Surface & Coatings Technology 319 (2017) 353–358

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Reduction of defects in self-assembling colloidal monolayer via surface modifiers and periodic mechanical vibration

Sayantan Das [a,*], El-shazly M. Duraia [a,c,*], Orlin D. Velev [b], Javad R. Gatabi [d], Gary W. Beall [a]

[a] Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, USA
[b] Department of Chemical and Biochemical Engineering, North Carolina State University, Raleigh, NC 27695, USA
[c] Physics Department, Faculty of Science, Suez Canal University, Ismailia, Egypt
[d] Material Science Engineering and Commercialization Program, Texas State University, San Marcos, TX 78666, USA

ARTICLE INFO

*Article history:*
Received 22 February 2017
Revised 29 March 2017
Accepted in revised form 13 April 2017
Available online 14 April 2017

*Keywords:*
Convective assembly
Nano spheres
Monolayer
Periodic vibrations
Defect reduction

ABSTRACT

Convective self-assembly has been demonstrated to be useful as a technique to generate self-assembled monolayers of nanoparticles over a given area. These films, however, suffer from defects that occur with misaligned grain boundaries and point defects from missing particles. We demonstrate the effect of surfactant modified substrate and external mechanical vibration on reducing the inherent defects in colloidal monolayers obtained using an industrially scalable process: convective assembly. Surface modified substrates coupled with vibration during the deposition resulted in a higher degree of ordering over a large deposition area. Numerical investigation further shows the increased capability of these external modifiers helps in producing better quality films. A significant 86% reduction in the defects, with larger crystal domains are realized in comparison to control, enabling this technique to easily be scaled up for various industrial applications.

## 1. Introduction

Ordered Microstructures using colloidal particles have plenty of applications in science and technology. In particular, bottom-up approaches for producing two-dimensional (2D) monolayers have gained much interest, for its potential uses as photonic devices [1–3], plasmonics [4], 2D sensor arrays [5,6], antireflection structures [7–9], and as bio templates [10–12]. Industrially, significant application include, use of 2D array of spheres to produce surface patterns for soft lithography [13–16] helping to replace non-versatile and expensive photolithography technique. Many methods exist for bottom-up self-assembly of particles. Among those, convective self-assembly is the most promising method due to its simplicity and scalability, which makes it favorable in industries [17–19]. The phenomenon, convective assembly primarily driven by solvent evaporation: a blade placed at an acute angle, on a horizontal substrate dragged along the surface with colloidal solution, dispensed in between blade and substrate. The colloidal self-assembly occurs at the substrate due to particle transfer at the tip of the meniscus induced by solvent evaporation. These self-assembled films yields ordered microstructures, but typically exhibit several kinds of defects [20], which hinder the usability of these films in several industrial applications where high quality/precision films required. These defects characterized into two categories [21]. The first type includes line defects that occur when there is a misalignment between two self-assembling domains. The second type includes point defects when a particle is missing in the array. Occasionally a third kind of defect occurs when a larger particle disrupts the pattern. These particles can cause either a point or a line defect [34]. Reducing the defects of these 2D monolayers is a standing problem, and several efforts to study the fundamental physics and techniques to reduce defects reported in the literature [22–27,35–37]. A few recent researchers have used vibration to study colloidal assembly [22–24]. Notably, work by Gilchrist et al. [21,24] utilized lateral vibration on the substrate during convective assembly. This work primarily focused on higher growth rates and packing quality of the films; however, there is no report on means to reduce inherent defects that occur in the 2D monolayers, over large areas. Some researchers considered few layer (3D) of particles instead of 2D monolayers [35,36], to combat defects. Other reports used methods like ultrasonic annealing, barrier sway, and modification of substrates. Ultrasonic and barrier-sway [25,27] reported to be useful for producing larger crystal domain; similarly, cracks were reduced using flexible and hydrophobic substrates [36,37] via assembly on liquid interfaces. These works reported no significant improvement of inherent defects, and the method used limited to processes like Langmuir-Blodgett, which is time-consuming and consists of several steps. Yan et al. [28] added surfactants to the sub-phase, to study a sessile drop, and reported ionic surfactants significantly improved ordering of soft spheres. As the work performed on

---

* Corresponding author at: Texas State University, Department of Chemistry and Biochemistry, 601 University Drive, San Marcos, 78666, TX, USA.
*E-mail addresses:* s_d65@txstate.edu (S. Das), Shazly_duraia@yahoo.com, ed24@txstate.edu (E.M. Duraia).

http://dx.doi.org/10.1016/j.surfcoat.2017.04.034
0257-8972/© 2017 Published by Elsevier B.V.

an individual sessile drop, quantitative scalability is an issue. We utilized industrially scalable convective assembly processes and exploited defect reduction techniques of the particle monolayer, by employing pre-coated substrate with surfactant and via periodic external vibrations. Both techniques alone facilitated some reduction of defects, significant reduction in defects (~86%), only occurred when both vibration and surfactant-modified substrates used during the deposition of the particles. In addition, numerical investigation showed higher diffusivity of particles when under the effect of external modifiers, promoting the formation of high quality films.

## 2. Experimental section

### 2.1. Colloidal particles

The colloidal particle used in this study was polystyrene. Polystyrene particles were commercially available and obtained from Thermo-Fischer Scientific. Monodispersed polystyrene particles with a mean diameter of 600 nm and a polydispersity <4% were obtained and redispersed in Ultrapure water (milliQ-grade; resistivity = 18.2 MΩ-cm) for the required solid loading (0.1–2 vol%).

### 2.2. Reverse convective assembly (RCA)

Using convective self-assembly, structured thin films from colloidal particles in the solution were prepared by dragging a liquid meniscus unidirectional at a constant velocity along a solid surface.

Instead of moving the blade in the conventional direction, one also can move the blade in the reverse direction [17], as seen in Fig. 1. The blade placed at an acute angle above the substrate, and a small volume of colloidal suspension injected in the trapped corner formed between the blade and the substrate. The blade moved (withdrawal speed) at desired range of speed. As a result, the phenomenon of evaporation-induced self-assembly takes place at the three phase contact line of the meniscus of the evaporating liquid film/drying front. The particles in the thin films are drawn together, due to the combination of hydrodynamic flux and capillary forces [20].

### 2.3. Periodic vibration

A piezoelectric transducer connected to a function generator placed beneath the substrate to create periodic vibrations during the convective deposition. The piezo transducer obtained from Multicomp-piezo, with the following specifications: 27 mm diameter; resonant frequency: 2500 ± 500 Hz; and operating temperature: 20 to 60 °C. We used the function generator (ZJ Chao DS Function Signal Generator Module), with the maximum output- amplitude equals ±10 V p-p (no-load) - output frequency - square wave ranging 1 Hz–20 kHz. Frequencies used for this particular experiment with load (substrate) ranged from 0-3KHz at 10Vp-p (square wave). To reduce dampening of the applied vibration, a thin sheet of insulating polyurethane foam placed underneath the transducer.

### 2.4. Coating parameter and its control

The substrate used is a P-type Si wafer of [100] orientation (obtained from Wacker Siltronic Corp.,525 μm ± 20 μm,10–15 Ω-cm) and plain pre-cleaned glass slides (obtained from Fischer Scientific) used as a blade. The Silicon wafer cut into desired sizes and pre-cleaned in an ultra-sonicating bath to remove any organic or macro particles by using Methanol and Isopropyl alcohol followed by rinsing with ultra-pure water. To obtain a hydrophilic surface, physical cleaning performed using Oxygen Plasma Etcher (RF power of 100 W, 25 SCCM of Oxygen for 300 s). Using Malvern Zetasizer, the zeta potential of the particles measured: −72 mV, hence, we used an anionic surfactant SDS (Sodium Dodecyl Sulfate), to help increase the surface tension of the substrate and prevent coagulation of the particles. SDS is spin-coated on pre-cleaned silicon substrate by using a spin coater, with its parameters optimized for different concentrations of SDS for a uniform coating, over the entire substrate. The whole setup for convective

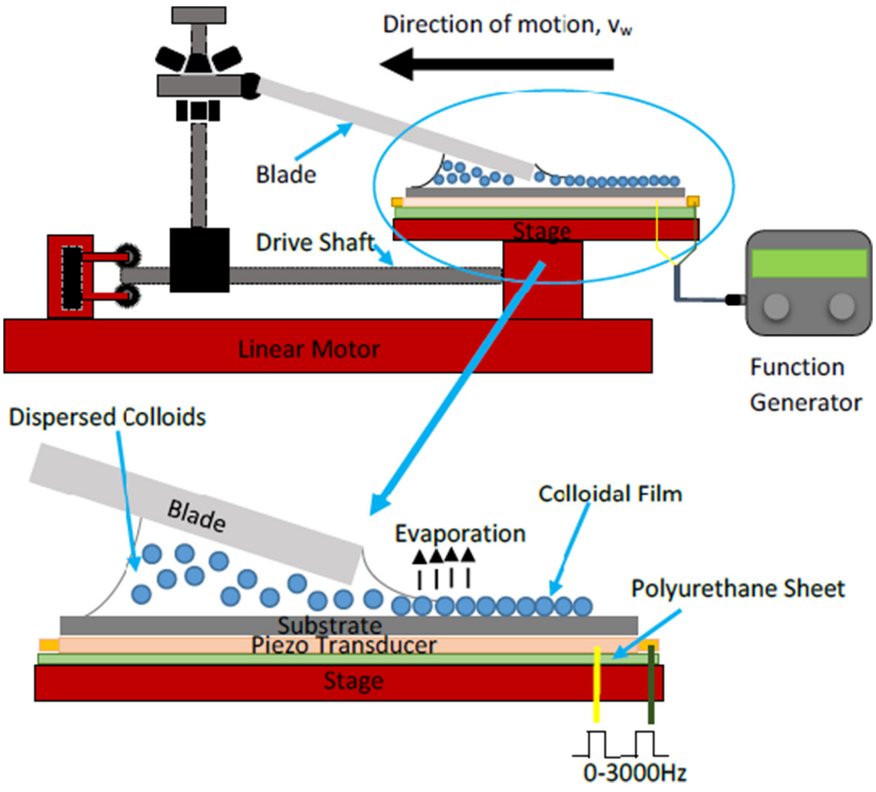

**Fig. 1.** Schematic representation of the RCA deposition process.