Two-dimensional Micro- and Nanoparticle Monolayer Films

Carlos A. Silvera Batista and Ilona Kretzschmar (Faculty Mentor)
Chemical Engineering Department
The City College of New York
New York, USA
csilver00@ccny.cuny.edu
kretzschmar@ccny.cuny.edu

***Abstract* —** *Close-packed particle monolayer films are interesting precursors for many applications such as sensors, catalyst carrying templates for membranes, and can even be employed as shadow masks.*
This project aims to determine the optimum volume-fraction required for the formation of large-area, self-assembled micro- and nanoparticle monolayers in a cylindrical crystallization cell under constant humidity. The results show that large-area particle monolayers can be obtained for particle volume fractions of 0.0020, but that the cylindrical cell setup is limited with respect to the range of applicable volume fractions and control over the speed of the receding meniscus.

I. INTRODUCTION

The inherent challenge in the formation of particle monolayers is to find conditions under which the formation of multilayer domains, voids, and point defects is suppressed. Among the techniques available, convective self-assembly is of special interest because of its simplicity and reported ability to fabricate large areas of close-packed monolayers [1]. As indicated by Deegan et al. [2], the driving force for the self-assembly of particles is the convective fluid flow resulting from the evaporation of the solvent from the particle solution. Dushkin et al. [3] report that the most influential factors required to get large areas of particle monolayers without defects are the solvent evaporation rate, the concentration of particles in the solution (volume fraction), the particle size distribution, and the contour of the contact line.

In this paper we report our experimental findings on the convective assembly of 2.4 μm diameter particle monolayers in a cylindrical crystallization cell and the influence of the particle volume fraction on the monolayer quality.

II. MATERIALS AND METHODS

Solutions of 2.4 μm sulfonated polystyrene particles (PS) from IDC (USA) are used for the experiments. The working solutions are prepared based on the number of particles needed to cover 100, 75, 50, and 25% of the available substrate surface in the hypothetical case of complete monolayer formation with hexagonal close packing. The cell load is the amount of solvent placed in the cell (20, 25, and 30 μl). A total of ten solutions with volume fractions from 0.0038 to 0.0008 are studied (Table 1). The substrate is a single-crystal silicon wafer with a natural oxide layer. Prior to an experiment, the substrate is submerged in a sulfuric acid-Nocromix mix (components purchased from Fisher) for one hour and thoroughly rinsed with di-ionized water.

	Theoretical Substrate Area Covered by Particles			
Cell Load	100%	75%	50%	25%
30μl	0.0034	**0.0025**	**0.0017**	0.0008
25μl	0.0041	**0.0031**	**0.0020**	0.0010
20μl	0.0051	0.0038		

Table 1: Volume fractions of solutions.

The crystallization cell consists of a Teflon ring, a glass slide that protects the substrate, and two clamps that press the ring onto the substrate to prevent leaking. The Teflon ring with an inner diameter of 1 cm is used to create a concave meniscus profile during the assembly process. The cell is placed in a chamber with a constant nitrogen flow providing a relative humidity of (14 ± 1) %. The nitrogen flow rate is low enough to prevent the disturbance of the gas-liquid interface during the assembly. The cell is loaded with the respective amounts of solution (Table 1) and left in the N_2 chamber until all solvent has evaporated.

III. RESULTS AND DISCUSSION

Optical inspection of the ten samples prepared from the solutions listed in Table 1 reveals that the films prepared from the 100% solutions (column 1, Table 1) show mutilayer domains while the 25% solutions (column 4) show loosely packed structures. The 20μl/75% solution forms large multilayer domains. Solutions with volume fractions between 0.0017 – 0.0031 show large-area monolayers. Scanning electron microscope (SEM) images reveal further details about the films obtained with the 50%/25μl, 75%/25μl, 50%/30μl, and 75%/30μl solutions (Figure 1).

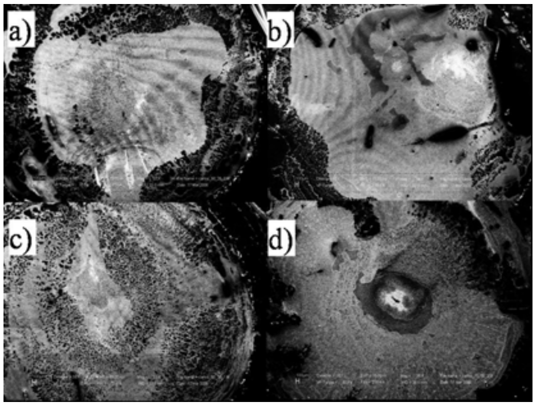

Figure 1: Scanning Electron Images at 34× of assembled crystals: a) 50%/25μl, b) 75%/25μl, c) 50%/30μl, and d) 75%/30μl.

Birefringence patterns are observed for the films obtained with the 50%/25μl and 75%/25μl solutions (stripped patterns in Figures 1a and b). Observation of birefringence is indicative of thin domains of hexagonal-packed particles. The pattern extends over areas as large as 45 mm^2. On the other hand, no birefringence is observed for the films formed with the 50%/30μl and 75%/30μl solutions pointing to less dense packing. High magnification SEM images of films from the 50%/25μl and 75%/25μl solutions show that the 50%/25μl crystal is indeed a compact monolayer, while the 75%/25μl film has small areas of bilayers (Figure 2). However, note the 50%/25μl monolayer still has voids and grain boundaries.

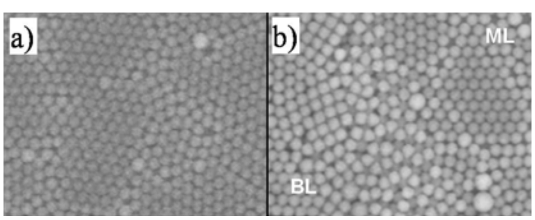

Figure 2: High magnification SEM images in variable pressure mode: a) 50%/25μl and b) 75%/25μl. ML = monolayer, BL = bilayer.

In results presented by Velev [4], close-packed monolayers were obtained using a set-up that allows pulling a volume of the working solution at a specific speed, which is equivalent to the speed with which the meniscus recedes in our crystallization cell. They find that for each volume fraction there are specific pulling speeds at which the particles assemble into monolayers, bilayers, multilayers, or submonolayers. As a result, they developed an operational phase diagram for their set up. Using their phase diagram, we can assess the limitations of our set up: (i) limited control of the speed of the receding meniscus and (ii) narrow range of volume fractions that can be explore. The fact that some samples present monolayers and multilayers simultaneously is a consequence of the quite low volume fractions used in our experiments. However, our crystallization cell is much simpler than the set-up used in [4], and further exploration of the assembly of nanoparticles (i.e., small volumes) is warranted.

IV. Conclusion

Large domains of particle monolayers are obtained with the cylindrical crystallization cell. The 0.0020 volume fraction solution results in the largest domains of close-packed monolayers. Although the particle monolayers are usable for further experiments, it is still desirable to reduce the number of grain boundaries and voids even more.

Acknowledgments

We are grateful for the continuous support received from the NYC-LSAMP program, the generous CCNY start up funds, and CCNY travel support.

References

[1] X. M. Lin, H. M. Jaeger, C. M. Sorensen, K. J. Klabunde. Formation of Long-Range-Ordered Nanocrystal Superlattices on Silicon Nitride Substrates. J. Phys. Chem. B 105: 3353-3357, 2001.

[2] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten. Capillary Flow as the cause of ring stains from dried liquid drops. Nature 389: 827-829, 1997.

[3] C. D Dushkin, G. S Lazarov, S. N Kotsev, H.Yoshimura and K. Nagayama. Effect of growth conditions on the structure of two-dimensional latex crystals: experiment. Colloid Polym. Sci., 277: 914 – 930, 1999.

[4] B. G. Prevo and O. D. Velev. Controlled, rapid deposition of structure coatings from micro- and nanoparticle suspension. Langmuir 20: 2099-2107, 2004.