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**NANYANG
TECHNOLOGICAL
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GUIDED COLLOIDAL CRYSTALLIZATION

ERIC NG CHIN HONG

SINGAPORE-MIT ALLIANCE

2018

GUIDED COLLOIDAL CRYSTALLIZATION

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(B.ENG. (Hons), NTU)

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2018

DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

ERIC NG CHIN HONG
15 MARCH 2018

Abstract

The expanse of single crystallinity in two-dimensional colloidal crystal is limited by the difficulty to control its nucleation, leading to multi-domain growth, empty bands and voids. Using a straight nucleation line, this thesis demonstrates techniques to engineer preferential nucleation and in-plane growth of monolayer colloidal crystal in both convective-induced self-assembly and electric field assisted self-assembly. In convective driven self-assembly, a straight nucleation line is achieved by pinning the air-liquid-solid contact line along the edge of a straight surface relief. With evaporation, convective driven particle flux to the edge of surface relief enables the formation of a perfect nucleation seed, followed by subsequent in-plane growth to produce large area single domain of monolayer colloidal crystal. A model describing the criteria for successful meniscus pinning near the surface relief is proposed, with consideration of surface relief height. A similar surface relief with conductive coating is used in electric field assisted self-assembly, to attract particle accumulation and ordering by both Dielectrophoresis (DEP) and AC Electro-osmosis (ACEO) forces, respectively. Near the surface relief of an electrode, preferential particle adsorption and nucleation of colloidal arrays are achieved, giving rise to in-plane growth of monolayer colloidal crystal. In addition, by analysing DEP and ACEO using finite-element method, DEP is found to be crucial in the nucleation of colloidal crystal near the surface relief, preceding the growth driven by ACEO forces. Lastly, both convective-induced self-assembly and electric field assisted self-assembly using straight surface reliefs are compared in terms of crystal quality, processing advantages and limitations. In conclusion, both approaches enable $\langle 11 \rangle$ (or $\langle 10 \rangle$) crystal-packing

directions aligned next to the straight surface relief, leading to the success of guided colloidal crystallization.

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List of Common Abbreviations and Symbols

ACEO Alternating Current induced Electro-osmosis

DEP Dielectrophoresis

SEM Scanning Electron Microscope

PS Polystyrene

Chapter 1: Introduction

1.1 Background

Analogous to periodic arrangement of repeating sub-units of atoms or molecules in solid crystals, a colloidal crystal consists of an ordered array of colloidal particles [1]. Natural occurring examples can be found in gem opal [2], where amorphous silica spheres assume a periodic array of close-packed structures, appearing colourful by diffraction of incident light.

Due to its light diffracting nature, colloidal crystal made of particles with high refractive indices provide great potential in photonic devices [3-7]. Embedded photonic crystals in solar cells [4, 5] and sensors [7, 8] have been shown to offer enhancement in performance. Other than optical advantage, the periodic structure of submicron particles offers a versatile template of high surface area for catalytic reactions [9-11], fuel cells [12, 13], battery anodes [14, 15], absorbent [16] and biomedical devices [17-20]. Also, low cost and easily obtained three-dimensional colloidal crystals through bottom-up methods like convective driven self-assembly [21-23], electrophoretic deposition [24, 25], gravitational sedimentation [26-29], spin-coating [30] and pressure-driven assembly through physical confined flow cells [31, 32] have attracted tremendous applications throughout the research community.

Besides three-dimensional periodical structures, a single layer of colloidal crystal offers practical advantages as an economical mask template for micropatterning [33, 34], providing surface coating for plasmonic, bio- and chemical sensing, as well as the fabrication of microelectronic devices [35]. Most importantly, its periodicity can be manipulated with the right size of particles.

In two-dimensional self-assembly, evaporation-driven self-assembly, ranging from a ring formation of sessile droplets [36, 37] to colloidal crystal formation in thin wetting films [21, 23, 38] is attractive simply by convectively moving particles from the bulk suspension towards the contact line of air-liquid-solid interface. The accumulation of particles in this thin and confined wetting film will give rise to onset of nucleation [39], once the packing fraction reaches above 0.5 [40]. Despite the ease of fabrication, the grown colloidal crystal under the action of capillary forces suffers common non-idealities [21, 22, 37, 38, 41, 42] like restricted domain size, thickness non-uniformity, voids and empty bands. A detailed review is given in Chapter 2.

The second bottom-up approach is to use an AC electric field to induce hydrodynamic clustering in a thin gap of parallel electrodes. This unique transverse motion parallel to the electrode surface enables two-dimensional ordering of colloidal crystals in seconds, offering great advantage in immediate application. In addition, induced ordering can be reversed by the removal of electric field, making it suitable for switching devices [43]. The nucleation of clusters and the initiation of ordering depend strongly on local particle density [44] and the perturbation of polarization layer near the electrode surface [45]. Over a flat electrode, it can occur randomly due to Brownian motion, leading to multi-domain growth and interconnecting network [44, 46, 47].

1.2 Motivation

Without the assistance of pre-patterned templates made by lithography processes, the assembly of monolayer colloidal crystal either suffers from long

assembly time or poor crystal quality. One of the key factors leading to poor crystal quality is the lack of control of nucleation and the direction of subsequent in-plane growth (growth direction). In most assembly methods, the onset of colloidal crystallization is determined by the packing fraction of particles occupied in a confined space [39, 40], either being bounded by physical confinement or meniscus capillary. In electric field self-assembly, the nucleation of clusters depends on the supersaturation of particle density near the electrode surface. Although pre-aggregation or clustering in bulk suspension can be avoided with the help of surfactants and low particle density, driving all the particles to concentrate at a desired location is not easy, let alone achieving preferred nucleation for subsequent in-plane growth.

In convective self-assembly, the nucleation often occurs near the contact line, under the confinement of capillary meniscus. However, wavy contact line [48] often gives rise to wavy nucleation seeds, creating multiple growth directions and domain mismatches in the later stage. While on an electrode surface, approaching particles in close proximity will often feel each other and attract each other, undergo clustering [45, 49]. Supersaturation described by Zhang and Liu [44] is required for stable clusters to grow. However, multiple sites of nucleation lead to domain mismatch, if not voids, and a network of finite elongated patches or interconnected bands [46] (if continuous supply of particles is disrupted).

1.3 Objective and Scope

This thesis aims to engineer straight nucleation line of colloidal arrays using simple and standard lithography patterning, subsequently controlling its in-plane growth of colloidal arrays in both

- 1) Convective Colloidal Self-Assembly (Evaporation-driven), and
- 2) Electric Field Assisted Self-Assembly

This thesis is built on the fact that preferential accumulation of particles at one specific location is the first requirement to a perfect nucleation seed of colloidal crystal. This is followed by a single direction of in-plane growth, and a single domain of monolayer colloidal crystal could thus be achieved, leading to guided colloidal crystallization.

1.3.1 Meniscus Pinning

In the first assembly method, a straight line of surface relief patterned on flat substrate is utilized to engineer a straight line of air-liquid-solid contact boundary, aiming to confine the colloidal ordering next to a straight drying edge (Figure 1.1).

Figure 1.1 Proposed design of surface relief that aims to stabilize the pinning of the three-phase contact line of wetting film. By keeping the meniscus pinned at the patterned surface relief, the distance bulk meniscus travels is defined as pinning distance, d .

To improve the affinity of wetting film (pure water) to the proposed hydrophobic surface relief, UV-ozone treatment was carried out to improve its hydrophilicity. To quantify the pinning strength of water film on the treated surface relief, an in-house measurement setup of pinning force based on the concept of Wilhelmy plate [50, 51] was used. The Wilhelmy plate method determines the surface tension of a liquid and the interfacial tension at a liquid–liquid interface by measuring the force acting on a vertically immersed thin plate (e.g. platinum or filter paper).

Also, quantitative visual measurement of pinning strength was carried out to verify the stability of contact line made by the wetting film of pure water and colloidal suspension of various surfactant concentrations (SDS). Here, pinning strength is quantified in terms of pinning distance – the distance travelled by bulk meniscus before the detachment or depinning of wetting film (Figure 1.1).

Followed by the success of straight meniscus pinning, colloidal ordering was pursued using the mentioned templates and characterized as elaborated in Chapter 4.

1.3.2 Edge as an Enhanced Electric Field Line

In the second approach, the edge of conductive surface relief is introduced onto a flat conductive electrode, creating a linear zone of high field intensity (Figure 1.2). Using Dielectrophoresis (DEP), this edge is expected to attract the accumulation of colloidal particles, so that electrohydrodynamic clustering could occur along the edge of surface relief. With preferential particle adsorption and formation of nucleation seed, it is aimed to control the in-plane growth with subsequent influx of particles.

To verify the effect of DEP and AC Electro-osmosis (ACEO), Finite-Element Method was used to compute the electric field intensity, DEP force and electro-osmotic flow near the edge, which are discussed in Chapter 5. For comparison, the electric field plots and electro-osmotic flows near the following designs of bottom electrodes are presented.

- (a) Conductive surface relief on conductive substrate
- (b) Conductive surface relief on insulated substrate
- (c) Insulated surface relief on conductive substrate

Finally, colloidal assembly on the first type of bottom electrode (a) was used, in order to demonstrate preferential accumulation of particles and the in-plane ordering starting from this edge (Chapter 6).

Figure 1.2 Diagram shows a proposed experimental cell with a conductive surface relief used to induce the preferred colloidal nucleation and in-plane growth. The white arrow indicates the injection of colloidal suspension. This diagram is not drawn to scale.

1.4 Flow Diagram of Thesis Work

Two flow charts (Figure 1.3 and 1.4) are illustrated to describe the sequences of theoretical and experimental works executed in this thesis to achieve preferential colloidal nucleations and in-plane control of monolayer colloidal

crystallizations, in both convective colloidal self-assembly and electric field assisted self-assembly.

Figure 1.3 The flow of works executed to achieve guided colloidal crystallization in convective colloidal self-assembly

Figure 1.4 The flow of works executed to achieve guided colloidal crystallization in electric field assisted self-assembly

Chapter 2: Literature Review

2.1 Nature of Colloidal Particles

Almost all colloidal particles are not electrically neutral. They either contain functional groups attached to the surface or have a large number of acid or base groups, susceptible to dissociation in polar solvent. Their functional groups are normally inherited from the synthesis path or catalysts used. For example, negatively charged polystyrene beads with sulphate group are normally synthesized using emulsion polymerization, using potassium persulphate (KPS) as a catalyst. In a polar solvent like water, surface charge of particles will tend to achieve electrical neutrality by attracting counterions to form a double layer (Figure 2.1). As a result, part of the counterions are attracted to the near surface of negatively charged particles, while the remaining can still move around in bulk suspension (after the slip plane). Figure 2.1 depicts the charge distribution surrounding the negatively charged particles in water suspension. Given a neutral system of suspension, each colloidal particle of radius R carries negative charges of ze . The water solvent contains an equivalent amount of counterions as well as possible stray ions such as salt (Na^+ and Cl^-).

Figure 2.1 In polar solvent, negatively charged colloidal particles of radius R are surrounded by positive counterions (+) in vicinity. A stern model is shown to describe the drop of potential across the double layer [52].

As particles approach one another in proximity, the DLVO (Derjaguin, Landau, Vervay, and Overbeek) interaction potential will arise [53], giving

$$V_{\text{DLVO}} = \frac{64\pi R c_0 G_o^2 kT}{k^2} \exp(-\kappa r) - \frac{AR}{12r} \quad (2.1)$$

$$\text{where } \Gamma_o = \tanh\left(\frac{ze\Phi_o}{4kT}\right) \quad (2.2)$$

where k is Boltzmann constant, R is particle radius, c_0 is ion concentration, ϕ_0 is surface potential of particle, T is temperature, κ is inverse double layer thickness, r is the separation between particles, and A is the Hamaker constant. The first term in Equation (2.1) describes the electrostatic interaction while the second term describes the van der Waals interaction. Both interactions result in

a profile of potential with a primary and secondary minimum, where the latter indicates the equilibrium distance between particles in an electrolyte medium (Figure 2.2). Further reduction of interparticle distance will give rise to strong repulsion, preventing particles from irreversible aggregation. Besides, this metastable state allows scientists to “anneal” the ordered arrays of wet colloidal crystal [54, 55], before the final irreversible dry state of colloidal crystal forms.

Figure 2.2 A comparison of interaction potentials between two colloidal particles in close proximity, described by DLVO potential [50].

Other than DLVO theory, zeta potential (ζ), a parameter that characterizes the electrochemical equilibrium of interfaces, is often used to describe the stability of particles in a solvent. In the interfacial double layer described in Figure 2.1, ζ is the electric potential at the location of the slipping plane relative to a point in the bulk. The fluid layer attached to the particle before the slipping plane is assumed to be stationary. The formation of counterions screens the negative charge of polystyrene beads, causing the surface potential to drop across the double layer. If a small amount of NaCl salt is added into the colloidal system (Figure 2.1), positive Na^+ ions will be attracted to the particle surface, further screening the repulsion between negatively charged particles. This causes interparticle repulsion to drop, and the attraction between particles to

rise. Often, particles form agglomerates at high salt concentration [55, 56], especially when the absolute value of zeta potential drops below 25 mV. Thermal fluctuation due to temperature increase could also increase particle collision, bringing particles into physical contact by chance (Brownian motion). Hence, the electrical double layer serves as an energy barrier (V_{max} in Figure 2.2) against irreversible agglomeration, at the same time controlling its electrokinetic behaviour [57, 58], ease of crystallization and final packing arrangement [59, 60].

2.2 Nucleation of Colloidal Crystals in Bulk Suspension

A stable suspension containing colloidal particles of uniform size appears milky white in nature. As local concentration of particles increases, the suspension may become iridescent when the interparticle distance shrinks to submicron range, satisfying Bragg's diffraction. Extensive study by Hales revealed that the equilibrium phase of monodisperse colloidal system is face-centered cubic (fcc) [61]. The nucleation is found to start above a threshold volume fraction of 0.40 [62]. Interestingly, body centered cubic (bcc) system was discovered at ionic strength lower than 2.7×10^{-6} M KCl and volume fraction less than 0.008 [63]. This discovery later leads to the exploration of ionic strength to control interparticle force and distance between charged dielectric particles [54, 55, 64].

However, long range ordering is almost impossible by controlling ionic strength or electrostatic attraction alone [55, 56]. With Brownian motion, aggregates often form before ordering takes place, even at below its maximum packing limit. These amorphous colloidal aggregates will then prevent further packing of colloidal crystal.

Although slow sedimentation of large particles in less concentrated suspension (volume fraction, v.f. $\ll 0.5$) by gravitational forces provide a single platform for nucleation to happen [29, 65, 66], it is rather slow and may take a few days or up to weeks, depending on the initial particle concentration and desired volume of crystal grown. Also, small particles ($< 1 \mu\text{m}$) or particles of low density are less likely to sediment, limiting its applications.

In the scope of this thesis, two bottom-up approaches of colloidal self-assembly will be discussed, particularly on the nucleation mechanism. They are convective self-assembly and electric field assisted self-assembly. They are attractive, as they require only simple and economical experimental setup. No vacuum or complex lithography system is needed to grow two-dimensional and three-dimensional colloidal close-packed arrays. Unlike gravitational forces, the forces responsible to drive particle motion in both methods – evaporation-induced convective flow and electric field, can be controlled with ease. However, the quality of crystal packing especially in two-dimensional arrays is often limited by the random nucleation of colloidal domains and subsequent multi-directional domain growth. It is believed that understanding the origins of nucleation and its preferential sites of occurrence will possibly lead us to produce in-plane control of single domain monolayer colloidal crystal in these two conventional methods.

2.3 Nucleation in Convective Self-Assembly

“Coffee-ring” experiment by Deegan *et al.* can best describe this evaporation-induced colloidal self-assembly, under the influence of capillary force [36]. A single coffee drop spilled onto a solid substrate will leave behind a dense ring

of stain upon drying, leaving the center of the initial droplet empty. This signifies an intense movement of coffee solids from the droplet interior to the drying perimeter of coffee drops. It is found that faster evaporation at the outer perimeter of drying droplet generates outward capillary flow (both solvent and solids) to replenish solvent loss from the drying edge [39]. Interestingly, the driving force is only due to evaporation rate, being independent of substrate type, carrier fluid and deposited solids [36]. Example of colloidal particles moving to the drying edge of water droplet is shown in Figures 2.3 and 2.4.

Figure 2.3 A sessile drop of colloidal suspension on a horizontal substrate is shown on the left and a magnified version of thinning water layer near the drying edge is depicted on the right. The scaling is for illustration purpose only. Straight arrows indicate the convective transport of particles to the drying edge of sessile droplet while curvy arrows indicate the evaporation or water loss. [36]

Figure 2.4 Evaporation driven self-assembly in sessile droplet where colloidal particles move convectively to the drying edge, forming monolayer crystal at the outer perimeter. Arrow indicates the direction of particle movement. Scale bar: 5 μm . [67]

Figure 2.5 Two partially immersed particles in a water layer during the drying stage. The deformation of water meniscus gives rise to attractive capillary force, indicated by dash arrows [38].

Using a thin well containing monodisperse micrometer-size latex particles, Denkov *et al.* investigated the mechanism and stages of evaporation-induced assembly via *in-situ* microscopic observation [38]. He found that the ordering of particles (nucleation) starts when the meniscus thickness of water approaches the underlying diameter of particles. Neither electrostatic interaction nor van der Waals forces contributes to the nucleation of colloidal domain. Rather, attractive capillary force [38, 68] is the key, attributed to the deformation of menisci (shown in Figure 2.5) between particles at the drying front (thinning of water layer due to evaporation). According to Figure 2.5, the thinning meniscus in the wetting film presses the latex particles toward the water-glass interface, exposing part of the particles out of the water-air interface. As a result, menisci slope near the particle surface causes the x-component of the surface tension force σ_x to vary, giving rise to attractive immersion capillary force.

$$F_c \approx 2\pi\sigma r_c^2 (\sin^2 \psi_c) \left(\frac{1}{L}\right) \quad r_c \ll L \ll \left(\frac{\sigma}{(\Delta\rho)g}\right)^{\frac{1}{2}} \quad (2.3)$$

where σ is the surface tension of the wetting film, r_c is the radius of the meniscus (three-phase contact line) formed at the particle surface, ψ_c is the angle of meniscus slope formed at the contact line, L is the distance between two

particles ($L=2s$), g is the gravitational acceleration, and $\Delta\rho$ is the difference between the mass densities of the gas and liquid phases.

In contrast to flotation capillary force [68] in which the meniscus deformation is strongly driven by particle weight and buoyancy at air-liquid interface (or liquid-liquid interface), wettability of liquid film on particle surface determines the degree of meniscus deformation, and hence the immersion capillary force. In addition, evaporation-driven water flux from thicker region of water layer shown in Figure 2.3 could produce additional horizontal force of packing to form close-packed crystal. This makes convective self-assembly at thinning meniscus (on solid substrate) more attractive compared to interfacial assembly at air-liquid or liquid-liquid interface [69-71].

Also, it is worth noting that the thinning water layer can immobilize partially submerged particles on solid surface as the vertical component of surface tension force presses the particles against the horizontal substrate. This serves as a condition for contact line pinning by particle arrays [37, 72, 73].

To conclude, the meniscus thickness of the drying edge of suspension film is the key to the fixing of contact line by colloidal particles, which can later lead to the accumulation of particles near the drying edge, before attractive capillary force induces the packing and ordering. This leads to the motivation of this thesis work that proposes the engineering of straight contact line of meniscus to induce perfect nucleation and seed growth.

2.3.1 Flow-Controlled Vertical Deposition

Due to the almost fixed contact line and meniscus confinement by colloidal sessile droplet on a horizontal substrate, thickness variation of colloidal crystal

is often observed, from monolayer near the edge to multilayer further away from the contact line (Figure 2.4). Therefore, substrate withdrawal or flow-controlled vertical deposition was introduced to move the contact line along the deposition direction [22, 23]. Figure 2.6 illustrates an experimental setup of flow-controlled vertical deposition, where a substrate is submerged vertically or at an inclined angle inside a colloidal suspension of dilute concentration (v.f. < 0.1). Water bath can be used to control the evaporation rate, driving convective transport of particles to the three-phase contact line made on the substrate. By withdrawing the colloidal suspension out of the chamber, contact line can be moved vertically down to give a uniform deposition of colloidal crystals. Besides, substrate withdrawal at a controlled speed can be used instead of pumping. Other than the contact angle made on the substrate, the relative speed of the moving contact line to the colloidal deposition rate will determine the thickness of colloidal crystal obtained [21, 41, 68, 74, 75]. However, it is still challenging to control the large area deposition of monolayer colloidal crystal or uniform colloidal crystal of few particle layers. As pure water film pinning on a bare and hydrophilic wafer appears weak with small hysteresis of contact angle [76], the dynamic nature of contact angle hysteresis and stick-slip mechanism often leave behind alternating bands of colloidal depositions with thickness variation (Figure 2.7 and Figure 2.8).

Figure 2.6 A flow-controlled vertical deposition setup [23], to control uniformity of multilayer colloidal deposition with the movement of contact line along crystal growth direction. Inset on the right shows capillary rise region near the submerged substrate.

2.3.2 Stick-Slip Mechanism

Although the initial pinning of liquid film onto the substrate will first allow particle deposition along the contact line, but substrate withdrawal or suspension withdrawal will stretch the pinned contact line and deform the receding meniscus (see Figure 2.7). Relatively fast withdrawal of substrate compared to colloidal deposition speed will cause the pinned contact line to depin and move in fingering pattern [77, 78]. Often, the contact line slips over a long distance, and pins at a region well after the previous crystal growth front, giving rise to repeated stripes and empty bands [42, 72].

If the early meniscus confinement is more than one particle diameter thick and recedes much slower than particle deposition, multilayer band with hexagonal close-packed orientation could be obtained. When the bulk meniscus of suspension recedes further with contact angle reaching the critical receding angle, the three-phase contact line will also slip to a lower pinning level with a new contact angle. This repeated Stick-Slip motion of meniscus growth front – pinning of contact line, dynamic change of contact angle and slipping of contact

line to a new zone was best described by Teh *et al.* in Figure 2.7. The alternating bands of colloidal deposition with thickness variation (colloidal bulge) can be referred in Figure 2.8, formed from 0.1 v.f. of 476 nm polystyrene suspension. Besides, it is also believed that weak pinning strength of the meniscus contact line may also contribute to this phenomenon.

Figure 2.7 Diagram depicts a cycle of Stick-Slip motion of meniscus contact line [42].

Figure 2.8 Colloidal stripes (multilayer thickness) formed due to stick-slip motion of meniscus in flow-controlled vertical deposition. The arrow

indicates the growing direction. (Polystyrene beads of 476 nm diameter, 0.1 v.f.) [79]

2.3.3 Wavy Contact Line

The forced contact line movement during the withdrawal of substrate in dip coating [22] or receding meniscus in flow-control vertical deposition [23] often experiences fingering instability, where some short lengths of contact line remaining pinned temporarily while the remaining segments of contact line are breaking loose and slipping rapidly over short distances, forming a wavy contact line. This "stick-and-slip" phenomenon is strongly dominated by surface irregularities [80] and contamination, and can probably be influenced by capillary waves propagating along the fluid interface [78, 81, 82]. At withdrawal of substrate or receding of three-phase contact line, the trapped colloidal particles under meniscus confinement may pin at any point along the contact line (as observed in Figure 2.4, 2.8 and 2.9a). The subsequent stretching of pinned wetting film will then increase the exposure of water-air interface, increasing the surface energy of wetting film. A retrenchment of any point of weakly pinned three-phase contact line will then follow to minimize the total energy. As a result, a wavy contact line is normally observed during the movement of three-phase contact line. A continuous flux of particles to this wavy meniscus confinement will then form the initial crystal growth front, leading to multiple directions of domain growth (Figure 2.9a). This will eventually limit the final domain size of grown colloidal crystal (Figure 2.9b). If a full retrenchment of pinned contact line follows with fast substrate withdrawal rate, stick-slip mechanism will then dominate.

Figure 2.9 (a) In convective driven self-assembly, wavy contact line formed on bare wafer substrate dominates the nucleation and growth of colloidal crystal, leading to polydomain growth (different growth directions). As indicated by the purple zone, fingering effect of wetting solvent appears above the assembled colloidal crystal. Scale bar: 8 μm (b) SEM image describing colloidal assembly on bare substrate is shown, explaining the effect of wavy line that results in domain growth of various directions. The growth directions are indicated by yellow arrows. [79]

2.4 Nucleation in Electric Field Assisted Self-Assembly

Analogous to gravitational sedimentation [29, 65, 66], electric field can be used to move polarized particles or charged particles perpendicularly to the substrate of deposition – in this case, electrode surface of opposite charge [24, 25]. In contrast to sedimentation, deposition rate can be easily controlled with the change in voltage applied, regardless of particle size and density. However, obtaining a monolayer of colloidal crystal using direct current (DC) mode is difficult, as three-dimensional clusters and structures form almost instantly upon the application of field.

Using AC electric field or alternating electric field, the formation of two-dimensional colloidal aggregates and crystals on electrode surface becomes possible [49, 83], especially within a thin gap of parallel electrodes ($< 200\mu\text{m}$). Extensive studies have shown that particles near the electrode surface can move

perpendicularly to the applied electric field, as long as the particles do not adhere to the electrode surface [45, 47, 84-86]. This behaviour is unexpected as electrostatic interactions between particles of the same charge are repulsive. Furthermore, ionic strength was found to reduce the aggregation tendency, indicating that this unique behaviour is not a consequence of DLVO type interaction [49].

Many then attributed this to electro-osmotic force that moves the fluid adjacent to the electrode surface towards the particles, pushing them towards one another [47, 85-87]. This transverse motion eventually gives rise to in-plane aggregation or clustering of particles, forming densely packed planar colloidal crystals. Interestingly, induced clustering due to electro-osmotic flow takes place over a few particle distances away, signifying a long-range hydrodynamic interaction.

Ristenpart *et al.* later attributed this transverse motion to an electrohydrodynamic (EHD) phenomenon where the perturbation of polarization layer (electrode) by particles creates fluid flow that carries particles towards one another [83, 85]. At electrode surfaces, migration of hydronium and hydroxide ions from water electrolysis towards each electrode forms a concentration gradient. The presence of particles near an electrode alters the local electric field, distorting the charge layer. In both DC and AC fields (<10 kHz), these perturbations result in fluid motion that drives the transverse movement of particles into two- or three-dimensional colloidal crystals [45].

In classical electro-osmosis model, a charge that is chemically bound to solid-liquid interfaces is balanced by the mobile equilibrium charge in the fluid. The fluid flow due to the tangential electric field on electrode surface can be simply described by Helmholtz-Smoluchowski approximation [87]:

$$\mathbf{u}_t = \frac{\varepsilon_m \zeta}{\eta} E_t \quad (2.4)$$

where $\mathbf{u}_t$ is the tangential component of fluid velocity, η is the medium viscosity, ε_m is the permittivity of the fluid medium, ζ is the zeta potential at the electrode surface ($\sim 0.01 - 0.1$ V) and E_t is the tangential component of electric field in the diffuse double layer.

In EHD model by Ristenpart *et al.*, the charge in the fluid fluctuates in response to alternating field (time-dependent potential). The amount of induced electric charge is thus proportional to the applied electric field. The resulting tangential electric field in the presence of particles can then be related to the electrohydrodynamic flow using Equation (2.4).

Since there is no net production or consumption of ions at low-voltage alternating field, the interruption of colloidal crystal growth by gas bubbles can be prevented. Besides, the negligible DC component allows the lateral motion to dominate the final packing of colloidal particles on electrodes. With strong electro-osmotic forces, second particle layer may not be stable against the flow if the underlying layer is not fully occupied. Given this nature, alternating field becomes very useful if one needs to obtain two-dimensional particle arrays in minutes [45, 85]. Furthermore, the ordering is

also reversible once the field is off, making it suitable for switching devices [43].

However, electrohydrodynamic clustering of particles can occur in random fashion. Nucleation could occur anywhere on the electrode surface, if the local particle density is sufficient or perturbation of charged layer is sufficiently strong. As a result, uncontrolled nucleation of clusters or colloidal domains often leads to multi-domain growth (Figure 2.10). If the nucleated clusters or domains are too bulky to move and join each other, they could possibly leave behind empty voids, vacancies, and network of finite elongated patches or interconnected bands [46, 47, 49].

Figure 2.10. Colloidal aggregation of 2.7 μm polystyrene on one of the parallel electrodes (flat gold surface) was immediately observed after 30s of electric field application (AC 6Vpp at 500Hz). [45]

Using real-time direct imaging, Zhang and Liu quantitatively measured the kinetics of pre- and post-nucleation processes of colloidal particles, driven by an alternating electric field [44]. As the nucleation tendency depends strongly on the local concentration, the critical nuclei size was determined. Also, the frequency of alternating field was observed to influence transport of particles to

the electrode surface, determining the area fraction of electrodes being occupied (local concentration of particles).

2.5 Towards Perfect Crystallization

2.5.1 Template-assisted Self-Assembly

To grow near-perfect colloidal crystal, high-resolution lithography templates were introduced to provide better nucleation site, by controlling interparticle spacing of pattern feature. For example, square-symmetric pillars fabricated using electron-beam lithography and reactive-ion etching [88] assist the accurate positioning of colloidal particles in square arrangement (Figure 2.11). Other than individual lattice fixing, a trench of v-groove could enable a vectorial control of colloidal crystal growth, right from the pyramidal pit of the groove. As a result, fcc close-packing of colloidal crystal with (100) crystal plane facing up was obtained [89] (Figure 2.12).

Figure 2.11 SEM images depict square arrangement of colloidal particles on square-symmetric pillar-shaped silicon template. The thickness of the crystal: (a) one layer to (b) two layers. The white dots in (a) are the square arrays of pillars. Small defects resulted from in-plane close packing are indicated by arrows. Adapted from [88].

Figure 2.12 (a) Using lithography, Si(100) wafer is anisotropically etched, producing V-shaped channels. (b) The V-grooved channel enables the assembly of single crystal of (100) orientation (silica particles). (c) Vacancy defects observed in the top layer of colloidal crystal. Adapted from [89].

Other than using sedimentation to bring particles into the confined patterns, dewetting of colloidal suspension over the patterned templates is often used to trap the suspended colloids by capillary forces [88-90]. This method is especially useful when one intends to control the formation of complex colloidal aggregates, and improve the domain quality of single or thin layer of colloidal crystal. For example, Yin *et al.* demonstrated the relative correlation between patterned feature size and particle diameter to obtain complex aggregate clusters [91] (Figure 2.13). Xia *et al.* later showed that grating with commensurate width could improve the domain quality of two-dimensional close-packed arrays [88]. Figure 2.14 shows a repeated work to improve the domain quality of polystyrene arrays within a grating width of 6 μm . As the grating width becomes larger, the commensurability effect may not work effectively to maintain the single domain quality. The surface minimization of dewetting film may give rise to curvy contact angle and multi-domain growth, as discussed in Section 2.3.2.

Figure 2.13 Two-dimensional arrays of colloidal aggregates formed by trapping of dewetting suspension film over the patterned substrates. (a)

Cylindrical holes ($6\mu\text{m}$) with $2\text{-}\mu\text{m}$ posts in their centers (b) square templates with $2\mu\text{m}$ side length. The arrow indicates the dewetting direction of suspension film. [91]

Figure 2.14 Dewetting of colloidal suspension film (650nm Polystyrene) over the gratings of SU8 on silicon substrate. The arrow indicates the dewetting direction of meniscus. Grating width = $6\mu\text{m}$. [79]

Combining commensurability and electrostatic interaction of particles (control of Debye length), Sharma *et al.* demonstrated the control of sparse occupancy of colloidal particles in each of the patterned lattice location [92]. The repulsive interaction of colloidal particles allows the polystyrene particles to deposit in every other site as shown in Figure 2.15a. Then, a subsequent deposition of silica particles led to ordered formation of binary particle layers in checkerboard order. This work was the first demonstration that non-close-packed multilayers could be obtained by template-assisted growth, with the knowledge of interparticle interaction.

Figure 2.15 (a) Figure shows a sparse occupancy of polystyrene particles in every other lattice site. (b) Subsequent deposition of silica particles leads to formation of 2D ordered heterostructure of polystyrene and silica. Adapted from [92].

Despite progressive advancements in micro- and nano-fabrication systems, most do not offer sound practicality for economical large-scale integration. Large areas of serial patterning by e-beam is time consuming and costly. The area of patterning is also limited by the cost of mask fabrication if standard lithography is used. Besides, the dewetting of suspension film over the patterned templates is always limited by the stick-slip mechanism, especially when trapped particles contribute to the pinning of contact line. As a result, large area of particle arrays without empty bands, and uniformity of particle deposition (lattice occupancy) could be hard to achieve. Also, as shown in Figure 2.14, the pinning of particles outside of the gratings is possible, contributing to particle retentions outside of gratings.

Chapter 3: Meniscus Pinning – Measurement and Model

Development

3.1 Theoretical Basis of Pinning

Motion of three-phase contact line (three-phase boundaries) along the hydrophilic substrate during the evaporation-induced self-assembly remains an open problem of general interest [42, 72, 91, 92]. As discussed in Chapter 2, the dynamics of Stick-Slip mechanism or pinning-depinning process has great influence over the thickness uniformity of colloidal crystal deposited and the area of successive depositions. As the aim is to achieve a straight contact line for three-phase boundaries (air-suspension-silicon substrate), the pinning strength along this edge must be quantified.

According to our understanding, pinning can be defined as the immobilization of three-phase contact line, strongly influenced by the interactions between the molecules from each phase. Consider a partial wetting of water droplet on a flat, smooth and chemically homogeneous solid surface, the equilibrium contact angle made at air-liquid-solid interface (contact line) is θ_o . The balance of interfacial tensions shown in Figure 3.1a can be described by Young-Dupré equation:

$$\gamma_{sv} - \gamma_{sl} - \gamma_{lv}\cos\theta_o = 0 \quad (3.1a)$$

where γ_{sv} , γ_{sl} and γ_{lv} are interfacial tensions of substrate-air, substrate-water and water-air, respectively.

Figure 3.1 Definition of the interfacial tension at (a) static equilibrium, (b) advancing and (c) receding angle.

A hydrophilic substrate will tend to have larger γ_{sv} (or smaller γ_{sl} with water), giving positive spreading coefficient: $\gamma_{sv} - \gamma_{sl} > 0$. In contrast, hydrophobic surface tends to discourage interaction between solid surface and water, reducing its interfacial area or increasing its equilibrium contact angle θ_o . Ideally, a directional force exerting on this static water droplet will move the interface as the lateral force balance at the three-phase contact line would be non-zero (assume constant γ_{sl} and γ_{sv}). However, most surfaces are not homogeneously smooth, and may contain chemically and structurally different regions. These inhomogeneities often give rise to immobilization of contact line (pinning) and dynamic change of contact angle in the presence of external force (Figure 3.1b and 3.1c) [93]. For instance, many surfaces may appear flat to naked eyes, but they are indeed rough at the submicroscopic scale (<100 nm). Assuming an advancing droplet of contact angle θ_o moving towards a microscopically small spherical protrusion as shown in Figure 3.2a, it will always maintain its local contact angle at its three-phase contact line either on a flat surface or over the microscopic protrusion. Microscopically the contact line moves over the top of spherical protrusion, but it appears static or pinned macroscopically, giving an apparent contact angle of more than 90° . Over this

protrusion, receding droplet will also give apparent contact angle smaller than θ_o (Figure 3.2b). Only after overcoming this protrusion, macroscopically the droplet will appear moving or “spreading”, with a fixed contact angle θ_o .

Figure 3.2 (a) Figure shows an advancing droplet that moves from a smooth surface to a small microscopic protrusion. Apparent contact angle made at $\angle A'B'C$ appears to be visually larger than the contact angle made at $\angle ABC$. (b) On the contrary, a receding droplet that moves across a microscopic protrusion will appear to have a smaller receding angle $\angle A'B'C$ than it makes on a smooth surface $\angle ABC$. The arrows indicate the moving directions of the droplet.

Other than physical heterogeneity, an interface between materials of different surface chemistry would also give rise to Stick-Slip phenomenon. In Figure 3.3, region CB and region BD are made of hydrophilic and hydrophobic materials where B indicates the interface between these two regions. At advancing motion, the three-phase contact line will be pinned by the relatively hydrophobic surface (BD) while the three-phase contact line will be pinned by the more hydrophilic region at receding motion. Hence at small microscopic movement across the interface, the resulting apparent angle at the interface

between these two surfaces will appear differently while the three-phase contact line could appear pinned at macroscopic view.

Figure 3.3 Schematic shows the a) receding three-phase contact line at B' and b) advancing three-phase contact line near the interface between two different surface chemistry. CB: hydrophilic and BD: hydrophobic

For easy representation and purpose of application, Joanny and Gennes described the hysteresis as the difference between the perturbed and unperturbed system [93]:

$$-h(x, y) = \gamma_{sl}(x, y) - \gamma_{sv}(x, y) - [\gamma_{sl} - \gamma_{sv}]_o \quad (3.1b)$$

where (x, y) denotes the coordinates on solid surface and bracket $[]_o$ denotes the unperturbed value.

With the presence of a large defect size like a step-height or particle contamination over flat surface, the anchorage of three-phase contact line and dynamic range of contact angle ($\theta_{rec} < \theta < \theta_{adv}$) could give rise to a pinning strength. As shown in equation 3.1c, this force can be estimated from the difference between critical receding angle, θ_{rec} (or advancing angle, θ_{adv}) and the static contact angle at equilibrium.

$$F_{pinning} = l\gamma_{lv}[\cos\theta_{rec} - \cos\theta_o] \quad (3.1c)$$

where l is the length of three-phase contact line.

In this work, a straight surface relief of SU8 photoresist was developed to provide a line interface of heterogeneity, separating the hydrophobic nature

($\sim 70^\circ$) of surface relief and the hydrophilic silicon surface ($\sim 10^\circ$). The aim is to combine both the physical and chemical inhomogeneity to achieve meniscus pinning and confinement, ultimately enabling controllable in-plane growth of colloidal crystal. A hydrophobic surface would be able to screen the three-phase contact line to the edge of surface relief, preventing undesirable colloidal crystal growth on SU8 surface. Despite possible hysteresis across this step height of 100 nm, the hydrophobic SU8 surface relief will not assist the adhesion of water film along its line edge or edge front. Hence, a light UV-ozone treatment [94, 95] is introduced to modify the SU8 surface, creating more hydrophilic functional groups to gain affinity to water molecules. However, this will increase γ_{sv} and decrease the wetting angle of water droplet or film. A slightly larger critical receding angle on SU8 surface is still required to prevent the pinning of particles and uncontrollable nucleation or aggregation.

In this chapter, a method is first developed to measure the pinning strength of water film along the edge of UV-Ozone treated SU8 film. Following this, the pinning strength in terms of pinning distance is measured using optical inspection. This serves to obtain the travel distance of bulk meniscus upon successful pinning along the straight edge of surface relief. The stretching limit could indicate the maximum area of colloidal crystal growth front before depinning occurs along the surface relief. Based on the experimental observations, a theoretical analysis of pinning events is demonstrated, followed by a model to predict the requirement of successful pinning by colloidal wetting film, especially in the presence of particles.

3.2 Measurement of Pinning Force

3.2.1 Instrumentation

To measure the pinning strength along the interface of less hydrophilic and more hydrophilic region (UV-ozone treated SU8 and silicon wafer respectively), a measurement system based on the concept of Wilhelmy plate tensiometer [50, 51] is built.

In standard Wilhelmy-plate method (Figure 3.4a), the force of liquid surface or interface acting on a vertically suspended plate is measured. If an infinitely thin and superhydrophilic flat substrate is immersed into a liquid, the surface tension force can be obtained from the following relationship:

$$F_{read} = \sigma L \cdot \cos\theta \quad (3.2a)$$

where F_{read} is the force recorded by the tensiometer or pressure-transducer, σ is the surface tension of liquid and L is the wetting length of liquid film (or length of three-phase contact line made on plate). $\theta \approx 0$ when a superhydrophilic substrate is used, simplifying Equation (3.2a) into $F = \sigma L$.

Figure 3.4 a) A schematic diagram of the Wilhelmy plate method and b) a system that is designed for an inverse measurement of pinning force using a weighing balance.

As the pressure transducer can directly measure the force a liquid exerts on a substrate of inhomogeneity or patterned substrate, the time-dependent pinning force can also be estimated. Although sensitive pressure transducer can measure up to 0.001 mN resolution, it can only hold a limited load of the substrate (<210 g) [96]. This limits the measurement of liquid exerting force on substrate of large size or weight. Furthermore, the hanging substrate connected to the transducer could be subjected to vibration or swinging of substrate in the case of perturbation.

Hence, a design that uses the analytical balance (weighing machine) to measure the “weight loss” due to the pulling of vertically submerged substrate is proposed (see Figure 3.4b). Here, the substrate is mounted to the motion actuator, stabilizing it from air blow and vibration. Instead of measuring the force taken to hold the sample of measurement and the force against the pulling of liquid film, “weight loss” due to the pulling of liquid meniscus against the gravity is directly obtained. The maximum weight loss recorded by weighing balance upon detachment of wetting film can be directly related to the pinning strength, $F_{pinning}$.

$$F_{pinning} = -\Delta W_{water \text{ or } liquid} \quad (3.2b)$$

Similar to Wilhelmy-plate tensiometer, this method can be used to measure surface tension of liquid. However, it is not within the thesis scope to explore further. This design is aimed to investigate the water affinity to SU8 surface upon UV-ozone treatment. More specifically, the pinning force of water along

the edge of 200 nm thick SU8 film (interfacing with silica surface) is emphasized here. (Figure 3.5).

Table 1 summarizes the comparison between the proposed system with commercial tensiometers. The specifications provided for the proposed system are based mostly on the resolution of the weighing balance used (Mettler Toledo CT-3100) and the specifications of the linear positioning actuator (Zaber T-LS series).

Table 1: Table compares the specifications offered by the in-house tensiometry, Attension Sigma 700 and KRUSS K100. * indicates that the limit is due to linear positioning actuator, which could be replaced easily.

Brands	Balance Specification		
	In-house Tensiometry	Attension Sigma 700	KRUSS K100
Displayed resolution (mN/m)	0.01	0.001	0.001
Maximum load (g)	2000 *	210	250
Weighing resolution (mg)	0.1	0.01	0.01
Force resolution (μ N)	1	0.1	0.1
Sample stage speed (mm/min)	0.005 – 360 *	0.01 – 500	0.01 – 500
Stage positioning resolution (mm)	0.001 *	0.015	0.01

3.2.2 Substrates

To investigate the affinity of water to SU8 surface, SU8 photoresist was spin-coated onto a clean borosilicate glass. Upon curing with UV, the substrates were exposed to UV-ozone treatment (Novascan PSD-UV) for 1, 2, 3, 4 and 5 minutes. This is to render the surface relief slightly hydrophilic [94, 95, 97-99], improving the adhesion and pinning of water film along the surface relief edges. The substrate without UV-ozone treatment was used as a reference sample. The

pinning force of water film along the flat edges of untreated and treated borosilicate glasses were studied (see Figure 3.5).

Figure 3.5 Schematic shows the pinning of water film along the flat edge of 25 mm wide borosilicate glass.

3.2.3 Measurement and Operation:

First, a beaker containing DI water was loaded onto the weighing balance. The sample was then mounted to the motion actuator (which moves in z-direction) and the bottom edge of sample was aligned to the bulk meniscus of water.

With the start of weight recording, the mounted sample was moved into the water (partially submerged). Then the sample was moved out at $10 \mu\text{m/s}$, until the water wetting film depinned from the flat edge of sample. The recording was then stopped. The same procedure was repeated for other sets of samples. 5 readings were taken for each set of samples.

3.2.4 Results and Discussion

A sample of raw data obtained from the weighing balance is provided in Figure 3.6, with labelling of the stages of substrate insertion, advancing wetting film, receding wetting film, pinning and depinning. It is obvious that at the instant

the substrate touched the water surface by the insertion of sample, it immediately caused a reduction in recorded weight. This signifies the first pinning of water wetting film. As the insertion proceeded, the dynamic change of weight reading indicated the advancing behaviour of the wetting film. At 83 seconds, the sample was removed slowly, causing the wetting film to recede. A significant weight reduction was observed after 92 seconds, when pinning occurred along the edge of sample. Further stretching of this pinned film drew a huge volume of water up, giving a maximum pinning force (pinning strength) of 3.87 mN. As the aim of this study is to quantify the pinning strength of water along the edge of SU8 resist, only the final two stages are important.

Figure 3.6: a) Schematic shows the stages of pinning and depinning when a glass substrate coated with 200 nm SU8 film (with two-minute UV-ozone treatment) was moved into and out of DI water. b) These stages can be distinctly differentiated from the weight of solution obtained from a weighing balance described in Figure 3.4b.

As indicated in Figure 3.7, the pinning strength derived from Figure 3.6 could refer to the pinning along both the perimeter edge of borosilicate glass and SU8. A separate measurement on bare glass substrate of the same dimension could be used as a reference. By considering the perimeter of the edges ($25 \text{ mm} \times 2 + 1 \text{ mm} \times 2$), the average pinning force per length, f in mN/m could also be computed. A very thin and negligible thickness of SU8 film was assumed.

Figure 3.7 Plot shows the average pinning force measured along the lower edges of both bare glass and SU8/glass substrate with and without UV-ozone treatments. The average pinning force per length was computed from averaging the force over the perimeter edges of glass and SU8 film. 5 measurements were acquired for each substrate.

According to Figure 3.7, glass substrate gives the highest pinning force at 4.21 mN and the highest average pinning force per length at 80.98 mN/m. A

200 nm thick coating of SU8 reduces its pinning strength by 20%. With UV-ozone treatment, the pinning strength is observed to increase, reaching up to 77.26 mN/m after 5 minutes of exposure. This gives an indication that successful pinning can be enhanced along the hydrophilic and hydrophobic interface by UV-ozone treatment. It is also important to emphasize that the described method gives a very small standard deviation ($<0.5\%$) among all samples measured. More details can be referred to Appendix I.

The obtained value of average pinning force per length is slightly higher than air-water tension force. This could indicate that the breakup of wetting film is possible prior to depinning. A slightly larger reduction of weight reading could be measured if water droplets are being retained by substrate after depinning. However, higher value of pinning force per length could also be due to geometrical effect (edges and corners) of thick substrate and significant area of water-glass interface (bottom facing water surface) that contributed to the enhanced adhesion of wetting film. Therefore, the average pinning force per length may not be the real quantification behind the pinning strength along the “thick edge front”. Pinning force could be used instead as it simply represents the total force acting along the edge front of the substrate. This metric could be more useful than dimensionless pinning force as it directly indicates the weight of water or solution that the thick substrate can hold before the onset of depinning. It can also be used on substrate with irregular shapes or edges.

In this section, a methodology to measure pinning force was developed and used to understand the impact of UV-ozone treatment on SU8 surface. Pinning force of water on the proposed substrates were measured and proven to be

sufficiently strong enough to sustain pinning upon substrate withdrawal, for more than 30 s (equivalent to 300 μm travel distance).

3.3 Quantification of Pinning Distance by Visual Inspection

To verify the success of pinning along the edge of SU8 relief (as of the proposed substrate in Figure 1.1), a straight surface relief line of the same thickness was patterned on silicon. According to previous study of pinning force, 2 min of UV-ozone treatment is sufficient to increase the affinity of water film. Long exposure to UV-ozone treatment may roughen the thin film or render it porous, causing complication to the motion of three-phase contact line or even nucleation of colloidal clusters (trapping of particles). Also the contact angle made by the three-phase contact line could be too small, limiting the confinement of colloidal particles used.

In this section, only samples with 2-min UV-ozone exposure are discussed. The verification of water film pinning along the edge of surface relief was first visually inspected to obtain its pinning distance. The pinning distance here refers to the distance travelled by the bulk meniscus of water (or suspension) surface upon the successful pinning along the edge surface relief (Figure 1.1). The maximum pinning distance was recorded after the depinning occurred at any point along the SU8 surface relief. Subsequently, the pinning distance for pure colloidal suspension, and suspensions with various surfactant concentrations were measured. Here, the addition of surfactant was expected to

improve the affinity of colloidal suspension to the surface relief and reduce the wetting angle of colloidal suspension.

The measurement of pinning strength of pure water film and colloidal suspension film (with varying surfactant concentration) along surface relief is important as a uniform and linear contact line of colloidal suspension film is required, with minimal fingering instability [48, 77, 78] upon the pulling of the pinned film. The maximum pinning distances under the influence of surfactant concentration and particle accumulation (particle trapping) was then compared with the pinning of pure water film on the physical surface relief.

3.3.1 Sample Preparation

The silicon wafers were first pretreated with piranha solution, with a ratio of one volume of 30% H_2O_2 to three volumes of concentrated H_2SO_4 . Using optical lithography, the substrates were then patterned with numerous straight lines of surface reliefs, made of hydrophobic photoresist (SU 8 2000.5) of 200 nm thickness. Each surface relief was designed to have a length of 7 mm. After the hard-bake process, the patterned wafers were treated with UV-ozone for 2 min.

3.3.2 Colloidal Suspension

Monodisperse polystyrene (PS) spheres with sulphate groups (1wt% aqueous dispersions, 800 nm in diameter, surfactant-free) were obtained from Duke Scientific. The aqueous suspension was then diluted to 0.25 wt% with DI water. To investigate the pinning capability of suspension film under the influence of sodium dodecyl sulphate (SDS) surfactant, another batch of colloidal

suspension was prepared with surfactant concentration ranging from 0.05 mg/ml to 1.5 mg/ml.

3.3.3 Instrumentation

A similar laboratory setup (Figure 3.8) used by Dimitrov *et al.* [21] for vertical deposition was adopted. The chamber wall (25 mm) was made relatively wider than the surface relief length of 7 mm, such that the wall would not cause an influence over the meniscus near the substrate. The substrate was mounted on a rotation stage attached to the vertical motorized stage. The rotation stage was then used to align the linear surface relief such that it stayed parallel to the bulk meniscus. A small gap of 2 mm between the substrate and chamber wall was kept to confine the evaporation to the edge of the pinned meniscus, such that solvent evaporation from the meniscus could be minimized. The vertical motorized stage (T-LS Series) was sourced from Zaber. It was programmed to withdraw the substrate at a predetermined speed. The pinning behaviour of liquid film (5x objective lens) and array growth (50x objective lens) was monitored using a horizontal long-focus microscope.

Figure 3.8 Laboratory setup used to measure maximum pinning distance by wetting film of pure water and colloidal suspensions of various SDS concentration. This setup was later used to grow monolayer colloidal crystal with predetermined orientation as discussed in Chapter 4.

3.3.4 Operation

To obtain the pinning distance, the chamber was slowly filled with respective solutions up to the edge of surface relief, using micropipette. Two-minute of equilibrium time was given to establish pinning. Precaution must be taken to prevent pre-compression or pre-stretching of the pinned liquid film. Then the lower stage holding the chamber was moved vertically downward at 1 $\mu\text{m/s}$ to stretch the pinned film. Once depinning occurred along the edge of surface relief (desired contact line), the distance travelled was recorded as pinning distance. At least three readings were taken for each set of solution.

3.3.5 Results and Discussion

The pinning capability of colloidal suspension, pure surfactant solution and pure water on surface relief are plotted and compared in Figure 3.9. Without a surface relief, pure water film pinning on a bare and hydrophilic wafer appears weak, the three-phase contact line moves over the hydrophilic surface with small hysteresis of contact angle [76]. Similar to hydrophilic borosilicate glass used in pinning force measurement (section 3.2.4), strong pinning was only observed near the bottom edge of the silicon wafer. With a proposed UV-ozone treated surface relief printed on a bare silicon wafer, it was observed that pinned meniscus wedge of pure water film along the edge surface relief can be stretched up to 1 mm away from the resist edge (star icon in Figure 3.9). This enhancement is attributed to the carboxylic groups created along the edges of surface relief during UV-ozone treatment [99], as discussed in section 3.2.4.

With addition of colloidal particles, pinned meniscus wedge of colloidal suspension film can be stretched to 1.5 mm, giving a 50% increment compared to that of pure water. In agreement with previous studies [37], particles being trapped under the thin meniscus wedge are able to provide friction against the movement of contact line.

Figure 3.9 The plot illustrates the effect of SDS concentration over both the distance a pinned liquid film was stretched before depinning along surface relief (absence of particles) and the distance stretched before rupturing near colloidal crystal growth front (presence of particles).

With addition of SDS surfactant (0.05–0.10 mg/ml), the pinning was enhanced to 1850 μm, giving a 20% increment. This could be explained by the cooperative interaction of hydrophobic surfactant tails with hydrophobic region of SU-8 resist and polystyrene beads, and hydrogen bonding between water molecules with hydroxyl groups created by UV-ozone treatment (Figure 3.10b). However, higher SDS concentration (>1.00 mg/ml) shows weakening of pinning distance. In accordance with equation 3.1c, significant reduction of

water surface tension (γ_{lv}) with the adsorption of SDS at air-water interface would reduce the pinning force of wetting film. This weakening is more obvious in the case of pure SDS solutions in the absence of colloidal particles. Above 0.10 mg/ml SDS concentration, significant weakening of pinning strength is observed with depinning occurring from meniscus wedge. Other than weakening of γ_{lv} , SDS adsorption on solid surfaces could screen the water affinity for both treated SU8 and silicon surfaces, increasing the wetting angle (Figure 3.10a).

Figure 3.10 a) Adsorption of surfactant molecules (SDS) at surface relief could render the surface relief more hydrophobic, at which the polar groups interact with the treated SU8 while the projected hydrophobic tails interact with the three phase contact line of water film. b) In the presence of polystyrene (PS) particles, polystyrene surface could become more hydrophilic with the attachment of SDS molecules, at which the polar heads interact with the water wetting film.

It is also worth mentioning that the presence of particles did not cause depinning along the surface relief, instead the stretched meniscus wedge was found to rupture at a region located after the colloidal crystal growth front (Figure 3.11b). Comparing to solution without particles (Figure 3.11a), the defined pinning distance refers to the distance travelled by bulk meniscus before the rupturing of wetting films, leaving behind wet colloidal crystals next to

surface relief (Figure 3.11b). As the pinning strength cannot be stronger than the surface tension that holds the solvent film together (Equation 3.1c), the nucleation of such rupturing could be due to particle protrusion out of the stretched film. The accumulation or surface adsorption of surfactants on particle could further lower the local surface tension, leading to retraction of wetting film held stronger to the surface relief and bulk meniscus. This rupturing left behind a wet colloidal crystal growth front, with a width of about 5 – 10 μm (Figure 3.11(b)). As equilibrium time was given prior to substrate withdrawal, the crystal growth front here contained multilayer of colloidal crystals.

Figure 3.11 (a) The absence of colloidal particles in suspension results in early depinning along the surface relief, indicated by red circle. A smaller pinning distance is thus observed. (b) The presence of colloidal particles stabilizes the pinning of liquid film along the surface relief. A similar speed of film stretching (relatively faster than crystal growth rate), causes liquid film to rupture near colloidal crystal growth front, leaving behind wet colloidal crystal along surface relief.

3.4 Theoretical Analysis of Pinning

3.4.1 Contact Angles of Wetting Drop and Wetting Film

The static contact angle of water droplet on UV-treated SU8 (2 min) is about 57° (Figure 3.12). When a drop was placed near the edge of SU8 surface relief,

the drop wetted and pinned at the edge of surface relief (Figure 3.12). When a similar substrate was inserted vertically into bulk water and pulled out at 10 $\mu\text{m/s}$, the critical receding angles (before depinning or slip occurred) on SU8 surface relief and edge of SU8 surface relief were observed at 47.89° and 25.08° , respectively (Figure 3.13). Particularly for pinning near the edge of SU8 surface relief, straight three-phase contact line could be observed (Figure 3.14).

Figure 3.12 Using contact angle goniometer with optical recording system, contact angles of two static sessile drops on both SU8 surface relief and silicon region were measured. The drop on the silicon surface wetted and pinned near the edge of SU8 surface relief, giving rise to a contact angle of 32.93° . The bottom diagram depicts the structure of SU8 surface relief sitting on a silicon substrate.

Figure 3.13 When a template with a straight SU8 surface relief (Figure 3.12) was inserted into pure water and pulled out at 10 $\mu\text{m/s}$, the critical receding angle formed on treated SU8 surface (Left) and along the edge of SU8 surface relief (Right) were obtained at 47.89° and 25.08° .

Figure 3.14 a) Snapshot shows a successful pinning of colloidal suspension film along the edge of SU8 surface relief. b) The stretching of pinned suspension film reduces the meniscus wedge down to a thickness close to a particle diameter. Diagrams in c) and d) illustrate the side-view of meniscus profiles that correspond to the snapshots shown in a) and b), respectively. Particle size: 476 nm. UV-ozone treatment of SU8 surface relief: 2 minutes.

3.4.2 Edge of the Surface Relief

Figure 3.15 describes the capillary pinning of three-phase contact line by pure water wetting film, over the surface relief and along the edge of the relief. If pinning is allowed near the slightly hydrophilic surface relief, the stretching of water wetting film will cause the initial static contact angle ($\sim 57^\circ$) to reduce. At equilibrium, the three-phase contact line on SU8 surface relief has a frictional pinning force of $-\gamma_{lv} \sin \omega$ [100, 101]. If the contact angle reduces to its critical receding angle ($\sim 45^\circ$), it may slip to the edge of SU8 surface relief. Here, the force vector (σ_{sl}) due to the interaction of water molecules with treated SU8

surface points downward, providing additional vertical pinning force to enhance the pinning of three-phase contact line. As a result, the critical receding angle of pinned wetting film along the edge is observed to be about 25° , much lower than that on a flat SU8 surface relief (see Figure 3.13). This finding could explain the delayed detachment of wetting film reported in previous sections and the success of engineering a straight pinning of three-phase contact line along the edge of SU8 surface relief, as shown in Figure 3.14. As a result, a gradual reduction of meniscus confinement by meniscus stretching (substrate withdrawal) can be carried out to a larger extent, before the critical receding angle is met (Figure 3.13b).

Figure 3.15 Diagram shows the force vectors contributing to the stability of contact line on SU8 surface relief and along the edge of surface relief.

As the stretching of pinned wetting film or increase of “pinning distance” will create more surface area of water-air interface, a larger area of vertical side front of surface relief (or larger relief height) may help in improving the pinning force. However, the correlation between this height and pinning force is not investigated in this thesis. The limitation of this height will be discussed in next section.

3.4.3 Capillary Pinning of Particles under Meniscus Confinement

From Figure 3.9 in section 3.3.5, the addition of colloidal particles was observed to enhance pinning of three-phase contact line by 50% (even without SDS addition). According to Kralchevsky's work, the additional capillary pinning force originates from the force vector of water surface tension (f_v) that presses the perimeter of protruded spheres (see Figure 3.16 and 3.17).

When the thickness of wetting film falls below the diameter of particle, meniscus deforms [68] around the particle surface. The degree of deformation will then influence the magnitude of capillary force exerted on the trapped colloid. Figure 3.16 shows a cross section of a trapped particle of radius R , within a thin wetting film of height h . The deformed meniscus forms a circular circumference of radius r_c around the particle surface, giving a tension vector indicated by f . f_c and f_v can be defined as lateral capillary force and vertical capillary pinning force, respectively.

$$r_c = R \sin \alpha \quad (3.3)$$

$$F = f_v = 2\pi r_c \gamma_{lv} \cos \left(\theta + \frac{\pi}{2} - \alpha \right) \quad (3.4)$$

From equation (3.4), θ must be smaller than α for a vertical pinning force to exist. Else, capillary force will be able to lift particle away from the substrate.

Figure 3.16 Diagram depicts a cross section of a trapped particle of radius R , within a thin wetting film of height h . Capillary force F acts on the trapped particle, giving a vertical stress that prevents movement of particles. Water meniscus is indicated by blue line.

Gao *et al.* later correlated the capillary pinning of particles with the surface property of substrate, by simplifying the geometry of meniscus connecting the substrate and particle surface (Figure 3.17) [100]. The capillary pinning and lateral capillary force can be described by the following equation:

$$F_v = F \cos \beta = 2\pi r_c \gamma_{lv} \cos \left(\theta + \frac{\pi}{2} - \alpha \right) \cos \beta \quad (3.5)$$

$$F_L = F \sin \beta = 2\pi r_c \gamma_{lv} \cos \left(\theta + \frac{\pi}{2} - \alpha \right) \sin \beta \quad (3.6)$$

Figure 3.17 Schematic of capillary forces F on particle that is trapped by a straight air-water interface made on a substrate (blue line).

At successful pinning, the magnitude of friction force must be equal to the lateral force that moves the particle away from meniscus wedge, but acts in opposite direction. Using a static friction coefficient μ , $F_L \leq \mu F_v$

$$\mu > \tan\beta \quad (3.7)$$

If μ is assumed to be 1 [100],

$$\beta \leq 45^\circ \quad (3.8)$$

As μ is unlikely to be larger than 1 for colloidal particles over a flat surface [100], a sessile drop placed on a hydrophobic substrate will not be able to pin particles successfully. The lateral capillary force F_L could be larger than the vertical pinning force F_v , pushing the particles back into bulk water. According to Figure 3.13, the critical receding angle of the treated SU8 surface is larger than 45° . This implies that the movement of three-phase contact line over the SU8 surface will not be able to pin particles successfully. As the contact line moves to the edge of SU8 surface relief, successful pinning along this edge would allow meniscus to stretch and the contact angle to reduce well below 45° .

Hence, the condition for successful particle pinning and colloidal nucleation could be achieved here.

As discussed earlier, the initial pinning is contributed by the interaction of water molecules with treated SU8 surface by a vertical force vector, σ_{sl} . This additional pinning component caused the observed critical receding angle to reduce further to 25.08° (Figure 3.13). As a result, the thickness and contact angle of meniscus wedge formed at the edge of surface relief can be controlled easily with the pulling of substrate or water withdrawal (Figure 3.14). Upon particle accumulation along the edge of surface relief by convective forces, the gradual reduction of meniscus thickness and contact angle β ($<45^\circ$) will then enable the immediate pinning of colloidal particles. As the particle used is taller than the thin surface relief, the thinning of meniscus wedge will expose the particle surface earlier before the critical receding angle is reached.

The particles being trapped by the meniscus deformation can be best described in Figure 3.18. Unlike triangular meniscus wedge proposed in Figure 3.17, the stretching and deforming meniscus (on both right and left sides of particle) could strongly immobilize the particle by capillary pinning, F_v . Due to slight hydrophilicity of both surface relief and particle surface, the meniscus connecting both surfaces is no longer straight. Instead of β , a smaller β' could best describe the net force vector F acting on the circumference of meniscus on trapped particle (Figure 3.18).

Figure 3.18 At successful water film pinning at SU8 surface, the deformation of menisci is shown during the decrease of meniscus wedge confinement.

Figure 3.19 Assuming same water thickness that exposes particle at P and S (or S'), the apparent contact angles made at point O (or O') in the absence (or presence) are shown, giving rise to different force vector F and F' .

It is obvious that the height of surface relief and contact angle β can be correlated to achieve maximum capillary pinning contributed by particle. Figure 3.19 compares the menisci pinned at O (without surface relief) and O' (the edge of surface relief). Assuming similar water thickness beyond point P (h) and a large hysteresis window for critical advancing angle and receding angle at point O or O' , the circumference formed by both menisci at P and S (or S') contributes to force vector F or F' on the particle. During the relative movement of

substrate, a large wetting angle may give force F that has stronger lateral component than the vertical one. Even with successful pinning at point O , particle pinning will not enhance the pinning of three-phase contact line here. With the presence of surface relief of height t , edge pinning could give lower apparent wetting angle, giving smaller β' at O' , compared to β at O . As a result, a stronger vertical component of capillary force will be produced as compared to the case with thinner or without surface relief. As described by equation 3.7, lower static friction is required to pin the particle successfully. The relationship between β and β' can be further described with the inclusion of surface relief height:

$$\tan\beta' = \tan\beta - t/l \quad (3.9)$$

Assuming L to be R when particle is at closest distance to the surface relief, the minimal requirement to achieve particle pinning next to surface relief would be

$$\mu \geq \tan\beta - t/R \quad (3.10)$$

where a smaller particle friction is only required with increment of t , as compared to no surface relief in equation 3.7.

However, thicker relief height may increase the thickness of meniscus wedge formed along the surface relief. A smaller critical receding angle will then be required to prevent early depinning of meniscus away from surface relief, before particles are successfully pinned.

$$\mu \geq \tan\beta'_{crit} \quad (3.11)$$

where β'_{crit} is the critical receding angle near the relief edge, which must be lower according to equation 3.7. This imposes stricter tolerance of β_{crit} if higher thickness of surface relief is used. Also, thickness larger than particle diameter

will not pin single-particle layer, but could possibly give rise to multilayer formation.

In contrast, a thin surface relief will allow one to pin the arriving particles well before the critical receding angle made at surface relief. For a large particle size (1.2 μm), the arrival of particles next to the thin surface relief could push the three-phase contact line onto SU8 surface. The fingering effect of three-phase contact line near the edge of SU8 surface can be found in Figure 4.1a, compared to no fingering effect of three-phase contact line pinned exactly at the edge of surface relief when a smaller particle size is used (Figure 3.14b).

3.5 Thermodynamic State of Pinned, Depinned and Rupture of Wetting Film and Force Analysis

The friction and capillary force analysis in section 3.4 assists the understanding of important criteria required to obtain successful pinning of wetting film and particles. In this section, the thermodynamics of experimentally observed states will be further discussed, by comparing the free energies of each pre-defined system.

To simplify the analysis and comparison, the area of curvy menisci is ignored and only the area of flat menisci in proximity to the surface relief is considered. Referring to Fig. 3.20, the wetting film is pinned slightly before the edge of surface relief, in the case of a), c) and d). In the case of b), depinning of wetting film in a) forms a new pinning line slightly after the relief. This is to describe the first state right after the event of depinning from surface relief.

a) Case 1: Pinning

b) Case 2: Depinning

c) Case 3: Particle Pinning

d) Case 4: Rupture of pinning film

Figure 3.20 Diagrams of different pre-defined state: a) pinning, b) depinning, c) particle-pinning, d) rupturing of wetting film near surface relief. Assuming a flat meniscus (away from surface relief) under meniscus stretching by gravitational force, the minimal area of curvature formed near the surface relief could be ignored in free-energy analysis. The nomenclature can be referred in Table 2.

Table 2: Nomenclature used in thermodynamic analysis of different predefined states depicted in Figure 3.20.

P	Particle	R	Particle radius
L	Liquid phase	ρ	Liquid density
V	Vapour phase	h_1, h_2	Meniscus thickness
A	Substrate	t	Surface relief height
B	Surface Relief	g	Gravitational acceleration
A_b	Area of surface relief expose to vapour phase in Case 1	w	Length of surface relief / pinning width
z_1	Pinning distance (from surface relief to bulk meniscus)	z_2	New pinning distance / Capillary rise from bulk meniscus
z_3	An empty band with no particle deposition and solvent left	a	Radius of spherical cap exposed to vapour phase
μ	Friction coefficient of particle on substrate A	θ_a	Contact angle formed on substrate
γ_{lv}	Liquid surface tension	θ_b	Contact angle formed on relief B
γ_{av}	Interfacial energy between substrate A and vapour phase	γ_{al}	Interfacial energy between substrate A and liquid L
γ_{bv}	Interfacial energy between relief B and vapour phase	γ_{bl}	Interfacial energy between relief B and liquid L
γ_{pv}	Interfacial energy between particle and vapour phase	γ_{pl}	Interfacial energy between particle and liquid L

The free energy of the system where the wetting film is pinned near the edge of surface relief can be described as follows.

Case 1: Pinned Wetting film

$$FE_{pinned} \approx \gamma_{bv}(A_b) + \gamma_{bt}(tw) + \gamma_{lv}(wz_1) + \gamma_{al}(wz_1) + \rho gwz_1^2 h_1 \quad (3.12)$$

If the film is stretched or stressed by holding a mass of wetting film to the surface relief, a gravitational energy (last term in equation 3.12) is stored in the system. This energy state can be increased by pulling the substrate out of liquid phase (increase z), while maintaining the pinning state. At maximum pinning distance z_l , wetting film will undergo depinning, moving to the next pinning site. Hence the free energy state becomes:

Case 2: Depinning of wetting film

$$FE_{depinning} = \gamma_{bv}(A_b + tw) + \gamma_{lv}w(z_2) + \gamma_{av}w(z_1 - z_2) + \gamma_{al}(wz_2) + \rho gwz_2^2 h_2 \quad (3.13)$$

The change of free energy state would be:

$$\begin{aligned} \Delta FE_{pinned \text{ to depinned}} &= FE_{depinning} - FE_{pinned} \\ &= tw\gamma_{bv} - \gamma_{bt}(tw) + \gamma_{av}w(z_1 - z_2) + w(\gamma_{lv} + \gamma_{al})(z_2 - z_1) + \rho gw(z_2^2 h_2 - z_1^2 h_1) \\ &= tw\gamma_{lv} \cos \theta_b + \gamma_{av}w(z_1 - z_2) + w(\gamma_{lv} + \gamma_{al})(z_2 - z_1) + \rho gw(z_2^2 h_2 - z_1^2 h_1) \end{aligned} \quad (3.14)$$

Since $z_2 < z_l$ and $h_2 < h_l$, the third term and fourth term in equation 3.14 will become negative. To maintain pinning state, the absolute magnitude of the first term and second term must be larger than that of the third term and fourth term. This can be achieved by using liquid of higher surface tension, substrate A of higher surface energy and surface relief of larger thickness and better wettability. Wettability of liquid film over substrate A and surface relief will

stabilize the pinning of wetting film. Depinning is prone to occur if θ_b is more than 90° , which is in accordance to the force analysis in section 3.4. Higher thickness of surface relief could help to reduce the particle friction required to achieve pinning, as concluded in equation 3.10.

In section 3.3.5, particles were observed to assist pinning of water film, giving rise to larger pinning distance (>1.5 mm). In case 3, thinning of wetting film exposes particles partially to the air, giving free energy state of:

Case 3: Particles are pinned by wetting film

$$FE_{particle\ pinning} = \gamma_{bv}(A_b) + \gamma_{bl}(tw) + \gamma_{lv}\{wz_1 - \sum_{i=1}^n \pi h_1(2R - h_1)\} + \gamma_{pv} \sum_{i=1}^n 2\pi R(2R - h_1) + \gamma_{pl}(\sum_{i=1}^n 2\pi R h_1) + \gamma_{al}(wz_1) + \rho g w z_1^2 h_1 \quad (3.15)$$

where $a = \sqrt{h(2R - h)}$ is the base radius of the spherical cap of particle which is exposed to air.

As compared to case 1 (equation 3.12), the partially submerged particle reduces the exposure of wetting film to the vapour phase, giving the third term in equation 3.15. The fourth term and fifth term describe the exposures of particle surface to the vapour phase and liquid phase, respectively.

Hence, the change of free energy state from case 3 to case 2 would be:

$$\begin{aligned} \Delta FE_{pinned\ to\ depinned} &= FE_{depinned} - FE_{particle-pinned} \\ &= tw\gamma_{lv} \cos \theta_b + \gamma_{av}w(z_1 - z_2) + w(\gamma_{lv} + \gamma_{al})(z_2 - z_1 + \sum_{i=1}^n \pi h_1(2R - h_1)) - \gamma_{pv} \sum_{i=1}^n 2\pi R(2R - h_1) - \gamma_{pl}(\sum_{i=1}^n 2\pi R h_1) + \rho g w(z_2^2 h_2 - z_1^2 h_1) \end{aligned} \quad (3.16)$$

Similar to equation 3.14, the first term and second term are positive while the contribution of potential energy stored by pinned wetting film is negative

(the last term). However, the change of free energy state from particle-pinned wetting film to depinning state could be less favourable, if interfacial energy of particle-air γ_{pv} and particle-liquid γ_{pl} are much smaller than that of liquid-air γ_{lv} and substrate A-liquid γ_{al} . The addition of particles to the wetting front could strengthen the contribution of third term in equation 3.16. The strongest contribution of this term occurs when the particle is half submerged in the wetting film ($h_l = R$).

However, equation 3.16 does not guarantee successful pinning of particles by wetting film and then the protrusion of particles out of liquid phase. Well-stabilized colloidal particles in colloidal suspension form are indeed stable thermodynamically and do not form aggregates without thermal agitation. In vertical deposition, particles are kinetically driven to the thin meniscus (drying front) by evaporation-induced convective force. The loss of liquid at drying front increases the area of particle exposure. The continuous flux of particles to the edge of meniscus or surface relief will then stabilize the pinning, increasing the friction against the depinning tendency. This explains why an “incubation period” (1 min) is given to the self-assembly system, prior to stretching of meniscus which could possibly sweep the particles back into bulk solution. This procedure can be referred in section 4.1.2.

It is believed that the immobility of colloidal crystal formed near the surface relief could prevent early depinning of wetting film, possibility giving rise to the rupture of wetting film (under extreme stressing of the meniscus or high substrate withdrawal rate). This rupturing state leaves behind wet colloidal crystal near the surface relief and a new pinning site, giving a free energy state of:

Case 4: Rupturing of pinned wetting film

$$\begin{aligned}
 FE_{rupture} = & \gamma_{bv}(A_b) + \gamma_{bl}(tw) + \gamma_{lv}\{wz_1 - \sum_{i=1}^n \pi h_1(2R - h_1) - wz_3\} + \\
 & wz_3(\gamma_{av}) + \gamma_{pv} \sum_{i=1}^n 2\pi R(2R - h_1) + \gamma_{pl}\{\sum_{i=1}^n 2\pi R h_1\} + \\
 & \gamma_{al}(wz_1 - wz_3) + \rho g z_2^2 w h_2
 \end{aligned} \tag{3.17}$$

Since $z_3 = z_1 - z_2$, equation 3.17 can be further reduced to

$$\begin{aligned}
 FE_{rupture} = & \gamma_{bv}(A_b) + \gamma_{bl}(tw) + \gamma_{lv}\{wz_2 - \sum_{i=1}^n \pi h_1(2R - h_1)\} + \\
 & w\gamma_{av}(z_1 - z_2) + \gamma_{pv} \sum_{i=1}^n 2\pi R(2R - h_1) + \gamma_{pl}\{\sum_{i=1}^n 2\pi R h_1\} + \\
 & \gamma_{al}(wz_2) + \rho g z_2^2 w h_2
 \end{aligned} \tag{3.18}$$

Free energy change from case 3 to case 4,

$$\begin{aligned}
 \Delta FE_{particle-pinned \text{ to rupture}} &= FE_{rupture} - FE_{particle-pinned} \\
 \Delta FE_{particle-pinned \text{ to rupture}} &= w\gamma_{av}(z_1 - z_2) - w\gamma_{al}(z_1 - z_2) - w\gamma_{lv}(z_1 - \\
 & \quad z_2) + \rho g w(h_2 z_2^2 - h_1 z_1^2) \\
 &= w(z_1 - z_2)[\gamma_{lv}(\cos\theta_a - 1)] + \rho g w(h_2 z_2^2 - \\
 & \quad h_1 z_1^2)
 \end{aligned} \tag{3.19}$$

where $\gamma_{av} - \gamma_{al} = \gamma_{lv}\cos\theta_a$

Since $z_1 > z_2$, $h_1 > h_2$ and $0^\circ < \theta_a < 90^\circ$, both terms in equation 3.19 are hence negative, giving $\Delta FE_{rupture,particle, pinning} < 0$.

This shows that rupturing of wetting film is favourable as it reduces the energy state. It is also difficult to prevent such rupturing as θ_a is normally larger than 0. To minimize the rupturing tendency, the wetting on substrate should be maximized ($\theta_a \approx 0$) and the thickness of surface relief should be minimized (so that $h_1 \approx h_2$). As discussed in case 3, slower withdrawal rate of substrate may help to stabilize particle-pinned wetting film, allowing new pinning lines to be

formed near the circumference of the spherical cap of protruding particles (out of wetting film), as shown in Figure 3.18.

However, the trapping and adsorption of surfactants near the particle surfaces could significantly lower the local surface tension of wetting film, possibly causing the cleavage of wetting film near the particle surface. As a result, the limit of gravitational force used to stretch the meniscus before rupturing should be measured (as per discussion in section 3.2). In the next experimental chapter, the meniscus would be stretched at a moderate rate such that sufficient particle flux is allowed to assist pinning and avoid rupturing. For growth front longer than 1 mm, new pinning site could be expected to form near at the growth front, without experiencing rupturing and total depinning from the growth front. Most importantly, a perfect crystal seed could be formed and stabilized before colloidal film depinning or rupturing, leading to the inplane control of monolayer colloidal crystal.

3.6 Conclusion

This chapter serves the purpose to verify the water affinity to SU8 surface upon UV-ozone treatment. At the same time, the quantification of pinning force is demonstrated using a weighing balance. In contrast to the standard tensiometer which holds the substrate of measurement to the pressure transducer, this method does not limit the size of patterned substrate, offering great advantage in metrology of large-scale production.

The second part of the chapter discusses an optical inspection method of successful meniscus pinning, followed by the measurement of pinning distance. Colloidal suspension with various SDS concentrations were studied, revealing

the optimum condition of SDS interaction with the interface of SU8/silicon wafer.

The third part provides an analysis of capillary pinning near the surface relief and the pinning of particles under the formation of meniscus wedge near surface relief. This analysis discusses the importance of obtaining smaller critical receding angle ($\mu \geq \tan\beta$) to achieve capillary pinning of particles. This step is critical to prevent early depinning of wetting film before the formation of nucleation seed. A relationship describing the apparent contact angle β' (with surface relief), β (without surface relief) and the thickness of surface relief t is given, indicating lower required particle friction for successful pinning: $\mu \geq \tan\beta - t/R$

Also, a thermodynamic model is provided to analyse the different states of pinning, depinning and rupturing of wetting film, with the consideration of surface relief height. It is recommended to use substrate of higher wettability and the thickness of surface relief must be optimized to improve pinning and prevent film-rupturing. To better complement the explanation, a force analysis involving particle friction is provided to explain the contribution of particles in pinning. Despite the possibility to increase the pinning force, it cannot exceed the surface tension of wetting film, which holds the solvent molecules together.

To conclude, this chapter serves as the foundation to achieve a straight three-phase contact line of wetting film, prior to the in-plane control of monolayer colloidal crystal growth, which will be discussed in the next chapter.

Chapter 4: Controlling In-plane Growth by Meniscus Pinning

The study of pinning enhancement in previous chapter serves as a guide to obtain stable and straight contact line of meniscus confinement, prior to in-plane growth of colloidal crystal. Here, strong pinning line not only maintains the required meniscus wedge for seeding colloidal crystal growth, it could also prevent depinning during the in-plane growth of colloidal crystal.

4.1 Experimental Procedure

4.1.1 Materials

Monodisperse polystyrene (PS) spheres with sulphate groups (1wt% aqueous dispersions, 800 nm in diameter, surfactant-free) were obtained from Duke Scientific. The aqueous suspension was then diluted to 0.25 wt% with DI water. As the effect of SDS concentration [98, 100] to the surface tension of liquid film must be minimized to prevent undesired rupturing of film during stretching, only 0.05 mg/ml of SDS concentration was added.

4.1.2 Experimental Setup

Similar to the setup used in pinning studies, the chamber was first filled slowly with colloidal suspension up to the edge of surface relief (Figure 3.5). Alternatively, lower stage can also be moved vertically upwards (1-20 $\mu\text{m/s}$) to achieve pinning of meniscus along the edge of surface relief. Upon successful pinning, one minute of equilibrium time was given for particle accumulation and seed nucleation of colloidal crystal. To minimize the evaporation rate and particle flux, the assembly of particles was done at room temperature (25°C).

At slow convective flow, the substrate was withdrawn at a speed of $1.5 \mu\text{m/s}$ for one min, and gradually slowed to $0.5 \mu\text{m/s}$ for subsequent growth.

4.1.3 Characterization

Using scanning electron microscope (JEOL JSM 6360), the quality of monolayer colloidal crystal was analyzed. Along the surface relief and the growth direction, consecutive SEM photos were recorded to quantify its domain orientation and size. A wide scan up to $100 \mu\text{m} \times 1 \text{mm}$ is presented in the Appendices for evidence.

4.2 Results and Discussion

4.2.1 In-plane Growth of Colloidal Crystal

The understanding acquired in the observation of pinning distance by various composition of colloidal suspension helps in the formulation of growing perfect colloidal crystal of a single layer. The following sequence of photos shows the initial pinning of colloidal suspension, followed by nucleation of colloidal domain next to SU8 surface relief and compression of bilayer colloidal crystal into monolayer colloidal crystal, upon meniscus stretching (Figure 4.1(a) – (f)).

Figure 4.1 Using meniscus pinning, capillary pressing of multilayer colloidal crystal growth front into monolayer colloidal crystal (C) is demonstrated in microscopic photo sequence above. The diagram below each photo sequence further depicts the meniscus profile during the pinning, stretching and compression. (a) Pinning is first established along surface relief (R) by advancing of three-phase contact line. (b) A minute of equilibrium enables particle accumulation near the pinned edge. (c) Buckling (B) phases are observed at region of thicker meniscus wedge. (d) A slight withdrawal of substrate stretches the pinned film to thinner meniscus, pressing multilayer crystal into monolayer colloidal crystal. (e) and (f) Further stretching of liquid film with substrate withdrawal gives uniform monolayer, limiting the buckling phase to growth front only. Yellow arrows indicate the growing direction of domain-oriented colloidal crystal while black arrows indicate the advancing or receding of bulk meniscus. Larger particle size ($1.2\ \mu\text{m}$) is used here for better clarity of multilayer formation (M).

The initial pinning of colloidal suspension allowed the accumulation of particles by convective flow. As the evaporation was minimal and the convective flux of particles was slow, an equilibrium time of one minute was given to enhance the pinning. Also, large area of particle accumulation along the surface relief was required to serve as a pinning base, giving extra friction against the detachment of contact line (and depinning) from the edge of surface relief. As the particles were trapped under the confinement of meniscus wedge,

the following substrate withdrawal (after equilibrium time) at $1.5 \mu\text{m/s}$ caused the pinned film to be stretched, resulting in thinner meniscus confinement and compression of bilayer or multilayer of colloidal structures into monolayer formation (Figure 4.1c to 4.1f). Then the gradual adjustment of withdrawal speed to $0.5 \mu\text{m/s}$ enabled the continuous growth of monolayer colloidal crystal (Figure 4.1f). This speed is in accordance to the observed growth rate of monolayer colloidal crystal.

In Figure 4.1 and Figure 4.2, the microscopic observation shows that the straight contact line successfully pinned along the surface relief sets a straight seeding line for nucleation and growth of colloidal crystal. Without surface relief, a wavy contact line was observed to give different growing directions from the non-straight initiation edge, resulting in distinct domain boundaries (Figure 2.9). As the close-packed arrays formed along surface relief will subsequently become the crystal seed for in-plane oriented growth, successful pinning of straight contact line is critical and the crystal seed formed must be perfect, or else non-uniform growth direction will give rise to domain boundaries. In both cases of bare substrate and substrate with surface relief, vivid fingering effects are observed above the assembled crystal at regions away from the pinned contact lines, where the meniscus thickness is slightly higher. Continuous pulling (or stretching) of bulk meniscus and drying of wet colloidal crystal near the original pinned line may possibly allow part of the assembled colloidal particles to protrude out of the meniscus. Eventually, this may create many microscopic pinning lines surrounding partially submerged particles. As more surface area to water film is being created, the local pinning strength may not be sufficient to resist dewetting at the particle level. As a result, Rayleigh

instability may prevail to minimize surface area, creating fingering effects over assembled crystal.

Figure 4.2 (a) Similar to larger particle size in Figure 4.1, straight contact line assisted by surface relief sets a straight initiation line for nucleation and growth of colloidal crystal. (b) SEM shows the result of domain-oriented growth of colloidal crystal from the edge of straight surface relief, with particles being lined up in the close-packed direction $\langle 10 \rangle$ or $\langle 11 \rangle$, along the surface relief. Red lines drawn serve as a guide to illustrate the high degree of directionality and perfect orientation under the straight pinning effect. Particle size used: 800 nm. Scale bar: 8 μm .

Despite vivid fingering effects of wetting solvent observed above the assembled colloidal crystal, as indicated in Figure 4.2a, they do not cause significant disturbance to the in-plane-oriented growth of colloidal crystal from the straight pinning line. Also, the assembled colloidal crystal before the fingering zone remains wet, pinned at respective contact lines which nucleate the growth. Hence, it can be concluded that Rayleigh-instability induced wavy contact lines could be minimized or eliminated using the engineered surface relief, prior to colloidal crystal nucleation and growth.

Figures 4.2(a) and 4.2(b) show the monolayer formation of colloidal particles packed along the surface relief, in a close-packed direction of $\langle 11 \rangle$ or $\langle 10 \rangle$. This straight line-up of particles forms a straight crystal growth front,

leading to unidirectional domain growth. Since evaporation is confined only to the meniscus edge, the directional convective flow of particles supplies free particles to the growth front, maintaining the array growth. Here, a few precautions were made to ensure no interruption of colloidal deposition. For example, withdrawal speed of substrate is critical to ensure relatively fast colloidal deposition to prevent pre-rupturing of liquid film, leaving behind empty bands or colloidal stripes [37, 73]. As discussed earlier in the pinning studies (Chapter 3), the assembled crystal could serve as pinning sites to prevent the early depinning of meniscus from the surface relief or delay the stick-slip phenomena. Also, extremely slow withdrawal speed may give rise to rigid multilayer formation, which are difficult to be compressed by capillary meniscus. Often, the reduction of meniscus height causes particle protrusion and rapid drying of assembled colloidal crystal.

A slow and controllable speed of particle flux to the ordered and oriented growth front results in large monolayer crystal domain (Figure 4.2(b) and Appendix II). Although this assembly process takes longer than that of spin coating [30], it offers control over domain orientation relative to the predetermined surface relief. Red lines drawn in Figure 4.2(b) and Appendix II indicate the excellent control over intended domain growth direction that leads to uniformity of domain orientation. The perfect orientation with respect to the surface relief and the high degree of directionality for engineered pinning assembly in Figure 4.2 are supported by intensity line-plot profile generated using ImageJ [102], shown in Figure 4.3(a). For comparison, similar line-plot obtained from colloidal assembly on bare substrate Figure 2.9(b) is presented in Figure 4.3(b). In addition, consecutive scans of SEM photos over large area are

provided in Appendix II to demonstrate the predetermined domain orientations, with respect to the surface reliefs.

Figure 4.3 From SEM photos from Figure 2.9(b) and 4.2(b), the directionality and quality of colloidal crystal are analyzed using line-line plot profile in Image J, along the middle red line in 4.2(b) and 2.9(b) respectively.

4.2.2 Domain Size and Quality

Conservatively, the observed domain size of monolayer colloidal crystal is as large as 1 mm^2 . As prolonged solvent evaporation could increase the particle concentration, higher flux of colloidal particles to the growth front is observed after growing 1 mm distance from the edge. As a result, the growth becomes uncontrollable at large area and multilayer formation is often observed. Hence, larger volume of chamber could be used to minimize the change of particle concentration over time.

According to the SEM photos in Appendix II, the domain orientation of large crystal domain remains similar, despite the existence of small misoriented domains found within the crystal. The creation of misoriented domains can be attributed to unclean colloidal suspension, non-uniformity of particle size or presence of foreign particles on substrate. Besides, defects like twinning and particle vacancies are also observed during the characterization. Twinning can be attributed to the crystal strain created within large domain of colloidal crystal

while the vacancy formation can be explained thermodynamically. From the observation, these small defect formations did not bring much disturbance to the direction of crystal growth front. Occasional occurrence of small multilayer domain seems correlated to dirt and dust particles (Figure 4.4), which alter the surrounding meniscus thickness during the growth. This multilayer domain could however disturb the unidirectional growth of colloidal crystal, giving rise to domain boundaries and mismatches.

Figure 4.4 Presence of dust particle could alter the meniscus in vicinity, leading to multilayer formation. Scale bar: 8 μm .

4.2.3 Size of Particles

For visual clarity under the optical microscope, large colloidal particles (> 800 nm) were used in this study. Relatively smaller particles under the current meniscus thickness induced by 200 nm surface relief may produce bilayer or multilayer colloidal crystal. Other than high monodispersity of particle size and suspension quality, it is important to engineer a uniform thickness of meniscus relative to the size of particles used. For smaller particle assembly, smaller heights of surface relief or self-assembled monolayers of organic molecules (SAMs) can be coated to engineer pinning line with the suitable meniscus

wedge of the right thickness and contact angle. Most importantly, straight pinning line must be achieved and fingering instability of contact line must be greatly eliminated, prior to colloidal crystal nucleation and growth.

4.3 Conclusion

By engineering the pinning of a straight contact line, the control of in-plane orientation of monolayer colloidal crystal growth is demonstrated. The formation of straight contact line allows a unidirectional flux of colloidal particles to the linear evaporative edge of pinning line, giving rise to a linear nucleation of $\langle 11 \rangle$ colloidal lines (or $\langle 10 \rangle$ as of hexagonally close-packed lattice). Subsequent colloidal deposition in a uniform direction perpendicular to the most close-packed directions will eventually lead to a large single domain of monolayer colloidal crystal (1 mm^2). Also, an insight on how engineered pinning could allow excellent control over growth direction of particle arrays and desired domain orientation is given. Despite the unique advantage of this method and its potential use in applications that require high crystallinity, better control over array growth must be achieved with dilute and constant concentration of colloidal suspension during the particle deposition. This is because long period of evaporation and increased concentration could lead to accumulation of extra particles, resulting in multilayer formation. Besides, contamination-free substrate and uniform thickness of pinned suspension film are critically required.

Chapter 5: Electric Field Induced Kinetics Near A Surface

Relief

The use of alternating electric field to induce two-dimensional nucleation and growth of colloidal crystals on electrode surface has been fascinating [49, 78], especially when it comes to the ease to use voltage to control clustering rate. However, the nucleation of particle clusters can occur anywhere on the electrode, leading to multi-domain growth. Without induced evaporation, driving all the particles to concentrate at a desired location is not easy, let alone achieving preferred nucleation for subsequent in-plane growth. Here in this chapter, two electrokinetics phenomena are explored to propose an electrode design that can enable preferred nucleation of two-dimensional colloidal crystal growth:

- a. Alternating Current induced Electro-osmosis (ACEO)
- b. Dielectrophoresis (DEP)

5.1 Theoretical Basis

In most electrokinetics studies [103, 104], ACEO and DEP often complicate each other. The presence of surface irregularities, or protruding electrode surface like surface relief in this case, often produces non-uniform field that gives rise to DEP forces. The concentration gradient of conducting ions due to alternating electric field [105] also produces ACEO stress to drive ion movement around the edge of surface relief. As DEP is known to be short-

ranged, particles suspended away from the surface relief may not experience the distorted non-uniform field produced. Hence, contributions of DEP and ACEO caused by surface irregularities like surface relief or approaching particles must be clearly determined and identified.

5.2 Dielectrophoresis

DEP is a directed motion driven by the interaction of non-uniform field with the induced dipole moment [106]. In AC electric field, the time-averaged DEP force on a spherical particle is proportional to the gradient of the square of the electric field [106, 107]:

$$\langle F_{DEP} \rangle = \pi r^3 \epsilon_m \text{Re} \left(\frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{\tilde{\epsilon}_p + 2\tilde{\epsilon}_m} \right) \nabla |\vec{E}|^2 \quad (5.1)$$

where r is the particle radius. Assuming there is no spatially varying phase, $\text{Re}[(\tilde{\epsilon}_p - \tilde{\epsilon}_m)/(\tilde{\epsilon}_p + 2\tilde{\epsilon}_m)]$ is the real part of the Clausius-Mossotti factor (CMF). $\tilde{\epsilon}_p$ and $\tilde{\epsilon}_m$ are the complex permittivity of particle and medium respectively. Then the real part of CMF could be expanded into:

$$\text{Re} \left(\frac{\tilde{\epsilon}_p(\omega) - \tilde{\epsilon}_m(\omega)}{\tilde{\epsilon}_p(\omega) + 2\tilde{\epsilon}_m(\omega)} \right) = \left(\frac{(\epsilon_p^2 + \epsilon_p \epsilon_m - 2\epsilon_m^2)\omega^2 - (2\sigma_m^2 - \sigma_p^2 - \sigma_m \sigma_p)}{(\epsilon_p + 2\epsilon_m)^2 \omega^2 + (2\sigma_m + \sigma_p)^2} \right) \quad (5.2)$$

where σ_p and σ_m are the electric conductivities of particle and medium, respectively. In low-frequency AC or DC electric fields, the real part of CMF factor could be approximated to

$$\text{Re} \left(\frac{\tilde{\epsilon}_p(\omega) - \tilde{\epsilon}_m(\omega)}{\tilde{\epsilon}_p(\omega) + 2\tilde{\epsilon}_m(\omega)} \right) \approx \left(\frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m} \right) \quad (5.3)$$

In aqueous solution, diffuse double layer forms at the interface of a charged particle and its suspending medium. The associated double layer will contribute to the permittivity of particle. As diffuse double layer responds to alternating electric field at low frequency, surface conductivity of particle can be more polarized than that of medium conductivity, giving positive CMF below the crossover frequency [106, 108, 109]. Above this, polarization of diffuse layer cannot respond fast enough, and hence the CMF factor can only be influenced by the electronic polarization of electron clouds surrounding the atomic nucleus.

At positive CMF, non-uniform field will drive polarized particles to the high field region, giving rise to positive Dielectrophoresis (p-DEP). On the other hand, less polarized particles in a relatively conductive medium will give negative value of CMF and negative DEP force, driving particles towards low field region.

In the scope of this thesis, low-frequency (< 2 kHz) regime is used to apply the electro-osmosis effect to induce aggregation of particles on electrode surface. In this regime, p-DEP can be used to drive charged particles towards the high field region – the edge of protruding electrode surface, prior to surface aggregation or clustering of particles by electro-osmosis.

Assuming a smooth surface of homogeneous particle in a system of small Reynolds number (< 1) where viscous forces are dominant with laminar flow,

spherical particles in a fluid medium of viscosity η will experience Stokes' drag [110] during the acceleration induced by DEP force. Using Newton's second law of motion,

$$F_{DEP} - \text{Stokes' drag} = m\mathbf{a}$$

$$F_{DEP} - 6\pi\eta rv = m\mathbf{a} \quad (5.4a)$$

Since the m constant is small, " $m\mathbf{a}$ " term could be neglected. The terminal velocity of particles can then be estimated.

$$F_{DEP} = 6\pi\eta rv \quad (5.4b)$$

5.3 AC Electro-osmosis

Other than DEP, the tangential component of the external alternating field can drive ion movements near the electrode [103], contributing to ACEO flow and particle motion. In an AC switching field, the counterions that form the diffuse double layer near electrode surface will experience the constant reversal of electrode charge. Near electrode surface, the presence of surface irregularities like surface relief and particles (or particle clusters) could give rise to uneven charging speed and non-uniform distribution of screened counterions. At low frequency (< 3 kHz), this imbalance of ion distribution is able to produce a tangential flow over the electrode surface [105], driving particle motion. This phenomenon also explains the particle aggregation and clustering observed on flat surface of parallel electrode arrangement [45, 85]. To account for the electrokinetic effect in the absence

or presence of particles near the surface relief, the ion species concentration c_i , electric potential ϕ in a weakly conducting dielectric liquid and the electrostatic-driven local bulk fluid velocity $\mathbf{u}$ can be described by Poisson-Nernst-Planck equations [111]. Assuming a dilute solution of 0.5 mM KCl, the conservation of mass in Nernst-Planck would give:

$$\left(\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i\right) = \nabla[D_i \nabla c_i] + D_i z_i c_i \nabla \frac{e\phi}{k_B T} \quad (5.5)$$

where the electrostatic potential is described by Poisson equation, which relates the electric potential to the charge density.

$$-\nabla \cdot (\epsilon \nabla \phi) = \sum_{i=1}^n z_i e c_i \quad (5.6)$$

where D_i , k_B and z_i refer to the diffusion coefficient, Boltzmann constant and charge number of the ion species, respectively.

The imbalance of ion distribution near the surface irregularities will produce electrostatic force that will drive the motion of ion species, adding a body force density term $\mathbf{f}_e$ into Navier-Stokes equation of incompressible flow.

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}\right) = -\nabla p + \eta \nabla^2 \mathbf{u} + \mathbf{f}_e \quad (5.7)$$

$$\mathbf{f}_e = -\sum_{i=1}^n z_i e c_i (\nabla \phi) = (\epsilon \nabla^2 \phi)(\nabla \phi) \quad (5.8)$$

where η is the dynamic viscosity (10^{-3} Pa·s), $\mathbf{u}$ is the velocity, ρ equals the fluid density (1000 kg/m³), and p refers to the pressure (Pa). For an incompressible fluid that describes the conservation of mass of the fluid, the continuity equation $\nabla \cdot \mathbf{u} = \mathbf{0}$ will be used in the numerical calculation in COMSOL®.

However, ions close to the electrode surfaces will experience large viscous drag, forming a non-slip plane. Electroosmotic flow will occur mostly outside the diffuse double layer, like a plug flow slipping over the surface. This can be represented by Helmholtz-Smoluchowski equation in Equation 2.4.

5.4 Finite Element Method of Modeling

Since the flat electrode surface in parallel arrangement provides an excellent platform for electrohydrodynamic-driven particle clustering, the idea to introduce a line of insulating or conducting surface relief was studied using COMSOL® modeling. A simple line of surface relief is preferred to the submicron resolution of gratings or patterning, as they require expensive and complex lithography tools which are not practical for mass production.

5.4.1 Electric Field Intensity Profile

In an electrolyte environment in which the suspended particles are more polarized like charged silica particles at low frequency [12, 109] and gold nanoparticles, they will experience positive DEP and move toward the region of high field intensity. As edges and sharp corners are commonly observed to produce highest field intensity, these zones can be the preferential adsorption sites for silica particles [107]. To engineer a perfect

nucleation seed of colloidal domain, a straight edge of conductive surface relief can be produced to attract a line of silica arrays. Hopefully, the accumulated silica particles along this edge could later undergo clustering and ordering (by AC electro-osmosis), subsequently giving rise to in-plane growth of colloidal crystal. Using Finite Element Modeling (FEM) in COMSOL®, the electric field intensity profile for surface reliefs made of insulating surface and conductive surface are first compared (Figure 5.1a and 5.1b), then followed by designs where the elevated and depressed zone are fully coated with conductive layer (Figure 5.1c and 5.1d).

Figure 5.1 Electric field intensity plots for flow cells with ITO forming the top electrodes, and the bottom substrates are each made of (a) conductive surface relief on insulator substrate, (b) insulated surface relief on conductive substrate, (c) conductive surface relief on conductive substrate, and (d) conductive gratings of 10 μm pitch and 1 μm height. The gap between each

set of the parallel electrodes is 100 μm . Yellow lines indicate conductive gold layer.

According to the electric field distributions plotted in Figure 5.1, the sharp corners of both the elevated conductive and insulating surface relief produce the highest field intensity. This could explain preferential adsorption of highly polarized particles like gold nanoparticles to these edges if electric field is applied, or if the positive dielectrophoresis is allowed for charged dielectric particles under certain frequency regimes [107, 112-114]. For instance, 2 μm silica particles were observed to be attracted to the edge of insulated SU8 surface relief at 150 kHz (Figure 5.2) and edge of conductive surface relief below 1 MHz (Figure 5.3a). The movement of particles from suspending medium to the edge is slow at these intermediate frequencies (about 2 to 5 min), as the contribution by electro-osmosis is minimal. No clustering, ordering or packing of particles was observed. The adsorbed particles remain stationary on electrode surface. This is in accordance to DEP experiment using micrometer-spaced electrodes [107], where particles being attracted to low field or high field region without clustering and ordering.

When the frequency is reduced to 10 kHz, significant movement of particles were found, giving rise to weak ordering of colloidal arrays along the edge of conductive surface relief. The elevated and depressed zone of this bottom electrode was both coated with gold, similar to the case shown in Figure 5.1c and 5.1d. It is also interesting to note that the depressed zone could serve as a zone for low field intensity. This could explain a slight

repulsion of particles away from the side of surface relief observed in Figure 5.3.

Figure 5.2 Silica particles are being attracted to edges of insulating SU8 surface relief, which is sitting on top of conductive silicon wafer. The ITO substrate serves as counter electrode above this template (Grating with 120 μm pitch), giving a gap of 100 μm . Scale bar: 20 μm

Figure 5.3 Silica particles are attracted to the edge of conductive surface relief (both depressed **V** and elevated **E** zones are coated with gold) at a) 1 MHz) and b) 10 kHz alternating field. $V_{pp} = 10$ V. Scale bar: 20 μm

If local concentration of approaching particles near the edge of surface relief can be concentrated, it is likely to observe electrohydrodynamic clustering and ordering of close-packed colloidal domains here [85] preferentially. Although the edges of insulating surface relief (sitting on

conductive substrate) could assist the preferential adsorption of particles, it may not allow hydrodynamic clustering due to electro-osmosis. Insulated surface may not provide sufficient electro-osmotic flow, as it does not generate charged ions with the response to electric field.

A very good example is shown in Figure 5.4, where distinct accumulation of particles on insulated surface relief (yellow) was observed at low frequency (10 kHz). There is no clustering and ordering observed on this insulated surface. The effect of p-DEP on silica particles was not significant here, and almost all particles were observed to be repelled from the polarized surface of electrode (white). This phenomenon is in contrast to the DEP effect shown in Figure 5.2 and 5.3, where electro-osmosis could be negligible. At 10 kHz, electro-osmotic flow generated from conductive surface (depressed zone: silicon) cannot be ignored as it pushes particles away from the electrode surface. It is also clear that particles were less likely to attach to the edges of insulating SU8, which produces highest field intensity. This could be due to stronger osmotic flow from the silicon surface, competing with the attraction of particles to the edges by p-DEP.

It is important to note that there is no clustering or ordering of particles hovering above the insulated SU8 surface. It is also obvious that electro-osmotic flow generated over electrode surface is pushing particles to the insulated SU8 surface at low frequency (<10 kHz), increasing particle density

over insulated surface. More discussion on electro-osmosis can be found in the following section.

Figure 5.4 a) Microscopic photo shows the accumulation of particles over the insulated SU8 surface relief. b) Diagram shows the electro-osmotic forces generated over the conductive region, repelling particles to SU8 surface. Regions in yellow are surface reliefs made of SU8 photoresist while the white areas are conductive silicon surface (80 μm pitch of SU-8 gratings). Scale bar: 20 μm

5.4.2 DEP Force

As DEP depends strongly on the gradient of the square of electric field intensity (Equation 5.1), the force that acts on charged silica particles can be computed from the electric field intensity profile produced in COMSOL®. In a cell of parallel electrodes with 100 μm gap, the highest field intensity near the edge of conductive surface relief can reach up to 10^4 V/m (assuming $V_{rms} = 5$ V). Using the time-average value of Equation (5.1), DEP force is thus computed and plotted based on the electric field profile in Figure 4.5a. Near the edge of conductive surface relief, the force of attraction could be as high as 0.2 pN.

Figure 5.5 a) Electric field intensity produced near the edge of conductive surface relief. b) Dielectrophoretic force induced by enhanced electric field near the edge of surface relief in a). $V_{rms} = 5$ V, $2\text{ }\mu\text{m}$ silica particle, and $CMF = 0.2$.

The terminal velocity of $2\text{ }\mu\text{m}$ silica particle is then estimated by considering the Stokes' drag in Equation (5.4), as shown in Figure 5.6. It is obvious that the velocity field of silica particle (DEP force vector) is pointing from the bulk towards the edge of surface relief. However, the low field region near the side front of surface relief could cause the particles in this zone to move away, eventually moving back to the edge of surface relief if possible.

Figure 5.6 Simulation plot shows the velocity vector and magnitude of DEP driven particle, computed based on the electric field intensity profile in Figure 5.5 a).

Without the consideration of electro-osmotic flow near electrode surface, particles are only attracted by p-DEP to the highest field zone. The strong adhesion of particles to this edge by p-DEP force is important, as strong electro-osmosis or other electrohydrodynamic forces at low frequency may cause disturbance to the nucleated colloidal domain here.

5.4.3 ACEO Flow

To further investigate the contribution of AC electro-osmosis, ACEO induced flow in the absence or presence of approaching particles near the edge of insulating and conducting surface relief are compared (Figure 5.7). In the case of insulated surface relief partially deposited on conductive surface, electrode surface (yellow) is charging in response to alternating electric field, serving as a source of ion flow. This strong osmotic flow ($\sim 400 \mu\text{m/s}$) is responsible for the instant repulsion of silica particles from charged

electrode to SU8 surface, as shown in Figure 5.7a. Similar flow is also observed from an elevated conductive surface relief that is patterned on an insulated SU8 substrate (Figure 5.7b). This explains why the tangential component of electric field over polarized electrode could play an important role in driving fluid movement, especially near the interface of different electrical properties. As described by Trau *et al.*, a spatially varying “free charge” could be produced by lateral variations in the amount of concentration polarization across the interface of insulated SU8 and conductive gold electrode. Tangential component of electric field will then act on these free charges, producing fluid motion.

Figure 5.7 AC electro-osmotic flow near the edge of a) insulated SU8 surface relief on conductive electrode and b) conductive relief on SU8 substrate. Yellow and white zones represent the conductive surface and SU8 layer, respectively. The red arrows indicate the directions of osmotic flow.

As electrode surface is required for clustering of silica particles, electrode design shown in both Figure 5.7a and 5.7b cannot be used, as osmotic-induced fluid flow will repel particles away from electrode surface.

Figure 5.8 Surface velocity plots with flow fields describing the ACEO flow, in the a) absence of particle, and the presence of particle at b) $x=150 \mu\text{m}$, c) $135 \mu\text{m}$ and d) $165 \mu\text{m}$ over the conductive surface with a thin surface relief. The yellow dashed arrows indicate the position of the edge of surface relief at $x=150 \mu\text{m}$. The surface relief has a height of 200 nm ($0 \mu\text{m} < x < 150 \mu\text{m}$). The red arrows indicate the directions of osmotic flow.

Hence, a thin conductive surface relief patterned on a flat conductive substrate is proposed, serving as a bottom electrode (in a parallel electrode arrangement) for guided colloidal crystallization. From ACEO simulation (Figure 5.8a), the flow is rather weak and negligible near a thin (200 nm) conductive relief on a flat electrode surface. According to Bazant's model [105] of induced charged electro-osmosis, higher electric field could attract denser layer of charged ions, giving rise to a gradient flow from denser charged layer to a region of low charge concentration. However, the density of induced charges between the depressed zone and elevated zone of electrode surface could be almost similar since the elevated zone is only 200 nm higher.

In the presence of a single particle at $x = 135 \mu\text{m}$ (Figure 5.8c) and $165 \mu\text{m}$ (Figure 5.8d), electro-osmotic induced flows increase significantly to $15 \mu\text{m/s}$, pushing the particles towards the edge of surface relief at $x = 150 \mu\text{m}$, as indicated by the yellow dashed arrows. In accordance to experimental observation [45, 85, 103], ACEO induced flow is rather long-range compared to the contribution of DEP (Figure 5.6 and 5.7), extending throughout the simulation cell. When the particle approaches near the edge of surface relief, the fluid flows from both sides become almost equal (Figure 5.8b), with only flow reversal coming from the top of the particle surface. This could indicate high tendency of particle clustering induced by ACEO along the edge of

surface relief, potentially leading to the preferential nucleation of colloidal crystal (Figure 5.3b). The finding here is analogous to the sweeping of colloidal particles into densely packed assemblies by the disruption of concentration polarization of electrode surface in the presence of surface inhomogeneity or colloidal particle over a flat electrode surface [85, 86]. However, strong reversal from the top of particle surface in Figure 5.8b may destabilize colloidal clusters grown along the edge of surface relief, unless they are strongly attracted to the high field region by p-DEP. In our experiment, the observed horizontal speed towards the edge of surface relief is about 10 – 20 $\mu\text{m/s}$. Interestingly, the terminal velocity due to DEP-driven motion is estimated to be comparable to that obtained via ACEO flow.

Also, it is important to note that there could be overestimation of ACEO induced flow from the widely used Helmholtz-Smoluchowski model (Equation 2.4) [115-117]. This theoretical velocity is strongly dependent on the fixed zeta potential of both the electrode and particle surface, which may not be true when there is a spatial variation of charge density over the polarized electrode, or if the double layer is not infinitely thin. The standard model used could sometimes overestimate the osmotic flow by an order, let alone the complication given by the presence of ions in the systems or strong dynamic ion crowding on electrode surface. (The correction factors can be obtained from the comprehensive review published by Bazant *et al.* [117]). Despite the reported discrepancies, the standard model is sufficiently

accurate to provide the flow fields and induced velocity near the edge of conductive surface relief, especially in the presence of colloidal particle.

5.4.4 Size-dependent behaviour and binary colloidal crystal

To study if binary colloidal crystal could be engineered, the size-dependent effect of DEP and ACEO in the proposed experimental cell would be discussed here. From equation (5.4), DEP-driven particle velocity scales with the square of particle size [106]. Particles with twice the size will experience stronger DEP force by four times, if the CMF factor remains similar.

$$v = \frac{r^2 \epsilon_m}{6\eta} Re \left(\frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{\tilde{\epsilon}_p + 2\tilde{\epsilon}_m} \right) \nabla |\vec{E}|^2 \quad (5.9)$$

The size-dependent or polarizability-dependent DEP force could be useful in achieving stoichiometry combination of binary concentration. For example, 1 μm and 2 μm particles could accumulate near the conductive edge in a local ratio of 1 to 4, giving the possibility of forming binary clusters [118]. However this may not be true as the growth continues, as the adsorption of particles near the conductive edge will reduce the induced electric field gradient. ACEO flow will then become the dominant force to grow the colloidal clusters. As a result, particle speed in a ratio of 1 to 4 could not be maintained, and hence the binary concentration of 1 μm and 2 μm particles.

Helmholtz-Smoluchowski model in equation 2.4 indicates that electro-osmotic flow near electrodes is independent of particle size and shape.

However this may not be true, as the size and geometry of particles will distort the electric field in different fashions. Finite element model used in section 5.3 is used to demonstrate ACEO flow if a larger particle ($4\text{ }\mu\text{m}$) is located $15\text{ }\mu\text{m}$ away from the edge of conductive surface relief. It is found that the ACEO flow velocity near the particle increases by two times (Figure 5.9). The direction of flow remains similar to that of smaller particle ($2\text{ }\mu\text{m}$), shown in Figure 5.8d.

Figure 5.9 Surface velocity plots with flow fields describing the ACEO flow, in the presence of particle at $x = 165\text{ }\mu\text{m}$ over the conductive surface with a thin surface relief. The yellow dashed arrow indicates the position of the edge of surface relief at $x = 150\text{ }\mu\text{m}$. The surface relief has a height of 200 nm ($0\text{ }\mu\text{m} < x < 150\text{ }\mu\text{m}$).

Without considering DEP force, it is clear that the larger particle could move faster in the proposed experimental cell, adding difficulty in maintaining identical flux rate of particles of different sizes during binary colloidal crystal growth. Additional control could be introduced by engineering the surface or functional group of particles, in order to modify the polarizability of particle or CMF factor [118, 119], as indicated in

equation 5.3. For example, CMF factor could be reduced to compensate the effects of larger size. With identical DEP contribution, binary particles of different size could be moved by ACEO force in a predictable fashion. However, controlling in-plane growth of binary colloidal crystal is not within the scope of this thesis.

5.5 Conclusion

In this chapter, the contribution of DEP and ACEO forces near the edge of conductive or insulated surface relief are presented with COMSOL® modeling. To supplement the simulation, experimental observations are also presented to explain the electro-kinetics near the surface relief under action of alternating electric field.

From electric field intensity plot (Figure 5.1), particles will be attracted by p-DEP to the highest field zone near the edge of surface relief, regardless of conductive or insulated surface relief. However in both simulation and experiment, ACEO forces was observed to push particles away from the conductive zone to the insulated zone. As electrode surface is required for clustering of silica particles, electrode design shown in both Figure 5.1a and 5.1b cannot be used to induce nucleation of particle clusters.

Hence, a cell design with conductive surface relief on one side of conductive substrate (Figure 5.1c) was chosen to enable both the contributions of DEP and ACEO to induce preferential nucleation of particle

clusters and ordering near the surface relief. To further validate the tendency of particle clustering and its sustainability near the edge of surface relief, ACEO simulations considering the approaching particles were demonstrated in Figure 5.8. It is also believed that the particle clusters induced along the edge of surface relief are further stabilized by p-DEP force, that could potentially sustain the colloidal crystal growth. This chapter will serve as the foundation to the in-plane growth of monolayer colloidal crystal, presented in the next chapter.

Chapter 6: Electric Field Induced In-plane Nucleation and Growth of Monolayer Colloidal Crystal

The simulations of DEP and ACEO in previous chapter serves as a guide to design the experimental cell for electric field induced in-plane nucleation and growth of monolayer colloidal crystal. Here, the straight conductive edge of surface relief not only induces the strongest electric field gradient to attract particles by p-DEP force, it also helps to seed the subsequent colloidal crystal growth by ACEO force.

6.1 Materials and Methods

The experimental cell is described in Figure 1.2. Using standard photolithography, a straight line of surface relief, V-corner of 90° and 45 μm pitch of grating was developed, with SU8 resist height of 200 nm. The templates (both valley and elevated surface) were then sputter-coated with 40 nm – thick platinum and 100 nm - thick gold, forming the bottom electrodes. In a parallel arrangement, the top electrode was made of transparent ITO-coated glass (surface resistivity of 8-12 Ω/sq), sourced from Sigma-Aldrich. The cell has a gap of 120 μm , with PTFE spacer sourced from Cole Parmer.

Under the action of electric field, sufficiently high density of particles in close proximity near an electrode surface will experience electrohydrodynamic forces [44, 45], moving towards each other to form

clusters. To prevent colloidal clustering on electrode surface away from the surface relief, a dilute silica particle concentration (0.1 %Vf) was used. 2.28 μm SiO_2 particles with natural hydroxyl (SiOH) surface groups were obtained from Bangs Laboratories, Inc. The conductivity of the final suspension is about 1×10^{-3} S/m and the zeta potential of the SiO_2 particles is about -62.7 mV.

The experimental cell (Figure 1.2) was then injected with the prepared silica colloidal suspension. Immediately, an alternating field of sinusoidal wave (2 kHz, 10 Vpp) was applied to drive the just-injected particles to the surface relief by p-DEP. Subsequently, the frequency was slowly reduced to the range of 500 Hz to 1 kHz to increase the electro-osmotic flow. The assembly process was monitored and recorded using optical microscope and CCD camera.

6.2 Results and Discussion

6.2.1 Nucleation of Colloidal Domains along the Edge

Unlike most DEP-driven self assembly works [107, 113, 114, 120], the electrode surface serves as a clustering and ordering platform. Approaching particles near an electrode surface will tend to experience ACEO forces, being swept into densely packed assemblies in transverse motion. Making use of a straight conductive surface relief on the flat electrode surface, preferential adsorption of particles can be achieved along the edge of the

surface relief by p-DEP, resulting in rapid nucleation of particle clusters or colloidal domains (Figure 6.1). In short, in-plane control of colloidal crystal growth can be achieved with continuous supply of colloidal particles into the experimental cell.

Figure 6.1 Pinning of silica particles along the edge of straight surface relief in (a), followed by clustering and ordering of colloidal arrays in (b), under the action of AC sinusoidal wave at 1 kHz. V and E indicate the depressed zone and elevated zone of conductive surface, respectively. Scale bar: 20 μm

At small crystal domain or cluster size, the colloidal domain may move or reorganize along the surface relief. This could indicate strong osmotic flow to the edge of surface relief, in accordance to simulated results obtained previously in Figure 4.8. Perturbation of diffuse double layer close to electrode surface by approaching particles (or growing size of crystal domain) could further complicate the ACEO induced flow in the vicinity. It is indeed difficult to maintain $\langle 11 \rangle$ or $\langle 10 \rangle$ packing direction (as in 2D hexagonal lattice) along the straight conductive surface relief, unless field induced electro-osmotic flow is reduced with higher frequency (> 1 kHz) or smaller voltage amplitude. Interestingly, domain stability was observed to improve as it grew (> 10 rows of particle arrays), probably due to increasing

friction between colloidal domains with the double layer of electrode surface. Once the crystal domain formed along the surface relief is stable (no longer moving), incoming flux of particles will just join the nucleated crystal domain. Those particles that hover across the top of surface relief will be driven back by ACEO force to join the existing domain. Ultimately, continuous supply of particles will deposit onto both the elevated zone and depressed zone of conductive surface (Figure 6.2a). Furthermore, attractive force (0.2 pN) given by p-DEP on silica particles could also help to stabilize $\langle 11 \rangle$ or $\langle 10 \rangle$ packing direction along the edge of surface relief, as observed in Figure 6.2.

With effective preferential nucleation and clustering starting from the edge of surface relief, successful growth of monolayer colloidal arrays from the proposed designs of surface relief is demonstrated in Figure 6.2. In addition, the effectiveness of preferential adsorption and nucleation of colloidal domain is not affected by the edges positioned at different orientation to the direction of injecting particles (Figure 6.2b). As dilute concentration is required in controlling the initial stage of preferential nucleation along edges, continuous supply of particles must be supported by injection from each of the opening side. Hence, the particle arrival rate along the tilted lines shown in Figure 6.2b and 6.2c will not be uniform, giving rise to faster growth of crystal domain along the edge that is closer to the side of

cell. Following that, larger grown domains could attract any approaching particles in close proximity, rendering difficulty in epitaxial growth.

Figure 6.2 Using sinusoidal wave of alternating field at 10 Vpp, preferred nucleations were first induced by p-DEP along the edges of (a) straight surface relief (parallel to substrate edges), (b) straight surface relief tilted at 60° from the direction of particle injection, (c) V-corner of 90° and (d) grating of 45μm pitch, followed by subsequent in-plane growth and monolayer formation of colloidal crystals. Scale bar: 10 μm. E and V represent elevated surface and depressed zone (valley), respectively. Yellow arrows indicate the direction of particle injection. Red circles indicate the occurrence of voids.

6.2.2 Multiple Nucleation Sites

From the observations in Figure 6.2c and 6.2d, the presence of multiple nucleation sites during colloidal crystal growth could potentially give rise to lattice vacancy (or void) and domain mismatch, which is structurally better

than the network of finite elongated patches or interconnected bands [46] commonly found over a flat electrode (Figure 2.10). For example, V-corner of 90° shown in Figure 6.2c offers two lines of preferential nucleation. Each of them attracts neighbouring particles, driving colloidal clustering along the surface relief. If “extended arms” of V-corner is closer to the opening side, approaching particles will get adsorbed, giving rise to faster growth. It is also found that adsorbed particles along the “extended arms” do not move further to the tip of V-corner, which is expected to produce the highest field intensity. An opposite flow of particles from the other opening channel does not give significant difference either. This could possibly due to intense current flow near the tip, pushing the particles away hydrodynamically. A three dimensional ACEO flow field near the tip of V-corner is presented in Figure 6.3, where three planes of flow field (xy-, xz- and yz-planes) are given. From yz-plane, net flow from the elevated surface relief near the tip is observed, pushing particles away to the depressed zone.

Figure 6.3 The top right shows the cell containing V-corner surface relief on a surface electrode. Assuming a particle approaches near the tip of V-corner, the simulated AC electro-osmotic flows near the tip are described in the cross sections or planes at: xy-plane (bottom electrode), xz-plane and yz-plane.

Since edges of surface relief compete for approaching particles, colloidal domains grow in direction perpendicular to each other in a V-corner (Figure 6.2c) and in opposite direction in conductive gratings (Figure 6.2d). Both the 90° of V-corner and gratings of 45 μm pitch do not provide ideal commensurability to hexagonally close-packed lattices, and hence stacking faults or small voids can be found (Figure 6.2c). In addition, gratings with multiple edges of surface relief also diminish the overall DEP effect, competing with each other to attract silica particles. As a result, clustering could start anywhere along the surface relief, potentially giving rise to multi-domain growth.

Despite these, the most close-packed direction $\langle 11 \rangle$ or $\langle 10 \rangle$ can be clearly seen along all the edges of surface relief (Figure 6.2). This proves strong stabilization by p-DEP force and excellent packing quality next to the surface relief.

6.2.3 Annealing of Colloidal Crystal

Thermal cycling is frequently used to anneal atomic and molecular solids in the crystal to enhance defect recombination. Unfortunately, the free-energy barriers (V_{max} in Figure 2.2) to collective rearrangement of colloidal particles

within the formed crystals are usually large [121, 122]. The temperature range over which a desired “transition state of high particle mobility” [54] is stable can be relatively small (secondary minimum in Figure 2.2). Thermal cycling the entire suspension can easily give rise to undesirable disordering or induce disruptive convection currents.

In contrast to other methods of colloidal self-assembly [23, 30, 69, 123], alternating field induced structure is reversible. A small increase in applied potential (by 1 – 2 V_{pp}) could help to enhance p-DEP force and ACEO force by a square factor. A temporary increase in frequency to 3 kHz could provide particle mobility for crystal reorganization, improving the packing quality of colloidal particles along the surface relief. This process is called electrically-induced annealing [124].

If vertical protrusion of particles occurs above the existing layer (buckling), reducing the voltage amplitude can reverse the structure. This indicates the potential of annealing over the grown colloidal crystal. The snapshots in Figure 6.4 indicate the reversibility of in-plane growth when the applied field was removed (Figure 6.4b) and reinforced (Figure 6.4c). Figure 6.5 shows a slight improvement of particle coverage when an increase to 12 V_{pp} was used to enhance p-DEP and ACEO force.

Figure 6.4 (a) The in-plane growth of colloidal crystal along the edge of gold surface relief can be dispersed into (b) disordered state at the removal of electric field. (c) The nucleation and growth of colloidal arrays along the edge of surface relief can be restored once the electric field is reapplied. E and V indicate the elevated and depressed zone of gold surface, respectively. Yellow arrows indicate the direction of particles injection. Scale bar: 20 μm

Figure 6.5 (a) The presence of voids in colloidal assembly due to uneven flux of particles to the edge of surface relief. (b) This can be slightly improved by increasing the applied voltage ($12V_{pp}$). As a result, colloidal domains are observed to move towards the edge of surface relief. Red circles indicate the zone of improvement while yellow arrows indicate the direction of particle injection. Scale bar: 20 μm

6.3 Advantages of Technique

Like conventional methods of colloidal self-assembly [42, 70, 72, 83, 125], particle vacancies and voids are commonly observed, even under the great influence of capillary force. Although vertical electric field can occasionally give rise to stacking faults or buckling of small clusters out of the existing layer, the described control of in-plane growth prevents the formation of interconnecting bands or networks, and large voids. With the assistance of AC hydrodynamics and DC component of electric field, particle mobility on the electrode surface can be controlled with ease, enabling the

annealing of colloidal packing. Also, the sharp edges generate p-DEP force to stabilize the packing of particle array along $\langle 10 \rangle$ or $\langle 11 \rangle$ direction. In addition, the reversible nature of colloidal assemblies under the action of alternating electric field offers great advantage in switching device for photonic applications [126]. Besides, successful in-plane growth introduced here may also enable the growth of binary and hybrid colloidal crystal using a premix solution [118], rather than a time-consuming layer-by-layer growth [64].

6.4 Limitations of Technique

Despite the unique reversible capability of grown colloidal crystal in an alternating electric field, fixing the final structure permanently remains challenging. Although off-setting the alternating field or using DC offset after the assembly has been suggested by others [83], the quality of final colloidal crystal grown under in-plane control is compromised as DC offset often gives a sudden shock to the diffuse double layer of electrodes, leaving behind voids and particle vacancies. Alternatively, cross-linkable polymeric beads or silica particles coated with cross-linkable molecular chains can be used, but additional step of photo-polymerization is required at the final stage.

Because of the strong particle mobility due to the strong current and reversible polarization above the electrode surface, single domain of

monolayer colloidal crystal could not be achieved. Despite large area of monolayer colloidal crystal grown under this technique ($\sim \text{mm}^2$, no interconnecting bands and voids), domain size is often limited by the buckling of clusters out of existing layer. (Please refer to Appendix III for consecutive snapshots of colloidal arrays after the edge of surface relief).

6.5 Conclusion

In an AC electric field, guided colloidal crystallization can be realized from a straight edge of conductive relief patterned on a flat electrode surface. With the help of p-DEP, this simple conductive relief serves as the guide for $\langle 11 \rangle$ (or $\langle 10 \rangle$) colloidal crystal packing direction. ACEO-induced flow can then be used to assist the clustering and ordering of colloidal arrays along the edge of surface relief, leading to in-plane control of monolayer colloidal crystal growth.

Chapter 7: Comparison between Guided Colloidal

Crystallization by Meniscus Pinning and Dielectrophoresis

In Chapter 4 and 6, in-plane growth of monolayer colloidal crystal was demonstrated by meniscus pinning and dielectrophoresis, respectively. As both approaches are driven by different principles and mechanisms, the advantages and limitations of each method are discussed respectively in this chapter.

7.1 Sample Preparation

Both techniques require a simple patterning of straight surface relief or edge on a flat substrate. In contrast to template-assisted self-assembly which requires complex lithography tools like e-beam lithography, standard photomask or shadow mask can be used for patterning a single linear surface relief.

In the method of meniscus pinning, a straight interface between surfaces of different hydrophilicity is required. In contrast to hydrophilic silicon surface (contact angle $< 30^\circ$), patterned SU8 surface relief is almost hydrophobic in nature ($\sim 80^\circ$), it tends to prevent water adhesion from the interface (edge of surface relief). Pretreatment of silicon substrate with Piranha solution prior to SU8 patterning and also UV-ozone treatment of patterned SU8 are required to ensure water film adhesion along the edge of SU8 surface relief.

In the case of dielectrophoresis, the patterned substrate is sputter-coated with gold and no pretreatment is required. However, making the substrate conductive may incur higher cost compared to the colloidal crystal growth by meniscus pinning. Vacuum system is required in the process of gold coating.

7.2 Ease of Control

As meniscus pinning of colloidal suspension film along the edge of surface relief is required prior to guided nucleation, the orientation of straight edge must be aligned to the bulk meniscus of water film to achieve perfect pinning. In the case of electric field, p-DEP will allow the edge to attract particles from all directions, regardless of the orientation of surface relief.

Furthermore, the speed of substrate removal (suspension film stretching rate) must be carried out slowly (typically $< 3 \mu\text{m/s}$), to prevent early meniscus depinning (Figure 3.7a). Upon meniscus pinning and nucleation of colloidal arrays, the growth speed is determined by particle flux driven by evaporation. Hence, the growth will be influenced by moisture, temperature and particle size [21, 39]. The matching of colloidal crystal growth rate to the speed of substrate withdrawal is critical, as faster colloidal deposition could lead to multilayer formation or faster substrate withdrawal could lead to rupturing of pinned meniscus film (Figure 3.7b).

In electric-field assisted assembly, no mechanical movement of substrate is required, bypassing issues of alignment or disruption of grown colloidal crystal. The preferential nucleation is driven by both p-DEP and ACEO forces, along the field of highest intensity – edge of surface relief. The growth speed is generally one order faster (10 $\mu\text{m/s}$) than that of meniscus pinning, and can be controlled easily with the amplitude of voltage applied. According to Equations 5.1 and 2.4, DEP and ACEO forces depend on the square of electric field induced near the edge of surface relief.

7.3 Readiness to Harvest

Under the influence of capillary force, the drying of grown colloidal crystal film will render the film irreversible and permanent. Excellent quality of colloidal arrays obtained with predetermined orientation can be ready for applications.

In contrast, alternating electric field enables reversible colloidal structures in an electrolyte environment, making it useful for switching devices. However, applications requiring dried colloidal crystal film in permanent nature will cost an extra step to fix the colloidal film obtained under electric field. Using particles or electrolyte medium with cross-linkable properties may help, but it may compromise its economical advantage.

7.4 Quality of Monolayer Colloidal Crystal

Colloidal array growth under the influence of capillary pressure tends to give stable and most-close-packed crystal lattices, especially during the drying stage where the menisci form contact lines with the particle surface (protrusion of particles out of meniscus film). Using meniscus pinning, the stretching of meniscus film becomes possible, as well as the thickness control. Multilayer colloidal arrays can be compressed by controlling the thickness of capillary meniscus or meniscus confinement (see Figure 3.10 and 4.1). Pinned meniscus film can be stretched without depinning if the meniscus pinning force is sufficiently strong.

In electric field assisted self-assembly, multilayer formation of colloidal domains is unfavourable as ACEO-induced osmotic flow will blow them away to unoccupied electrode surface. Vertical buckling of colloidal clusters out of existing film can be observed from time to time. Although they are reversible and can be annealed with higher frequency or lower voltage amplitude, sometimes it could be difficult to repair the disrupted domain orientations due to vertical buckling. If possible, any instability of electrical current noise in the system must be eliminated.

Besides, the elimination of major voids in the proposed design of bottom electrode may indicate the dominant role of directional flow induced by ACEO forces, towards the edge of surface relief. Perhaps because of this,

strong strains could be felt within the grown colloidal crystal, causing vertical buckling as described earlier. In contrast to capillary force which presses the particles down to single particle layer, the z-movement of particles is being influenced by the dynamic nature of polarized double layer above electrode surface.

The following sequences of SEM and microscopic snapshots compare the qualities of in-plane oriented growth of monolayer colloidal crystal by meniscus pinning and dielectrophoresis.

Figure 7.1 Sequential scanning of colloidal arrays formed after the straight surface relief by meniscus pinning (Left) and DEP (Right), recorded using SEM and optical microscope, respectively. The red lines serve as the visual guides to compare the crystal packing directions $\langle 10 \rangle$ (or $\langle 11 \rangle$) to the edges of surface reliefs. Scale bar: 10 μm

Chapter 8: Conclusions & Future Work

8.1 Conclusions

This thesis demonstrates two-dimensional guided colloidal crystallization through the engineering of meniscus pinning and dielectrophoresis. With the control of in-plane nucleation of colloidal domains, in-plane growth of colloidal crystal could be achieved with the continuous transport of colloidal particles to the nucleated seeds, giving rise to a large area of monolayer colloidal crystal. Particularly with meniscus pinning, the predetermined orientation of colloidal crystal is achieved, with single domain size up to 1 mm².

The key findings and major contributions of this work are summarized as follows:

1. Demonstration of a Method to Measure Pinning Force

Using a weighing balance, the inverse method of measuring the loss of original water weight due to the pinning of wetting film was measured. The maximum force prior to the depinning of wetting film from the bottom edge of glass/SU8 interface was then quantified. The effect of UV-ozone exposure that improves the water film affinity to hydrophobic surface of SU8 was also quantified.

2. Successful Meniscus Pinning to Obtain Straight Three-Phase Contact Line

Successful meniscus pinning was then verified with visual inspection by optical microscope, and the stretching of pinned meniscus was then quantified. The pinning of suspension film of various SDS concentrations was investigated, revealing cooperative interaction of SDS with both the polystyrene and SU8/silicon interface. The pinning capability was observed to almost double (~ 1 mm) at small concentration of SDS (0.10 mg/ml) and in the presence of colloidal particles, compared to pure water solvent. To prevent early depinning before particles are successfully pinned, the relationship between critical receding angle and friction coefficient of particle ($\tan\beta'_{crit} < \mu$) was further developed with the consideration of surface relief. With the presence of surface relief, smaller apparent wetting angle β' could be induced near the edge, enhancing the pinning capability by introducing a stronger vertical component of capillary force as described in Figure 3.19. The developed relationship between its height and the apparent wetting angle is given in equation 3.11 ($\tan\beta' = \tan\beta - t/L$).

3. Successful Nucleation Next to Meniscus Contact Line and In-plane Growth

Capillary pinning of particles next to the straight surface relief was demonstrated experimentally, followed by the guided formation of most close-packed colloidal direction ($\langle 11 \rangle$ or $\langle 10 \rangle$) along the surface

relief. This enables the in-plane growth of monolayer colloidal crystal with the supply of unidirectional particle flux to the straight drying edge. This predetermined orientation of colloidal crystal growth produced a large area of single domain arrays up to 1 mm².

4. Contribution of DEP and ACEO to In-plane Nucleation and Growth of Colloidal Crystal

(a) Using COMSOL® simulation, the individual contribution of DEP and ACEO by the edge of conductive and insulated surface relief were presented.

(b) This finite-element method serves as the guide to understand the control of in-plane nucleation and growth of monolayer colloidal crystal near the edge of surface relief. Ultimately, a cell design with conductive surface relief on one side of conductive substrate was chosen.

(c) DEP is found to be critical in the nucleation of colloidal crystal near the surface relief (a linear zone of high field intensity), preceding the growth driven by ACEO forces.

5. Demonstration of In-plane Nucleation along the Edge of Conductive Surface Relief and In-Plane Growth

Using p-DEP, in-plane nucleation of two-dimensional colloidal domains along the edge of conductive surface relief was demonstrated. The in-plane growth of colloidal domains was then

succeeded by ACEO, giving rise to large area of monolayer colloidal crystal. Though limited by domain size and disruption of buckled clusters, major voids were significantly reduced.

8.2 Future Work

Despite the demonstration of in-plane nucleation and guided growth of colloidal crystallization along a straight surface relief through simple patterning, the following work could be explored further to improve the results discussed in this thesis.

1. Better affinity of suspension film along the surface relief can be improved with the exploration of new material. Smaller critical receding angle or longer pinning distance could further extend the growth area of single-domain colloidal crystal. Longer surface relief could also be explored to probe the practical non-idealities of sustaining an ultra-long straight meniscus edge, which is important for engineering this technique to meet industrial and commercial applications.
2. SAMs (Self-assembled monolayers) with negligible thickness and required wetting capability could be explored to grow colloidal arrays of small particle size.
3. Harvesting the reversible colloidal crystal formed by AC field is difficult. Other than using particles coated with UV-cross-linkable

polymer chains [127, 128], colloidal arrays grown by AC field could be fixed by additional adsorption of binding agents. For example, metal precursor like copper sulfate can be reduced near the electrode surface where the colloidal arrays deposit, binding the bottom region of colloidal arrays (Figure 8.1). However, the addition of metal salt may increase the conductivity of the medium, and subsequently the conduction current near the electrode surface. This effect must be accounted for to prevent distortion made to the existing colloidal arrays.

Figure 8.1 Diagram shows a potential method to introduce binding agents near the grown colloidal arrays by the reduction of metal precursor.

4. The assembly of binary colloidal solution or Janus particles near the conductive edge of surface relief could be studied. The electrokinetic-driven particle flux rate along the edge of surface relief could be further investigated and fine-tuned to engineer the formation of binary clusters or structure of higher complexity. The advantage of having a linear edge will give a single directional flux towards the

induced nucleated zone, leading to better control of binary colloidal crystallization.

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List of Publications

1. Zhao, Q.; Ng, E.; Kang, H. K.; Yip, C. H.; Hartono, M. R.; Wong, C. C. Real Time Visualization of Surfactant Effects on Colloidal Self-Assembly. *International Journal of Nanoscience* **2010**, 09, 113–118.
2. Ng, E. C. H.; Chin, K. M.; Wong, C. C. Controlling Inplane Orientation of a Monolayer Colloidal Crystal by Meniscus Pinning. *Langmuir* **2011**, 27, 2244–2249.

Book Chapter

3. Ng, E. C. H.; K, Y.; Wong, C. C. Colloidal Crystals. In *Modern Aspects of Bulk Crystal and Thin Film Preparation*; Kolesnikov, N., Ed.; InTech, 2012.

Appendix I: Measurement of Pinning Force and Pinning

Distance

T1. Table shows the measurements of pinning force of pure water film along the edge of SU8/Glass substrate, pre-treated with UV-Ozone exposure.

	Reading	Pinning Force, mN						
		1	2	3	4	5	Average	Standard deviation
UV-Ozone Exposure	0 min	3.389	3.398	3.392	3.396	3.401	3.395	0.005
	1 min	3.669	3.708	3.698	3.718	3.710	3.701	0.019
	2 min	3.875	3.877	3.868	3.864	3.859	3.869	0.007
	3 min	3.957	3.935	3.965	3.949	3.938	3.949	0.013
	4 min	4.022	3.990	3.997	4.022	4.019	4.010	0.016
	5 min	4.033	4.032	4.045	4.042	4.036	4.037	0.006

T2. Table shows the pinning force per length of pure water film along the edge of SU8/Glass substrate (after conversion from Table T1). Total perimeter length of three-phase contact line is assumed to be $25 \text{ mm} \times 2 + 1 \text{ mm} \times 2 = 52 \text{ mm}$.

	Reading	Pinning Force per Length, mN/m						
		1	2	3	4	5	Average	Standard deviation
UV-Ozone Exposure	0 min	64.856	65.025	64.912	64.987	65.081	64.972	0.089
	1 min	70.206	70.956	70.769	71.144	70.994	70.814	0.365
	2 min	74.148	74.185	74.016	73.941	73.847	74.027	0.141
	3 min	75.724	75.293	75.875	75.555	75.349	75.559	0.246
	4 min	76.963	76.344	76.475	76.963	76.907	76.730	0.298
	5 min	77.170	77.151	77.395	77.339	77.226	77.256	0.107

T3. Table shows the records of pinning distances measured at various SDS concentrations.

Concentration (mM)	Reading (μm)			Average Pinning Distance (μm)
	1	2	3	
0.05	1044	902	952	966
0.1	40	44	39	41
0.5	27	34	35	32
1	29	29	26	28
1.5	43	44	49	45
5	54	50	52	52

T4. Table shows the records of pinning distances measured at various SDS concentrations, in the presence of colloidal particles at 0.25 wt%.

Concentration (mM)	Reading (μm)			Average Pinning Distance (μm)
	1	2	3	
0	1473	1495	1525	1473
0.05	1690	1725	1606	1674
0.1	1850	1821	1891	1854
0.5	1052	1024	1055	1044
1	968	1068	936	991
1.5	605	601	655	620
5	413	375	523	437

Appendix II: In-plane Growth by Meniscus Pinning

Appendix III: Electric Field Induced In-plane Nucleation and Growth of Monolayer Colloidal Crystal