

Formation of Two-Dimensional Colloidal Sphere Arrays on Micro-Patterns

Neil A. Bernotski¹, Xiaorong Xiong², Kerwin Wang³, Nels E. Jewell-Larsen⁴, and Karl F. Böhringer⁵

Department of Electrical Engineering, University of Washington, Seattle, WA 98105, USA

Abstract: A hydrophobic substrate patterned with hydrophilic squares is used as a template for the selective deposition of two-dimensional micron and sub-micron polystyrene sphere arrays. In experiment, a monodisperse colloidal solution is applied to a patterned substrate. When the colloid is drawn off the substrate, two-dimensional arrays of colloidal spheres are selectively formed in the center of the hydrophilic squares. Optical microscopy coupled with high-speed photography allows the observation of this process for 1 μ m and 290nm polystyrene spheres. The observations reveal that as the body of colloid recedes off the substrate, the three-phase contact line becomes pinned at the pattern edges. This pinning causes the colloid to stretch across the hydrophilic areas, forming liquid films that neck and break off from the main body of colloid. The film is sufficiently thin to force the colloidal particles into a single layer. Capillary forces from the remaining liquid centers and packs the two-dimensional arrays in the hydrophilic patterns.

Introduction

Two-dimensional arrays of colloidal particles are being applied in technologies such as surface plasmon resonance sensors [1] and solar cells [2]. The arrays are used as lithographic masks to produce surface textures. The potential application of these arrays has fueled interest in various colloidal methods of two-dimensional array formation [3-7]. Some of these methods form arrays only on selected areas of the substrate [3-5]. The resulting patterned arrays may be useful as micro and nanostructures themselves. Patterned arrays of colloidal particles could potentially be refloated to form other micro/nano structures such as wires or lenses.

The formation of colloidal particle arrays on selected areas of a hydrophilic-hydrophobic patterned substrate was recently proposed by authors of this paper as a method to transform traditional lithography micro-patterns into nano-structures [3]. A substrate patterning and colloidal deposition technique was presented that can produce self-assembled arrays with feature sizes smaller than found in the original pattern. The technique was used to form two and three-dimensional arrays on both rectangular and circular patterns. The arrays feature tightly packed hexagonal lattice

¹ nbernots@ee.washington.edu

² xrxiong@ee.washington.edu

³ kerwin@ee.washington.edu

⁴ nelsjl@ee.washington.edu

⁵ karl@ee.washington.edu

structures that are centered within the substrate patterns. Here, we report on experimental observations of this technique, which were made during array formation. The experiments focused on two-dimensional array formation on substrates with simple patterns of squares. Figure 1 shows final arrays of 290nm spheres, self-assembled on a pattern of hydrophilic squares.

Other groups have used patterned substrates to guide two-dimensional array formation. Xia et al. [4] employed patterns of recesses with depths similar to the diameter of the colloidal spheres. The deposition process packs each recess with spheres, forming arrays that are the length and width of the recess. Due to the finite number of lattice structures available for a given perimeter shape, the final arrays have continuous, tightly packed lattice structures only when the original recess is properly dimensioned. This implies that the recess fabrication method must have dimensional tolerances that are less than some fraction of the sphere diameter. While the method presented here has less control over the shape and size of the final arrays, the lattice structure is not affected by such small variation in the pattern dimensions.

Guo et al. [5] used gold patterned on mica to selectively form two-dimensional arrays of colloidal spheres. Negatively charged spheres are attracted to the gold patterns by their image charges while being repelled from the negatively charged mica background. The electrostatic interaction between the colloidal spheres and substrate guides the selective formation of arrays on the gold patterns. In contrast, for the method presented in this paper it is the interaction between the colloidal liquid and substrate that guides the selective formation of arrays on patterns. This may allow a greater degree of freedom in the types of colloidal particles

and substrates applicable to this process. Further, the electrostatic attraction and subsequent evaporation of the colloidal liquid does not center the array in the original pattern. The natural centering of this deposition process allows formation of arrays that have features smaller than the original patterning.

Experimental Setup

In experiment, a substrate coated with colloid is brought into contact with a water bath. When the water contacts the colloid/substrate/air interface, some of the colloid is drawn off the substrate and into the bath. The colloid that remains on the substrate selectively wets hydrophilic squares that have been patterned against a hydrophobic

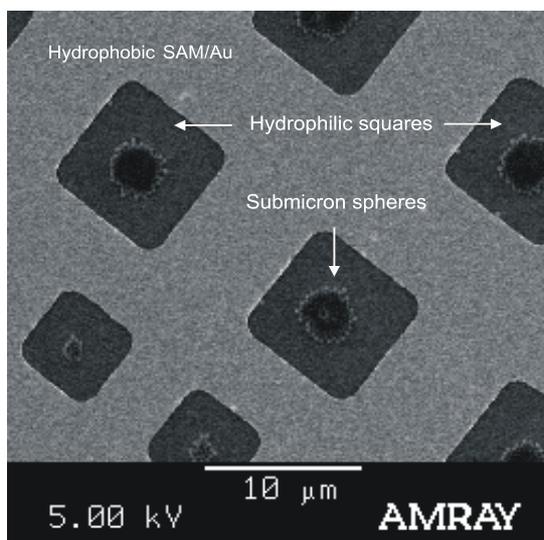


Figure 1. SEM image of micro-patterned two-dimensional arrays composed of 290nm polystyrene spheres.

background. The colloid liquid in each square evaporates leaving two-dimensional arrays of colloidal particles. Images of the process were captured with a high-speed digital camera coupled with an optical microscope (Figure 2).

Two monodisperse colloids were studied on patterned substrates. One colloid contained 290nm mean diameter polystyrene spheres and the other, 1 μ m (0.99 μ m mean diameter) polystyrene spheres (Bangs Labs, Inc.). Both colloids contained a 10% by weight concentration of spheres (density 1.050 g/cm³), suspended in a solution of deionized water with 0.1% sodium dodecylsulfate (SDS). Substrates were prepared with patterns of hydrophilic silicon oxide squares against a hydrophobic background. The hydrophobic background consists of a self-assembled monolayer (SAM) of dodecanethiol molecules on gold. Substrate fabrication begins with a silicon wafer on which a 400nm thick silicon oxide layer is thermally grown. Then a 10/20nm layer of TiW/Au is sputtered and patterned by photolithography, and a lift-off process is used to expose the hydrophilic silicon oxide patterns. It is cleaned by two minutes of oxygen plasma, followed by a soaking of at least twenty-four hours in 1mM ethanolic dodecanethiol solution to make the Au background hydrophobic.

After fabrication, the substrates were diced into rectangular chips with approximate dimensions of 4.5mm by 10mm. Each substrate contained patterns of hydrophilic squares. Some substrates contained a mixture of squares ranging in length from 3 to 20 μ m, while others contained arrays of homogeneous squares of either 20, 40, 80 or 160 μ m in length.

For each deposition process, a patterned substrate is removed from the SAM solution and then rinsed with pure ethanol, acetone, and isopropyl alcohol (in that order). The substrate is blown dry by a stream of nitrogen. It is then mounted into a fixture and held at a 40° (+/- 3°) angle above a bath of deionized water (Figure 2a). Using a micropipette, approximately 40 μ L of colloid is applied to the substrate surface. The continuous drop of colloid covers approximately 20mm² of the sample surface (Figure 2b). With colloid applied, the bath is slowly raised until the water contacts the bottom edge of the substrate and colloid. Fluid flow results, drawing most of the colloid into the bath, leaving only the hydrophilic patterns wetted. The remaining colloid liquid evaporates leaving self-assembled, two-dimensional arrays of spheres centered in the hydrophilic patterns (Figure 2c).

This process was captured with a digital camera capable of 1000 frames per second (fps), mounted on a 20 times optical microscope. The field of view was approximately 600 μ m in diameter. The camera settings for most of the images in this paper were taken at 500 fps with a shutter speed of $1/500$ second.

Results and Discussion

Two-dimensional array formation was observed to occur in three key steps. Initially, contact between the bathwater and substrate/colloid/air interface draws the colloid into the bath. The receding three-phase contact line of the colloid moves across the patterned substrate (Figure 3). Second, the moving contact line reaches the interface of a hydrophilic square and pins strongly at the pattern edge (Figure 3a). While remaining pinned, the main body of colloid moves past the square, necks, and separates, depositing a thin film of colloid onto the square (Figure 3b). The liquid film contains a single layer of colloidal spheres. The droplet shape of the pinned colloid naturally centers the spheres in the pattern (Figure 3c). In the final step, as the

colloidal liquid evaporates, thin film capillary forces ensure that a tightly packed two-dimensional array is formed (Figure 4).

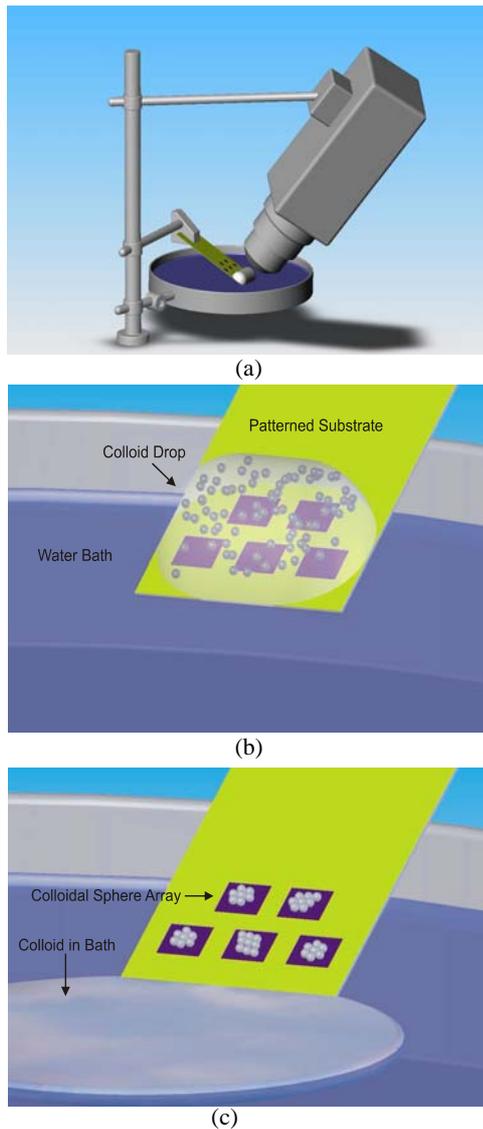


Figure 2. Illustrations of (a) the experimental setup including a substrate, D.I. water bath, and high-speed camera coupled with a microscope lens; (b) a closeup of a substrate with colloid applied; and (c) patterned arrays of colloidal spheres after colloid is drawn into the bath.

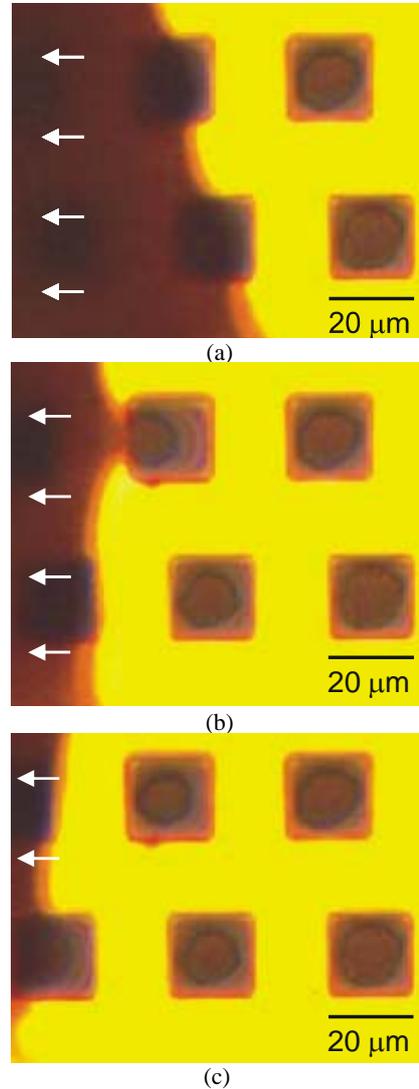


Figure 3. Two-dimensional arrays of $1\mu\text{m}$ polystyrene spheres form on $20\mu\text{m}$ square patterns as the colloid contact line sweeps over the patterns. Arrows indicate the direction of colloid travel: (a) the contact line pins at the hydrophobic-hydrophilic boundary of several squares; (b) 8ms later necking occurs between one of the squares and the main body of colloid; (c) 4ms later the colloid has separated and the two-dimensional array has moved toward the center of the square.

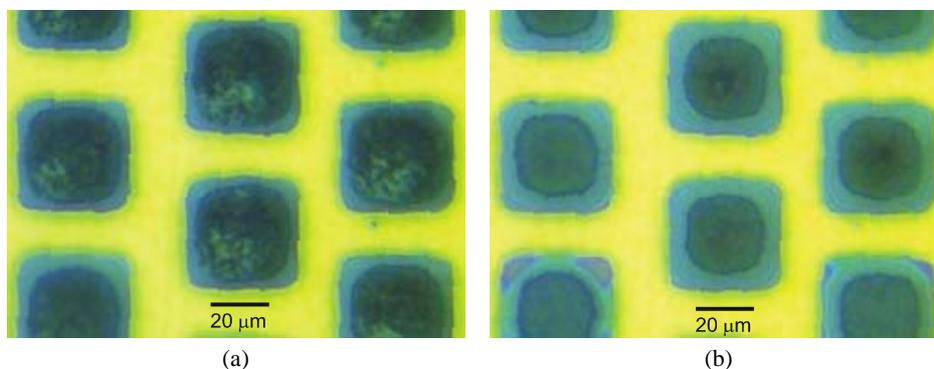


Figure 4. (a) loosely packed two-dimensional arrays of $1\mu\text{m}$ diameter polystyrene spheres immediately after deposition on $40\mu\text{m}$ squares; (b) 1.4 seconds later, capillary forces have tightly packed the arrays as evaporation tightens the water film around them.

The initial step of this process occurs when the main body of colloid is drawn off the substrate providing a moving three-phase contact line. The water bath method used to draw the colloid off the substrate was chosen because it is relatively simple and provides consistent results. The resulting contact line velocity for both the 290nm and $1\mu\text{m}$ colloids was found to be on the order of 1 cm/s .

Examination of the high-speed video reveals a region of densely packed polystyrene spheres that extends from the moving contact line into the main body of colloid. The spheres travel very close to the contact line. Photographic frames taken with an increased camera shutter speed of $1/5000$ second verify that the $1\mu\text{m}$ colloidal spheres travel within $1\mu\text{m}$ of the contact line.

As the main body of colloid moves across the hydrophobic background, various factors influence colloidal sphere movement in the plane of the substrate surface. Liquid forces arising from viscosity and potential interactions with the liquid surface will influence spheres to move in the direction of liquid movement. Inertia resists change in the spheres movement. Gravity exerts a constant pull due to the 40° tilt of the substrate. Potential adhesion and friction forces between the spheres and substrate impede sphere movement. Because the spheres remain in the moving colloid, it is reasonable to assume that the dominant forces on the spheres are those that act in the direction of liquid movement. This indicates that some combination of the liquid viscous and surface tension forces dominate. The Reynolds number of micro/nanospheres in the moving colloid and a comparison of the known forces supports this [8].

The second step of the array formation process occurs when the colloid contact line reaches the leading edge of a square and pins at the hydrophobic-hydrophilic substrate junction. The pinning can be attributed to the heterogeneity at the pattern edge where the SAM/Au surface takes a 30nm step down to the SiO_2 surface [9]. As the colloid continues to move past the square, visible interference fringes from the colloid liquid reveal these pin lines (Figure 3b). Each transition of the interference pattern from dark to light or vice versa corresponds to an approximately 100nm change in height [7]. Close examination of the width of each dark and light band reveals that the liquid surface between the pin line and spheres is concave (Figure 5a). The main body of colloid continues to move away from the square and the pinned

colloid necks and breaks off. Liquid surface tension pulls the deposited colloid onto the square, pinning at the pattern's perimeter and roughly centering the spheres in the square (Figure 3c, Figure 5b).

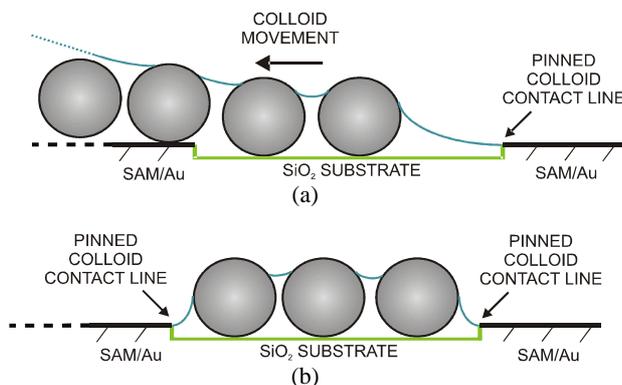


Figure 5. Cross sections of colloidal spheres and liquid as they are deposited on a hydrophilic square: (a) the main body of colloid pins at the pattern edge and stretches over the square (compare to the necking colloid in Figure 3b); (b) the spheres and liquid have been pulled into the pattern by liquid surface tension immediately after separation from the main body of colloid (Figure 3c).

The concave shape of the liquid surface between the pin line and spheres indicates that the spheres are hydrophilic. A “floating” contact angle measurement as described by Lubarsky et al. [10] of the colloidal liquid contact angle on the polystyrene spheres at the air/liquid interface verifies this. The measurement was made by observing spheres at the liquid/vapor interface through a microscope. Because particles with such small Bond numbers do not disturb the liquid surface (i.e. the fluid/vapor interface is flat), the proportion of the sphere that protrudes from the liquid is directly related to the contact angle. The measured contact angle was 73° , in agreement with typical values found in the literature.

In the final step, as the colloid liquid evaporates, the arrays become tightly packed. This phenomenon is attributable to lateral immersion capillary forces as described by Kralchevsky and Nagayama [11]. For submillimeter particles, the hydrostatic pressure contribution to the lateral capillary force is insignificant compared to the interfacial tension contribution. Figure 6 illustrates how the net surface tension along the three phase contact line will influence the arrays to pack and center themselves in the hydrophilic patterns. Due to the curvature of the liquid surface between the pattern edge and spheres, calculation of the lateral force is non-trivial and beyond the scope of this paper.

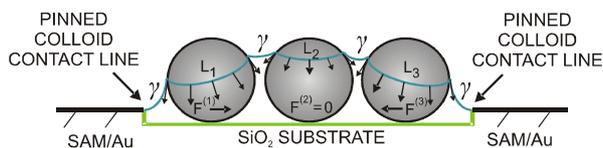


Figure 6. Lateral immersion capillary forces arise from the integral of the surface tension γ along the contact line L_k of the spheres.

It is important to note that when the length of the patterned square became too large in relation to the sphere diameter, three-dimensional arrays were observed to form. For the 290nm colloid, 10 μ m length squares contained two-dimensional arrays while 15 μ m squares (and larger) contained three-dimensional arrays. For the 1 μ m colloid, three-dimensional arrays began to occur on the 40 μ m length squares and always occurred on the 80 μ m and 160 μ m squares.

Conclusions and Future Work

A novel method of patterning two-dimensional arrays of micron and sub-micron colloidal particles was presented. Preliminary modeling and key stages of the self-assembly process were introduced. High-speed photography was shown to be an effective method for observing colloidal sphere deposition and array formation on micro-patterns. Because this array formation process is largely dependent on the liquid interaction with the spheres and substrate, it should be applicable to a wide variety of colloidal particles, pattern shapes, and substrates. Work is currently underway to characterize the effect of altering the colloidal liquid surface tension on particle deposition. Future work is planned to determine the size range of colloidal particles to which this process is applicable.

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