Asymmetric liquid wetting on controllable magnetic micro-pillar surfaces

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magnetic micro-pillar surfaces

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Abstract

Wetting is the ability of a liquid to maintain contact with a solid surface, and spreading is the displacement process from a surface of air or one fluid by another. The wetting and spreading is a ubiquitous phenomenon in nature and daily life and has attracted numerous research interests in many applications, such as lubrication, coating, painting and drug delivery. Unidirectional liquid wetting and spreading on asymmetric nanostructured surfaces was also reported recently, such as water droplets roll off rice leaves due to their anisotropic microstructured leaf surfaces. For developing new process and technologies in which wetting and spreading are involved, many research efforts have been devoted in these areas. In this work, we studied the liquid wetting and spreading behaviors on different surfaces, and tried to understand the mechanism and utilize it in applications.

First, we studied the wettability ageing behaviors of the silicon wafers which had been cleaned by piranha solution (a 3:1 mixture of sulfuric acid), SC1 (a mixture of NH_4OH , H_2O_2 and H_2O with a ratio of 1:1:5) and HF solution (a mixture of 40% NH_4F and 49% HF with a ratio of 6:1), and treated by gaseous plasma. It is found that both piranha and SC1 solution cleaned silicon wafers were hydrophilic, and the water contact angles on the surfaces would increase along with ageing time, until they reached the saturated point $\sim 70^\circ$. The contact angle increase rate of these wafers in vacuum was much faster than in open air, because of loss of water, which was physically adsorbed on wafer surfaces. The silicon wafer cleaned by HF solution was hydrophobic, and the contact angle decreased in atmosphere, while it increased in vacuum up

to 95°. Gold thin films deposited on the hydrophilic wafers were smoother than the ones deposited on the hydrophobic wafers, because the numerous oxygen groups linked on hydrophilic surfaces would react with gold adatoms in the sputtering process to form continuous thin film at nucleation stage. The argon, nitrogen, oxygen gas plasma treatments could change the silicon wafer surfaces from hydrophobic to hydrophilic by creating a thin (around 2.5 nm) silicon dioxide film, which would be used to improve the gold thin film roughness and adhesion.

Next, we invented a novel technique for fabricating high-aspect-ratio magnetic PDMS micro-pillars which are capable of vibrating with considerable amplitudes under a gradient magnetic field. We dispersed the special treated Fe_3O_4 super-paramagnetic nanoparticles (refer as Fe_3O_4 nanoparticles, similarly hereinafter) in acetone solution and sonicate for disaggregation, and pour the solution with Fe_3O_4 nanoparticles over the silicon mold, which has been pre-etched with deep micro-holes. Then, nanoparticles are attracted into micro-holes by a strong rotating permanent magnet at the backside of the silicon mold. Soft lithography is used to make the PDMS fluid flow into the micro-structures in a vacuum, and peel it off after sufficient baking. The PDMS magnetic pillars have been fabricated with diameters ranging from 1 μm to 10 μm , and with heights of 30 μm and 50 μm . The pillar tip displacement, for 1 μm diameter pillars with an aspect ratio of 50, could be as much as 12 μm under a gradient magnetic field. The magnetic pillar tip vibration in a liquid was also validated, which enables the application as actuators in micro-fluidics, miniaturized devices on a chip, and dynamic substrate for cell culture in biomimetic researches. The key to drive micro-pillar tip deflection is high-aspect-ratio. EDS data shows that the weight percentage of iron embedding in PDMS pillars is

from 42% to 81.4% with a median value 59.6%, which is the highest value reported in the literature, to our best knowledge.

Last, we studied the uni-directional liquid spreading phenomena on asymmetric silicone-fabricated nanostructured surfaces. The uniformly deflected Polydimethylsiloxane (PDMS) micro-pillars covered with silver films were fabricated. Asymmetric liquid wetting and spreading behaviors in a preferential direction were observed on the slanted micro-pillar surfaces and a micro-scale thin liquid film advancing ahead of the bulk liquid droplet was clearly observed by high-speed video imaging. The slanted micro-pillar array is able to promote or inhibit the propagation of this thin liquid film in different directions by the asymmetric capillary force. The spreading behavior of the bulk liquid was guided and finally controlled by this micro-scale liquid film. Different spreading regimes are defined by the relationship between the liquid intrinsic contact angle and the critical angles which were defined by the micro-pillar height, deflection angle and inter-pillar spacing.

We incorporated Fe_3O_4 magnetic particles into the PDMS micro-pillars to make them be controllable to external magnetic field, which in turn was used to turn the liquid spreading direction. However, it was proven that the magnetic force is not stronger than capillary force for controlling the liquid flow direction. Once the drop is placed on the micro-pillar surfaces, the micro-pillars with partial wetting are deflected in different directions. Based on the magnetic pillars deflection angles measured, it was found the magnetic force calculated is around $5.9\text{E-}5$ for $1\text{ }\mu\text{m}$ pillar in diameter and $5.9\text{E-}4\text{ N/m}$ for $10\text{ }\mu\text{m}$ in diameter. These forces are much smaller than the capillary force (0.072 N/m) exerted on micro pillar surface. Therefore, the

conclusion is that magnetic force is not able to overcome the surface tension. Nevertheless, the capillary force could be tuned by appropriately selecting the wetting liquid or the liquid mixtures and the magnetic pillar surface coating materials and the features. It will be the next research focus. Moreover, the magnetic micro-pillars also could be used as actuators in micro-fluidic and other applications for controlling the liquid flow rate and direction.

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List of Figures

Figure 2.1 The apparent contact angle determines the drop shape, when a drop partially wets and spreads on the solid substrate. It is shown that the interface near the corner is highly curved.....	18
Figure 2.2 The continuum modeling procedure illustration.....	20
Figure 2.3 (1) is the spherical part of the drop, in which a dynamic contact angle θ is formed on the solid surface; (2) A region the hydrodynamic force distorts the spherical shape; (3) A region capillary force is gradually overwhelming by the disjoining pressure; (4) A region with surface diffusion only and no macroscopic spreading process.....	22
Figure 2.4 On PPX nano-film coated pipes, it shows the drop motion. It is the experiment schematic. One is coated with PPX nano-film and the other is uncoated. The frequency of the low amplitude vibration at half-pipes is $\sim 85\text{Hz}$	29
Figure 2.5 Images show the droplet motions with time on the coated and uncoated half pipe surfaces. Water drops were translated axially on the half-pipe coated with the PPX nano-film, but there is no motion for those on the uncoated half-pipe. The glue layer can be seen on uncoated pipes. The arrows indicate droplet position.....	30
Figure 2.6 With different obliquity AONWAs the PET sheets changed the surface water wetting property. The nano-wire growth direction on the PET surface was indicated. (a) Contact angles aligned with the projection direction. (b) Contact angles upright to the projection direction. (c-f) Top-views of water drop on PET surfaces with different obliquity AONWAs. From (c) to (f), they are 10° , 20° , 30° , and 40° , respectively.....	31
Figure 2.7 (a) (a) After annealing in a high temperature oven, the schematic shows that the nano-pillar is bended against to the metal side. (b) A titled image showing the bent nano-pillars. It is achieved by coating a 6 nm platinum thin film on one side of the pillars and conducted	

thermal annealing in an oven with the temperature of 120 °C for 30 min. (c) A schematic illustrating the nano-pillars bending against the polymer side after electron-beam treatment. A platinum thin film was coated on one side of the pillars to prevent the decomposition of polymer material in CO₂ atmosphere during the electro-beam irradiation. (d) A title image showing nano-pillar bending after 6 seconds electron-beam irradiation33

Figure 2.8 (a) The titled nano-hair arrays fabrication by adjusting surface energy. (b) The schematic of experimental set-up for macroscopic shear adhesion force measurements on hydrophobic (SiO₂-C) and hydrophilic (SiO₂) surfaces34

Figure 2.9 Images of the anisotropic rolling behavior on rice leave. a) A water drop on a rice leaf with an inset showing the optical images of a roll-off angle measurement for a 4 µL water drop being perpendicular or parallel to the longitudinal direction on the rice leaf. b) A image of the rice leaf upper surface. The rice leaf surface CLSM topographical image is displaced in the inset. c) A magnified images of (b). The magnified image of the papillae with wax is displaced in inset37

Figure 2.10 Schematic showing the fabrication process of the rice leaf-like surface. a) The fabrication procedure includes surface wrinkling, LBL deposition and PDMS surface treatment. b) The fabricated rice leaf-like surface CLSM images with an inset showing the cross-section SEM image of the wavy PDMS substrate. c-e) the nano-structured film images on the PDMS substrates which had gone through various deposition cycles; (c), (d), and (e) indicate 2, 5 9, respectively.....38

Figure 2.11 Images of a water droplet on the lotus leaf surface (a) and the silicon wafer surface with PVB nano-fibers coating (b). The fuchsine solution with the concentration of 1×10^{-5} M was used to have a clear view. (c) PVB nano-fibers image with the scale bar 2 µm39

Figure 2.12 (a) Image of a water droplet on the bamboo leaf surface.....40

Figure 2.12 (b) Image of a water droplet on the silicon wafer surface which was coated by aligned electro-spun PVB nano-fibers. (c) SEM image of the aligned PVB nano-fibers with the scale bar of 1 µm. (d) the fiber array surface AFM image41

Figure 2.13 The comparison images of the wetting behaviors on symmetric and asymmetric nano-patterned surfaces. a), axially symmetric liquid spreading of a 1 μl DI water droplet with 0.002% by volume of surfactants (Triton X-100) deposited on the vertical nano-pillar array surface which has the nano-pillar with diameters of 500 nm, spacings of 3.5 μm and height of 10 μm (inset). The scale bars in the image are 10 μm	42
Figure 2.14 Increasing the distance from magnet surface, the magnetic flux decreases rapidly. This data was plotted based on the data on a NdFeB magnet	49
Figure 2.15 A magnetically permeable material influences on the magnetic field lines.....	49
Figure 2.16 (A) the experiment setup schematic shows magnetic field gradients creation. A large array of magnetic micro-pillars can be obtained by applying spherical magnetic aggregates. The piezoelectric micromanipulator has a sharp metallic needle mounted. Once a strong magnetic field gradient is applied, the substrate is spontaneously deformed. The pillar deformation and tip position were detected by the analysis software. When the magnetic tip moves, each pillar follows the movement. (B) The side-view of the pillars with a 10 μm diameter 20 μm height. The pillars were filled with ferromagnetic black iron oxide particles. The magnetic nano-particles were concentrated at pillar tips with their fabrication technique. (C) The moving pillar optical images. The pillar rotation movement is induced by the moving needle (first and third pictures).....	54
Figure 2.17 The illustration shows the working principle of the circular ferro-fluid pump. Ferro-fluid plugs was controlled by the two magnets (M) in a circular micro-channel.....	56
Figure 2.18 Schematic of nano-magnetic pillar array Fabrication process flow.....	57
Figure 2.19 The Scanning Electron Microscope (SEM) image shows Si(100) pillar with about 500 nm in height and the ellipsoid shape $\text{Fe}_{55}\text{Pd}_{45}$ wrapping around each Si (100)-pillar top with a length L around 108 nm.....	58

Figure 2.20 Schematic showing process steps of the fabrication and images of the pattern magnetic media. The isolated domain with quantized up and down magnetization was displayed the final panel with magnetic force microscope images.....	60
Figure 2.21 Cell separation procedure diagram for the micro separator: (a) the magnetic field is generated and the pre-treated sample flows into the separator; (b) Capture the target cells by the micro-pillars; (c) wash the non-target cells out of the separator; (d) cut off the external current and release the target cells.....	62
Figure 2.22 Schematic illustration of magnetic micro-pillar chip process flow.....	63
Figure 2.23 SEM image of the captured magnetic beads on the micro-pillar surface.....	64
Figure 2.24 Cross-section view of the fabrication steps used to template magnetically actuated composite polymer rod arrays.....	65
Figure 3.1 (a) Diagram showing the contact angle measurement method; (b) Image of the contact angle of a water drop on a wafer surface that has gone through an oxygen plasma treatment for three minutes; (c) Image of the contact angle of a water drop on a silicon wafer in a vacuum for 2 hours after the piranha cleaning; (d) Image of the contact angle of a wafer drop in a vacuum for 96 hours after the piranha cleaning; (e) Image of the contact angle of a wafer drop in a vacuum for 96 hours after the HF solution cleaning.....	70
Figure 3.2 The contact angle trend chart of the silicon wafers cleaned with different solutions, and then aged in various conditions.....	72
Figure 3.3 The contact angle trend charts of the silicon wafers that were cleaned with the HF solution, treated by the gas plasma, and then aged in the open air or a vacuum oven.....	74
Figure 3.4 The contact angle trend charts of the silicon wafers that were cleaned with different cleaning solutions, treated by the gas plasma, and then aged in a vacuum. All wafers have the similar aging behavior after plasma treatments.....	75

Figure 3.5 are the XPS spectra collected on silicon sample surfaces obtained with various cleaning methods and plasma treatments.....77

Figure 3.6 are the XPS spectra collected on silicon sample surfaces obtained with various cleaning methods and plasma treatments.....78

Figure 3.7 is the XPS spectra collected on silicon sample surfaces obtained with various cleaning methods, plasma treatments and aging processes.....79

Figure 3.8 (a1) and (b1) are the AFM 3D and 2D images, and (c1) is the SEM image of the gold thin film deposited on a hydrophilic silicon wafer, which was cleaned with the piranha solution. (a2) and (b2) are the AFM 3D and 2D images, and (c2) is the SEM image of the gold thin film deposited on a hydrophobic silicon wafer, which was cleaned with the HF solution; (d) The film roughness bar chart of the gold thin films.....81-82

Figure 3.9 (a1) The cross-section image of the gold thin film deposited on a hydrophobic silicon sample, S2. The gold film is porous and has big vacancies, and the gold atoms diffuse into the silicon substrate. (a2) the high magnification cross-section image of the gold thin film on S2. (b1) the cross-section image of the gold thin film deposited on a hydrophilic silicon sample, S3. (b2) the high magnification cross-section image of the gold thin film on S1.....84

Figure 4.1 Schematic showing the PDMS magnetic pillar arrays fabrication process: (a) micro-holes patterning on a silicon wafer; (b) the silicon wafer was etched in a deep RIE chamber; (c) fill Fe_3O_4 nanoparticle into micro-holes; (d) remove the redundant Fe_3O_4 and acetone solution; (e) pour over the PDMS mixture on the silicon wafer, and (f) peel off the cross-linked PDMS from the silicon mold.....89

Figure 4.2 SEM images of the magnetic micro pillar arrays with various pillar dimensions and spaces. (a) Image of the micro-pillar with diameter 2 μm , height 50 μm and inter-pillar spacing

10 μm , (b) Image of the micro-pillar diameter 3 μm , height 30 μm and inter-pillar spacing 30 μm , (c) Image of the micro-pillar diameter 10 μm , height 50 μm and inter-pillar spacing 20 μm90

Figure 4.3 (a) The micro-pillars filled with nanoparticles (diameter: 5 μm); (b1) The EDS element spectra on PDMS substrate background; (b2) the EDS element spectra on PDMS micro-pillars; (c) The Bar chart of iron percentage on micro-pillars with various dimensions (A1: diameter 2 μm with height 30 μm , A2: diameter 2 μm with height 50 μm , B1: diameter 3 μm with height 30 μm , B2: diameter 3 μm with height 50 μm , C1: diameter 5 μm with height 30 μm , C2: diameter 5 μm with height 50 μm , D1: diameter 10 μm with height 30 μm , D2: diameter 10 μm with height 50 μm); (d) The diagram of iron percentage distribution in micro-pillars (Weight %) regardless of the pillar diameter and height.....92

Figure 4.4 Schematic showing two scenarios that the unit force F_1 applies to the whole pillar uniformly (a) and the focused force F_2 applies to pillar's tip only (b).....96

Figure 4.5 (a) the trend charts of the required force per length and force per volume for the micor-pillars which have the aspect-ratio 10; (b) The trend chart of the required force per length and force per volume for the micro-pillar which have the height of 50 μm . (c) The trend chart of the required force per length and force per volume for the micro-pillar which have the diameter of 2 μm98

Figure 4.6 (a1) The optical image of the micro-pillars (diameter 2 μm , space 4 μm , height 50 μm) without magnetic force; (a2) the optical image of the micro-pillars while they are under magnetic field; (b1) The optical image of 5 μm micro-pillars (space 10 μm , height 50 μm); (b2) the optical image of the same micro-pillars which are under the magnetic field. (c) The trend chart of the micro-pillars tip displacement under the same magnetic field.....100

Figure 4.7 (a) Images of micro-pillars fall down on ground and (b) collapsing each other.....102

Figure 4.8 (a) Trend chart of the critical aspect-ratio for ground collapse and neighboring collapse. The images of (b1) to (b4) verified the calculation results that the lateral collapse

become less and less when the inter-pillar space increases (diameter 5 μm , height 50 μm).....105

Figure 5.1 Diagrams of the straight micro-pillar array fabrication: (a) Lithography patterning; (b) Deep reactive ion etching to fabricate silicon wafer mold; (c) Pour PDMS polymer over the silicon mold and degassing; (d) Peel off PDMS micro-pillars from silicon mold and drying.....116

Figure 5.2 Schematic shows the slanted micro-pillars fabrication. (a) A thick silver metal film was deposited on one side of micro-pillars in an electron beam evaporator to make micro-pillars deflected; (b) followed by 300nm Ag film deposition on the other side of pillars in the electron beam evaporator, and (c) 200nm gold thin film was coated on the entire of the pillars on the rotating and tilted substrate in a sputtering chamber.....117

Figure 5.3 (a) Schematic presentation of Young's equation as the force balance at the three phase contact line when a droplet is placed on a flat solid surface; (b) Wenzel model for a liquid wets on a homogenous material; and (c) Cassie-Baxter model for a liquid rests on composite material.....119

Figure 5.4 SEM images of micro-pillar arrays with various micro-pillar bending angles. (a) Straight micro-pillars and the definition of micro-pillar deflection angle α . (b) Micro-pillars were bended with 24° with micro-pillar length 30 μm and inter-pillar spacing 20 μm . (c) Micro-pillars were bended with 39° with micro-pillar length 40 μm and inter-pillar spacing 30 μm . (d) Micro-pillars were bended with 52° with micro-pillar length 40 μm and inter-pillar spacing 30 μm ...121

Figure 5.5 (a) The side view of the time-lapse color images of the unidirectional spreading of a drop (75% ethanol in DI water (v/v)) spreading on a gold coated slanted PDMS micro-pillar surface.....123

Figure 5.5 (b1) and (b2) compare the early stage spreading of a drop (75% ethanol in DI water (v/v)) on a pillared surface to that on a flat surface of the same material. (c1) and (c2) shows the spreading approach the typical Tanner's law.....124

Figure 5.5 (d1) and (d2) show close-up images of the micro-scale thin liquid film propagation on a slanted micro-pillar array surface.....125

Figure 5.5(e) shows the motion of the thin liquid film in Video 2. Once the three-phase contact line reaches the bottom of a pillar, the liquid climbed along the micro-pillar and moves forward very fast. Then, the liquid front moves slowly until it reaches the next pillar.....126

Figure 5.6 (a) A schematic showing the definition of θ_{front} and θ_{rear} . (b1) Video frames showing the fast motion of the meniscus as it touches the next pillar. The scale bar is 20 μm long and the frames are spaced by 50 μs . (b2) Liquid touches with the bottom of the next pillar and (b3) liquid climbs along the pillar as well as spreads along the substrate.....127

Figure 5.6 (c) A schematic showing that the requirement for the liquid to move forward and get touch with the next pillar is $\theta_{\text{eq}} < \theta_{\text{front}}$. (d) A schematic showing spreading stops when the liquid level is not high enough to make the liquid get touch with the next pillar, even $\theta_{\text{eq}} < \theta_{\text{front}}$ is satisfied here. (e) A schematic showing spreading stops when $\theta_{\text{eq}} > \theta_{\text{front}}$...130

Figure 5.7 (a) Image of the liquid pinning at reversed direction of pillar deflection. The purple dash line is the profile of the liquid. (b1) Schematic showing the situation in which the liquid is able to propagate in the reversed direction when θ_{eq} is smaller than θ_{rear} and (b2) showing that the liquid stops spreading when θ_{eq} is larger than θ_{rear}131

Figure 5.8 (a) Trend chart of θ_{front} , θ_{rear} and θ_{im} and the different zones for all-directional, unidirectional propagating and non-propagating.....133

Figure 5.8 (b) Trend chart of θ_{front} , θ_{rear} and θ_{im} when inter-pillar spacing is changed from 10 μm to 70 μm134

Figure 5.8 (c) Trend chart of θ_{front} , θ_{rear} and θ_{im} when pillar length is altered from 5 μm to 60 μm . (d) The simplified diagram describing the lateral angles.....136

Figure 6.1 Papillose and non-papillose leaf surfaces with an intact coating of wax crystals: (a) Lotus, (b) *Euphorbia mysinites*, (c) *Brassica oleraces*, (d) *Yucca filamentosa*. In comparison with

other plant surfaces, lotus has the highest density of papillae with smaller diameters. The contact angle on lotus leave can exceed 160° 145

List of Tables:

Table 2-1 Chemical and PDMS substrate characterization after immersion.....	43
Table 3-1 Element concentration values of the silicon sample surfaces were calculated based on the XPS spectra collected.....	74

List of Publications

1. **X.M. Yang**, Z.W. Zhong, E.Q. Li, Z.H. Wang, W. Xu, S.T. Thoroddsen and X.X. Zhang, Asymmetric liquid wetting and spreading on slanted micro-pillar surfaces, *Soft Matter*, 9 (2013), 11113-11119
2. **X.M. Yang**, Z.W. Zhong, E.M. Diallo, Z.H. Wang, W.S. Yue, Silicon wafer wettability and aging behaviors: Impact on gold thin-film morphology, *Materials Science in Semiconductor Processing*, 26 (2014), 25-32

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Nomenclature and Symbols

A	Interface area, [m^2]
Ca	Capillary number
E	Elastic modulus, [MPa]
f	Driving force, [mN/m]
f_c	Ratio of the contact surface area to the total horizontal surface area, [-]
h	Height of liquid droplets [mm]
L	Contact radius of liquid droplets, [mm]
L_p	Precursor film length, [mm]
r	Roughness factor, [-]
S	Spreading parameter, [mN/m]
t	Time, [s]
T_g	Glass transition temperature, [$^{\circ}C$]
V	Volume, [μ l]
v	Velocity of the contact line, [mm/s]
g	Gravitational acceleration, [m/s^2]
P_{atm}	Atmospheric pressure, [Pa]
P_c	Capillary pressure, [Pa]
P_{nw}	Pressure of the non-wetting fluid, [Pa]
P_w	Pressure of the wetting fluid, [Pa]
Ca	Capillary Length
Re	Reynolds number
γ	Surface or Interfacial tension in the liquid/vapor/solid system, [N/m]

θ	Contact angle, [°]
θ_{ap}	Apparent contact angle, [°]
θ_c	Critical contact angle from Wenzel state to Cassie state, [°]
η	Viscosity, [Pa s]
ϕ	Partial volume fraction, [mN/m]
ϕ_s	Fraction of wet surface, [-]
B	Magnetic field, [T]
H	Magnetic field, [A/m]
M	Magnetization, [A/m]
m	Magnetic dipole moment
F_m	Magnetic force, [N]
ρ	Density (kg/m^3)
δ	Differential
Δ	Difference
μ	Liquid viscosity, [$mN \cdot s/m^2$]
μ_0	Permeability, $4\pi \times 10^{-7} \text{ H} \cdot \text{m}^{-1}$
ρ	Poisson ratio
θ_{im}	Imbibition contact angle, [°]

Abbreviations and Acronym

Si	Silicon
CO ₂	Carbon Dioxide
CA:	Contact Angle
E-Beam	Electron Beam
DI wafer	Deionized Water
PECVD	Plasma Enhanced Chemical Vapor Deposition
CLSM	Confocal Laser Scanning Microscope
RIE	Reactive Ionized Etching
PDMS	Polydimethylsiloxane
PMMA	Polymethyl methacrylate
PAM	Polyacrylamide
PAA	Polyacrylic acid
MEMS	Microelectromechanical Systems
PPX	Poly(p-xylylene)
PET	Poly(ethylene terephthalate)
PS	Polystyrene
PUA	Poly(urethane acrylate)
PVB	Poly(vinyl butyral)
AONWA	Align Oblique Nanowire Array
NW	Nanowire
HAR	High-Aspect-Ratio
UV	Ultraviolet
CAH	Contact Angle Hysteresis

XPS	X-ray Photoelectron Spectroscopy
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
SOI	Silicon-on-Insulator
MHD	Magnetohydrodynamic
EDS	Energy-dispersive X-ray spectroscopy
CTC	Circulating Tumor Cells
PCTE	Polycarbonate Track-Etched
NIB	Neobymium-Iron-Boride

Table of Contents

Asymmetric liquid wetting on controllable magnetic micro-pillar surfaces.....	I
Abstract.....	i
Acknowledgements.....	v
List of Figures	vi
List of Publications	xvi
Nomenclature and Symbols.....	xvii
Table of Contents.....	xxi
Chapter 1 Introduction	1
1.1 Background	1
1.2 Research objectives	4
1.3 Research scope	Error! Bookmark not defined.
Chapter 2 Literature review.....	6
2.1 Introduction to wetting and spreading.....	6
2.1.1 Basic surface thermodynamics	6
2.1.2 Basic concepts of a drop spreading	10
2.1.3 Apparent and microscopic contact angles.....	15
2.1.4 Wetting on structured surfaces	21
2.2 Anisotropic wetting and spreading research works	22
2.3 PDMS and properties	37
2.4 Magnetic field, forces and applications	43
2.4.1 Magnetic field	43
2.4.2 Magnetic forces	45
2.4.3 Magnetic micro-devices and applications	48

Chapter 3 Silicon wafer surface wettability ageing behavior	61
3.1 Background of silicon wettability	61
3.2 Experimental	62
3.3 Results and discussion	64
3.3.1 Impact of cleaning methods and aging atmosphere	65
3.3.2 Impacts of plasma treatment.....	67
3.3.3 XPS survey on silicon wafers	70
3.3.4 The influence of surface wettability on gold thin film	74
3.4 Summary	79
Chapter 4 Magnetic Micro-pillar array fabrication and characterization	80
4.1 Magnetic micro-pillar research background.....	80
4.2 Experimental	82
4.2.1 PDMS polymer preparation	82
4.2.2 Micro pillar array fabrication	83
4.3 Results and discussion	86
4.3.1 Micro pillars morphology	86
4.3.2 Magnetic pillar composition	88
4.3.3 Magnetic force calculation.....	91
4.3.4 Magnetic micro-pillar movement	98
4.3.5 Surface energy and capillary force.....	100
4.4 Summary	105
Chapter 5 Asymmetric liquid wetting and spreading	107
5.1 Wetting and spreading.....	107
5.2 Experimental	109
5.3 Results and discussion	113
5.4 Summary	137

Chapter 6 Conclusions and Future work.....	138
6.1 Conclusions	138
6.2 Asymmetric wetting modeling on micro-pillar surfaces.....	140
6.3 Super-hydrophobic study on micro-pillars surfaces	144
References	147

Chapter 1 Introduction

1.1 Research background

Early in the morning, it is common to see beads of water droplets gleaming on a spider web or grass leaves. The film of dew that settles on the threads or plant leave surface is in unstable, and it is prone to breaks up instantly into droplets. This phenomenon with implications has many applications on the surface treatment of textile fiber, glass, metal and other materials. A falling rain drops on the window glass, water boiling, crystal growth, surface coating and painting are the samples of the wetting and spreading phenomena and applications in nature and industry. Thus, understanding of the wetting and spreading behavior is of very importance in our daily life, inventing new machines, and taming new process and technologies, in which the wetting, spreading, interface evolution and adhesion are involved. Particularly, the surface wetting is prevalent around us with numerous biological surfaces exhibiting favorable wetting properties that have been developed during the long history species evolution and adaption. Biomimetic researches have been inspired to discover the surface wetting properties of plants and insects, such as some plant leave surfaces have specialized micro-structural and chemical modification to manipulate surface wetting. For example, it is explored that the surface of the lotus leaf exhibits super-hydrophobicity with water contact angle of more than 150° for self-cleaning. The super-hydrophilic water plant surface, like peat moss, is able to absorb water to maintain the wet surface. Some parts of animals, like butterfly wings, and desert beetle exhibit

distinct wettability properties, which help enable the adoption of surrounding and promote survivals.

Furthermore, grass and rice leaves were intriguingly found to be favorable for water droplets rolling off and directional movement because of the anisotropic microstructures. When a droplet drops on a typical flat surface, the droplet spreads symmetrically, and its final size is controlled by the minimized total surface energy. When micro-grooves or micro-features are introduced to create localized energy barriers on lateral directions, a droplet will spread in parallel. More than one axis energy barriers can force the liquid to propagate in one direction only. Anisotropic wetting behavior involves the inhomogeneous liquid distribution and it is associated with surface wetting properties. The physical discontinuity is the origin of physical anisotropic wetting, and the chemical heterogeneity can cause the chemical anisotropic wetting on smooth solid surfaces. The anisotropic wetting behaviors can be found on both natural and synthetic surfaces, which have chemical or physical dissimilarities in the surface properties. Therefore, both surface chemistry and surface morphology have impacts on the surface wettability, and it is determined by how a liquid contacts with a solid surface. The macroscopic and observable wetting behaviors can be determined and affected by the micro- and nano-scale surface topographical structures.

Anisotropic wetting phenomenon could have both dynamic properties, like different sliding angles in different directions, and static properties, like different static contact angles in different directions. Some novel and complex anisotropic wetting behaviors can be created by the chemical gradient or spatial structures, which support the designs for liquid movement in

one or two designated directions to guide the liquid flow in microfluidics and other applications. However, the current understanding and models of the universal liquid spreading on the micro scale still remains tentative and controversial, especially for the micro-level liquid propagation occurring near the three-phase contact line, although many researchers have devoted much effort on this topic. Furthermore, the recent found asymmetric wetting and spreading behaviors become very popular, while the understanding and models are very limited and not conclusive yet. The further efforts for thorough investigation on this phenomenon are desirable. The surfaces with chemical gradient from hydrophobic to hydrophilic along certain directions may be able to lead anisotropic liquid wetting and moving. The structural gradient surfaces with the periodic heights change or special patterns may also create some amazing anisotropic wetting behaviors. From fabrication aspects, making the chemical gradient on surfaces is relatively easier than processing structural gradient, while we are trying to achieve the asymmetric liquid spreading in a physical way.

The great subtlety in the design of asymmetric nanostructured surfaces, beautiful unidirectional liquid spreading was first achieved by Wang's groups ^[1]. A theory from an energy point of view, to predict the liquid spreading characteristics, was also proposed and verified by their experimental results. However, in their work, they did not give the detailed explanation of the liquid flow around pillars at a micro-level in detail, and also did not have micro-level vivid dynamic flowing observation to support their findings.

1.2 Research objectives and scope

The characterization of the silicon wafer surface wettability and aging behaviors is the first objective of this work. As we know, the silicon surface hydrophilic property plays an important role in many applications, like direct wafer bonding, silicon-on-insulator process, silicon-based sensors, biochemical systems, and microelectromechanical systems. In general, the silicon surface is hydrophilic because a thin native oxide layer covers on the silicon surface, and a variety of cleaning processes can modify the silicon surface wettability. However, few works were done systematically to investigate the silicon surface wettability and aging behaviors in different environments, and what is the impact on the noble metal thin film deposition and growth. This is the first aim of this project.

The second objective is to study the asymmetric wetting and spreading behaviors of liquids on rough surfaces, especially for the micro-level liquid propagation occurring near the moving the three-phase contact line. It is interesting to examine surface forces, liquid flow profile and the wetting process dynamics. We will try to demonstrate the asymmetric liquid wetting and spreading on slanted micro-pillar array surfaces, which are fabricated by oblique metal film deposition on PDMS straight micro-pillars by the help of magnetic fields. The PDMS material is versatile and easily processed with low cost for mass production and large area, as compared to the fragile silicon pillar process in other research works. Then, by utilizing a high-speed video imaging, the micro-level thin precursor liquid film advancing ahead of the bulk droplet is the point of interest for us to observe. Based on the vivid dynamic flowing, we will be able to provide a more detailed explanation of the liquid flow mechanism around pillars in micro-level.

Third, we will also work on the micro-pillar array surface fabrication by incorporating the magnetic nano-particles, which enable the micro-pillars to be bended in a controllable direction under magnetic fields. It will be magic to control the non-magnetic liquid spreading flow directions through the magnetic flux and strength. Therefore, it was proposed to fabricate the controllable magnetic micro-pillar array surfaces leading the liquid spreading directions. The difficulty here are how to fabricate magnetic micro-pillars which could be deflected without clashing together in a magnetic field and how strong the magnetic field is required. Many people have attempted to produce magnetic micro-pillar devices in various methods. A conventional way for fabricating magnetic polymer structures relied on the techniques of solvent-casting, in which the magnetic nano-particles were dispersed in a fluidic medium. However, it is a formidable challenge to make magnetic nanoparticles homogeneously embedded and disturbed inside the polymeric micro-features. It is nature that the nanoparticles always cluster or aggregate together due to high surface energy of the high surface to volume ratio particles. And it becomes much worse for magnetic nanoparticles. In chapter 5, we will introduce a new technique for fabricating the magic controllable magnetic micro-pillar array surface with less process step and high reproducibility. The high aspect-ratio magnetic polymeric pillars will be able to vibrate with considerable amplitudes under gradient magnetic fields. In addition, the applications of the polymeric magnetic micro-pillar can be extended to microfluidics, micro sensors, micro actuators and traps, electrospray, tunable wetting surfaces and structure substrates for cell culture.

Chapter 2 Literature review

2.1 Introduction to wetting and spreading

2.4.1 Basic surface thermodynamics

A liquid is considered as a condensed state in which molecules attract each other. When the attraction force is stronger than thermal agitation, molecules is condensed from the gas phase to liquid phase, though it is still disordered. When two immiscible fluids, like water-oil or water to air, are in contact, the two fluids are separated by a definite interface that is only a few molecular diameters thick. In the bulk liquid, because the molecules are away from the interface, they exert an attractive force with their neighbors in all directions. The molecules in the midst of a liquid are in the “steady” state. In contrast, the molecules that are wandering to the surface lose half of their cohesive interactions, and they become “unsteady” state. There is an inward directed force attempting to minimize the surface by pulling it into the shape of a sphere. The molecular activity at the surface creates a layer of molecules that in tension. We can view the surface tension as a force per unit length, which is capillary force. Capillarity is the science of the interactions and interfaces between a liquid and air, or between two immiscible liquids, which are free to change their shapes. Thus, the interfaces can be deformed for minimizing the total surface free energy. Therefore, wetting and spreading phenomena and dynamics are the area with intersection of chemistry, physics and engineering. The surface energy is the decisive fact to determine the liquid wetting and spreading behaviors. The very high surface tension of mercury, typical of values for metals, is resulting from the short-range

electron exchange interactions (the origin of the metal bonds). It is notable that the surface tension of water is remarkably higher than all of the organic liquids, because water is a highly polar hydrogen-bond liquid. Experimentally, it was found that the air-water interfacial tension decreases almost linearly with temperature ^[2]. It will be zero at the critical temperature, where the interface disappears. There are many research groups having been working on manipulating all kind of solid surface chemistry in order to obtain certain specific wetting properties and behaviors ^[3]. Plasma treatment ^[4] or silanization ^[5] are usually used to adjust the surface chemical properties, and thus the contact energy of the surface with materials, such as water and air. The “short-range” interaction was referred to the interactions acting over the molecule scale. However, the surface forces are paramount to determine if a fluid will wet a given surface or not, besides the surface chemistries. Hence, van der Waals and electrostatic forces are the basis for the various states of wettability, and they are the intermolecular forces that control the attraction, repulsion and adhesion of condensed states of matter. The gas could be compressed easily, while the liquid has the limited compressibility because the strong repulsive forces oppose the molecules being brought together further. Short-range forces where electron clouds interact, London dispersion forces develop from asymmetric charge distributions of molecules, Deybe interactions are resulted from induced dipole moments. As the decay is rather slow for Van der Waals forces, generally they can act over the distance of a few tens of molecules. Therefore, they are considered as “long-rang.” It is believed that the van der Waal forces are the main cause to determine the liquid wetting equilibrium film thickness, and they are of very importance for controlling the fluids spreading behaviors over solid surfaces. For example, the soap film stability is determined by both van der Waals and electrostatic forces ^[6].

In order to play with soap bubbles, it is required to add some special additives in water to foam. People have clearly understood why a soap film can be formed and stretched with additives. In some cases, foams are desirable, such a shampoo. However it could be a nuisance in other circumstances, like a dishwasher detergent. Another important application is antifoam agents, which have been well developed and employed in many places.

It is necessary to introduce *Laplace Pressure*. Laplace published his work in 1805 ^[7]. He believed that surface tension is the origin of the overpressure existing inside of droplets. This pressure difference between the outside and inside bubbles has resulted in many interesting facts. In one example, smaller drops disappear ahead of larger ones in emulsions because the smaller drops with smaller surface curvatures have bigger surface forces stretching on the droplet surfaces, and they are always evaporating preferably in aerosol cooling phase. The phenomenon of capillary adhesion between two plates also can be explained by the pressure difference. And the capillary adhesion between hairs or fibers is induced by capillary bridges as well.

As the matter of fact, wetting and spreading dynamics are really very important for multiple science and engineering, many process and technologies. One example with a large scale is the wetting and non-wetting plays the key important role in oil industry ^[8] and the efficient pesticides deposition on plant leaves ^[9]. An small scale example is wetting engineering have been extensively employed in microfluidics devices, nano-printing ^[10], etc. The surface and interfacial interactions are deeply involved in all these applications. The interaction range is

from less than one nanometer to a few nanometers, which are the range of van der Waals or electrostatic interactions.

Considering a liquid droplet drops on a horizontal solid surface, the liquid droplet will adopt a position between completely spreading on the surface and around drop resting lightly on the surface. When three different phases present in a system: solid, liquid and vapor, three surface tensions are formed: solid-liquid, liquid-vapor, and solid-vapor. By applying Young's equation, the relationship between the equilibrium contact angle θ_{eq} and the three surface tensions can be expressed as

$$\cos \theta_{eq} = (\gamma_{SG} - \gamma_{SL}) / \gamma_{LG} \quad (2-1)$$

where γ_{SG} , γ_{SL} and γ_{LG} are the interfacial energy of the solid-gas, solid-liquid, and liquid-gas interfaces, respectively.

As stated by de Gennes^[11], Eq. (2-1) is obtained by considering the reversible interchange at the three phase contact line, using energy theories. Accordingly, θ_{eq} is the value which can be measured macroscopically. In the case of $\gamma_{SG} < \gamma_{SL} + \gamma_{LG}$, a droplet with a finite contact angle, it is the partial wetting. In another case of $\gamma_{SG} = \gamma_{SL} + \gamma_{LG}$, the contact angle will be zero and it is called as complete wetting, in which a macro scale uniform liquid film will finally cover the whole solid surface and the system is at the equilibrium state. The different wetting states is

usually distinguished by the equilibrium spreading coefficient $S_{eq} \leq 0$, which is the surface free energy γ_{SG} comparing to its value at complete wetting:

$$S_{eq} \equiv \gamma_{SG} - (\gamma_{SL} + \gamma_{LG}) = \gamma_{LG}(\cos \theta_{eq} - 1) \quad (2-2)$$

If it is complete drying in a solid-liquid-gas system, it implies there is a macroscopic intrusion vapor layer between the solid and the liquid, and it is almost impossible in real. Actually, the drying and wetting are very similar In respect of the thermodynamic view. In the real world, drying is rather rare because van der Waal forces tend to form thin vapor layers on surfaces. Partial wetting corresponds to the formation of drops, which are surrounded by a microscopically thin film adsorbed and formed on the surfaces, while the complete wetting is to form a uniform macroscopic thick liquid layer. Some molecules are always adsorbed onto the substrate when it is at the thermodynamic equilibrium status, because it is favor of increasing the total entropy in the whole system.

2.4.2 Basic concepts of a drop spreading

When a liquid droplet drops on a solid substrate, it is generally not in its equilibrium state at the beginning. Thus, the liquid will be in motion to reach its equilibrium state, unless it is stuck at some metastable state due to localized energy barriers. For complete wetting, the drop can spread for a very long time. It stops spreading when it reaches a thin film with a thickness

set by van der Waal forces. When the liquid static contact angle is finite and not large, the liquid spreading initial stages are similar. It follows the relaxation principle and towards a static shape. The capillary force is dominant when the capillary length $l_c = \sqrt{\gamma/\rho g}$ larger than the drop radius, so it is negligible for the gravity. When the immiscible fluids (like water-air) are in contact with each other in a capillary tube, a clear interface exists between them. As we know, there is an interfacial tension at the interface between two surfaces (liquid and solid, or two immiscible liquids). This interfacial tension induces the Capillary pressure. As stated, the interfacial tension is originated from the imbalance molecular forces being attracted by the molecules at the surface. The pressure on the concave side is higher than that in the convex side to balance the forces creating the interfacial tension. The pressure difference is defined as the capillary pressure where, it is

$$P_c = P_{nw} - P_w = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = 2\sigma \cos \theta / r_t \quad (2-3)$$

Where P_{nw} is the non-wetting fluid's pressure, P_w is the wetting fluid's pressure, r_1 and r_2 are the curvatures' radii of the interface, r_t is the capillary tube's radius. In the ideal case, the relationship between fluid saturation and capillary pressure could be calculated, but it is rarely conducted except for idealized models of some porous materials. A liquid flow process with the wetting phase saturation increases is called as imbibition. When the capillary pressure declines

and is close to zero, the wetting phase imbibition occurs. The capillary number is used to measure the viscous to surface tension force ratio,

$$Ca = U \eta / \gamma \quad (2-4)$$

Here $U = \dot{R}$ is the contact line moving velocity and η is the viscosity of the liquid. Ca is usually very small ($Ca \approx 10^{-5} - 10^{-3}$) in most spreading cases. For a small Ca , it tells us the surface tension is dominant over the whole droplet. Thus, the drop is in spherical shape. Whereas, it is an exception in the near vicinity of the three phases contact line. In the case of low capillary numbers ($Ca \ll 1$), the spreading behaviors are very much different from the one with intermediate capillary numbers ($Ca \sim 1$). This is the same with the case of the Reynolds number: the flows at high Reynolds numbers are fairly different from the ones at low Reynolds numbers. It also indicates the interface shape is rarely affected by viscous forces, except in a region very close to the apparent three-phase contact line. If the drop is sufficiently flat ($h' \ll 1$), its thickness $h(r, t)$ is described by^[12]

$$h(r) = \frac{2V}{\pi R^2} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (2-5)$$

At a fixed volume V , the drop shape is almost entirely decided by the apparent contact angle θ_{ap} between the solid substrate and the spherical cap. From a flat droplet $[-h'(R)] = \tan(\theta_{ap})$ one obtains ^[12]

$$\theta_{ap} = 4V/\pi R^3 \quad (2-6)$$

As the drop spreads, the apparent contact angle $\theta_{ap}(t)$ will be close to zero at the rate of $1/R^3(t)$. As a function of time, the drop radius can be expressed as ^[13]

$$R(t) \approx \left[\frac{10\gamma}{9B\eta} \left(\frac{4V}{\pi} \right)^3 \right]^{1/10} \propto t^n \quad (2-7)$$

Please note that the initial spreading coefficient S_i is not going to affect the spreading law. S_i is used to measure the total surface energy available to the system. And the constant B is found to be close to $B^{1/10} = 1.186$. Eq. (2-6) is universally known as Tanner's Law ^[13].

As we know, in the complete and partial wetting, in the vicinity of the three-phase contact line, a thin liquid film is always adsorbed or spreading on the surface. The combined available surface energy and gravitational energy determines the thin liquid film spreading speed and dissipation, and further affect the drop bulk liquid. The major force that should be considered is

the surface energy only when the drop is small. The spreading process has two stages: a thin precursor film is moving ahead of the macroscopic wetting, and the typical thickness of the thin precursor film is between 100 Å ^[14] and a single molecular layer ^[15]. Konisho *et al.* had experimentally studied the dynamics and thickness of the thin liquid precursor film by using high-speed cameras and an interferometer ^[16], and they found the precursor film appearance occurs when the dynamic contact angle is smaller than 5.7° under their experimental conditions. It is earlier to appear the precursor film when the liquid has a low viscosity. It is an inverse relation between the precursor film length and the liquid spreading velocity in an adiabatic system, and it can be calculated by ^[17]

$$L_p = \sqrt{\frac{SA}{6\pi\sigma^2}} \frac{1}{Ca} \quad (2-8)$$

where A is the effective Hamaker constant, S is the spreading coefficient, U is the spreading velocity of the droplet, and $Ca \equiv \mu U / \sigma$ is the capillary number. The dynamical structure can be differentiated from the adsorbed thin liquid film surround the partially wetting drop. A small quantity of molecules movement reveals a more efficient run-path with the most of the energy than moving the whole drop at once.

The effective spreading coefficient has been minimized to focus on its equilibrium value $S_{eq} = 0$, as we consider the macroscopic drop spreads along with time. Thus, it is going to help to enhance the overall liquid spreading rate by increasing the surface energy only. The decrease

of F_s is very small if R is large for a vanishing S_i . The very small exponent $n = 1/10$ in Eq. (2-7) has explained why spreading is pretty slow. In order to calculate the power n , the energy dissipation rate will also need to be calculated. The point of interest is near the three-phase contact line where the capillary numbers are usually very small. As the matter of fact, near the drop region the viscous energy dissipation rate increases so dramatically. From here, we can see the fundamental difficulties for calculating the hydrodynamic spreading with a moving contact line.

2.4.3 Apparent and microscopic contact angles

If we consider a liquid spreading in a non-equilibrium state, the concept of a contact angle becomes more difficult to deal with a moving three-phase contact line. Eq. (2-1), which was obtained based on the thermodynamic theory, will be no longer valid. In real, it is found that the local contact angle at the liquid interface strongly depends on the scale and the distance from the contact line. From the hydrodynamic scales, the interface curvature, which varies with the distance from the contact line, is the result of the strong divergence of viscous force. It has been confirmed in experiments ^{[18] [19] [20]}. The dynamic contact θ_d is the local angle, which can be macroscopically measured at a specified distance from the contact line.

When the “intermediate” region is concerned, the size of the crossover region between microscopic and macroscopic can be calculated approximately based on Eq. (2-9) ^[21]:

$$h_{out}(r, t) = h_0(r) + Ca h_1(r) + O(Ca^2) \quad (2-9)$$

As the drop radius increases with time, the profile h_0 changes as well. From the Eq. (2-9), the curvature of h_0 is negative, while $h_1''(r)$ is positive. When the curvatures become comparable, the point r leads to the estimate $3CaR/\theta_{ap}$ at the intermediate region. Both the profile height h_0 and drop radius R have an implicit dependence on time.

Fig. 2.1 The apparent contact angle determines the drop shape, when a drop partially wets and spreads on the solid substrate. It is shown that the interface near the corner is highly curved^[12].

As shown in Fig. 2.1, when we approach the three-phase contact line, the long-range forces also affect the micro-angle. Due to diffusiveness and thermal fluctuations, the interface position may not be fixed if we are going to examine it in the molecular scale. Thus, a real microscopic contact angle is directly determined at the contact line. When it is applied, by taking into account the diffusiveness of the interfaces, it requires to calculate the average microscopic data with well-defined theoretical models,.

However, the apparent contact angle can be uniquely defined with macroscopic angle by calculation with Eq. (2-6). Unfortunately, its requirement is contingent that the interface shape should be fairly far away from the micro- contact line and it is quasi-static. Meanwhile, the spreading speed only has limited impact on the drop shape. If the capillary number is sufficiently large in some cases, the viscous forces can deform the surface extensively, and no general formula can be applied for certain interface shapes. This fact even makes it more difficult to define an apparent angle with a formula. For a partially wetting drop spreading on a solid surface, three distinct spreading regions can be seen. The macroscopic bulk flow with the scale of its radius R is called as macroscopic fluid region. The contact line region is the second one, which is balanced by viscous and surface tension forces. At this region, the interface is exceedingly bent and interface slope is greatly changed as well. It is the “intermediate” region, where the profile turns from concave to convex. The third one is an “inner” region, where the nanometer size contact line is formed.

When the drop radius $R \ll l_c$ and the Tanner’s Law is fulfilled, the drop spreading analysis is easy to conduct. Whereas, the gravity will play a more important role in liquid spreading once

the radius is larger than the capillary length. Then, the drop will turn out to be like a “pancake”, which is curved at the edge part only with a constant thickness on the bulk liquid. At that moment, the gravity is the main driving force. The competition between capillary forces and the disjoining pressure determine the final thickness of the “pancake”. The capillary force has the intent to spread the thin liquid film and thus reduce its thickness, while the disjoining pressure tends to thicken the film by decreasing the wetting area. It can be balanced against dissipation either in the drop bulk or near the three-phase contact line, leading to $n = 1/8$ or $1/7$ respectively. The gravity will be very important and compete the surface tension and contact line dynamics and it should not be ignored, once the drop is sufficient large. It is found that the spreading exponent is $n = 1/8$, when gravity and bulk dissipation are balanced.

Fig. 2.2 The continuum modeling procedure illustration ^[22].

There are three regions from bulk liquid to the dynamic contact line, outer regions, intermediate and microscopic (Fig. 2.2). In the intermediate region, the viscous and surface tension forces are balanced. At that region, the macroscopic drop is generally preceded by a mesoscopic precursor thin film in front of the contact line. The precursor liquid thin film is formed by the van der Waals forces and static-electrics. The initial spreading coefficient S_i is negative, and the unit length work done through the contact line is $U[S_i + \gamma(1 - \cos \theta_d)]$. The free energy balance becomes

$$US_i + U\gamma h'^2(x) = 6\eta U^2 \int_{-L_p}^x \frac{1}{h} dx \quad (2-10)$$

Where the interaction doesn't start at the position of the bulk film or macroscopic contact line $x = 0$. It actually starts at the front edge of the precursor thin film. Hervet and de Gennes ^[23] had explained that the integral in Eq. (2-10) can be interpreted as two parts: one is covering the bulk fluid from 0 to x , and another is from the tip of the precursor thin film $-L_p$ to the macroscopic contact line at $x = 0$. Radke *et al.* ^[24] described it in more detail, as shown in Fig. 2.3, we can see four distinct regions comprise the entire moving apparent contact line front tip. In region 1, it is a spherical meniscus as a part of the spreading bulk droplet. It includes the dynamic contact angle θ ; In region 2, the hydrodynamic flow distorts the spherical shape. Then, disjoining pressure comes to play a role in the region 3. Disjoining pressure is the interactions of a variety of forces, such as van der Waals, electrostatic, hydrodynamics and structural. Over

region 3, capillary force is gradually overwhelmed by the disjoining pressure. The concept of disjoining pressure was introduced by Derjaguin ^[25] and developed from thermodynamic and hydrodynamic analysis and has been widely used as a means of modeling the liquid-solid molecular forces interactions in a liquid thin film on a surface; The last part is region 4. In the vertical direction, the characteristic scale is in the order of a few molecules only, thus there is no macroscopic spreading process in this region. Hence, it is referred as the surface diffusion region.

Fig. 2.3 (1) is the spherical part of the drop, in which a dynamic contact angle θ is formed on the solid surface; (2) A region the hydrodynamic force distorts the spherical shape; (3) A region capillary force is gradually overwhelming by the disjoining pressure; (4) A region with surface diffusion only and no macroscopic spreading process ^[24].

However, many other research groups also split the overall equilibrium fluid profile into three portions: the first portion is the liquid bulk in spherical shape, in which the dominant force is capillary forces, and gradually gravity take the role. The second portion is thin equilibrium films in the front tip. In this part, the disjoining pressure acts primarily as the surface forces. In-between part is the transition region, in which the capillary and surface forces compete with each other. The true liquid spreading progress is driven by the disjoining pressure by acting the forces in the vicinity of the apparent contact line through the chemical heterogeneity and surface roughness. Here, it is no wonder why accelerating the spreading through the bulk liquids is so difficult.

2.4.4 Wetting on structured surfaces

Wetting can be expressed by the Young's equation. It is commonly called as partial wetting since the droplet is placed and sustained on the surface. The three surface tensions will change if we change some thermodynamic variables, like temperature. And the contact angle will be changed as well. It is observable that there is a difference between the advancing and receding contact angles of a liquid droplet on a solid surface in many cases. It is called a hysteresis. It is commonly believed that the surface roughness or chemical heterogeneity of the solid substrate result in the "contact angle hysteresis". It also says the surface wettability can be changed by the surface structure and chemistries. It is notable that the static advancing and receding contact angles are different. For the micro-structures with the dimensions above 100 nm, we still can apply the macroscopic laws in the bulk liquid and local wetting front, while the surface

parts have to be resolved differently. In another aspect, thermal fluctuations and the intermolecular forces spatial variation become important, even though the structures are on the nano-scale. Micro-texturing is one of the ways which are able to change surface properties. Based on the researches and studies undertaken so far, two main ways have been proven as efficient approaches to alter the wettability of surfaces: patterned surfaces and structured surface. On patterned surfaces, the surface is flat, but the wetting properties vary spatially in a controlled way. On structured surface, the chemical properties are identical everywhere, but the geometry of the surface is manipulated in certain way. By minimizing of the total surface free energy, an equilibrium contact angle can be reached on the rough or patterned surfaces. We will go through the details of this topic in the discussion of Chapter 5 in order to integrate it with this research topic more naturally.

2.2 Anisotropic wetting and spreading research works

Owing to the anisotropic structured surface on the feet, water strider is allowed to walk on water. With the same reason, water is auto shed on the butterfly wings and insects can be trapped on plant leaves. Seizing and learning these naturals in biomimetic science is one of the hot research fields. It is often observed that the water contact angles of more than 150° on the lotus leaves, which are super-hydrophobic and on which water drops can roll off as a ball ^[26]. Similarly, the rice, bamboo and some grass leaves exhibit a different property that the water can roll off and flow more easily in one or two preferable directions, which is called as anisotropic ^[27]. It is worth to note another phenomenon that water droplets can roll outwards

only along its vein on gull and duck feathers, and the motion inward and in the perpendicular directions are extremely inhibited ^[28]. A lot of effects have been continuously devoted by scientists to investigate and explain the nature magic. It has been found that the special wettability on the animal and plants is less to do with the intrinsic property of materials, but is more related to their unique surface micro/nano structures and morphologies. More research data has indicated that the excellent water repellence of the lotus leaf is as a result of their strong surface roughness ^[29].

Malvadkar *et al.* report an engineered nano-film, which was made of by an array of poly (*p*-xylylene) nano-rods, demonstrates excellent anisotropic wetting behaviors by using a pin-release droplet ratchet mechanism. The experiment schematic and nano-film cross-section are illustrated in Fig. 2.4 ^[30].

Fig. 2.4 On PPX nano-film coated pipes, it shows the drop motion. It is the experiment schematic. One is coated with PPX nano-film and the other is uncoated. The frequency of the low amplitude vibration at half-pipes is $\sim 85\text{HZ}$ ^[30].

In the paper, it states the retention force in the pin and release directions differs by up to 80 μN , which is over ten times greater than the value reported on other engineered anisotropic surfaces. The micro-scale smooth surfaces can be made by the nano-film, and they can be employed to transport microliter droplets. It is also an easy way for synthesizing the nano-films with a bottom-up vapor-phase process. It is described that the film's anisotropic wetting and spreading behavior is a film morphology parameters to measure functions. With the random vibration shown in Fig. 2.5, the wafer drop moves on the half pipe along with the nano-film direction.

Fig. 2.5 Images show the droplet motions with time on the coated and uncoated half pipe surfaces. Water drops were translated axially on the half-pipe coated with the PPX nano-film,

but there is no motion for those on the uncoated half-pipe. The glue layer can be seen on uncoated pipes. The arrows indicate droplet position ^[30].

Wu *et al.* presented a mask-assisted low energy with a few kilo-electron volts focused ion milling technique to fabricate polymer textured micro/nano-surfaces with a large scale and low cost ^[31].

Fig. 2.6 With different obliquity AONWAs the PET sheets changed the surface water wetting property. The nano-wire growth direction on the PET surface was indicated. (a) Contact angles aligned with the projection direction. (b) Contact angles upright to the projection direction. (c-f)

Top-views of water drop on PET surfaces with different obliquity AONWAs. From (c) to (f), they are 10°, 20°, 30°, and 40°, respectively ^[31].

The method can be used to exactly manipulate the nanowire arrays' obliquity, length, diameter, and density, and nanowires also have good mechanical properties. With stimulation of the music sound wave vibrations, a poly(ethylene terephthalate) (PET) sheet with an align oblique nanowire array (AONWA) can unidirectional move liquid horizontally, and it can even climb up a 3.6° slope. Moreover, by using that kind of PET AONWA, a polystyrene (PS) microsphere can be directional transported for a distance of 0.28 cm with a slope of 1.6°, shown in Fig. 2.6.

Furthermore, the water droplets unidirectional wetting property shown by PET AONWAs, is similar with the anisotropic parylene nano-rod films ^[30] and polymer-coated silicon nano-pillar arrays ^[1]. In order to fabricate the PET AONWAs in their experiments, a PET sheet is covered by a gold film and is bombarded by Argon+ ions. The Ion acceleration voltage is 4 kV and incident angle is fixed. By modifying the Argon+ ions incident direction, the AONWAs obliquity can be adjusted. The process mechanism was elucidated clearly with charged surface, shadow mask protection and incident ions deflection. The objects with the sizes from a microscopic PS microsphere to a macroscopic PET sheet can be transported by the surfaces with AONWAs structures. Moreover, AONWAs show a property of unidirectional wetting for water drops, and there is a close relationship between the anisotropy of the NW's obliquity and the wetting property. These AONWAs has found its utility in a lot of applications ranging from self-cleaning

without a liquid, drug delivery systems, biomimetic mechanical research, fluidic diodes, to microfluidic devices.

Kwak *et al.* developed a nanofabrication technique for fabricating various slanted polymer nano-hairs with a poly(urethane acrylate) (PUA) mold material, shown in Fig 2.7 ^[32]. The flexibility and adjustable modulus of the PUA material provide the opportunities for large area replication and enable its usage in the techniques from micro-contact printing to imprint with lithography. The tensile modulus of PUA material is around from 19.8 to 320 MPa ^[33].

Fig. 2.7 (a) After annealing in a high temperature oven, the schematic shows that the nano-pillar is bended against to the metal side. (b) A titled image showing the bent nano-pillars. It is

achieved by coating a 6 nm platinum thin film on one side of the pillars and conducted thermal annealing in an oven with the temperature of 120 °C for 30 min. (c) A schematic illustrating the nano-pillars bending against the polymer side after electron-beam treatment. A platinum thin film was coated on one side of the pillars to prevent the decomposition of polymer material in CO₂ atmosphere during the electro-beam irradiation. (d) A title image showing nano-pillar bending after 6 seconds electron-beam irradiation ^[32].

By introducing the usage of the PUA mold, the structure resolution has been remarkably increased to approximate 50 nm without increasing cost, thus it opens the seam for preparing a variety of nano-hairy structures with a less-expertise and simple method. By utilizing the materials properties and employing appropriate physics and chemicals, it is possible to manipulate the pillar aspect ratio, tip shape, slanted angle, and surface energy in a low-cost, but high fidelity approach.

Fig. 2.8 (a) The titled nano-hair arrays fabrication by adjusting surface energy.

Fig. 2.8 (b) The schematic of experimental set-up for macroscopic shear adhesion force measurements on hydrophobic ($\text{SiO}_2\text{-C}$) and hydrophilic (SiO_2) surfaces^[34].

The soft lithography is the technique which can be used to fabricate the high aspect-ratio nano-pillars, such as UV-assisted CFL and replica molding. This is one-step process, while some structures with vertical hairs are produced by the two-step process, which is replica molding or photolithography with a post treatment. They had demonstrated a unidirectional spreading experiment on the PUA stooped nanohairs surface showing the anisotropic wetting. With the help of the small scale mechanical movements, like vibration or physical loading, the liquid front gradually migrated along with the pillar deflection direction at a speed of around $50 \mu\text{m s}^{-1}$, while the other frond pinned to the surface.

Rahmawan *et al.* presented a similar process approach to adjust tilting nano-hairy structure angles and the surface energy by using broad ion beam irradiation (Fig. 2.8)^[34]. Their work was inspired by the “adhesive” gecko foot-hair, which was discovered having the strong adhesive force on almost all surfaces. The gecko lizard is able to cling to these surfaces regardless of angle and roughness is attributed to these complex micro and nano features on the feet. Besides environment conditions such as humidity and temperature, it has been proven that the

hairs contract geometry like tip shape and hair density is the primary factor to decide the adhesion force in the gecko-inspired system ^{[35] [36]}. First, they made the vertical high aspect-ratio nano-hair arrays by replica molding process with UV-curable PUA material, and the nano-hairs have the diameter of 100 nm and height of 1 μm . Next, the nano-hairs were bent to a variety of bending angles from 0° to 75° by the oblique Argon ion beam irradiation. The surface energy was adjusted by the oxygen ion beam irradiation with aging processing (47.1 to 71.9 mJ m^{-2}). The prepared hairy surface properties can be altered from hydrophobic into hydrophilic by the oxygen ion-beam treatment, accompanying the notable shear adhesion force increase. The data, which were measured on the tilted nano-hairs with surface energy modifications, shows the nano-hairs tilting angle plays a major role in determining the macroscopic shear adhesion force. The adhesion force increased two times when the titled angle increased from 0° to 75°.

Inspired by the plant leave surfaces shown in Fig. 2.9, which feature hierarchical nanostructures on anisotropic wavy microstructures, the mimic grass-leaf surfaces have been produced by Lee *et al.* by tuning anisotropic wettability properties via a combination of Layer by Layer assembly on anisotropic micro-wrinkled substrates ^[37]. That paper exploited explained the properties of rice leaf surface with the hierarchical wavy structured topography. With this understanding, they also fabricated the artificial rice leaf surfaces with micro-structures where a number of nano-porous layers are presented on the given wavy micro-structures. There is an electrostatic layer-by-layer assembly with the combination of surface wrinkling in the fabrication process. With the anisotropic wrinkling patterns, the micro-scale roughness was maintained as a constant as shown in Fig. 2.10 ^{[27] [38]}. A wide range of wettability states, such as

anisotropic / pinned, anisotropic / rollable, or isotropic / rollable state, have been exhibited on the fabricated surfaces, and they are adjustable by changing the surface hierarchical nano-patterns and the overall roughness. They made the same conclusion with the findings that the water anisotropic droplet rolling and water repellence behaviors mainly result from the multiple-level roughness with anisotropic microstructures on rice leaf surfaces.

Fig. 2.9 Images of the anisotropic rolling behavior on rice leaves. a) A water drop on a rice leaf with an inset showing the optical images of a roll-off angle measurement for a 4 μL water drop being perpendicular or parallel to the longitudinal direction on the rice leaf. b) A image of the rice leaf upper surface. The rice leaf surface CLSM topographical image is displaced in the inset.

c) A magnified images of (b). The magnified image of the papillae with wax is displaced in inset
[37]

Fig. 2.10 Schematic showing the fabrication process of the rice leaf-like surface. a) The fabrication procedure includes surface wrinkling, LBL deposition and PDMS surface treatment. b) The fabricated rice leaf-like surface CLSM images with an inset showing the cross-section SEM image of the wavy PDMS substrate. c-e) the nano-structured film images on the PDMS

substrates which had gone through various deposition cycles; (c), (d), and (e) indicate 2, 5, 9, respectively^[37].

Wu *et al.* reported they used electro-spinning to generate biomimetic surface with one dimensional nano-fibers for wettability manipulations, shown in Fig. 2.11.^[39]

Fig. 2.11 (a) Images of a water droplet on the lotus leaf surface (a) and the silicon wafer surface with PVB nano-fibers coating (b). The fuchsine solution with the concentration of 1×10^{-5} M was used to have a clear view. (c) PVB nano-fibers image with the scale bar $2 \mu\text{m}$ ^[39].

In many research papers, it has been introduced that the bio-surfaces wetting properties have been mimicked with different patterns of electro-spun polymer nano-fibers, including bamboo leaves, lotus leaves, goose feathers and water stride's legs. By producing the bio-surfaces with an electro-spinning technique, the artificial water strider's legs with anisotropic wetting in two or three directions have the maximal supporting force of more than 200 dynes cm⁻¹. These polymer nano-fiber patterns help the design of fluid-controllable interfaces that can be applied in microfluidic applications and self-cleaning surfaces. In their paper, a new approach is introduced to mimic certain bio-surface topographies. By using electro-spinning process, the bio-surface topographies were mocked with the patterned polymer nano-fibers. It is a versatile process to generate the one dimensional nano-fibers. The fiber diameter can be easily manipulated by modifying the spinning parameters and solution concentration, and the fiber orientation could be adjusted by changing fiber collections.

Fig. 2.12 (a) Image of a water droplet on the bamboo leaf surface, and (b) Image of a water droplet on the silicon wafer surface which was coated by aligned electro-spun PVB nano-fibers. (c) SEM image of the aligned PVB nano-fibers with the scale bar of 1 μm . (d) the fiber array surface AFM image^[40].

Poly(vinyl butyral) (PVB) an oil-soluble polymer and was chosen as the raw material to fabricate fibers from PVB-alcohol solution with the electro-spinning process. The smooth spin coating PVB surface has the contact angle of 60° , while the contact angle on the surfaces with PVB nano-fibers is as high as $143 \pm 1^\circ$. The enhanced surface roughness is the main root cause of the higher contact angle of PVB nano-fiber surface (Fig. 2.12). After modifying the solution

concentration, the fabricated fiber diameters can be also changed, and then the surface wettability with these PVB nano-fibers will be modified accordingly^[40].

With the fabrication methods of a variety of micro- and nano- structures and selective chemical modulations on surfaces, advancements in surface engineering have utilized to enhance the surface wettability and enable the controllability of the liquid spreading. In Wang's works^[1], they successfully demonstrated the asymmetric nano-featured surface to accomplish uni-directional liquid spreading, in which the liquid propagates in a or two designated directions. Based on energy theory, they proposed a simple two-dimensional model to illustrate the the liquid thin film spreading behaviors. The model they proposed assumes that the liquid thin film propagates only when the moving contact line is able to reach the next row of pillars. In this situation, the local contact angle of the liquid, which is the intrinsic contact angle, must be equal to or smaller than a critical angle defined by the effective pillar height, pillar deflection angle and the spacing between pillars. This work gives us an insight on the design of asymmetric nanostructures and offer exciting opportunities to achieve unidirectional liquid spreading in future applications. Nevertheless, the dynamic process of the liquid spreading was not still studied in micro-level. Inspired by this seminal work, we will aim to gaining a deeper understanding of the unidirectional liquid spreading around micro/nano-pillars, particularly the dynamics of spreading near the three-phase contact line.

Fig. 2.13 The comparison images of the wetting behaviors on symmetric and asymmetric nano-patterned surfaces. a), axially symmetric liquid spreading of a 1 μl DI water droplet with 0.002% by volume of surfactants (Triton X-100) deposited on the vertical nano-pillar array surface which has the nano-pillar with diameters of 500 nm, spacings of 3.5 μm and height of 10 μm (inset). The scale bars in the image are 10 μm ^[1].

2.3 PDMS and properties

Polydimethylsiloxane, which is also called as PDMS briefly, is a widely used material. It has been utilized in microfluidic chips, bio-chemicals, MEMS and other applications. It is also known as a mineral-organic polymer with the structures containing silicon, carbon and oxygen. Besides

the applications in microfluidics, we also can find it in shampoo as an additive and in lubricating oils as an anti-foaming agent. Once the PDMS liquid is mixed with a cross-linking agent and pours the mixture into a micro-structured mold and heat up, a replica of the elastomer mold can be obtained, which is the basic use in microfluidic devices.

The PDMS can be expressed with an empirical formula as $(\text{C}_2\text{H}_6\text{OSi})_n$, while it is $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$ with a fragmented formula. Here, n is the number of repetitions of the monomer. The PDMS strength and fluidity can be modulated by the size of the monomer string. With a small n , the PDMS is almost non-cross-linked and like a liquid; with large n , it becomes a semi-solid. A certain viscoelasticity can be obtained with a flexible polymer by controlling the siloxane bonds. PDMS becomes a hydrophobic elastomer after fully cross-linked. PDMS cannot be wetted by the polar solvents, like water. It will appear as water beads on the PDMS surface and does not spread. It will adsorb the hydrophobic contaminants if it is placed in water. Plasma treatment can oxidize PDMS and change the surface chemistry of PDMS by creating silanol termination (Si-OH) on its surface, and then it can keep being hydrophilic for around half an hour. The plasma treatment also helps the surface resistant to adsorption of negative-charges and hydrophobic contaminants. Furthermore, the plasma process also can be employed to functionalize the PDMS surface with tri-chlorosilane, which enables the PDMS material to be covalently bond on an oxidized glass surface on an atomic scale with Si-O-Si bonds. PDMS material is not deformed or infiltrated in methanol, glycerol, ethanol or water, no matter whether it is oxidized by plasma. That is the advantage of PDMS being widely used in micro-fluids and bio-chemicals without deformation concerns. Whereas, if put PDMS in the

solution containing chloroform or diisopropylamine, it still will swell or deform. In the presence of pyridine and acetone it also will perform a lesser extent.

As aforementioned, PDMS is an extensively used as bio-chemical compatible material in various microfluidic devices. Here are the a few examples of the applications in the microfluidic chips. Owing to the high fidelity of the molding process, it is possible to mass production by replicating microfluidic chips from a mold. The process procedure is discussed below.

- Step 1: prepare a mold, like a silicon wafer mold, on which the surface is treated by release agents.
- Step 2: Drop 10% v/v amount of the cross-linking agent in PDMS liquid, and mix them up thoroughly by stirring, and then pours the mixed liquid on the set mold and place in an oven.
- Step 3: The PDMS hardening time depends on the percentage of cross-link agent in PDMS and the bake temperature. In general, 30 minutes is sufficient with 200 °C. PDMS can be peeled off from the mold, once it is hardened.

There are many advantages using PDMS for microfluidic and micro structured device fabrication.

- PDMS is transparent to the light with the optical wavelength between 24 nm and 1100 nm. This property can be utilized to visually inspect the micro-flow and flux contents in micro-channels under a microscope.

- PDMS is also a low auto-fluorescence material. When the light is absorbed by biological structures, like lysosomes, there is a natural emission, which is called as auto-fluorescence. It is allowed us to distinguish whether the light originating from bio-chemicals or artificially fluorescent markers ^[41], so it is considered as biocompatible.
- By oxidizing the surface with a plasma treatment, PDMS is able to sticks to another PDMS or glass surface tightly. With this advantage, it is possible to stack multilayer PDMS devices together and integrate it with a glass substrate, and enable the process of depositing thin film on functioning surfaces.
- With using spin-coating, PDMS is able to be coated with a controlled thickness before it is fully cross-linked on the substrate. This ability opens a door for integrating micro-valves with multilayer devices.
- It is deformable. With this flexible mechanical property, the microfluidic valves are possible to be connected with the small channels by deformation.
- PDMS is a less expensive material and a simple process as compared to the silicon and metal.
- It is easy to mold PDMS. The PDMS keeps as liquid for a few hours at room temperature, even it is fully mixed with the cross-linking agent.
- It is able to mold the structures with PDMS material with a high resolution, up to several nanometers ^[42].

- It is permeable to gas for PDMS. By taking this advantage, it is possible to control the gas flux through PDMS in cell culture. During molding process, PDMS is able to fill in small channels with no outputs. Since it is gas permeable, the residual air can escape through PDMS and balance the pressure with atmospheric.
- PDMS is a material with little ageing decay. It is verified that the PDMS material can keep the good mechanical properties for a few years.

As a coin has two sides, the problems of PDMS materials for microfluidics and micro-structure applications are also listed here:

- It is difficult to deposit metal films or dielectric films on PDMS. This weakness greatly restricts the usage on micro-devices and many applications which have the integration with resistors and electrodes. However, this shortcoming can be overcome attaching the PDMS a glass slide with the prior plasma processing, and then the glass slide can be used a substrate for depositing various dielectric or metals thin films, and it is alleviated when glue layer is applied in between.
- In contact with a liquid, PDMS can absorb hydrophobic materials and some new molecules are released from the cross-linking agents. This disadvantage will raise big concerns on some biological experiments and it should be handled with care.
- Since PDMS is gas permeable, including water vapor. Some gases are evaporated in PDMS device, and it makes difficult to monitor and calculate the gas flows. PDMS is also sensitive to exposure to some chemicals, shown in table 2-1 ^[43].

Chemical	Concentration (wt.%)	Time (min)	No	Mild	Medium	Total	Weight gain (%)
Buffered hydrofluoric acid	49.0	10	x				-0.97
Hydrochloric acid	37.9	10	x				-0.34
Potassium hydroxide ^a	86.9	10	x				-0.27
Hydrogen peroxide (H ₂ O ₂)	31.8	10	x				2.01
Piranha	3(H ₂ O ₂) : 1(H ₂ SO ₄)	10, 30	x				0.64
Photoresist developer ^b	100.0	10	x				-0.97
Water (deionized)	100.0	10, 30	x				-0.33
Hexane	99.9	10	x				4.67
Toluene	99.9	10	x				45.51
Acetone	99.7	10, 30	x				2.78
Methanol	100.0	10	x				-0.34
Isopropanol	100.0	10	x				-0.97
Potassium hydroxide ^a	86.9	60		x			0.75
Buffered hydrofluoric acid	49.0	30			x		1.39
Nitric acid	69.8	10			x		4.13
Hydrofluoric acid	49.0	10				x	-1.38
Sulfuric acid (H ₂ SO ₄)	96.0	10				x	-14.00
Potassium hydroxide ^a	86.9	1620				x	-0.90

Table 2-1 The characterizations of PDMS after immersion in Chemicals ^[43].

Note: The chemicals were gotten from Mallinckrodt Baker Inc., Phillipsburg, NJ. Photoresist developer (Shipley 351) was purchased from Rohm and Hass Electronic materials, Sunnyvale, CA, and the potassium hydroxide was purchased from Fisher Scientific (Fairlawn, NJ).

^a 800 g of Potassium hydroxide were mixed up with 4 L of deionized water. Immersion experiments were done at the temperature of 55 °C.

^b Photo-resist developer was diluted with deionized water with a ratio of 1:4.

2.4 Magnetic field, forces and applications

2.4.1 Magnetic field

A magnetic field is the magnetic influence of magnetic materials and electric currents. Magnetic field lines can be quantified by the magnetic permeability, and they form complete cycles and reach a certain density in a material. The magnetic flux density describes the number of field lines per unit area. Along with the distance from the magnet surface, this magnetic flux density decreases quickly (Fig. 2.14). The magnetic field lines will be re-directed through the material when a magnetic material is placed in a magnetic field iron to take advantage of the greater permeability (Fig. 2.15). The magnetic magnitude and direction at a given point can be used to specify the magnetic field. Basically, the moving electric charges generate magnetic fields, while the intrinsic magnetic moments of elementary particles in a material is associated with the electron spin, which is the fundamental quantum property ^[44]. Based on the relativity theory, magnetic fields and electric are two interrelated aspects of a single object, which is called as the electromagnetic. According to the quantum physics, the photons exchange results in electromagnetic interactions and the electromagnetic field is quantized ^[45]. Permanent magnets can pull on ferromagnetic materials, such iron, nickel and cobalt, and they can attract or repel each other. The invisible force is the most often form magnetic fields show us in daily life. The magnetic fields are used very extensively in modern technology, particularly in electrical engineering and electro-mechanics.

Fig. 2.14 Increasing the distance from magnet surface, the magnetic flux decreases rapidly. This data was plotted based on the data on a NdFeB magnet ^[46].

Fig. 2.15 A magnetically permeable material influences on the magnetic field lines ^[46].

The magnetic field can be defined by the force exerting on a moving charge. In electrostatics, a particle of charge q in an electric field $\mathbf{E}$ has a force of $\mathbf{F} = q\mathbf{E}$. On the other hand, the force also depends on the particle's velocity when a charged particle moves in the vicinity of a current-carrying wire. *Lorentz force law* is the principle defining the velocity separation,

$$\mathbf{F} = q (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2-16)$$

Where $\times$ denotes the cross product and $\mathbf{v}$ is the particles' velocity. The vector $\mathbf{B}$ is the term of the magnetic field, and it defines the vector field. The moving charged particle should satisfy the Lorentz force law. Alternatively, it produces on a magnetic dipole when the magnetic field is defined as a torque. $\mathbf{H}$ is the "magnetic field", besides there is a $\mathbf{B}$. In a vacuum, $\mathbf{B}$ and $\mathbf{H}$ are proportional to each other, with multiplicative constant which is also related to the physical units.

2.4.2 Magnetic forces

It is quite complicated when we deal with the magnetic force. It is associated with the orientation and strength of both magnets. It also depends on direction and the distance of the magnets relative to each other. The magnetism rotation is special sensitive to the force, since magnetic torque is direction related. The force on each magnet depends on the magnetic field

and its magnetic moment. It is essential to visit the magnetic pole model to understand the force between magnets. In this model, the ***H**-field* of one magnet pulls and pushes on both poles of a second magnet. There is no net force on that magnet if both poles of the second magnet in the ***H**-field* are the same with the opposite force. However, in the situation that the magnetic field of the first magnet is non-uniform, each pole of the second magnet sees a different field and they are subject to a different force. The two different forces will move the magnet in the direction of increasing magnetic field, and a net torque may be induced.

A general rule is that magnets are attracted or repulsed into the higher magnetic field regions. Any non-uniform magnetic field, which may be caused by electric currents or permanent magnets, exerts a force on small magnets. From the math perspective, the force on a small magnet have a magnetic moment ***m*** due to a magnetic field ***B*** is ^[47],

$$\mathbf{F} = \nabla (\mathbf{m} \cdot \mathbf{B}) \quad (2-17)$$

where the gradient ∇ is the unit different of the quantity $\mathbf{m} \cdot \mathbf{B}$ per unit distance, and the direction is that of maximum increase of $\mathbf{m} \cdot \mathbf{B}$. The dot product $\mathbf{m} \cdot \mathbf{B} = mB \cos(\theta)$, where θ is the angle between $\mathbf{m}$ and $\mathbf{B}$. If $\mathbf{B}$ has the same direction of $\mathbf{m}$, the dot product will be positive and the gradient points pulling the magnet into the higher $\mathbf{B}$ -field regions. This equation is strictly only valid for magnets with zero size, but it is often a good approximation for

the magnets with “small size”. By dividing them into smaller regions, the magnetic force can be calculated by summing up the forces on each of these regions.

When two pole-like separate magnets are brought close to each other and one of them is fixed and another can free rotate, the flexible one will rotate promptly to align itself with the first one. The fact here is that a magnetic torque is created by the magnetic field of the static magnet and imposes on the free magnet to rotate. The magnet’s poles will align with the magnetic field lines by the effect of the magnetic torque. We can utilize the magnetic torque to drive electric motors in many applications. In the motor, the magnet is fixed and the shaft is free rotating. The shaft can rotate fast when the magnet is subjected to a magnetic field, which was created by an array of electromagnets. With the flipping of the magnetic fields polarity by switching the electric current through the electromagnets continuously, the poles are kept next to the rotor and the shaft keeps on receiving the torque.

Moving charged particles can produce magnetic fields and electron is one type of them. When many moving point charges are combined, the magnetic is complicated. The final magnetic field depends on the charge, velocity, and acceleration of the particles ^[48]. When a cylindrical current flows around a conductor, it can create complete and concentric circles magnetic field lines around it. The “right hand grip rule” is applied to determine the magnetic field direction. Increasing the distance from the wire, the magnetic field strength decreases. The magnetic field is strengthened inside the loop by bending a current-carrying wire as a loop, while it weakens the outside. And this effect is particularly enhanced by bending a wire into multiple closely loops to form a coil. Inserting an iron in the coil forms a device, which can act

as an electromagnet to generate a well-controlled strong magnetic field. A finite length electromagnet is produced by the current flowing through the coil, and the strength and polarity of electromagnet are also determined by the current flow. The magnetic field generated by a steady current I can be described by the Biot-Savart law ^[49].

$$B = \frac{\mu_0 I}{4\pi} \int_{wire} \frac{dl \times r}{r^2} \quad (2-18)$$

where r is the distance between the locations of dl and the location at which the magnetic field is being calculated, and the integral sums over the wire length where vector dl is the vector line element with direction in the same sense as the current I . $\hat{r}$ is a unit vector in the direction of r , and μ_0 is the magnetic constant.

2.4.3 Magnetic micro-devices and applications

In this project, we are going to discuss the magnetic micro-pillar application in control of the liquid wetting and spreading. In the past many decades, people have extensively utilized the kind of polymeric materials in a variety of applications with micro- and nano-structured to create novel devices.

Fig. 2.16 (A) the experiment setup schematic shows magnetic field gradients creation. A large array of magnetic micro-pillars can be obtained by applying spherical magnetic aggregates. The piezoelectric micromanipulator has a sharp metallic needle mounted. Once a strong magnetic field gradient is applied, the substrate is spontaneously deformed. The pillar deformation and tip position were detected by the analysis software. When the magnetic tip moves, each pillar follows the movement. (B) The side-view of the pillars with a 10 μm diameter 20 μm height. The pillars were filled with ferromagnetic black iron oxide particles. The magnetic nanoparticles were concentrated at pillar tips with their fabrication technique. (C) The moving pillar optical images. The pillar rotation movement is induced by the moving needle (first and third pictures) ^[50].

For instant, magnetic actuated micro-devices can be employed to accomplish various complex functions in micro-fluidics and micro-fabricated devices, as shown in Fig. 2.16. An

example is the magnetic actuators and magnetic mixers have been introduced to handle micro-fluids. Digabel Jimmy Le *et al.* had showed us a new strategy to create micro-pillar arrays which can be magnetically actuated. It enables it as a tool to govern substrate deformations ^[50]. The micro-fabrication techniques were used to fabricate the micro-pillar arrays by incorporating the magnetic aggregates inside polymeric matrices with dispersion methods. Near the substrate, a magnetic field gradient was created to impose the well-defined forces on these magnetic aggregates, which in turn affect the micro-pillar deflections. Owing to the magnetic nanoparticles embedded in the micro-pillars, an isolated pillar movement or the synchronized motion of a batch of pillars can be achieved in a magnetic field gradient. This versatile ability enables the possibility that the substrate actuations can be controlled locally or globally within a range of micro-dimensions, which could be used for micro-fluidics and biological applications.

Magnetohydrodynamic (MHD) flow is generated when a magnetic field and an electric field are applied to each other perpendicularly across the height and width of a micro-channel filled with a conducting solution. It has been applied to the pumping of fluids through micro-channels. A *Lorentz* force acts in the direction of the channel length and induces fluid movement. Any conducting liquid is suitable to use MHD pumping technique. Both straight channels and circular channels are able to take advantage of it. By changing magnetic field and the current flow or the buffer solution ionic concentration, the flow velocity is adjustable. MHD micro-pumps can be operated with DC or homogeneous magnetic fields.

Magnetic materials, like ferro-fluids, and PDMS with embedded magnetic particles have also been widely used as valves. A circular ferro-fluidic micro-pump (Fig. 2.17) was fabricated by

Hatch *et al.* based on two plugs of ferro-fluid and two Nd magnets ^[51]. Acting as a closed valve, one plug could be held in place between the inlet and outlet channel. By a rotating external magnet, the second plug could move around the circle. With this repeated action, this plug pulled liquid in and then pushed it out of the circular channel.

Fig. 2.17 The illustration shows the working principle of the circular ferro-fluid pump. Ferro-fluid plugs was controlled by the two magnets (M) in a circular micro-channel ^[46].

By employing electroplating process and electron beam nanolithography technique, ultrahigh density single domain magnetic nickel pillar arrays were fabricated by Chou *et al.* ^[52]. The nickel pillar arrays on the silicon substrate have a uniform height of 120 nm and diameter of 35 nm, and a period space of 100 nm. The density of the pillar arrays can be as high as 65

Gbits/in². Each nickel pillar is a single domain with only two quantized perpendicular magnetization states: up and down, and it is attributed from the nano-scale size, shape anisotropy, and isolation each other. Therefore, each pillar is able to store one bit of information.

Fig. 2.18 Schematic of nano-magnetic pillar array Fabrication process ^[52].

Figure 2.18 shows the nickel pillar fabrication process flow. A thin gold was deposited on a silicon substrate with electrical plating process. A high resolution electron beam resist, poly(methyl methacrylate) (PMMA), was then spun onto the substrate. Depending on the desired pillar height, the thickness of the PMMA can be adjusted. It is around 130 nm in their works. Dot arrays with diameter from 35 to 40 nm and spacing from 50 to 1000 nm were exposed in the PMMA using a high-resolution electron-beam lithography equipment, which has the electron beam diameter of 4 nm. Then, the nickel post was deposited by electroplating method on the holes, which developed in a cellosolve and methanol solution.

Fig. 2.19 The Scanning Electron Microscope (SEM) image shows Si (100) pillar with about 500 nm in height and the ellipsoid shape $\text{Fe}_{55}\text{Pd}_{45}$ wrapping around each Si (100)-pillar top with a

length L around 108 nm. The short-axis (or planar) diameter of the ellipsoid is around 67-83 nm [53].

Another high-density magnetic recording work was done by Liu *et al.* making use of the titled or perpendicular anisotropic magnetic nano-dot arrays [53], which were deposited by two kinds of ferromagnetic sample: $\text{Fe}_{55}\text{Pd}_{45}/\text{Si}$ (100)-plane and $\text{Fe}_{55}\text{Pd}_{45}/\text{Si}$ (100)-pillar. The key properties for the magnetic recording media with high-density and low noise are associated with the high square-ness in the perpendicular hysteresis loops and reduced magnetic domain sizes properties.

A theoretical estimation shows that the magnetic state of the FePd ellipsoid should be in a single-domain or vortex-domain state. They made single-domain or vortex-domain state sample by depositing $\text{Fe}_{55}\text{Pd}_{45}$ on nano-meter silicon pillars. This is a good and economic way for the magnetic recording media with high-density and low noise in the perpendicular magnetic recording.

Fruchart *et al.* reported a method for fabricating epitaxial nanometer-thick self-organized magnetic structures on atomic step arrays, such as Fe/Mo (110) stripes, and surface features, such as Co/Au (111) pillars [54]. At room temperature, these structures are remanent due to the high volume. However, the conventional self-aligned flat systems obtained in the sub-monolayer deposition are super-paramagnetic even at the low temperatures. Au is (111) surface, so it will undergo a surface reconstruction with the lattice parameters much larger the

atomic dimensions, 7 x 20 nm. We can use the template to fabricate self-organized arrays of flat Co, Ni or Fe dots with diameters of 1-5 nm. In their report, by sequential depositing Au and Co sub atomic layer amounts under suitable conditions, the flat Co dots could be extended vertically.

It was reported by McClelland *et al.* that nano-scale magnetic islands patterning could be produced by imprinting lithography with a flexible mold ^[55]. They used a mask with SiO₂ holes array pattern to form the polymeric mold, and in turn used it to mold a photo-resist film on substrates. This latter film is used as a resist to etch SiO₂ and yield the pillar array patterns. Last step is to deposit the 11-nm-CoPt multilayer film.

Fig. 2.20 Schematic showing process steps of the fabrication and images of the pattern magnetic media. The isolated domain with quantized up and down magnetization was displayed the final panel with magnetic force microscope images ^[55].

The process steps are described here. The first step is to use electron-beam lithography to fabricate a master. Next, imprint the pattern on the mask with a photo-cured stamp, and then mold a photo-cured etch mask on the silicon substrate. Following that, it is plasma etching to create SiO_2 pillars (Fig. 2.20). Last, deposit the magnetic film with the electron-beam evaporation process. The magnetic film on the tops of the pillar is isolated into independent islands defined by pillars. The CoPt multilayer film thickness on the patterned small selected regions is around 3 nm and their magnetic properties are examined. Owing to the perpendicular, high remanent and high anisotropy magnetization, the CoPt multilayers are the good candidate for magnetic recording on patterned media.

Dong *et al.* had invented an integrated micro-separator by utilizing the soft magnetic micro-pillar array patterns^[56]. As we know, in medical samples, we need to isolate or separate certain kinds of cells from the bulk. A lot of methods have been introduced for separating the specific cells based on electrical charge, antigenic surface properties, light-scattering properties, density and size from liquid suspensions. Because of the fragility and accumulation of the cells, it is a big challenge by using a physical filter only to bio-purify the cells in the bulk samples. In their work, they accomplished the cell isolation by using an independent lab-on-chip device. In that device, Micro-coils are used to generate the electromagnetic field and the cells were simplified and re-distributed with the soft magnetic micro-pillar arrays. Here is the micro separator fabrication process flow: by using the technique of the Electro- chemical plating process, NiCo/NiFe was deposited to fabricate the micro-pillar arrays, which was used to isolate the lymphocytes in their work. The results show that the separation ratio reaching up to 90%.

The mechanism is that, at an extremely low current, the target lymphocytes can be recognized and captured by the electromagnetic micro separator with a high efficiency. Fig. 2.21 shows the cell isolation mechanism in the micro-pillar device.

Fig. 2.21 Cell separation procedure diagram for the micro separator: (a) the magnetic field is generated and the pre-treated sample flows into the separator; (b) Capture the target cells by the micro-pillars; (c) wash the non-target cells out of the separator; (d) cut off the external current and release the target cells ^[56].

Xia *et al.* presented a similar creative method to fabricate the cell capture device with integrated magnetic micro-pillars in Figs. 2.23 – 2.34 ^[57]. CTCs (circulating tumor cells) have been identified in peripheral blood from patients with various kinds of cancers. However, CTCs capture and counting is facing the technical difficulty because of the low abundance of CTCs

among an extremely large number of hematologic cells in the bulk blood. Microfluidic lab-on-chip devices have been successfully used for cell separation. The magnetic pillar fabrication process is shown here. The arrays of cavity structure were created using the conventional soft lithography. Fabrication of the masters was done by spin coating with the material US-8 (MicroChem US Inc.) on silicon wafers. These cavities were filled with the ferroferric oxide powder and remove the excess powder with brushing, and leave the intervals clear. PDMS was treated following the instructions and poured onto the masters. It was then degassed in a desiccator and cured at 80 °C for two hours. When peeling the PDMS from the masters, magnetic micro-pillars were fabricated finally. By using oxygen plasma treatment, the PDMS micro-device is strongly bonding to a glass slide irreversibly.

Fig. 2.22 Schematic illustration of magnetic micro-pillar chip process flow ^[57].

Fig. 2.23 The SEM image of the captured magnetic beads on the micro-pillar surface. The white bar is 20 μm ^[57].

Then, it was used to test the bead capture and release. Initially, the super-paramagnetic beads can be distributed evenly within the chip. When a small external magnet was applied, micro-pillars were instantly magnetized and deliver a strong magnetic force to capture almost all of the beads around them. When the external magnet was removed, the beads captured on the micro-pillars were immediately released into solution.

Owing to the potential applications for sensors and actuators and the adhesion and wetting properties presented on the material surface, a lot of research interests have been attracted by the high-aspect-ratio micro/nano-structures in the nanotechnology fields. By using polycarbonate track-etched (PCTE) membranes as a template, Evans *et al.* had produced high-aspect-ratio structures with variable pillar spacing and diameter ^[58].

Fig. 2.24 Cross-section view of the template fabrication process ^[58].

The low elastic modulus of the PDMS material and the high-aspect-ratio (HAR) of the pillars give us the flexibility, and they can be the good candidates for actuators. The iron oxide nanoparticles are embedded in the PDMS rods, so that the flexible super-paramagnetic rods can be actuated by under the controllable and adjustable external magnetic fields. Fig. 2.24 summarizes the process procedure to prepare the magnetically controllable pillar arrays. The actuation of the pillar arrays is induced through the externally magnetic field, which is created by permanent magnets of neobymium-iron-boride (NIB). There are the applications giving us an idea how the magnetic devices were fabricated and utilized by researchers. Here, I am going to introduce the approaches to fabricate the micro-pillars in my research work.

Chapter 3 Silicon wafer surface wettability ageing behavior

3.1 Background of silicon wettability

The terms of “hydrophilic” and “hydrophobic” are used to describe the surface wettability by water or non-polar liquids, respectively. A surface is hydrophilic if it tends to adsorb water or be wetted by water with a low contact angle; otherwise it is hydrophobic. The surface hydrophobicity of a silicon wafer is important in many applications ^[59-66]. For example, the silicon hydrophilic property plays a crucial role in the process of direct wafer bonding ^[59, 60], silicon-on-insulator (SOI) products ^[61], silicon-based sensors ^[60, 62], biochemical systems ^[63, 64], and Micro Electro-Mechanical Systems (MEMS) ^[66].

A silicon surface is hydrophilic because the silicon surface is generally covered by a thin native oxide layer, which links many silanol (Si-OH) groups, and physically adsorbs 1 or 2 monolayers of water on top ^[65, 67]. The native silicon oxide (SiO₂) on a silicon surface could be formed in the presence of water molecules, which might be extracted from moisture or from polymerization of Si-OH on the surface ^[59]. The singular and associated -OH groups are relatively stable on a silicon dioxide surface during heating ^[60, 68]. A variety of cleaning methods could be utilized to modify the silicon surface wettability. The silicon wafer cleaned using a piranha solution is hydrophilic, but the silicon wafer cleaned by a HF solution is hydrophobic, and the hydrophilicity could be restored after long time exposure to moisture or by a plasma activation treatment ^[69]. However, most of these studies were carried out in atmosphere

environments, and few works systematically investigated the silicon wafer surface wettability and aging behaviors in a vacuum condition and the impact on the noble-metal thin-film deposition and growth. For example, the influence of the silicon surface wettability on the morphology of the sputtered noble materials, like gold film, is still not clear. By measuring the surface contact angle, and using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and high-resolution Transmission Electron Microscopy (TEM), we studied silicon surface wettability and its aging process, and the sputtered gold thin-film growth mechanism on silicon wafers. In-situ plasma treatments were performed to lower the film roughness and improve the adhesion of the sputtered gold thin film on silicon wafers. It is a low cost and effective technique, especially for some applications, such as magnetic-nanowire gold thin-film coating, in which a metal glue layer is strictly prohibited.

3.2 Experimental

P-type silicon wafers were used in the experiments, and they were purchased from Semiconductor Wafer, Inc. We used a piranha solution, SC1 solution or HF solution to clean the silicon wafers in this study. The piranha solution is a 3:1 mixture of sulfuric acid (H_2SO_4 , 96%) and hydrogen peroxide (H_2O_2 , 30%), and is heated up to 120 °C. The SC1 solution used is a mixture of NH_4OH , H_2O_2 and H_2O with a ratio of 1:1:5 at 80 °C^[70]. The HF solution is a mixture of 6 parts of 40% NH_4F and 1 part of 49% HF. The wafers were rinsed in deionized (DI) water for three cleaning cycles, which lasted for ten minutes with a continuous DI wafer purge, and then were dried in a spun drier with a hot N_2 purge. A vacuum oven (DZ-1BZ, China) was used to

provide a vacuum condition with a pressure less than 1 Torr, and it was placed in a class 100 cleaning room with 42% humidity at 23 °C. A plasma treatment was carried out in a sputtering chamber (RD4, ESC, UK) for the silicon surface wettability modification at a pressure of 15 mTorr and RF power of 100 W with argon, nitrogen or oxygen gas. The base pressure of the plasma treatment chamber was around 3.0×10^{-8} Torr. The duration of the plasma treatment was three minutes. We measured the water contact angles using a contact angle system (DSA100, KRUSS) with a sessile mode. At least three measurements were conducted for each sample, and their average value was taken to be the contact angle for that sample. Every measurement was performed at a fresh site to avoid the potential impacts from previous measurement water marks. An X-ray photoelectron spectroscope (XPS, KRATOS Axis Ultra DLD, UK) was used to analyze the wafer surface composition. It is equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and a delay line detector in a 1.0×10^{-9} Torr vacuum. XPS Surveys were collected at the fixed analyzer pass energies of 160 eV. Charge neutralization was performed for all samples. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination, which was taken to be 284.8 eV.

The gold thin films were deposited in a magnetron sputtering system (RD4, ESC, UK) with a process pressure of 5 mTorr at the room temperature. Before film deposition, the chamber was pumped to a base pressure of around 3.0×10^{-8} Torr, and the pre-sputtering time was three minutes to remove contaminants on the target surfaces. The thickness of the gold thin film was measured using a profile-meter (Dektak 8, Advanced Development Profiler, US), and the surface roughness was examined using an atomic force microscope (AFM, D3100, Topometrix Instrument). A transmission electron microscope (TEM, FEI Titan 80-300 s-twin) was also

employed to exam the cross-section of the gold thin film texture and the interface layer between the silicon substrate and gold film.

3.3 Results and discussion

A simple way to evaluate the hydrophobicity of a surface is to measure the contact angle of a water drop on it, as shown in Fig. 3.1 (a). Various contact angles are exhibited in Fig. 3.1 (b) - (e).

Fig. 3.1 (a) Diagram showing the contact angle measurement method; (b) Image of the contact angle of a water drop on a wafer surface that has gone through an oxygen plasma treatment for three minutes; (c) Image of the contact angle of a water drop on a silicon wafer in a vacuum for 2 hours after the piranha cleaning; (d) Image of the contact angle of a wafer drop in a vacuum for 96 hours after the piranha cleaning; (e) Image of the contact angle of a wafer drop in a vacuum for 96 hours after the HF solution cleaning.

The hydrophilicity of the silicon wafer results from singular and associated -OH groups presented on the surface ^[59, 60, 67, 68]. It was reported that drying in a vacuum at a low temperature is the way to remove the physically adsorbed water without disturbing the -OH groups ^[62]. Here, we monitored the silicon wafer wettability and behavior by measuring the water contact angles, and reviewing the surface species change.

3.3.1 Impact of cleaning methods and aging atmosphere

Sample W1 and sample W2 in Fig. 3.2, which were cleaned with the piranha solution (10 min, the same as below), were hydrophilic, because of a very thin native oxide layer on the surfaces, and plenty of hydroxyl (-OH) groups linked to the native oxide ^[64]. The contact angles of W1 and W2 were less than 5° immediately after the piranha cleaning. Next, W1 was put in an open oven, exposing to the cleanroom environment, and W2 was put in a vacuum oven (<1.0 Torr) at the same temperature (23 °C). Fig. 3.2 shows that the contact angles of W1 were around 5°, 15.3°, 18.2°, 22.9°, 24.6° after 5 hours, 24 hours, 48 hours, 72 hours and 96 hours, respectively. After two weeks, it reached 27.3° and it might continuously increase with a slower rate. This contact angle increases as the result of the fact that the water molecules were slowly evaporated from the silicon surface, and some organics and particles in the air dropped on the surface ^[62]. W2 was put in a vacuum oven immediately after the piranha cleaning. Because the physically trapped water desorption from the silicon wafer surface in the vacuum was much faster than that in the air, the contact angle increase rate of W2 was much faster than that of W1. The contact angle rose to 18.3° in 2 hours, 28.2° in 5 hours, and 47.1° after 12 hours. After that, the increase rate became slower, and eventually the contact angle reached 68.7° two

weeks later. This indicates that the vacuum condition accelerated the aging process by evaporating water molecules without adsorbing contaminants [62, 63, 65].

Fig. 3.2 The contact angle trend chart of the silicon wafers cleaned with different solutions, and then aged in various conditions.

Both W21 and W22 were cleaned with the SC1 solution. W21 was then put in the open oven, and it experienced the similar surface wettability with W1, while W22 was then put in the vacuum oven, and it had the wettability trend similar to that of W2. However, there was a 5 - 10° gap between the contact angles of W22 and W2, because the piranha solution is a strong

oxidizing agent, and it would remove most organic matters to make the silicon surface highly hydrophilic by adding -OH groups. The SC1 cleaning is also a good cleaning process to remove organic residues and particles from silicon surfaces, but it might bring a certain degree of metallic contaminants, like iron, which makes W2 even more hydrophilic.

Both W11 and W12 had gone through the HF solution, and they were hydrophobic. The contact angles were around 81° immediately after cleaning. W11 was then put in the open oven, and W12 was put in the vacuum oven. Interestingly, the contact angle of W11 decreased to around 71° in the first 12 hours probably due to a few water molecules adsorbed on the surface and a very thin native oxide film formed, and then it went to a plateau. On the contrary, the contact angle of W12 increased to 88.4° after 5 hours, climbed to 91.3° after 12 hours in the vacuum, and then slowly crept to its saturated point around 95° after two weeks.

3.3.2 Impacts of plasma treatment

The utilization of a plasma treatment offers an innovative and economical solution for the cleaning and surface activation of silicon wafers ^[71, 72], PDMS ^[73, 74], SU8 ^[66, 75] and other materials ^[76, 77]. It provides an alternative for solvent cleaning, and it is a favorable, environmentally friendly process on micro-devices. The gas could be argon, oxygen, nitrogen, hydrogen, SF₆ or air. Suni *et al.* stated that argon or nitrogen plasma activation yields stronger bonds than oxygen plasma in the vacuum wafer bonding ^[59]. However, in terms of the surface wettability and surface composition detected by XPS in our experiments, the impacts of the three (argon, nitrogen, and oxygen) gases are almost the same. W4, W5, and W6 were cleaned

by us with the HF solution, and then treated by the argon, nitrogen, and oxygen plasma (RF 100 W, 15 mTorr, 3 minutes), respectively. They were then put in the open oven.

Fig. 3.3 The contact angle trend charts of the silicon wafers that were cleaned with the HF solution, treated by the gas plasma, and then aged in the open air or a vacuum oven.

All of the three wafers had very similar water-contact-angle aging behaviors, as shown in Fig. 3.3. W23, W24, and W25 were cleaned with the HF solution, and then treated by the argon, nitrogen and oxygen plasma, respectively. After that, these three wafers were put in the vacuum oven for aging, and three similar aging curves were observed. Their contact angles increased to 70° after 10 hours, and then stabilized at that level. W7, W8, and W9 were cleaned

with the piranha solution, and then went through argon, nitrogen, oxygen plasma treatments, respectively. They were put in a vacuum oven together with W23, W24 and W25. The results show in Fig. 3.4 that there is no obvious difference among all wafers, no matter if the silicon wafer surface was hydrophilic or hydrophobic prior to the plasma treatments. This indicates that they have the same surface properties after the plasma treatments.

Fig. 3.4 The contact angle trend charts of the silicon wafers that were cleaned with different cleaning solutions, treated by the gas plasma, and then aged in a vacuum. All wafers have the similar aging behavior after plasma treatments.

3.3.3 XPS survey on silicon wafers

The XPS survey was carried out to analyze the surface composition after the cleaning, plasma treatment and aging. The silicon samples process conditions are: S1 was cleaned with the piranha solution; S2 was cleaned with the HF solution; S3 was cleaned with the HF solution and argon plasma treatment; S4 was cleaned with the HF solution and nitrogen plasma treatment; S5 was cleaned with the HF solution and oxygen plasma treatment; S1_P was cleaned with the piranha solution and then aged in a vacuum oven for two weeks; S2_P was cleaned with the HF solution and then aged in a vacuum oven for 2 weeks; and S3_P was cleaned with the HF cleaning, experienced the argon plasma treatment, and then was aged in a vacuum oven for 2 weeks. The XPS survey was conducted on these samples immediately after they went through the cleaning or plasma treatments. The XPS spectra are shown in Figs. 3.5 - 3.7, and the element results are presented in Table 3-1. S1 has a higher concentration of oxygen (22.3%) and a lower concentration of carbon (3.9%) than S2, which has 5.1% oxygen, 15.1% carbon and 30.4% fluorine. After plasma treatments, S3, S4 and S5 have similar elements. The plasma treatments resulted in a remarkable increase in the concentration of oxygen from 5.1% (S2, HF cleaned without a plasma treatment) to 52.4% (S3, argon plasma treated after the HF cleaning), 39.7% (S4, nitrogen plasma treated after the HF cleaning) and 55% (S5, oxygen plasma treated after the HF cleaning). It is noticed that S3, S4 and S5 have similar oxygen levels, although there is no oxygen flow during the plasma treatments of S3 and S4. It is most likely that the energetic ion bombardments during an RF plasma treatment broke Si-Si, Si-H or other bonds and activated the sites to the high surface energy status^[78], and then the activated sites attracted atomic or molecular oxygen or water instantly when the silicon wafer was taken out

from the plasma chamber to the open environment. Meanwhile, the plasma treatments dramatically decrease the fluorine element concentration from 30.4% to less than 0.2%, and the carbon concentration from 15.1% to around 9%. This result explicitly shows that the hydrophilic silicon surface has a high concentration of S-OH groups, while the hydrophobic silicon surface has more Si-H, Si-CH_x and Si-F groups, and low –OH groups^[62, 65].

Fig. 3.5 XPS spectra collected on silicon sample surfaces obtained with various cleaning methods and plasma treatments. The process conditions of the samples are listed in Table 3-1.

Fig. 3.6 XPS spectra collected on silicon sample surfaces obtained with various cleaning methods and plasma treatments. The process conditions of the samples are listed in Table 3-1.

It is also noticed that a certain amount of the aluminum element was detected on all plasma-treated samples, and there was no aluminum element on non-plasma-treated samples. The size of the samples was 2 cm x 2 cm, and they were placed on top of an 8-inch aluminum pallet in the sputtering chamber during the gaseous plasma treatments. It is very likely that the aluminum contamination was from the aluminum pallet during the plasma treatments. S1_P, S2_P and S3_P were the samples after two weeks of aging, and they had larger contact angles than their counterparts, S1, S2 and S3, which did not go through aging. From the XPS data, we can see that the aged S1_P had slightly higher carbon and oxygen concentrations than S1.

Similarly, aged sample S2_P also had slightly higher carbon and oxygen concentrations, while the fluorine concentration on S2_P was smaller than S1. S3_P had a higher carbon concentration than S3 as well. Therefore, the silicon surface hydrophobicity is mainly contributed from $-CH_x$ groups, rather than $-F$ groups.

Fig. 3.7 XPS spectra collected on silicon sample surfaces obtained with various cleaning methods, plasma treatments and aging processes. The process conditions of the samples are listed in Table 3-1.

Elements	Si	C	O	F	N	Al	Ar	Sample	Process condition
Atomic concentration (%)	72.1	3.9	22.3	1.1	0.6	-	-	S1	Piranha cleaning
	49.4	15.1	5.1	30.4	-	-	-	S2	HF cleaning
	15.1	9.6	52.4	0.2	-	22.7	2.1	S3	HF cleaning and Ar plasma treatment
	22.3	8.5	39.7	0.2	14.6	14.7	-	S4	HF cleaning and N2 plasma treatment
	22.5	8.8	55.0	0.1	0.6	13.0	-	S5	HF cleaning and O2 plasma treatment
	64.3	10.1	25.6	0.6	-	-	-	S1_P	Piranha cleaning and two weeks ageing in vacuum
	47.1	19.2	16.7	17.0	-	-	-	S2_P	HF cleaning and two weeks ageing in vacuum
	14.6	13.2	45.9	0.6	0.4	23.2	2.1	S3_P	HF cleaning, Ar plasma treatment, and two weeks ageing in vacuum

Table 3-1 Element concentration values of the silicon sample surfaces were calculated based on the XPS spectra collected.

3.3.4 The influence of surface wettability on gold thin film

Thin film nucleation and a film growth process could be significantly affected by silicon substrate chemistry ^[79-81]. As aforementioned, S1 was hydrophilic after the piranha cleaning, and S2 to S7 were hydrophobic after the HF cleaning, and then S3, S4, and S5 surfaces were then modified to be hydrophilic by argon, nitrogen and oxygen plasma treatments, respectively. Next, a gold thin film was deposited on S1-S5 in a magnetron sputtering chamber. An AuO_x (non-stoichiometric Au₂O₃, which is considered one of the most smooth gold compound films) thin film was deposited on S6 by incorporating 25% oxygen in the argon gas during the sputtering process in the same chamber. A sputtered gold thin film with a thin AuO_x transition layer was deposited on S7. The thin film thicknesses of all samples were modulated to around 55 nm. In Fig. 3.8 (c), the AFM roughness bar chart shows that S6 has the best surface roughness (RMS 1.49nm). However, AuO_x is a metastable material ^[82-84] and will decompose at the temperature of 360-450 K ^[85]. The hydrophobic sample, S2 (RMS 3.62 nm), has the worst

film roughness. The film roughness of the other samples (S1, S3-S5, and S7) is between those of S2 and S6. The SEM (Quanta 600, FEG) images have confirmed that the gold thin film deposited on a hydrophobic surface (Fig. 3.8 (c2)) has a worse film roughness than the hydrophilic one (Fig. 3.8 (c1)).

Fig. 3.8 (a1) and (b1) are the AFM 3D and 2D images, and (c1) is the SEM image of the gold thin film deposited on a hydrophilic silicon wafer, which was cleaned with the piranha solution. (a2) and (b2) are the AFM 3D and 2D images.

Fig. 3.8 (c2) is the SEM image of the gold thin film deposited on a hydrophobic silicon wafer, which was cleaned with the HF solution.

Fig. 3.8 (d) The film roughness bar chart of the gold thin films. The thicknesses of all gold thin films are around 55 nm.

A better understanding is required for the gold-thin-film roughness-formation mechanism on the hydrophobic and hydrophilic silicon wafers, and the cross-section film interfaces were inspected through TEM images. In Fig. 3.9 (a1-a2), the gold film on S2, which was hydrophobic after the HF cleaning, is very rough with big grains, holes or cavities. Due to the inertness of the gold material, the sputtered gold atoms tend to be clustered to form three-dimensional clusters or islands at the nucleation stage (Volmer–Weber growth), rather than forming the continuous thin films (Frank–van der Merwe growth) ^[86, 87]. However, as shown in Fig. 3.9 (b1-b2), the gold thin film deposited on S3, which was hydrophilic after the plasma treatment, is much smoother. A thin (around 2.5 nm) silicon oxide layer was observed between the gold thin film and silicon substrate of S3, and it was verified that this silicon oxide film was created by the gas plasma pre-treatment ^[69, 78]. The plasma treatment is able to activate the surface energy of the silicon surface via breaking existing chemical bonds and creating plenty of functional oxygen groups on the silicon surface ^[88]. These oxygen function species on the silicon surfaces reacted with gold adatoms in plasma to form a continuous gold ultrathin-film at the nucleation stage, and then the smooth nucleation gold ultrathin-film grew to be a smooth bulk gold thin-film. The physical adhesion stability of the gold thin films deposited on the modified hydrophilic silicon wafers (S3, S4 and S5) has also been qualitatively examined by sonication in DI water, acetone, isopropyl alcohol (IPA), methanol, and ethyl ethanol. The gold thin films were adhered to the substrates very well without peeling off during the tests. However, the gold thin film of S2, which did not have a plasma treatment, was easily peeled off during sonication.

Fig. 3.9 (a1) the cross-section image of the gold thin film deposited on a hydrophobic silicon sample, S2. The gold film is porous and has big vacancies, and the gold atoms diffuse into the silicon substrate. (a2) the high magnification cross-section image of the gold thin film on S2.

Fig. 3.9 (b1) the cross-section image of the gold thin film deposited on a hydrophilic silicon sample, S3. (b2) the high magnification cross-section image of the gold thin film on S1. The gold film of (a1) is smooth with uniform gold grains. Between the gold thin film and silicon substrate in (a2), a thin silicon dioxide layer was observed. No gold atom diffused through the silicon dioxide layer into the silicon substrate.

3.4 Summary

We studied the surface wettability and aging behaviors of silicon wafers that went through the piranha, SC1, or HF solution cleaning, was treated by argon, nitrogen or oxygen plasma, and was aged in a vacuum or open-air environment. The water contact angles on these silicon wafers were measured up to two weeks to monitor the aging trends. The contact angle increases of the silicon wafers in a vacuum were much faster than that in the open air, because the water molecules trapped on the silicon wafer surfaces had been continuously evaporated in the vacuum. The XPS data indicates that the hydrophilic silicon surfaces have more -OH groups, while the hydrophobic silicon surfaces have more -CH_x groups. Argon, nitrogen and oxygen plasma treatments could be used to modify the silicon surfaces from hydrophobic to hydrophilic by creating a thin silicon dioxide layer, which could improve the gold thin film roughness and adhesion. In one application, we successfully coated a very thin (~ 5nm) gold film on magnetic nano-wires without clustering of gold atoms by pre-plasma treatment.

Chapter 4 Magnetic Micro-pillar array fabrication and characterization

4.1 Magnetic micro-pillar research background

Over the past decades, polymeric micro-pillar devices are of importance and have gained a great deal of intense attentions in micro and nanotechnology researches because of their potential and practical applications ^{[89] [90] [91] [92] [93] [94] [95] [96]}. For instance, it has been used in biological for cell division, cell extraction, cell growth, cell adhesion and migration ^[89], as electrodes and electrophysiology for electro-analysis ^[90], and as micro traps ^[91]. Micro-pillar arrays also have been found the utilizations in electrospray ionization device for mass spectrometric analysis ^[92], and in measurement of the mechanical interaction forces generated by living cells ^[96]. Most of these devices are comprised of arrays from micrometer to nanometer sized pillars made from various polymeric ^{[89] [90] [91] [92]} or composite materials ^[93]. They are mainly categorized into two basic groups: passive devices in which there are no actuation mechanisms and active devices which are used as actuators. For the active devices, actuation is commonly realized through magnetic force ^[93].

Many approaches have been used to produce magnetic micro-pillar devices ^[94, 95]. The conventional ways for fabricating magnetic polymer structures rely on the solvent-casting technique, in which the magnetic nanoparticles were dispersed in a fluidic medium ^{[96] [97] [98]}. However, it is a formidable challenge to make magnetic nanoparticles homogeneously

embedded and distributed inside polydimethylsiloxane (PDMS) pillars due to particle cluster or aggregation in micrometer scale, causing by surface energy and magnetic attraction force^[99]^[100]. People have attempted to modify the surface energy of nanoparticles via chemical methods making them repel each other and stably disperse in aqueous medium, such as using polyacrylamide (PAM) gel^[97] and others^[98]^[100]^[101]. Liao *et al.* prepared the Fe₃O₄ superparamagnetic nanoparticles by co-precipitating Fe²⁺ and Fe³⁺ ions in an ammonia solution and treated them with polyacrylic acid (PAA), thus Fe₃O₄ nanoparticles could be steadily dispersed in water^[98]^[100]. Hui *et al.* reported that hydrophilic Fe₃O₄ nanoparticles with citrate-capped could be dispersed in water for more than one month in air^[101]. However, the disadvantage of these processes is that they are too complicated and labor consuming. Moreover, the concentration of single isolated particles decreases with an increase in the particle volume percentage (up to 0.56% w/w, which is far below the expectation in this research work), meanwhile the aggregation increases with decreasing particle size^[100]. J. Le *et al.* proposed to mix magnetic nanoparticles with a polymer hardener, and cast them together into a mold to obtain a final device, while this approach is also limited by the aggregation of magnetic particles in high viscous polymers^[97].

Now we are going to introduce a simple but novel technique for polymeric magnetic micro-pillars fabrication. A small amount of magnetic Fe₃O₄ nanoparticles were put into acetone solution and ultra sonicated for thoroughly dispersed in ferrofluid mixture. Then, a drop of mixed ferrofluid was inhaled by a pipet and put on a silicon mold. The magnetic nanoparticles were attracted into the deep holes by a strong magnet. The next step was to pour the PDMS polymer on silicon mold, degas in a vacuum and cure until it was fully cross-linked. It was

peeled off in ethanol solution and dried in a supercritical dryer chamber. In this work, we focus on the high-aspect-ratio magnetic micro-pillar fabrication and characterization, including analyzing iron concentration in pillars and demonstrating micro-pillar movement under a gradient magnetic field.

4.2 Experimental

4.2.1 PDMS polymer preparation

PDMS is a widely used polymeric material in many applications, such as bio-Microelectromechanical Systems (MEMS) devices because of its biocompatibility ^{[[102]}. The PDMS rigidity or Young's modulus is tunable by adjusting the cross-linker agent concentration in the PDMS solution, baking temperature and baking time ^[103]. In our experiments, the PDMS prepolymer (Sylgard 184 kit, Dow corning) was prepared by mixing PDMS base with a curing agent in a 10:1 ratio by weight. The mixer was thoroughly stirred and degassed in a vacuum chamber until bubbles completely disappeared. The PDMS samples were baked at temperature 100°C for 30 minutes to make them fully cross-linked ^{[103] [104]}. In such condition, the PDMS Young modulus is around 1.5 MPa from the literature ^[103]. Ghanbari *et al.* has validated that the difference of the Young's modulus characterized from bulk PDMS and a micro-PDMS structure is within 5% ^[105]. However, the Young's modulus would be slightly altered when the pillars were filled with certain percentage of magnetic nanoparticles.

4.2.2 Micro pillar array fabrication

Soft lithography technique is broadly used to fabricate micro structures by virtue of it can be easily performed on polymeric and curved substrates^[106]. It is also relatively cheap, simple and flexible. The micro-pillars fabrication processes are shown in Fig. 4.1 (a) to (f). First, the photoresist was coated on silicon wafers (Semiconductor Wafer, Inc., Taiwan) and exposed in a Mask Aligner machine (EVG6200, Infinity double sided mask aligner) with a mask, which was pre-prepared in a Mask Laser Write machine (DWL2000, Heidelberg Instruments). Then, the silicon wafers were etched in a plasma etching chamber (Plasmalab 100 ICP380 deep Reactive Ion Etch, Oxford, UK) to certain depth based on pre-designed aspect-ratio. In order for the PDMS material could be easily peeled off from silicon molds, the silicon molds were treated by mold release agent trimethylchlorosilane (Sigma Aldrich) for three days. Superparamagnetic Fe_3O_4 nanoparticles (20-30 nm, coated with 1% PVP, NanoAmor, France) were dispersed in acetone solution and sonicated in ultrasonic bath (2510E-DTH, Branson) for five hours before use. A small drop of the mixer of Fe_3O_4 acetone solution was put on the treated silicon wafer mold by a pipet. A strong permanent magnet was at the backside of the silicon mold and rotating to attract Fe_3O_4 nanoparticles to fully fill in small features of silicon mold, including micro-holes. The remaining Fe_3O_4 nanoparticles on the top of silicon mold surface were quickly removed by taking away the magnet. 10 minutes later, acetone liquid was completely evaporated from silicon mold in air. There are always some process tricks to effectively fill the Fe_3O_4 nanoparticles into the micro-holes and make high quality PDMS pillars. First, it is important to well control an appropriate Fe_3O_4 concentration in acetone solution. Too many Fe_3O_4 nanoparticles in a small droplet of acetone may cause them too dry to be thoroughly

dispersed in solution. The big nanoparticle clusters may block the entrance of micro-holes. On the other hand, if the concentration of Fe_3O_4 nanoparticles in acetone solution is too low, some of the Fe_3O_4 nanoparticles which are already in micro-holes would be re-dispersed in acetone solution and flow out of micro-holes. Second, the area of micro-hole arrays should be smaller than the size of the rotating permanent magnet. Otherwise, nanoparticles which were inside the micro holes at the periphery area of permanent magnet might be re-pulled out. Third, the sufficient silicon mold treatment by release agent is crucially essential to easily peel the PDMS micro-pillar device from silicon mold without stretching. Any small stretching or adhesion between PDMS micro-pillars and silicon mold may cause micro-pillars be falling down or collapsing each other, even breaking inside silicon holes. The silicon mold condition might become worse and worse after being used for some times, so that the first a few batches of PDMS pillars have the best quality in consideration of the F_3O_4 nanoparticle contents in PDMS pillars and the standing proportion of pillars. The next step was to pour over the PDMS mixing with 10% curing agent on the silicon wafer mold, and then the whole silicon mold was put in a vacuum oven (DZ-1BZ, Dalian Instrument Ltd.) for degassing. The pressure in the vacuum oven was less than 1.0 Torr, under which the PDMS mixture was completely filled in micro-holes by squeezing air out. Subsequently, the silicon mold coated with PDMS material was put on a hotplate at temperature 100 °C for curing. Insufficient bake time would make the PDMS pillars too soft to be standing up. After 30 minutes, we peeled the PDMS film from silicon mold in ethanol solution, and dried in a CO_2 supercritical point dryer machine (Automegamdri-916B series C, Tousimis) to avoid the surface tension on the pillars and prevent the micro pillars from falling down or collapsing with neighboring ones.

Fig. 4.1 Schematic showing the PDMS magnetic pillar arrays fabrication process: (a) micro-holes pattern on a silicon wafer, (b) the silicon wafer was etched in a deep RIE chamber.

Fig. 4.1 Schematic showing the PDMS magnetic pillar arrays fabrication process: (c) fill Fe_3O_4 nanoparticles into micro-holes, (d) remove the redundant Fe_3O_4 and acetone solution.

Fig. 4.1 Schematic showing the PDMS magnetic pillar arrays fabrication process: (e) pour over the PDMS mixture on the silicon wafer, and (f) peel off the cross-linked PDMS from the silicon mold.

4.3 Results and discussion

4.3.1 Micro pillars morphology

In order to clearly inspect micro-pillars in a scanning electron microscopy (SEM, FEI, Quanta 3D FEG), a very thin layer of titanium was coated on the PDMS surface to avoid charging problem induced by electron beam. Fig. 4.2 shows that PDMS pillars with the diameters 2 μm , 3 μm and 10 μm and height 30 μm or 50 μm can stand up firmly. However, only a few 1 μm pillars were standing upright after drying. Presumably, 30 μm and 50 μm are too high for 1 μm diameter PDMS pillars, which have quite low Young's modulus and the actual micro holes sizes are even smaller after mold release agent treatment.

Fig. 4.2 (a) SEM Image of the micro-pillar with diameter 2 μm , height 50 μm and inter-pillar spacing 10 μm .

Fig. 4.2 (b) SEM image of the micro-pillar diameter 3 μm , height 30 μm and inter-pillar spacing 30 μm .

Fig. 4.2 (c) SEM image of the micro-pillar diameter 10 μm , height 50 μm and inter-pillar spacing 20 μm .

4.3.2 Magnetic pillar composition

For the convenience of the inspection conducted in an optical microscopy, we purposely made the pillars sleeping down to check their iron oxide concentrations. The optical picture (Figure 4.3 (a)) shows that the entire pillars had been fully filled with magnetic nanoparticles. The iron concentration and its distribution of the PDMS pillars with various sizes were analyzed by energy-dispersive X-ray spectroscopy (EDS). A series of scanning spots were selected at the top or at the bottom of the pillars with a variety of diameters from 2 μm , 3 μm , 5 μm to 10 μm and heights of 30 μm and 50 μm . At least three points were measured at different locations for each type of pillars. As compared to PDMS substrate background, which has elements of silicon, carbon and oxygen only (Fig. 4.3(b1)), the pillars have iron element up to 81.4% in weight and 57.8% in atom percentage (Fig. 4.3(b2)). No significant iron percentage difference is found

among these spots located at various dimension pillars (Fig. 4.3(c)), which indicates nanoparticles can be successfully filled in all these micro-holes of silicon mold by this technique. The statistical data shows (Fig. 4.3(d)) the median value of iron element percentage in pillars is 59.6% and the average value is 59.3% with a standard deviation of 8.4%, in a normal distribution. To best of our knowledge, this is the highest iron percentage embedding in PDMS micro pillars, reported in the literature, with feature sizes in a few micro-meters in diameter and tens micro-meters in height. Khademolhosseini *et al.* had reported that the percentage of iron in polymer pillars fabricated by their technique is in a range of 35% to 43% by weight ^[93].

Fig. 4.3 (a) The optical image showing micro-pillars filled with nanoparticles (diameter: 5 μm).

Fig. 4.3 (b1) The EDS element spectra on PDMS substrate background; (b2) the EDS element spectra on PDMS micro-pillars.

Fig. 4.3 (c) The bar chart of iron percentage on micro-pillars with various dimensions (A1: diameter 2 μm with height 30 μm , A2: diameter 2 μm with height 50 μm , B1: diameter 3 μm with height 30 μm , B2: diameter 3 μm with height 50 μm , C1: diameter 5 μm with height 30 μm , C2: diameter 5 μm with height 50 μm , D1: diameter 10 μm with height 30 μm , D2: diameter 10 μm with height 50 μm);

Fig. 4.3 (d) The diagram of iron percentage distribution in micro-pillars (Weight %) regardless of the pillar diameter and height.

4.3.3 Magnetic force calculation

In order to bend PDMS magnetic pillar tips, a neodymium iron boron permanent magnet (D2.5 x 2.5 mm) was used to create a non-uniform magnetic field. It was measured by a magnetometer (Mag-01H, Bartington Instruments, USA) that the magnetic field was around 0.06T at the distance of 20 mm and the magnetic field gradient was around 5 mT/mm. For magnetic force calculation, the magnetic field should be known first. Assuming there is a permanent magnet with the limited volume V , and the elementary atomic dipoles inside are

the source of the magnetic field, the magnetization M is the magnetic momentum of unit volume of the uniform material, and an elementary magnetic momentum is expressed as ^[104]

$$d m = M dV \quad (4-1)$$

Where dm is the elementary magnetic momentum, and dV is the elementary volume. The magnetic flux density is written as

$$B = \mu_0 \cdot (H + M) \quad (4-2)$$

Where μ_0 is the permeability of free space, and H is the magnetic field ^[107]. The magnetic force acting on a magnetic dipole moment m can be expressed as the gradient of the magnetic potential energy, assuming m is constant.

$$F_m = \nabla (m \cdot B) = (\nabla m) \cdot B + m \cdot \nabla B \approx (m \cdot \nabla) B \quad (4-3)$$

When the superparamagnetic nanoparticle is embedded in a non-magnetic medium like PDMS, which has negligible susceptibility, the magnetic dipole moment can be written as

$$m = VM = V\chi H. \quad (4-4)$$

Here V is the volume of nanoparticle, and χ is the effective magnetic susceptibility. As H and B differ only by the constant μ_0 , the magnetic force can finally be written as

$$F_m = \frac{V\chi}{\mu_0} (B \cdot \nabla) B \quad (4-5)$$

This equation shows that a magnetic field gradient is required to exert a translation force on a particle. In a homogeneous field, the particle would only be submitted to a torque, forcing it to align along the direction of the magnetic field ^[108]. It is complex to calculate the magnetic force for an object with a certain volume according to the magnetic theory. Therefore, we can examine the force in an alternative way.

Based on the mechanics of material, the relationship between pillar tip deflection under a force and its dimensions can be expressed by the following equations (4-6, 4-7) ^{[93] [97]}:

$$F_1 = K\Delta x = \frac{8EI\Delta x}{l^4} = 2\pi E \frac{r^4 \Delta x}{l^4} \quad (4-6)$$

$$F_2 = K\Delta x = \frac{3EI\Delta x}{l^3} = \frac{3}{4}\pi E \frac{r^4 \Delta x}{l^3} \quad (4-7)$$

Where K is the spring constant, Δx is the deflection, E is the PDMS Young's modulus, I is the area moment of inertia of the pillar cross-section (for circular cross-section, $I = \frac{\pi r^4}{4}$), and L and r

are the height and radius of the pillar respectively. Note F_1 is the force per length with a unit of $\mu\text{N}/\mu\text{m}$ and F_2 is the total force focusing on the pillar tip with a unit of μN . The difference between formula (4-6) and formula (4-7) is illustrated in Fig. 4.4. In this work, the magnetic force was loaded on the entire PDMS pillars, which were fully filled with nanoparticles. If all magnetic nanoparticles could be compressed at the top of the micro-pillar, the magnetic force will be focused on the micro-pillar tip only, and then the force required for a same pillar tip displacement is $F_1 / l = 2.67F_2$, assuming it contains the same volume magnetic material and under the same magnetization M .

Fig. 4.4 Schematic showing two scenarios that the unit force F_1 acts to the whole pillar uniformly (a) and the focused force F_2 puts to the pillar's tip only (b).

On the basis of the theory of materials mechanics, we calculated the required magnetic forces for micro-pillar tips deflection. Fig. 4.5(a) shows that the required magnetic force for a

micro-pillar tip deflecting its own diameter distance (e.g., a 2 μm diameter pillar has the tip displacement of 2 μm .) increases when the pillar diameter increases, given a fixed aspect-ratio of 10. It is understandable that a bigger size micro-pillar needs a larger force for the tip deflection, whereas it is worthy to note that the required magnetic force per unit volume decreases with diameter size. This is the reason why the large size magnetic micro-pillar tips are easy to be deflected in the same gradient magnetic field compared with small ones, besides it is relatively easy to fabricate the pillars with large dimensions. For example, a 2 μm diameter pillar with an aspect-ratio of 10 needs a force of 0.02 $\mu\text{N}/\mu\text{m}^3$ for 2 μm tip displacement. While, for a 10 μm diameter pillar with the same aspect-ratio, the magnetic force needed is 0.039 $\mu\text{N}/\mu\text{m}^3$ for a 10 μm tip displacement, which is 5 times less than the 2 μm pillar's.

Fig. 4.5 (a) The trench chart of the required force per length and force per volume for the micro-pillars which have the aspect-ratio 10. In order to make the micro-pillars deflected with a

distance of their own diameter, the required force increases with the micro-pillar diameter, while the required force per unit volume decreases with the micro-pillar diameter.

Fig. 4.5 (b) The trend chart of the required force per length and force per volume for the micro-pillars which have the height of 50 μm. The required force increases with the micro-pillar diameter.

Fig. 4.5 (c) The trend chart of the required force per length and force per volume for the micro-pillars which have the diameter of 2 μm . The required force decreases with the micro-pillar height. In the calculations, we assume that all micro-pillars contain the same percentage (30% v/v) of magnetic nanoparticles with homogeneous distribution.

Once the pillar height is fixed (Fig. 4.5 (b)), the required force, which is to make the pillar tip displacement of its own diameter distance, increases when the pillar size increases. It is obvious and was verified with our experiments (Fig. 4.6(c)). Once the pillar diameter is fixed (Fig. 4.5(c)), the required force decreases dramatically when the pillar height increases, in order to make the pillar tip be deflected for its own diameter distance. For instance, in Fig. 4.5(c), for a pillar with the diameter 2 μm and aspect ratio 2, the required unit force to make 2 μm pillar tip deflection is $1.9\text{E-}2 \mu\text{N}/\mu\text{m}^3$. If the aspect ratio is increased to 20, the unit force required for a same tip deflection is $2\text{E-}6 \mu\text{N}/\mu\text{m}^3$, which is around 10000 times less. It explicitly and

quantitatively elucidates why high-aspect-ratio is so critical for moving magnetic micro-pillar tip. Hence, we are motivated to fabricate the PDMS pillars aspect-ratio as high as possible in order to obtain considerable pillar tips deflection. However, due to the limited selection of materials and the techniques available, it is a great challenge to fabricate extraordinary high-aspect-ratio micro-pillar structures.

4.3.4 Magnetic micro-pillar movement

The amplitudes of the pillar tip deflection were measured when devices were under a varying magnetic field, which was created by a strong permanent magnet moving back and forth slowly at distances from 18 mm to 22 mm. It was observed that the maximum tip deflection of 1 μm pillars with a height 50 μm (aspect ratio 50, only a few can stand up after drying) is around 12 μm . For 2 μm pillars, the maximum tip deflection is around 10 μm (height 50 μm , aspect-ratio 25, Fig. 4.6(a2)) and for 5 μm pillars, the max tip deflection is around 6 μm (height 50 μm , AR 10, Fig. 4.6(b2)). Some variations and inconsistencies among pillars were also observed, probably due to the difference of the iron concentration in PDMS pillars and the attraction force between adjacent pillars. The pillar array (diameter 2 μm , space 6 μm and height 50 μm) tip movement under a varying magnetic field was recorded as a video. We further examined the micro-pillar tips vibration in deionized (DI) water, which has similar viscosity with cell culture medium. Hence, this PDMS micro-pillar surface could be used as dynamic substrates for cell cultures in biomimetic researches.

Fig. 4.6 (a1) The optical image of the micro-pillars (diameter $2\text{ }\mu\text{m}$, space $4\text{ }\mu\text{m}$, height $50\text{ }\mu\text{m}$) without magnetic force; (a2) the optical image of the micro-pillars while they are under magnetic field, all pillar tips deflected in one direction.

Fig. 4.6 (b1) The optical image of $5\text{ }\mu\text{m}$ micro-pillars (space $10\text{ }\mu\text{m}$, height $50\text{ }\mu\text{m}$), (b2) the optical image of the same micro-pillars which are under a magnetic field.

Fig. 4.6 (c) The trend chart of the micro-pillars tip displacement under the same magnetic field.

4.3.5 Surface energy and capillary force

Despite we peeled the PDMS micro-pillar arrays in ethanol solution and dried in a CO_2 supercritical point dryer machine, many 1 μm pillars and some 2 μm pillars with a height of 50 μm still fell down because of the low rigidity of PDMS, gravity force, surface energy and capillary forces. These forces exerting stresses on the soft polymeric features may cause high-aspect-ratio micro-pillars difficult to stand up straightly ^{[106] [109]}. Two major common failure phenomena were observed: one is ground collapses due to adhesive forces between pillars and

the ground surface (Fig. 4.7(a)); another one is lateral collapse due to attractions between neighboring pillars (Fig. 4.7(b)).

Fig. 4.7 SEM images of micro-pillars fall down on ground (a) and collapsing each other (b).

Although the silicon wafer molds were thoroughly pre-treated by the release agent trimethylchlorosilane, the adhesive force between the PDMS material and silicon holes sidewalls and bottoms may always exist, which may cause micro-pillars to be stretched when PDMS pillars peel off from the silicon mold. A small stretch force may cause pillars touching on ground or neighboring pillars. Then, pillars cannot stand upright independently. When we peel off the PDMS from the silicon wafer mold in ethanol solution, the situation becomes much better. However, when pillars dry from a liquid, the capillary force may cause pillars to fall down or cluster together^{[106] [109]}, especially when polymer microstructures have a high-aspect-

ratio up to 15 and the feature sizes in the range of tens to hundreds of micrometers^{[110] [111] [112]}.

Hui *et al.* believe that soft high-aspect-ratio microstructures can buckle under their own weight^[113]. Roca-Cusachs *et al.* have derived the equation of the critical aspect-ratio for neighboring collapse as follows^[114]:

$$\left(\frac{h}{d}\right)_c = \frac{\pi^{5/3}}{2^{11/3} 3^{1/2}} (1 - \nu^2)^{-\frac{1}{6}} \left(\frac{E}{2\gamma_{sv}}\right)^{2/3} d^{2/3} \quad (4-8)$$

where h is the height of the micro-pillar, d is the diameter of the micro-pillar, E is the elastic modulus of material, ν is the Poisson's ratio (here is 0.5 for PDMS), and γ_{sv} is the surface energy of the micro-pillar material (here is 29.8 mJ/m²). With regards to lateral collapse for pillars with circular cross-section, Glassmaker *et al.* gave the following expression^[115]:

$$\left(\frac{h}{d}\right)_c = \left(\frac{3^{3/4} \pi E w^{3/2}}{2^{1/4} 3^2 \gamma_{sv} (1 - \nu^2)^{1/4} d^{1/2}} \right)^{1/3} \quad (4-9)$$

Where w is the lateral separation / spacing between adjacent micro pillars. Based on Eq. (4-8) and Eq. (4-9), the critical aspect-ratio was calculated for 5 μm diameter PDMS micro-pillars to collapse and listed in Fig. 4.8. When the inter-pillar spacing is less than 30 μm , the lateral collapse is dominant. The ground collapse becomes a dominate failure mode when the inter-

pillar spacing is larger than 30 μm . The real situation may not be exactly overlaid these theoretical calculation results, because other factors may be involved in as well, like material properties, surface roughness, elastic, and rheological behavior. In general, the experiments in this work validated the theory that when the inter-pillar spacing became larger, the neighboring collapse was getting less. Eventually all pillars can be firmly standing upright when space was more than 30 μm .

Fig. 4.8 (a) The trend chart of the critical aspect-ratio for ground collapse and neighboring collapse. The lateral collapse is dominant when the inter-pillar space is less than 30 μm .

Fig. 4.8 (b1) The SEM image of the pillar array with space 10 μm ; (b2) The SEM image of the pillar array with space 15 μm ; (b3) The SEM image of the pillar array with space 20 μm ; (b4) The

SEM image with space 30 μm . It is clearly shown that the lateral collapse becomes less and less when the inter-pillar space increases (diameter 5 μm , height 50 μm).

The magnetic pillars were originally fabricated to guide the liquid spreading. However, when a drop is placed on the micro-pillar array surfaces, the partial wetting micro-pillars are deflected in different directions. Basically, the magnetic forces generated by Fe_3O_4 nanoparticles inside the micro-pillars are not able to overcome the capillary force, which is 0.072 N/m for pure water. It is verified by the mechanical force calculated based on the magnetic pillars deflection angles measured that the magnetic forces calculated is around $5.9\text{E-}5$ for 1 μm pillar in diameter and $5.9\text{E-}4$ N/m for 10 μm in diameter. Therefore, the conclusion is that magnetic force is too smaller to overcome the surface tension and guide the liquid spreading. A new technique is required to bend the micro-pillars firmly and fabricate the uniform slanted micro-pillar array surfaces for asymmetric wetting and spreading experiments, and it will be discussed in Chapter 5.

4.4 Summary

We invented a novel technique to fabricate a series of PDMS micro-pillars with diameters of 1 μm to 10 μm and heights of 30 μm and 50 μm . They are upright firmly after drying, and their tips are able to vibrate with considerable amplitudes under the gradient magnetic field. The maximum micro-pillar tip deflections are around 12 μm for 1 μm pillars, 10 μm for 2 μm pillars, and 5 μm for 10 μm pillars with a height of 50 μm . The micro-pillar tip vibrations were also examined under DI water, which enables its applications as actuators in micro-fluidics, and

particularly as dynamic substrate for cell culture in biomimetic researches. The EDS data revealed that the weight percentage of iron embedded in PDMS pillars is as high as 81.4% with median value 59.6%, which is the highest value reported in the literature. With this method, we are able to fabricate the magnetic micro-pillar array surfaces. By applying gradient magnetic fields carefully, the micro-pillars can be bended instantly to guide the liquid flow. This function will be utilized in many applications, and more discussion will be extended in Chapter 5.

Chapter 5 Asymmetric liquid wetting and spreading

5.1 Wetting and spreading

Wetting and spreading are ubiquitous phenomena in nature, industry and daily life. Very interesting wetting phenomena have been observed on natural biological surfaces. For example, the surface of the lotus leaf exhibits super-hydrophobicity with water contact angle of more than 150° for self-cleaning^[39]; whereas the super-hydrophilic surfaces of water plants (like peat moss) are able to absorb water to maintain a wet surface^[116, 117]. Similarly, water droplets roll off rice leaves due to their anisotropic micro-structured leave surface^[27]. Therefore, understanding of the wetting and spreading behavior on different surfaces is not only very important on a fundamental level, but also critical to developing new devices and technologies in which wetting, spreading, interface evolution, and adhesion can be controlled^[118].

It is commonly found that a droplet will spread symmetrically when it is deposited on a flat surface and its final shape is determined by the total surface energy. However, when anisotropic micro/nano structures, such as micro-grooves or channel features, are fabricated on a surface, an asymmetric spreading of the droplet can be caused by the creation of localized energy barriers. However, the mechanism of the asymmetric wetting and spreading behavior of liquids on rough surfaces are still not well understood, especially for the micro-level liquid propagation occurring in the vicinity of the moving three-phase contact line, although it has recently been studied extensively^[1, 118-125].

The recent demonstration of unidirectional liquid spreading on asymmetric nanostructured surfaces ^[1] has generated much interest. Wang *et al.* ^[1] have also successfully modeled their observed phenomenon. However, the dynamic process of the spreading was not studied in detail. Inspired by this seminal work, we aim to gain a deeper understanding of the unidirectional liquid spreading, particularly the dynamics of spreading at the micro-level. By utilizing a high-speed video imaging with a pixel resolution of 0.5 μm and a recording rate of 20,000 frames per second, we have observed for the first time the micro-level thin liquid film advancing ahead of the bulk droplet with high spatial resolution. Based on the time-resolved flow dynamics, we provide a more detailed explanation of the liquid flow mechanism around pillars at the micro-level. The mechanism of the asymmetric and unidirectional liquid spreading on the surfaces with slanted micro-pillar arrays has been discussed, and different spreading regimes, such as all-directional asymmetric spreading, unidirectional spreading and no spreading, have been successfully predicted. We believe that this study together with the study of Wang's group can lay a foundation to detailed understanding of this intriguing phenomenon.

In addition to the above dynamics, we have developed a much simpler and cheaper fabrication method for the asymmetric nanostructured devices. In the work of Wang's group, the asymmetric nanostructured surface was fabricated using the conventional and expensive silicon etching technique. In my project, the slanted micro-pillar array surfaces are fabricated by oblique metal film deposition on the straight PDMS pillars that have been produced by soft lithography. The PDMS material is more versatile and easily processed with low cost for mass production over larger areas, in comparison to the fragile silicon pillar process. Particularly, the soft lithography replication technique is much easier and simpler process.

5.2 Experimental

We fabricated the micro-pillar arrays by using a soft lithography replication technique. First, micro-hole arrays were made on a silicon wafer (<100>, Semiconductor wafer Inc.,) by the conventional photolithography on a mask aligner machine (EVG6200, Infinity). Then, the silicon wafer was etched in a plasma etching chamber (Plasma-lab 100 ICP380, deep reactive ion etch, Oxford) to create silicon micro-hole array. Subsequently, the silicon mold was treated with release agent trimethylchlorosilane (Sigma Aldrich) for three days in order to easily peel off the PDMS pillars from the silicon mold. The PDMS polymer (mixture of PDMS base (Sylgard 184 kit, Dow Corning) with the cyclic hydride curing agent (MDX4-4210, Dow Corning) in a 10:1 ratio by weight) was poured over the silicon mold, and degased in a vacuum oven (DZ-1BZ, China). After degassing, the samples were cured at 100 °C for 30 minutes to make the PDMS fully cross-linked. Finally, the PDMS micro-pillars were peeled off from the silicon mold in ethanol and dried them in a CO₂ supercritical point drying chamber (Automegamdri-916B series C, Tousimis). This technique proved to be very effective to fabricate high-aspect-ratio micro-pillars which stick straight up and do not fall down or collapse. We have successfully fabricated straight pillars with a diameter of 3 μm, lengths of 30 μm and 40 μm and with micro-pillar lattice spacings of 20 μm, 30 μm or 40 μm.

Fig. 5.1 Diagrams of the straight micro-pillar array fabrication: (a) Lithography patterning; (b) Deep reactive ion etching to fabricate silicon wafer mold; (c) Pour PDMS polymer over the silicon mold and degassing; (d) Peel off PDMS micro-pillars from silicon mold and drying.

In order to deflect the pillars, the magnetic nanoparticles were embedded in the PDMS pillars with the method discussed in Chapter 4. Whereas, it is found the magnetic force driven by the nanoparticles were not strong enough to bend the micro-pillars to a certain degree required, and the deflection angles for the micro-pillars are also not uniform. It is understandable that the magnetic force imposed by the external magnetic field is not uniform cross the entire the surface. Furthermore, the interactions between magnetic pillars are not inevitable, which always make the pillars collapse and cluster together when a strong magnetic force is used.

Therefore, an alternative approach with a better manipulation was used to serve this purpose. A thick silver layer (~ 500 nm) was deposited obliquely on one side of the micro-pillars

with a deposition rate of 5 to 10 Å per second, using an electron-beam evaporator (Vacuum Explorer 14, Denton). By tuning the deposition incidence angle (from 50° to nearly 90°) and the metal film deposition rate, the bending angles α of the micro-pillars can be varied ranging from 10° to near 55°, as defined in Fig. 5.5 (a). The deflection of micro-pillars was a result of the combination of the tensile stresses ^[126], which accumulating during the silver film growth on one side of PDMS pillars, and residual stresses induced by the thermal expansion mismatch between the PDMS material ^[127] and the silver material. Actually, we also tried an alternative method to make the micro-pillar deflected. First, we fabricated the magnetic PDMS micro-pillar array surfaces via the method discussing in chapter 4. Then, we put a strong NIB magnet near the magnetic micro-pillar surfaces to make the pillar deflected. Later, we put the samples into a sputtered chamber to coat a thick 300nm silver layer to solidify the whole samples, including the deflected micro-pillars. However, we found the micro-pillar deflections were not well controlled and also not uniform. That was why we go back to seek for a better process approach.

After the micro-pillars have been deflected, a thin layer (300 nm) of silver film was deposited on the other side of the pillars with a low deposition rate (1 Å per second) in the vertical direction within the same evaporator. An additional 200 nm thin gold film was homogeneously deposited on the entire PDMS device in a sputtering system (RD4, Equipment Support Company, UK) by rotating the tilted substrate. After addition of the metal film coating, the micro-pillar diameter becomes around 5 µm.

Fig. 5.2 Schematic shows the slanted micro-pillars fabrication. (a) A thick silver metal film was deposited on one side of micro-pillars in an electron beam evaporator to make micro-pillars deflected; (b) followed by 300nm Ag film deposition on the other side of pillars in the electron beam evaporator, and (c) 200nm gold thin film was coated on the entire of the pillars on the rotating and tilted substrate in a sputtering chamber.

The drop spreading behavior depends critically on the intrinsic contact angles on the solid material. Different liquids were used to tailor this intrinsic contact angle on a flat gold coated PDMS surface, which has gone through the same process as the micro-pillar surfaces. The contact angles were measured with a contact angle analyzer (DSA 100, KRUS) with sessile droplet method. The static contact angles are 63° , 39° , 28° and 15° for ethanol in DI water, at 0%, 33% (v/v), 50% (v/v), and 75% (v/v), respectively. Moreover, an oxygen plasma treatment machine (PDC-002, Harrick Plasma, US) was used to produce a super-hydrophilic gold coated PDMS surface with a contact angle less than 5° . Contact angle hysteresis (CAH) is an important parameter which might affect the motion of the contact line. We have tried to measure the CAH, but the number is so small on the flat gold coated surface and the measurement error is

comparable with the CAH. We discuss possible effects of CAH when describing the directional spreading mechanism.

A Photron SA-3 color video camera was used to record the overall liquid droplet spreading with a frame rate of 50 fps. The micro-scale rapid thin liquid film requires high-speed video at a frame rate up to 300,000 fps, acquired with a Phantom V1610 CMOS video camera. Backlighting was accomplished with a 350 W metal-halide lamp (Sumita Optical Glass, Inc.), which was shone onto a diffuser.

5.3 Results and discussion

When a droplet is deposited on a surface, the adhesive forces between the liquid and the solid surface tend to spread the droplet as large as possible ^[128], whereas the cohesive forces within the droplet try to minimize the water-solid interface area and keep the liquid droplet spherical ^[129]. Therefore, the wettability is determined by a balance force between adhesive and cohesive forces to maintain the minimum surface energy. At the equilibrium state, the contact angle θ is the measure of wettability on a flat surface. It is defined as the angle between a tangent to the droplet and the substrate (Fig. 5.3(a)), and expressed by Young's equation ^[130].

Fig. 5.3 (a) Schematic presentation of Young's equation as the force balance at the three phase contact line when a droplet is placed on a flat solid surface; (b) Wenzel model for a liquid wets on a homogenous material; and (c) Cassie-Baxter model for a liquid rests on composite material.

As expressed in Eq. (2-1), it implied that the reversible interchange at the three phase contact line was taken into account from the energy point of view. Obviously, θ_{eq} is measurable macroscopically. In partial wetting, $\gamma_{SG} < \gamma_{SL} + \gamma_{LG}$, a droplet has a finite contact angle. While in the case of completing wetting, $\gamma_{SG} = \gamma_{SL} + \gamma_{LG}$ and the contact angle will be zero. In such scenario, the whole solid surface will be covered by a macro scale uniform liquid film and the system is at the equilibrium state. The different wetting states is usually distinguished by the equilibrium spreading coefficient $S_{eq} \leq 0$. If the system is complete drying in a solid-liquid-gas system, it indicates there is a macroscopic intrusion vapor layer between the solid and the liquid, and it is impossible in reality. In the real world, drying is rather rare because van der Waal forces tend to form thin vapor layers on surfaces. Partial wetting corresponds to the formation of drops, which are surrounded by a microscopically thin film adsorbed and formed on the surfaces, while the complete wetting is to form a uniform macroscopic thick liquid layer. Some molecules are always adsorbed onto the substrate when it is at the thermodynamic

equilibrium status, because it is favor of increasing the total entropy in the system. This liquid thin film is nanoscopic, and the average thickness varies from less than one molecule to a few molecules. It depends on the liquid chemistries to the solid surface and the distance from the bulk liquid critical point.

The Young equation describes the mechanical equilibrium only, and the actual surface wettability depends on both the material chemistry and the surface topography ^[37, 39, 128, 131-133]. There are two classical models that account for the wetting on rough surfaces: the Wenzel model (Fig. 5.3(b)) addresses the homogeneous surface wettability from thermodynamic point of view, and the Cassie-Baxter model (Fig. 5.3(c)) which describes the scenario of a liquid sitting on a heterogeneous composite surface, such as when air is trapped under the liquid in the roughness grooves or pits. Micro-texturing is one of the ways which are able to change surface properties. Based on the researches and studies undertaken so far, two main ways have been proven as efficient approaches to alter the wettability of surfaces: patterned surfaces and structured surface. On patterned surfaces, the surface is flat, but the wetting properties vary spatially in a controlled way. On structured surface, the chemical properties are identical everywhere, but the geometry of the surface is manipulated in certain way. By minimizing of the total surface free energy, an equilibrium contact angle can be reached on the rough or patterned surfaces.

If a low roughness is exhibited on a surface, the liquid flows along with the surface, and it is impacted by the roughness. In such case, $r\gamma_{SL}$ and $r\gamma_{SG}$ are the solid surface/liquid and solid/gas energies, respectively. Here, r is the roughness being defined as the relationship between real surface and apparent surface. If $r > 1$, it is a rough surface, and it is a perfectly

smooth surface for $r = 1$ ^[134]. A variation of energy can be expressed with a dx displacement of the three-phase contact line with the following equation, Eq. (5-1),

$$dE = r(\gamma_{SL} - \gamma_{SG})dx + \gamma_{LG}dx \cos \theta^* \quad (5-1)$$

When $dE = 0$, it is at the equilibrium state. For $r = 1$, which means it a perfect smooth surface, Young equation is applied. However, the Wenzel ^[135] obtained the expression for a rough surface:

$$\cos \theta^* = r \cos \theta \quad (5-2)$$

Thus, what kind of the condition we can use this equation? We need to know this configuration of Wenzel model. In this equation, the Young angle θ cannot be changed as it is the equilibrium contact angle on a planar surface, and it is around 120° for water. Furthermore, it also gives us an implication that there is a possibility to reach an apparent contact angle of 180° from the theoretical point of view, as far as $r \cos \theta$ is equal to -1. Nevertheless, it is impossible to have the 180° apparent angle θ^* in real, as it must preserve a contact surface area with the substrate to sustain the drop. Thus, the roughness is the only parameter that can be manipulated with care. If a surface has a strong roughness, the system will go into another

configuration, Cassie-Baxter model ^[136]. The energy is smaller, while a liquid droplet remains on a rough surface, than the one that penetrates into asperities. Thus, the Wenzel is applicable to the low roughness surfaces only, and the apparent angles are lower than 180°.

Actually, super-hydrophobic surface properties with wetting behaviors were not in the research scope of Cassie and Baxter, but they did examine the heterogeneous surfaces in chemistry. The surface with two distinct materials was investigated by them. The two materials were present in a pattern way and occupies a certain fraction of the total surface. In the case material #1 is hydrophobic and material #2 is air, a drop in contact with each of the two phases of material #1 and air forms the contact angles of θ_E and 180°, respectively, and the fractions of the hydrophobic surface and hydrophilic surface of the total surface area are ϕ_s and $(1 - \phi_s)$. If a dx displacement of the three-phase contact line is considered, the energy change dE could be written as

$$dE = \phi_s (\gamma_{SL} - \gamma_{SG})dx + (1 - \phi_s)\gamma_{LG}dx + \gamma_{LG}dx \cos \theta^* \quad (5-3)$$

After the Young's equation is applied, the Cassie-Baxter relation is obtained by minimizing E :

$$\cos \theta^* = -1 + \phi_s (\cos \theta_E + 1) \quad (5-4)$$

Wenzel model is applicable to a low roughness surface, while Cassie-Baxter model is for a strong roughness one. It can be calculated that for the air pocket appears and sustains, the roughness must be larger than 1.75^[11], for a sinusoidal surface and a Young angle of 120°. Furthermore, it had been demonstrated by Bico *et al.* that the Cassie-Baxter mode is thermodynamically more stable than Wenzel model for a given value threshold θ_c ^[134]. For a drop is placed in the Cassie-Baxter state, the energy is minimized and it is lower than that in Wenzel mode. The energy variation calculated with Eq. (5-4) is thus weaker than that calculated with Eq. (5-2). As described in Fig. 5.4, there is a coexistence of the two modes.

Fig. 5.4 A schematic chart showing the coexistence of two hydrophobic modes^[137].

However, after a drop is placed on a feeble roughness surface, a Cassie-Baxter regime may occur for a short time, though θ is less than θ_c . This is a metastable state. By applying a pressure to the drop, it is most likely the drop will transfer from the Cassie-Baxter regime to the Wenzel regime ^[138]. Many plants super-hydrophobic properties were investigated by Neinhuis and Barthlott, including the Lotus Effect ^[26]. In most cases, there are two different roughness scales on the surfaces: one is micro-metric and another one is nano-metric. The drops in the Wenzel state could be avoided by this unique double roughness ^[139]. Air are trapped in the small asperities, which results in the drop will be in an intermediate state between Cassie-Baxter and Wenzel model ^[134]. Imbibition angle is expressed in Eq. (5-5) and it is useful when the Cassie-Baxter model is applied in experiments.

$$\cos \theta_c = \frac{\phi_s - 1}{r - \phi_s} \quad (5-5)$$

When a liquid spreads on a hydrophilic surface, there is generally a thin precursor liquid film ahead of macroscopic liquid motion ^[12, 140-143]. The behavior of the thin precursor liquid film is governed by long-range intermolecular forces between the molecules of the liquid and the molecules of the substrate ^[141]. Such an interaction occurs at the front of the precursor film

rather than at the macroscopic contact line that is behind of the precursor film ^[12]. In this work, we focus on the motion of the micro-scale thin liquid film ahead of the bulk droplet, which spreads on slanted micro-pillar surfaces.

Fig. 5.5 SEM images of micro-pillar arrays with various micro-pillar bending angles. (a) Straight micro-pillars and the definition of micro-pillar deflection angle α . (b) Micro-pillars were bended

with 24° with micro-pillar length $30\text{ }\mu\text{m}$ and inter-pillar spacing $20\text{ }\mu\text{m}$. (c) Micro-pillars were bended with 39° with micro-pillar length $40\text{ }\mu\text{m}$ and inter-pillar spacing $30\text{ }\mu\text{m}$. (d) Micro-pillars were bended with 52° with micro-pillar length $40\text{ }\mu\text{m}$ and inter-pillar spacing $30\text{ }\mu\text{m}$.

The images in Figure 5.5(a) – (d) are the micro-pillar array surfaces with different pillar deflection angles by obliquely depositing silver thin film on one side of the micro-pillars with electron-beam evaporation process. From the images, we can see clearly that the micro-pillars are suitable for liquid wetting and spreading experiment. Compared the work done by Kwak's work shown on page 27 in Chapter 2, Literature review, the pillars deflections are more uniform, and beautiful.

On the microscopic scale, the behavior of droplets and streams of liquid in contact with solid walls is dominated by capillary pressure ^[143]. We find that when a droplet was deposited on a smooth surface or straight micro-pillars surface (Fig. 5.5(a)), the droplet shape is symmetric, and the liquid spreads out uniformly and symmetrically, because the energy barriers are the same in all directions. However, when a droplet was deposited on the surface of deflected micro-pillar array surfaces (Fig. 5.5(b) to (d)), the liquid would under some conditions spread only in the direction of the micro-pillar deflection, i.e. we observe unidirectional liquid spreading as previously reported by Wang's group ^[1].

In Fig. 5.6(a) we show a time-sequence of images of a drop undergoing unidirectional spreading on a slanted micro-pillar array surface (see Video 1 in the supplementary material). The spreading is in the direction which the pillars are slanted. Keep in mind that gravity plays only a minor role in the dynamics, as the height of the droplet hemisphere is always smaller

than the capillary-length $a = \sqrt{\sigma/\rho g}$. The capillary length takes the smallest value of $a = 1.75$ mm for the 75% ethanol/water (v/v) droplets. Fig. 5.6(b) shows that the earliest spreading is fastest, being in the capillary-inertial regime ^[144-148], where the wetted radius grows as $t^{1/2}$, while the spreading velocity slows as $t^{-1/2}$. Following this initial phase, Fig. 5.6(c) shows the spreading approach the typical Tanner's law with $r \sim t^{1/10}$ and $V \sim t^{-0.9}$ ^[24].

Fig. 5.6 (a) The side view of the time-lapse color optical images of the unidirectional spreading of a drop (75% ethanol in DI water (v/v)) spreading on a gold coated slanted PDMS micro-pillar surface. It was recorded by a Photron SA-3 CMOS video camera with 1X lens, which gave the corresponding pixel resolution of $17.5 \mu\text{m}$. The snapshots shown are 60 ms, 240 ms, 1 s, 17 s and 100 s relative to the time at which the droplet touches the substrate.

Fig. 5.6 (b1) and (b2) compare the early stage spreading of a drop (75% ethanol in DI water (v/v)) on a pillared surface to that on a flat surface of the same material. (c1) and (c2) show the spreading approach the typical Tanner's law with $r \sim t^{1/10}$ and $V \sim t^{-0.9}$.

Fig. 5.6 (d1) and (d2) high-magnification camera images of the micro-scale thin liquid film propagation on a slanted micro-pillar array surface. They were captured by a Phantom V1610 high-speed video camera with a 50X magnification, at 20,000 fps. The purple dashed line is the profile of the liquid flow. (e) Location of the front of the micro-scale thin liquid film.

It should be noted that our overall spreading velocity is about 5 times faster than those observed in Wang *et al.* ^[1], which is most likely due to the difference in the micro-pillar topography (larger pillars and lower coverage in our study) and in equilibrium contact angles. Keep in mind that overall the presence of the pillars slows down slightly the early spreading speed, compared to spreading on a flat smooth surface of the same material. This is demonstrated in Fig. 5.6(b) where we compare the early stage spreading on a pillared surface

to that on a flat surface of the same material. The later stage spreading differs as the pillars can sustain the unidirectional spreading further than the equilibrium contact angle on a flat surface.

By combining high-speed video imaging and a long-distance microscope we have successfully imaged the contact line motion between the individual pillars. This reveals the spontaneous formation of a thin liquid film in the vicinity of the bulk droplet front edge. This faster expanding thin film guides the bulk liquid spreading. The slanted micro-pillars were nearly immersed by the moving micro-scale liquid film (Fig. 5.6(d1) and 5.6(d2)).

Fig. 5.6(e) shows the motion of the thin liquid film in Video 2. Once the three-phase contact line reaches the bottom of a pillar, the liquid climbed along the micro-pillar and moves forward very fast. Then, the liquid front moves slowly until it reaches the next pillar. The forward spreading behavior of the thin liquid film followed a “stick-jumping” process.

Fig. 5.7 (a) A schematic showing the definition of θ_{front} and θ_{rear} . (b1) Video frames showing the fast motion of the meniscus as it touches the next pillar. The scale bar is 20 μm long and the frames are spaced by 50 μs . (b2) Liquid touches with the bottom of the next pillar and (b3) liquid climbs along the pillar as well as spreads along the substrate. Here $L \cos \alpha$ is the pillar height, $L \sin \alpha$ is the pillar shadow length.

To understand the unique spreading behavior described above, a simplified model was proposed. We defined the front angle θ_{front} and rear angle θ_{rear} shown here. The values of θ_{front} and θ_{rear} can be obtained from Eq. (5-6) and Eq. (5-7)

$$\theta_{front} = \tan^{-1}\left(\frac{L \cos \alpha}{S - L \sin \alpha}\right) \quad (5-6)$$

$$\theta_{rear} = \tan^{-1}\left(\frac{L \cos \alpha}{S + L \sin \alpha}\right) \quad (5-7)$$

where L is the pillar length, and S is the spacing between pillars. It was observed that once the three-phase contact line touched the bottom of a pillar (shown in Fig. 5.7(b1) and illustrated in Fig. 5.7(b2)), the liquid climbed along a pillar very fast like a “jump”, as a result of the capillary force which wants to minimize the surface energy ^[149, 150]. Here the liquid spreading velocity obtained from Fig. 5.7(b1), along both the pillar up-side surface and substrate directions, is in the order of 100 mm/s, which is over 10 times higher than the average spreading speed shown in Fig. 5.6(e). The liquid front spreading speed reduces rapidly to the average level after a short time following the pillar contact. As shown in Fig. 5.7(b1), three contact angles can be defined as the liquid tries to reach its equilibrium state on the surfaces of pillar and substrate. θ_1 is the contact angle of the liquid on the pillar up-side surface; θ_2 is the liquid contact angle on the pillar down-side surface and θ_3 is the contact angle of the liquid on the bottom flat substrate. To measure these three angles is difficult in the fast-moving flow, but we still can comprehend the dynamic process in the following qualitative way: from Fig. 5.7(b2), at the moment when the liquid touches the next pillar, we will have $\theta_1 > \theta_{eq}$, which will lead to a rapid climbing of liquid along the pillar up-side surface, as has been calculated in above (~ 100 mm/s). This large

advancing contact line speed could be able to produce a large advancing contact angle θ_1 , according to the Cox-Voinov-type theory, in which $\theta_1^3 = \theta_{eq}^3 + 9Ca \ln(R\theta_{eq}/(6e\lambda))$, where Ca is the capillary number, R is the contact-line radius and λ is the dimensional slip length. This will be significant only for the rapid wetting when the contact line reaches the bottom of a pillar during the “jump”. Even if the CAH makes the angle too large to reach the next pillar, the contact line will automatically slow down its motion thereby reducing the contact angle and minimizing this effect, allowing forward spreading. Furthermore, as was mentioned in the “Experimental” section the contact angle hysteresis on the flat gold coated surface is very small here, thus we do not expect a large difference between θ_1 and θ_{eq} will be sustained for a long time. The same situation is applicable to θ_2 and θ_3 . When the liquid wets the down-side surface of the pillar and touches the bottom substrate, contact angles θ_2 and θ_3 also need to reach the equilibrium contact angle θ_{eq} . Despite the large spreading speed occurring during the “jump”, the spreading speed along the substrate drops rapidly to the average value after a short time of around 100 μs , as shown in Fig. 5.6(e). Spreading continues until the liquid is unable to reach the next pillar, with θ_1 , θ_2 and θ_3 reaching θ_{eq} by curving the liquid profile, as illustrated in Fig. 5.7(b3). In this process, liquid is continuously driven to fill in the volume under the pillars and move forward along the pillar deflection direction.

Fig. 5.7 (c) A schematic showing that the requirement for the liquid to move forward and get touch with the next pillar is $\theta_{eq} < \theta_{front}$. (d) A schematic showing spreading stops when the liquid level is not high enough to make the liquid get touch with the next pillar, even $\theta_{eq} < \theta_{front}$ is satisfied here. (e) A schematic showing spreading stops when $\theta_{eq} > \theta_{front}$.

The requirement for the thin liquid film to move forward is that θ_{eq} must be smaller than θ_{front} (Fig. 5.7(c)), so that the liquid front is able to reach the next pillar before it stops at θ_{eq} . This leads to a continuous liquid spreading in the direction of the micro-pillar deflection. When the liquid level is not high enough to make the thin liquid film reach the next pillar, as shown in

Fig. 5.7(d), the liquid will propagate no further, even though θ_{eq} is still smaller than θ_{front} . Pinning can also happen when θ_{eq} is larger than θ_{front} (Fig. 5.7(e)).

In the opposite direction of the pillar deflection, a pinning phenomenon is shown in Fig. 5.8(a). The requirement for a liquid spreading in this direction is that θ_{eq} must be smaller than θ_{rear} , which is quite small in most cases. Thus, it is unlikely for a liquid moving back in an opposite pillar deflection direction.

Fig. 5.8 (a) The high magnification optical image of the liquid pinning at reversed direction of pillar deflection. The purple dash line is the profile of the liquid. (b1) Schematic showing the situation in which the liquid is able to propagate in the reversed direction when θ_{eq} is smaller than θ_{rear} and (b2) showing that the liquid stops spreading when θ_{eq} is larger than θ_{rear} .

If the liquid is able to reach the next pillar, it will creep up the pillar from the base (Fig. 5.8(b1)). The liquid accumulating at the bottom of the pillar will reach the equilibrium state on

the substrate (Fig. 5.8(b2), θ_1) and pillar surfaces (Fig. 5.8(b2), θ_2). Meanwhile, the liquid at θ_2 is slightly lifted up by the liquid on the other side of the pillar. During this process, there is no driving force to push liquid moving in the reversed direction of the pillar deflection. Consequently, the liquid is pulled back by the slanted pillars, and pinning occurs.

To validate the model of the asymmetric spreading proposed above, we investigated the behaviors of the liquid on the surfaces with different pillar deflection angles, inter-pillar spacing and micro-pillar lengths experimentally. The front angle and rear angle were also calculated using Eq. (5-6) and (5-7) and these parameters (deflection angles, spacing etc). Shown in Fig. 5.9(a) are the experimental data and the calculated front, rear and imbibition angles that define clearly three different zones, no-spreading (zone I), unidirectional spreading (zone II) and asymmetric all directional spreading (zone III). Here, the imbibition angle is given by

$$\cos \theta_{im} = \frac{1 - \phi_s}{r - \phi_s} \quad (5-8)$$

where r is the solid roughness factor, and ϕ_s is the solid surface fraction remaining dry^{[16] [33]}. As is well known, the prerequisite for the liquid propagating on the micro-pillars surface is that the liquid should be imbibed first to reach the flat substrate.

Three zones are clearly defined based on the curves of critical imbibition angle (θ_{im}), critical front angle (θ_{front}) and critical rear angle (θ_{rear}) in the figure, which can be understood: 1) when the intrinsic contact angle θ_{eq} is larger than θ_{im} or θ_{front} (zone I), the liquid will not propagate; 2) when θ_{eq} is larger than θ_{rear} but smaller than θ_{im} and θ_{front} (zone II), unidirectional spreading occurs; 3) in the scenario that θ_{eq} is smaller than all three critical

angles (zone III), the liquid will spread in all directions, *i.e.*, asymmetric all directional spreading. The lateral angles are described in Fig. 5.7(d) with a simplified diagram. However, when θ_{eq} is in zone III, the liquid moving in the direction of the pillar deflection is more favorable, and the spreading in this direction is much faster than other directions. Therefore, the spreading in zone III is also asymmetric. It was found that the experimental results matched well with this simple model. Fig. 5.9(b) shows the results of three zones by varying the inter-pillar spacing S , for a bending angle $\alpha = 30^\circ$ and $L = 30 \mu\text{m}$. The smaller S is, the bigger the difference between θ_{front} and θ_{rear} is.

Fig. 5.9 (a) Trend chart of θ_{front} , θ_{rear} and θ_{im} and the different zones for all-directional, unidirectional propagating and non-propagating. The calculation is based on a simplified model of pillar length $30 \mu\text{m}$, inter-pillar spacing $30 \mu\text{m}$, and pillar deflection angles from 5° to 85° .

The liquid intrinsic contact angles were altered by the liquids with the different ethanol percentage (v/v) in water. It was well validated by experiments.

Fig. 5.9 (b) Trend chart of θ_{front} , θ_{rear} and θ_{im} when inter-pillar spacing is changed from 10 μm to 70 μm .

Fig. 5.9 (c) Trend chart of θ_{front} , θ_{rear} and θ_{im} when pillar length is altered from 5 μm to 60 μm .

However, when S is too small, the pillars are overlaid. In this situation, the liquid sits on the surface like a sphere, as described by the Cassie-Baxter state ^[127], where the Laplace pressure inside the cavities is negative and air is trapped under the droplet ^[143]. In Fig. 5.9(c), the results were obtained by varying L , while keep pillar deflection angle $\alpha = 30^\circ$ and $S = 30 \mu\text{m}$.

Fig. 5.9 (d) The simplified diagram describing the lateral angles which can be defined by the following expressions, $\theta_{l1} = \tan^{-1}\left(\frac{L \cos \alpha}{\sqrt{S^2 + (S-L \sin \alpha)^2}}\right)$, $\theta_{l2} = \tan^{-1}\left(\frac{L \cos \alpha}{\sqrt{S^2 + (L \sin \alpha)^2}}\right)$ and $\theta_{l3} = \tan^{-1}\left(\frac{L \cos \alpha}{\sqrt{S^2 + (S+L \sin \alpha)^2}}\right)$. The lateral angles are generally larger than θ_{front} , but less than θ_{rear} .

Some fluctuations are observed at the boundaries between zones, which could be due to the non-uniform metal film coating and defects, such as particles, missing and broken pillars, and surface cracks. At micro-level the gravity effect is negligible. Therefore, this unique effect of wetting and spreading can be explored for a vertical self-driving pump in micro-fluidics. The preliminary results show that the 75% ethanol solution can be transported from the bottom reservoir to the top of a sample (3 cm height), along the pillar deflection direction and, the flat surface and the micro-pillar array surface with the reversed pillar deflection do not have such a capability. Although we have tried very hard to obtain a clear image to demonstrate this result, the contrast of the images was not good enough. Therefore, the images are not shown here.

5.4 Summary

In this work, we have investigated the asymmetric wetting and spreading behavior of a liquid on slanted micro-pillar array surfaces. The dynamics of the micro-scale liquid film ahead of the bulk liquid was recorded by using a high-speed imaging. A simple model was proposed to understand the unique behavior of the asymmetric spreading. Based on the model, the unidirectional spreading of the liquid can be understood as follows: a) the micro-scale liquid film spreading characteristic in the pillar deflection direction is different from the one in the reversed pillar deflection direction, which is the basic mechanism behind the unidirectional liquid spreading on asymmetric structured surface with slanted pillar array; b) The thin liquid film can promote the front spreading of bulk liquid in the pillar deflection direction, and inhibit the spreading in the opposite direction; and c) the forward spreading behavior of the micro-scale thin liquid film follows a “stick-jumping” process, which was introduced for the first time, to be best of our knowledge.

Furthermore, different types of liquid spreading behavior, such as all directional asymmetric spreading, unidirectional spreading and non-spreading, have been demonstrated by controlling the relationship between the intrinsic contact angle and critical angles. This work provides a clear understanding of the asymmetric liquid wetting and spreading behavior on stooped micro/nano-structure surfaces, and offers opportunities for precisely manipulated or self-motivated liquid spreading in micro-fluidics and other applications.

Chapter 6 Conclusions and Future work

6.1 Conclusions

In this project, to have a basic understanding of the wetting and spreading science, first we studied the surface wettability and aging behaviors of silicon wafers that went through the piranha, SC1, or HF solution cleaning, and was treated by argon, nitrogen or oxygen plasma, and then aged in a vacuum or open-air environment. It was found that the contact angle increase rates on the silicon wafers in a vacuum were much faster than that in the open air, due to the water molecules trapped on the silicon wafer surfaces had been continuously evaporated in the vacuum, while the water molecules on the silicon wafers in room atmosphere keep dynamical balanced. The XPS data reveals that the -OH groups contribute the properties of hydrophilic silicon surfaces, while the hydrophobic silicon surfaces have more -CH_x groups. Argon, nitrogen and oxygen plasma treatments had be used to modify the silicon surfaces from hydrophobic to hydrophilic by creating a thin silicon dioxide layer and activating the surface energy, which could improve the gold thin film roughness and adhesion. In the application, we had successfully coated a very thin (~ 5nm) gold film on magnetic nano-wires without adhesion layer by pre-plasma treatment.

In the second part, we invented a novel technique for fabricating a series of PDMS micro-pillars with diameters of 1 μm to 10 μm and heights of 30 μm and 50 μm . They are upright firmly after drying in CO₂ supercritical dryer, and the micro-pillar tips are able to vibrate with

considerable amplitudes under the gradient magnetic fields. The maximum micro-pillar tip deflections are 12 μm for 1 μm pillars, 10 μm for 2 μm pillars, and 5 μm for 10 μm pillars with a height of 50 μm . The micro-pillar tip vibrations were also examined under DI water, which enables its applications as actuators in micro-fluidics, and particularly as dynamic substrate for cell culture in biomimetic researches. The EDS data revealed that the weight percentage of iron embedded in PDMS pillars is as high as 81.4% with median value 59.6%, which is the highest value reported in the literature.

Last, we successfully made a couple of devices with asymmetric-deflected micro-pillar arrays by the help of the magnetic PDMS micro-pillar fabrication method. These devices were utilized to investigate the asymmetric wetting and spreading behavior of a liquid on non-symmetric rough surfaces. The dynamics of the micro-scale liquid film moving ahead of the bulk liquid was the key of this process and was recorded by using a high-speed imaging. A simple model was proposed to understand this unique behavior of the asymmetric spreading. Based on the model, the unidirectional spreading of the liquid are understood as follows: a) the micro-scale liquid film spreading characteristic in the pillar deflection direction is different from the one in the reversed pillar deflection direction, which is the basic mechanism behind the unidirectional liquid spreading on asymmetric structured surface with slanted pillar array; b) The thin precursor liquid film can promote the front spreading of bulk liquid in the pillar deflection direction, and inhibit the spreading in the opposite direction; and c) the forward spreading behavior of the micro-scale thin liquid film follows a “stick-jumping” process, which was by us for the first time, to be best of our knowledge.

Furthermore, following the models, different types of liquid spreading behavior, such as all directional asymmetric spreading, unidirectional spreading and non-spreading, have also been demonstrated by and manipulating the relationship between the intrinsic contact angle and critical angles. This work gives us a clear understanding of the asymmetric liquid wetting and spreading behavior on stooped micro/nano-structure surfaces which was produced by the help of magnetic PDMS micro-pillar fabrication method, and offers opportunities for precisely manipulated or self-motivated liquid spreading in micro-fluidics and other applications. However, the experiments revealed that the magnetic force is too weak to control the liquid spreading direction, because the capillary force on the micro-pillar is much more overwhelming. Furthermore, the PDMS material is hydrophobic, it is necessary to coat a thin hydrophilic film, gold film, on the micro-pillar surfaces to make it hydrophilic. While the metallic thin film increases the stiffness and reduces flexibility of the micro-pillar under magnetic fields. Last, the micro-pillars with high-aspect-ratio are easy to clash together if they are not solidified before liquid spreading experiments.

6.2 Asymmetric wetting modeling on micro-pillar surfaces

As discussed in the previous chapters, the science of wetting describes how a liquid spread out when it is deposited on a solid or liquid substrate. This phenomenon is becoming increasingly important role in many applications in which the liquid wetting are involved. The dynamic wetting and spreading process is far from being thoroughly understood, though this liquid behavior has been as a subject with intensive research interest for many decades. It is a

challenge to numerical modeling of the three-phase contact line movement due to the widely different length-scales interactions are involved in this process. However, many research groups have been still attempting many studies in this field. For example, several power laws have been proposed to predict the drop spreading degree with time, by considering the forces exerted on the drop, such as gravity, surface tension, and viscous forces,. Based on the understanding of the spreading of a small liquid droplet is driven by surface tension and resisted by viscosity, Tanner ^[13] proposed a power law of the spreading radius, $R \sim t^{1/10}$, where t is time. While at the late spreading stage, the large drop spreading is mainly driven by gravity, and the radius increases with $t^{1/7}$ and with $t^{1/8}$ when the dissipation occurs in the bulk liquid ^[151] and near the three phase contact line ^[152], respectively. If the solid surface is micro-texted, the intrinsic wettability is magnified so that the hydrophilic surface becomes super-hydrophilic. We recognize there are two important distinct features in the spreading process on the micro-pillar arrays: one is that the drop may spread into polygonal, and the spreading edge propagates through a zipping profile in the late spreading stages so that the wet area expands by filling the rows of pillars along the edge ^[153]. When a water droplet wets into the micro-pillars of a super-hydrophobic surface, it also has such features. Once the air pockets supporting the drop collapse, it is the transition phenomenon from the Cassie-Baxter state to the Wenzel state.

When a drop is in contact with a super-hydrophilic micro-pillar array surface, the upper part of the drop collapses, but the drop bottom penetrates into the gaps of the array. When the liquid film expansion dominates the flow spreading at the end of the spreading process, the

bulk liquid vanishes. There are two distinct liquid motions: the fringe film propagation and the bulk liquid collapsing, when a drop spreads on a super-hydrophilic surface.

By using the finite element modeling, wetting experiments and dimensional analysis, Srivastava *et al.* ^[154] developed a predictive scaling law for a liquid flows through an finite micro-pillar array substrates. The viscous resistance from both the pillar surface and supporting substrate was taken into account in the viscous scaling model, and it is valid over a wide spectrum of post geometries. As we know, Washburn dynamics describe the interaction between viscous forces and surface tension in the circular capillary wetting process. It has been attempted to combine the model with the capillary pressure to obtain a unified scaling law that is analogous to Washburn dynamics. Based on the basic principles of Washburn dynamics, the distance, l , penetrated by a liquid driven by capillary pressure into a horizontal tube is given as $l = \sqrt{\frac{\gamma r t \cos \theta}{2\mu}}$, γ is the liquid surface tension, t is the time, r is radius of the capillary, θ is the contact angle and μ is the liquid viscosity. The liquid wetting is obtained by driving to minimize the surface energies difference ($dE_{non-wetted} - dE_{wetted}$). By considering the surface energy change of wetting liquid front with a small wetting distance dx through the pillars, a capillary pressure expression can be derived

$$\Delta P_{cap} = \frac{\gamma}{p^2 h} \left[\cos \theta \left(\pi d h + p^2 - \frac{\pi d^2}{4} \right) - \left(p^2 - \frac{\pi d^2}{4} \right) \right] \quad (6-1)$$

where the pitch is p , the center to center distance between pillars. It is not easy to derive the universal expression with the first principles for viscous losses through the micro-pillar structure. A few aspects must be considered in this expression, for example, the viscous drag from the pillars, viscous losses from the supporting substrate and interactions between the pillars. As a result of the complexity, the finite-element simulation and dimensional analysis are combined in order to derive a scaling law that is applicable to a large range of the geometric parameters. Finally, Srivastava *et al.* ^[154] found the liquid flow rate per unit gap between two adjacent pillars are $h^{1.17}$, $d^{-0.5}$ and $g^{1.33}$. This modeling is used for straight micro-pillar array.

Cavalli *et al.* successfully modeled the unidirectional imbibition phenomena by using a two-phase lattice Boltzmann algorithm ^[155]. This is the hydrophilic surface and has the tilted angle posts patterns with varying contact angles with the substrate. Each post has a square cross-section, rather than cylindrical pillar, for better simulation. The dimensions of the square posts w , which was equal to 5 or 10 computational grid spacing. The posts have the tilted angles ϕ at the positive x-axis, and extend to a height $h = 4w$. They defined a fluid reservoir in the center of the post array reaching to the top of the posts and extending to around $10w$. The new mass is slowly added to feed the imbibition, once the fluid density inside the reservoir decreases below the equilibrium density of the liquid phase. θ is the liquid contact angle with both the posts and the substrate, and it varies from 30° to 70° . This range is the representative of a variety of hydrophilic materials ^[156]. A quasi 2D geometry was considered in the modeling, which allows them to concentrate on the x-direction spreading. The simulation box has $40w$ in length in the x-direction, $4w$ in the y-direction and $6w$ in the z-direction. The period boundary condition is along both x and y . When simulating a cylindrical drop spreading from a reservoir, the

interfaces are in parallel to the y -direction on average. The average of any fluid motion is along x . We will then present results for a full 3D geometry, using a simulation box with typical dimensions along x and y . In the simulation process, defining a governing equation is the most challenge work. In Cavalli's work ^[155], they used a diffuse interface model. Based on the liquid thermodynamic theory, the state is define at every point x and time t by its density $\rho(\vec{x},t)$. The free energy of the system, ψ , is taken as a Landau double-well potential tension, and a surface contribution form, which was introduced by Cahn ^[157].

6.3 Super-hydrophobic study on micro-pillars surfaces

Since the "Lotus phenomenon" was introduced decades ago, the lotus leaf has become the original example for super-hydrophobicity and surface self-cleaning properties, and it is a model inspired in many technical applications. The Lotus is a semi-aquatic plant, and its leave have the marvelous water repellency property to adapt itself to the aquatic environment. The combination of micro- and nano-structures with optimized geometry and the unique chemical composition of waxes results in these super-hydrophobic properties ^[158]. The Images in Fig. 6.1 show the micro-structure of lotus leaves and other similar plant leaves, and all of them have the similar water repellent properties. With such combination, the Cassie-Baxter state is retained with partial contact between surface and water, and the intrusion of the water in between the surface structures is avoided. If water replaces the water and enters the spaces between structures, it is Wenzel state and the water repellency is lost.

Fig. 6.1 The leaf surfaces of papillose and non-papillose, and the intact wax crystals coating: (a) Lotus, (b) *Euphorbia mysinites*, (c) *Brassica oleraces*, (d) *Yucca filamentosa*. Lotus is one of plants which have the highest density of papillae with smaller diameters. The contact angle on lotus leave can exceed 160° ^[158].

These super-hydrophobic surfaces are able to make the water and even oils to roll off, and it leaves little or no residue on the surface, which can be utilized for self-cleaning to carry away any resting surface contamination. Many super-hydrophobic materials have been developed by the inspiration of this kind of biological models. Recently, more research groups are interested in this field, and devoted a great of efforts to develop process for producing such super-hydrophobic surfaces. With this simpler and cheaper method, the high water-contact angles and low hysteresis can be achieved. They can be used as self-cleaning, anti-fog or anti-corrosion surfaces. Here, I would like to mention that this slanted micro-pillar array surface has the high

potential in super-hydrophobic applications by adjusting the pillar size, density and deflection angle and coating a thin hydrophobic polymer films, and will be my research works in near future.

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