth of the structures in a range from 400 nm down to 100 nm.

Patterned substrates can be used for a variety of applications. Here we have realized the creation of different geometric patterns and the direct patterned deposition of organic (polymer films)<sup>9</sup> and inorganic [ $\text{CaCO}_3$  and  $\text{Zn}(\text{OH})_2$ ]<sup>10</sup> materials as well as colloids.<sup>11</sup>

Using multiple exposures of the sample at different angles we were able to generate line, square, and triangular patterns. An example of a square pattern obtained after double exposure is shown in Fig. 3. Here  $\text{CaCO}_3$  was deposited according to the procedure described in Ref. 10 in the hydrophilic regions of SAMs (bright regions in SEM). The design of the patterns provided by any absorption mask is limited only by diffraction.

We also prepared samples coated with oppositely charged monolayers on which we deposited patterns of charged colloidal spheres. Starting out with a sample coated with positively charged thiols [ $25 \text{ mM HS}(\text{CH}_2)_2\text{NH}_3$ ], the UV-oxidized regions were derivatized by immersion of the

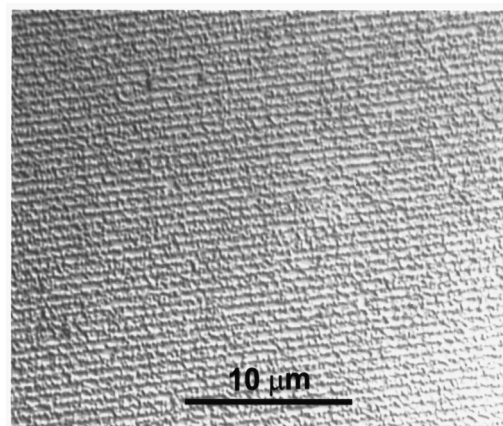


FIG. 4. Light micrograph of a patterned colloidal deposition of positively charged amidine-terminated polystyrene spheres with the diameter of 190 nm on a sample coated with positively and negatively charged thiols. The periodicity of the line pattern is 532 nm.

sample into negatively charged thiol [25 mM HS(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H] resulting in a pattern of oppositely charged regions. The colloids used were positively charged amidine-terminated polystyrene spheres with a diameter of 190 nm ±1.5%. Figure 4 shows an example of a high-resolution 2D array of colloidal particles formed on the template. Diffraction of a laser beam from all the decorated patterns could be observed.

We have demonstrated that UV lithography can be used to prepare chemically patterned substrates on a submicron scale using SAMs as a resist. This lithographic technique combines high resolution and—due to the short wavelength—short exposure times. These substrates can be used as templates for high resolution deposition of a wide variety of organic and inorganic materials. We have shown here the direct deposition of patterned mineral, polymer, and colloidal films with submicron pattern resolution. We plan to exploit this technique further to fabricate 2D photonic structures as well as to use square arrays of colloids as templates for the growth of three-dimensional colloidal crystals.

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