ADVANCED MATERIALS

DOI: 10.1002/adma.200602521

Micropatterning by Non-Densely Packed Interfacial Colloidal Crystals**

By *Matthew A. Ray* and *Li Jia**

Methods for patterning solid surfaces are the focus of significant scientific efforts because micropatterned surfaces are important materials for modern technologies, such as microelectronics, optoelectronics, optics, and biological microanalysis.[1] Among the many surface-patterning options, nanosphere lithography[2] is unique in that it uses a self-assembled mask with hexagonal symmetry, consisting of densely packed monodispersed colloidal particles deposited on a substrate by either a Langmuir-type technique[3] or by direct evaporation of the aqueous particle suspension.[4] Non-densely packed 2D colloidal crystals also form at air/water or oil/water interfaces.[5] In these cases, charged particles with a hydrophobic surface self-organize into large 2D hexagonal lattices directed by electrostatic repulsion and capillary attraction between neighboring particles.[6] The interparticle spacing in the lattice is adjustable by varying the surface pressure of the film. Such interfacial films would be very attractive for surface patterning if they could be transferred intact from the aqueous interface onto solid substrates. Although densely packed particle films are routinely transferred, the transfer of *non-densely packed* films, where the particles are not physically touching each other and can easily be moved out of their lattice positions, is yet to be accomplished. We report on a methodology for the transfer of non-densely packed particle films at an air/water interface onto silicon substrates (Scheme 1) and also demonstrate that the transferred particle arrays can be used as an etching mask to generate hexagonal arrays of divot-like holes in the surface of the silicon-wafer substrate.

In this work, monodispersed polystyrene latex particles were used with an average diameter of 2.7 μm and a sulfate-functionalized surface having a charge density of 8.9 $\mu C\,cm^{-2}$. The particles were suspended in isopropyl alcohol (IPA) and allowed to age for 10 days before use. During this time, the water/particle surface contact angle progressively increased until approaching an asymptote at ca. 84° (see Supporting Information). The high contact angle was critical for irreversible particle attachment to the interface[5] and also strengthens the interparticle repulsion at the aqueous/air interface.[6a,b] After aging in IPA, the particles had readily spread over the air/water interface with minimal particle flocculation and virtually no loss to the bulk aqueous phase. A continuous non-densely packed hexagonal particle array formed when the particle coverage on the surface approached 1.1×10^4 particles mm^{-2}.

Under the pragmatic assumption that strong attractive forces between the substrate surface and the particle surface were necessary for the successful transfer of the interfacial film onto the solid substrate, we modified the surface of the silicon wafer to have a compatible degree of hydrophobicity and an opposite charge to that of the particle surface. This was achieved by treating the silicon wafer with tetradecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride (TDAC) or *N*-trimethoxysilylpropyl-*N*,*N*,*N*,-tri-*n*-butylammonium chloride (TBAC) following standard procedures until both the water contact angles (77.8 ± 1.9° and 65.6 ± 2.5°, respectively for TDAC and TBAC) and the ellipsometric thicknesses of the organosilane monolayers (10.4 ± 1.1 Å and 10.2 ± 1.5 Å, respectively) reached their asymptotic values. Assuming that full monolayers were indeed achieved and that the monolayer parking areas of the TDAC and TBAC motifs are approximately 100 and 70 $Å^2/NR_4^+$ (from molecular mechanics calculation using PC Spartan version 1.0.2), the theoretical surface charge densities would be approximately 16 and 23 $\mu C\,cm^{-2}$, respectively.

In our initial attempts of transferring the interfacial films, the substrate prepared as described above was steadily lowered parallel to the aqueous surface until it contacted and slightly passed through the aqueous surface to ensure full contact with the interfacial film. After being withdrawn immediately from the aqueous phase, the substrate was invariably covered by randomly positioned particle clusters. However, the average particle density on the silicon wafer was very similar to the initial particle density at the air/water interface. We thus speculated that the initial transfer might be successful but the ordered array was destroyed during the dewetting and drying process, when the particle array was subject to strong lateral capillary forces.[3] To circumvent this problem, the withdrawing procedure was modified. After contacting the interfacial film, the substrate was lowered further into the aqueous phase and flipped facing up. A glass cover slip with dimensions slightly larger than the substrate was floated on top

[*] Prof. L. Jia,[+] Dr. M. A. Ray
Department of Chemistry, Lehigh University
Bethlehem, Pennsylvania 18015 (USA)

[+] Current address: Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA. E-mail: ljia@uakron.edu

[**] The authors thank the Center of Optical Technologies at Lehigh University for financial support. M.R. thanks the Lehigh University Department of Chemistry for a research fellowship. Supporting information is available online from Wiley InterScience or from the author.

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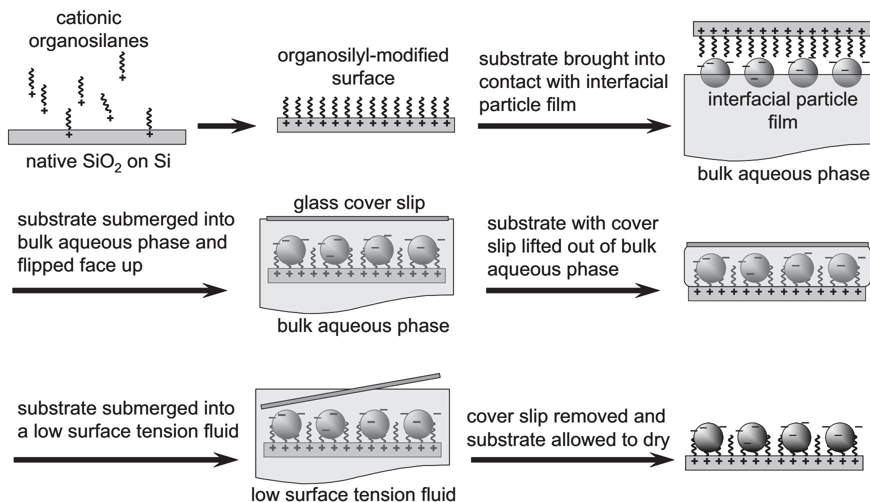

Scheme 1. Schematic summary of the procedure of transferring a non-densely packed interfacial particle film intact onto a silicon substrate.

of the water. This covered the substrate while it was raised out of the liquid, sandwiching the adsorbed particle array and a thin film of water between the substrate and the cover slip. This method ensures that the transferred particle films remain in water and allows them to be observed before being subjected to the drying process. As we suspected, optical microscopy revealed that the hexagonal lattice was fully preserved at this stage. The process of the ordered array being destroyed upon drying could be observed after the cover slip was removed.

A "fluid-exchange" approach was then used to preserve the surface pattern during drying. In this approach, the cover glass was removed while the substrate was submerged in ethanol. This allowed water to be replaced by ethanol, which has a much lower surface tension. The capillary force caused by ethanol was low enough so that the hexagonal particle lattice was left undisturbed on the silicon wafer after the surface had dried completely as shown in Figure 1. The interparticle spacings in the representative optical microscopy image of the patterned surface were measured by nearest-neighbor analysis (NN)[7] and fast-Fourier-transform analysis (FFT). The NN and FFT analysis gave average interparticle spacings of 7.89 ± 0.33 μm (standard deviation, 1121 measurements) and 7.93 ± 0.32 μm (standard deviation, 60 measurements), respectively. Using a He:Ne laser with an incident beam spot on the order of 1 mm^2, a clear hexagonal diffraction pattern was generated throughout almost the entire substrate, except when the laser scanned across the domain boundaries. This indicates that the individual domain sizes of the hexagonal crystals exceed several square millimeters. The average interparticle spacing measured from the laser diffraction pattern in Figure 1 was 8.05 ± 0.33 (standard deviation, 60 measurements), which is consistent with the NN and FFT analysis.

The fluid-exchange process was used for an additional purpose. The particles could be deformed by certain fluids, such as acetone or diethyl ether, to create "footprints" of increased size on the substrate (Fig. 2A). In these cases, the improved adhesion due to the expanded contact area was likely also a major factor in preserving the pattern against capillary destructive forces. Once a particle array was deformed at the interface, it could function as a lithographic mask. As illustrated in Figure 2, the starting silicon wafer was patterned with a hexagonal array of particles that were in contact with acetone for 1 min during the fluid-exchange process. The heights of the polystyrene mounds were approximately 1.5 μm, measured by atomic force microscopy (AFM). The wafer was then treated by a 40 % potassium hydroxide (KOH) solution in water and IPA (4:1) at 60 °C for 3 min, rinsed with IPA, washed with toluene to remove any residual polystyrene, again rinsed with IPA, and then blown dry with a nitrogen jet. Somewhat surprisingly, this procedure caused selective etching of the areas where the particles were, creating a hexagonal array of holes in the substrate. The diameter of the holes (3.9 ± 0.1 μm, 25 measurements) was approximately equal to or slightly smaller than the diameter of the circular footprints (4.1 ± 0.1 μm, 25 measurements). The depth of the holes measured by AFM was about 200 nm. Apparently, the organosilane monolayer acted as a barrier to the etchant. Selective etching occurred in the areas where the integrity of the organosilane monolayer was compromised by the deformed particles.

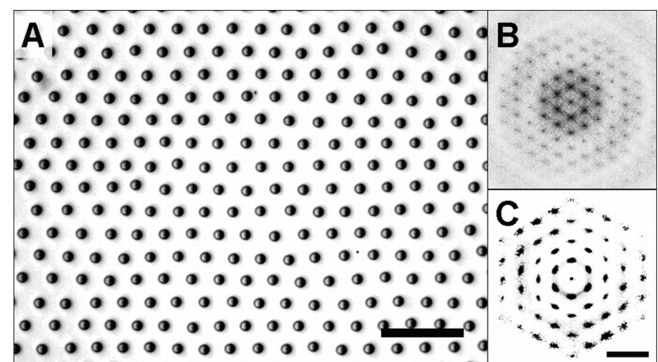

Figure 1. A) Optical microscopy image of the hexagonal particle pattern transferred to a TBAC-modified substrate. Scale bar: 25 μm. B) Central region of the fast-Fourier-transform of the image shown in A. C) Contrast-corrected laser-diffraction pattern of the particle array shown in A. The backscattered diffraction pattern was recorded at a projection length of 10 cm. Scale bar: 2 cm.

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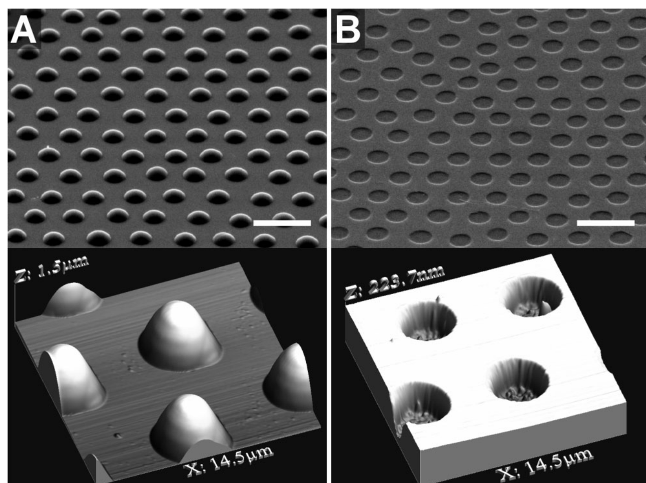

Figure 2. A) Polystyrene latex particles in hexagonal lattice on the wafer surface after being treated by acetone for 1 min. Top: SEM image. Scale bar: 10 µm. Bottom: AFM image. B) Wafer surface of the sample in A after KOH etching and removal of the polystyrene on the surface. Top: SEM image. Scale bar: 10 µm. Bottom: AFM image.

In summary, a method has been developed to transfer interfacial films of non-densely packed particle arrays onto surface-modified silicon substrates. The substrate surfaces can be easily prepared by treating silicon wafers with organosilane compounds. The resulting surface, with functionality complementary to that of the latex particles, rapidly adsorbs particles at the aqueous interface with the pattern intact. Fluids with low surface tension or capable of deforming the latex particles were used to replace water to prevent disorganization caused by strong lateral capillary forces during the drying process. Ordered arrays of deformed particles may be used as a mask for lithographically patterning the surface topography of the substrate through chemical etching. The interparticle spacing can be controlled by the surface pressure and the size of the particle/substrate contact area can be tuned by the choice of the immersion fluid and time. Therefore, the spatial parameters should be adjustable with the herein described micropatterning methodology. Although the present examples involve patterns on the micrometer scale, the method can likely be extended to the nanometer scale.[7] This methodology also provides a high incentive to explore the complexity of patterns achievable at aqueous interfaces by using, for example, binary particles or an external electric field.

Received: November 7, 2006
Revised: March 15, 2007
Published online: July 11, 2007

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[7] We have had preliminary successes using latex particles with a diameter of 258 nm. The size limit is likely going to be the range in which the thermal energy of the interfacial particles becomes comparable to the interfacial trapping energy. This limit is somewhere between a few nanometers to a few tens of nanometers (as reported previously [5]).

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