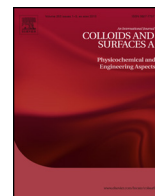




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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

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## Statistical characterization of self-assembled colloidal crystals by single-step vertical deposition



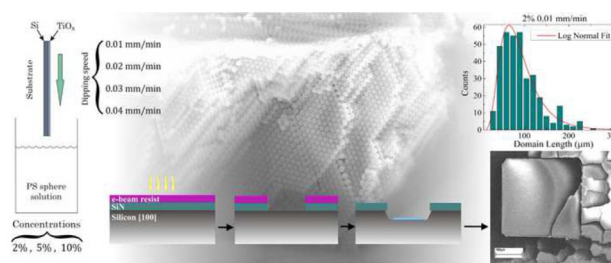
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### HIGHLIGHTS

- Multilayer polystyrene colloidal crystals are formed by one vertical deposition step.
- Domain sizes are characterized as a function of dip speed and solution concentration.
- Variations in domain sizes are found to follow a log-normal distribution.
- Lithographically assisted assembly is used to control lateral domain size.
- Minimum domain size is significantly increased and size variations are suppressed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We have statistically characterized the self-assembly of multi-layer polystyrene colloidal crystals, using the technique of vertical deposition, with parameters chosen to produce thick layers of self-assembled crystals in one deposition step. The size distribution of domains produced with this technique was seen to follow a log-normal distribution, hinting that aggregation or fragmentation phenomena play a role. In addition, using a lithographically directed self-assembly method, we have shown that the size of multi-layer, continuous crack-free domains in lithographically defined areas can be many times larger than in the surrounding areas. In a single deposition step, we have produced continuous colloidal crystal films of 260 nm diameter polystyrene spheres approximately 30–40 layers thick, with a controllable lateral size of 80–100  $\mu\text{m}$  without lithography, and as high as 250  $\mu\text{m}$  with the lithographic template. This method allows us to suppress the domain size fluctuations and produces mesoscopically thick colloidal crystals of selected size at a selected location.

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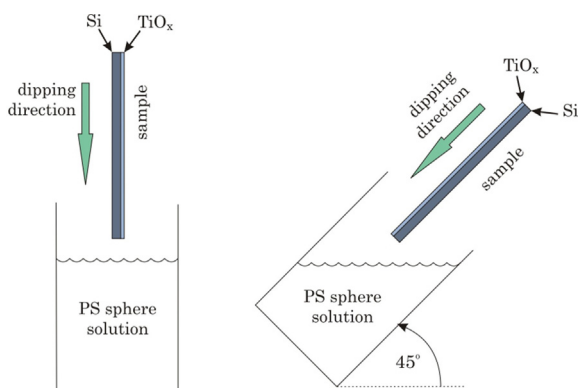
## 1. Introduction

Colloidal crystallization of mono-disperse spherical sub-micron particles has been used successfully in the fabrication of three-dimensional (3-D) photonic crystals [1,2] for a wide variety of applications [3]. These artificial opals, as they are commonly known, can also exhibit an acoustic or a phononic band gap, whose frequency depends on the particle diameter. While the properties

of 3-D phononic crystals have recently been studied by various groups in the millimeter and micrometer scale at acoustic frequencies [4–6], much less work has been performed on 3-D hyper-sonic phononic crystals with 100 nm scale dimensions, which produce phononic band gaps in the GHz range [7]. This frequency range is even relevant for thermal properties, as the dominant thermal phonons at low temperatures below 1 K have frequencies in that same range. One possibility for GHz 3-D phononic crystal fabrication is therefore the use of polystyrene (PS) nano-spheres of  $\sim 100$  nm size range, as they are commercially available as colloidal suspensions. As demonstrated before [1,8–10], these particles can be self-assembled into crystals from suspensions, allowing a

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**Fig. 1.** Schematics of the dipping setups are shown.  $\text{TiO}_x$  coated substrates were dipped vertically and also at a  $45^\circ$  angle.

convenient bottom-up assembly of a GHz phononic crystal with possible applications in thermal management [11] or phononic waveguiding [12].

Common methods for self-assembly of colloidal particles include gravitational sedimentation, capillary assembly and vertical deposition [13]. Typically, closed-packed lattices (face-centered cubic, hexagonal closed packed, or a random combination of the two) are produced in each of these methods, with face-centered cubic being more common. Here, we use the vertical deposition method for producing large area, thick 3-D closed packed lattices using colloidal suspensions of PS nanospheres. This technique in its simplest form has been documented in the literature [1,8–10] quite extensively. We concentrate on increasing the lateral crystal domain size for the crystals and characterize the domain size results statistically, as a function of dipping speed and nanosphere concentration. The domain sizes are found to follow a log-normal distribution, a fact that to our knowledge has not been reported before for colloidal crystals.

We also combine the vertical deposition with lithographically patterned and etched substrates, not to control the crystal structure itself as has been suggested often before [14–17], but to increase the size of single crystalline domains and to reduce cracking. In contrast, most other lithography directed methods are typically monolayer [15–17] or few-layer [18,19] techniques. These have the drawbacks of multiple process steps and lengthy fabrication time, if thicker crystals are required. Some initial work on vertical deposition of colloidal crystals in deeper trenches was presented in [20].

## 2. Materials and methods

Samples were coated with a solution of PS nanospheres using vertical deposition [1] and the resulting crystals were characterized by scanning electron microscopy (SEM). All substrates used in the experiments were either oxidized or nitridized silicon chips with dimensions of approximately  $8\text{ mm} \times 16\text{ mm}$ , and coated with a layer of titanium oxide ( $\text{TiO}_x$ ) approximately 10 nm thick on the surface. A titanium coating was first applied by electron-beam evaporation in an UHV chamber with a pressure  $10^{-8}$  mbar, and the resulting film was then oxidized in a vacuum chamber at 100 mbar of oxygen pressure for 2 min. The  $\text{TiO}_x$  provided a hydrophilic surface for improved wetting by the nanosphere solution [21].

A schematic of the dipping setup is shown in Fig. 1.

Samples without lithographically patterned surfaces were submerged into and withdrawn from solutions with concentrations of 0.02%, 0.2%, 2%, 5% and 10%. The original solution of 10% concentration, purchased from Duke Scientific, was diluted with de-ionized water to produce the lower concentrations. Each concentration was

tested at withdrawal speeds from 0.01 mm/min up to 0.04 mm/min. It is well known that self-assembly by vertical deposition, like evaporative deposition, is dominated by fluid dynamics at the meniscus [22–25]. Consistent with that, we also determined that the speed of withdrawal from the solution was the dominant factor in self-assembly and thus, a higher speed could be used for submersion in order to reduce total dipping time. In addition to vertical dipping, some experiments were performed at a  $45^\circ$  angle for select combinations of dipping speed and solution concentration.

Lithographically assisted self-assembly was investigated with patterned surfaces made by a two-step electron-beam lithography technique, shown schematically in Fig. 2. Samples were fabricated by first etching troughs into silicon substrates, using the overlay  $\text{SiN}_x$  layer (750 nm) as an etch mask. The nitride mask was defined by etching it reactively in  $\text{CF}_4$  or  $\text{CHF}_3$  plasma (for  $\text{CHF}_3$ , we typically had to etch for 20 min with parameters 100 W, 55 mTorr). The troughs with sidewalls angled at  $54.74^\circ$  were produced by wet chemical etching in potassium hydroxide (KOH) at  $90^\circ\text{C}$ . The depth of the troughs were varied from a few  $\mu\text{m}$  up to nearly  $100\ \mu\text{m}$ . These troughs were then selectively coated with a hydrophilic  $\text{TiO}_x$  layer by a second e-beam lithography step with lift-off aligned with the previous pattern, which produced  $\text{TiO}_x$  coating only at the bottom of the troughs.

## 3. Results

### 3.1. Deposition characteristics on flat surfaces

The fabricated crystals typically consisted of a set of domains, separated by cracks produced by the drying process. Domain size data were collected by taking several SEM images from each sample, and using the SEM scale bar as a calibration length. All measurements take into account the direction of dipping, where measurements taken along the dipping direction were defined as vertical lengths, while those which are perpendicular were defined as horizontal.

A total of 2398 measurement pairs (horizontal and vertical lengths) were collected from over 50 SEM images to produce the statistical data in this report. Representative SEM measurement images for three dipping speeds at three concentrations are shown in Fig. 3. The image for each combination of dipping speed and concentration is marked with its respective average vertical domain length. A typical top view of a colloidal crystal structure is shown in Fig. 4 (left) with its respective Fourier transformed k-space image shown in the inset. A clear hexagonal symmetry is seen in both the real space and k-space data. Also shown in Fig. 4 (right), is a side-view close up of a thick multi-layer colloidal crystal displaying the 3-D structure. The 3-D structure typically seen in these images was face-centered cubic. Large data sets were collected from each sample in order to improve statistics and reduce the inherent inaccuracies of the measurement method. From the scatter plots of vertical vs. horizontal length, we always saw a distribution of domain sizes for all speeds and solution concentrations.

The plain, unpatterned samples dipped into solutions of 0.02% and 0.2% concentration did not produce any crystalline order even at the lowest dipping speeds and thus, no data is shown for these concentrations. For the higher concentrations crystalline domains always formed, and an example of the scatter plot of domain size measurement results for 2%, 5% and 10% solutions dipped at 0.02 mm/min is shown in Fig. 5(a). From these, a clear trend can be seen with increasing concentration. While there is a trend toward larger average domains with increasing concentration, the size distribution also increases. This variability in domain size becomes quite large, as seen in the data for 10% concentration, where the vertical domain size varies from a few tens of  $\mu\text{m}$  up to approximately

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