Epitaxial Crystal Growth of Colloids with Short Range Attraction

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Abstract:

This study modeled epitaxial crystal growth of atomic structures using PMMA colloids with depletant polymer. The suspension was sedimented onto square lattice templates to simulate substrate surfaces. Different types of substrates were modeled by using templates of varying lattice constants. Analysis showed that the templates force square packing instead of hexagonal close pack (hcp). However, the effect can be diminished if the lattice constant is larger than the natural packing distance of the colloids. Square templates with Gaussian noise were also fabricated and preliminary results have shown forced square packing, but not at the same magnitude as non-noisy lattices.

Introduction:

When performing epitaxial growth of atoms, it is advantageous to control the morphology of film growth as much as possible. While it is difficult to perform experimentation upon actual atoms due to their size and high kinetic energy, atomic behavior can be mimicked using colloidal particles. Their ability to self-assemble and, in the presence of depletant polymer, crystallize in an atomic matter makes colloids an ideal candidate for experimentation. This study capitalized upon colloids' ability to exhibit such behavior.

Experiment:

Micropatterned templates were fabricated using plasma-cleaned coverslides that were coated with PMMA, anti-reflective coating (ARC), and photoresist (PR). Using photolithography methods, arrays of 1 μm circles with three different lattice constants (l.c.) (1.212μm, 1.362 μm, 1.412 μm) were projected onto the PR of the glass slide. The PR was then developed away, exposing regions of ARC and PMMA, which were then etched off using oxygen plasma. Finally, the PR was removed, leaving a pattern of holes in a layer of pure PMMA. An identical procedure was carried out upon another set of coverslides that were instead patterned with a square lattice that contained program-generated random Gaussian noise.

PMMA particles averaging 0.9 μm in diameter were stained using a rhodamine solution. These particles were then experimentally density mismatched until the particles experienced Brownian motion while in freefall. Polystyerene polymer was also added to the solution. When the PMMA particles were closer than the radius of gyration of the polymer, the osmotic pressure around the two colloids becomes unbalanced, causing a net attractive force between them. This phenomenon is described by:

$$U_{dep} = \begin{cases} +\infty & \text{for } r \le \sigma \\ -\Pi_p V_{overlap} & \text{for } \sigma < r \le \sigma + 2r_g \\ 0 & \text{for } r > \sigma + 2r_g \end{cases}$$

where U_{dep} is the depletant potential, σ is the diameter of the particle, and Π_p is the osmotic pressure of the polymer. $V_{overlap}$ is the volume of the overlapping depletion zones between particles at a separation. Confocal microscopy was then used to observe the dynamically changing system while the PMMA particles sedimented onto the templates.

The sedimentation container consisted of a coverslide with a micropipette tube glued to the slide using a combination of UV glue and epoxy. The density mismatched particles were then inserted. Samples were analyzed using confocal microscopy two days after dispersion of colloids into the container. Using confocal

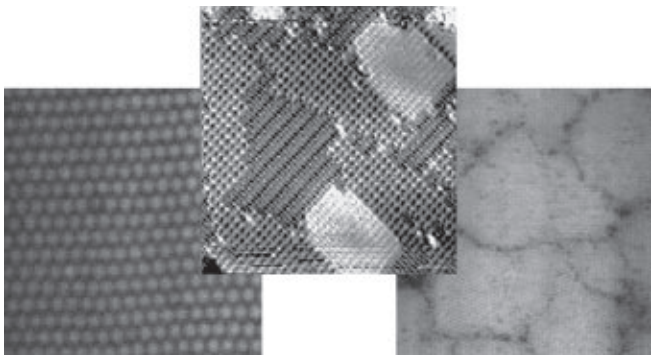

Figure 1: [L-R] Colloids without depletant exhibiting hexagonal close packing (hcp); Island-like growth of oxygen and nitrogen in epitaxial growth; Island-like growth of colloids after depletant effect.

microscopy, the samples were scanned both in the horizontal and vertical direction to locate sites of crystal growth.

After these sites were located, particle tracking was performed and the pair correlation function, g(r), was calculated. G(r) is the normalized probability of finding a particle a radial distance away from another particle. The form of the g(r) contains information describing the structure of the ordered phase.

Results & Discussion:

Sedimentation upon 1.412 μm Lattice Constant Template: G(r)s for colloidal sedimentation upon a flat surface showed that packing was hcp while colloidal sedimentation upon the 1.412 μm template was square. This order was shown to persist through at least two layers. Further analysis of the pair correlation functions showed that the peaks were consistent with predicted radial values for a square lattice with 1.412 μm spacing. However it was visually observed that the affect of the template diminished as the confocal microscope scanned through z at sites of crystal growth. 1.412 μm lattice spacing is larger than the natural packing distance of the PMMA particles and as layers of particles sediment above the template, the structure began to revert back to hexagonal close-packing.

Sedimentation upon 1.212 μm Lattice Constant Template: The 1.212 μm template also showed that the colloids were conforming to the square lattice. The 1.212 μm template, however, showed no signs of lost ordering when visually observed using confocal microscopy. This would seem to indicate that a spacing of 1.212 μm is closer to the natural packing distance of PMMA particles than 1.412 μm.

Sedimentation upon Noisy Lattice: The noisy lattice was created by adding random Gaussian noise to the original 1.362 μm square lattice. First layer g(r)s showed similar ordering to non-noisy lattices. Since the noise added was subtle, this was not unexpected. However, in the second layer the subtle stacking disorder of the colloids began to propagate resulting in a g(r) graph that showed that while square packing was evident, it was not as ordered as the standard square lattices. This demonstrates that even a substrate surface with minor variations can have an impact on developing film layers.

Future Work:

While this project has begun to simulate the possible effects of the substrate surface on epitaxial growth, the picture is not yet complete. Further experiments need to be done investigating the effects of the noisy lattices as these more accurately model a realistic substrate. Further work will also be done to see at what level the disorder diminishes in noisy lattices and, as in the case of the 1.412 μm lattice, a lattice with a large lattice constant.

Acknowledgements:

I would like to thank my Principal Investigator Itai Cohen and mentor Sharon Gerbode for being interactive, supportive and knowledgeable advisors. I would also like to thank the Cohen lab and CNF staff along with Jalina Keeling for density mismatching the PMMA particles used in this experiment. Finally, many thanks to the Intel Foundation and the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program.

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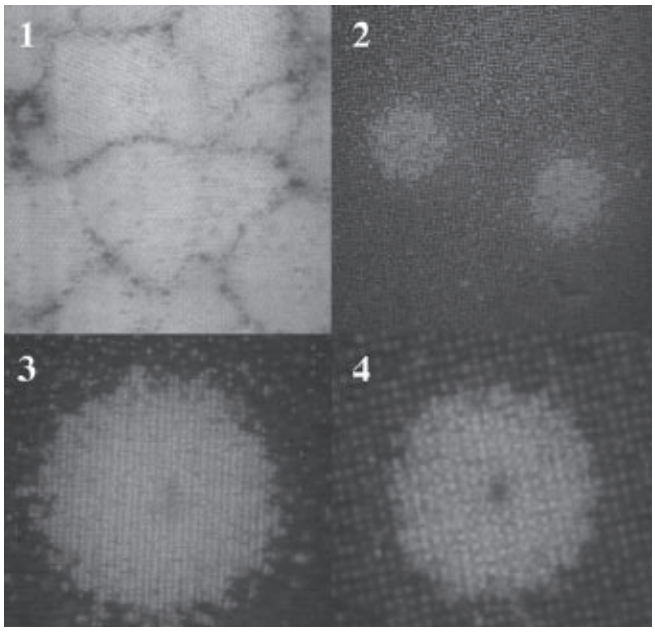

Figure 2: Colloidal sedimentation: 1) Smooth wall, 2) 1.212 µm l.c., 3) 1.412 µm l.c., 4) Random lattice based on 1.362 µm template.

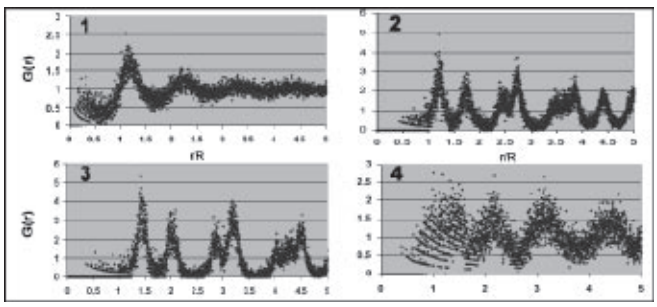

Figure 3: 1) G(r) for sedimentation on a smooth wall, 2) G(r) for 1.212 µm lattice, 3) G(r) for 1.412 µm lattice, 4) G(r) for noisy template.