

Defects in Self Assembled Colloidal Crystals

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Abstract — Colloidal self assembly is an efficient method for making 3-D ordered nanostructures suitable for materials such as photonic crystals and macroporous solids for catalysis and sensor applications. Colloidal crystals grown by convective methods exhibit defects on two different scales. Macro defects such as cracks and void bands originate from the dynamics of meniscus motion during colloidal crystal growth while micro defects like vacancies, dislocations and stacking faults are indigenous to the colloidal crystalline structure. This paper analyses the crystallography and energetics of the microscopic defects from the point of view of classical thermodynamics and discusses the strategy for the control of the macroscopic defects through optimization of the liquid-vapor interface.

Index Terms—Colloidal self assembly, macroporous solids, photonic crystal, defects.

I. INTRODUCTION

COLLOIDS are particles of size 10-0.1 micrometers suspended in a fluid medium. They have been experimentally observed to form a homogenous crystal at a volume fraction 0.536. [1] These colloidal crystals have close-packed structure and theoretical considerations have shown that the stable structure is the FCC structure. Colloidal crystals exhibit interesting optical properties like photonic bandgap. Yablonovitch first suggested that it is possible to localize light in a material that has a periodically modulating dielectric constant. [2] These ordered structures have a photonic bandgap (PBG) which prevents light of certain frequency from propagating through the material. Monodispersed colloids will assemble themselves into the FCC crystal structure under the right conditions. This natural process of self assembly makes colloidal crystal an attractive method of fabricating

large scale ordered nanostructures, useful as templates for subsequent infiltration into 3-d photonic crystal structures, for nanosphere lithography [3,4], and as templates for other interesting porous media applications [5]

It is important to understand defect formation and control in self assembled colloidal crystals in order to fully harness the engineering potential of these materials. In this work, colloidal crystals are grown by immersing a substrate into a colloid solution and the colloid solution is allowed to dry by evaporation. At the meniscus region, the self assembly process occurs and forms the colloidal crystal. The conditions at this region are very important in determining the quality of the colloidal crystal grown.

There are 2 boundaries at the meniscus region, namely the liquid-vapor interface and the substrate [Fig. 1]. They have different characteristics and consequently, will have different effects. The substrate is rigid and most likely charged. One obvious requirement is that it must be smooth, at least on the order of the dimension of the colloid. The conditions of the substrate affect the process of self-assembly profoundly. Work will be done to investigate the effects and optimized them for better defect control. The liquid-vapor interface is very much different from the substrate. It is deformable and moves as the fluid evaporates. Capillary forces are the main type of forces responsible for agglomerating the colloids together into the FCC structure. Earlier theoretical work by others [6] has shown that the capillary forces acting on the colloids can be either attractive or repulsive depending on the colloids. In this initial stage, most of our work has been concentrated on the effect of the meniscus.

Defects that are observed in colloidal crystals are classified under two categories, macro and micro. Macro defects are growth bands and cracks. Micro defects include vacancies and stacking faults. The origin of these defects will be discussed.

Manuscript received November 18, 2004. This work was supported in part by the Singapore-MIT Alliance.

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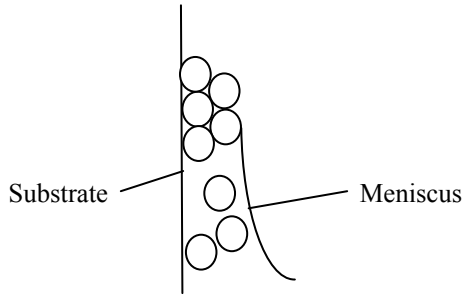


Fig. 1 Schematic of the self assembly process at the meniscus region.

II. EXPERIMENTAL PROCEDURE

A. Colloids

The colloids used in the experiment are polystyrene (PS) nanospheres dispersed in water. They are made in our lab by emulsion polymerization. A particle sizer (Brookhaven Zetaplus) is used to characterize their size and polydispersity. The size of the colloids is 295nm and the polydispersity is 8%. Measurement under FE-SEM confirms the size as 287nm. [Fig. 2] The discrepancy is due to the double layer of water around the colloids which the particle sizer cannot resolve.

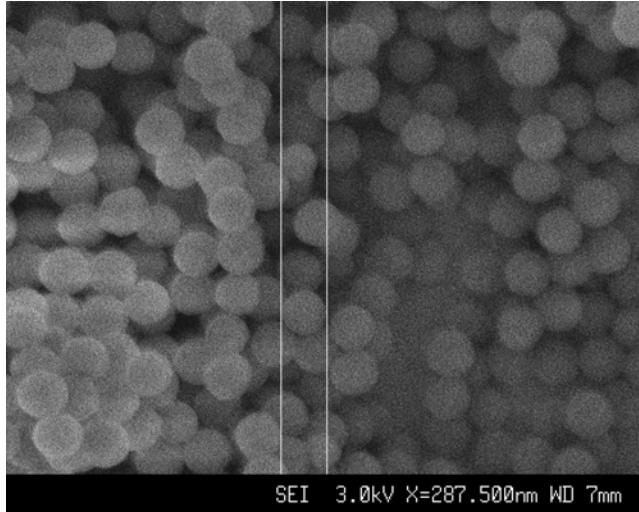


Fig. 2 FE-SEM image to show the measurement of the colloid size. It can be seen that the PS nanospheres are uniform in shape and sizes.

B. Vertical deposition

The vertical deposition process is developed by Dimitrov et al. [7] For this experiment, it is carried out in an oven at a temperature of 60°C. At this temperature, the colloids dry up completely after 2 days. A slow evaporation is preferred as it gives enough time for the colloids to self assemble into their energetically stable FCC structure. There is no convection in the oven and so no disturbance of the meniscus is expected. Most of the

colloidal crystals are deposited on Si substrate.

III. RESULT AND DISCUSSION

A. Macroscopic defects

Growth bands are bands of colloidal crystals formed before the colloidal crystals becomes continuous. [Fig. 3] This has been reported in another paper by our group. [8] A “stick-slip” model is proposed to explain the mechanism of their formation. It is postulated that the meniscus undergoes a hysteresis process and “slip” down the substrate without deposition between the bands. This highlights the importance of understanding the interplay of forces that is taking place at the meniscus.

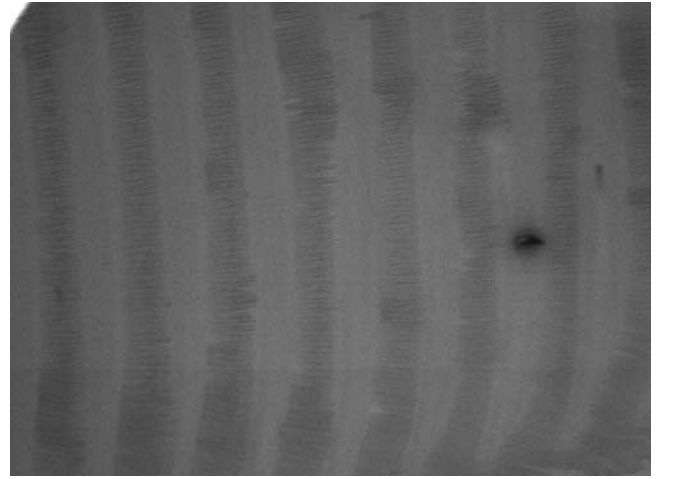


Fig. 3 Growth bands in as-deposited colloidal crystals.

Subsequent investigation on the effect of the liquid-vapor interface has confirmed its significance. This interface is characterized by the contact angle and the contact line. A simple model using the surface energy of the interfaces gives the Young’s equation for contact angle.

$$\cos \theta = \frac{\gamma_{SL} - \gamma_{SV}}{\gamma_{LV}}$$

where θ is the contact angle and γ are the surface energies for different interfaces.

In order to verify the effect of the contact angle, deposition is done on different materials like aluminum and silicon and the quality of the colloidal crystal is characterized under an optical microscope. The substrate is prepared by evaporating some Al on Si so that part of the Si is covered by the Al. Measurement of the contact angle in a sessile drop configuration has confirmed that there is a difference of around 30° in contact angle between Al and Si. Si, with higher surface energy, has a contact angle of

29° whereas Al has a contact angle of 61°. It is possible to do the vertical deposition in one step so there is no difference in the quality of the colloids.

The self-assembled colloidal crystals are observed under the optical microscope after the deposition. It is apparent that the crystal formed on the Al has more macroscopic defects than that on the Si. This helps to support that a major driving force for colloidal self assembly is by capillary forces. From the results, we can see that in order to have better colloidal crystals from deposition with capillary forces, a smaller contact angle is required. A possible explanation is that the smaller meniscus region restricts the number of layers of colloids that can form. Thinner colloidal crystals can cover larger areas. However, the contact angle cannot be too small as growth band may appear when the growth front slips. More work will be done on the contact angle dependence on other factors like colloid concentration, surfactant and ionic strength. By controlling the meniscus, it is possible to control some of the macroscopic defects.

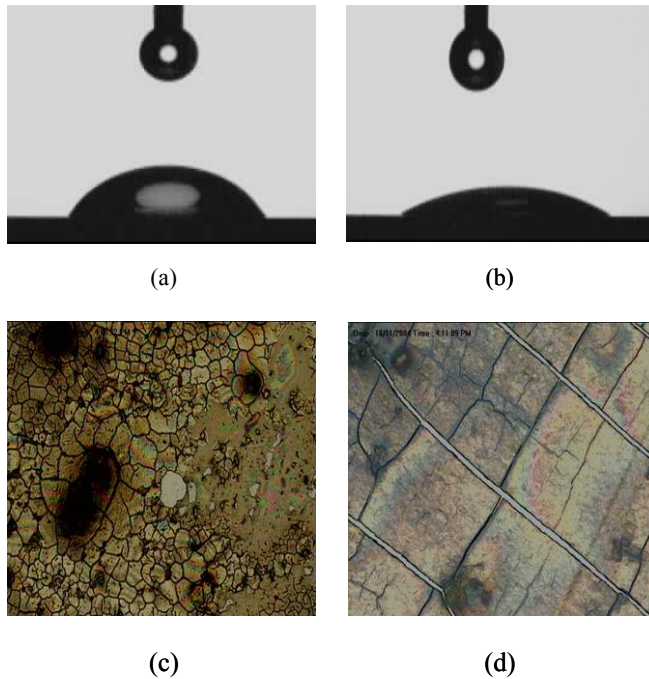


Fig. 4 (a), (c) on Al, (b), (d) on Si. Notice that the contact angle on Al is larger than on Si. (Al: 61°, Si: 29°) Magnification in (c) and (d) is 10x. The quality of the deposited film is very different. In some regions of the colloidal crystal, there seems to be some iridescence suggesting that the colloidal crystal has a PBG.

Other macroscopic like cracks can be seen in the optical microscope image. There are two possible explanations. Firstly, it can be due to thermal expansion mismatch between the substrate and the colloidal crystal film.

Another explanation is that the colloids have a thin layer of water (double layer) around them even after they have assembled. This corresponds to the secondary minimum in the energy predicted by the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid interaction. As the water dries completely, the separation between the colloids narrows and there is volume shrinkage. The thickness of double layer is controlled by the zeta potential of the colloids and can be reduced by either changing the charge of the colloids or the ionic concentration. However, the colloids will tend to agglomerate before they assemble if their zeta potential is too low.

B. Microscopic defects

The colloidal crystal on Si is viewed under the FE-SEM to look at their structure at the microscopic level. [Fig. 5] The close packed structure can be seen with the closest packed plane of FCC crystal, the (111) planes, being parallel to the substrate plane. Point defects such as vacancies can be seen in the SEM micrograph. This is expected as it is entropically favorable for the system to have some vacancies.

At a finite temperature, the colloids undergo random Brownian motion. When they have just assembled into the close packed structure, the double layer of water around them allow them to oscillate about their lattice position before they dry up totally and become mechanically bounded. Point defects can form at this period of mobility. In order to form vacancies or interstitial, there must be cooperative displacements among the packed colloids. In other words, the defect formation energies may be different with different colloids condition as the permissible displacement is related to the double layer thickness.

In classical materials, the concentration of the vacancies is associated with the vacancy formation energy and it is a strong function of temperature.

$$C_v = A_0 \exp\left(\frac{\Delta G_v}{kT}\right)$$

where C_v is the concentration of the vacancies, A_0 is a constant and ΔG_v is the driving force for vacancy formation.

The vacancy formation energy is related to how strongly the atoms are bounded to each other. In colloidal crystal, the permissible displacement will affect how strongly the colloids are bonded mechanically. Also, it is still unclear whether there is similarly strong temperature dependence in the colloidal crystal vacancies. Further work will be done to investigate the temperature effects. Temperature in the colloids also needs to be defined properly. Classically,

temperature is related to the average kinetic energy of the particles. In colloids as a model system, this is not just dependent on the temperature of the medium but also on other factors like size and viscosity. This has profound effect on the analysis of the energetics of the vacancies formation.

There seems to be an absence of interstitial defect. This may be due to the relatively uniform colloids. The colloids are generally spherical and the polydispersity is relatively low for significant amounts of small particle to go into the interstitials. Also, the interstitial sizes in the colloidal crystal are related to the double layer thickness around the colloids. If these are small compared to the colloids, there must be significant strain in the lattice to accommodate any self-interstitial defect. However, there may be “impurity” interstitial that are smaller colloids from the colloid synthesis process. This has not been observed in the colloidal crystal prepared. In the absence of interstitial defects, there is no way of annihilating the vacancies by recombining with interstitial like in classical materials. Thus, it appears that vacancies are indigenous in colloidal crystals.

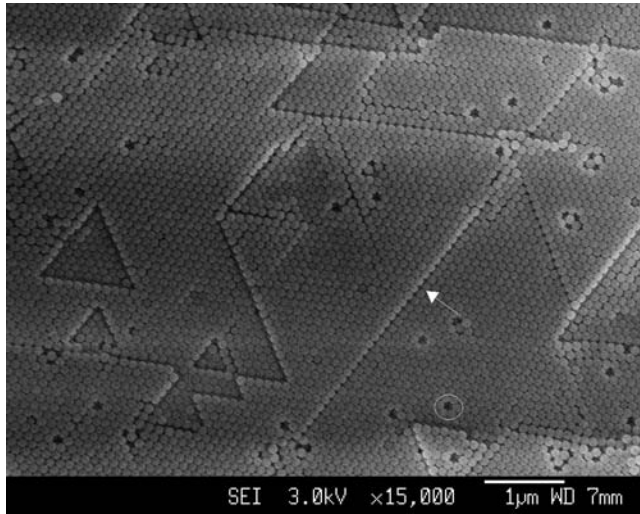


Fig. 5 FE-SEM image of the colloidal crystal on Si. The white circle marks a vacancy and the arrow points to a surface step.

In the FE-SEM, it is difficult to check for stacking faults. These defects are likely to exist in colloidal crystals as the energy difference between the HCP and FCC phase is very small. It is reported that the FCC crystal has a slightly lower energy than HCP crystal. [9] In vertical deposition, it may be more difficult to prevent the stacking faults due to the confined geometry. In some preliminary work, the stacking in the colloidal crystal has been checked by observing the packing pattern under the vacancies in different layers. [Fig. 6] More advanced characterization method will be explored to identify the stacking faults. Subsequently, it is possible to try to eliminate these

stacking faults by employing layer by layer method of deposition.

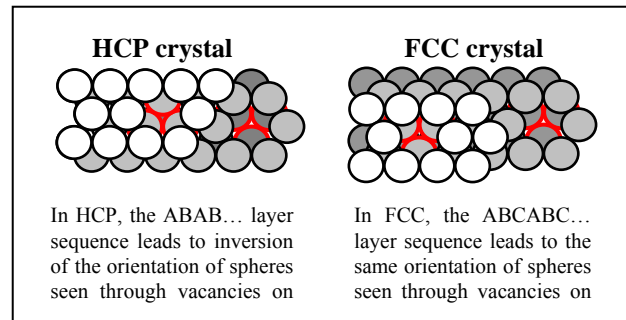
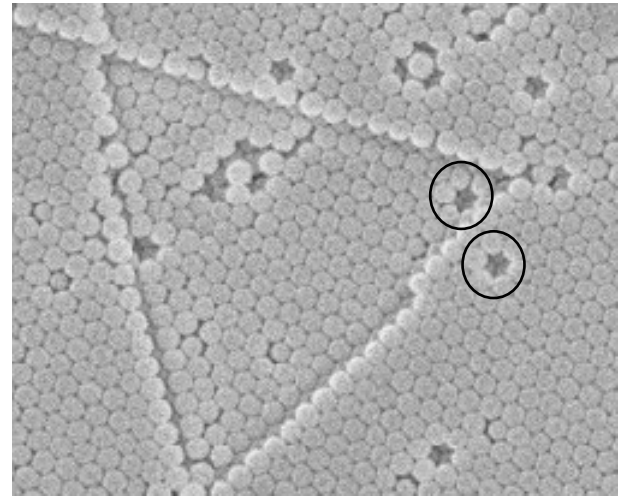


Fig. 6 The stacking in the colloidal crystal is checked by looking through the vacancies at different layers. The FE-SEM image at the top shows a colloidal crystal with FCC stacking.

The analysis so far suggests that certain microscopic defects like vacancies cannot be eliminated totally. In order for colloidal crystal to be useful as PBG materials, the effect of the defects on the PBG needs to be investigated. The presence of defects is not necessarily bad. In fact, application of PBG materials often requires carefully engineered defects in them as in semiconductors.

IV. CONCLUSION

Through the work so far, we have identified two classes of defects in colloidal crystals. This is important for PBG materials application as defect control is the key to achieving useful optical devices. Evidently, the understanding of the influence liquid-vapor interface will help to control the defects better. More advanced technique has to be developed to observe the meniscus fluctuations dynamically. The effect of the substrate will also be investigated. Modifications on the substrate like templating and applied fields will be implemented. Another issue worth investigating is the effect of the presence of the defects on the PBG. Certain defects may always be present

in the colloidal crystals. If the effect can be quantified, it is possible to get a threshold that future optical application can tolerate and ability to engineer the defects.

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