A Convenient Method to Produce Close- and Non-close-Packed Monolayers using Direct Assembly at the Air–Water Interface and Subsequent Plasma-Induced Size Reduction

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An extremely facile approach to produce close-packed colloidal monolayers over large areas using direct assembly at the air–water interface is presented. The influence of small amounts of sodium dodecyl sulfate (SDS) as well as the influence of the pH value of the subphase on the quality of the resulting monolayer is investigated. It is found that small amounts of SDS at the interface influence capillary forces and form a soft barrier that facilitates the crystallization process. Increased electrostatic repulsion arising from a higher pH of the subphase induced a higher order using carboxylic acid functionalized particles. The deposited close-packed monolayers were subjected to plasma treatment in order to shrink the colloids and produce non-close packed monolayers with lattice spacing and symmetry reflecting the order of the initial close-packed monolayer. A detailed examination of etching conditions and their influence on the shrinkage of the particles was performed, including effects of plasma power, composition, flow rates as well as polymeric- and substrate material. The monolayers exhibit vivid coloration, which is determined by their size and packing density. UV–Vis–NIR spectroscopy was used to investigate the change of monolayer color during the size reduction of the individual particles. A simple theoretical model was elaborated to explain the optical properties. Finally, the non-close-packed monolayers were used as masks to produce gold nanostructures to exemplify the versatility of the monolayer architectures in nanosphere lithography.

Introduction

Colloidal particles have been attracting attention from various research fields for their ability to crystallize in highly symmetric arrangements. Two dimensional crystals, commonly referred to as colloidal monolayers, are widely used for lithographic processes to create metal nanostructures in a cheap and highly parallel fashion.\textsuperscript{[1,2]}

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Supporting Information for this article is available from the Wiley Online Library or from the author.
As no light has to be applied for the lithographic process, the diffraction limit is conveniently circumvented and nanostructures with only several tens of nanometers are created with ease. Compared to other nanofabrication processes such as electron beam lithography or focussed ion beam patterning, colloidal lithography offers the advantage of being a parallel process that does not require expensive equipment to yield structures with comparable resolution. While the conventional process, leading to arrays of triangular shaped particles, has long been established, further research focuses on the creation of more sophisticated structures, including embedded objects, rings, and crescent shaped particles. In order to create these kinds of structures in symmetric arrays, the controlled preparation of non-close packed monolayers is a key step. Several approaches have recently been demonstrated. Isa et al. prepared non-close packed arrays of colloidal particles by assembly at the oil–water interface and demonstrated high control over interparticle spacing. Similarly, assembly at the air–water interface has been exploited for the preparation of non-close packed monolayers.

Spin-coating has been applied as well by Jiang and McFarland using a sophisticated coating protocol and a non-volatile acrylate matrix, high ordering of silica particles in a non-close packed architecture was achieved. Subsequent combustion of the matrix materials generated non-close packed monolayers. An alternative strategy consists of the preparation of close-packed monolayers which are subsequently converted into non-close packed architectures. This technique reduces the time needed for the crystallization process significantly. However, several preparation steps are necessary and requires special equipment. Retsch et al. used a preassembly of individual spheres on a parental substrate to produce highly ordered monolayers by immersion of the substrate into a water subphase. During the process, the colloidal particles detach from the parental substrate and form a freely floating monolayer at the air–water interface. This technique reduces the time needed for the crystallization process significantly. However, several preparation steps are necessary and crystallization of arbitrary large monolayers is cumbersome due to size limitations of the parental substrate.

Here, we present a method to produce high quality colloidal monolayers over large areas without the need of any special equipment. The process uses a direct assembly of colloids at the air–water interface in a way that no additional compression of the monolayer is necessary prior to transfer. The close-packed monolayer directly forms at the air–water interface and can be transferred to arbitrary substrates simply by immersion of the substrate into the water phase and picking up the monolayer with a transfer substrate of arbitrary material or topography. Thus, the technique presents an essential simplification of the crystallization procedure and holds promise to make colloidal monolayers available wherever needed even to untrained persons.

The close packed monolayers produced were used in a plasma assisted size reduction to yield non-close packed 2D...
crystals. As a plasma source, a simple, readily available plasma cleaning device was used. A detailed investigation on the effect of plasma power, gas flow rates, and composition as well as the effects of substrate temperature and colloidal material on the etching process was performed. Most importantly, it was investigated until which diameter the plasma etched particles retain their spherical shape before completely collapsing. This point is of special interest for colloidal lithographic applications that require round shapes and space available underneath the colloids for the creation of complex nanostructures. A careful examination on process conditions and their influence on the shape and morphology of the resulting size-reduced colloids is thus a key requisite to control the process.

The colloidal monolayers showed a vivid coloration that was highly sensitive to the size and packing density of the array. The change of color of the colloidal monolayer during the etching time was investigated by UV–Vis spectroscopy. A simple theoretical model was used to explain the optical features. The dependence of the color on the diameter and spacing provides a simple mean for control over the etching conditions and the resulting monolayer.

**Experimental Section**

**Materials**

The monomers styrene, methyl methacrylate (MMA), and acrylic acid were purchased from Sigma Aldrich and distilled under reduced pressure prior to remove the inhibitor. The initiator, potassium peroxodisulfate (KPS), and the comonomer sodium para-styrene sulfonate were purchased from Sigma Aldrich and used as received. Gold and chromium were purchased from Balzers AG. Silicon wafers were obtained from Crystec GmbH (Germany), boron-doped (1–20 \( V/V \) C1 cm) with a thickness of 624 \( m \). Photoresist SU-8 was purchased from Microchemicals (USA) and prepared as specified by the manufacturer. As glass slides, standard microscopy slides (BK7 glass) were used.

**Colloid Synthesis**

All colloids were synthesized by surfactant free emulsion polymerization. The procedure was similar for all samples used. Ultrapure water (MilliQ grade) was heated to 80 °C and degassed by bubbling with Argon gas. Monomer (styrene or MMA, respectively) was added to the water phase and vigorously stirred for 10 min. The comonomer (sodium styrene sulfonate or acrylic acid) was dissolved in a small amount of water and added to the mixture. After 5 min, the initiator, potassium peroxodisulfate (KPS), dissolved in a small amount of water, was added to the mixture. The polymerization was carried out for 24 h at 80 °C. After cooling to room temperature, the dispersion was filtered and dialyzed extensively (Visking Membranes; MWCO = 14 000 g·mol\(^{-1}\), Carl Roth AG).

**Monolayer Crystallization Procedure**

The aqueous colloidal suspensions (typically \( \approx 5 \) wt.\%-\%) were diluted with ethanol to form a 50 vol.-% mixture of dispersion and ethanol and applied to the water surface via a partially immersed hydrophilic glass slide with at a tilt angle of approximately 45° with respect to the water surface following a procedure adapted from Weekes et al.\(^{[19]}\) To help the direct crystallization process, small amounts of SDS were added to the water phase prior spreading of the colloids. The monolayer readily formed at the air–water interface as could be seen by the bright, colorful Bragg reflexes. A hydrophilic substrate (typically a silicon wafer) was immersed into the subphase and elevated under a shallow angle to transfer the monolayer. The substrate was dried under an angle of approximately 45°.

**Plasma-Induced Size Reduction**

All process parameters are specified in the main text. Generally, the etching reactions were carried out in a commercially available plasma cleaner (Model femto, Diener electronic, Nagold, Germany). After placing the samples into the plasma chamber, the chamber was evacuated and flushed with the gas used for the etching experiment for three consecutive cycles. The temperature of the bottom plate of the plasma chamber was controlled by a cryostat with a water/ethylene glycol mixture.

**Nanostructure Fabrication**

All evaporations were carried out in a Balzers PLS500 evaporation chamber with a Pfeiffer vacuum pump (Balzers AG, Liechtenstein). The samples were etched with a reactive ion beam (RR-15Q76, Roth & Rau, Wüstenbrand, Germany) normal to the surface of the substrate. As etching gas, a mixture of Ar, CF\(_4\), and O\(_2\) was used. After the etching procedure, the colloids were removed using elastomeric glue (Marabu Fixogum, Tamms, Germany) that was applied onto the sample surface, hardened for 12 h at room temperature and then removed mechanically.

**Sample Characterization**

Scanning electron micrographs were recorded on a Gemini 1530 microscope (Carl Zeiss AG, Oberkochen, Germany). Polarization-dependent UV–visible spectra were recorded on a Perkin Elmer Lambda 900 spectrometer.

**Results and Discussion**

**Formation of Colloidal Monolayers by Direct Assembly at the Air–Water Interface**

Figure 1a–e shows the process flow for the monolayer crystallization at the air/water interface and the subsequent transfer to a solid substrate. The colloidal dispersion was diluted with 50 wt.-% ethanol to facilitate spreading.
Addition to the air–water interface was performed via a glass slide tilted with an angle of approximately 45° (Figure 1a). Upon spreading, patches of colloidal monolayers formed and remained afloat at the interface (Figure 1b,c). The monolayer patches continued to grow in size upon further addition of colloids until the complete interface was covered. A solid substrate was immersed into the water phase (Figure 1d) and elevated at a shallow angle through the interface in order to collect the monolayer (Figure 1e). Drying was performed at a tilted angle of approximately 45°. Photographs of the process using 1 μm colloids are shown in Figure 1f–h. Figure 1f shows the addition of the colloidal dispersion to the air/water interface via a tilted glass slide. Patches of ordered monolayers are already afloat on the interface as can be seen by the vivid colors that arise due to Bragg reflections of the different crystal domains. In Figure 1g, the transfer to a 200-wafer is shown. The wafer is immersed into the subphase and lifted at a shallow angle to transfer the monolayer. The same wafer after drying is shown in Figure 1h. A uniform coverage with colloids is visible. Individual crystal domains can be distinguished by their distinct coloration.

The process is versatile with respect to colloidal size and substrate material. Polystyrene particles with diameters between 130 and 1,000 nm were successfully applied in the process. Transfer to solid substrates is straightforward and conveniently done by hand. There are no special requirements for the substrate except for that it must be sufficiently hydrophilic in order not to completely dewet during the deposition process. However, even hydrophobic substrates can be used if they are treated with oxygen plasma for a short time prior to transfer. Planarity of the surface is generally not a requirement for the deposition process and substrates with arbitrary topographies have been covered by a similar transfer process.[5,33] This is demonstrated in Figure 1i that presents an electron micrograph of a monolayer of 1 μm colloids deposited onto an array of photoresist micropillars produced by conventional photolithography. The coverage of 50 μm polystyrene latex particles with monolayers is shown in the Supporting Information, Figure SI2.

The quality of the resulting monolayer is strongly affected by the composition of the continuous phase. Using pure water for the assembly led to the formation of a monolayer of colloids at the interface that did not possess a high degree of short- or long range order. Figure 2a shows a monolayer of 408 nm polystyrene colloids crystallized at a pure water interface. Two ways of increasing the order in the resulting monolayers were investigated. First, small amounts of sodium dodecyl sulfate (SDS) were added to the water subphase. As these molecules are amphiphilic, they will accumulate at the air/water interface and constitute a soft barrier for the colloids added to the interface. This barrier facilitates the packing process of the individual colloidal particles into a hexagonal lattice. On a molecular scale, the particles detaching from the glass slide at the interface are pushing against the floating surfactant layer which in turn pushes the particles closer together and thus

Figure 1. Schematic illustration and photographs of the monolayer fabrication process. a,b) Addition of colloids to the interface via a tilted glass slide; c) formation of a close-packed monolayer; d,e) monolayer transfer by immersion of the transfer substrate and subsequent elevation under a shallow angle; f) photograph of the deposition of 1 μm colloids onto the air/water interface; Individual, crystalline monolayer patches floating at the interface can be seen; g) photograph of the monolayer transfer onto a 2″ wafer; h) the same wafer after drying; and i) electron micrograph of a colloidal monolayer deposited onto arrays of micropillars produced by photolithography.
facilitates the nucleation of 2D crystals. This feature has been coined “piston oil effect.”\cite{33} It has been shown that monolayers, which were floated in the presence of surfactants, exhibited a higher mechanical stability and fractured less easily at the edges.\cite{33} This higher stability facilitates the transfer to solid substrates as well. Additionally, free surfactant molecules can adsorb to the particle surfaces and introduce further negative charges. As will be shown below, this leads to an increase in electrostatic repulsion that counteracts van der Waals and capillary attractions and induces a higher degree of order in the monolayer. Finally, the presence of a surfactant lowers the surface tension of the subphase. As the capillary forces acting on the particles is proportional to the surface- or interface tension, the addition of surfactants significantly lowers the magnitude of capillary attraction.\cite{36} The reduced attraction increases the time that is available for the colloids to find their minimum free energy position and thus, further increases the order of the monolayer.

The SDS concentration was varied between 0.1 and 1 mmol·L$^{-1}$. Characteristic electron micrographs of monolayers crystallized with these concentrations are shown in Figure 2. Highest order was achieved using the lowest SDS concentration (0.1 mmol·L$^{-1}$) as can be seen in Figure 2b. An excellent short range order is visible. The long range order is further highlighted in a lower magnification image (Figure 2e) that shows single crystalline domains with dimensions of several hundreds of square micrometers. An increase in SDS concentration up to 0.5 mmol·L$^{-1}$ still produced monolayers with a high degree of order. Nevertheless, individual particles were found on top of the monolayer, thus indicating an increasing stiffness of the surfactant layer that started to interfere with the crystallization process (Figure 2c). At a SDS concentration of 1 mmol·L$^{-1}$, no complete colloidal monolayer is formed. Instead, small patches of colloidal monolayer and free surfactant were present at the surface (Figure 2d). The amount of SDS is high enough to cover extensive parts of the surface and impedes the crystallization process.

Furthermore, the pH value of the water subphase was used to tune the assembly process. The particles featured carboxylic acid groups at their surface. Increasing the pH value induces a higher charge density at the particle surfaces as the acidic groups are more and more deprotonated.\cite{5} This induces an increase in electrostatic repulsion that counteracts attractive van der Waals and capillary forces and allows better ordering of the monolayer.\cite{6,35,37} A higher crystalline order in the monolayer results as the particles remain mobile for a longer time which is a requirement for the ordering process. At lower pH values (i.e., screened electrostatic repulsion), colloids brought into close vicinity by capillary forces immediately feel the attractive van der Waals forces that drive them into close contact. By increasing the electrostatic repulsion, the energy barrier for a close contact is increased and the individual particles have sufficient time and mobility to find the energetic minimum and crystallize in their minimum free energy position as a hexagonally ordered lattice. An additional contribution to the increased energy barrier of the interaction potential is the lowering of the contact angle of the colloids that is a consequence of the increased charge density on the particle surface. Recently, this has been directly visualized by our group.\cite{5} In other words, the colloids are more immersed in the subphase. As a consequence, the capillary forces will be reduced with similar benefits for the crystallization process as mentioned above.

Figure 3 shows examples of a monolayer of polystyrene particles with a diameter of 422 nm at pH values of 6 (Figure 3a) and 11 (Figure 3b). The higher order of the latter is clearly observable.
Controlling Size and Lattice Spacing in Colloidal Monolayer Architectures by Plasma-Induced Size Reduction

After the successful establishment of a simple and straightforward assembly method for close-packed monolayers, a conventional plasma cleaner was used to produce non-close packed monolayers by plasma-induced size reduction. Some articles have been published reporting on plasma-induced shrinkage of colloidal monolayers to form non-close-packed systems.[10,21,22] However, most do not focus on the etching process but rather on the construction of nanostructures themselves. Recently, the etching process has been carefully examined by Plettl and co-workers.[22] Using sophisticated equipment and temperatures of ~150 °C, they demonstrated an isotropic etching process that led to ordered non-close-packed architectures with particles that retained their spherical shape and lattice position. In this study, a commercially available, standard plasma cleaning apparatus (model femto, diener electronics, Nagold, Germany) was used to investigate the etching process and to determine etching rates and the limitations of the process. Besides an accurate investigation on the etching conditions, the shape and lattice positions of the particles at different stages of the etching process were investigated by electron microscopy. This is of special interest for colloidal lithographic applications that require round shapes and space available underneath the colloids for the creation of complex nanostructures.

In general, the diameter of the particles decreased linearly with increasing etching time until reaching a saturation regime upon which no further decrease in size was detected. As will be examined in detail below, the saturation regime represents the threshold value for a controlled size reduction process: in the linear regime, the particles retain a roughly spherical shape that is increasingly transformed into a lentil-like shape for longer etching times (a detailed electron microscopy study is presented in Figure 6 and 7). At the saturation diameter, the particles lose their spherical character and collapse to the surface forming an ill-defined residue. A characteristic image of a monolayer in the collapsed, destroyed state is shown in the Supporting Information, Figure SI3. The linear dependency of the decrease in particle diameter with etching time has also been found by Plettl[22] and Blättler.[38] With an etching rate that is assumed to be constant in time, a shell of the thickness \(d_r\) is etched off the particle by the plasma in the time \(d_t\). Thus, the radius of the particle will decrease linearly. The model is valid as long as the shape of the colloid is still reasonable spherical and the surface remains homogeneous. In the course of the etching process, deviations from the linear relationship are expected due to the deformation of the colloids into a more lentil-like shape and the increase in roughness of the particle surface.

The rates determined for all different conditions are summarized in Table 1.

**Effect of Plasma Power**

In a first set of experiments, the effect of plasma power on the colloidal particles was investigated. As plasma gas, oxygen was used with a flow rate of 3 sccm (standard cubic centimeters per minute). The substrate temperature was fixed to 20 °C using a water/ethylene glycol unit to cool the sample tray.

Figure 4a,b shows the resulting diameter versus etching time diagrams for polystyrene colloids with a diameter of 408 (Figure 4a) and 246 nm (Figure 4b). As expected, a higher plasma power induces a faster shrinkage of the colloids. The etching rates for both different colloid sizes close resemble each other (44 and 23 nm · min\(^{-1}\) for the 408 nm colloids at high/low power; 37 and 22 nm · min\(^{-1}\) for the 246 nm colloids at high/low power, respectively), indicating that the size reduction is not dependent on the size of the colloids as long as both are composed of identical polymers. Using high plasma power, the saturation regime that indicates the break-down of the controlled size reduction is reached.

**Figure 3.** Effect of the pH value of the subphase on the quality of the resulting monolayer for carboxylic acid functionalized particles.
within minutes. Hence, in order to gain a better control on the etching process, 15 W plasma power was applied for all following experiments. The value represents the threshold energy that needs to be applied to reach stable plasma conditions in the set-up used, being necessary for a controlled size reduction.

Next, the effect of different oxygen flow rates on the etching process was investigated. Figures 4c,d show the diameter versus etching time diagrams for the same colloids subjected to oxygen plasma with a power setting of 15 W and flow rates of 3 and 10 sccm, respectively. The lower flow rates induce a faster etching process with etch rates of 23 (408 nm colloids) and 22 nm/\text{min}^1 (246 nm colloids) in agreement with investigations on plasma processes from literature.[39,40] 10 sccm oxygen flow significantly reduced the etching rates to 16 (408 nm colloids) and 18 nm/\text{min}^1 (246 nm colloids). The diagrams also show the linear dependency of the colloidal diameter with etching time. Except for small particles with low flow rates (Figure 6b, black data points), the saturation regime is not reached after the maximum etching time of 10 min. This is desired as it allows very precise control the etching process in order to adjust both colloidal diameters and interparticle distances in the monolayer.

**Effect of Polymer Material of the Colloids**

To test the behavior of different polymeric materials during the etching process, poly(methyl methacrylate) colloids with a diameter of 239 nm and polystyrene particles with a similar diameter (246 nm) were subjected to identical plasma conditions. Figure 5 compares the etch rates of the two types of particles for 15 W plasma power and oxygen plasma flow rates of 3 and 10 sccm. The etching is much faster with the PMMA particles and rates of 71 (3 sccm O₂) and 50 nm/\text{min}^1 (10 sccm O₂) were determined. The finding is in good agreement with reports on polymer and block-copolymer thin film etching processes reported in the literature.[41–43] The slower etch rates of polystyrene are attributed to the higher chemical stability of the aromatic ring. It is concluded that PMMA is not the material of choice

<table>
<thead>
<tr>
<th>Initial colloid size$^a$ [nm]</th>
<th>Plasma gas$^b$</th>
<th>Flow rate [sccm]</th>
<th>Substrate</th>
<th>Substrate temperature [°C]</th>
<th>Etch rate [nm·min$^{-1}$]</th>
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<tr>
<td>408</td>
<td>O₂ (50W)</td>
<td>3</td>
<td>Si</td>
<td>20</td>
<td>44 ± 5.0</td>
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<td>O₂</td>
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<td>20</td>
<td>37 ± 1.1</td>
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<tr>
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<td>3</td>
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<td>20</td>
<td>23 ± 0.8</td>
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<tr>
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<td>20</td>
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<td>3</td>
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<td>20</td>
<td>18 ± 2.1</td>
</tr>
<tr>
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<td>3</td>
<td>Si</td>
<td>20</td>
<td>10 ± 1.3</td>
</tr>
<tr>
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<td>20</td>
<td>11 ± 1.0</td>
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</tr>
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</tbody>
</table>

$^a$Unless otherwise stated, the polymer material was polystyrene; $^b$the plasma power was 15W unless specified.

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**Table 1. Summary of the etching experiments.**

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for a controlled fabrication of non-close-packed monolayers as the rates are too high to allow for a precise adjustment of the colloidal diameter. It should be noted that an increase in etching rates can be readily achieved by increasing the plasma power. Hence, if short etching times were required, e.g., for industrial applications, the combination of polystyrene particles with 50 W plasma power allows a more precise adjustment of diameters and distances in the monolayer as compared to PMMA.

Electron Microscopy Investigations on the Shape of the Colloids During the Etching Process

Three characteristics of the colloids subjected to the etching process are of key importance for any lithographic application. First, the diameters need to be precisely adjusted in order to tailor nanostructure arrays with defined sizes. Second, the symmetry of monolayer should not be lost during the etching process in order to produce metal nanostructure arrays with a high order. Therefore, during the etching process, the colloidal particles need to retain their individual positions and shrink without lateral movement. Third, the particles need to retain their spherical shape in order to produce architectures with the maximum flexibility with regards to colloidal lithography. This becomes obvious when realizing that many processes for complex structure construction take advantage of the substrate regions shaded by the colloids. Once the particles completely lose their shapes, they can still be used for the construction of e.g., disk-like structures or as etching masks for substrate patterning but any more complicated geometries (i.e., evaporation and etching under varying angles to exploit the area shaded by the colloid) cannot be produced by a lithographic process anymore. In this chapter, electron microscopy is used to image the monolayers at different stages of the etching process in order to access possibilities and limitations of the etching process.

Figure 6 presents electron micrographs of a colloidal monolayer comprised of 408 nm polystyrene latex particles in the course of the plasma etching process. In the top-view images (Figure 6, left row), the high symmetry of the monolayer at all etching stages is well visible. Hence, it can be concluded that plasma etching does not induce any lateral disorder to the non-close-packed monolayer. The side-view images (Figure 6, right row) reveal the shape of the individual particles. It can be seen that the particles do...
not shrink isotropically. Instead, the etching is more efficient on the top of the particles, resulting in lentil-shaped colloids after several minutes of etching. Increasing etching times roughens the particle surfaces of the top parts. After long etching times (10 min), the deviation from a spherical shape is pronounced. However, keeping in mind applications in colloidal lithography it should be noted that even for the longest etching time investigated (Figure 6g,h), the particles still feature a round shape at the bottom and are not completely collapsed. Thus, it is still possible to use them as evaporation masks because they continue to shade a certain amount of substrate space (Figure 6h). At that stage, the particle diameter is reduced to approximately half its initial value. Further etching induced a collapse of the already strongly deformed particles into irregular shaped structures (Figure S13).

Figure 6. Examination of shape and position of the individual colloids of a polystyrene monolayer subjected to oxygen plasma (15 W, 10 sccm) with an initial size of 408 nm. The left column shows top view images, the right column side view images. The insets show lower magnifications of the same sample. The scale bars are: left row: 500 nm; insets: 1 μm. Right row: 200 nm; insets: 500 nm. Plasma was applied for the following times: a, b) 4; c,d) 6; e,f) 8; g,h) 10 min.

Figure 7 shows the electron micrographs of monolayers made of polystyrene particles with a diameter of 246 nm in the course of the etching process. In agreement with all observations on the larger colloids, it can again be stated that the lateral symmetry is retained during all stages of the etching process. The shape of the individual particles is gradually transformed into a more flattened, ellipsoidal structure; accompanied by an increase in roughness for longer etching times. However, until the particle diameter is reduced to less than half its initial value (Figure 7g and h), the shape of the particles is still suitable for any lithographic application.

It can thus be estimated that the etching procedure described here produces non-close-packed monolayer with the same, high symmetry as the parental, close-packed monolayers. For polystyrene as colloid material, the size can...
Finally, the PMMA colloids used in Figure 5c were investigated by electron microscopy as well. Melting of the colloids in the electron beam inhibited the recording of side-view images. Please note that the etching times applied for the individual stages of the process are substantially shorter than the ones for the polystyrene monolayers shown above. The top view images shown in Figure 8, highlight the symmetry of the monolayers, which is retained in a way similar to polystyrene colloids. The individual spheres, however, seem to be more roughened than the polystyrene particles shown above. We attribute this behavior to the low resistance of PMMA toward the plasma, which leads to particles, being more severely attacked by the oxygen species generated in the plasma. The last picture in the row shows a particle array in the saturation regime. The spherical shape is lost and the particles are flattened and irregularly shaped. Once this stage is reached, further plasma treatment does not induce any changes in shape or diameter of the colloids.

Effect of Plasma Composition

The effect of the plasma gas was investigated as well. Figure 9 summarize all etching experiments performed with different gas compositions. All colloids in the study were subjected to oxygen and argon plasma with similar...
flow rates (3 sccm). As can be seen from Figure 10a–c, oxygen plasma leads to a more rapid shrinking of the particles than argon. For polystyrene particles, the etch rates were 22 (246 nm colloids) and 23 nm·min⁻¹ (408 nm colloids) for oxygen and 10 (246 nm) and 11 nm·min⁻¹ (408 nm) for argon, respectively. For PMMA as colloid material, oxygen plasma induced a decrease in diameter of 71 nm·min⁻¹; application of argon led to rate of 34 nm·min⁻¹. For all samples investigated, the etch rate of oxygen is approximately two times higher than that of argon. Hence, another means of controlling the etch rate and by this, the final colloidal diameter is at hand. It should be mentioned that argon plasma produced particles with a rougher colloid surface compared to oxygen plasma treated particles with a similar diameter.

Figure 9d shows a more detailed examination of plasma compositions with 408 nm colloids. The composition was systematically varied from pure oxygen (3 sccm; same data as Figure 9a) via ratios of 2:1 oxygen:argon, 1:1, 1:2 to pure argon (equaling the second graph of Figure 9a). The etch rates of all oxygen containing plasmas did not differ significantly and the non-close-packed monolayers produced by the different mixtures resembled each other. Only pure argon led to a drastic reduction of the shrinking process. It can be concluded that the presence even of small amounts of oxygen molecules in the plasma strongly accelerate the etching process. Oxygen molecules are the more efficient species in the decomposition process of the polymeric material as chemical decomposition by insertion of peroxy-radicals into the backbone followed by chain scission is the dominating process of the plasma etching.[42] In contrast, argon species generated in the plasma are chemically inert and physical decomposition by surface bombardment of ions is the dominating mechanism. This also explains the higher roughness of colloids etched with argon as they are subjected to higher impact energies by the heavier argon ions. Surface functionalization, related to chemical etching, has been reported to only occur due to water impurities in the argon plasma or by environmental oxygen after the plasma treatment.[43,49]

Effect of Substrate Temperature on the Etching Process

The substrate temperature was varied in order to examine possible changes in the etching process. Using a water/ethylene glycol mixture in a cryostat connected to the bottom of the plasma chamber, the substrate temperature was controlled between 20 and 0 °C. Figure 10 shows the resulting diameter vs. etching time diagrams. Decreasing the substrate temperature led to a slight decrease in etching rates; both for oxygen and argon plasma applied. The effect was not very pronounced and limited to few nanometers per minute. Concluding this set of experiments, it should be...
stated that the substrate temperature does not have a significant effect on the etch rates and particle morphologies for the temperature range investigated. However, controlling the temperature of the plasma chamber is important as uncontrolled temperature led to strong increases of the temperature of the substrate in the course of the etching process with the drastic consequences on the resulting particle arrays. First, the etching rates were not reproducible and featured strong deviations from the typical linear dependencies of the controlled process. Furthermore, etching times of 5 min and longer resulted in particles with a completely destroyed shape; somewhat resembling popcorn. Hence, even though the precise adjustment of temperature does not seem to be very significant for the process, cooling of the plasma chamber is an important requisite for successful size reduction processes.

Effect of Substrate

Finally, the effect of the substrate on the plasma-induced size reduction process was accessed experimentally. Colloidal monolayers were deposited on substrates typically applied in colloidal lithography (Si-wafer and glass) and treated with oxygen plasma with a flow rate of 10 sccm. As glass substrate, conventional microscopy slides were chosen. Both the microscopy slide as well as the silicon wafer were also covered with a thin gold film (50 nm), as typically applied for lithographic processes. Furthermore, the silicon wafer was covered with a \( \sim 10 \mu m \) thick film of photoresist (SU-8) to investigate effects of a thicker, insulating layer on the silicon wafer. Figure 11 shows the resulting diameter-versus-etching time diagrams. The etch rates on silicon was twice as high as compared to glass as substrate material (16 nm \( \cdot \) min\(^{-1} \) for Si and 7 nm \( \cdot \) min\(^{-1} \) for SiO\(_2\)). The effect of thin film of gold is not pronounced and the etch rates resemble the native substrates. The thicker film of insulating photoresist significantly reduces the etch rate by approximately 30%. We attribute this phenomenon to a higher density of charges on insulating surfaces. In contrast to a (semi)conductor that can remove the charges introduced by ions and electrons in the plasma, insulators accumulate charges on their surfaces. In the course of the etching process, the substrate is increasingly charged and thus shield like charges in the plasma that cannot contribute to the etching process, resulting in smaller etch rates. The phenomenon is related to smaller etch rates of silicon dioxide compared to silicon that are reported for reactive ion beam etching experiments.\(^{[39]}\)

Figure 11. Effect of substrate material on the size reduction process. a) Silicon wafer and wafer with thin films of gold and photoresist; b) microscope slide and slide with a thin gold film.

The color strongly depends on the colloids’ size, lattice orientation, and interparticle spacing. One has to distinguish two different phenomena that lead to the color. First, highly crystalline monolayers with a size above \( \sim 400 \text{ nm} \) exhibit strong iridescence in dependence of illumination and observation angles. This phenomenon, known e.g., from butterfly wings in nature,\(^{[53]}\) results from diffraction of light in the layered arrangement of particles in a colloidal monolayer. Light waves scattered by individual particles interfere with beams scattered from neighboring particles and give rise to amplification (constructive interference) or annihilation (destructive interference) of light with certain wavelengths.\(^{[52]}\) In total, brilliant intermixing of colors with strong angular dependence and a clear distinction between individual crystal domains result. Second, monolayers of sizes below \( \sim 500 \text{ nm} \) show continuous, uniform coloring. This color is a result of interference of light at parallel planes of the monolayer surface and the substrate.\(^{[50,51]}\) Crystallinity is not a requirement for this type of color as the monolayer merely acts as a thin, continuous film. The uniform coloration strongly depends on the size of the particles and can thus be used as a simple means to control the etching process. This might be of interest e.g., for quality control in industrial applications where electron microscopy control is time consuming and cumbersome.
Figure 12 presents UV–Vis–NIR spectra recorded in transmission of monolayers consisting of polystyrene spheres with an initial diameter of 408 nm at plasma etching times between 0 and 10 min. To illustrate the strong differences in coloration of the two-dimensional colloidal crystals at different etching times, photographs of 2 inch silicon wafers covered with monolayers where taken and are presented in Figure 12b–e. The wafer was illuminated normal to the wafer surface.

The extinction maxima shift toward shorter wavelength for longer etching times (i.e., smaller particle diameters and larger interparticle spacing). A second, more pronounced peak appears in the visible range at around 500 nm for the initial monolayer. A blue-shift in the course of the etching process is detected for the second maxima as well (see inset for a more detailed picture). Both shifts are indicated by arrows in the Figure. In order to explain the spectral features, a theoretical model was adopted from literature\(^{[50]}\) and extended to non-close-packed architectures.

Treating the monolayer that consists of individual particles as a continuous, plane parallel film, one can apply classical optics to describe the interference between waves reflected at the surface of the thin film and substrate surface.\(^{[50,54]}\) The intensity of the reflected light depends on the path difference between the waves reflected at the air–colloid and the colloid–substrate interface. When illumination occurs normal to the surface, angular dependencies of the phase shift cancel out\(^{[50]}\) and constructive interference is obtained for a path difference of integers \((m = 1, 2, \ldots)\) of \(\lambda\) (see Supporting Information Figure SI4 for a sketch and derivation of the equation). Hence, reflective maxima can be calculated as

\[
m\lambda = 2d_{\text{coll}}n_{\text{mono}}(m = 1, 2, \ldots)
\]  

(1)

In the equation, \(\lambda\) represents the wavelength at maximum reflection, \(d_{\text{coll}}\) the diameter (or, more precisely the height) of the particle and \(n_{\text{mono}}\) the refractive index of the colloidal monolayer.

The refractive index of the monolayer \(n_{\text{mono}}\) depends on the refractive index of the polymer material (here: polystyrene) \(n_{\text{PS}}\), the volume fraction of the colloids \(\varphi_{\text{coll}}\) and the refractive index of the surrounding medium (here: air) \(n_{\text{med}}\) and can be expressed as\(^{[55]}\)

\[
n_{\text{mono}} = n_{\text{PS}}\varphi_{\text{coll}} + n_{\text{med}}(1-\varphi_{\text{coll}})
\]  

(2)

Substituting Equation (2) into (1) and taking \(n_{\text{med}} = 1\) for air as surrounding medium, an expression for the reflection maxima is obtained:

\[
\lambda = \frac{2}{m}d_{\text{coll}}[n_{\text{PS}}\varphi_{\text{coll}} + (1-\varphi_{\text{coll}})]
\]  

(3)

The last task for the calculation of the constructive interference peaks is the determination of the volume fraction of the colloids in the non-close-packed monolayer. Using geometric arguments, the volume fraction can be approximated as the volume fraction of a sphere with the diameter \(d_{\text{ncp}}\) (being the diameter of the colloid in the non-close-packed monolayer) in a hexagonal prism with the base determined by \(d_0\) (\(d_0\) being the initial diameter of the
spheres in the close-packed arrangement) and the height $d_{ncp}$ (sketch and derivation presented in the Supporting Information, Figure SI5):

$$\psi_{coll} = \frac{\pi \sqrt{3}}{9} \frac{d_{ncp}^2}{d_0}$$  \hspace{1cm} (4)

Table 2 compares the theoretical values for the constructive interference with the experimental data extracted from Figure 12a. A refractive index for polystyrene of $n_{PS} = 1.57$ was used and the wavelength dependence was neglected.

A qualitative agreement between theory and experimental data is obvious. Both first ($m = 1$) and second ($m = 2$) interference maxima are reproduced and the shift toward shorter wavelengths for increasingly less densely packed architectures as found experimentally is confirmed theoretically. Quantitatively, a discrepancy between experimental data and theory is found. This can readily be explained by oversimplification of the model. The order of the monolayer is assumed to be perfect and defects are neglected. Thus, the volume fraction of the colloids is overestimated in the model. Additionally and more severely the colloids are assumed to fully retain their spherical shape while in reality, their shape deforms into a lentil-like form. As the model uses the experimentally determined top view diameter of the colloids as the height of the thin film, the volume fraction is further overestimated as the real height is reduced due to the shape deformation. Further refinements of the model, e.g., by taking into account the deviations from spherical shape are expected to increase the quantitative agreement between model and experimental data. Considering the simplicity of the theoretical model, the qualitative agreement with experimental data was surprisingly good.

### Applications in Colloidal Lithography

In order to demonstrate the versatility of the non-close packed monolayer in colloidal lithography applications, arrays of differently shaped nanoparticles were produced. A detailed elaboration of size-dependencies, optical properties, or limitations of the structure generation is not scope of this article. However, plenty of literature exist on the plasmonic properties of differently shaped metal nanostructures\cite{56,57} and their use, e.g., in sensing applications\cite{7,58–60}.

Figure 13 shows different structures which are produced with ease using non-close packed monolayers as masks. Figure 13a shows nanoscopic holes in a continuous gold film produced simply by evaporation of gold onto the non-close packed monolayer and subsequent removal of the

### Table 2. Constructive interference maxima of a monolayer of PS colloids subjected to plasma treatment.

<table>
<thead>
<tr>
<th>Etching time [min]</th>
<th>Colloid diameter [nm]</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st order maximum [nm]</td>
<td>2nd order maximum [nm]</td>
</tr>
<tr>
<td>0</td>
<td>408</td>
<td>1097</td>
<td>549</td>
</tr>
<tr>
<td>2</td>
<td>393</td>
<td>1049</td>
<td>524</td>
</tr>
<tr>
<td>4</td>
<td>388</td>
<td>1018</td>
<td>509</td>
</tr>
<tr>
<td>6</td>
<td>370</td>
<td>950</td>
<td>475</td>
</tr>
<tr>
<td>8</td>
<td>355</td>
<td>895</td>
<td>448</td>
</tr>
<tr>
<td>10</td>
<td>344</td>
<td>834</td>
<td>428</td>
</tr>
</tbody>
</table>

![Figure 13. Application of non-close-packed monolayers in colloidal lithography: a variety of gold nanostructures can be readily created in highly ordered arrays. (a) Holes in a continuous gold film; (b) gold nanocrescents; (c) gold disks; (d) gold rings.](image-url)
colloids. Figure 13b shows arrays of gold nanocrescents that are produced by evaporation of gold under an angle of 30° with respect to the surface normal followed by reactive ion beam etching normal to the surface.\[10\] Figure 13c presents arrays of gold nanodisks that are produced by assembly of a monolayer onto a continuous gold film. After plasma-induced size reduction, reactive ion beam etching is used to remove the gold not shaded by the colloids. Finally, gold nanorings can be produced as well (Figure 13d). Ring formation is achieved by multiple evaporation of gold with an angle of 30° with respect to the surface normal, followed by reactive ion beam etching similar to the process used for the nanocrescent fabrication.\[57\]

**Conclusion**

In conclusion, this article presents a convenient method for the preparation of close-packed monolayers, examines a plasma-induced size reduction process in detail and provides a simple model to explain the optical features of the resulting non-close packed monolayers.

The monolayer preparation method uses a direct assembly of a highly ordered, close-packed monolayer at the air–water interface that can be transferred manually to arbitrary, hydrophilic substrates. The quality of the monolayer can be increased by controlled addition of small amounts of SDS to the subphase that acts as a soft barrier to facilitate monolayer crystallization. Furthermore, when carboxylic acid functionalized colloids were used for the monolayer crystallization, an increase in the pH of the subphase was found to increase the order in the resulting monolayer.

The monolayers were subjected to oxygen plasma in a standard plasma cleaning device. A detailed investigation of the etching process was performed and the following conclusions can be drawn. During the etching process, no lateral movement of the colloids was observed and the non-close packed architectures exhibited the same, high lateral symmetry and order as the initial close-packed monolayers. In the course of the etching process, the particles’ initial spherical shape deforms into lentil-like structures. The particles can be decreased up to approximately 50% of their initial diameter before completely collapsing and losing their structural integrity. Polystyrene proved to be the more suitable colloidal material than poly(methyl methacrylate), as the latter exhibited high etching rates and thus little control over resulting particle diameters. Oxygen plasma showed significantly higher etch rates than argon and the latter induced higher surface corrugation on the colloids. The substrate material drastically affected the etch rates while temperature of the substrates only marginally influenced the process. However, a control of the temperature was necessary for a successful preparation of non-close packed monolayers to prevent high temperatures and “explosion” of the individual colloids.

The color of the monolayer changed characteristically upon reduction of colloidal size and surface fraction in the non-close packed crystals. UV–Vis–NIR spectroscopy was applied to assess the optical properties of the monolayers. A simple model to predict constructive interference between the colloids that are treated as a continuous thin film and the surface was adopted and extended to describe the non-close packed architectures. Considering the simplicity of the theoretical model, the qualitative agreement with experimental data was surprisingly good and all characteristic features were reproduced. More elaborate geometrical considerations would certainly help to describe the experimental results more quantitatively.

The processes for the monolayer crystallization and size reduction are conceptually extremely simple, do not require any sophisticated instruments and are able to pattern large areas in short time scales with a high precision. Thus, they provide a method to make colloidal monolayers available wherever needed even for persons untrained in colloidal crystallization processes. Additionally, due to the simplicity, the process might be easily amenable for industrial applications. The characterization method using UV–Vis spectroscopy is fast and simple as well and would provide an excellent means for quality control of the resulting non-close packed monolayers.

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