

Macroscopic Patterning via Dynamic Self-assembly and Wrinkling Instability

Item Type	Dissertation (Open Access)
Authors	Kim, Hyun Suk
DOI	10.7275/zkk4-xm95
Download date	2025-03-28 11:22:25
Link to Item	https://hdl.handle.net/20.500.14394/39054

MACROSCOPIC PATTERNING VIA DYNAMIC SELF-ASSEMBLY AND WRINKLING INSTABILITY

A Dissertation Presented

by

HYUN SUK KIM

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

SEPTEMBER 2012

Polymer Science and Engineering

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Approved as to style and content by:

Alfred J. Crosby, Chair

Todd Emrick, Member

Narayanan Menon, Member

David A. Hoagland, Department Head Polymer Science and Engineering

DEDICATION

To my family and friends

ACKNOWLEDGMENTS

First of all, I would like to express my sincere gratitude to my advisor, Professor Alfred J. Crosby, for his constant guidance and encouragement. I am very proud of what I have learned from him, which is an invaluable asset for my future career. I believe we have worked together synergically and his point of view was always refreshing and motivating. I also appreciate his care on my personal life. I am also thankful to my research committee members, Professor Todd Emrick and Professor Narayanan Menon for their constructive comments and constant academic support throughout this work. I also thank Prof. Chin and Prof. Jin at Inha Univ., who motivated and led me into the polymer science.

I would like to thank my past and present group members in the Crosby group for their kind and warm friendship throughout my Ph.D years. I would like to thank Charles, Jessica, Doug, Derek, Chelsea, Santanu, Guillaume, Dinesh, Andrew, Aline, Dong Yun, Shelby, Jun, Yuri, Sam, Mike, Cheol Hee, Yujie, Marcos, Sami, Dan, Jon, Yu-Cheng, Mike, and Minchao for their readiness to help me either in research or in my personal life.

I want to express my warm gratitude to my classmates in the Department of Polymer Science and Engineerning. Our first year was tough but it was fun with them. I would like to thank friends in Amherst with whom I have enjoyed my life through these past five years.

Finally I would like to thank my family, including my parents, father (Doosun Kim) and mother (Hyesook Hong), my sister (Kyungha and Jeungeun) for their love and support. I am deeply thankful to them as they have shaped me into who I am now. Without them, it would not be possible to continue this journey and complete my thesis.

ABSTRACT

MACROSCOPIC PATTERNING VIA DYNAMIC SELF-ASSEMBLY AND WRINKLING INSTABILITY SEPTEMBER 2012 HYUN SUK KIM, B.S., INHA UNIVERSITY M.S., INHA UNIVERSITY M.S., UNIVERSITY OF MASSACHUSETTS AMHERST Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST Directed by: Professor Alfred J. Crosby My PhD work focuses on developing new methods to create the macroscopic patterns in

a simple, robust, and versatile way. For macroscopic pattern formation, we first use flow coating as an assembly technique, uniquely balancing two driving forces: (i) evaporative deposition of nonvolatile solutes at a three-phase contact line and (ii) precision movement of a confined meniscus layer. This balance leads to the formation of line-based patterns that range in height and width from nanometers to microns, with lengths greater than centimeters. Moreover, we couple this deposition methodology with functional ligand chemistry on the nanoparticle surface, which allows us to create complex nanoparticle structures. By lifting crosslinked nanoparticle ribbons and ropes, exceptionally intriguing structures emanate from this process. The nanoparticle ribbons and ropes demonstrate a leap forward in nanomaterials fabrication, since the nanoscale properties are embedded within a macroscale object that can be manipulated with conventional methods and engineered into advanced technologies.

Using mechanical instability, we fabricate a simple, robust stimuli-responsive surface with periodic structures over a large area based upon osmotically-driven surface wrinkling. Although surface wrinkling has received considerable attention in the scientific literature, only a handful of papers have shown the ability to harness perhaps the greatest potential attribute of

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surface wrinkles: their active reversible nature. The ability to precisely control surface topographic morphologies in accordance with established scaling relationships opens a wide array of advanced materials applications, which do not rely upon cost-limiting fabrication techniques. Specifically, the surfaces respond to solvent exposure by developing well-defined topographic structures over laterally extensive areas due to osmotically-driven differential strains between a surface layer and underlying soft substrate. The observed wrinkling occurs spontaneously, forming hierarchical morphologies with controlled dimensions, and vanishes upon removal of the solvent driving force. The combined responsiveness and reversibility of wrinkling allow for the realization of functional devices, such as smart windows, smart microlens arrays, reversible channels in microfluidic devices. Moreover, by using thermal and osmotic approaches, we study the influence of geometry and material properties on surface instability such as cracking and wrinkling in a trilayer system consisting of a thin film on a soft foundation supported by a rigid substrate.

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CHAPTER 1

INTRODUCTION

1.1 Project Overview

Spontaneous formation of ordered complex structures that extend over macroscopic distances is both interesting and potentially useful for many applications in photonics, electronics, catalysts, and biotechnology [1-5]. It offers opportunities to simplify processes, lower costs, develop new processes, impart new types of functionality and combinations of functionalities, and generate structures in three dimensions and on curved surfaces. A number of examples of spontaneous pattern formation have been reported, yet controlled and predictable formation of ordered structures over large areas is highly required to realize full potential. Our goal is to develop simple, robust, and versatile methods to create the spontaneous formation of well-organized pattern over a large area in a controlled fashion. To achieve this goal, we need to understand the underlying mechanisms of patterning techniques as well as examine the key characteristics to produce novel, complex structures and to control the morphology.

This thesis is divided into two major sections based on different approaches. Firstly, one promising route for well-ordered structures is the use of self-assembly [6-7]. A variety of self-assembly methods, by which the autonomous and spontaneous organization of components into ordered and/or functional structures occurs, have been extensively investigated as a route for well-ordered structures at the different length scales, because such procedures are more cost-effective and technologically simple than conventional microfabrication techniques. Most of the concepts and general principles of self-assembly have been developed or elucidated in molecular systems. Components of any size, however, can self-assemble under appropriate

conditions, making structures that are too large to be prepared by chemical synthesis, but too small to be easily generated by photolithography or ink-jet printing. This self-assembly of nanometer- to millimeter-sized components (mesoscale self-assembly) can offer flexible routes to the fabrication of 3D and large-area structures [7]. In this study, the dynamic self-assembly of nonvolatile solutes through irreversible solvent evaporation will be explored for creation of complex, large-scale structures of nanoparticles and polymers. The focus of this study is to investigate how these structures can be well organized with high regularity and how selfassembled patterns can be controlled in a programmed way. Specifically, we will use the flowcoating to combine the "coffee ring" effect with the controlled stick-and-slip motion of contact line, resulting in line-based patterns with high spatial accuracy. Furthermore, we will examine how the geometry (*e.g.* height and width) of deposit affect the line formation (*e.g.* spacing between neighboring lines).

In addition to evaporative self-assembly, wrinkling of thin films has been shown to achieve highly ordered patterns over large areas, showing great promise in vast potential applications [8-9]. In this study, the wrinkling instability will be exploited to fabricate the spontaneous formation of hierarchical periodic structures triggered by swelling. We will examine how geometric parameters and materials properties affect wrinkle morphologies. Moreover, a system consisting of a thin film on a soft foundation supported by a rigid substrate will be used to study how the geometry of a system determines the stress state to the thin film, and controls the observed surface deformation of either cracking or wrinkling.

1.2 Dynamic Self-assembly

1.2.1 Self-assembly

Self-assembly is a process in which isolated components organize autonomously and spontaneously into ordered and/or functional structures [6]. This process can occur with components having various length scales when appropriate conditions are met. It is now being intensively studied in chemistry, physics, biology, and materials engineering and has been recognized as an important "bottom-up" approach to create intriguing structures including hierarchical structures with orders on different length scales for various applications.



Figure 1.1 Examples of self-assembly. (a) Static and (b) dynamic self-assembly [Reprinted from ref 10].

There exist two main classes of self-assembly systems: static and dynamic. The distinction between them refers to the thermodynamic description of the resulting assemblies [10]. Static self-assembly involves systems that are at equilibrium and do not dissipate energy:

crystal structure of a ribosome, electrostatic assembly of polymeric particles. Dynamic selfassembly is when the ordered state requires dissipation of energy: bacterial colony growth, and school of fish. Examples of self-assembly are shown in Figure 1.1. The most well-studied subfield of self-assembly is molecular self-assembly. Besides the well-studied molecular self-assembly in a solution (*e.g.* micelles, liposomes, vesicles, liquid crystals, and gels), self-assembled structures with different length scales formed at interfaces have been recently attracted significant attention owing to the ease of producing complex structures with small feature sizes [2, 11-12]. Among them, drying mediated self-assembly of nonvolatile solutes (such as polymers, nanoparticles, DNA, and colloids) through irreversible solvent evaporation represents one such case [13].

1.2.2 Evaporation-induced Self-assembly

When a suspension droplet dries on a solid substrate, nonvolatile solutes readily assemble into a diverse range of intriguing surface patterns and structures. When a drop of coffee is placed on a solid surface, a dense, ring-like stain is formed along the perimeter of the drop after evaporation of solvent, which is commonly known as the "coffee ring" effect [14]. "Coffee ring" patterns are often observed in evaporative deposition process from colloidal suspensions. The underlying physics of this process was first explained by Deegan *et al.*, who visually observed the particles moving toward the contact line and forming a deposit in a sessile droplet (Figure 1.2) [14]. They ascribed the formation of coffee-ring patterns to an outward capillary flow, induced by the differential evaporation rate across the drop surface. The model is based on two conditions: (i) the solvent wets the surface well and (ii) the gas–liquid–solid contact line is pinned. Since the solvent evaporation rate is the greatest at the edge, pinning of the contact line of the drying drop results in an outward flow to replenish the evaporative losses.

This non-uniform evaporation is attributed to the large vapor diffusion gradients that arise as a result of the strong curvature at the solid-liquid-vapor interface. The outward flow carries the dispersed particles from the interior to the edge of the drop and deposits them at the perimeter of the drop forming a ring pattern. They also found that the drop itself could generate the pinning of the contact line on smooth substrates without surface heterogeneities that is referred to this phenomenon as "self-pinning", which is not well understood [15]. While mechanisms typically responsible for solute transport, such as surface-tension gradients, solute diffusion, electrostatic and gravity effects, are negligible in the Deegan's model for a single phase of particles in water, these mechanisms become dominating in the case of organic solvents or multi-phase solutions. In a certain condition, the evaporation can induce a Marangoni effect inside a droplet [16]. A gradient of temperature across the droplet surface due to solvent evaporation leads to a Marangoni-Benard convection (*i.e.* closed-loop circular convection), which results in irregular Benard cells caused by the upward flow of lower, warmer liquid. A flow induced by the Marangoni effect can reverse the coffee stain effect, as a result of which depositing the particles at the center rather than the edge of the droplet [17]. In this sense, the formation of coffee-ring patterns requires not only the pinning of the contact line but also suppression of the Marangoni effect.

The contact line is not kept pinned during the whole drying process but can move at a certain stage of drying, resulting in a stick-slip motion of contact line (repeated pinning and depinning). The solutes transport to the edge during pinning of the contact line (*i.e.* "stick"), thereby forming a coffee ring. The contact line jumps (*i.e.* "slip") to a new position and a new coffee ring is then deposited. These pinning and depinning events alternate as solvent evaporates and, ultimately, lead to the formation of concentric multiple rings that are governed by a competition between the capillary force and the pinning force. Numerous studies have

been devoted to investigating the mechanism behind multiple rings formed via pinningdepinning contact line dynamics and influencing parameters of ring formation [18-21]. Importantly, the coffee ring effect and the stick-slip motion of contact line are not restricted to typical colloidal particles but can be applied to a wide variety of materials, including nanomaterials [22-23], polymers [24], and DNA [21]. However, the concentric ring patterns from drying mediated self-assembly are generally irregular due to the essentially stochastic pinning– depinning cycles of the contact line motion.



Figure 1.2 Evaporation-mediated self-assembly of nonvolatile solutes. (a) Coffee stain on a solid substrate and (b) schematic representation of outward flow during evaporation [Reprinted from ref 14].

1.2.3 Evaporation under a Confine Geometry

Recently, several elegant approaches have been successfully utilized to control the evaporation of droplet in confined geometries including two plates with two plates with the top one sliding on the lower stationary substrate [25], cylindrical tube [26], and curve-on-flat geometries [27], as shown in Figure 1.3. The confined geometries provide a unique environment for remarkable control over the flow within an evaporating droplet, leading to well-ordered

structure. Because of imposed geometrical constraint, the controlled pinning and depinning of the three-phase contact line produces a lateral surface morphology spontaneously that consists of hundreds of highly ordered deposits with regular spacing. Other ordered yet complex structures including spokes, fingers, serpentines, and hierarchically organized structures can also be produced [22, 28-29].



Figure 1.3 Evaporation-induced self-assembly under confined geometries. (a) Two parallel plate, (b) capillary tube, and (c) sphere-on-flat geometry [Reprinted from ref 24, 25, 19].

1.3 Surface wrinkling

1.3.1 Wrinkling Mechanics

Wrinkling is commonly exhibited in our daily life across a broad range of length scales for a wide variety of material systems [9]. Wrinkles may form on the skin of dried fruits such as apples or a paper being stretched in one direction. Other representative examples of wrinkling are our fingerprints and the folding of the Earth's crust into domes and mountains. All phenomena originate from the same mechanism, although the detailed stress distributions may differ significantly. Before discussing wrinkling, it is important to elaborate on general concepts of elastic instability.





The question of the stability of various forms of equilibrium of a compressed beam or plates can be addressed by considering the stability of equilibrium configurations of rigid-body systems [30]. Consider three cases of equilibrium of the ball shown in Figure 1.4. The ball on the concave surface is in stable equilibrium (Figure 1.4a) and the ball on the convex surface is in unstable equilibrium (Figure 1.4b), while the ball on the flat surface is in neutral equilibrium (Figure 1.4c). In the case of the ball on the concave surface, any lateral displacement of the ball from its equilibrium position requires the addition of work, thereby increasing the potential energy of the system. For the ball resting on the convex surface, any displacement will decrease in potential energy. Therefore, in a stable equilibrium the energy is at a minimum, while in an unstable equilibrium the energy is at a maximum. For the ball on the flat surface, lateral displacement has no influence on the system's potential energy. The compressed beam shown in Figure 1.5 can be similarly considered. In the state of stable equilibrium, if the beam is given any small displacement by some external influence, it remains stable and undeflected. The applied stress, σ_{r} is smaller than the critical stress, σ_{cr} . On the other hand, in the state of unstable equilibrium, the beam becomes unstable, resulting in a lateral deflection because the energy required for simple compression becomes larger than the energy required to buckle the beam. By definition, the state of neutral equilibrium is the one at which critical stress for when the equilibrium configuration changes from stable to unstable, as shown in Figure 1.5, is applied.

Therefore, instability occurring in elastic systems such as buckling of beams and plates refers to the ability to resist additional stress.



Figure 1.5 Response of a beam to an applied compressive stress.

Wrinkling is a mechanical instability occurring when compressive strains are imposed on a material system comprising a stiff film on an elastic foundation. A material system for the wrinkling is schematically shown in Figure 1.6. When a sample is compressed, the film buckles into a sinusoidal shape to relieve the applied stress. The film deformation is dictated by the bending and stretching energy of the film. Assuming that thin film is inextensible, the stretching energy of the film and the elastic deformation energy of a foundation are equated. Therefore, Wrinkles form due to the competition between the bending energy of a stiff film and the elastic deformation energy of a soft foundation [31].



Figure 1.6 Schematic drawing for surface wrinkling of a stiff film on a compliant substrate.

We consider cylindrical symmetry with a sinusoidal deformation of the stiff layer. The inextensibility condition of a stiff layer implies that $\varepsilon \sim A^2/\lambda^2$, where ε is the imposed compressive strain, λ the wavelength, and A the amplitude of wrinkles, respectively. The bending energy (U_b) of a stiff layer and the stretching energy (U_s) of an underlying soft layer can be described by assuming inextensibility of stiff layer [31]:

$$U_b = B \left(\frac{A}{\lambda^2}\right)^2 , \qquad (1.1)$$

$$U_s = KA^2 , \qquad (1.2)$$

where *B* is the bending stiffness of the stiff layer, $B = E_f h_f^3$, with *E* and *h* being the modulus and thickness. The subscripts *f* and *s* denote stiff and soft layer, respectively.

Minimization of the total energy for wrinkling, $U_{tot} = U_b + U_s$, yields the wavelength (λ):

$$\lambda = \left(\frac{B}{K}\right)^{\frac{1}{4}},\tag{1.3}$$

where K is the stiffness of a soft layer (Note that $K = \rho g$ for a fluid, where ρ is the fluid density and g is the acceleration due to gravity). In the case of $\lambda \gg h_s$, the stiffness of substrate scales as $K \sim E_s \lambda^2 / h_s^3$, giving:

$$\lambda \sim \left(\frac{h_f}{h_s}\right)^{1/2} \left(\frac{E_f}{E_s}\right)^{1/6}$$
(1.4)

In the opposite case of $\lambda \ll h_s$, K scales as E_s/λ , yielding:

$$\lambda \sim h_f \left(\frac{E_f}{E_s}\right)^{\frac{1}{3}}.$$
(1.5)

Other key parameters are the critical strain (ε_c) and stress (σ_c) that is necessary for wrinkling to occur. The critical strain and stress can be determined by comparing the total energy corresponding to the optimum wrinkled state and the compression energy of thin stiff layer $(U_c \sim E_f h_f \varepsilon^2)$.

$$\varepsilon_c \sim \left(\frac{E_f}{E_s}\right)^{2/3}$$
, $\sigma_c \sim \left(E_f E_s^2\right)^{1/3} \quad \left(\lambda \ll h_s\right)$, (1.6)

$$\varepsilon_c \sim \frac{h_f}{h_s} \left(\frac{E_f}{E_s} \right)^{\frac{1}{3}}, \quad \sigma_c \sim \frac{t_f}{t_s} \left(E_f^2 E_s \right)^{\frac{1}{3}} \quad \left(\lambda \gg h_s \right).$$
(1.7)

1.3.2 Morphological Patterns of Wrinkled Surface

Although the critical wrinkling point and wavelength are set by the material and geometry of a buckling system as shown above, the wrinkling patterns are much more strongly dependent on the magnitude and directionality of applied stress to the thin film [32]. The simplest case is a uniaxial stress state in which compression of the wrinkling system is applied mechanically along a single axis. This results in the formation of straight wrinkles aligned perpendicular to the direction of the applied compression (Figure 1.7a) [33]. In addition to the aligned straight wrinkle pattern, a variety of patterns can be achieved through the application of biaxial stresses, in particular equibiaxial stress states (Figure 1.7b). An energy minimization approach has been used to determine the preferred ordering of a wrinkled surface. This analytical method considers the energetic contributions from the bending of the thin film, the stretching of the thin film, and the stretching of the attached substrate for a prescribed periodic wrinkle pattern, compared to the strain energy incurred if the bilayer remains unbuckled. At the critical buckling point, these energies are equal by definition. Above the critical point, wrinkling

reduces the overall energy of the system. The exact amount of the energy reduction is dependent on the chosen wrinkling pattern as well as the degree to which the critical buckling stress is exceeded, which defines the final morphology of wrinkle patterns. Wrinkling wavelength is still determined by Equation 1.3 for any buckling mode whose wavenumbers ($k = 1/\lambda$) satisfy [34]:

$$k = \sqrt{k_1^2 + k_2^2} = \left(\frac{K}{B}\right)^{\frac{1}{4}},$$
(1.8)

which includes the equibiaxial case $(k_1 = k_2)$ as well as the uniaxial case $(k_1 = 0 \text{ or } k_2 = 0)$. However, these analytical techniques do not account for differences in the pathway through which the final stress state is achieved. Kinetic effects of the stress application process deriving from such transient aspects as diffusion, heat transfer, or sequential application of stresses may prevent the surface from attaining its lowest energy conformation.

In the past century, wrinkling has been recognized as a model of failure for lamellar composites such as airplane wing panels. The mechanics of the wrinkling process were intensively studied to avoid this wrinkling, focusing on appropriate material selection or product design. Recently, a renewed interest in the study of wrinkling has occurred with the opposite motivation to introduce topographical patterning onto surfaces. Since wrinkling is a spontaneous and responsive process by which periodic structures are generated out of a uniformly flat surface, it represents a pathway for rapidly creating regular surface topography over large surface areas without the use of expensive machinery or time consuming prepatterning steps [3]. The length scale of the generated wrinkle patterns is easily tunable from nanometers to centimeters, making wrinkling a highly versatile patterning method. Additionally, wrinkling is a highly reversible process, and there is significant interest in using wrinkled

structures as smart, responsive materials [35-37]. Because of these inherent advantages, surface wrinkling has been used for a number of specialty materials or processes [38-39].



Figure 1.7 Examples of wrinkle morphologies with different stress states. (a) Uniaxial stress state and (b) equibiaxial stress state [Reprinted from ref 32].

1.4 Thesis organization

In Chapter 2, we will build upon lessons from the "coffee ring" effect and a flow-coating process to develop a novel method for assembling periodic polymer and nanoparticle line patterns. This new method can provides an easy, robust, and lithography-free method to control the deposition of line pattern of polymer and nanoparticle. We will demonstrate that the dimensions and the spacing of deposits can be controlled over a wide range by programming the velocity profiles for the translating stage. Deposition of solutes is induced when contact lines "stick" at slow or zero velocity, while limited deposition occurs during "slip" at high velocity. We will investigate the effect of velocity, concentration, and gap height on the pattern formation. A simple geometric consideration will be implemented for the minimum spacing between neighboring lines obtained by the programmed flow-coating technique, giving a relationship between the minimum spacing and the geometry of deposits.

In Chapter 3, we will extend our previous method to assemble inorganic nanoparticles that are tailored with ligands into line patterns with controlled spacing between neighboring lines. Building upon the tailored chemistry of the nanoparticles, complex assemblies with precise arrangements of CdSe quantum dots with different sizes are achieved. This method provides an easy, robust, and lithography-free method for the formation of hierarchical assemblies, which will have advantageous effects on properties ranging from mechanics to optoelectronics. Also, crosslinking and lift-off of stripes lead to free-floating structures of nanoparticles that are flexible and fluorescent.

In Chapter 4, we will exploit reversible surface wrinkling to design responsive or adaptive materials. We will investigate the reversibility and geometry of surface wrinkles driven by swelling an elastically-supported stiff plate by solvent vapor and liquid. We will use crosslinked polydimethylsiloxane (PDMS) substrates with surfaces modified by ultraviolet-ozone (UVO) processing, creating materials with rigid, surface films that swell differentially in comparison to the underlying substrates. We will study the dependence of the wrinkle wavelength on the UVO time and thickness of elastomers. Taking advantage of the reversibility and geometric relations, we will demonstrate advanced applications such as smart windows with swichable optical transparency and responsive channels in microfluidics.

In Chapter 5, we will build upon our understanding on swelling-induced surface instabilities that can form in a trilayer system, in which the compliant PDMS is sandwiched between a stiff thin film and a rigid substrate. Through osmotic and thermal approaches, we will investigate the stress state of the top layer by observing the wrinkling and the cracking on the surface of trilayer. When the expansion of top layer is larger than that of PDMS layer, a

compressive state is always induced, leading to the formation of wrinkles. We will study the effect of geometry and materials properties on the surface instability by varying the PDMS thickness and modulus in the case when the expansion of PDMS is larger than that of top layer.

CHAPTER 2

CONTROLLED FORMATION OF STRIPE PATTERNS VIA FLOW-COATING

2.1 Introduction

Dynamic self-assembly of nonvolatile solutes (*e.g.* polymers, nanoparticles, colloids, or DNA) through irreversible solvent evaporation has received significant attention, since it is recognized as a lithography- and external-field-free route to generate complex, intriguing structures at the micron- or nano-length scales in a simple and cost-effective manner [2, 21, 40-46]. However, flow instabilities within the droplet often lead to irregular structures such as polygonal network structures [47] and fingering instability [48]. Thus, to realize the full potential of evaporative self-assembly as a versatile way to produce well-ordered structures over large areas for a variety of technological applications [4, 49-50], a delicate control over the evaporation process is highly required. To date, several methods have been used to obtain wellordered structures such as concentric rings [51-52], parallel lines [25, 53-54], and complex patterns [27] under a confined geometry. The confined geometry enables remarkable control over the flow within an evaporating droplet, which results in well-ordered patterns of nonvolatile solutes. Despite on-going research over several decades to enhance pattern regularity, the control of self-organized patterns with high fidelity and regularity is still lacking. However, prior studies suggested to us that combining restricted geometries with a controlled deposition process would lead to distinct advantages in controlling evaporative self-assembly.

In this chapter, we created line patterns of polymers and nanoparticles in a controlled manner and investigated the role of experimental conditions in the coating and patterning of polymers via a flow-coating method. We demonstrated that well-ordered line patterns of Poly(methyl methacrylate) (PMMA) and CdSe nanoparticle formed spontaneously over large

area in a programmed way using flow-coating. The dimensions of lines and the spacing between two neighboring lines were separately controlled by manipulating the stick-slip motion of contact line under a confined geometry. Geometry-based scaling for a minimum spacing between neighboring lines was developed and we found good agreement with experimental observations, giving physical insight of the evaporative self-assembly process based on the "coffee ring" effect.

2.2 Experimental Section

Poly(methyl methacrylate) (PMMA, $M_n = 120 \text{ kg/mol}$, PDI = 1.05) was obtained from Aldrich. TOPO-covered CdSe quantum dots (QDs, 6 nm diameter) were synthesized by methods described in the literature by the Emrick (PSE, UMass) research group and kindly provided [55]. PMMA and QDs solutions were prepared with different concentration and different solvents. All solutions were filtered through a PTFE membrane with a pore size of 0.45 μ m (Millipore Corp., Bedford, MA) prior to flow-coating. Silicon wafers with native oxide layer were obtained from University wafer, Inc., and rinsed by DI water, ethanol, and toluene, followed by drying in a nitrogen stream.

A flow-coating apparatus consists of an angled blade that was rigidly attached to a vertical translation stage with rotational alignment capabilities. This angled blade was positioned above a motorized linear translation stage with servo motors (Parker Daedal, Parker Hannifin Corp., Cleveland, OH) on which the flat substrate was fixed. For coating, the blade was brought down into contact with the substrate, adjusting the blade tilt to bring the blade level with the surface of the substrate. The blade was then elevated to a given height above the substrate ($100 \sim 400 \mu$ m). A defined solution (100μ L) was placed between the angled blade and the silicon wafer fixed to the linear translation stage. Once the solution was held by capillary

forces under the knife blade, the velocity of translation stage during the coating process was controlled in a programmable manner through Motion Planner software (Parker Hannifin Corp., Cleveland, OH) or custom software based on LabView (National Instruments, Austin, TX). The linear translation stage was moved at a defined velocity from 1 µm to 15 mm/s.

Optical microscopy was performed to observe the deposited patterns formed on the Si wafer in reflective mode under white light. To quantify the surface profiles of the deposits, AFM images of patterns formed on the Si substrate were obtained using a scanning force microscope (Nanoscope III, Digital Instrument Co., Santa Barbara, CA) in tapping mode. Nanoscope software in version 5.12 was used for image processing (1st and 2nd order flattening) and analysis. Fluorescence microscope images were obtained by a reflected fluorescence microscope (Olympus BX51 equipped with a CCD camera DP 71 and a 100 W Mercury arc lamp, Tokyo, Japan) using SWB (420-480 nm) excitation wavelengths.

2.3 Results and Discussion

2.3.1 Three Regimes in Flow-coating

Flow-coating has been used to create thin films with a thickness gradient for a variety of applications [56]. As shown in Figure 2.1, an angled knife blade is positioned above the flat substrate at a fixed distance in the flow-coting setup. A motorized linear translation stage, on which the substrate is fixed, allows for control over stage translation. When a solution is placed between the knife blade and substrate that is attached to a moving stage, a capillary force holds the solution under the blade. As the substrate is moved under the fixed blade, a thin layer of solution is deposited on the substrate caused by the frictional drag of the substrate on the solution. The balance of capillary and friction forces determines the quantity of solution deposited. Since friction force is proportional to the substrate velocity and capillary force is

independent of this velocity, the amount of solution left behind is directly proportional to the velocity of the substrate. Hence, a lower velocity generates a thinner film. By accelerating the substrate (4 mm/s²) from 5 mm/s to 15 mm/s at 400 μ m of gap height (h_{gap}), a Polystyrene (PS) film with a gradient thickness was fabricated from a 4 wt% solution of 131 k PS in toluene (Figure 2.1b-iii).

The above-described deposition dynamics control film formation for substrate velocities above a critical velocity, called *v***. Below *v***, a transition from continuous films to line patterns was observed. For 1 mg/mL of PMMA solution in toluene, the formation of line patterns emerged from stick-slip motion of contact line below the withdrawal velocity (*v***) of 2 mm/s. Since the solvent evaporation rate is the greatest at the edge, solvent evaporating from the edge is replenished by solvent from the bulk. A resulting outward flow carries the nonvolatile solute to the edge, depositing them along the contact line, causing the critical receding contact angle of the solution/substrate interface to decrease. This decreased receding contact angle causes the contact line to be pinned. As a pinned meniscus is stretched by moving the stage, the contact angle decreases and the contact line recedes to a new pinning position on the substrate when the contact angle reaches the critical contact angle. This repetitive stick-slip motion produces the periodic line patterns of PMMA parallel to the contact line (Figure 2.1b-ii). A thin PMMA film was stable on a Si substrate, making a well-defined line pattern, whereas PS was found to form a fingering instability due to a positive value of Hamaker constant between PS and Si wafer with a native oxide layer [24].

For substrate velocities below a second critical velocity, v^* , no stick-slip motion of contact line occurred. In this regime, continuous convective deposition of PMMA near the contact line is observed (Figure 2.1b-i). For the 1mg/mL PMMA, the transition velocity from the convective deposition to the line patterning by the stick-slip motion was $v^* \sim 2 \mu m/s$, which is

dependent on the solution concentration (c), that is, v^* increased with the increase in c. The accessibility of these different regimes by simply adjusting the withdrawal velocity of the substrate provides an opportunity to create well-ordered structures over large.







Figure 2.1 Schematic of flow-coating process and images of coating and patterning using flowcoating. (a) Schematic diagram of flow-coating apparatus for coating and patterning of nonvolatile solutes on a solid substrate. (b) Three regions for coating and line patterning of polymers produced by a flow-coating method as a function of the withdrawal velocity: convective deposition by a slowly receding meniscus (i), line patterning by stick-slip motion of the contact line (ii), and casting film by a friction drag between the solution and the substrate (iii).

2.3.2 Controlled Formation of Stripe Patterns

Taking advantage of the velocity-controlled transitions described above, the stick-slip motion of contact line can be controlled by imposing programmed velocity transitions during a coating process, leading to the formation of well-defined line patterns with predictable shape and size. The stick and slip events were programmed independently by using a motorized linear translation stage, on which the substrate is fixed. Between intermittent time steps (t_s), the stage velocity (v) is changed (Figure 2.2a). Controlling v relative to v^* and v^{**} and t_s allowed us to control the dimensions of deposits and the spacing between neighboring lines (d) in well-aligned



Figure 2.2 The velocity profile of flow-coating and optical images of PMMA line patterns. (a) The velocity profile of translation stage for manipulating stick-slip motion of contact line. (b-d) optical images of PMMA line patterns on a silicon wafer in which the spacing between neighboring lines were controlled by programming the velocity profile (v = 2 mm/s, $t_s = 1 \text{ s}$, $h_{gap} = 200 \mu\text{m}$, and c = 1 mg/mL toluene solution).

line patterns (Figure 2.2b-d). The distance moved when $v > v^{**}$ defines the programmed spacing between deposited line structures (d_p).

The versatility of this deposition and stripe fabrication method was demonstrated not only with PMMA, but also using nanoparticles and polydimethylsiloxane (PDMS) (Figure 2.3).



Figure 2.3 Stripe patterns of various materials using flow-coating. (a) An optical micrograph of stripe patterns produced by flow coating of 1-pentanethiol-covered Au NPs with the diameter of $\sim 2 \text{ nm} (0.5 \text{ mg/mL} \text{ toluene solution}, t_s = 1 \text{ s})$. (b) A fluorescent micrograph of stripe patterns of CdSe quantum dots with the diameter of 6 nm (0.1 mg/mL toluene solution, $t_s = 1 \text{ s})$. (c) Stripe patterns of polydimethylsiloxane (PDMS) are fabricated on a silicon wafer, followed by curing at 70 °c. Pre-cured Dow Corning Sylgrad[®] 184 oligomer with crosslinker (10:1 by weight) was dissolved in heptane at the concentration of 10 mg/mL.
Moreover, the stripe patterns of CdSe nanoparticles were produced on flexible substrates, such as aluminum foil, and extension to any of a variety of other flexible backings, such as PDMS, is feasible (Figure 2.4).



Figure 2.4 Formation of QDs stripe patterns on flexible substrates. (a) PS-QD stripe patterns are formed on an aluminum foil with the spacing of 40 μ m. Aluminum foils were attached to glass slide with a tape. (b) TOPO-QD stripe patterns on the PDMS treated with UVO for 20 min. A crosslinked PDMS substrate was prepared by combining Dow Corning Sylgrad[®] 184 oligomer with crosslinker (10:1 by weight).

A representative 3D AFM height image of deposited PMMA lines revealed that the deposited structures are ridge-like, as shown in Figure 2.5a-b, when v = 0 during the time t_s . The height (*h*) and width (*w*) of lines were controlled by varying t_s . Figure 2.5c-d show *h* and *w* of PMMA line patterns as a function of t_s . Both *h* and *w* increased with increasing t_s . When chlorobenzene was used as a solvent, the slower evaporation rate of chlorobenzene (b.p. ~ 131 °C) compared to toluene (b.p. ~ 110 °C) led to smaller line patterns. Conversely, an increase in *c* resulted in the formation of PMMA line patterns with larger *h* and *w* at equivalent t_s . This can be qualitatively rationalized as a higher concentration drives more solute to the edge of meniscus[57], resulting in thicker and wider lines. A line pattern of QDs was also produced with tens of nanometer height and micron width.



Figure 2.5 AFM images of line patterns and dimensions of line patterns as a function of stopping time. (a-b) A representative AFM image and a corresponding line profile trace from PMMA line patterns obtained with $t_s = 0.5 \text{ sec}$, $d_p = 20 \text{ }\mu\text{m}$, c = 4 mg/mL toluene solution, and v = 2 mm/s, showing ridge-like structures with the actual spacing of 20 μm . (c-d) Height (*h*) and width (*w*) of the lines with different experimental conditions are plotted as a function of t_s with $\lambda_p = 20 \text{ }\mu\text{m}$ (Δ : PMMA from 4 mg/mL toluene, \circ : PMMA from 1 mg/mL toluene, \Box : PMMA from 1 mg/mL coluene, ∇ : CdSe nanoparticle from 0.1 mg/mL toluene).

Instead of stopping (v = 0) during t_s , the width of PMMA lines could be increased simply by moving the substrate at a slow withdrawal velocity to allow the convective deposition (Figure 2.6). In this strategy, the line width, w, was controlled by programming the distance moving at the slow velocity (w_p). Between periods of t_s , the spacing between neighboring lines was controlled by moving the substrate at 2 mm/s. As the line width increased, the height of lines also increased. In addition, the length of the stripes (L) was determined by the blade width, which is adaptable to any blade width (meters or more in principle).



Figure 2.6 Line patterns with the controlled width. (a-c) Optical images of PMMA lines with different width produced by controlling the withdrawn velocity of the substrate. (d) Width (w) of the lines are plotted as a function of w_p that is the distance moving at the speed of 1 µm/s (v = 2 mm/s, $d_p = 100 \text{ µm}$, $h_{qap} = 200 \text{ µm}$, and c = 1 mg/mL toluene solution).

Moreover, *d* was regulated by the slipping distance of the contact line, which is controlled by d_p . Figure 2.7a shows that *d* of PMMA lines was determined by d_p , allowing for formations such as a gradient line pattern of PMMA to be easily fabricated (Figure 2.7b). Although no upper limit in *d* was observed, a lower limit was discovered as the programmed spacing decreased below a critical limit, *e.g.* 20 µm for 1 mg/mL PMMA in toluene with the stopping time of 0.5 s and a gap height of 200 µm. When d_p is smaller than this minimum spacing (d_m), both *d* and the dimensions (*h* and *w*) of lines were found to increase as d_p decreased (Figure 2.7c). This result suggests that the larger deposit pattern required an extended translation to withdraw the contact line to a new position, thus resulting in the observed larger spacing. Consistent with this qualitative description, d_m depended on t_s by which the height and width of the line structures were controlled (Figure 2.7d). For example, as t_s increased from 0.5 sec to 1 sec, d_m increased from 10 µm to 20 µm; h and w was increased from 100 nm and 6 µm to 125 nm and 8 µm, respectively.



Figure 2.7 The minimum spacing of line patterns using a programmed flow-coating. (a) Spacing between neighboring lines (*d*) is controlled by programmed spacing (d_p) until a minimum spacing (d_m) is reached (0: PMMA from 1 mg/mL toluene, \bigtriangledown : CdSe nanoparticle with the diameter of ~ 6 nm from 0.1 mg/mL toluene). (b) An optical image of gradient line pattern of PMMA spaced at 20, 30, 50, 60, 70, 80, 100, and 200 µm. (c) Height (*h*) and width (*w*) of the lines are plotted as a function of d_p (v = 2 mm/s, $t_s = 1$ s, c = 1 mg/mL toluene solution). (d) d_m is plotted as a function of stopping time (t_s). Solutions used were the same as in (a).

2.3.3 Simple Geometric Consideration for Minimum Spacing

To understand this observation, we propose a simple geometric argument to account for the contact angle variation caused by the shape of the deposited line structures and the moving distance of translation stage. This simple scaling establishes a relationship between d_m and the geometry of the deposits, which can be related to t_s , solution concentration, and the meniscus shape.

To consider the effect of the deposited line geometry on the local contact angle between the solution and substrate, we assume that high evaporation rate of solvent at the contact line allows the deposited structures to be considered as a glassy or gel due to the sudden increase in local concentration of solute. Thus, the deposited ridge-like, triangular-shape structures can be considered to act as new topographical features on the substrate, on which the solution contact line is residing. Under this assumption, the effective contact angle (θ^*) between the solution and the substrate can be described by

$$\theta^* = \theta + \varphi \,, \tag{2.1}$$

where θ is the contact angle between the flat substrate and solution without a deposit and φ is the slope of the deposit (Figure 2.8a).



Figure 2.8 Schematic representation of a simple geometric consideration for a minimum spacing obtained by programmed flow-coating.

We further assume that the stretched meniscus can be modeled as a parabolic surface, allowing the meniscus profile to be related to the position of the flow-coating blade relative to the position of three phase contact line (Figure 2.8b):

$$x = \frac{a}{h_{gap}^{2}} \left(h_{gap}^{2} - \left(h_{gap} - y \right)^{2} \right),$$
(2.2)

$$\theta \approx \tan \theta = \frac{\partial y}{\partial x}\Big|_{x,y=o} \approx \frac{h_{gap}}{2a},$$
(2.3)

where h_{gap} is the gap height between substrate and flow-coating blade, and a is the distance between the position of the flow-coating blade and the position of three phase contact line. x and y are positional coordinates along the capillary meniscus surface, and θ is the contact angle between the flat substrate and the solution. Thus, the change in contact angle caused by translating the substrate relative to the flow-coating blade scales as:

$$\Delta \theta \propto \frac{\Delta x}{h_{gap} \left(1 + \frac{\Delta x}{a}\right)},$$
(2.4)

where Δx is the translated distance.

When the effective contact angle, θ^* , reaches a critical receding contact angle, θ^*_c , the contact line will slip. Thus, the translated distance of flow-coating blade is equal to the minimum spacing ($\Delta x = d_m$), giving:

$$\theta^* - \theta_c^* \propto \frac{d_m}{h_{gap} \left(1 + \frac{d_m}{a}\right)}.$$
(2.5)

Substituting Equation 2.1 into Equation 2.5 gives the relationship between d_m and φ :

$$d_{\rm m} \propto \frac{\varphi h_{gap}}{1 - \varphi h_{gap} / a} \,. \tag{2.6}$$

Based on the measurement of line dimensions and shape of meniscus for our experiments, $\varphi h_{gap} / a$ is relatively small (< 0.1) and can be neglected. Therefore, we find this scaling relationship simplifies to

$$d_{\rm m} \propto \varphi h_{gap}$$
 (2.7)

This scaling relationship suggests that the minimum possible spacing between successive deposited line structures is governed by two parameters, which are dependent on the geometry of the deposits (φ) and the flow-coating blading position (h_{gap}). To validate this relationship, the minimum spacing results were obtained from different experimental conditions such as concentration, solvent, and solute. In addition, h_{gap} was varied from 200 to 400 µm for 1 mg/mL PMMA in toluene to study the influence of h_{gap} in a programmed flow-coating on d_m . It was found that d_m increased with the increase of h_{gap} under the same t_s . In Figure 2.9, the experimental minimum spacing is plotted as a function of φh_{gap} , where φ was estimated by 2h/wbased on AFM data. The linear relation between d_m and φh_{gap} is in good agreement with the experimental data.



Figure 2.9 A plot of the minimum spacing, d_m , versus φh_{gap} from various experimental conditions (Δ : PMMA from 4 mg/mL toluene (h_{gap} = 200 µm), \odot : PMMA from 1 mg/mL toluene, \Box : PMMA from 1 mg/mL chlorobenzene (h_{gap} = 200 µm), \bigtriangledown : CdSe nanoparticle from 0.1 mg/mL toluene (h_{gap} = 100 µm)). For PMMA from 1 mg/mL toluene solution, the gap height, h_{gap} , was varied from 200 to 400 µm.

Not only can this model predict the minimum spacing of line patterns by the flowcoating method, it also provides an understanding of the origin of contact line pinning in the evaporative deposition process. When a suspension droplet dries on a solid substrate, single or multiple ring patterns are formed. The patterns of the deposition are ascribed to a capillary flow in which solvent evaporating from the edge is replenished by solvent from the interior. The stick-slip motion of contact line results from the competition between the capillary force and the pinning force [19]. The contact angle decreases during the receding of substrates due to the pinning of contact line, which increases the capillary force. In a controlled experiment, the larger w and h of deposit yielded the larger d between the neighboring lines. Therefore, the pinning force should increase as the deposit grows during the pinning time. Our result indicates that the pinning force strongly depends on the geometry of the deposit, more precisely the slope of the deposit (φ). Similarly, Bodiguel *et al.* reported that the maximum pinning force has been correlated to the slope of the deposit [53, 58]. Therefore, it strongly supports the concept that deposited structure geometry is the dominant cause of pinning.

2.4 Conclusions

In conclusion, the line patterns of polymer and nanoparticle with unprecedented regularity were obtained by programming flow-coating process with a confined geometry. The height and width of lines were controlled by the stopping time. Both line height and width increases with the stopping time, showing the dependence of concentration and solvent. The width of lines could be increased to ~ 100 μ m by moving the substrate very slowly instead of stopping. The spacing between the neighboring lines was regulated by programming the stick-slip motion of contact line with the lower limit of spacing. This minimum spacing between the neighboring lines could be explained and predicted by a simple geometric consideration. The studies demonstrate that programmed flow-coating can offer a powerful means to create the well-controlled line patterns as well as the thin film with a gradient thickness. Further experiments to investigate the influence of the materials and the substrate on the formation of line patterns are currently under way.

CHAPTER 3

NANNOPARTICLE STRIPES, ROPES, AND RIBBONS

3.1 Introduction

Nanoscale materials represent attractive building blocks towards ordered hierarchical assembly for applications in photonics [59-60], electronics [61], catalysis [62], and biotechnology [63]. To realize their full potential, controlled and predictable assembly of nanoscale materials into well-ordered structures over multiple length scales is required. A variety of techniques have been developed to allow the multi-component patterning of nanomaterials at the micro- and nanoscale, including dip-pen nanolithography (DPN) [64], selective deposition [65], e-jet printing [66], micro-contact printing (μ CP) [67], wet stamping [68], microfluidic interfacial assembly [69], and nanopipetting [70]. However, each method has inherent limitations. Patterning of several different types and/or sizes of nanomaterials at different spatial locations typically requires multiple steps, introducing problems associated with precise spatial alignment of consecutive patterns or elaborate fabrication of stamps having complex, three-dimensional structures [71]. DPN, while advantageous for high resolution, has the drawback of low throughput. Thus, progress toward controlling the assembly of nanomaterials, in a simple and robust manner, is still critically important in achieving fine control over hierarchical nanomaterials-based structures.

In this Chapter, using a programmed flow-coating we fabricated nanoparticle stripes, ribbons, and ropes that are comprised of individual nanoparticle components. The assemblies have lengths up to several centimeters in length, yet the nanoscale properties are still maintained. Taking advantage of polymer ligand chemistry on the nanoparticle surface, we covalently link neighboring particles to create robust nanoparticle ribbons, as well as

multicomponent patterns such as grid structures. These structures, which are nearly 70% inorganic, exhibit extreme flexibility.

3.2 Experimental Section

All commercial chemicals were used as received. Silicon wafers with native oxide layer and thermal oxide layer (250 nm thickness) were obtained from University wafer, Inc., and rinsed by DI water, ethanol, and toluene sequentially, followed by drying in a nitrogen stream. TOPO-covered CdSe QDs (TOPO-QDs, 6 nm diameter), vinylbenzene-functionalized CdSe QDs (VB-QDs, ~3 nm diameter), and Polystyrene-functionalized CdSe QDs (PS-QDs, 3~4 nm diameter) were synthesized (Figure 3.1) and subsequently dispersed in toluene solution to 0.1 mg/mL. The molecular weight of the PS ligand is 1 kg/mol. All CdSe QD solutions were filtered through a PTFE membrane with a pore size of 0.45 μm (Millipore Corp., Bedford, MA) prior to flow-coating.



Figure 3.1 Chemical structures of ligands. (a) Vinylbenzene-functionalized CdSe QDs (VB-QDs). (b) Trioctylphosphine oxide-covered CdSe QDs (TOPO-QDs). (c) Polystyrene-functionalized QDs (PS-QDs).

Flow-coating: The flow coating instrument consists of an angled blade that is rigidly attached to a vertical translation stage with rotational alignment capabilities. This angled blade is positioned above a linear translation stage with servo motors (Parker Daedal, Parker Hannifin Corp., Cleveland, OH) on which the flat substrate is fixed. For a coating process, the blade was

brought down into contact with the substrate, adjusting the blade tilt to bring the blade level with the surface of the substrate. The blade was then elevated to a given height above the substrate (typically 100 µm). A defined CdSe QD solution (100 µL) is placed between the angled blade and the silicon wafer fixed to the linear translation stage. Once the solution was held by capillary forces under the knife blade, the velocity of translation stage during process was controlled in a programmable way through Motion Planner program (Parker Hannifin Corp., Cleveland, OH) or computer interface based on LabView (National Instruments, Austin, TX). The linear translation stage was moved at a defined velocity of 3 mm/s. A microscope (VZMTM 1000i, Edmund optics, Barrington, NJ) with a digital camera (EO USB 2.0, Edmund optics) was mounted to provide direct observation of the assembly process. A custom-built positioning system was developed for producing multicolor patterns of CdSe QDs with controlled alignment.

UV-crosslinking and lift-off of QD stripes: To withstand stripe patterns during further depositions, QD stripes were crosslinked under 254 nm UV irradiation at 400 μ W/cm² for a certain time (UVP, model CL-1000, Upland, CA) at room temperature. For all VB-QDs, UV irradiation was carried out for 30 min, while PS-QDs were crosslinked for 1 hr. Stripe patterns of VB- or PS-QDs are formed on thermal oxide layer with a thickness of 250 nm as a sacrificial layer. After crosslinking the stripes of CdSe QDs, 5 vol.-% HF solution was used to etch underlying oxide layer, leaving fluorescent stripes floating.

Characterization: AFM images of patterns formed on a silicon wafer were performed using a scanning force microscope (Nanoscope III, Digital Instrument Co., Santa Barbara, CA) in tapping mode. Nanoscope software in version 5.12 was used for image processing (1st and 2nd order flattening) and analysis. Fluorescence microscope images were obtained by a reflected fluorescence microscope (Olympus BX51 equipped with a CCD camera DP 71 and a 100 W Mercury arc lamp, Tokyo, Japan) using SWB (420-480 nm) exciting wavelengths. Stripes were floated by putting a drop of a 5 vol.-% HF solution, and then picked up on a carbon-coated TEM grid. TEM measurements were taken on a JEOL 2000 FX MARK II microscope operating at 200 kV.

3.3 Results and Discussion

3.3.1 Control of Stick-slip Motion by Flow-coating

The prerequisites for controlled formation of nanomaterials by evaporation-induced self-assembly are a restricted geometry to improve the regularity of features by confining the deposition solution and a programmable deposition process to control the positioning and deposition time. The flow coating technique, used in conjunction with functionalized nanoparticles, is ideal for self-assembly and the control of pattern formation with high throughput over a large area. Thus, we demonstrated the spontaneous, controlled formation of striped patterns of CdSe nanoparitices (*i.e.* quantum dots, QDs) on underlying substrates by flow coating.

The flow coating apparatus consists of an angled knife blade attached rigidly to a vertical translation stage. The blade is positioned above the flat substrate at a fixed distance, providing a restricted geometry for NP deposition and assembly. When the NP solution is loaded and trapped between two plates by capillary forces, there is a migration and deposition of NPs towards the contact line, caused by an outward flow driven by solvent evaporation (Figure 3.2a-i). A motorized linear translation stage, on which the substrate is fixed, allows for control over stage translation. Between intermittent stopping times (t_s), the stage shifts by a programmed distance (d_p) at a fixed velocity (v) (Figure 3.2a). As the meniscus is stretched by moving the stage, the contact angle is decreased below the critical receding contact angle, at which point



Figure 3.2 Schematic of nanoparticle deposition using a programmed flow-coating and a fluorescent image of gradient stripe patterns. (a) The velocity profile of translation stage for manipulating stick-and-slip motion of contact line. Schematic illustration of deposition of QDs at intermittent stopping times (i) and slipping of contact line upon moving of translation stage (ii). (b)) A fluorescence micrograph of a gradient stripe pattern of TOPO-QDs.

capillary forces exceed the pinning force, and the contact line slips to a new position. This programmed translation leads to controllable distance (*d*) between neighboring stripes (Figure 3.2a-ii), producing well-aligned stripes of NPs. Such a deposition mechanism can be used to generate simple lines and more complex patterns.



Figure 3.3 Morphology and dimensions of lines of nanoparticles. (a) A representative AFM image of stripe patterns of TOPO-QDs. (b) Height (*h*) and width (*w*) of the stripes are plotted as a function of t_s ($d_p = 20 \ \mu m$).

To control the distance between neighboring lines (d), consecutive stick-and-slip events were regulated by programming the velocity profile of the translating stage. The distance between the neighboring lines was determined by the slipping distance, which is controlled by programmed distance (d_n) . A gradient stripe pattern of TOPO-covered QDs (~6 nm diameter), spaced at 20, 30, 50, 80, 100 and 200 μ m, is shown in Figure 3.2b. The spacing follows linearly with d_p , as expected, until a minimum spacing (d_m) is reached as shown in the Chapter 2. For example, a 0.1 mg/mL CdSe solution produced $d \sim 20 \,\mu\text{m}$ when $d_0 = 10 \,\mu\text{m}$, thus defining $d_m \sim 20$ μ m. This suggests that an extended translation is required to release the pinned contact line for $d_p < d_m$. This extended translation correlates to a decrease in the effective critical receding contact angle (θ_c) associated with contact line slip. We found d_m to be dependent on t_s . As t_s was decreased from 1 sec to 0.2 s, d_m was seen to decrease from 20 μ m to 10 μ m (see Chapter 2 for detail). We also found that both the width (w) and height (h) of the NP stripe patterns increased with t_s and. Examination of surface morphology of the NP stripes by AFM revealed ridge-like structures, represented in Figure 3.3a (obtained using $t_s = 1$ s and $d_p = 20 \mu$ m), with $w \simeq 1.6 \mu$ m and $h \sim 82$ nm. For $t_s = 0.2$ s, $w \sim 1.2 \ \mu m$ and $h \sim 28$ nm (Figure 3.3b). From this result, it is apparent that there is strong correlation between the geometry of deposits and minimum spacing between neighboring lines. In order to explain this, in the part of proposed research, we propose a possible mechanism, by which minimum spacing of line pattern using flow-coating is dependent on the feature morphology (see Chapter 2 for detail). Importantly, no upper limit has been observed, or would be expected, for d, thus providing a significant advantage to processes such as micro contact printing (μ CP), where small patterns separated by large distances are difficult to obtain due to collapse in commonly used negative stamps [72].

3.3.2 Multi-color Patterning

There is a need for a novel, simple, and cost-effective approach in nanotechnology that allows fabrication of multi-component materials with high precision over large areas. Both parallel and crossed multi-component stripe patterns were prepared by controlling the direction of the stage translation and cross-linking of these NP stripes (Figure 3.4). To create robust, multi-colored patterns of QDs by flow coating, we first deposited stripes of vinylbenzenefunctionalized CdSe QDs (VB-QDs) of ~ 3 nm diameter (green fluorescence). These stripes were subjected to UV-irradiation (254 nm, 400 μ W/cm²), cross-linking the stripes by polymerization of the vinylbenzene-containing QD ligands, making the stripes sufficiently robust to withstand the solvent flow associated with a second deposition (note that in the absence of such cross-linking, an attempted second deposition results in complete dissolution of the originally deposited stripes).

A second striped pattern of QDs, using ~ 6 nm tri-*n*-octylphosphine oxide-covered CdSe QDs (TOPO-QDs, red fluorescence), was then deposited either perpendicular, or parallel, to the first pattern. As shown in Figure 3.5a, well-defined multi-color QD grids were obtained by perpendicular deposition, achieved by rotating the substrate 90 degrees between deposition steps. AFM characterization of the junction points revealed that the second set of lines stacked cleanly onto the first, without noticeable deformation or breaking of the overlying stripe (Figure 3.5b). This experiment confirms the adaptability of the deposition technique to hierarchical assembly, and its amenability to a layer-by-layer approach. We note that such grid structures would be difficult to obtain by other lithographic techniques, such as μ CP, since conformal contact is not readily achieved in stamp deformation during a second printing step [73].

Moreover, when we applied a second stripe pattern parallel to the first pattern, highly aligned multi-color stripes formed with high fidelity and pre-defined spacing between the red



Figure 3.4 A schematic of flow-coating and crosslinking process to make multicomponent patterns.

and green lines (Figure 3.5c). For parallel stripes, the spatial separation between the \sim 3 nm (green) and \sim 6 nm (red) QD stripes could be reduced to zero (Figure 3.5d), representing a completely overlaid deposition, which was confirmed by the observed disruption of the line deposition caused by a dust particle introduced between flow stages. Thus, spatial alignment is

limited at most by the precision of the equipment positioning, while the overall throughput and scale is enhanced significantly over other techniques.





By repeated flow-coating and crosslinking processes with QDs of different sizes, grid

patterns with homo- or hetero-junction configuration at each crossed point were generated

from controlled positioning of each line (Figure 3.6). Such structures may be useful for

understanding electromagnetic coupling effects in layered QD structures [74].



Figure 3.6 A fluorescent micrograph of grid patterns with homo- or hetero-junction configuration at each crossed point generated by a three step flow-coating process.

3.3.3 Floating Nanoparticle Stripes

Combining inherent functionality and flexibility of organic-inorganic mesostructures with ease fabrication can create new opportunities in many areas of nanotechnology. We utilized this flow coating technique to fabricate robust ribbon- and rope-like structures of QDs that are exceptionally long, flexible, and fluorescent. For this, cross-linked stripes were deposited successfully on a silicon substrate containing a sacrificial oxide layer (~ 250 nm thickness). Following stripe deposition, etching the substrate by immersing in aqueous HF liberated the stripes, leaving flexible semiconductor QD lines floating freely in solution. We observed the different structures of floated stripes (Figure 3.7). Inside the droplet, the NP stripes were shrunk due to the low dispersion of QDs in water, resulting in the coiled structures. On the contrary, the NP stripes were floated on the solution surface near edge of droplet,

leading to the straight and flexible ropes because of the surface tension of water.



Figure 3.7 Fluorescence micrographs of floating stripes of CdSe QDs crosslinked by UV irradiation. Release of crosslinked stripes of VB-QDs from sacrificial oxide layer inside aqueous HF solution (left) and at the edge of the droplet of HF solution (right).

Figure 3.8a shows a fluorescence micrograph of floating stripes at the edge of drop, reflecting the combined flexibility and mechanical strength of these QD-based objects. The controlled and very long length of these lines (Figure 3.8b), combined with their ease of fabrication, leads to the creation of numerous structures (Figure 3.8c) that display conformations related to the QD packing density and mechanics of the crosslinked material. The impact of particle packing and cross-linking is evident in the statistically different conformations seen in Figure 3.8d, where polystyrene-functionalized QD (PS-QD) ropes are seen. Notably, the dimensions of these PS-QD ropes are preserved in solution without further deformation (inset, Figure 3.8d), and the very sharp bends and curves in the lines are indicative of substantial mechanical properties possessed by these freely floating structures. In order to understand the properties of floating structures, we should control the interparticle distances and packing density.





We also investigated the effect of UV crosslinking time on the structure of floated QD stripes. Although it is difficult to measure the crosslinking density, the longer UV crosslinking time should make NP structures to form stable and robust. Below 15 min UV time, the floated stripes were broken into small pieces. As shown in Figure 3.9, the structures became more robust and flexible as the UV time increased. This result suggests that very long, robust, and flexible NP ropes can be obtained with the increased crosslinking density through the ligand chemistry of NPs.



UV exposure time

Figure 3.9 Effect of UV exposure time on the structures of PS-QD stripes floating on the droplet.

3.4 Conclusions

In conclusion, we have described a nanoparticle deposition/assembly process, by flowcoating, that contains several attractive features, including (i) the ability to create well-aligned stripes over large areas without lithographic steps or external-fields; (ii) control over the stripe dimensions, by regulating the motion of translation stage; (iii) the generation of multicomponent stripe patterns with parallel and/or perpendicular orientation; and (iv) a simplicity in fabricating freely-floating and robust structures over multiple length scales (*i.e.* nanoscale height, sub-micron width, and very long lengths). These nanoparticle-based structures, and the method used to produce them, represent a new paradigm for integrating nanoscale materials properties into macroscale structures, opening opportunities in optoelectronics, reinforcement, and encapsulation/release strategies.

CHAPTER 4

SOLVENT-RESPONSIVE SURFACE VIA SUFACE WRINKLING

4.1 Introduction

Periodic surface structures have attracted tremendous attention from scientists and engineers, since they give rise to novel properties and functionality such as wettability and structural color [75-76]. Surface wrinkles have been used to create such periodic structures in a simple, robust manner. Since Bowden *et al.* utilized wrinkling to fabricate ordered surface structures in a thin film on a compliant substrate [3], considerable effort, both theoretical and experimental, has developed to decode the wrinkling phenomena, leading to greater physical understanding and application of wrinkling.

Surface wrinkles spontaneously occur when a thin stiff layered material on a compliant foundation is compressed at small strain. The compressive stress can be provided by methods such as mechanical compression, thermal expansion, swelling or shrinkage. In all cases, the wrinkle morphology (*e.g.* characteristic wavelength) is defined by a compromise between bending energy of the top layer and deformation energy of its foundation as explained in the Chapter 1. Thus, wrinkle patterns can be controlled by the geometry and properties of constituent materials. Furthermore, since wrinkling is an elastic instability, upon removing the compressive stress the wrinkles disappear and the surface returns to the initial state, if the materials remain within the elastic limit through the wrinkling deformation.

Recently, the stimuli-responsive surfaces with periodic structures have been created via wrinkling instability by capitalizing on both its reversibility and responsiveness [37, 77]. Stimuliresponsive materials that undergo large changes in their properties and structures in response to external stimuli such as pH, temperature, light, and solvent environment have attracted a

great deal of attention due to a wide range of potential applications in switchable surfaces, drug delivery, optical systems, coating, and biosensors [78]. While most previous studies have centered on mechanical or thermal approaches, few attempts have been made to fabricate solvent-responsive surfaces. Also, a delicate control of the dimension and morphology of wrinkle patterns is greatly required for fulfilling its potential in many applications. Previous studies from our group have demonstrated the formation of wrinkle patterns through swelling by solvent vapors and acrylate monomer [79-80]. However, these studies have not demonstrated the reversibility of wrinkling associated with osmotically-driven stress. Therefore, we focus on both the reversibility and responsiveness of osmotically-driven wrinkling to fabricate the solvent-responsive surfaces.

In this Chapter, we introduce a simple, robust approach for fabricating stimuliresponsive surfaces based on osmotically-driven wrinkling with hierarchical morphology and controlled wavelength. By taking advantage of reversible wrinkling mechanisms, we demonstrated the ability to produce reversible channels and microlens arrays by controlling the region with local moduli-mismatch coupled with osmotic pressure. In addition, this stimuliresponsive surface allowed for a one-step deposition of colloidal patterns by utilizing the reversible wrinkle patterns to guide colloidal deposition.

4.2 Experimental Section

Sample preparation: Crosslinked poly(dimethylsiloxane) (PDMS) films were prepared by mixing Dow Corning Sylgard 184 base thoroughly with its crosslinking agent (20:1 by weight) and then degassing for 1 hour. The degassed mixture was spun-coated onto a rigid substrate and cured at 70°C for at least 3 hours. The prepared PDMS sample was exposed to Ultraviolet/ozone (UVO) oxidation (Jelight 342) for 10-60 minutes to form a stiff oxidized layer on the surface. TEM

grids as stencil mask were placed on the samples to produce selectively oxidized regions for microlens array. To generate the wrinkle patterns, an ethanol droplet was placed on the oxidized PDMS surface (Figure 4.1).



Figure 4.1 A schematic of sample preparation and swelling experiments.

Wrinkle alignment: The confined geometry consists of an upper glass that is positioned above a linear translation stage with compact motorized actuator (Newport, model: CMA-25PP) on which the flat substrate is fixed. A defined solvent (500 μ L) was placed between the glass and

the oxidized PDMS fixed to the linear translation stage with a gap height of 200 μ m. Once the solution was held by capillary forces under the upper plate, the velocity of translation stage was controlled during process. Optical microscope was mounted to provide direct observation of the process.

Reversible channels: To prepare microfluidic devices, degassed PDMS prepolymer with a base-to-crosslinker ratio of 20:1 was cast against a photolithographically-prepared (SU 8-100, MicroChem Corp.) mold and cured at 70°C for 4 hours to produce PDMS slabs with two microchannel features (100 μm wide and 80 μm deep). These were then masked with scotch tape and treated with UVO for 40 mins to define the oxidized layer. The PDMS slab having relief patterns of microchannels was treated with UVO for 3 mins and sealsed against a flat PDMS slab oxidized under the same UVO treatment conditions to generate enclosed microchannels. The microfluidic device was mounted on an inverted microscope with a CCD camera. A flow rate in each microchannel was controlled by a syringe pump (New Era Syringe Pump NE1000). Water and ethanol were colored by green and red food dyes, respectively.

Characterization: Optical microscopy was used to observe the surface wrinkling that was formed in response to solvent environment. The thickness of bare PDMS films was measured by interferometery (Filmetrics, Inc.) and a stylus profilometry (Veeco Dektak 3 Stylus Profilometer). In small angle light scattering, a laser beam (532 nm) was transmitted through the sample and projected onto a screen. The 2-dimensional diffraction patterns were collected by a CCD camera (EO 0312C) with a time resolution 92 ms. The transmittance at 550 nm was determined by UV-Vis spectrophotometer (Agilent 8453, model: G1103A). Fluorescence microscope images were obtained by a reflected fluorescence microscope (Olympus BX51 equipped with a CCD camera DP 71 and a 100 W Mercury arc lamp) using SWB (420-480 nm) exciting wavelengths. The amplitude of the wrinkles and the microlenses which were wet by

solvent was quantified using a stylus profilometry. The cross-section of sample was prepared by cutting it in liquid nitrogen, and then was characterized by Scanning Electron Microscopy (SEM, JEOL JSM 6320F) at 5 kV.

4.3 Results and Discussion

4.3.1 Osmotically-driven Wrinkling

UVO oxidation of a crosslinked PDMS film spun-coated onto Si substrate converted the PDMS surface into a thin oxidized layer [81]. When an ethanol droplet was placed on the oxidized PDMS surface and wrinkles formed spontaneously, confined within the trace of the droplet, and then disappeared upon evaporation of ethanol (Figure 4.2). In this simple experiment, the ethanol solvent preferentially swelled the oxidized layer more than the underlying non-modified PDMS layer. To confirm this differential swelling, we characterized the bending of an oxidized PDMS beam in ethanol vapor, showing that the relatively larger expansion of the top oxidized layer caused the beam to bend away from this layer (Figure 4.3). Therefore, when the PDMS layer was supported by a Si substrate, the swollen oxidized layer experienced a biaxial compression due to lateral confinement. Once the compressive stress reached a material-defined critical stress, wrinkles were formed spontaneously and persisted over regions of the ethanol droplet. After evaporation of ethanol, compressive stress was relieved, leading to the recovery to the optically flat surface (Figure 4.2c). This response could also be achieved by other volatile solvents, such as alcohols, acetone, pyridine, etc. Although wrinkle wavelength and amplitude were altered by the choice of solvent due to different swelling properties, the primary concepts were consistent for all tested solvents.



Figure 4.2 Solvent-responsive surfaces via wrinkling instability. (a) A schematic showing reversible surface wrinkling of UVO-treated PDMS in response to solvent. (b) Optical microscopy images of surface wrinkles with hierarchical patterns that are spontaneously formed when the surface is exposed to an ethanol droplet. (c) Upon complete evaporation of ethanol, wrinkle patterns disappear and the surface become smooth.



Figure 4.3 Bending experiments of UVO-treated PDMS beam (thickness ~ 2 mm) with different solvents. (a) initially flat (b) Curvature of beam after exposure to ethanol. The relatively larger expansion of the top oxidized layer causes the beam to bend downward.

4.3.2 Control of Wrinkle Morphology

The ability to control the morphology of self-organized features has significant advantages in the design of robust, adaptable materials. For low strain, wrinkle wavelength depends only on the material properties (Young's modulus and Poisson ratio) of the materials involved and the film thickness. According to the Equations 1.6 and 1.7, the thickness of an underlying soft layer (h_f) has an effect on wavelength only when λ is larger than h_f . We observed this transition in the scaling of wavelength within a single material system, which have not been reported experimentally to the best of our knowledge. In the osmotically-driven wrinkling of UVO treated PDMS, we found that wrinkle wavelength depended on the total thickness of the composite film, $h_t = h_f + h_s$, as illustrated in Figure 4.4a. The results showed two regions: for small h_t , λ increased with h_t , while λ reached a plateau value for large h_t . This behavior of wavelength dependence on film thickness was explained with Equations 1.6 and 1.7. The same UVO oxidation time (t_{uvo}) with different h_t of UVO-treated PDMS film ($h_t \ge 10 \ \mu m$) leads to the constant E_f and h_f . In addition, h_f ranges from 10 to 100 nm, which is very small compared with h_s such that h_s is nearly equal to h_t . Therefore, the dependence of λ on h_t is adequately described: λ is proportional to the $h_t^{1/2}$ for $\lambda > h_t$, and λ is independent of h_t for $\lambda < h_t$, which is in excellent agreement with our observations (Figure 4.4).



Figure 4.4 The effect of film thickness on wrinkle wavelength. (a) Dependence of λ on the total thickness of composite films (h_t). Dotted lines are the power laws ($\lambda \propto h_t^{0.5}$) expected from scaling theory. (b-e) optical microscopy images of swelling-induced wrinkled structures with different film thickness.

With the increase in UVO time, λ increased as a consequence of increase in *B* from the greater stiffness and the larger thickness of an oxidized layer (Figure 4.5). The wrinkle amplitude (*A*) also increased with increasing UVO time, as *A* is proportional to λ with the assumption of a constant imposed strain, which was consistent with the observation by Chan *et al.* [79]. Under our experimental conditions, dimple and random line patterns were observed after relatively short t_{uvo} (~ 20 min), while we typically observed labyrinth patterns for moderately long t_{uvo} (30 min ~ 60 min).

In addition to the wrinkle wavelength, the amplitude of wrinkles could be controlled by varying the composition of the solvent mixture. The ethanol/water mixture was used as a swelling agent. Note that no wrinkle was observed within the droplet of water, which indicates that water has low swelling degree of oxidized layer. As the ethanol content in the ethanol/water mixture increased, the amplitude of wrinkles increased without the change in wrinkle wavelength. As shown in Figure 4.6, the amplitude of wrinkle was ~ 500 nm when 60% ethanol/water mixture was used, which is smaller than ~ 1 μ m obtained using pure ethanol. As the content of water increases, the swelling degree of oxidized layer might decrease, resulting in the low compressive strain. When the solvent mixture less than 40% ethanol, the surface was flat or the amplitude was too small to observe the wrinkles.



Figure 4.5 The effect of UVO time on wrinkle morphology. (a) Wavelength (λ) and amplitude (A) of wrinkles are plotted as a function of UVO oxidation time (t_{uvo}) of 27 µm thick PDMS. Dotted lines indicate observed transitions in pattern morphology. (b-e) optical microscopy images of morphologies of the wrinkled structures observed in different UVO time: (b) 15, (c) 20, (d) 30, and (e) 40 min, respectively.



Figure 4.6 The control of amplitude with solvent mixtures. (a) Height profiles of wrinkled structures induced by swelling with solvent mixture. (b-e) optical images of wrinkled structures obtained with different ethanol/water mixtures (scale bar = $200 \ \mu$ m): (b) 100 % ethanol, (c) 80 % ethanol, (d) 60 % ethanol, and (e) 20 % ethanol.

One of the key features in smart responsive materials is to undergo numerous reversible changes in some property. The reversible switching by external stimuli in wrinkling instability can offer exciting possibilities in a diverse range of applications for functional, 'smart' devices. In order to test reversibility of the osmotically-driven wrinkling, we measured the transmittance of UVO treatment of PDMS spun-coated on the glass. Figure 4.7 shows a representative result of reversible change in transmittance at 550 nm measured by UV-Vis spectroscopy in drying and wetting cycles: transmittance was reduced when the film wrinkled, whereas the surface of film became smoother and transmittance increased to over 95% as the ethanol evaporated. This response could be cycled numerous times at the same location simply through the wetting/drying process. During several cycles, transmittance at 550 nm did not change significantly. Upon exposure to ethanol, the sample with UVO-treated PDMS changed from optically transparent to translucent as a result of the scattering of light by surface wrinkles. In the dry state, the wrinkled film transformed back to a smooth surface, providing a clear view of image behind the window. We found that transmittance was dependent on wrinkle structures. Figure 4.7d shows transmittance at 550 nm and the curvature of wrinkles ($\kappa = A/\lambda^2$) as a function of t_{uvo} . Transmittance decreased with t_{uvo} until a plateau was reached. We found a strong correlation between transmittance and κ with the changes in t_{uvo} . Periodic micrometersized surface structures should be related to the scattering intensity, affecting transmittance of film. In other words, larger wrinkle curvature enabled the light to scatter to a larger degree, resulting in a smaller transmittance.


Figure 4.7 Reversibility of wrinkled structures. (a) Optical microscopy images showing the change in surface morphology of UVO-treated PDMS with thickness of 27µm spun-coated on glass before (left image) and after (right image) ethanol exposure (t_{uvo} =40 min). Insets: optical images demonstrating the reversible optical switching capability between optically transparent and translucent. (b) Reversible transmittance variations at 550 nm in a wetting/drying cycle of UVO-treated PDMS (h_t = 27µm, t_{uvo} = 40 min). (c) The change of transmittance at 550 nm and curvature of wrinkles as a function of t_{uvo} (h_t = 27µm).

4.3.3 Alignment

Equally and simultaneously applied stresses to a stiff thin layer on a compliant substrate generally create labyrinth structures (*e.g.* thermally-induced wrinkling). Similarly, an isotropic compressive stress field by solvent exposure resulted in patterns with no preferred orientation as confirmed with the ring shape of the Fast Fourier Transform (FFT) image and diffraction pattern (Figure 4.8). Recently, Yang *et al.* have reported that highly ordered herringbone structures can be formed, when equal but sequential stresses are applied to the oxide-on-PDMS layer [33]. It suggested to us that we could create well-ordered wrinkle patterns by controlling the stress state of a system.



Figure 4.8 Random wrinkle patterns. (a) An optical microscopy image of morphologies of the wrinkled structures observed with the 30 min of t_{uvo} . (b) A representative 2D FFT analysis of microscopy image in (a).

We found that controlling the advancing front of solvent exposure played a key role in the orientation of wrinkles. During swelling of a UVO-treated PDMS, the oxide layer near the advancing solvent front was stretched perpendicular to the solvent front, associated with the out-of-plane strain due to swelling the network behind the front. This uniaxial stretching caused a compressive stress component perpendicular to the front, which induced aligned wrinkles perpendicular to the front. As the effect of uniaxial stretching reduces away from the front, the stress perpendicular to the front becomes similar to the stress component along the swelling front, leading to the biaxial-stress induced morphology (Figure 4.9).



Figure 4.9 Sequences of optical micrographs near the advancing ethanol. The time interval for frames is 1 s.

Following these observations, we used a confined geometry composed of an upper glass plate positioned above the system at a fixed distance rather than an uncontrolled droplet (Figure 4.10a). As the swelling solvent advanced under confined geometry at a constant velocity of 5 μ m/s, the herringbone morphology structure was formed over an impressively large area without noticeable defect (Figure 4.10b). With increasing velocity, more defects were observed and isotropic labyrinth patterns were obtained at high velocity



Figure 4.10 Alignment of wrinkle patterns using a confined geometry. (a) A schematic diagram of apparatus for aligning wrinkle patterns of UVO-treated PDMS. (b) Optical microscopy image acquired during the advancing solvent at 5 μ m/s on the surface of PDMS. The arrow indicates the direction of the advancing front of ethanol.

In order to characterize the dynamics of wrinkle formation and extinction, we measured the first order diffraction intensity as a function of time using small angle light scattering (Figure 4.11a). When the UVO-treated PDMS (t_{uvo} = 30 min) was exposed to ethanol, wrinkles were formed within 2 s and A increased to an equilibrium value with a constant λ within 4 s (Figure. 4.11b). After evaporation of ethanol droplet, A rapidly decreased, by ~80 % in less than 14 s, and returned to a non-wrinkled surface over a total time of 120 s (Figure 4.11c).



Figure 4.11 Dynamics of wrinkle formation. (a) Schematic of small angle light scattering apparatus for observing the dynamics of wrinkling. (b-c) Representative normalized diffraction intensity as calculated from the first-order peak as a function of elapsed time ($h_t = 10 \mu m$, $t_{uvo} = 30 \text{ min}$). t_{wet} and t_{dry} are elapsed time after exposure and disappearance of ethanol droplet, respectively. The diffraction efficiency is proportional to A^2 .

4.3.4 Potential Applications

Given the range of structure control shown to obey robust scaling relationships and the combined reversibility and responsiveness, surface coatings fabricated in this manner could have numerous applications. Here, we highlight initial applications to demonstrate the unique aspects of this top-constrained, osmotically-driven wrinkling system, which develop micron or sub-micron features spontaneously across large lateral lengths or locally in a specific region.



Figure 4.12 Reversible wrinkle channels in a microfluidic device. Wrinkles were generated within the selectively oxidized area between two microfluidic channels when ethanol was introduced into one microchannel. Water and ethanol were colored by green food dye and red one, respectively. Flow rate: 0.5 mL/hr (left) and 2 mL/hr (right).

We first demonstrate the use of dynamic wrinkle patterns to provide reversible channels in microfluidic systems. A representative result is shown in Figure 4.12. Two parallel microchannels (100 μ m wide and 80 μ m deep) of crosslinked PDMS, non-treated with UVO, were separated by 400 μ m within a single device, and green-dyed water was flowed through each. When red-dyed ethanol was introduced into one microchannel instead of water, wrinkles were formed within the oxidized area separating the two microchannels. The wrinkle amplitude and wavelength define an open channel of cross-sectional area ~ $A\lambda$. Once the wrinkles connect the two microchannels, ethanol solution began to flow through the wrinkle channels. These wrinkle channels are opened and closed reversibly in response to the introduction of swelling solvent. The ability to fabricate reversible structures within microfluidic devices has the potential to create, control and manipulate various types of fluidic transport for both synthetic and biological applications.



Figure 4.13 Smart microlens array using solvent-responsive surface. (a) Experimental set-up with a projection template of the emblem (bottom) for demonstrating optical functionality of microlens array. Optical microscopy image (upper) of a selectively oxidized PDMS surface using a stencil mask (scale bar = 100 μ m). (b) Projected emblem images are observed on every optical element when microlens structures are formed by ethanol-wetting, demonstrating the reversible microlens array.

In addition, the morphology of a wrinkled surface can also be controlled such that the wrinkle features serve as local focusing lenses, or a microlens array. To demonstrate the utility of these surfaces as responsive microlens arrays for optical display applications, we controlled the lateral dimensions by defining the oxidized region of PDMS surface by using stencil masks [82]. Upon swelling, the finite boundaries led to the generation of microlens structures when the diameter of oxidized region (*D*) was smaller than the wrinkle wavelength (λ). With 1 hr of UVO treatment, we prepared a microlens array with a hexagon diameter of 38 µm that was smaller than wavelength of 55 µm. Figure 4.13 illustrates the ability to focus on an object over a hexagonal array of microlenses in response to solvent environment. When the sample was exposed to ethanol, microlenses were formed spontaneously with ~ 3 µm of height, and they transmitted an image focused at the focal point of the microscope objective. As the ethanol evaporated and smooth surface was recovered, the image was no longer projected onto the objective due to the change in focal point. Further, tuning of the focal length of the microlens can be achieved simply by changing oxidation time and/or the lateral dimensions of the oxidized region.

Dynamic wrinkle patterns were also used as templates for guided assembly of colloidal particles. Previously, Lu *et al.* have used wrinkles as a template to produce the colloidal assembly with tunable wavelength [39]. Hyun *et al.* have assembled colloids in a wrinkled film and transfer to a flat substrate [77]. Although these approaches simplify the fabrication of well-defined colloidal assembly, a sequential methodology is required for deposition of the colloids and the complexity of pattern is relatively low due to their mechanical process, in that only straight lines can be fabricate without confinement-induced wrinkling. Thanks to the sinusoidal nature of wrinkling, the deposition of fluorescent polystyrene (PS) colloids with the diameter of 500 nm dispersed in ethanol takes place selectively in the troughs of the wrinkle patterns during

solvent evaporation (Figure 4.14a). After complete evaporation of solvent, colloidal assemblies are embossed as the surface snaps back to the smooth state (Figure 4.14b).



Figure 4.14 Particle patterning using wrinkle patterns. (a) A schematic. (b) A cross-sectional view SEM image of colloidal pattern on UVO-treated PDMS.

In addition to the wrinkle patterns (e.g. dimple, random lines, and labyrinth), more

complex patterns of particles could be achieved by pattering the wrinkling regions with local

moduli difference using a stencil mask (Figure 4.15).



Figure 4.15 Fluorescence microscopy images of selective deposition of fluorescent PS colloidal particles (diameter =500 nm) on wrinkle patterns.

4.4 Conclusions

In conclusion, this study presented a stimuli-responsive surface that changed surfacerelief structures over a large area by osmotically-driven wrinkling. We controlled the dimension and morphology of wrinkle patterns by changing the oxidation time and the thickness of soft layer. The versatility of this method allowed for a realization of a variety of functional devices, such as reversible channels, and tunable microlens arrays, and facile printing of nanoparticle assemblies. Overall, the results of this study exploited proposed scaling relationships and wrinkling mechanisms that until now have not been demonstrated, opening new avenues for technological development with significant promise.

CHAPTER 5

WRINKLING INSTABILITY IN A TRILAYER SYSTEM

5.1 Introduction

Wrinkling occurs across a broad range of length scales for a wide variety of material systems such as skin being squeezed, paper being stretched, or thin rigid materials trying to expand while being bound to a compliant substrate [9]. This phenomenon is a type of mechanical instability that develops in response to the applied compressive stress (thermal, mechanical, or osmotic), showing unique, periodic surface patterns. When a thin stiff film on a compliant foundation is compressed, wrinkling occurs to minimize the total energy of the system. Wrinkling has been exploited recently to create intriguing patterns such as microlens arrays, to fabricate novel devices such as stretchable electronics, and to measure materials properties [36, 82-83].

Contrary to mechanical compression on a bilayer, trilayer systems have mostly been used to obtain wrinkle patterns through thermal and osmotic approaches [84-85]. Metal/polymer/substrate trilayers have recently been reported to exhibit wrinkling when heated above the T_g of the polymer [86-87]. Also, Crosby *et al.* demonstrated the wrinkling of an oxidized PDMS surface under a compressive stress induced by absorptive swelling of a liquid solvent into the different layers [32, 34]. Although there is general agreement that the lateral stress arises from the strain mismatch of the different layers, the effect of geometry and material properties in a trilayer system has not been studied systematically.

In this Chapter, we present methods to create osmotically- or thermally-induced wrinkle patterns in a trilayer system. We observe a transition from wrinkling to cracking as the thickness or modulus of compliant layer sandwiched between a rigid substrate and the thin stiff surface

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layer increases. A theoretical model based on the strain mismatch between the surface layer and an underlying layer, which is constrained by a rigid substrate, is used to provide a quantitative analysis of the observed transition in surface deformation mechanisms.

5.2 Experimental Section

Osmotically-induced wrinkling: The trilayers were prepared as same in the Chapter 4 by UVO treatment of PDMS film spun-coated onto Si substrate. UVO treatment converted the PDMS surface into a thin oxidized layer, giving a SiO_x/PDMS/Si trilayer. Samples were placed inside a sealed glass chamber along with a small volume (2–3 mL) of solvents. The oxidized samples were placed inside a cylindrical glass chamber, which was then covered by a watch glass, using vacuum grease to seal the chamber. Immediately prior to sealing, a small volume (2–3 mL) of solvent was dispensed via syringe into the chamber, taking care to keep the sample itself from contacting the liquid solvent. Optical microscopy was used to characterize the wrinkled surfaces inside the chamber. Figure 5.1 shows a schematic of the sample preparation and exposure to solvent vapor.



Figure 5.1 Schematic of sample preparation and experiment set-up for solvent vapor-induced swelling.

Thermally-induced wrinkling: Trilayers of gold (Au) film (top layer) on PDMS (middle layer) supported by Si wafer (bottom layer) were prepared in two steps. Crosslinked PDMS films were prepared by mixing Dow Corning Sylgard 184 base thoroughly with its crosslinking agent (40:1, 50:1, 60:1 by weight) and then degassing for 1 hour. The degassed mixture was spuncoated onto a silicon wafer and cured at 70°C for at least 4 hours with thickness ranging from 10 μ m to 500 μ m. A thin gold (Au) film with thickness between 2 to 10 nm was deposited onto the PDMS surface by Cressington 108 sputter coater for varying times, by which sputtering was achieved with an efficient DC magnetron, offering fine-grain coatings and negligible sample heating. Stencil masks were placed on the samples to selectively deposit the thin Au film. Thickness of the PDMS and the Au layers were measured by Filmetrics optical Interferometer. For the wrinkle formation, the whole samples were heated to 300 °C at 5 °C/min using a hot stage and then examined using a Zeiss optical microscopy and an optical profilometer (Zygo New View 7300) to obtain the amplitude and wavelength of wrinkle patterns.

5.3 Results and Discussion

5.3.1 Swelling-induced Surface Instability

To prepare osmotically-induced wrinkling, UVO-treated PDMS on a silicon wafer was used as shown in the Chapter 4. To induce wrinkling, we exposed prepared samples to solvent vapor. Upon exposure to the solvent vapor, solvent molecules diffuse into the oxidized layer toward the PDMS layer. The swelling ratio of PDMS layer is inversely related to the solubility parameter of the solvent [88]. Solvents such as ether, THF, and chloroform swell the PDMS to a large extent, while acetone, pyridine, and alcohol swell it to a small extent (Table 5.1). The oxidized layer is a hydrophilic material, so a high affinity for polar solvents such as THF, acetone, and alcohol is expected. To qualitatively characterize the swelling mismatch of UVO-treated PDMS by solvent vapors, we conducted simple beam bending experiments, where UVO-treated PDMS films were placed on, but not adhered to, metal posts with a diameter of 1 cm. Upon swelling, the beam curled due to the differential strain induced by differences in the swelling extent of the oxidized layer and the non-modified PDMS layer. For example, the UVO-treated PDMS bent downward after ethanol or acetone vapor exposure, indicating that ethanol swelled the top oxidized layer to a greater extent as compared to the underlying PDMS (Figure 5.2a). On

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the other hand, toluene, hexane, THF, and ether swelled the PDMS layer more than the oxidized layer and caused the beam to bend upward (Figure 5.2b).

Table 5.1 Beam bending test and surface morphology with solvent exposure of UVO-treated PDMS (20:1 PDMS, PDMS thickness ~ 30 μ m, UVO time = 30 min). The swelling degree (*S*) that was measured experimentally for 10:1 PDMS: $S = D/D_0$, where *D* is the length of PDMS in the solvent and D_0 is the length of the dry PDMS.

Solvent	Beam bending test	Surface morphology	Swelling degree of PDMS (S _s) [88]
Ethanol	$S_f > S_s$	wrinkle	1.04
Acetone	$S_f > S_s$	wrinkle	1.06
Toluene	$S_f < S_s$	flat	1.31
Hexane	$S_f < S_s$	flat	1.35
THF	$S_f < S_s$	wrinkle and/or crack	1.38
Ether	$S_f < S_s$	wrinkle and/or crack	1.38

For SiO_x/PDMS/Si trilayer with the thin PDMS layer (thickness ~ 12 μ m), the rigid substrate resists the swelling-induced stress, putting the oxidized layer into a compressive stress state. When this compressive stress exceeds the critical stress value, wrinkles appear over large areas. Figure 5.2 shows representative results for the wrinkling of a UVO-treated PDMS supported by Si substrates with ethanol and THF. With equibiaxial stress, the resulting wrinkles exhibited no regular order. We could control the wrinkle wavelength and amplitude by changing the thickness of PDMS layer, the ratio of PDMS and crosslinker, and the UVO time (see details in the Chapter 4). While only wrinkle patterns were obtained from ethanol vapor regardless of the PDMS thickness, cracking was observed prior to wrinkling for thick PDMS (thickness ~ 100 μ m) exposed to THF vapor. For the very thick PDMS (thickness ~ 5 mm), no wrinkles, only cracks, were observed for samples exposed to THF vapor.

(a)



Figure 5.2 Wrinkling and cracking in a trilayer induced by swelling. (a-b) Images of beam bending and surface morphologies of UVO-treated PDMS after exposure to (a) ethanol and (b) THF vapor (t_{uvo} = 40 min, $h_s \sim 12 \mu$ m). (c) Surface instability of UVO-treated PDMS (t_{uvo} = 40 min $h_s \sim 100 \mu$ m) after THF vapor exposure. Cracking occurs prior to the formation of wrinkles.

This observation implies that the stress exerted in the oxidized layer changes with the thickness of PDMS, which can be qualitatively rationalized as follows. The swelling mismatch between the oxidized layer and the PDMS layer from THF vapor in the absence of Si substrate causes a tensile stress to the oxide layer. The attachment of UVO-treated PDMS to Si substrate constrains, or limits, the bending deformations caused by differential swelling. Hence, a compressive-stress is applied to the UVO-treated PDMS bilayer. For thin films of PDMS, this compressive stress is large and dominates swelling-induced tensile stresses near the SiO_x/PDMS interface, leading to wrinkle formation upon exceeding a critical strain. For PDMS layers with increasing thickness, the substrate constraint decreases, leading to tensile stresses dominating the SiO_x/PDMS interface. If the strain energy release rate associated with the applied tensile stress is greater than the critical strain energy release rate, cracking will ensue in the oxidized layer. As the tensile stress in the top oxidized layer is relieved by the process of cracking, compressive stresses imposed by the substrate constraint may lead to observed wrinkling patterns for PDMS films with intermediate thickness.

5.3.2 Thermally-induced Surface Instability

We used Au/PDMS/Si trilayers to study similar deformation mechanism transitions described in the above section. This system, which can be wrinkled by thermally induced strains, has advantages relative to SiO_x/PDMS/Si tirlayers in terms of control for the top layer thickness and knowledge of the differential mismatch strains, which can be directly determined by the coefficient of thermal expansion (CTE) of each material layer. The wavelength (λ) of wrinkles can be described when PDMS thickness is larger than wrinkle wavelength at small strains.

$$\lambda = 2\pi h_f \left(\frac{\overline{E}_{Au}}{3\overline{E}_{PDMS}}\right)^{\frac{1}{3}},\tag{5.1}$$

where h_f is the film thickness, $\overline{E}_i = E_i/(1 - v_i^2)$ is the plane-strain elastic moduli for material *i*. *E* is Young's modulus and v is the Poisson's ratio for material *i*. This equation predicts that the wavelength depends only on the film thickness and the film/substrate modulus ratio, and not on the strain. The wavelength of the wrinkle increased linearly with h_f , Au film thickness, as shown in Figure 5.3. A measurement of wavelength and thickness of Au film allows a determination of the modulus ratio ($\overline{E}_f / \overline{E}_s$) based on equation (5.1). We obtain $\overline{E}_f / \overline{E}_s \sim 5.59 \times 10^5$, 1.26 × 10^6 , and 1.82×10^7 for 40:1, 50:1, and 60:1 PDMS from the slope of the fit line in Figure 5.3, respectively. These values are of the same order of magnitude as calculated values based on the literature values [89-90].



Figure 5.3 A plot of wavelength of wrinkles (λ) vs Au thickness (h_f) with different PDMS ratios. The dotted lines represent best linear fit to data.

Two limiting cases help to understand the resulting stress on the Au film in such a trilayer system: (i) when $h_s \rightarrow 0$, the mismatch in the thermal expansion coefficients between

the Au film ($\alpha_{Au} \sim 14 \times 10^{-6} \text{ K}^{-1}$) [89] and the Si substrate ($\alpha_{Si} \sim 3 \times 10^{-6} \text{ K}^{-1}$) [91] leads to compressive stress, $\sigma_f = E_f (\alpha_{si} - \alpha_{Au}) \Delta T$. (ii) When $h_s \rightarrow \infty$, the lateral constraint by the substrate becomes negligible and the stress on the Au film is defined by the mismatch in thermal expansion coefficients between the Au film and the PDMS elastomer ($\alpha_{PDMS} \sim 3 \times 10^{-4} \text{ K}^{-1}$) [92], $\sigma_f = E_f (\alpha_{PDMS} - \alpha_{Au}) \Delta T$. In this regime, the stresses on the Au film will be tensile. These limits imply that a transition in the Au film stress state from compression to tension occurs as the PDMS thickness increases. Figure 5.4 shows representative results of wrinkle patterns in trilayer system with different PDMS thickness (60:1 PDMS ratio). For thin PDMS, wrinkling emerged at ~ 120 °C without cracking and disappeared by cooling. On the other hand, in the case of thick and more stiff PDMS films (40:1 ratio, 140 µm thick), cracks were observed before wrinkling. This observation is consistent with the results from swelling of UVO-treated PDMS film supported by Si substrate.



Figure 5.4 Wrinkling and cracking in a trilayer induced by heating. Optical micrographs of (a) 12 um and (b) 200 um PDMS layer sandwiched between the 5 nm Au film and Si substrate during heating from room temperature to 200 °C.

5.3.3 Stress State in a Trilayer

The thermally- and osmotically-driven deformation transitions observed in both trilayer systems described above indicate that the resultant stress in the top layer, which controls wrinkling or cracking, is determined by the balance of geometry and mechanical properties for the layered materials. An understanding of this stress state can be developed by applying the principle of superposition, such that the stress in the top layer can be determined by the summation of the mismatch stress that would develop in a hypothetical bilayer of the top and middle layers and the mistmach stress that would develop in a hypothetical bilayer of the top and bottom layers. The effect of middle layer thickness can be considered to modulate the stress in the bilayer of the top and bottom layers. For a film/substrate bilayer, Stoney's formula (Equation 5.2) can be applied to quantify the stress in thin top film layer [93].

$$\kappa = \frac{6(\varepsilon_s - \varepsilon_f)}{h_s} \left(\frac{h_f E_f}{h_s E_s}\right) \left[\frac{1 + \frac{h_f}{h_s}}{1 + \frac{h_f E_f}{h_s E_s} \left(4 + 6\frac{h_f}{h_s} + 4\left(\frac{h_f}{h_s}\right)^2\right) + \left(\frac{h_f}{h_s}\right)^4 \left(\frac{E_f}{E_s}\right)^2}\right], \quad (5.2)$$

where κ represents the curvature of bilayer. The subscripts *f* and *s* denote stiff, top film (*e.g.* Au) and underlying substrate (*e.g.* PDMS), respectively. With the given material properties and geometrical dimensions of top film and middle bilayer considered in our experiments, we expect the thickness ratio (h_f/h_s) to be small such that higher order terms are negligible and the extended Stoney's equation can be simplified to:

$$\varepsilon_s - \varepsilon_f \approx h_s \kappa \left(\frac{2}{3} + \frac{h_s E_s}{6h_f E_f} \right).$$
 (5.3)

The strain of the PDMS midplane (ε_0) is also given by:

$$\varepsilon_0 \approx -\frac{\left(\varepsilon_s - \varepsilon_f\right)h_f E_f}{h_s E_s + 4h_f E_f}.$$
(5.4)

The stress at the interface between the top and middle layers from the side of top film ($\sigma_{film/middle}$) given by:

$$\sigma_{film/middle} \approx \frac{E_f(\varepsilon_s - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_s E_s}}.$$
(5.5)

In the case of $\mathcal{E}_s > \mathcal{E}_{fr}$ the tensile stress is applied to the top film.

For a hypothetical bilayer between the top and bottom layers, the lateral stress on the top layer could be expressed as:

$$\sigma_{film/bottom} \approx \frac{E_f(\varepsilon_b - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_b E_b}},$$
(5.6)

where $\sigma_{film/bottom}$ is the stress on the top film from substrate constraints. The subscripts *b* denotes bottom layer (*e.g.* Si wafer.) In our experiments, the stress in the Au film will approach the stress predicted by Equation 5.6 when the thickness of the middle layer becomes infinitely small, *i.e.* $h_s \sim 0$. As the middle layer thickness increases, the contribution from the top/bottom bilayer will decrease to zero for an infinitely thick middle layer. Therefore, the following semi-empirical equation is suggested to describe the influence of middle layer thickness on the top film stress:

$$\sigma_{film/bottom} \approx \frac{E_f(\varepsilon_{Si} - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_b E_b}} \left(\frac{1}{1 + \frac{h_s}{L_0}}\right)^n,$$
(5.6)

where L_0 is a characteristic length and n (n > 0) is an exponent that defines the scaling for variation in the middle layer thickness. The stress state on the thin top film can be expressed as the superposition of these two stress contributions:

$$\sigma_{tri} \approx \frac{E_f(\varepsilon_s - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_s E_s}} + \frac{E_f(\varepsilon_{si} - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_{si} E_{si}}} \left(\frac{1}{1 + \frac{h_s}{L_0}}\right)^n = E_f \varepsilon_{tri}, \qquad (5.7)$$

where σ_{tri} and ε_{tri} is the stress and strain on a thin top film in a trilayer, respectively. This empirical equation satisfies the two limiting cases: (i) for $h_s \rightarrow 0$, $\sigma_{trilayer} \sim E_f(\varepsilon_b - \varepsilon_f)$, and (ii) for $h_s \rightarrow \infty$, $\sigma_{trilayer} \sim E_f(\varepsilon_s - \varepsilon_f)$.

To validate this approach for qualifying the lateral stress state on a thin top film in a trilayer, we first measured the wrinkle amplitude and wavelength to estimate the applied strain to the Au film in Au/PDMS/Si trilayer. The amplitude (*A*) of wrinkle pattern increases with a square-root dependence on the applied compressive strain (ε) as

$$A = h_f \left(\varepsilon / \varepsilon_c - 1 \right)^{1/2}. \tag{5.8}$$

Here, ε_c is the critical strain that is necessary for the wrinkling to occur:

$$\varepsilon_c = \frac{1}{4} \left(\frac{3\overline{E_s}}{\overline{E_f}} \right)^{2/3}.$$
(5.9)

Combining Equation 5.1 and Equation 5.8 yields an expression relating wrinkle amplitude and wavelength to the applied strain to the Au film:

$$\pi \frac{A}{\lambda} = \left(\varepsilon - \varepsilon_c\right)^{1/2}.$$
(5.10)

From the observed amplitude and wavelength with different temperatures, we estimated the applied strain induced by the CTE mismatch based on Equation 5.10. With the assumption of a

linear relationship between thermal strain and temperature ($\varepsilon = \alpha \Delta T$) and $\varepsilon_{tri} = -(\varepsilon - \varepsilon_c)$, Equation 5.10 becomes:

$$\frac{(\pi A)^2}{\lambda^2} = -\left[\frac{(\alpha_s - \alpha_f)}{1 + \frac{4h_f E_f}{h_s E_s}} + \frac{(\alpha_{si} - \alpha_f)}{1 + \frac{4h_f E_f}{h_{si} E_{si}}} \left(\frac{1}{1 + \frac{h_s}{L_0}}\right)^n\right] (T - T_c) = \alpha_a (T - T_c), \quad (5.11)$$

where T_c is the critical temperature at which wrinkles emerge. The parameter α_a is an apparent CTE of the Au film in Au/PDMS/Si trilayer. When $h_s \rightarrow 0$, α_a equals ($\alpha_f - \alpha_{Si}$) ~ 11 × 10⁻⁶ K⁻¹. It is qualitatively expected that as the PDMS thickness increases and approaches the critical thickness at which a transition of stress state from compression to tension occurs, α_a decrease, resulting in the decrease in magnitude of the applied compressive strain. As shown in Figure 5.5,



Figure 5.5 A plot of A/λ versus temperature variation from critical temperature to induce the wrinkling with different thickness of 60:1 PDMS layer (\Box : 12 µm, \circ : 140 µm, and \triangle : 400 µm). The dashed lines represent best square root curve fit to data.

the observed dependence of A/λ on temperature is adequately described by the allometric relation $A/\lambda \propto (T - T_c)^{1/2}$ given by Equation 5.11. By fitting the data, we obtain the value of α_a with three different PDMS thickness (4.20×10^{-6} , 2.37×10^{-6} , 0.96×10^{-6} K⁻¹ for 12, 140, 400 µm, respectively), which is in good agreement with the expectation. As shown in Figure 5.6, α_a decreased as the PDMS layer in thickness increased. The dashed line was obtained from Equation 5.11 with $L_a = 10$ µm and n = 0.6.



Figure 5.6 A plot of α_a versus 60:1 PDMS thickness. The dashed line was obtained from Equation 5.11 with $L_a = 10 \ \mu m$ and n = 0.6.

Above the critical PDMS thickness, the cracking was observed as the dominant deformation mechanism, followed by wrinkling as shown in Figure 5.4. We observed the surface morphology in Au/PDMS/Si trilayer systems at 300 °C by varying the PDMS thickness from 10 to 500 μm with three different PDMS/crosslinker ratios (40:1, 50:1, and 60:1). Figure 5.7 shows two different forms of surface deformation (*i.e.* wrinkle and crack) of Au/PDMS/Si trilayer system in



Figure 5.7 Morphological phase diagram of surface instability in a trilayer. Phase boundary is drawn to guide the eye. O: wrinkling and Δ : cracking prior to wrinkling. E_s is estimated from Figure 5.3 with the E_f of 82 GPa.

the PDMS thickness-modulus phase diagram. The dashed line guides the boundary between the two regions of wrinkling and cracking prior to wrinkling. The data below the dashed line exhibit the formation of wrinkles in the Au film. The data above the dashed line show the cracking prior to wrinkling. This can be qualitatively rationalized with Equation 5.7. As the PDMS layer increase in thickness, the thermal mismatch between the Au and PDMS increases the tensile stress while the compressive stress induced by thermal mismatch between Au and Si decreases in Equation 5.7. As a result, a transition from compression to tension occurs at the critical thickness. For PDMS layer with thickness above the critical thickness, the tensile stress leads to the formation of cracks. As cracking relieves the tension stress in the Au film induced by the thermal mismatch

with PDMS, the stress in the remaining regions of Au transitions to compression, which is attributed to the second term of Equation 5.13. This compressive stress leads to the formation of wrinkles after cracking. It should be noted that only cracks were observed for very thick PDMS ($h_s \sim 5$ mm), which implies that the effect of substrate constraint, *i.e.* the contribution from the second term in Equation 5.7, is negligible.

The dashed line in Figure 5.7 is empirical, but some insight into the stress state of the Au film can be gained: the effect of substrate constraint on the PDMS layer becomes more significant as the PDMS layer becomes thinner and softer, which increases the compressive stress on the Au film in Au/PDMS/Si trilayer system. This result infers that L_0 is related to wrinkle wavelength (λ), as it is the only relevant length scale that depends on the modulus of PDMS. Considering the residual stress (σ_t), Equation 5.7 can be written as:

$$\sigma_{tri} \approx \frac{E_f(\varepsilon_s - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_s E_s}} + \frac{E_f(\varepsilon_{si} - \varepsilon_f)}{1 + \frac{4h_f E_f}{h_{si} E_{si}}} \left(\frac{1}{1 + A\binom{h_s}{\lambda}}\right)^n + \sigma_r = E_f \varepsilon_{tri} + \sigma_r, \quad (5.13)$$

where A is the constant ($L_0 = \lambda/A$). Equation 5.13 shows that σ_{tri} is dependent on not only geometry but also material properties of each layer in a trilayer system.

From the Equation 5.13, there must be a mismatch strain between top layer and substrate to induce the compressive stress for wrinkling. For the swelling test of UVO-treated PDMS on Si with hexane or toluene vapor, no wrinkling was observed (Table 5.1). It might be due to the fact that these solvents swell the oxidized layer to no extent at all or to a very small extent compared to the THF and ether, while swelling the PDMS at a large extent. Okayasu *et al.* also showed no wrinkling in the absence of the mismatch strain between a top film and a substrate. Equation 5.13 explains the stress state of a thin top layer in a trilayer qualitatively,

but more intensive study is needed to develop the more accurate expression of quantitative relationships.



Figure 5.8 Schematic showing the sample preparation for Au/PDMS/Si trilayer to generate wrinkling instability.

Lastly, the lateral configuration of Au film on PDMS layer plays a role in determining the magnitude of the stress profiles. These boundary effects were observed specifically in the case when the PDMS edge coincided with the film edge than in the case when the PDMS extended far beyond the film edge (Figure 5.8).

5.5 Conclusions

In this chapter, we discussed the surface instability in the trilayer that consists of a compliant PDMS layer sandwiched between a stiff top film and a rigid Si substrate through osmotic and thermal approaches. The constraint by a rigid Si substrate leads to compressive stress on a stiff thin film, resulting in the wrinkle formation. Wrinkling was observed for thin

and/or soft PDMS layers, while cracking occurred prior to the wrinkle formation for relatively thick and/or hard PDMS layers. Understanding the effect of geometry and material properties in a trilayer system on surface instability provides critical insight toward its use in various applications.

CHAPTER 6

CONCLUSION

The main focus of this thesis was to create the spontaneous formation of wellcontrolled patterns over large areas in a simple, robust, and versatile manner. By taking advantage of dynamic self-assembly and wrinkling instability we were able to develop new strategies for macroscopic patterning that will have a broad impact on many applications in optics, electronics, and adhesion.

This study demonstrated that a programmed flow-coating can offer a powerful means to create the well-ordered line patterns of numerous materials over large areas in a simple manner as well as a new, exciting class of inorganic nanoparticle materials. Combining the "coffee ring" effect with the precise control over the contact lines by using the programmed flow-coating resulted in line-based patterns with high positioning accuracy. By programming the velocity profile of a translation stage, we mimicked the stick-slip motion of the contact line, leading to the controlled macroscopic patterns. Spacing and dimensions of lines were controlled by a programmed flow-coating. By studying the minimum spacing between the neighboring lines based on geometric consideration, the geometry of deposit structures was found to play a significant role in pinning the contact line. With the help of polymer ligand chemistry on the nanoparticle surface, multicomponent patterning of nanoparticles was realized with welldefined structures and 1-D nanoparticle structures that exhibited extreme flexibility when they were floated by removing the sacrificial layer were readily fabricated. The ease of macroscopic patterning by the programmed flow-coating method creates new opportunities for organization and assembly of functional materials with preserved materials properties into macroscale devices.

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Inspired by the mechanical instability, we also fabricated the solvent-responsive surfaces with periodic structures over large areas that dynamically transform their topography through wrinkling. By changing the geometry and material properties of systems, we controlled the dimension and morphology of wrinkle patterns over large areas, which allowed for a realization of a variety of advanced devices, such as reversible channels, and smart microlens arrays, and patterning of nanoparticle assemblies. Taken together, this study provided promising avenues of future work and potential applications of stimuli-responsive materials, while raising many questions regarding the origin of stress in a multilayer system. Therefore, we studied the influence of geometry and material properties of system on the stress state in a trilayer system. A compliant middle layer played a significant role in determining the surface structures, which is determined by the stress state on a top layer. In the pursuit of new functional materials, fundamental understanding of the stress state in this study which causes the formation of wrinkles enables the possibility to create more complex patterns over large areas through the creative use of geometry, material choice, and process. However, more work remains to be done in order to study the kinetic effects that can provide a number of useful starting points for both the generation of novel patterns as well as in exploiting the reversibility of wrinkled surfaces for practical applications.

The results and analysis presented here will undoubtedly provide useful stepping stones for the beginning of understanding and utilizing dynamic self-assembly and wrinkling instability not only to generate novel macroscopic patterns but also to probe fundamental and practical questions. Thus, it lays the foundation to develop novel patterns and advanced materials for a wide range of future studies from the fundamental to the applied.

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BIBLIOGRAPHY

1. Yoo, P. J.; Nam, K. T.; Qi, J.; Lee, S. K.; Park, J.; Belcher, A. M.; Hammond, P. T., Spontaneous assembly of viruses on multilayered polymer surfaces. *Nature Materials* **2006**, *5* (3), 234-40.

2. Bigioni, T. P.; Lin, X. M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M., Kinetically driven self assembly of highly ordered nanoparticle monolayers. *Nature Materials* **2006**, *5* (4), 265-270.

3. Bowden, N.; Brittain, S.; Evans, A. G.; Hutchinson, J. W.; Whitesides, G. M., Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature* **1998**, *393* (6681), 146-149.

4. van Hameren, R.; Schon, P.; van Buul, A. M.; Hoogboom, J.; Lazarenko, S. V.; Gerritsen, J. W.; Engelkamp, H.; Christianen, P. C. M.; Heus, H. A.; Maan, J. C.; Rasing, T.; Speller, S.; Rowan, A. E.; Elemans, J. A. A. W.; Nolte, R. J. M., Macroscopic hierarchical surface patterning of porphyrin trimers via self-assembly and dewetting. *Science* **2006**, *314* (5804), 1433-1436.

5. Park, S.; Lee, D. H.; Xu, J.; Kim, B.; Hong, S. W.; Jeong, U.; Xu, T.; Russell, T. P., Macroscopic 10-Terabit-per-Square- Inch Arrays from Block Copolymers with Lateral Order. *Science* **2009**, *323* (5917), 1030-1033.

6. Whitesides, G. M., Self-Assembly at All Scales. *Science* **2002**, *295* (5564), 2418-2421.

7. Whitesides, G. M.; Boncheva, M., Beyond molecules: Self-assembly of mesoscopic and macroscopic components. *Proceedings of the National Academy of Sciences of the United States of America* **2002**, *99* (8), 4769-4774.

8. Khang, D.-Y.; Rogers, J. A.; Lee, H. H., Mechanical Buckling: Mechanics, Metrology, and Stretchable Electronics. *Advanced Functional Materials* **2009**, *19* (10), 1526-1536.

9. Genzer, J.; Groenewold, J., Soft matter with hard skin: From skin wrinkles to templating and material characterization. *Soft Matter* **2006**, *2* (4), 310-323.

10. Grzybowski, B. A.; Fialkowski, M.; Bishop, K. J. M.; Klajn, R.; Smoukov, S. K.; Campbell, C. J., Principles and implementations of dissipative (dynamic) self-assembly. *Journal of Physical Chemistry B* **2006**, *110* (6), 2482-2496.

11. Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P., Nanoparticle assembly and transport at liquid-liquid interfaces. *Science* **2003**, *299* (5604), 226-229.

12. Skaff, H.; Lin, Y.; Tangirala, R.; Breitenkamp, K.; Boker, A.; Russell, T. P.; Emrick, T., Crosslinked capsules of quantum dots by interfacial assembly and ligand crosslinking. *Advanced Materials* **2005**, *17* (17), 2082-+.

13. Lin, Z. Q., Controlled Evaporative Assembly of Polymers from Confined Solutions. *Journal of Polymer Science Part B-Polymer Physics* **2010**, *48* (24), 2552-2557.

14. Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A., Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **1997**, *389* (6653), 827-829.

15. Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A., Contact line deposits in an evaporating drop. *Physical Review E* **2000**, *62* (1), 756-765.

16. Maillard, M.; Motte, L.; Ngo, A. T.; Pileni, M. P., Rings and hexagons made of nanocrystals: A Marangoni effect. *Journal of Physical Chemistry B* **2000**, *104* (50), 11871-11877.

17. Hu, H.; Larson, R. G., Marangoni Effect Reverses Coffee-Ring Depositions. *The Journal of Physical Chemistry B* **2006**, *110* (14), 7090-7094.

18. Adachi, E.; Dimitrov, A. S.; Nagayama, K., Stripe Patterns Formed on a Glass-Surface during Droplet Evaporation. *Langmuir* **1995**, *11* (4), 1057-1060.

19. Xu, J.; Xia, J.; Hong, S. W.; Lin, Z.; Qiu, F.; Yang, Y., Self-Assembly of Gradient Concentric Rings via Solvent Evaporation from a Capillary Bridge. *Physical Review Letters* **2006**, *96* (6), 066104.

20. Watanabe, S.; Inukai, K.; Mizuta, S.; Miyahara, M. T., Mechanism for Stripe Pattern Formation on Hydrophilic Surfaces by Using Convective Self-Assembly. *Langmuir* **2009**, *25* (13), 7287-7295.

21. Maheshwari, S.; Zhang, L.; Zhu, Y. X.; Chang, H. C., Coupling between precipitation and contact-line dynamics: Multiring stains and stick-slip motion. *Physical Review Letters* **2008**, *100* (4), 044503.

22. Xu, J.; Xia, J. F.; Lin, Z. Q., Evaporation-induced self-assembly of nanoparticles from a sphere-on-flat geometry. *Angewandte Chemie-International Edition* **2007**, *46* (11), 1860-1863.

23. Chengyi Zhang, X. Z. X. Z. X. F. J. J. J. C. C. C.-S. L. W. Z. S.-T. L., Facile One-Step Growth and Patterning of Aligned Squaraine Nanowires via Evaporation-Induced Self-Assembly. *Advanced Materials* **2008**, *20* (9), 1716-1720.

24. Hong, S. W.; Xia, J.; Lin, Z., Spontaneous Formation of Mesoscale Polymer Patterns in an Evaporating Bound Solution. *Advanced Materials* **2007**, *19* (10), 1413-1417.

25. Yabu, H.; Shimomura, M., Preparation of self-organized mesoscale polymer patterns on a solid substrate: Continuous pattern formation from a receding meniscus. *Advanced Functional Materials* **2005**, *15* (4), 575-581.

26. Li, F.; Josephson, D. P.; Stein, A., Colloidal Assembly: The Road from Particles to Colloidal Molecules and Crystals. *Angewandte Chemie International Edition*, n/a-n/a.

27. Hong, S. W.; Byun, M.; Lin, Z. Q., Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids. *Angewandte Chemie-International Edition* **2009**, *48* (3), 512-516.

28. Hong, S. W.; Xia, J. F.; Byun, M.; Zou, Q. Z.; Lin, Z. Q., Mesoscale patterns formed by evaporation of a polymer solution in the proximity of a sphere on a smooth substrate: Molecular weight and curvature effects. *Macromolecules* **2007**, *40* (8), 2831-2836.

29. Hong, S. W.; Wang, J.; Lin, Z. Q., Evolution of Ordered Block Copolymer Serpentines into a Macroscopic, Hierarchically Ordered Web. *Angewandte Chemie-International Edition* **2009**, *48* (44), 8356-8360.

30. Landau, L. D.; Lifshitz, E. M.; Kosevich, A. M.; Pitaevskiĭ, L. P., *Theory of Elasticity*. Butterworth-Heinemann: 1986.

31. Cerda, E.; Mahadevan, L., Geometry and physics of wrinkling. *Physical Review Letters* **2003**, *90* (7), -.

32. Breid, D.; Crosby, A. J., Effect of stress state on wrinkle morphology. *Soft Matter* **2011**, 7 (9), 4490.

33. Lin, P. C.; Yang, S., Spontaneous formation of one-dimensional ripples in transit to highly ordered two-dimensional herringbone structures through sequential and unequal biaxial mechanical stretching. *Applied Physics Letters* **2007**, *90* (24), -.

34. Breid, D.; Crosby, A. J., Surface wrinkling behavior of finite circular plates. *Soft Matter* **2009**, *5* (2), 425-431.

35. Lee, S. G.; Lee, D. Y.; Lim, H. S.; Lee, D. H.; Lee, S.; Cho, K., Switchable Transparency and Wetting of Elastomeric Smart Windows. *Advanced Materials* **2010**, *22* (44), 5013-5017.

36. Khang, D.-Y.; Jiang, H.; Huang, Y.; Rogers, J. A., A Stretchable Form of Single-Crystal Silicon for High-Performance Electronics on Rubber Substrates. *Science* **2006**, *311* (5758), 208-212.

37. Takahashi, M.; Inoue, M.; Ihara, R.; Yoko, T.; Nemoto, T.; Isoda, S.; Malfatti, L.; Costacurta, S.; Innocenzi, P., Photo-Fabrication of Titania Hybrid Films with Tunable Hierarchical Structures and Stimuli-Responsive Properties. *Advanced Materials* **2010**, *22* (30), 3303-3306.

38. Schweikart, A.; Fortini, A.; Wittemann, A.; Schmidt, M.; Fery, A., Nanoparticle assembly by confinement in wrinkles: experiment and simulations. *Soft Matter* **2010**.

39. Lu, C. H.; Mohwald, H.; Fery, A., A lithography-free method for directed colloidal crystal assembly based on wrinkling. *Soft Matter* **2007**, *3* (12), 1530-1536.

40. Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E., Drying-mediated self-assembly of nanoparticles. *Nature* **2003**, *426* (6964), 271-274.

41. Lin, Z. Q.; Granick, S., Patterns formed by droplet evaporation from a restricted geometry. *Journal of the American Chemical Society* **2005**, *127* (9), 2816-2817.

42. Yeon, W. C.; Kannan, B.; Wohland, T.; Ng, V., Colloidal Crystals from Surface-Tension-Assisted Self-Assembly: A Novel Matrix for Single-Molecule Experiments. *Langmuir* **2008**, *24* (21), 12142-12149.

43. Huang, J. X.; Tao, A. R.; Connor, S.; He, R. R.; Yang, P. D., A general method for assembling single colloidal particle lines. *Nano Letters* **2006**, *6* (3), 524-529.

44. Malaquin, L.; Kraus, T.; Schmid, H.; Delamarche, E.; Wolf, H., Controlled particle placement through convective and capillary assembly. *Langmuir* **2007**, *23* (23), 11513-11521.

45. Kumnorkaew, P.; Ee, Y.-K.; Tansu, N.; Gilchrist, J. F., Investigation of the Deposition of Microsphere Monolayers for Fabrication of Microlens Arrays. *Langmuir* **2008**, *24* (21), 12150-12157.

46. Smalyukh, I. I.; Zribi, O. V.; Butler, J. C.; Lavrentovich, O. D.; Wong, G. C. L., Structure and dynamics of liquid crystalline pattern formation in drying droplets of DNA. *Physical Review Letters* **2006**, *96* (17), 177801.

47. Nguyen, V.; Stebe, K., Patterning of Small Particles by a Surfactant-Enhanced Marangoni-Bénard Instability. *Physical Review Letters* **2002**, *88* (16), 164501.

48. Stannard, A., Dewetting-mediated pattern formation in nanoparticle assemblies. *Journal of Physics-Condensed Matter* **2011**, *23* (8), 083001.

49. Huang, J. X.; Fan, R.; Connor, S.; Yang, P. D., One-step patterning of aligned nanowire arrays by programmed dip coating. *Angewandte Chemie-International Edition* **2007**, *46* (14), 2414-2417.

50. Nie, Z. H.; Petukhova, A.; Kumacheva, E., Properties and emerging applications of selfassembled structures made from inorganic nanoparticles. *Nature Nanotechnology* **2010**, *5* (1), 15-25.

51. Chen, J. X.; Liao, W. S.; Chen, X.; Yang, T. L.; Wark, S. E.; Son, D. H.; Batteas, J. D.; Cremer, P. S., Evaporation-Induced Assembly of Quantum Dots into Nanorings. *ACS Nano* **2009**, *3* (1), 173-180.

52. Hong, S. W.; Xu, J.; Lin, Z. Q., Template-assisted formation of gradient concentric gold rings. *Nano Letters* **2006**, *6* (12), 2949-2954.

53. Bodiguel, H.; Doumenc, F.; Guerrier, B., Stick-Slip Patterning at Low Capillary Numbers for an Evaporating Colloidal Suspension. *Langmuir* **2010**, *26* (13), 10758-10763.

54. Lin, Y.; Balizan, E.; Lee, L. A.; Niu, Z. W.; Wang, Q., Self-Assembly of Rodlike Bionanoparticles in Capillary Tubes. *Angewandte Chemie-International Edition* **2010**, *49* (5), 868-872. 55. Skaff, H.; Ilker, M. F.; Coughlin, E. B.; Emrick, T., Preparation of Cadmium Selenide Polyolefin Composites from Functional Phosphine Oxides and Ruthenium-Based Metathesis. *Journal of the American Chemical Society* **2002**, *124* (20), 5729-5733.

56. Stafford, C. M.; Roskov, K. E.; Epps, T. H.; Fasolka, M. J., Generating thickness gradients of thin polymer films via flow coating. *Review of Scientific Instruments* **2006**, *77* (2), 023908.

57. Zheng, R., A study of the evaporative deposition process: Pipes and truncated transport dynamics. *European Physical Journal E* **2009**, *29* (2), 205-218.

58. Bodiguel, H.; Doumenc, F.; Guerrier, B., Pattern formation during the drying of a colloidal suspension. *European Physical Journal-Special Topics* **2009**, *166*, 29-32.

59. Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G., Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides. *Nature Materials* **2003**, *2* (4), 229-232.

60. Vaia, R. A.; Dennis, C. L.; Natarajan, L. V.; Tondiglia, V. P.; Tomlin, D. W.; Bunning, T. J., One-Step, Micrometer-Scale Organization of Nano- and Mesoparticles Using Holographic Photopolymerization: A Generic Technique. *Advanced Materials* **2001**, *13* (20), 1570-1574.

61. Jacobs, H. O.; Whitesides, G. M., Submicrometer patterning of charge in thin-film electrets. *Science* **2001**, *291* (5509), 1763-1766.

62. Daniel, M. C.; Astruc, D., Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews* **2004**, *104* (1), 293-346.

63. Lee, K. B.; Park, S. J.; Mirkin, C. A.; Smith, J. C.; Mrksich, M., Protein nanoarrays generated by dip-pen nanolithography. *Science* **2002**, *295* (5560), 1702-1705.

64. Hong, S. H.; Zhu, J.; Mirkin, C. A., Multiple ink nanolithography: Toward a multiple-pen nano-plotter. *Science* **1999**, *286* (5439), 523-525.

5. Jiang, X. P.; Clark, S. L.; Hammond, P. T., Side-by-side directed multilayer patterning using surface templates. *Advanced Materials* **2001**, *13* (22), 1669-1673.

66. Park, J. U.; Hardy, M.; Kang, S. J.; Barton, K.; Adair, K.; Mukhopadhyay, D. K.; Lee, C. Y.; Strano, M. S.; Alleyne, A. G.; Georgiadis, J. G.; Ferreira, P. M.; Rogers, J. A., High-resolution electrohydrodynamic jet printing. *Nature Materials* **2007**, *6* (10), 782-789.

67. Tien, J.; Nelson, C. M.; Chen, C. S., Fabrication of aligned microstructures with a single elastomeric stamp. *Proceedings of the National Academy of Sciences of the United States of America* **2002**, *99* (4), 1758-1762.

68. Klajn, R.; Fialkowski, M.; Bensemann, I. T.; Bitner, A.; Campbell, C. J.; Bishop, K.; Smoukov, S.; Grzybowski, B. A., Multicolour micropatterning of thin films of dry gels. *Nature Materials* **2004**, *3* (10), 729-735.
69. Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A., Colloidosomes: Selectively permeable capsules composed of colloidal particles. *Science* **2002**, *298* (5595), 1006-1009.

70. Bruckbauer, A.; Zhou, D. J.; Ying, L. M.; Korchev, Y. E.; Abell, C.; Klenerman, D., Multicomponent submicron features of biomolecules created by voltage controlled deposition from a nanopipet. *Journal of the American Chemical Society* **2003**, *125* (32), 9834-9839.

71. Xia, Y. N.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M., Unconventional methods for fabricating and patterning nanostructures. *Chemical Reviews* **1999**, *99* (7), 1823-1848.

72. Santhanam, V.; Andres, R. P., Microcontact printing of uniform nanoparticle arrays. *Nano Letters* **2004**, *4* (1), 41-44.

73. Perl, A.; Reinhoudt, D. N.; Huskens, J., Microcontact Printing: Limitations and Achievements. *Advanced Materials* **2009**, *21* (22), 2257-2268.

74. Song, J. H.; Atay, T.; Shi, S. F.; Urabe, H.; Nurmikko, A. V., Large enhancement of fluorescence efficiency from CdSe/ZnS quantum dots induced by resonant coupling to spatially controlled surface plasmons. *Nano Letters* **2005**, *5* (8), 1557-1561.

75. Xie, T.; Xiao, X.; Li, J.; Wang, R., Encoding Localized Strain History Through Wrinkle Based Structural Colors. *Advanced Materials* **2010**, *22* (39), 4390-4394.

76. Singamaneni, S.; Tsukruk, V. V., Buckling instabilities in periodic composite polymeric materials. *Soft Matter* **2010**, *6* (22), 5681-5692.

77. Hyun, D. C.; Moon, G. D.; Cho, E. C.; Jeong, U. Y., Repeated Transfer of Colloidal Patterns by Using Reversible Buckling Process. *Advanced Functional Materials* **2009**, *19* (13), 2155-2162.

78. Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Muller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S., Emerging applications of stimuli-responsive polymer materials. *Nature Materials* **2010**, *9* (2), 101-113.

79. Chan, E. P.; Crosby, A. J., Spontaneous formation of stable aligned wrinkling patterns. *Soft Matter* **2006**, *2* (4), 324-328.

80. Chan, E. P.; Smith, E. J.; Hayward, R. C.; Crosby, A. J., Surface wrinkles for smart adhesion. *Advanced Materials* **2008**, *20* (4), 711-+.

81. Efimenko, K.; Rackaitis, M.; Manias, E.; Vaziri, A.; Mahadevan, L.; Genzer, J., Nested selfsimilar wrinkling patterns in skins. *Nature Materials* **2005**, *4* (4), 293-297.

82. Chan, E. P.; Crosby, A. J., Fabricating microlens arrays by surface wrinkling. *Advanced Materials* **2006**, *18* (24), 3238-+.

83. Stafford, C. M.; Harrison, C.; Beers, K. L.; Karim, A.; Amis, E. J.; Vanlandingham, M. R.; Kim, H. C.; Volksen, W.; Miller, R. D.; Simonyi, E. E., A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nature Materials* **2004**, *3* (8), 545-550.

84. Vandeparre, H.; Damman, P., Wrinkling of Stimuloresponsive Surfaces: Mechanical Instability Coupled to Diffusion. *Physical Review Letters* **2008**, *101* (12), 124301.

85. Vandeparre, H.; Leopoldes, J.; Poulard, C.; Desprez, S.; Derue, G.; Gay, C.; Damman, P., Slippery or sticky boundary conditions: Control of wrinkling in metal-capped thin polymer films by selective adhesion to substrates. *Physical Review Letters* **2007**, *99* (18), -.

86. Yoo, P. J.; Lee, H. H., Evolution of a Stress-Driven Pattern in Thin Bilayer Films: Spinodal Wrinkling. *Physical Review Letters* **2003**, *91* (15), 154502.

87. Yoo, P. J.; Suh, K. Y.; Kang, H.; Lee, H. H., Polymer Elasticity-Driven Wrinkling and Coarsening in High Temperature Buckling of Metal-Capped Polymer Thin Films. *Physical Review Letters* **2004**, *93* (3), 034301.

88. Lee, J. N.; Park, C.; Whitesides, G. M., Solvent compatibility of poly(dimethylsiloxane)based microfluidic devices. *Analytical Chemistry* **2003**, *75* (23), 6544-6554.

89. Lacour, S. P.; Wagner, S.; Huang, Z. Y.; Suo, Z., Stretchable gold conductors on elastomeric substrates. *Applied Physics Letters* **2003**, *82* (15), 2404-2406.

90. Ochsner, M.; Dusseiller, M. R.; Grandin, H. M.; Luna-Morris, S.; Textor, M.; Vogel, V.; Smith, M. L., Micro-well arrays for 3D shape control and high resolution analysis of single cells. *Lab on a Chip* **2007**, *7* (8), 1074-1077.

91. Okayasu, T.; Zhang, H. L.; Bucknall, D. G.; Briggs, G. A. D., Spontaneous formation of ordered lateral patterns in polymer thin-film structures. *Advanced Functional Materials* **2004**, *14* (11), 1081-1088.

92. Kim, B.; Park, M.; Kim, Y. S.; Jeong, U., Thermal expansion and contraction of an elastomer stamp causes position-dependent polymer patterns in capillary force lithography. *ACS Applied Materials & Interfaces* **2011**, *3* (12), 4695-702.

93. Freund, L. B.; Floro, J. A.; Chason, E., Extensions of the Stoney formula for substrate curvature to configurations with thin substrates or large deformations. *Applied Physics Letters* **1999**, *74* (14), 1987.