Fabrication of gecko mimicking nanostructures using colloidal nanolithography and porous alumina

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FABRICATION OF GECKO MIMICKING NANOSTRUCTURES USING COLLOIDAL NANOLITHOGRAPHY AND POROUS ALUMINA

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School of Mechanical & Aerospace Engineering
NANYANG TECHNOLOGICAL UNIVERSITY
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In Proverbs 30:24, King Solomon proclaimed:

“There are four animals in the world that are small, but very very clever...

(30:28) Lizards: you can hold one in your hand, but you can find them in palaces.”

According to him, wise counselors are those who are skilled at life, including the ability to observe the natural realm and deduce knowledge and skills at living.

Gecko lizards are indeed small insignificant creatures, yet they have great power underneath their feet allowing them to manoeuvre any kind of surfaces.

ABSTRACT

Geckos have adopted nanoscale fibrillar structures on their feet as adhesion devices, allowing them to maneuver on vertical walls and ceilings. Despite more than 300 years of studies on hairy attachment systems, there is still a debate concerning the attachment mechanism of geckos walking on smooth and rough surfaces. Based on experimental data, some of the theories, such as sticking fluid, microsuckers, and electrostatic forces, have been rejected and adhesion has been attributed to either a combination of molecular interactions and capillary attractive forces or purely van der Waals interactions. This finding has inspired the creation of novel adhesives by manufacturing small, closely packed arrays mimicking adhesive hairs.

A good understanding of the origin of the force between gecko foot-hair and the surface is essential for providing insight into the mechanism of gecko climbing as well as guidance in fabricating artificial gecko mimicking devices. Direct measurement of force between a single gecko nanohair and a tipless cantilever was obtained by the force-displacement method using an atomic force microscope (AFM). The experimental results show that the force between gecko spatula and an AFM cantilever exhibits behavior consistent with an adsorbed surface water layer, suggesting that the dominating component of gecko adhesion force is the capillary attractive force.

Wafer-scale polymer nanofabrillar structures have been fabricated using the combination of colloidal nanolithography, deep-silicon etching, and nanomolding to mimic the nanostructure of gecko foot-hairs. The artificial surface features densely packed polymeric nanofibrils with super-hydrophobic, water-repellent, and “easy-to-clean” characteristics. In the macroscopic scale, the nanostructured surface can adhere firmly to a smooth glass substrate and is capable of supporting an object weighing approximately 70 g. In addition, the surface inherits the in-use, self-cleaning property of the setal nanostructures found in gecko lamellae.

Although the synthetic surface was able to adhere to the smooth glass substrate, the experimental results showed that it failed to demonstrate any useful adhesive properties on a rough substrate. The lack of adhesion was associated mainly with the compliance of the membrane-nanofibrils system, which was insufficient to deform elastically to make good contact between the nanofibrils and the substrate. In order to solve this problem, another novel fabrication process based on bonded porous alumina template is developed to fabricate hierarchical polymeric microfibrils array.

We have successfully created the binary-branched gecko setae and overcome the challenge of replicating the hierarchical pattern in gecko foot-hairs. However, our hierarchical structures resulted in a very small adhesive force of $\approx 0.01\text{ N}$ on glass surface, indicating that a very small amount of nanostructures were in actual contact with the substrate. This could be due to the over densely-packed arrangement of nanostructures, which was inherent in the fabrication technique using alumina membrane. Many other important aspects, such as the selection of synthetic materials, the integration of compliant layer on the nanofibrils tips, and the fabrication of slanted setae from the backing surface, have to be considered to optimize the compliance level of fibrillar structures to produce functional synthetic structures.

CONTENTS

Abstract.....	3
Contents	4
List of Figures.....	7
List of Tables	13
Notation.....	14
Glossary	16
Acknowledgements	18
1. Introduction and Background	20
1.1 Introduction.....	20
1.2 Research Motivation, Objectives, and Scopes	24
1.3 Thesis Organization	27
2. Literature Review	30
2.1 Mechanism of Adhesion in Geckos	31
2.2 Adhesive Force of a Single Seta	36
2.3 Mechanism of Detachment in Geckos	40
2.4 Mechanism of Self-Cleaning in Geckos	42
2.5 State-of-the-Art Artificial Gecko Tape	43
2.5.1 Nanorobotic Imprinting and Parallel Fabrication	44
2.5.2 Electron-beam lithography.....	46
2.5.3 Bulk Microfabrication Techniques	49
2.5.4 Wetting of Polymer in Commercial Alumina Template.....	52
2.5.5 Multiwalled Carbon Nanotubes	55
2.5.6 Summary	57
2.6 Contact Mechanics in Biological Attachment Systems	58
2.6.1 Downscaling Effect of Contact Elements	59
2.6.2 Influence of Surface Roughness on the Adhesion	62
2.7 Summary	64
3. Multi-Springs Model for Geckos Adhesion and Detachment Mechanisms.....	65
3.1 Detachment of Fibrillar Structures by Peeling.....	66
3.2 Attachment of Fibrillar Structures on Rough Surface	76
3.3 Anti-bunching Condition for Fibrillar Structures	81
3.4 Hierarchical Fibrillar Structures for Robust Adhesion and Efficient Detachment	84

3.5 Summary	89
4. Role of Capillary Forces in Geckos Adhesion	91
4.1 Capillary Forces Hypothesis	91
4.2 Materials and Methods.....	93
4.2.1 Single Seta and Multiple Setae Sample Preparation.....	93
4.2.2 Preparation of Hydrophobic and Hydrophilic Cantilever Surfaces	94
4.2.3 Adhesion force measurement of a single spatula.....	95
4.3 Results and Discussion	98
4.4 Summary	102
5. Self-Assembled Nanoparticles based Fabrication of Gecko Foot-Hairs Inspired Polymer Nanofibers.....	104
5.1 Polymeric Nanostructures Fabrication Process	104
5.1.1 Colloidal Nanolithography.....	106
Chemicals and materials	108
Experimental	109
Results and Discussions	110
5.1.2 Anisotropic Nano-scale Silicon Etching.....	112
Experimental	114
Results and Discussions	116
5.1.3 Nanomolding.....	117
Experimental	118
Results and Discussions	118
5.2 Nanoscopic Adhesive Properties	119
Experimental	119
Results and Discussions	120
5.3 Macroscopic Adhesive Properties.....	123
5.4 Self-cleaning Effect	127
5.5 Summary	129
6. Fabrication of Hierarchical Microfibrils Structure.....	131
6.1 Artificial Hierarchical Gecko Foot-Hairs	131
6.2 Nanoparticles Lithography by Stamping/Contact Printing.....	133
6.2.1 Conventional Lithography	136
Experimental	136
Results and Discussions	137
6.2.2 Colloidal / Nanoparticles Deposition.....	139
Experimental	139
Results and Discussions	139
6.2.3 Nanoparticles Lithography.....	142
Experimental	142
Results and Discussions	143
6.3 Anodic Porous Alumina Template.....	147
6.3.1 Electrochemistry and Pores Formation Mechanism	148
6.3.2 Anodization Set-up and Fabrication Process	152

6.3.3 Experimental	155
6.3.4 Results and discussions.....	157
Self-ordered alumina by two-step anodization	157
High aspect-ratio microporous alumina template	159
Ultra-thin nanoporous alumina template	161
Hierarchical microporous alumina template	162
Formation of hierarchical microfibrils.....	163
6.3.5 Superhydrophobic Effect of Double Roughness Structures	165
6.4 Summary	167
7. Conclusions.....	169
7.1 Summary and Conclusions	169
7.2 Outlook	171
7.3 List of Presentations and Publications	173
References.....	175
Appendix A Specifications and Properties of Parylene.....	184
Appendix B Properties of PMMA	190

List of Figures

Figure 2.1 (a) Digit surface of <i>Gekko gekko</i> covered with overlapping lamellae. (b) Oriented hair-like bristles or setae arising from lamella (c) Isolated single seta with multiple levels of branches at the tip. (d) Arrays of protruding spatulas with flattened ends. [9].....	31
Figure 2.2 (a) Shear force of a single seta as a function of initial preloading force. (b) Force of a single seta pulled parallel to the surface (t_s : the time when the seta began to slide off the sensor) [9]	37
Figure 2.3 Predicted adhesive force of gecko seta based on (a) capillary forces and (b) van der Waals forces. Measurement were conducted on hydrophilic and hydrophobic surfaces. (c) Experimental data of adhesive force of gecko seta on hydrophilic and hydrophobic surfaces [19].....	38
Figure 2.4 Detachment angle of a seta as a function of perpendicular force. Filled symbols represent seta pulled away from the surface until release. Open symbols represent seta held at constant force as angle is increased. Each symbol shape represents a different seta sample. [9].....	40
Figure 2.5 Peeling action of gecko's foot from a substrate (picture courtesy of Central Channel, MediaCorp, Singapore)	41
Figure 2.6 Recovery force by self-cleaning for (a) isolated setae arrays and (b) toes of live geckos. F_{clean} indicates the shear force of the setae arrays and geckos' toes on clean glass surface. F_{dirty} indicates the shear force measured immediately after the setae arrays and gecko's toes were contaminated by alumina-silica microsphere. F_n indicates the shear force measured after n simulated steps. Recovery index $R(n)$ represents the fraction of the initial loss in force that is recovered by step n . (c) Mean shear stress in clean, dirty, and self-cleaned gecko toes (dotted line indicates the minimum level to support gecko's weight). [18].....	41
Figure 2.7 (a) Setae arrays after dirtying with microspheres. (b) Setae arrays after five simulated steps. [18]	43
Figure 2.8 (a) Indenting a flat surface using a micro/nanofabricated probe nanotip. (b) Molding the template with polymer. (c) Separating the polymer from the template by peeling. (d) AFM image of indented flat surface. (e) Molded and peeled off polymer nanohairs [13]	45
Figure 2.9 (a) Molded silicone rubber nanohairs with 200 nm diameter, 60 μ m length, and about 100 nm spacing. (b) Molded polyimide nanohairs with 200 nm diameter and 60 μ m length. (c) Molded rubber hairs with 6 μ m diameter and length. [13]	46

Figure 2.10 (a) SEM images of microfabricated polyimide hairs. (b) Bunching due to the high flexibility of polyimide hairs. Both scale bars are 2 μm . [12].....	47
Figure 2.11 (a) The perpendicular force F_{pull} required for detaching various samples of polyimide hairs with periodicity P from a silicon surface. The experimental points are marked by ϕ/L , indicating the hairs' diameter ϕ and length L , respectively. (b) The adhesive force as a function of apparent contact area A_{app} . [12]	48
Figure 2.12 (a) Side view and (b) top view of silicon dioxide platforms supported by single slender silicon pillars. (c) polymer nanorods covering the platform surfaces. (d) Magnified image of (c). [14].....	49
Figure 2.13 Nanoindenter adhesion testing results and theoretical models for hydrophilic polymer surfaces. (a) van der Waals and (b) Johnson-Kendal-Roberts (JKR) adhesion models predicting the collective adhesion of organorods over a given contact area. Modified van der Waals accounting for the increased contact area attributed to the conformation of (c) two platform fingers and (d) four platform fingers. [14].....	51
Figure 2.14 Nanoindenter adhesion testing results and theoretical models for hydrophobic polymeric surfaces. (a) van der Waals adhesion model. (b) van der Waals and (c) JKR models compensating for an increased radius of organorods. (d) Reduction of the interaction distance in the van der Waals model. (e) van der Waals model for hydrophobic organorods and the compliant platform model with one finger. [14].....	52
Figure 2.15 SEM images of polystyrene nanotube layer: (a) Top view of the aligned tubes. (b) Magnified image of (a). (c) Cross sectional view of the aligned tubes. [16]....	53
Figure 2.16 Force-distance curves recorded before and after the water droplet makes contact with the as-prepared aligned nanotubes. [16].....	54
Figure 2.17 SEM images of vertically aligned multiwalled carbon nanotube structures: (a) grown on silicon by chemical vapor deposition. (b) transferred into a PMMA matrix and then exposed on the surface after solvent etching. [15].....	56
Figure 2.18 Terminal elements in animals with hairy design of attachment pads (all scale bars are 2 μm). [62].....	59
Figure 2.19 Dependence of the terminal element density N_A of the attachment pads on the body mass m of diverse animal groups. [62]	60
Figure 3.1 Spring-damper systems representing the setae arrays	67
Figure 3.2 Variable x and y Convergence Histories using Runge-Kutta method	71
Figure 3.3 Variable x and y Convergence Histories using the NDF Method	72

Figure 3.4 Relationship between position and magnitude of detachment force at $\alpha = 30^\circ$	73
Figure 3.5 Relationship between angle and magnitude of detachment force at $d = 0$	75
Figure 3.6 Contact of fibrillar structures and randomly rough surface	77
Figure 3.7 Relation between the separation and the load, assuming an exponential distribution of asperity heights	79
Figure 3.8 Relation between the load and the number of contact spots for patterned and solid surfaces. The load and number of contact spots is capped at the point when normalized separation $h = 0$	80
Figure 3.9 Two neighboring fibrils in contact	82
Figure 3.10 Contact of hierarchical fibrillar structures and randomly rough surface	86
Figure 3.11 Relation between seta stiffness and seta angle measured from the backing surface	88
Figure 4.1 Comparison of van der Waals and capillary forces between a SFM tip and a surface. z_0 indicates the distance at which the meniscus is built, γ is the surface tension, θ_1 and θ_2 is the contact angle of the liquid at the surface and the tip, respectively, c is a constant that defines the shape of the tip (approximated by the tip diameter), p_0 is the normal vapor pressure of meniscus liquid, and p is the pressure acting outside the meniscus surface, and D defines the separation distance between the tip and the surface. Values for the van der Waals curves (dashed): tip width 20 nm; Hamaker constants 0.04 and $3.0 \times 10^{-19} J$. The capillary forces show the range for different humidities. [85]	92
Figure 4.2 (a) Setae were sheared off a gecko finger using a sharp blade. (b) A group of setae was attracted to the needle tip by intermolecular attraction forces. (c) A single seta is glued to the needle tip.	94
Figure 4.3 Experimental setup for adhesion force measurement of a single spatula	96
Figure 4.4 Typical force-displacement curve of atomic force microscope	97
Figure 4.5 Force-displacement curves of geckos' spatulas using (a) an isolated seta and (b) multi-setae samples, measured with a silicon cantilever with a spring constant of 0.1 N/m, in air with relative humidity of 70%. The black and red lines are the extending and retracting curves, respectively.	98
Figure 4.6 Histograms of forces measured with (a) hydrophilic and (b) hydrophobic silicon cantilevers	99

Figure 5.1 Schematic flow of the fabrication process: (a) formation of monolayers, (b) etching back of polystyrene particles with oxygen plasma, (c) chromium deposition using e-beam evaporation, (d) polystyrene particles removal by ultrasonication in CHCl_3 , (e) deep silicon etch with $\text{SF}_6 + \text{C}_4\text{F}_8$, (f) parylene deposition, (g) complete silicon etch with XeF_2 105

Figure 5.2 Laboratory-made conical trough for the formation of colloidal monolayers. 108

Figure 5.3 (a) Colloidal monolayers of ~ 356 nm polystyrene particles on a silicon substrate. (b) Closed-packed hexagonally ordered array of nanoparticles. (c) ~ 250 nm etched back polystyrene particles after oxygen plasma treatment, (d) Non close-packed hexagonally ordered array of nanoparticles. (e) Nanoholes array of chromium layer. (f) Magnified image of (e). 111

Figure 5.4 (a-b) ~ 10 nm thick fluorocarbon polymer deposited around the nanoholes during silicon etching, (c-d) removal of the fluorocarbon polymer by baking inside a furnace at 600°C for 5 minutes, (e-f) cross-section view of deep silicon holes etched using a Bosch process with modified power and pulses durations (inset shows minimal mask under-cutting during the etching process). 115

Figure 5.5 SEM pictures of (a) densely packed nanofibrils structure at 15° angle, (b) enlarged view of (a), inset shows free standing parylene nanofibrils structure. 119

Figure 5.6 (a) AFM characterization of the adhesive properties of parylene nanostructures, (b) Mean adhesive force of individual nanofibril or artificial “nanohair” at 10 different locations (indicated by sample A, B, and so on). 121

Figure 5.7 Bunching of nanofibrils due to the unnecessarily high aspect-ratios and too compliant fibrils. 122

Figure 5.8 Surface topography of smooth glass substrate 125

Figure 5.9 (a) SEM picture of modulated height and inter-fibrils distance due to a deflected supporting parylene membrane. 127

Figure 5.10 (a) Contact angle of water droplets on bare parylene film (70°), (b) contact angle of water droplets on nanostructured parylene film (155°). 127

Figure 5.11 Proposed cleaning mechanism: (1) nanostructured surface was contaminated by particulates of $5\ \mu\text{m}$ in diameter, (2) thin layer of water attracts the particulates to the substrates, (3) nanostructured surface is cleaned from particulate contaminants. Two optical images showing the nanostructured surface before (A) and after (B) stepping onto a wetted mica surface. The nanofibrillar structures cannot be clearly seen in the images due to the limited resolution of the optical microscope. 128

Figure 6.1 Schematic diagram of artificial hierarchical gecko foot-hairs supported by flexible membrane.	132
Figure 6.2 Schematic diagram of fabrication process of hierarchical microfibrils structure using nanoparticles lithography and contact printing.	135
Figure 6.3 Microstructures with aspect ratio of 1:15; (a) 10 μm gap; (b) 25 μm gap	136
Figure 6.4 Challenges in fabricating high aspect ratio microfibrils: (a) lift-off, (b) collapse, (c-d) stiction.	138
Figure 6.5 Colloidal particles adsorption phenomena on surfaces: (a) with contact printing; (b) without contact printing.	140
Figure 6.6 SU-8 nanofibrils structure with 15 minutes etching time (~ 250 nm wide and 1 μm long).	144
Figure 6.7 Hierarchical microstructures on solid silicon substrate, showing nanofibrils structure on top of microfibril: (a-c) before, and (d) after discarding the nanoparticles in NaOH.	145
Figure 6.8 (a) Slender fibrils and (b) Collapse of nanofibrillar structures due to the excessive lateral etching.	146
Figure 6.9 Schematic diagram for barrier-type alumina and porous-type alumina.	150
Figure 6.10 Current density curve corresponding to the pore formation at the beginning of anodization. (1) Formation of barrier oxide on the entire area. (2) Local field distributions caused by surface fluctuations. (3) Creation of pores by field-enhanced or/and temperature-enhanced dissolution. (4) Stable pore growth.	151
Figure 6.11 Schematic diagram of the apparatus used for the anodization.	152
Figure 6.12 Schematic diagram of fabrication process of binary hierarchical structure: (a) First-step long anodization; (b) Concaves-textured pattern surface after removal of the porous alumina layer; (c) Second-step long anodization; (d) Sputter Au layer and coat photoresist AZ7220 for micropatterning; (e) Pattern transfer from the photoresist to the Au layer; (f) Separation of alumina from aluminum substrate; (g) Second short anodization; (h) Infiltration of PMMA; (i) Separation of alumina from aluminum substrate; (j) Selective etch of barrier layer; (k) Bonding two porous membranes; (l) UV-Ozone treatment; (m) Infiltrate a desired material into the template, which was subsequently etched away to obtain hierarchical polymeric structures on flexible membrane.	154
Figure 6.13 (a) Irregular arrays of pores. (b-c) Hexagonally ordered arrays of pores. (d) Cross-sectional view of porous alumina.	158

Figure 6.14 Cracks of oxide layer due to heat localization.....	158
Figure 6.15 Highly anisotropic microporous alumina template	160
Figure 6.16 (a) Undercut due to the too long period of etching time (b) Tapered microporous alumina due to the non-homogenous penetration of the etchant solution into the pores	161
Figure 6.17 Intimate contact between two membranes (inset shows clean nanoporous alumina template after UV-Ozone treatment).....	162
Figure 6.18 SEM micrographs of: (a) hierarchical microfibrils array featuring $\approx 10\ \mu\text{m}$ wide and $\approx 70\ \mu\text{m}$ long microfibrils, each branches into $\approx 60\ \text{nm}$ wide and $\approx 0.5\ \mu\text{m}$ long nanofibrils array; (b-c) magnified top view and (d) oblique view of the nanofibrils array.	164
Figure 6.19 Equilibrium water contact angle on: (a) non-patterned PMMA surface, (b) nanostructured PMMA surface, and (c) hierarchical microstructured PMMA surface..	166
Figure A.1 Chemical structures of Parylene N, C, and D.....	184
Figure A.2 Parylene Deposition Process	186

List of Tables

Table 4.1 Spatula Adhesion Force	100
Table A.1 Parylene Electrical Properties	188
Table A.2 Parylene Physical and Mechanical Properties	189
Table B.1 PMMA Properties	190

Notation

Notation	Description
α	Detachment angle, at which orientation the external force is applied (measured from the positive x-axis coordinate)
γ	Interfacial surface energy per unit area
$\Delta\gamma$	Differential surface energy
γ_{fs}	Surface energy of fibril-substrate interface
γ_s	Surface energy of substrate
γ_f	Surface energy of fibrils
ϕ	Diameter of synthetic or natural fibrils
$\phi(z)$	Height distribution
$\phi^*(s)$	standardized height distribution
ν	Poisson's ratio
δ	Surface deformation due to the applied external force
σ	Normal stress
σ_{th}	Theoretical adhesion strength
σ_h	Standard deviation of surface height distribution
θ	Tilting angle of the rigid beam
θ_1, θ_2	Contact angle of the meniscus liquid at the surface and the tip
ϑ	Angle at which the seta is oriented from the backing surface
φ	Area fraction of the fibrils array
η	Surface density of asperities
A	Material dependent Hamaker constant
A_{app}	Apparent contact area
b	Damping constant
D	Separation distance between two objects in close proximity
d	Detachment position, at which position the external force is applied
d_p	Separation distance between two reference planes in contact
E	Young's modulus
E_f	Electric field
$E^\#$	Effective elastic modulus
E_D	Dissipative energy
F_{vdw}	van der Waals force
F_{app}	Applied external force to cause deformation
F_{pull}	Applied external load to cause detachment
h	standardized separation distance between two reference planes in contact
h_i	Discrete surface roughness
I_C	Inertia mass about centre of mass of the rigid beam

j	Current density passing across the oxide film
j_a	Anion-contributing current density
j_c	Cation-contributing current density
j_e	Electron-contributing current density
j_i	Ionic current density
k	Spring constant
k_g	Spring constant of a fibril oriented at an angle θ
L	Length of synthetic or natural fibrils
L_0	Relaxed fibrils length
L_d	Deformed fibrils length
L^*	Minimum fibrils length to avoid bunching
L_C	Contact length
M	Mass of rigid beam
m	Mass of spring-damper system
N	Fibrils density
n	Splitted fibrils density
N_A	Number of asperities
n_c	Number of contacts
P	Fibrils periodicity
P_T	Total contact load
P_i	Contact load at a given asperity
p / p_0	Relative vapor pressure
q	Generalized coordinates
R	Fibrils radius
R_S	Sphere radius
R_A	Average surface roughness
R_q	Root mean square surface roughness
r_c	Contact radius
sl_i	Spring offset length
T	Kinetic energy
U	Potential energy
U_B	Strain energy associated with bending
U_C	Elastic energy
W_{ad}	Work of adhesion
w	Halved separation distance between neighboring fibrils
x, y	Cartesian coordinates of the leftmost spring
z_0	Distance at which meniscus is built

Glossary

Term	Description
AFM	Atomic Force Microscope
Anisotropic etch	Different etch rates in different directions in the material
A*STAR	Agency for Science, Technology, and Research
BMRC	Biomedical Research Council
Bunching	Phenomenon where neighboring fibrils are stuck one to another due to surface forces, such as van der Waals and capillary forces
CIMIL	Computer Integrated Medical Intervention Laboratory
Contact angle	The angle at which a liquid/vapor interface meets the solid surface
DMT theory	Derjaguin-Muller-Toporov theory
DRIE	Deep Reactive Ion Etching
Hydrophilic surface	Surface with a high surface energy (a liquid will spread out over a greater area on the surface)
Hydrophobic surface	Surface with a low surface energy (a liquid will form a droplet on the surface)
ICP	Inductively Coupled Plasma
Isotropic etch	Etch in which rate of etching reaction is the same in any direction in the material
JKR theory	Johnson-Kendall-Roberts theory
Lamella	Flexible membrane that supports gecko setae
Matting	Phenomenon where neighboring fibrils are stuck one to another due to surface forces, such as van der Waals and capillary forces
Mesoscopic scale	The length scale at which one can reasonably discuss the properties of a material without having to discuss the behavior of individual atoms (typically a few to ten nanometers)
MWNT	Multi-Walled carbon NanoTubes
NDF	Numerical Differential Formulas
Organorods	Polymer nanofibrils
Parylene	Inert and hydrophobic polymer coating, deposited by vapor deposition
PDMS	Poly (dimethyl siloxane)
Photoresist	A light sensitive material used in photolithography process to form a patterned coating on a surface
PS	Polystyrene
PMMA	Poly (methyl methacrylate)
PZT	Lead zirconate titanate, a material with piezoelectric effect
RH	Relative Humidity
RIE	Reactive Ion Etching
SAM	Self-Assembled Monolayers, surfaces consisting of a single layer of molecules on a substrate
sccm	A unit for volumetric flow rate (standard cubic centimeters per minute)

SD	Standard deviation
Self-cleaning	Surface property that enables a surface to remain clean despite external particulate contaminants
SEM	Scanning Electron Microscope
SERC	Science & Engineering Research Council
Seta	Microscopic projections underneath gecko's foot that is responsible for adhesion
Spatulae	Terminal elements in gecko foot-hairs
SPM	Scanning Probe Microscope
Superhydrophobic surface	Surface with very low surface energy (a water contact angle of more than 120°)
Surface energy	A measure of the energy required to form a unit area of new surface at the interface
Surface tension	An effect within the surface layer of a liquid that causes that layer to behave as an elastic sheet. It allows the water strider to walk on water.
Torr	A unit for pressure (equivalent to millimeter of mercury)
UV	Ultra-violet light

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CHAPTER 1

Introduction and Background

1.1 Introduction

The ability of geckos, insects, and other animals to adhere to smooth surfaces has always fascinated scientists. In the mid-twentieth century, there was considerable discussion on the fundamental issues of how the geckos can climb up walls without glue or suckers on their feet and hold onto the ceiling against the force of gravity. The subdigital pads of geckos were known to possess overlapping plates or lamellae, which bear fields of microscopic “hair”-like projections or setae. The gross structure of these setae and of the lamellae had been studied by various authors [1-3]. Under the light microscope the setae appear as densely packed hair-like projections about 100 μm long and 4.7 μm in diameter. Ruibal and Ernst [2] used electron microscope to reveal the structure at the free ends of the adhesive setae. They reported that the setae are complex structures with numerous branchings. The free ends of the setae consist of flattened spatulas of less than 1 μm in width. In addition, electron microscope studies indicated that the setae are composed of β -keratin, which is derived from the structural combination of crystalline polymeric fibers embedded in a highly cross-linked amorphous polymer matrix. It was described that the β -keratin of the setae is a rigid structural material and has a relatively high tensile and shear strength with higher strain at failure [4].

In the field of biological attachment system, there is an interesting structural parallel between the geckos' setae and the adhesive hairs that have been described in various

insects. The morphology of the insect setae varies considerably but in some reduviids (family: Reduviidae) the adhesive pads have setae with expanded terminal spatulas resembling the geckos' spatulas [5]. The spatulas are larger with a width of approximately 2.5 μm , and are supported by a hollow shaft about 40 μm long. The fundamental adhesion mechanism of the reduviid setae was previously explained by Gillet and Wigglesworth [6]. The hollow setae were reported to secrete an oily substance and the traction is provided by the adhesion of a wedge of oil between the free end of the setae and the substratum upon which the insect walks.

Much has been written about the mechanisms that may be involved in the adhesion of the geckos' lamellar setae to the substratum. Dellit [7] and Mahendra [8] had discounted the theories based on the secretion of adhesive substances, suction, and electrostatic charges. Both hypothesized that the traction is provided by the mechanical interaction and intermeshing of the ends of the setae with irregularities of the substratum. Based on the functional morphology of the digits and lamellae, Dellit emphasized that the structural complexity of the geckos' feet is responsible for their traction. The claws, the blood sinuses of the digits, the muscles of the digits and limbs, and the lamellar surface are all involved. A few decades later, Ruibal and Ernst [2] commented that the presence of the branches at the free end of the setae certainly indicates that these structures do not act like the spikes of climbing shoes. Rather the adhesion of the setae to the substratum appears to be a surface phenomenon, i.e. friction. Since the frictional force is proportional to the area of actual contact between two surfaces, the flattened spatulas therefore represent a mechanism that increases the total contact area between the setae and the substratum. Nevertheless, Maderson [1] suggested that electrostatic charges may serve as

an additional force in the adhesion of the setae. The movement of flat ends of the setae over a surface could generate electrostatic charges between the spatula and the substratum, he claimed.

It is obvious that considerable experimental works will have to be done before the mechanism of adhesion is fully explained. Indeed, today, well over fifty years later, there is still controversy about the actual mode(s) of adhesion employed by the geckos. The major problems in understanding the derivation of the adhesive force have been the dearth of accurate information on the detailed structure of the adhesive setae and the absence of high precision metrological tools to conduct the adhesion measurements. Recently, Autumn [9] has studied the morphology of adhesive setae in a Tokay gecko (*Gekko gekko*) more fully. He reported the first direct measurements of single seta adhesive force by using a two-dimensional micro-electro-mechanical systems force sensor [10] and a wire as a force gauge. Molecular adhesion by van der Waals interaction was proposed to play a dominant role to keep geckos firmly on their feet, even when upside down on a glass ceiling. Each seta produces a miniscule force $\approx 10^{-7} \text{ N}$, but hundreds of millions of them acting together could create a formidable adhesion of $\approx 10 \text{ N/cm}^2$.

In the past few years progress has been made in understanding the mechanism behind the geckos' amazing climbing ability, which relies on the hierarchical hairy structures covering the soles of geckos feet. Persson [11] described that the origin of the hierarchical structure of the adhesive microstructure could be well correlated to the fractal nature of all real surfaces, which have surface roughness on all length scales ranging from macroscopic to atomic scale. While the skin of the gecko foot-pads is able

to deform and follow the rough surface in the length scales beyond $\approx 1000\ \mu\text{m}$, the gecko relies on the long and thick fibrillar structure (setae) to conform to the roughness in the length scales between few μm and $1000\ \mu\text{m}$. At the shorter length scales (less than few μm), the thinner fibrils play the crucial role in ensuring the spatulas make a molecular level contact with the substrate. The unique hierarchical architecture makes the gecko adhesive system compliant on all surface length scales, enabling the gecko to adhere on the rough and smooth surfaces.

The fabrication of gecko-inspired adhesives has recently attracted considerable scientific and commercial attention due to the remarkable adhesive capabilities of the natural gecko's feet. Geim et al. [12] reported the first prototype of such "gecko tape" by microfabricating dense arrays of flexible plastic pillars from polyimide materials using electron-beam lithography and oxygen plasma etching. Sitti and Fearing [13] adopted nanomolding techniques using two different templates formed by atomic force microscope (AFM) probes and self-organized alumina and polycarbonate membranes. Northen and Turner [14] reported the batch fabrication of a multi-scale conformal system using standard bulk microfabrication techniques such as lithography, deep-reactive-ion-etching, and oxygen plasma etching. The system consists of arrays of flexible silicon dioxide platforms coated with organic looking polymeric nanorods supported by single high aspect-ratio silicon pillars. Yurdumakan et al. [15] used multi-walled carbon nanotubes to mimic the nanostructures found in geckos' feet and reported a remarkable adhesion forces at the nanometer level, about 200 times higher than that of a gecko foot-hair. Jin et al. [16] prepared a superhydrophobic aligned polystyrene nanotube layer via a

simple template-wetting method and described that the layer can hold water droplets through strong adhesive forces, even when the layer is turned upside down.

1.2 Research Motivation, Objectives, and Scope

How the geckos manage to stay attached has long been a mystery and the answer turns out to lie in the structure of the hairs on its feet. The gecko sticky feet can work in a vacuum environment [7], can be attached and detached rapidly without leaving any residue [17], and do not lose their stickiness with repeated use [18]. If it is possible to synthesize artificial hairs that can duplicate the adhesive strength and self-cleaning property of the natural hairs, the potential applications would be numerous. Some of the potential applications for a gecko-like adhesive include micromanipulation or pick and place manipulators in the micro-manufacturing industry. This could be used to handle delicate tiny objects without getting them dirty or damaging them. The gecko hair can stick tight, leave no residue, and detach without harming the material. Gecko-like adhesive could also find its application in surgery, in which the surgeon may need to pull on something, like a nerve or blood vessel, gently without damaging it. Another possible consumer application would include reusable and self-cleaning gecko adhesive tapes, gecko shoes and gloves for climbing in rocky mountains, and so on. But in order to develop replicates that could meet the benchmark performance of the real gecko, there are still a number of questions that need to be answered and understood: Is van der Waals interaction the only dominant force that explains the remarkable adhesive capability of geckos? What is the significance of the hierarchical structure of gecko foot-hairs in the

overall adhesion process? How do the geckos control the attachment and detachment of millions of hairs from the surface in a short period of time? How do the geckos keep their feet clean and use them repeatedly without any reduction in performance? What materials should the artificial hairs be made of, aiming for ease of processing and high durability? What technology would be appropriate in building the hierarchical structures of gecko foot-hairs with hundreds to thousands of nanohairs on the end of long and thick stalks in the order of 10 μm in diameter?

While this thesis does not seek to answer all these questions, its basic aims and scopes are to:

1. Develop a theoretical model to formulate an anti-bunching condition between neighboring fibrils. In an array of high aspect-ratio hairs planted on a flexible surface, a surface interaction such as van der Waals or capillary forces can arise between neighboring fibrils and cause them to bundle together [11-13]. Theories that explain (a) the significance of hierarchical structures in gecko foot-hairs and (b) the efficient detachment mechanism despite of geckos' excellent grip would also be targets of this research. A thorough understanding of these issues would be of value in the design of artificial gecko foot-hairs and the development of novel adhesives with a detachment process that is superior to current adhesives.
2. Measure the adhesive force of a single spatula in controlled environment to better understand the true nature of geckos' adhesion force. Numerous attempts have been made to study and understand the nature of the adhesive force between the spatula and the surface [19] as well as the effect of spatula orientation [9] but the complex structure of a gecko seta has made it difficult to determine how many spatulas are in

instantaneous physical contact with the sensor. The total force between two surfaces in close proximity consists of up to 11 components [20], including the van der Waals, dipole, and capillary forces. However, discrimination among the individual force components presents a considerable challenge especially for weak interaction forces such as the van der Waals force, because it is typically accompanied by stronger forces such as the capillary force in air or a dipole force in water. To determine the amplitude of the van der Waals force, the measurement has to be done either in a liquid or completely dry environment (high vacuum) to eliminate the capillary force [21]. Due to the fact that the relative humidity (RH) is at least 10% in any natural habitat, it would be essential to investigate the contribution of the capillary force in the gecko's remarkable adhesion. The adhesion measurement results of the single spatula could be further used as a benchmark for the manufacturing of artificial gecko foot-hairs.

3. Develop novel methods to manufacture the artificial structures of gecko foot-hairs. It should be noted that the development of a parallel process with the possibility to process large areas is especially important for developing future technological applications of sticky gecko foot-hairs. The artificial membrane should feature densely packed high aspect-ratio polymeric nanofibrils with super-hydrophobic, water-repellent, and self-cleaning characteristics similar to those found in gecko lamellae. Moreover, the back supporting membrane of the fibrillar structures has to be sufficiently flexible to ensure a good conformity between the membrane and the underlying substrate topography. The problems of lateral collapse and bunching between neighboring hairs have to be avoided to achieve the optimum adhesion

between the membrane and the substrates. Further development of manufacturing methods to mimic the hierarchical structure of gecko foot-hairs would become another focus of this research so as to achieve the aims of creating the true gecko-inspired adhesive structures. The hierarchical structure is expected to avoid the bunching problem commonly found in the high aspect-ratio nanofibrillar structures. Moreover, it is proposed to provide a multi-scale compliance to better conform to a rough and smooth surface.

1.3 Thesis Organization

The thesis chapters are organized as follows:

Chapter 2: This chapter provides a comprehensive review of several theories underlying geckos' adhesion, mechanisms of detachment and self-cleaning in geckos, state-of-the-art for the fabrication of gecko-inspired adhesive micro and nanostructures, and some theoretical models that explain the mechanism of adhesion in geckos' adhesive systems.

Chapter 3: This chapter discusses several important aspects that influence gecko's adhesion and should be considered in the design of synthetic fibrillar structures. Various orientations and positions of external loads are assessed to understand how the gecko can release its feet from the substrate despite its remarkable adhesion forces. A multi-spring model has been developed to describe the contact behavior between single-level fibrillar structures and

rough substrates. Furthermore, it is shown that the contact area depends on the topography of the substrate and that the initial preloading force could help mitigate the influence of surface roughness. The theory of an anti-bunching condition in fibrillar structures is also discussed and compared with the design of gecko's setae and spatulas in nature.

Chapter 4: This chapter presents direct experimental evidence for adhesion of gecko spatula by capillary force, rejecting van der Waals force as the dominant force in gecko's adhesion. The process of isolating a single seta and preparing a multiple setae sample is also discussed in this chapter. In addition, the modification of the surface properties of an atomic force microscope (AFM) cantilever is presented. This chapter is closed by discussing in detail the experimental setup of an AFM to conduct the adhesion force measurements.

Chapter 5: This chapter presents a novel approach to fabricate a nanofibrillar structure using the combination of colloidal nanolithography, deep-silicon etching, and nanomolding to mimic the nanostructure of gecko foot-hairs. The adhesion measurements of artificial structures, both in the macroscale and nanoscale, are also discussed in this chapter. A self-cleaning characteristic of the artificial structures is further discussed in relation to the role of water condensation between particulate contaminants and the substrate.

Chapter 6: This chapter presents an unprecedented approach to produce hierarchical microfibrils structures using micro- and nanoporous alumina membranes as templates. Some pioneering research groups in the gecko-inspired-adhesives community have proposed various fabrication methods to manufacture a fiber array system like those in geckos and have indeed shown some useful adhesion, but no man-made replica of the hierarchical nature used in geckos' adhesive systems has so far been reported. The fabrication method described in this chapter allows manufacturing of artificial gecko foot-hairs from different types of materials with multiple levels of hierarchical structure.

Chapter 7: Thesis contributions are summarized and the scope for future work is discussed. A list of presentations and publications made during the period of this candidature is also included in this chapter.

CHAPTER 2

Literature Review

Many animals bear structural aids on their feet to enhance their ability to climb the smooth and rough surfaces of plants, rocks, trees, and other substrates. In some climbing lizards, insects, and spiders, these take the form of specialized adhesive setae on their feet. The general morphology of digital setae in geckos has been described by Ruibal and Ernst [2] and Maderson [1] with other contributions by authors such as Hiller [22] and Williams and Peterson [23]. The detailed structure of digital setae in Tokay gecko has recently been reported by Autumn [9]. The expanded digital pad of geckos is composed of overlapping lamellae (Figure 2.1a) with the exposed outer portion of each lamella having a surface composed of microscopic setae (Figure 2.1b) formed from β -keratin [24, 25]. The Tokay gecko bears approximately 3,600 tetrads of setae per mm^2 , or about 14,400 setae per mm^2 [26]. A single seta of the Tokay gecko is approximately 100 μm in length and 5 μm in diameter (Figure 2.1c). The setae of the Tokay gecko arise independently from the keratinized skin surface and branch at the tip into hundreds to thousands structures known as spatulas (Figure 2.1d). A single spatula consists of a stalk with a flattened end, approximately 200 nm at their widest edge [2, 23]. While the Tokay (*Gekko gekko*) and house geckos (*Hemidactylus frenatus*) share a similar setae morphology and are currently the best studied among other gecko species, there exist many hundreds of species with adhesive toe pads, encompassing an impressive range of morphological variation at the lamella, seta, and spatula, which has yet to be fully characterized.

Figure 2.1 (a) Digit surface of *Gekko gecko* covered with overlapping lamellae. (b) Oriented hair-like bristles or setae arising from lamella (c) Isolated single seta with multiple levels of branches at the tip. (d) Arrays of protruding spatulas with flattened ends. [9]

2.1 Mechanism of Adhesion in Geckos

The remarkable ability of the gecko to move easily on walls and even upside down on ceilings has been a gripping topic of scientific research for a very long time and many authors have tried to elucidate the mechanism that makes these acrobatic feats possible.

While the structures of many geckos are now well documented, a full understanding of their function has been more elusive. This could be because of the complex physics involved at the interface when two surfaces are in intimate contact and of the difficulties to discriminate the individual force components among other different types of intermolecular surface forces.

Theories to explain the phenomena of geckos' adhesion have been propounded for well over a century [1-3, 7-9, 19, 22, 24, 26-35] and are summarized as follows:

1. Adhesive secretions theory

The old notion that geckos' feet secrete a sticky substance to adhere has been ruled out early in the study of gecko adhesion [36, 37]. There are three decisive objections against it. First, the most searching observations fail to establish the presence of such an adhesive substance. Second, the geckos lack glandular tissue on their toes to secrete it. Third, the supposed adhesive substance must be endowed with two qualities which are apparently contradictory to each other, i.e. it must be able to glue to geckos' feet firmly and readily to the substrates; but it must allow the separation of the geckos' feet from the substrate without the slightest obstruction.

2. Pneumatic theory

The idea that the individual setae acted as miniature suction cups was first debated in the insect adhesion literatures [38, 39], but was later proposed for geckos by Simmermacher [36] and Wagler [37]. It was believed that the adhesion takes place by the formation of interlamellar vacuum when the geckos press their feet upon a flat substrate. However, there are several inconsistencies in the vacuum theory. First, the absence of any arrangement to shut off the interlamellar grooves from the

atmospheric air outside makes it difficult to imagine how the vacuum is enclosed. Second, the fact that a freshly killed gecko can adhere on a substrate, even in a vacuum environment [7], indicates that the interlamellar space is not responsible for the phenomenon. Third, experiments carried out by Autumn [9] suggesting 10 atm of adhesion pressure strongly contradict the pneumatic theory hypothesis.

3. Electrostatic theory

Schmidt [34] and Maderson [1] pointed out that the contact of billions of spatulas with the substrate and the movement of the flat-end spatulas over a substrate could potentially produce enormous electric double-charges that are responsible for the geckos' adhesion. The arguments, however, are not substantiated by any experimental evidence. Experiments using Rontgen and Radium rays carried out by Dellit [7] suggested that an electrostatic attraction is not involved in the geckos' adhesion since the geckos were still able to adhere in ionized air. Further experiments using a galvanometer conducted by Mahendra [8] also failed to establish the presence of any electrical charges on the geckos' feet. He also reported that the geckos can adhere both on the conductive and non-conductive surfaces equally well. All these experimental findings eliminate electrostatic attraction as a mechanism for geckos' adhesion.

4. Friction theory

Hora [31] regarded the geckos' adhesion to vertical and horizontal surfaces as due to the phenomenon of friction. He argued that the presence of ridge-and-groove patterns and millions of hair-like projections, mere mechanical frictional devices, would help to prevent the geckos from slipping. Hora thought that in the geckos' adhesion to a

vertical surface, the weight of the animal itself causes pressure on the pads and makes them efficient. When the gecko is in the “upside-down” position, when the limbs are stretched outwards, the body weight instead of pulling the pads directly downwards causes them to slip along a surface for a short distance before exerting a vertical pressure on them. The pressing of the belly against an opposing surface is suspected to be an additional advantage since the scaly surface could help increase the frictional force.

The theory based on the frictional force as explained by Hora suffered from several drawbacks. When the geckos adhere to a vertical surface, the body weight, due to the force of gravity, can exert no pressure in the direction claimed by Hora. It would act parallel to the vertical surface and tend to pull the geckos downward. In the absence of pressure acting at right angles to the vertical surface, friction cannot come into play. In the “upside-down” position, the body weight can be expected to exert only a negative pressure, tending thereby to separate the pads from the horizontal surface [7]. The geckos in such cases do not use frictional force to adhere on the inverted horizontal surface.

5. Microinterlocking theory

Mahendra [8] and Altevogt [40] put forward a theory, which suggests that a gecko uses its adhesive pads in essentially the same way as a climber uses spiked boots. They believed that adhesion is achieved by the digital claws clinging to the major irregularities in the substrate, and, that the setae as well as the spatulas reinforce the action of the claws by entering the smaller irregularities. Moreover, the slight bending exhibited by each microscopic hair, considered together with the fan-wise disposition

of the five digits of a foot in five different directions and with the difference in the directions of the feet themselves, indicates that these microscopic hairs catch at the irregularities of the surface from different angles, and this would naturally increase the intensity of the gecko's hold. The explanation on the microinterlocking theory sounds plausible, but the ability of geckos to adhere on a molecularly smooth SiO_2 surface [9] shows that the surface irregularities are not necessary for adhesion, although it may play a secondary role in the geckos' adhesion.

6. Intermolecular adhesion theory

Haase [41] was one of the first who proposed intermolecular forces as the adhering mechanism of geckos. He explained that close contact of the digits surface with the substrate surface could be the cause of the geckos' adhesion. His adhesion theory is based on the attraction between molecules of different nature. If van der Waals force is the main source for the adhesion mechanism, the theory predicts that the force should exhibit no positive force dependence on velocity when pulled parallel to each other. Surprisingly, Sponberg [42] discovered that force increased dramatically with velocity: when pulled rapidly the setae arrays produced forces more than five times higher. Of all the theories about geckos' adhesion, the present intermolecular adhesion theory is the most difficult to prove or disprove. It will be discussed in more detail in the subsequent section of this chapter.

Despite all the hypotheses mentioned above, one may have questions in mind such as why do the setae have such a remarkable adhesion only to the surface to which the gecko adheres and not to neighboring setae. In [3], it was hypothesized that the form of the multi-branched setae and optimum mechanical compliance of the setae reduce the

possibility of matting between adjacent setae. The optimum mechanical compliance is offered by the combination of flexibility and rigidity in one structural design in the setae. While flexibility is derived from the fibrillar base and branched spatula filament tips, rigidity is derived from the large setae or thick matted fibril shaft. Such a combination of rigid and flexible patterns results in regular and compact spacing of the adhesive points without their interaction and resultant matting.

2.2 Adhesive Force of a Single Seta

Different theories have been proposed to explain the mechanism of geckos' adhesion, as described in the previous sections of this chapter. Based on experimental data, some of these theories have been rejected, and adhesion has been attributed to a combination of molecular interactions and capillary attractive forces or purely van der Waals interactions. Kellar Autumn, a professor from Lewis and Clark College, Portland, USA, initiated the research to measure the adhesive force of a single gecko foot-hair in ambient environment and provided a strong argument for the hypothesis of van der Waals force as the main contributor to geckos' adhesion [9]. The fact that gecko setae are strongly hydrophobic, as predicted for β -keratin structures, makes Autumn believe that capillary forces are not the reason behind geckos' adhesion [17, 43]. He further described that the highly hydrophobic setae may even aid in decreasing the gap distance between the setae and the substrate by excluding layers of water at points of contact, further reducing the role of capillary adhesion and increasing that of van der Waals forces [19].

Figure 2.2 (a) Shear force of a single seta as a function of initial preloading force. (b) Force of a single seta pulled parallel to the surface (t_s : the time when the seta began to slide off the sensor) [9]

It was reported that the geckos' adhesion is dependent upon preloading force and attachment orientation during the initial contact [9]. As shown in Figure 2.2a, the shear force of a single seta was found to increase linearly with the normal preloading force. Furthermore, the experimental results showed that setae that were pushed into the surface and then pulled parallel to it developed over ten times the force ($13.6 \pm 2.6 \mu\text{N}$) than those having only a normal preload ($0.6 \pm 0.7 \mu\text{N}$). It was suspected that the stronger adhesive force is due to the increase in the number of spatulas contacting the surface. Employing a dual-axis MEMS (Micro-Electro-Mechanical-System) cantilever to measure the adhesive force of single seta, Figure 2.2b describes the dynamic response of a single seta when the seta is sheared away from a surface. The maximum shear force that had been reported lies in the range of $194 \pm 25 \mu\text{N}$ [4].

Comparing the experimental result with theoretical calculation of van der Waals force:

$$F_{vdw} = \frac{A \cdot R}{6 \cdot D^2} \quad (2.1)$$

where A is the material dependent Hamaker constant, R is the radius of spatula tips, and D is the separation distance, Autumn claimed that his force measurement result ($\sim 200 \mu\text{N}/\text{seta}$) falls in the range of theoretical calculation ($40\text{--}400 \mu\text{N}/\text{seta}$). It is noted that the role of thin film capillary adhesion caused by condensation of water from the atmosphere cannot be excluded although the experimental result was consistent with the theoretical calculation of van der Waals forces. In [19], the adhesive force measurements of a single seta on hydrophobic and hydrophilic surfaces were carried out to verify the contribution of capillary forces on geckos' adhesion.

Figure 2.3 Predicted adhesive force (units are arbitrary) of gecko seta based on (a) capillary forces and (b) van der Waals forces. Measurement were conducted on hydrophilic and hydrophobic surfaces. (c) Experimental data of adhesive force of gecko seta on hydrophilic and hydrophobic surfaces [19]

Figure 2.3(a-b) illustrates the predicted adhesive force of a single seta when the capillary forces and van der Waals forces dominate the adhesion mechanisms, respectively. If capillary forces dominate the adhesion, a significant difference in adhesive force should be encountered when the seta touches on hydrophilic and hydrophobic surfaces, as depicted in Figure 2.3a. On the other hand, if van der Waals force is the dominant force, the measured adhesive force of a single seta is independent of the surface hydrophilicity, as shown in Figure 2.3b. The experimental results in Figure 2.3c show that the adhesion force of a single seta on both hydrophobic and hydrophilic surfaces of the same polarity (dielectric constant > 4.5) are equally strong, which indicates that capillary force is not the main factor of geckos' adhering capability. Adhesion of a single gecko seta on the hydrophobic MEMS cantilever was measured to be $41.3 \mu\text{N}$, which differs by only 2% from that measured on the hydrophilic sensor, which is $40.4 \mu\text{N}$.

Figure 2.4 Detachment angle of a seta as a function of perpendicular force. Filled symbols represent seta pulled away from the surface until release. Open symbols represent seta held at constant force as angle is increased. Each symbol shape represents a different seta sample. [9]

2.3 Mechanism of Detachment in Geckos

Besides the remarkable adhering mechanism, the secrets behind repeated and rapid detachment of geckos still remain unanswered. It is surprising to find out that a gecko manages to detach its feet in 15ms with no measurable detachment forces [17, 43]. The peeling behavior of geckos during running may contribute to the detachment process of the toes. The uncurling action was suspected to help the gecko put every individual seta at a critical angle that aids in its release [44]. However, the mechanism of how this peeling behavior results in reaching the critical angle of detachment is still unclear. As shown in Figure 2.4, it was observed that setae always detached at the angle α of $30.6^\circ \pm 1.8^\circ$ when pulled away from a sensor's surface. Stress increases at the trailing edge of the seta as the angle of the seta's shaft increases, causing crack nucleation at the periphery of the contact area and propagation towards the center during pull-off. As seen in Figure 2.5, geckos peel their toes up and away from the substrate rather than attempting to detach an entire foot at once, much like removing a piece of tape. Peeling action concentrates the detachment force on only a small subset of all attached setae at an instant and spreading detachment out over time.

Figure 2.5 Peeling action of gecko's foot from a substrate (picture courtesy of Central Channel, MediaCorp, Singapore)

Figure 2.6 Recovery force by self-cleaning for (a) isolated setae arrays and (b) toes of live geckos. F_{clean} indicates the shear force of the setae arrays and geckos' toes on clean glass surface. F_{dirty} indicates the shear force measured immediately after the setae arrays and gecko's toes were contaminated by alumina-silica microsphere. F_n indicates the shear force measured after n simulated steps. Recovery index $R(n)$ represents the fraction of the initial loss in force that is recovered by step n . (c) Mean shear stress in clean, dirty, and self-cleaned gecko toes (dotted line indicates the minimum level to support gecko's weight). [18]

2.4 Mechanism of Self-Cleaning in Geckos

It has been observed that gecko feet and setae remain clean from particles encountered during locomotion. Hansen and Autumn [18] studied the effects of particulate contamination on the toes of live geckos and on isolated setae arrays to determine whether cleaning of setae occurs apart from the gecko. The study was conducted by applying silica microspheres deliberately to the surface of gecko's foot-pads. Shear forces of the contaminated toes and setae arrays were measured by using a vertically mounted force sensor. After application of microspheres, both the toes and the isolated setae arrays lost more than 50% of the shear force relative to when they were clean. Particulate contaminants interfere with attachment of gecko toes and in isolated arrays, but repeated seta and substrate interactions would significantly restore the shear force capacity in both cases, as illustrated in Figure 2.6(a-b). Striding and toe movement may aid the speed and effectiveness of the cleaning process, possibly by sliding or rolling particles and thereby easing the detachment of the contaminating particles [45]; however the substrate-particle interactions are the basic phenomenon to explain the gecko self-cleaning mechanism. The results also imply that self-cleaning is an intrinsic property of arrays of setae and it occurs even under extreme exposure to clogging particles. It can be seen from Figure 2.6c that four steps on clean glass restore the shear force of setae arrays to a level sufficient to support the gecko by a single toe.

Figure 2.7 (a) Setae arrays after dirtying with microspheres. (b) Setae arrays after five simulated steps. [18]

Figure 2.7 shows that the spatulas are mostly clean even though microspheres are still present after five simulated steps. In order to inherit the dry self-cleaning property, it was proposed that the array of spatulas has the following properties: (i) surface area smaller than that of dirt particles, (ii) made of relatively hard, nontacky materials [46, 47], and (iii) having low surface energy.

2.5 State-of-the-Art Artificial Gecko Tape

The fabrication of gecko-inspired adhesives has recently attracted considerable scientific and commercial attention due to the remarkable adhesive and self-cleaning capabilities of the natural gecko's feet. If our hands were made up of tiny elastic structures that were able to deform and comply with different scales of surface roughness, then perhaps our hands could also adhere to the surfaces we touch [15]. In fact this achievement is not far away. There have been several recent attempts to fabricate surface patterns with polymers to mimic the thin fibrils structure of gecko foot-hairs [12-16]. The following subsections

of this chapter will discuss different micro and nanofabrication techniques to develop a remarkably effective adhesive inspired by the natural technology of gecko foot-hairs.

2.5.1 Nanorobotic Imprinting and Parallel Fabrication

In the nanorobotic imprinting method, arrays of high aspect ratio micro or nanostructures such as atomic force microscope (AFM) or scanning tunneling microscope (STM) probes are imprinted on a flat soft surface such as a polystyrene or poly(methyl methacrylate) / PMMA surface by indentation (see Figure 2.8a). The indented template is molded with a desired material (see Figure 2.8b), after which it will be freed from the template subsequently to obtain a free-standing nanopatterned surface (see Figure 2.8c). Sitti and Fearing [13] measured the adhesion of artificial hairs as 181 ± 9 nN for a silicone rubber nanobump with a tip radius range of 230-440 nm and 294 ± 21 nN for a polyester nanobump with tip radius of 350 nm.

Figure 2.8 (a) Indenting a flat surface using a micro/nanofabricated probe nanotip. (b) Molding the template with polymer. (c) Separating the polymer from the template by peeling. (d) AFM image of indented flat surface. (e) Molded and peeled off polymer nanohairs [13]

As a parallel fabrication method, membranes with self-organized high aspect-ratio pores (alumina and polycarbonate) were used as the master template and molded with a liquid polymer. Figure 2.9a shows 200 nm diameter and 60 μm long silicone rubber nanohairs molded from an alumina membrane. It can be clearly seen that the high aspect-ratio nanohairs are too compliant and too dense to prevent self-sticking. Another example of self-sticking nanohairs due to the high density and aspect ratio is shown in Figure 2.9b. Figure 2.9c shows 6 μm diameter and 6 μm long silicone rubber nanohairs molded from a polycarbonate membrane. Adhesion of the rubber arrays in Figure 2.9c was measured to be $2.8 \text{ mN}/\text{cm}^2$ or 60 nN adhesion for each single hair assuming all hairs make a contact with the substrate.

Figure 2.9 (a) Molded silicone rubber nanohairs with 200 nm diameter, 60 μm length, and about 100 nm spacing. (b) Molded polyimide nanohairs with 200 nm diameter and 60 μm length. (c) Molded rubber hairs with 6 μm diameter and length. [13]

2.5.2 Electron-beam lithography

Geim et al. [12] was among the first who successfully developed an artificial “gecko tape” using micro- and nanofabrication technology. Any submicrometer object, whether it is the tip of AFM, a small piece of dust or a single gecko hair, sticks to a solid surface with an adhesive force in the range of 10 to 1,000 nN, depending on the exact geometry and materials involved [3, 9, 19, 21, 48]. A formidable force could be produced when large arrays of these submicrometer objects make physical contacts with the opposing substrate. But the fact that all real surfaces are not ideally flat requires the submicrometer objects to be sufficiently long, thin, and flexible to attach to uneven surfaces all at the same time.

Figure 2.10 (a) SEM images of microfabricated polyimide hairs. (b) Bunching due to the high flexibility of polyimide hairs. Both scale bars are 2 μm . [12]

Arrays of submicrometer polyimide hairs, as shown in Figure 2.10, were prepared by using the following set of procedures. A polyimide film was coated on silicon wafer and an array of submicrometer aluminum disks was subsequently prepared using electron beam lithography, thermal evaporation of an aluminum film, and lift-off. The resulting aluminum pattern was then transferred onto the polyimide film by dry etching in oxygen. The whole structure is then peeled off and transferred to scotch tape to provide a flexible substrate as the base. The flexible substrate was used so as to maximize the number of hairs getting into contact with the surface and eventually enhances the overall adhesive force of artificial structures.

Figure 2.11 (a) The perpendicular force F_{pull} required for detaching various samples of polyimide hairs with periodicity P from a silicon surface. The experimental points are marked by ϕ/L , indicating the hairs' diameter ϕ and length L , respectively. (b) The adhesive force as a function of apparent contact area A_{app} . [12]

Adhesive properties of the resulting “gecko tape” were characterized and the average force per hair was found to be 70 nN and the whole 1 cm^2 patch was able to support 3 N. Figure 2.11a shows that the perpendicular force required to detach the samples from a substrate depends weakly on the length L and diameter ϕ of the hairs and it is inversely proportional to the hairs periodicity P . In addition, the force was found to vary linearly with the apparent contact area A_{app} , as shown in Figure 2.11b. The results suggest that, for maximum adhesion, one has to maximize the number of hairs capable of attaching to a surface, and their particular geometry is of less importance.

2.5.3 Bulk Microfabrication Techniques

In this work, a wafer-scale batch fabricated multiscale conformal system has been produced [14]. The multiscale structures consist of arrays of organic looking photoresist nanorods (organorods), approximately 2 μm tall and 50-200 nm in diameter, on top of photographically defined 2 μm thick silicon dioxide platforms 100-150 μm on a side (see Figure 2.12).

Figure 2.12 (a) Side view and (b) top view of silicon dioxide platforms supported by single slender silicon pillars. (c) polymer nanorods covering the platform surfaces. (d) Magnified image of (c). [14]

The platforms are supported by single high aspect ratio pillar down to 1 μm in diameter and with heights up to 50 μm . The structures were fabricated out of four-inch silicon wafers using standard bulk microfabrication techniques [49]. A 2 μm thick silicon dioxide film was grown on the silicon wafer using a wet oxidation process. The top platform geometry was defined using a standard stepper photolithography using a positive resist, Shipley SPR 220-7. The resist was then used as an etch mask in an inductively-coupled-plasma (ICP) etcher with CHF_3 chemistry to vertically etch through the silicon dioxide to the silicon. The exposed silicon was then etched using the Bosch process, also known as deep reactive ion etching (DRIE), where the plasma is cycled between a highly reactive SF_6 gas and a hydrocarbon forming CF_4 species, creating high aspect ratio vertical cavities. The depth of these cavities can be controlled depending on the desired final aspect ratio of the pillars. An extended SF_6 etch was subsequently used to isotropically etch the silicon and to create an undercut from all directions leaving behind only a single pillar in the middle (Figure 2.12a). By controlling the duration of the release it is possible to control the final size of the pillars supporting the platforms. Following the platform and pillar fabrication, the photoresist surface of the platforms was transformed into organorods by placing it into oxygen plasma. The plasma creates an electric field, which acts on the dielectric polymer inducing a force large enough to overcome surface tension, thus causing the growth of vertical polymeric columns. The samples were placed in a CF_4 plasma to change the organorod surface from hydrophilic to hydrophobic. This creates a fluorocarbon coating, increasing their size and altering their surface chemistry. The fluorocarbon coating leaves a $-\text{CF}_3$ terminated surface, greatly reducing the surface energy. It was found that the coating with the morphology of

the organorod surface creates a lotus leaf effect [50], making the surface highly hydrophobic.

Figure 2.13 Nanoindenter adhesion testing results and theoretical models for hydrophilic polymer surfaces. (a) van der Waals and (b) Johnson-Kendal-Roberts (JKR) adhesion models predicting the collective adhesion of organorods over a given contact area. Modified van der Waals accounting for the increased contact area attributed to the conformation of (c) two platform fingers and (d) four platform fingers. [14]

Adhesion testing was performed using a nanoindenter with a spherical aluminum tip. The adhesive force was found to significantly depend on the maximum applied normal load (Figure 2.13). This dependence was proposed due to the increase in contact area between the two surfaces as a result of increased conformation, and deformation (plastic and elastic), of the adhesive to the spherical indenter surface. It was found that the loading and unloading curves with hard flat silicon substrates were produced with no apparent adhesion (results are not presented in the figures). Figure 2.13 shows that the photoresist surfaces demonstrated little adhesion and the organorod coated surfaces

demonstrated much higher adhesion strengths. Figure 2.14 shows an improved adhesion when a hydrophobic coating was added to the organorod surface. The result was proposed to be associated with the increased organorod size. Combining the organorods with the compliant pillar structures offered a significant increase in adhesion, suggesting that the compliant structures aid in increasing the surface contact area. The fingers platform structures not only improve the surface conformation but also were able to bend out of the plane changing the adhesion vector to include a transverse component.

Figure 2.14 Nanoindenter adhesion testing results and theoretical models for hydrophobic polymeric surfaces. (a) van der Waals adhesion model. (b) van der Waals and (c) JKR models compensating for an increased radius of organorods. (d) Reduction of the interaction distance in the van der Waals model. (e) van der Waals model for hydrophobic organorods and the compliant platform model with one finger. [14]

2.5.4 Wetting of Polymer in Commercial Alumina Template

A polystyrene (PS) layer, which is composed of greater than 6 000 000 aligned nanotubes per square millimeter, has been fabricated to mimic the feet of a gecko [16]. In this

method, a commercial alumina template with 290 nm diameter pores, whose porosity consists of an array of parallel and straight channels, was brought into contact with a PS solution. A thin PS layer covered the pore walls of the membrane in the initial stages of wetting. The template was subsequently dissolved away and an aligned PS nanotube layer was obtained.

Figure 2.15 SEM images of polystyrene nanotube layer: (a) Top view of the aligned tubes. (b) Magnified image of (a). (c) Cross sectional view of the aligned tubes. [16]

Figure 2.15 shows the typical top view and cross sectional SEM images of the as-prepared PS nanotube layer, showing good alignment of the PS nanotubes with open end caps. The density of the PS nanotubes is $\approx 6.76 \times 10^6$ tubes mm^{-2} and their length is $\approx 57.9 \pm 0.8 \mu\text{m}$. The round aligned nanotubes are observed clearly with an average outer diameter of $\approx 283.4 \pm 4.1 \text{ nm}$ and a wall thickness of $\approx 59.8 \pm 1.9 \text{ nm}$, which is consistent with the dimensions of the template used. Interestingly, the PS nanotube layer was reported to be able to hold water droplets through strong van der Waals forces, even when the layer is turned upside down. A surface with a sufficiently high adhesive force to a liquid has many potential applications, such as in liquid transportation without loss and in the analysis of very small volumes of liquid samples. The adhesive force between a

water droplet and the PS layer was assessed by a high-sensitivity microelectromechanical balance system.

Figure 2.16 Force-distance curves recorded before and after the water droplet makes contact with the as-prepared aligned nanotubes. [16]

Figure 2.16 displays the recorded force-distance curves during the measuring process. First, the PS nanotube layer was placed on the plate of the balance system, a 3 mg water droplet was suspended on a metal ring, and the force of this balance system was initialized to zero. Then, the PS layer was brought into contact with the water droplet while maintaining the balance force at zero (process 1). When the PS layer left the water droplet after contact, the balance force increased gradually and reached its maximum at the end of process 2. Finally, the balance force decreased immediately when the PS layer broke away from the water droplet in process 3 to finish one cycle of the force measurement. The force that the water droplet was subjected to can be regarded as the

adhesive force between the PS nanotube layer and water. The maximum force was about 59.8 μN at the position just before the water droplet left the surface.

2.5.5 Multiwalled Carbon Nanotubes

A structure based on multiwalled carbon nanotubes (MWNT) constructed on polymer surfaces with strong nanometer level adhesion was reported to serve as a dry adhesive similar to or stronger than gecko foot-hairs [15]. The fabrication process involved the growth of 50-100 μm MWNT on quartz or silicon substrates through chemical vapor deposition [51]. A gaseous mixture of ferrocene, as a catalyst source, and xylene, as a carbon source, was heated and passed over the substrate which was itself heated in a quartz tube furnace. The MWNT grow selectively on the oxide layer with controlled thickness and length. The oxide layer of the substrate can be patterned by photolithography followed by a combination of wet and/or dry etching in order to create various patterns of MWNT [52].

Figure 2.17 SEM images of vertically aligned multiwalled carbon nanotube structures: (a) grown on silicon by chemical vapor deposition. (b) transferred into a PMMA matrix and then exposed on the surface after solvent etching. [15]

An SEM image of typical MWNT grown on silicon is shown in Figure 2.17a. These tubes are vertically aligned with a typical diameter of 10-20 nm and length of $\approx 65 \mu\text{m}$. The samples, with the MWNT side facing up, were gently dipped in a beaker containing methyl methacrylate monomer. After polymerization process, the MWNT were completely embedded and stabilized in the PMMA matrix. The PMMA-MWNT sheets are peeled off from the silicon substrates forming a very smooth surface. The MWNT were exposed from the silicon-facing side of the PMMA matrix by etching the top layer with acetone or toluene. The exposure length of the MWNT can be controlled by varying the solvent etching time. Figure 2.17b shows MWNT brushes on PMMA films. The brushes are mostly aligned vertically and in general form entangled bundles due to the

solvent drying process. The adhesive force of the MWNT brushes was measured with scanning probe microscope (SPM) and it was reported to be $1.6 \pm 0.5 \times 10^{-2} \text{ nN nm}^{-2}$.

2.5.6 Summary

Fabrication of fibril arrays of nanometer scale has recently attracted considerable interest because of the potential demand for development of novel adhesives based on the gecko attachment system. Various fabrication techniques have been discussed in the preceding sections. The very robust technique to fabricate these structures is electron beam lithography [12]. However, electron beam lithography has some drawbacks, such as low throughput due to its long exposure time, and high cost of equipment. Simplification of the process to allow large-scale fabrication of nanofibril arrays is desirable. The combination method of colloidal nanolithography, deep-silicon etching, and nanomolding is developed in Chapter 5 to overcome the obstacle of electron beam lithography. Other techniques that have been proposed to fabricate gecko micro- and nanostructures include template synthesis method [13, 16], MEMS fabrication techniques [14], and carbon nanotubes based structure [15]. However, in many cases the reported methods aim to produce the terminal bristle component of gecko foot-hairs, thereby limiting the applications of artificial structures for smooth substrates [53]. In gecko setae, the design of a solid shaft with branched tips combines the rigidity from the thick setae fibrils, and the flexibility from the fibrillar base and fine spatulae fibrils, to attain the most efficient adhesion without having the problems of matting. In Chapter 6, a novel fabrication technique based on the bonding of two alumina membranes of different pores size is used to replicate the branched structures in gecko setae.

2.6 Contact Mechanics in Biological Attachment Systems

Adhesion between surfaces becomes important with smooth surfaces on a small scale. From the point of view of mechanics, adhesion is expressed in terms of the ‘work of adhesion’, i.e. the external work done to separate a unit area of the adhering surfaces, whatever its physical origin; be it intermolecular forces, electrostatic forces or capillary action. Contact mechanics theories have been used to understand adhesion mechanism in both engineering and biology. The classical Hertz theory [54] assumes no adhesive interaction between contacting objects. Some experimental contradictions were reported by Johnson, Roberts, and Kendall [55] who noted that at low loads the contact areas between contacting bodies were considerably larger than those predicted by Hertz. These observations also suggested that attractive surface forces were operating between the solids and they become increasingly important as the load was reduced to zero. Hertz theory was then modified to account for the attractive surface forces in lightly loaded contacts. The JKR (Johnson-Kendall-Roberts) theory determines the size of contact area via a balance between elastic and surface energies. While the JKR theory is appropriate for modeling contact between soft elastic materials, the assumption of a crack-like singular field becomes increasingly inaccurate for materials of high elastic modulus, in which case different assumptions on the elastic deformation of contacting objects have led to DMT (Derjaguin-Muller-Toporov) theory [56]. Maugis [57] further extended these theories and developed a more general model that includes the JKR and DMT models as two limiting cases. It is interesting to note that the existing contact mechanics theories, including JKR, DMT, and Maugis models, all predicted infinite adhesion strength as the size of contacting objects is reduced to zero. The adhesion strength is defined as the

tensile force per unit contact area at pull-off, which can be maximized via size reduction [58-61].

2.6.1 Downscaling Effect of Contact Elements

Attachment pads of animals, such as insects, spiders, and lizards, are well known to contain surfaces covered by fine patterns of protuberances. The setae of these animals are structured down to the μm and sub- μm levels, as shown in Figure 2.18. The widest dimension of their terminal elements has been measured to range from 0.2 to 5 μm , with the heavier animals exhibiting finer adhesion structures. Comparative structural data, shown in Figure 2.19, indicate that the terminal elements density N increases with increasing body mass m . The finding was noteworthy that a single master curve exists for the different species and it is given by [62]:

$$\log N(m^{-2}) = 13.8 + 0.699 \cdot \log m(\text{kg}) \quad (2.2)$$

Figure 2.18 Terminal elements in animals with hairy design of attachment pads (all scale bars are 2 μm). [62]

Figure 2.19 Dependence of the terminal element density N_A of the attachment pads on the body mass m of diverse animal groups. [62]

Continuum mechanics models of the adhesion between elastic spherical surfaces predict a finite pull-off force given by:

$$F_{JKR} = \frac{3}{2} \cdot \pi \cdot R_S \cdot \gamma \quad (2.3)$$

where R_S is the radius of the sphere and γ is the interfacial surface energy per unit area. Assuming there are no hairy structures and $R_S = 100 \mu m$ is the radius of the complete surface of the attachment organ of a fly (*Drosophila melanogaster*), an adhesion energy in excess of $1 J/m^2$ would be required to support the weight of 80 mg. The value of adhesion energy is clearly unrealistic for intermolecular interaction forces, which typically falls in the range of few to tens of mJ/m^2 . However, in reality, the animal takes advantage of contact theory. By splitting up the contact into n subcontacts, each with radius $R/\sqrt{n}$, the total adhesion force is increased to:

$$F' = \sqrt{n} \cdot F \quad (2.4)$$

When the number of hairy structures is of order 10^3 to 10^4 setae, the typical adhesion energy falls in the range of 10 to 50 mJ/m^2 .

The patterned surfaces have an added advantage in that the adhesion with various surface profiles is more easily accomplished due to the increased tolerance to defects at individual contacts [63]. The failure of some microcontacts because of dust particles would minimally influence the contact adhesion. In the case of solitary contact, even a little damage of the contact caused by the dirt or surface asperities will reduce the adhesion to a very small value, between 100 to 1000 times smaller than the theoretical values [64], and immediately lead to contact breakage.

Recently, Gao and Yao [59] showed that the adhesion strength can in principle approach the theoretical strength via size reduction and shape optimization. In practice, interfacial crack-like flaws due to surface asperities or contaminants inevitably weaken the actual adhesion strength. By accurately adopting the optimal shape of the tip of the fiber and by reducing the diameter of the fiber, the theoretical strength can be achieved and failure occurs no longer by crack propagation [65] but rather by a uniform detachment over the entire contact region. At macroscopic sizes, a small variation in the tip shape of the fiber was said to result in large changes in pull-off forces. Although theoretically feasible, the design of the optimal shape is unrealizable in practice at the macroscopic scale. The sensitivity of adhesion strength to tip geometry of the fiber decreases as the fiber diameter is reduced, and a robust design of optimal adhesion becomes possible around a critical size on the order of $\approx 100 \text{ nm}$ at which the pull-off force is no longer sensitive to variations in tip geometry.

2.6.2 Influence of Surface Roughness on the Adhesion

The adhesion between an elastic solid and a hard rough substrate has been studied previously by Fuller and Tabor [64], Briggs and Briscoe [66], and more recently by Persson [67]. They reported that a relative small surface roughness may result in negligible adhesion. A surface roughness of $\approx 10 \mu m$ may completely remove the adhesion between a very soft rubber ball (elastic modulus $E \approx 0.06 MPa$) and a hard rough substrate. In view of geckos' attachment system, the outermost layer of the skin on the toes is made from a relatively stiff material, i.e. keratin (elastic modulus $E \approx 4 GPa$), which has an elastic modulus $\approx 10^5$ times higher than that of very soft rubber. Because of its high elastic modulus, the skin is not able to deform and follow the substrate surface roughness; it is for exactly this reason that the foot-pads skin is covered by the fiber array system, which forms a very soft compliant layer.

In [11], the elastic modulus of a solid block is compared with the effective elastic modulus of a fibrous material made from the same material. When a solid block of thickness t is exposed to the surface stress σ , it will deform a distance δ and the strain δ/t can be derived from:

$$\sigma = E \cdot \frac{\delta}{t} \quad (2.5)$$

where E is the elastic modulus.

On the other hand, if a solid block is replaced by a dense array of thin curved fibers, a displacement δ is given by:

$$\delta = \frac{F_{app}}{k} \quad (2.6)$$

where F_{app} is the force applied to a fiber and k is the effective spring constant:

$$k = \frac{CER^4}{L^3} \quad (2.7)$$

where C is a constant which depends on the shape of the fiber (typically of order 10), L and R is the length and radius of the fiber, respectively.

If there are N fibers on the area A then the normal stress is given by:

$$\sigma = N \cdot \frac{F_{app}}{A} = N \cdot \frac{k \cdot \delta}{A} = E^\# \cdot \frac{\delta}{L} \quad (2.8)$$

where the effective elastic modulus $E^\#$ is given by:

$$E^\# = \frac{N \cdot k \cdot L}{A} = C \cdot E \cdot \frac{N \cdot R^2}{A} \left(\frac{R}{L} \right)^2 \quad (2.9)$$

For the setae array we have $R/L \approx 0.02$ ($R = 1.5 \mu m$, $L = 80 \mu m$). The setae density of $\approx 10^4$ setae per mm^2 contact area gives $N \cdot R^2 / A \approx 0.02$ so that $E^\# \approx 10^{-4} E$. Thus the replacement of the solid block with an array of fibers reduces the effective elastic modulus from $E \approx 4 GPa$ to $E^\# \approx 0.4 MPa$, which is similar to that of soft rubber. This explains the fundamental mechanism by which many biological attachment systems generate “sticky” surfaces.

The fiber array system not only provides the compliance to geckos’ attachment pads, but it also has a unique hierarchical structure, that consists of “long thick” fibers followed by “short thin” fibers, to conform to the surface with roughness of different length scales, ranging from macroscopic to atomistic. The skin of geckos’ foot-pads is able to deform and follow the surface on length scales much longer than the thickness of the elastic keratin film, say, beyond $\approx 1000 \mu m$. At the shorter length scales, the geckos make use of the setae to penetrate into the surface “cavities” with a diameter less than $1000 \mu m$.

However, if the setae fiber tips would be blunt and compact, negligible atomic contact would occur between surfaces because they would not be able to penetrate into surface cavities with a diameter less than a few μm . For this reason, at the tip of the seta occurs an array of ≈ 1000 thinner fibers on the order of $\approx 0.1 \mu\text{m}$, also known as spatulas. Persson [11, 68] further explained that the hierarchical structure is present in geckos' attachment system because it is more durable and less prone to wear as compared to just a single layer of very thin and long fibers. In addition, a dense array of thin and long fibers would be unstable against condensation into a compact thin film with a high elastic modulus.

2.7 Summary

A comprehensive review of the digital setae structure of a gecko, published theories of adhesion mechanisms, proposed detachment and self-cleaning mechanisms, and some related contact mechanics theories are presented in this chapter. The topics under review in this chapter provide the theoretical basis for the proposed research project. The following conclusions are drawn from the literature review presented in this chapter. It has now been well recognized that van der Waals forces and capillary forces are the two competing forces that underlie the remarkable adhering capability of a gecko. Considerable efforts have been devoted to the development of synthetic gecko micro/nanostructures, but none has successfully produced manmade adhesives with a hierarchical structure incorporated in the design. It has also been shown that the effective elastic modulus of the fiber array system is very small on all relevant length scales (from mm to nm), which is of fundamental importance for adhesion on rough substrates.

CHAPTER 3

Multi-Springs Model for Geckos Adhesion and Detachment Mechanisms

There are several factors that need to be taken into consideration in the effort of emulating the adhesive properties of gecko-foot hairs. These include the array structure of synthetic setae, the material properties, and the design and geometry of each single seta. The gecko-setae have evolved many times to reach the present state providing the geckos with the most effective adhesion and the least detachment effort during locomotion. Reproducing the adhesive properties of a gecko foot does not imply that we have to follow exactly the same natural structure. The crucial aspect here is to understand how each level of the hierarchical structure contributes to the adhesion of single seta, and how it eventually integrates with hundreds of millions of the setae to create a remarkable adhesion. Nature may provide us with the best design of setae, in terms of geometry, compliance, and array structure, but due to the complexity of mimicking nature, we have to appreciate the importance of each component of the gecko foot-hairs, including the lamellae, the setae, and the spatulas. With this, we would be able to deduce and prioritize the compromises and emerge with our engineering model of the fabricated synthetic gecko foot-hairs.

In this chapter, a springs model of the setae arrays is introduced and followed by the derivation of equations of motion that describe the movement of seta arrays when the gecko peels its feet during detachment. The efficiency of Runge-Kutta and Numerical Differentiation methods in solving the initial value problems is compared in terms of

stability and convergence rate. Enhancement in work of adhesion by fibrillar structures with a high aspect ratio was previously reported by Jagota and Bennison [69], Persson [11], and Gao et al. [70]. However, the excessive length of the fibrils could cause an instability leading to fiber bunching, which eventually impairs the overall adhesion efficiency. In order to improve the design of the synthetic gecko foot-hairs, the anti-bunching condition in fibrillar structures is discussed in the following section.

3.1 Detachment of Fibrillar Structures by Peeling

In this study, a model for setae arrays is developed and equations of motion of the setae arrays are derived to simulate the dynamic movement of the gecko's peeling action. When external load is applied to the system, the setae experience tensile and compressive stresses, dependent upon the position, magnitude, and direction. The tensile stress developed within the setae keeps increasing up to the threshold value of the adhesive force, after which it results in the detachment of the setae from the substrate. A system of simple attached springs and dampers, as depicted in Figure 3.1, is used to model the setae arrays with an assumption that a small fraction of energy would be lost when an external force is applied to the system. The resistance to motion is assumed to be directly proportional to the velocity (viscous damping) and naturally opposes the motion. The springs are assumed to be linear and behave according to Hooke's Law. All the springs in the system are identical in length, have an equal separation, and are connected to a rigid beam. We assume that the stiffness of the fibrillar structures is much lower than that of the lamellae, so that considering the lamellae as rigid is a reasonable approximation. The model also assumes a constant adhesive force at the point of contact between the setae

tips and the substrate, regardless of the basic physical mechanism of adhesion, which may involve capillary attraction, van der Waals interactions, and other bonding mechanisms.

Figure 3.1 Spring-damper systems representing the setae arrays

The dynamic equations of any systems can be derived by the Newtonian approach or the Lagrangian approach. In the Lagrangian approach, the differential equations are formulated in terms of the two basic forms of energy contained in a system: the kinetic energy and the potential energy. While there are a large number of interacting forces in the modeled system, there are only two forms of energy. Thus by expressing the Newtonian mechanics in terms of energies, the formulation is simpler. Furthermore, the

energy in a system is a scalar quantity which is expressible in terms of the system coordinates. It is therefore convenient to express the dynamic equations in terms of the energy of the system. Including the dissipation term (E_D) to account for the expected energy loss, the Lagrangian equation can be written as [71],

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_i} \right) - \frac{\partial T}{\partial q_i} + \frac{\partial U}{\partial \dot{q}_i} + \frac{\partial E_D}{\partial \dot{q}_i} = 0 \quad (3.1)$$

where T , U , E_D , and q are the kinetic energy, potential energy, dissipation energy, and generalized coordinates involved in the system, respectively. As the external load is applied to the system, the rigid beam moves to its new equilibrium position and the load is transferred to each single spring that supports the beam. When the restoring force developed in the spring exceeds the binding adhesive force at the end of the setae, the seta is detached from the substrate and the rigid beam finds its new equilibrium position until all the springs in the system are detached. With this model, the effectiveness of detachment mechanisms is explored with respect to each single variable in the system. As seen in Figure 3.1, the variables encompass the mass of the spring-damper system m and the rigid beam M , the position d and orientation α of the applied load F_{pull} , and the contact length L_C . The solution of any specific problem provides us with the position of the leftmost spring in coordinates x , y and the tilting angle of the rigid beam θ that indicate the amount of deformation experienced by each single spring in the system.

The kinetic energy T of the systems above includes the translational and the rotational kinetic energy. The total kinetic energy can be written as,

$$T = \frac{1}{2} \left(\frac{1}{2} m \right) \sum_{i=0}^{n-1} [\dot{x}_i^2 + \dot{y}_i^2] + \frac{1}{2} M [\dot{x}_b^2 + \dot{y}_b^2] + \frac{1}{2} I_c \dot{\theta}^2 \quad (3.2)$$

The first and second terms of equation (3.2) are the translational kinetic energy of the springs and the rigid beam, respectively. The last term represents the rotational kinetic energy of the rigid beam, where I_c is the inertia mass about the centre of mass of the rigid beam.

The potential energy U has two components – one due to the spring and the other due to the gravitational potential. The potential energy can be written as,

$$U = \frac{1}{2} k_x \sum_{i=0}^{n-1} \left[x + \frac{iL_c}{n-1} (\cos \theta - 1) \right]^2 + \frac{1}{2} k_y \sum_{i=0}^{n-1} \left(y + \frac{iL_c}{n-1} \sin \theta \right)^2 - \\ Mg \left(y + \frac{L_c}{2} \sin \theta \right) - \left(\frac{1}{2} m \right) g \sum_{i=0}^{n-1} \left(y + \frac{iL_c}{n-1} \sin \theta \right) - F_x [x + d(\cos \theta - 1)] - \\ F_y (y + d \sin \theta) \quad (3.3)$$

The first and second terms of equation (3.3) are the potential energy due to the elongation or compression of the spring in the x - and y -directions, respectively. The third and fourth terms of equation (3.3) represent the potential energy due to the gravitational potential of the beam and springs, respectively. The last two terms of the equation represents the work done due to external load F_{pull} .

The dissipative term E_D needs to be included in the system to account for the frictional elements in the system. In fluid dynamics, the friction force is the force that resists the movement of a solid object through a fluid and its magnitude is approximately proportional to velocity, but opposite in direction. The frictional element (damper) represents the combined effects of all the various mechanisms for dissipating energy in the system, including friction, air resistance, deformation losses, and so on. The velocity dependent potential is introduced in equation (3.4) to give the resistive force upon differentiation by $\dot{q}$,

$$E_D = \frac{1}{2} b_x \sum_{i=0}^{n-1} \left[\dot{x} - \frac{iL_C}{n-1} \dot{\theta} \sin \theta \right]^2 + \frac{1}{2} b_y \sum_{i=0}^{n-1} \left[\dot{y} + \frac{iL_C}{n-1} \dot{\theta} \cos \theta \right]^2 \quad (3.4)$$

The first and second terms of equation (3.4) represent the dissipative elements developed in the x - and y -direction, respectively.

Having substituted the kinetic, potential, and dissipative terms back into equation (3.1), we obtain the second-order differential equations for the system. The system of differential equations of this model is too complicated to solve analytically, so a numerical approach is necessary to obtain the approximate solution of the problem. The traditional method for solving a system of higher order differential equations requires the equations to be converted to the equivalent first order equations. A solution to the system of ordinary differential equations (ODE) derived was first solved using the Runge-Kutta Method and Numerical Differentiation Formulas (NDF), as implemented in the commercial numerical algebra package, MATLAB (The MathWorks, Inc). However, the implementation of Runge-Kutta method in this problem was found to be inappropriate. Although Runge-Kutta method allows a variable step size, where the step size is continually adjusted to achieve a specified precision with a minimum number of steps, instabilities still arise due to the widely different decaying rates of the two variables in the system. When too small a value of step size was used, an unnecessary amount of computation was carried out and this could lead to round-off error. On the other hand, when the value of step size was too large, the desired accuracy requirements were not met due to the errors induced by discretization. As seen in Figure 3.2, variable y oscillates approximately in the range of three orders larger than variable x . This phenomenon indicates that the problem is stiff and in this case, the numerical solution has its step size

limited more severely by the stability of the numerical technique than by the accuracy of the technique [72].

Figure 3.2 Variable x and y Convergence Histories using Runge-Kutta method

The Runge-Kutta is a one-step solver, i.e. the value of $y(t)$ for t before t_i does not directly affect the values of $y(t)$ for t after t_i . Other methods such as Numerical Differentiation

Formulas (NDF) and Backward Differentiation Formulas (BDF) take advantage of previously computed solution values and are referred to as multi-step methods. As seen in Figure 3.3, the NDF method can overcome the convergence problem shown in the Runge-Kutta method.

Figure 3.3 Variable x and y Convergence Histories using the NDF Method

Figure 3.4 Relationship between position and magnitude of detachment force at $\alpha = 30^\circ$

The adhesive force at the contact area of the setae tips $F_{contact}$ is assumed to be constant, and the angle α and position d of an external load F are varied to examine how these two factors affect the detachment effectiveness of the system. Let us consider the behavior of a springs-dampers system with respect to the position of applied load when the angle of the applied load is maintained at $\alpha = 30^\circ$. As an illustration, the following values were used for the variables in equations (3.1)-(3.4): $N = 100$, $m = 40 \times 10^{-12} \text{ g}$, $M = 700 \times 10^{-9} \text{ g}$, $b_x = b_y = 0.1 \text{ N} \cdot \text{s}/\text{m}$, $k_x = \frac{3EI}{L^3} = 0.24 \text{ N}/\text{m}$, $k_y = \frac{\pi R^2 E}{L} = 30 \text{ N}/\text{m}$, $F_{contact} = 5 \text{ nN}$. As shown in Figure 3.4, the detachment is found to be more effective when the load F is applied at the edges ($d = 0$ and $d = L_c$). The amount of force required to pull the first spring off the substrate is about $2.3 \times 10^{-7} \text{ N}$ and its magnitude

decreases gradually as more springs are detached from the substrate. The detachment of the individual fibril occurs when the adhesion resistance due to the intermolecular forces cannot balance the external pulling force. Applying a load at the edges not only introduces a stress concentration at the edges, but it also aims to reduce the overall detachment forces by detaching only a small number of fibrils/springs at any moment. This finding is in a good agreement with the experimental results carried out by Autumn et al. [9, 19] who observed a difference in the calculated (based on the assumption that all the setae-substrate bonds break simultaneously) and the observed pull-off force. They observed the maximum force to break the bond between a single seta and a flat substrate is on the order of $\approx 200 \mu N$. If all 6.5 million setae of a gecko would have to be broken simultaneously, the pull-off force would be of order $\approx 1.3 kN$, about a factor 30 larger than the maximal observed gecko pull-off force. This can be explained as the detachment of gecko setae does not occur simultaneously and it starts at the periphery of the contact area and propagates towards the center during pull-off. In actual circumstances, the fibrillar structures do not separate from the substrate by a simple cracking mechanism but by drawing out fibrils/springs that continue to hold the surfaces together as significant separation occurs. This mechanism has similarities to the crazing behavior in polymers [73] and fiber reinforcement of composite materials [74]. Essentially this mechanism would allow extra energy dissipation and move the fracture of the joint further from equilibrium.

Autumn et al. [9] further reported experimental data that the detachment force of a single seta of a gecko on a surface strongly depends on the orientation of pulling, with the optimal value achieved as the seta is pulled at an inclined angle of 30° with respect to the

tangent of the surface. While this behavior suggests that the pull-off force of a single seta in contact can be controlled by pulling in different directions, an open question is whether the adhesive strength of a large array of fibers or a macroscopic attachment pad in contact with a rough surface would show similar behaviors. To address this question, we shall consider the issue of releasable adhesion from the point of view of a “system” rather than the individual seta. The springs and dampers model in Figure 3.1 is used to show that the pull-off force of a system also exhibits a directional dependence, similar to the behavior of a single seta.

Figure 3.5 Relationship between angle and magnitude of detachment force at $d = 0$

Figure 3.5 shows that the springs and dampers system demonstrate an anisotropic behavior with the optimal detachment angle at 90° with respect to the substrate. The

variation in pull-off force is observed as the pulling angle varies. By applying the external load perpendicular to the substrate, the pulling action of the fibrils/springs is accentuated and the separation distance between the two adhering surfaces increases, leading to a more effective detachment. This anisotropic behavior of fibrillar structures allows the adhesion strength to vary strongly with the direction of pulling. In other words, releasable adhesion can be achieved via an orientation-controlled switch between strong and weak adhesion.

3.2 Attachment of Fibrillar Structures on Rough Surface

It has long been realized that surface roughness on a microscopic scale causes the real area of contact to be extremely small compared to the nominal area. The calculation of the area of contact, or even the prediction of how this varies with load, is difficult because the area of the contact depends on the radius of the asperity, which is not usually known. Greenwood and Williamson [75] considered a flat surface covered with spherical asperities. They assumed that the heights of the asperities were represented by a well-defined continuous distribution function. The same approach is used here to solve the contact problem of fibrillar structures on a randomly rough surface whose height distribution is exponential.

Figure 3.6 Contact of fibrillar structures and randomly rough surface

The attachment pad of geckos was modeled by arrays of elastic springs attached to a rigid surface, as shown in Figure 3.6. The elastic springs were assumed to cover the entire area of the attachment pad and the stiffness is much lower than that of the backing surface, so that considering the backing surface as rigid is a reasonable approximation. The randomly rough surface is modeled as a nominally flat surface covered with a large number of asperities. If the two surfaces come together until their reference planes are separated by a distance d_p , then there will be contact at any asperity whose height was originally greater than d_p . Thus, the probability of making contact at any given asperity, of height z , is

$$prob(z \geq d_p - L_0) = \int_{d_p - L_0}^{\infty} \phi(z) dz \quad (3.5)$$

and if there are N_A asperities in all, the expected number of contacts will be

$$n_c = N_A \int_{d_p - L_0}^{\infty} \phi(z) dz \quad (3.6)$$

Also, since $L_d = d_p - z$ and the contact load $P_i = \frac{\pi R^2 E}{L_0} (L_0 - L_d)$, then the mean load is

$$\int_{d_p - L_0}^{\infty} \frac{\pi R^2 E}{L_0} (L_0 - d_p + z) \phi(z) dz \quad (3.7)$$

where R is the radius and E is the Young's modulus of the elastic spring. The expected total load is given by

$$P_T = \int_{d_p - L_0}^{\infty} \frac{\pi R^2 E N_A}{L_0} (L_0 - d_p + z) \phi(z) dz \quad (3.8)$$

It is convenient to introduce standardized variables, and describe the heights in terms of the standard deviation σ_h of the height distribution. The surface density of asperities η was introduced and $N_A = \eta A_{app}$ where A_{app} is the apparent contact area. This gives

$$P_T = \int_h^{\infty} \frac{\pi R^2 E \eta A_{app} \sigma_h}{L_0} (s - h) \phi^*(s) ds \quad (3.9)$$

where h , the standardized separation, is equal to $(d_p - L_0)/\sigma_h$ and $\phi^*(s)$, the standardized height distribution, is the height distribution scaled to make its standard deviation unity.

Assume that the probability density function $\phi^*(s)$ of the height distribution is exponential,

$$\phi^*(s) = e^{-s} \quad (3.10)$$

then

$$P_T = \int_h^{\infty} \frac{\pi R^2 E \eta A_{app} \sigma_h}{L_0} (s - h) e^{-s} ds \quad (3.11)$$

Similarly, we find the expected number of contacts is

$$n_c = \int_h^{\infty} \eta A_{app} e^{-s} ds \quad (3.12)$$

Using physically reasonable values for the parameters, we have calculated the relations between the load and the separation and the number of contact spots. Figure 3.7 shows how the separation varies with the load, calculated for a nominal area $A_{app} = 1 \text{ cm}^2$, asperities density $\eta = 4 \times 10^6 / \text{mm}^2$, fibrils' elastic modulus $E = 1 \times 10^9 \text{ Pa}$, fibrils' radius $R = 200 \text{ nm}$, and fibrils' length $L_0 = 5 \text{ }\mu\text{m}$.

Figure 3.7 Relation between the separation and the load, assuming an exponential distribution of asperity heights.

Though it is obvious from equation (3.12) that the number of contact spots could be increased by reducing the separation distance, merely reducing the separation from $3\sigma_h$ to σ_h would cause an increase of contact load nearly seven-fold from 0.15 N to 1 N . One major concern that arises from this finding is the durability of such fibrillar structures when they are exposed to frequent loading and unloading process. Northen and Turner [14] previously reported that their fabricated fibrillar structures can provide no further adhesion after going through frequent attachment and detachment cycles. This

durability problem could be resolved by adopting suitable materials and geometry (lower Young's modulus, slender and longer fibrils), which are sufficiently flexible so as to improve the resistance to attachment and detachment cycles. It should be noted, however, that reducing the separation distance by applying preload could only result in a temporary increase in the number of contacts. If the surface forces holding contacts in touch with the substrate is lower than the restoring force from the springs, the contacts will be lost as soon as the preload is removed.

Figure 3.8 Relation between the load and the number of contact spots for patterned and solid surfaces. The load and number of contact spots is capped at the point when normalized separation $h = 0$.

Figure 3.8 shows that the number of contacts is roughly proportional to the contact load for both patterned (fibrillar structures) and solid surfaces. The patterned surface, however, appears to be much more effective than the solid surface, in that amount of load exerted onto the contacting surface when achieving the same number of contact spots is

relatively lower than that on the solid surface. This could be explained due to the low effective elastic modulus of the fibrillar structures. Many biological attachment pads adopt the same fundamental mechanism to generate “sticky” surfaces [11]. They have the distinct ability to make contact with a variety of surfaces while using materials considerably stiffer than those used in pressure sensitive adhesives.

3.3 Anti-bunching Condition for Fibrillar Structures

In addition to the setae-substrate adhesion, the surface forces can lead to the setae-setae adhesion, giving rise to the problem of bunching. When two neighboring setae tips are in close proximity, surface forces cause the fibrils to jump into contact, effectively sticking the two together. Furthermore, if this sticking occurs on a large scale (many setae stuck together) bunching is said to have occurred. Bunching between neighboring setae is to be avoided as the adhesive capacity of the microstructure is reduced when only a small fraction of spatulas make physical contact with the surface. Bunching of the artificial setae has been reported to be one of the mechanisms responsible for reduction of adhesion strength [12]. Hence the anti-bunching condition in fibrillar structures has to be taken into consideration in the design of gecko-inspired adhesives. An anti-bunching condition has been previously derived by Hui et al. [76] and Gao et al. [58] for fibrils of square cross section. In this study, we focus on the cylindrical fibrils that have been considered by Glassmaker et al. [77].

Figure 3.9 Two neighboring fibrils in contact

Let us consider the fibrils as long beams with circular cross-sections of radius R and separated by a distance $2w$, as shown in Figure 3.9. When the two fibrils are in contact, the contact radius can be determined using the JKR theory [78],

$$r_c = \left(\frac{32R^2\gamma(1-\nu^2)}{\pi E} \right)^{1/3} \quad (3.13)$$

where γ is the fibrils' surface energy, and E and ν denote the Young's modulus and Poisson's ratio of the material, respectively. The elastic energy U_C stored in the fibrils is computed using contact equilibrium,

$$\frac{\partial U_C}{\partial r_c} = 4\gamma \quad (3.14)$$

The strain energy U_B associated with the fibrils bending in Figure 3.9 can be written as,

$$U_B = \frac{3E\pi R^4 w^2}{L^3} \quad (3.15)$$

When the length of the non-contact fibrils is increased by dL , the decrease in strain energy is,

$$-\frac{dU_B}{dL} = \frac{9E\pi R^4 w^2}{L^4} \quad (3.16)$$

By equating the decrease in strain energy with the energy required to separate the two surfaces, the length of the non-contact fibrils can be calculated as,

$$2\gamma(2r_c)dL - U_c dL \quad (3.17)$$

The length of the fibrils L^* has to be less than the length of the non-contact fibrils to avoid bunching,

$$L^* < \left(\frac{\pi^4 ER}{2^{11} \gamma (1 - \nu^2)} \right)^{1/12} \left(\frac{12ER^3 w^2}{\gamma} \right)^{1/4} \quad (3.18)$$

In addition to the geometric restrictions, it is apparent from equation (3.18) that the surface property of the materials could help avoid the bunching problem. A hydrophobic material has a lower surface energy than a hydrophilic material, resulting in the larger values of critical fibrils length to avoid bunching.

For the gecko setae, we have $\gamma = 5 \text{ mJ} / \text{m}^2$, $E = 1 \text{ GPa}$, $\nu = 0.3$, $R = 5 \text{ }\mu\text{m}$, $w = 2 \text{ }\mu\text{m}$ [9, 13], giving $L^* < \sim 485 \text{ }\mu\text{m}$ which is consistent with the length of natural seta, i.e. $100 \text{ }\mu\text{m}$. In the case of the gecko spatulas, we have exactly the same material properties, except $R \approx 200 \text{ nm}$ and $w \approx 200 \text{ nm}$, so that $L^* < \sim 14 \text{ }\mu\text{m}$. It should be noted that the fabrication of the synthetic gecko spatulas in Chapter 5 follows the anti-bunching condition, defined in equation (3.10), giving rise to the maximum length of nanofibrils of $\sim 2.5 \text{ }\mu\text{m}$ for a given set of material properties $\gamma \approx 30 \text{ mJ} / \text{m}^2$, $E \approx 2.8 \text{ GPa}$, $\nu = 0.3$, $R \approx 125 \text{ nm}$, and $w \approx 75 \text{ nm}$ [53, 79].

In Chapter 6, we will discuss a novel fabrication technique to develop synthetic hierarchical gecko foot-hairs using an alumina template with PMMA used as the filling

materials. The anti-bunching condition was also applied to the design of the synthetic setae and spatulas. For a given surface free energy $\gamma \approx 40 \text{ mJ/m}^2$ [80], geometries $R \approx 30 \text{ nm}$, $w \approx 20 \text{ nm}$, and material properties $E \approx 2.5 \text{ GPa}$, $\nu = 0.3$, we get $L^* < \sim 450 \text{ nm}$ as a constraint to avoid lateral collapse of the nanofibrils. We should note, however, that adjusting the geometrical arrangement of the spatulas array is not straightforward due to the nature of the hexagonal porous structure in an self-ordered alumina membrane. Therefore, choosing a suitable material with a lower surface free energy and a higher elastic modulus would help avoid the bunching problems yet still maximize the density and aspect ratio of the fibrils. These will be further elaborated in Chapter 6.

3.4 Hierarchical Fibrillar Structures for Robust Adhesion and Efficient Detachment

As discussed in the previous section, fibrillar interfaces are capable of making contact with and adhering to a variety of surfaces with varying degrees of roughness. This mechanism is important to biological adhesion as animals in their natural habitats encounter many types of surfaces, each with its own roughness characteristics. Many conventional adhesives suffer a reduction in adhesion when they make contact with a rough surface. For example, pressure sensitive adhesives are found to be ineffective on non-smooth surfaces and are easily fouled by particulate contaminants. On the other hand, a patterned fibrillar surface is capable of maintaining contact and adhesion properties against rough and dirty surfaces. Any particulate contaminants on the surface

would only result in the failures of some microcontacts, minimally affecting the overall contact adhesion.

From the theoretical standpoint, Yao and Gao [81] developed a bottom-up designed fractal hair structure as a model to demonstrate that hierarchical fibrillar structures can lead to robust adhesion at macroscopic scales. The work of adhesion of a single-level fibrillar structures is defined as the differential surface energy $\Delta\gamma = \gamma_f + \gamma_s - \gamma_{fs}$, where $\gamma_f, \gamma_s, \gamma_{fs}$ denote the surface energies of fibril, substrate, and fibril-substrate interface, respectively. This interpretation is valid only in the absence of other dissipation mechanisms. For a large fibril with a hairy surface in contact with a substrate, resulting in a two-leveled structure, the work of adhesion is no longer equal to $\Delta\gamma$ even though the small thin fibrils at the tip interact with the substrate only via intermolecular interaction forces. The elastic deformation of the fibrils makes significant contributions to the separation process and adhesion failure occurs by an abrupt drop in stress near the theoretical strength of surface interaction. The work of adhesion would, therefore, include the elastic energy stored in the fibrils when they are stretched to failure, i.e.

$$W_{ad} = \left(\Delta\gamma + \frac{\sigma_{th}^2 L}{2E} \right) \varphi, \text{ where } \sigma_{th}, L, \varphi \text{ denote the theoretical adhesion strength, the}$$

length of the fibrils, and the area fraction of the fibril array, respectively. Increasing the structural levels of the fibrillar structures could enhance the work of adhesion and therefore, contribute to the robust adhesion at the macroscopic scales.

Figure 3.10 Contact of hierarchical fibrillar structures and randomly rough surface

Now let us consider a large fibril with an array of thinner fibrils on its tip surface, as shown in Figure 3.10. At mechanical equilibrium of the system, the resulting force on B is zero. Now, suppose that point C be moved by a distance Δz_C , and that the free end of each of the n springs is immobile. To recover a null force on B , the latter moves over a distance Δz_B related to Δz_C by:

$$\Delta z_B = \frac{k_C}{K + k_C} \Delta z_C \quad (3.19)$$

in which $K = nk_B$. The increase of force applied to the n springs is therefore:

$$\Delta F = K \Delta z_B = \frac{K k_C}{K + k_C} \Delta z_C \quad (3.20)$$

This makes clear that the apparent loading $F_C = k_C \Delta z_C$ is in general not the loading actually applied to the n springs to be detached from the surface. The actual loading ΔF is smaller than F_C or at most equal to it because the equivalent stiffness k_{eq} of the n -

spring system, defined by $k_{eq} = \frac{Kk_C}{K + k_C}$, is smaller than or at most equal to k_C . If the global stiffness K is much smaller than the stiffness of the large fibril k_C (“stiff fibril”), equation (3.20) leads to:

$$\Delta F \approx nk_B \Delta z_C \ll F_C \quad (3.21)$$

On the other hand, if K is much larger than k_C (“soft fibril”), then:

$$\Delta F \approx k_C \Delta z_C = F_C \quad (3.22)$$

It follows from equation (3.20) that the loading on a bond is, in general, not uniquely determined by the pulling/pushing distance Δz_C and the stiffness k_C of the large fibril. In addition, it follows from equations (3.21) and (3.22) that the loading of an individual bond, $\Delta f = \frac{\Delta F}{n}$, is independent from the number of bonds in the limit of a very stiff fibril, whereas it is inversely proportional to the number of bonds in the limit of a very soft fibril.

For the gecko’s seta, we have $k_C \approx 800 \text{ N/m}$ for a given radius $R = 5 \mu\text{m}$, length $L = 100 \mu\text{m}$, and Young’s modulus $E = 1 \text{ GPa}$. At the end of the seta there exists an array of spatulas, each with a stiffness of $k_B \approx 60 \text{ N/m}$ for a given radius $R = 200 \text{ nm}$, length $L = 2 \mu\text{m}$, and Young’s modulus $E = 1 \text{ GPa}$. The two stiffness values imply the “stiff-fibril” condition as described in equation (3.21). The actual loading that is experienced by the spatulas ΔF happens to be much smaller than that being applied to the seta F_C , therefore hindering the influence of preloading force used to increase the surface contact with the substrate.

We should note, however, that the stiffness of the seta is considerably reduced when the setae are inclined at an angle other than 90° . One can use simple beam theory to obtain its value if the setae are oriented at angle ϑ to the backing,

$$k_{\vartheta} = \frac{\pi R^2 E}{L \sin \theta \left(1 + \frac{4L^2}{3R^2 \tan^2 \vartheta} \right)} \quad (3.23)$$

where R, L, E denote the radius, length, and Young's modulus of the seta, respectively.

Figure 3.11 Relation between seta stiffness and seta angle measured from the backing surface

Figure 3.11 plots the relation between the stiffness and the angle of individual seta measured from the backing surface. If we consider a seta oriented at an angle of 30° , the seta stiffness is reduced by nearly 800 times than the seta oriented normal to the backing surface, resulting in the “soft-fibril” condition as described in equation (3.22). In this case, the actual loading that is applied to the spatulas ΔF would be the same as that

being applied to the seta F_C . In other words, the preloading and detachment forces are most effectively applied when the seta is at its most compliant configuration. The above analysis is indeed consistent with Autumn's experimental data [9], that is the seta detaches from the substrate when the angle between the seta and the substrate reaches 30° angle. At this orientation, the seta is relatively compliant, ensuring an effective transfer of load from the seta to the spatulas array. The "soft-and-stiff-fibril" behavior appears to have enabled the geckos to switch between a strong adhesion and an effective detachment during locomotion. When the gecko is in the standstill position, it would orient the setae array perpendicularly to the substrate so as to minimize the body-weight gravity effect to achieve the optimum adhesion. On the other hand, the gecko would orient the setae array in its most compliant configuration when there is a need to detach and re-initiate the setae attachment to the substrate.

3.5 Summary

In this chapter, we studied four theoretical aspects of fibrillar structures. First, we have shown that the peeling action of the fibrillar structures is capable of reducing the overall detachment forces by detaching only a small number of fibrils/springs at any moment. Second, patterned surface was found to have a better contact with rough substrate due to the reduction of effective elastic modulus in fibrillar structures. The attachment and detachment effectiveness of fibrillar structures direct us to the fabrication of fibrillar nanostructures in Chapter 5. Third, we have confirmed that the anti-bunching condition derived theoretically matches the design of fibrillar structures (setae and spatulas) in nature. Similar geometrical control was adopted in the fabrication of synthetic gecko

foot-hairs (Chapter 5 and 6) to avoid the bunching problem between neighboring fibrils. And fourth, we have studied the effects of compliance and effective load transfer for robust and releasable adhesion in hierarchical fibrillar structures. The fabrication of hierarchical structures will be discussed in more detail in Chapter 6.

CHAPTER 4

Role of Capillary Forces in Geckos Adhesion

Understanding the adhesion mechanism of biological attachment systems is of great scientific interest and a prerequisite for developing biologically inspired adhesive systems. As already discussed in Chapter 2, intermolecular adhesion plays a dominant role in the adhesion of geckos' setae. Here, a new insight based on meniscus capillary forces will be presented.

4.1 Capillary Forces Hypothesis

To date, adhesion experiments have been conducted on a whole foot [22, 32] and a single seta [9, 19] of geckos. Early studies of geckos' adhesion proposed capillary forces due to liquid bridges [22, 82], but a recent investigation rejected the contribution of capillary forces and indicated that van der Waals forces alone can give rise to the high adhesion observed [19]. The reported experimental results, however, are inadequate to understand the nature of the force, given the fact that the total force between two surfaces in close proximity is very complex, consisting of up to eleven components, such as van der Waals forces, electrostatic forces, capillary forces, and so on [20]. Even under very dry conditions with relative humidity below 10%, the adsorbed water layer with a thickness ranging between a few Angstrom and several nanometers is still observed [83]. Liquids from the environment spontaneously condense from the vapor phase to the liquid state on the surface cavities of any substances. These capillary forces of water films can

significantly influence the attraction between two surfaces [84, 85]. Dependent upon the operating and environmental conditions (surface tension, relative humidity, contacting geometry), the capillary forces can be large for most cases as compared to weak van der Waals forces [85].

Figure 4.1 Comparison of van der Waals and capillary forces between a SFM tip and a surface. z_0 indicates the distance at which the meniscus is built, γ is the surface tension, θ_1 and θ_2 is the contact angle of the liquid at the surface and the tip, respectively, c is a constant that defines the shape of the tip (approximated by the tip diameter), p_0 is the normal vapor pressure of meniscus liquid, and p is the pressure acting outside the meniscus surface, and D defines the separation distance between the tip and the surface. Values for the van der Waals curves (dashed): tip width 20 nm; Hamaker constants 0.04 and 3.0×10^{-19} J. The capillary forces show the range for different humidities. [85]

The two dashed curves in Figure 4.1 show the spread of possible van der Waals forces for a SFM system. The two solid curves are capillary forces indicating the range

for different humidities. Capillary forces have weaker distance dependence as compared to van der Waals forces and its magnitude can be stronger or weaker than that of van der Waals forces for distances smaller than 0.5 nm. For greater distances the capillary forces were found to be stronger than the van der Waals forces.

4.2 Materials and Methods

The invention of the atomic force microscope (AFM) in 1986 by Binnig et al. [86] has brought about new opportunities to study surface and material properties at the subnanometer scale as well as to enable the study of interaction forces between two objects in a controlled environment by the force-distance method with sensitivity in the piconewton range [87]. It was previously used to determine the adhesion force between a spider leg seta and the flattened tip of a silicon nitride AFM cantilever [88]. In the following sections, we will discuss the experimental details of force measurement between a single gecko spatula and a tipless AFM cantilever in a controlled fluid environment.

4.2.1 Single Seta and Multiple Setae Sample Preparation

Analyses were performed on geckos of the species *Hemidactylus frenatus*. The adhesion force measurements were conducted on two different samples, which are a single seta and multiple setae samples. A single seta was prepared by shearing off a gecko's finger with the aid of sharp blade and a needle tip, as shown in Figure 4.2. An electrochemically etched tungsten tip was mounted to an X-Y-Z micromanipulator and a small amount of 5-

minute epoxy was applied to the tip. After waiting for about 1 minute, the tip was positioned to the vicinity of the seta by the manipulator, while the process was monitored through a stereomicroscope. After 30 seconds, the manipulator lifted the tip up. If the seta was not attached to the tip, the same procedure was repeated. Once the tip with a seta on it was obtained, it was glued to a magnetic plate with the seta pointing up. For multiple setae sample preparation, a fresh single gecko's finger was glued by 5 minute epoxy to a magnetic sample plate of an AFM with the gecko's setae facing up. In order to avoid sample contamination, the epoxy was applied only 2 minutes later to allow it to harden partially and increase its viscosity.

Figure 4.2 (a) Setae were sheared off a gecko finger using a sharp blade. (b) A group of setae was attracted to the needle tip by intermolecular attraction forces. (c) A single seta is glued to the needle tip.

4.2.2 Preparation of Hydrophobic and Hydrophilic Cantilever Surfaces

Cantilevers with surfaces of different contact angles were produced by varying the surface chemistry of silicon by silanization. The AFM silicon cantilever (CSG11, Nano Technology Instruments, Europe) is hydrophilic with a contact angle of 29° due to the native oxide layer on its surface. The hydrophobic surface was prepared by immersing

the silicon cantilever into a 2% weight/volume of dimethyldichlorosilane in octamethylcyclotetrasiloxane solution (Amersham Biosciences) for 15 minutes. The process was followed by baking the cantilever at 100 °C for one hour. The contact angle of the treated silicon cantilever was measured to be 110°.

4.2.3 Adhesion force measurement of a single spatula

Adhesion force measurements were performed using a commercial AFM (Multimode, Veeco, Santa Barbara, CA). A tipless silicon cantilever (250 ± 5 μm long and 35 ± 3 μm wide) with a spring constant of 1 N/m was used in this study and calibrated with resonant frequency measurements [89] prior to conducting any adhesion measurements. The sample was mounted on a piezoelectric lead zirconate titanate (PZT) tube scanner, which moved the sample in the x, y, and z directions. The sample was slowly brought into contact with the cantilever and subsequently retracted. The procedure was recorded by a PicoForce scanner (Veeco). The schematic diagram of experimental setup is shown in Figure 4.3.

Figure 4.3 Experimental setup for adhesion force measurement of a single spatula.

Two types of experiments were performed: First, hydrophobic and hydrophilic cantilevers were used to assess the capillary forces contribution in the adhesion of geckos' setae. Cantilever deflection was transformed into force values, according to the calibration of the instrumental set-up, and plotted against the sample displacement in the z-direction to obtain a force-displacement curve as shown in Figure 4.4. The adhesion force in AFM can be measured by measuring the force necessary to break the sample away from the cantilever, which can be deduced from a force-displacement plot. As the distance between the sample and the cantilever is reduced, the cantilever suddenly moves towards the sample (jump-in) when the attraction force exceeds the spring constant of the cantilever. Once the water layers on the cantilever and sample make contact, the capillary force will become important. Upon retracting the cantilever, the distance at which the cantilever breaks away from the sample is larger than the jump-in distance due to the adhesion force. This force can be calculated from the distance moved to break the cantilever away from the sample and the spring constant of the cantilever.

Figure 4.4 Typical force-displacement curve of atomic force microscope.

The second type of experiment involved controlled variation of air humidity. To control the relative humidity, the experiments were conducted in a chamber purged with nitrogen gas of known humidity. The desired relative humidity in the purge gas was obtained by mixing streams of dry and wet nitrogen (prepared by bubbling nitrogen gas through distilled water) at an appropriate flow ratio. The relative humidity in the chamber was measured by a digital hygrometer (VWR Scientific, Philadelphia, PA).

Figure 4.5 Force-displacement curves of geckos' spatulas using (a) an isolated seta and (b) multi-setae samples, measured with a silicon cantilever with a spring constant of 0.1 N/m, in air with relative humidity of 70%. The black and red lines are the extending and retracting curves, respectively.

4.3 Results and Discussion

Figure 4.5a shows the typical force-displacement curve of geckos' spatulas measured by a rectangular silicon cantilever using an isolated single seta sample. The force magnitude of a saw-tooth is related to the force contribution of individual spatulas through a complex interdependent network of effective spatula stalk springs. However the first (during contact) and last (during release) saw-tooth data represent isolated events. The saw-tooth pattern is proof that the cantilever touched only the spatulas rather than the gecko's skin. It is possible that more than one spatula may have almost the same height and contact or release from the cantilever surface simultaneously. In such a case, the measured adhesion force would be significantly stronger. More than 50 measurements were carried out in each experiment to find the most probable value, distinguishing multi-spatulas adhesion results from the more frequent single spatula event. The measured adhesion force for a single spatula can be deduced by this analysis although there are

hundreds of spatulas on each seta. Figure 4.5b shows a force-displacement curve of geckos' spatulas using multi-setae sample, which is similar to Figure 4.5a. The experimental observations indicate that the force interaction between a single spatula and the cantilever can be measured either with a single seta or multi-setae samples. For all subsequent testings multi-seta samples were used due to the simplicity of the sample preparation.

Figure 4.6 Histograms of forces measured with (a) hydrophobic and (b) hydrophilic silicon cantilevers.

As the variation in force with surface hydrophobicity is a major feature of capillary forces [90], modification of the cantilever hydrophobicity is a conventional way to determine its amplitude. We have measured the cantilever-gecko force interaction with hydrophilic and hydrophobic silicon cantilevers with surface water contact angles of 30° and 110° , respectively. The mean adhesion force derived from histograms (shown in Figure 4.6) was 11.8 and 4.9 nN, respectively, which suggests that the dominating component of the gecko force is the capillary force as the amplitude of van der Waals

force decreases instead of increases with the increase in water between the surface and the spatula [21].

Table 4.1 Spatula Adhesion Force

Contact angle	Environment	Force (nN)	Mean $\pm$ SD (nN)
30°	Dry nitrogen	4.4	0.8
30°	70% RH	11.8	2.2
30°	Wet nitrogen	6.2	1.2
110°	70% RH	4.9	0.9
N.A.	Water	1.8	0.5

Force-distance measurements at different relative humidity (RH) were performed to confirm the above derived conclusion. A measurement was first taken at normal laboratory conditions with RH of 70%, which yielded a mean adhesion force of 11.8 nN. The sample was then purged with dry nitrogen for 20 minutes, which caused the adhesion force to drop to 4.4 nN. Finally, the sample was exposed to wet nitrogen for 15 min, during which the mean force rose to 6.2 nN. The results confirmed that decreasing RH decreases the adhesion force and vice versa. All mean values of spatula's adhesion force and the standard deviations (SD) are listed in Table 4.1. It should be noted that the sample might change its position relative to the cantilever while blowing nitrogen. However, the statistical method adopted in the data analysis removes random error and we report the most probable force value of a single spatula rather than any specific spatula. When the sample was immersed into water, the adhesion force decreased to less than 20% of its original value (see Table 4.1). This eliminates the possibility that the hydrogen bonding force could play a major role because its amplitude does not decrease

with increase of water [91]. This confirms that the dominant force in an ambient air environment is the capillary force.

It has been accepted that the dominant adhesion force between silicon nitride AFM cantilever and a mica surface is the capillary force [92]. As a control experiment, the interaction between a silicon nitride AFM cantilever and a fresh mica surface was conducted under the same conditions as the experiments with the gecko seta, i.e., in different RH and under deionized water. Because both systems (gecko spatula—tipless cantilever and the silicon nitride AFM cantilever—mica) showed identical trends, i.e., adhesion forces in air are proportional to the RH, we can assume that the nature of forces in both systems is the same. Moreover, it is also noted that the van der Waals forces increase in a lower RH environment because there is less screening from water [21]. Therefore, we conclude here that the van der Waals forces do not play a dominating role in the geckos' adhesion.

The experimental results show that the force between gecko spatula and an AFM cantilever exhibits behavior consistent with an adsorbed surface water layer. As long as there is the presence of surface water, capillary forces will exist. The only exception is when the gecko setae were completely submerged in water where the adhesion force dropped to ≈ 2 nN. However, even in this case there are other forces that might be stronger than the van der Waals forces, such as the double-layer forces, the hydration forces, and the hydrophobic forces.

As a simple way to illustrate the importance of the capillary forces, a live gecko was allowed to climb a dry vertical surface. Once sprayed with water, the gecko was unable to adhere to the surface. This technique of spraying geckos with water to remove them from

vertical surfaces is well known to zoologists. It shows that the adhesive force of a gecko is significantly reduced in the absence of capillary forces. Van der Waals forces may still play a role, but in ambient air the capillary forces dominate.

An unsolved mystery remains as to how geckos' spatulas self-clean. It has been observed that dirty gecko footprints disappear after a few steps when it moves onto a clean surface, demonstrating a self-cleaning mechanism, i.e. transfer of dust particles attached to the foot seta to the surface. This self-cleaning mechanism is a key property worthy of further study in order to successfully fabricate gecko mimicking adhesive tape suitable for practically any surface and many detachment-attachment cycles. Based on the capillary force explanation presented in this chapter, the self-cleaning mechanism can be explained by the two menisci formed between the particle and a spatula, and the particle and the surface. Since the size of single spatula is only 100 – 200 nm, the meniscus circumference between the particle and the surface is usually much larger than the meniscus with the spatula, resulting in a larger force, and an overall effect of leaving small particles attached to the surface rather than the setae. Larger particles may adhere more strongly to the conformal setae however observations show that geckos also lick their paws occasionally, which could contribute to the self-cleaning effect [18].

4.4 Summary

In summary, the adhesion force produced by an individual gecko spatula was measured. As the gecko force was influenced by the surface hydrophobicity as well as the presence of water, it can be concluded that the dominating component of the adhesion force is the capillary force. This finding not only sets a benchmark for the performance of synthetic

structures, but it also epitomizes one of many intriguing natural phenomena that can be adapted to improve the technological know-how of humans, such as development of an artificial gecko mimicking device.

CHAPTER 5

Self-Assembled Nanoparticles based Fabrication of Gecko Foot-Hairs Inspired Polymer Nanofibers

As already discussed in Chapter 2, numerous fabrication techniques have been developed to produce novel adhesives by mimicking the nanostructures of gecko foot-hairs. In this chapter, the fabrication of gecko foot-hair inspired polymeric nanofibril structures by means of colloidal nanolithography, deep-silicon etching, and nanomolding will be introduced.

5.1 Polymeric Nanostructures Fabrication Process

Methods of fabricating patterned nanostructures include (i) lithography with photons [93], energetic particles [94], and scanning probes [95]; (ii) replication of masters using printing [96], molding [97], and embossing [98]; (iii) self-assembly [99]; (iv) shadowed evaporation [100]; and (v) size reduction such as an isotropic deformation of amorphous materials [101] and chemically anisotropic etching of single crystals [102]. In general most of the methods mentioned above are not meant for creating high aspect-ratio nanostructures. The development of cost-effective methods that are capable of forming high aspect-ratio nanostructures that do not suffer from lateral collapse represents one of the technical challenges facing nanofabrication.

In this chapter a new paradigm that combines a self-assembly patterning technique and semiconductor technologies is proposed to efficiently construct densely packed high

aspect-ratio nanostructures. The inexpensive method of colloidal nanolithography [103] as a facile patterning protocol, a modified silicon etching to form deep columnar trenches, and nanomolding are used to form the flexible polymeric nanostructures. The combination of methods offers the possibility of tailoring a compliant surface with nanofibrillar-features that replicate the basic morphology of gecko terminating nanostructures for potential adhesive applications. The role of the flexible membrane was further investigated in relation to the adhesion of the nanostructured surface on a macroscopic scale, and the “easy-to-clean” characteristic was associated with the role of water condensation / capillary forces formed between particulate contaminants and the substrate (see section 5.3).

Figure 5.1 Schematic flow of the fabrication process: (a) formation of monolayers, (b) etching back of polystyrene particles with oxygen plasma, (c) chromium deposition using e-beam evaporation, (d) polystyrene particles removal by ultrasonication in CHCl_3 , (e) deep silicon etch with $\text{SF}_6 + \text{C}_4\text{F}_8$, (f) parylene deposition, (g) complete silicon etch with XeF_2 .

Figure 5.1 shows a schematic illustration of the fabrication procedure developed for creating high aspect-ratio polymer nanofibrils supported by a flexible polymer film. The process started with the formation of monolayers of particles on a silicon substrate,

followed by etching back of the particles, metal deposition, and particle removal to obtain a regular array of nanoholes. Colloidal nanolithography was used here as it provides a much simpler, faster, and cheaper approach than complex semiconductor nanolithography technology for creating patterns in the nanometers and submicron range. A thorough understanding of the fundamental mechanisms that determine etching anisotropy is critical to meet the challenge of obtaining deep, narrow, columnar trenches in the submicron region with an aspect-ratio as high as 1:10. A parylene vapor deposition process was used to fill the nano-trenches in the silicon substrate and finally a complete sacrificial-etching of the silicon mold was performed to obtain a freestanding nanostructured parylene film.

5.1.1 Colloidal Nanolithography

Colloidal particles have a number of attractive properties for the purpose of surface nanofabrication. Their ability to self-organize can be utilized to form ordered structures, and the parallel nature of the assembly process makes it possible to produce large numbers of nano sized features that cover large surface areas. In comparison, conventional nanofabrication methods based on electron beam lithography are exceedingly slow, and they are normally used for electronics applications where precise control of a small number of nanostructures is more important than high throughput.

Monolayers of colloidal particles are formed by self-assembly. Such two dimensional particle arrays are interesting for applications such as lithographic masks, optical gratings, multilens arrays, antireflecting surface, synthetic membranes, data storage media, etc. Many techniques have been examined for the fabrication of such arrays,

namely Langmuir Blodgett (LB) deposition method [104], self-assembled monolayer (SAM) [105], layer-by-layer (LbL) [106], electrophoretic deposition [107], and evaporation driven self-assembly [108]. The formation of monolayers using LB technique can be stable and ordered at the air-water interface, but the process of transfer to the solid substrate often leads to pin-hole defects with a coverage not more than 80% [109]. Both SAM and LbL techniques require an additional chemical step of surface modification, which in turn could cause an inhomogenous distribution of the monolayers. Another approach relies on electrophoretic deposition of particles onto an electrode. It has a drawback in the difficulty to control monolayer formation as areas thicker than a monolayer can be formed. In the case of evaporation driven self-assembly, the rate of evaporation plays a crucial role and the self-organization is sensitive to the surface topography and properties of the substrate. Recently, Aveyard et al. [110] investigated the monolayer behavior of polystyrene (PS) particles at the water/octane interface and found a formation of highly ordered arrays of large 1.5 μm and 2.6 μm particles.

Here, a method of trapping colloidal particles at the liquid surface combined with a water seepage technique is adopted to form a close-packed two-dimensional array of colloidal particles on a solid substrate. It consists of the preparation of monolayers at the liquids interface followed by slow draining of the aqueous subphase, which causes gradual descent and finally deposition of the monolayer onto a surface located within the subphase. The method is both cost-effective and time-saving, and can be easily scaled up for industrial application or scaled down for the purpose of coating objects with expensive materials.

Chemicals and materials

All experiments were carried out in a class 100 cleanroom. Silicon wafers (n-/p- type, (100) oriented, 450-500 μm thick, and 4" diameter) were obtained from Cemat Silicon. Sulfuric acid, hydrogen peroxide, ethanol, and hexane were purchased from Aldrich and used without further purification. Polybead polystyrene (PS) microspheres, 356 ± 14 nm in diameter, were obtained from Polysciences and packaged in a 2.5% aqueous suspension. A laboratory-fabricated conical trough, as shown in Figure 5.2, was used in the experiment. The interior of the cylinder was made conical while the periphery was maintained in a cylindrical form in order to attain stability. A platform positioned at the center was firmly attached to the cylinder base and orifices located at the bottom connected to tubes that served as outlets for subphase seepage.

Figure 5.2 Laboratory-made conical trough for the formation of colloidal monolayers.

Experimental

Formation of a close-packed 2D array of colloidal particles on a solid substrate: Silicon wafers were cleaned in a piranha solution (a 3:1 mixture of 96% sulfuric acid with 30% hydrogen peroxide) at 120 °C for 20 minutes, rinsed with deionized water, and dried in a stream of dry nitrogen. The dispersion of PS microspheres was centrifuged at 7,500 rpm for 20 minutes, which caused sedimentation of the particles and allowed removal of the aqueous suspension. The precipitated particles were collected, washed twice with ethanol, and re-suspended in an ethanol solution of spectroscopic grade at a concentration of 1 wt %. A silicon wafer was kept on a platform that was located at the centre of a conical trough as in Figure 5.2. The trough was filled with deionized water and a thin layer of hexane was introduced onto the water surface for trapping the monolayers. The ethanol suspension of the PS particles was spread onto the interface between water and hexane by using a pipette until the water surface was totally covered with monolayers. The water was then allowed to slowly seep out from the conical trough through the bottom orifices at a rate of 10 $\mu\text{l/s}$ to transfer the monolayers to the silicon substrate.

Formation of a non-closed-packed nanohole array chromium mask: An oxygen plasma etcher (Technics, Micro 800 RIE) operated at 0.1 Torr oxygen pressure, 20 sccm oxygen flow rate, and a power of 200 W was used to etch back the polystyrene particles for 90 seconds. A 500 Å layer of chromium was deposited using e-beam evaporator (CHA Industries, SE-600-RAP) at a pressure of 10^{-6} Torr with an average deposition rate of 2 Å/s. The substrate was then placed in the ultrasound bath filled with chloroform for 20 minutes for a complete removal of the polystyrene particles.

Results and Discussions

Monolayers of monodisperse colloidal particles on a solid substrate were prepared by trapping the monolayers at the water/hexane interface and transferring them onto the substrate by decreasing the water level in a conical trough. The conical trough was fabricated to realize gradual compression of the monolayer as it descends. The reduction in the surface area due to the tapering walls of the conical trough caused compression of the monolayer. When the water level went below the level of the silicon substrate, the monolayer was deposited. The substrate was left undisturbed for few hours to ensure that the water layer adhering to the surface of the substrate had evaporated and the monolayer of colloids was firmly anchored on the surface of the substrate. Figure 5.3 (a-b) shows the scanning electron microscopy (SEM) image of the ordered structures of polystyrene particles, 356 ± 14 nm in diameter, on a silicon substrate. Large close packed monolayers of about 1 cm^2 could be easily and quickly obtained by this method. The particles were subsequently etched-back using an oxygen plasma etcher resulting in a mean particle diameter of 250 ± 10 nm and an inter-particle spacing of 100 ± 10 nm, as illustrated in Figure 5.3 (c-d). The pitch and size of nanostructures could be well controlled by the starting size and subsequent dry etching of the particles. Some structural nonuniformity in the particle size, shape, and arrangement was caused by the nonuniform etching rate of the particles and defects in the aligned particle lattice. A more uniform fashion of colloidal monolayer array can be achieved using a confined convective assembly method as proposed by Kim et al [111].

Figure 5.3 (a) Colloidal monolayers of ~356 nm polystyrene particles on a silicon substrate. (b) Closed-packed hexagonally ordered array of nanoparticles. (c) ~250 nm etched back polystyrene particles after oxygen plasma treatment, (d) Non close-packed hexagonally ordered array of nanoparticles. (e) Nanoholes array of chromium layer. (f) Magnified image of (e).

A 500 Å layer of chromium was deposited using an e-beam evaporator. As the chromium was deposited on the substrate, the colloidal particles function as shadow masks to obstruct material deposition underneath them. The chromium deposition with a line-of-sight deposition tool such as the e-beam evaporator was crucial in order to ensure the nonconformality of the metal film. This is not only necessary for the pattern transfer, but also facilitates particle removal during the wet etching process with chloroform. After the particles were completely removed from the substrate, a regular array of nanoholes was obtained and used as the mask for silicon etching as illustrated in Figure 5.3 (e-f).

5.1.2 Anisotropic Nano-scale Silicon Etching

Deep etching of silicon has become an attractive technique since the emergence of microelectromechanical systems (MEMS). New commercially available etching tools from manufacturers such as Surface Technology Systems, Alcatel, or Applied Materials have rapidly come out to meet the increasing demand and are now capable of deep etching silicon beyond 300 µm. A new challenge consists of increasing the aspect ratio (depth/width) while keeping both a high etch rate and a high anisotropy. Dry etching is increasingly used in silicon etching because it provides better anisotropy than traditional wet processes, which are crystal orientation dependent. For low etch rates and low aspect ratios, standard reactive ion etching (RIE) equipment can typically be used. However, when deep anisotropic etching with high aspect ratios and high etch rates is needed, high density plasma and low pressure tools such as electron cyclotron resonance, inductively coupled plasma (ICP) are more suitable. The ion density is at least an order of magnitude higher than reactive ion etching systems and ion energy is independently controlled

[112]. At high density and low pressure, the ion collision probability is reduced as the sheath thickness decreases and the ion mean free path increases. Ion directionality is improved and a better control of anisotropy is achieved.

Fluorine based chemistries are commonly used to achieve high etch rates, however lateral etching is also high; thus compromising anisotropy. One method of maintaining high anisotropy is to reduce spontaneous lateral etching by reducing sidewall reaction probability. Surface temperature has been demonstrated to directly influence the volatility of the reaction product. Tachi et al. [113] described that at low temperatures (below approximately $-100\text{ }^{\circ}\text{C}$), lateral etching was considerably reduced while vertical etch rate was sustained because of the ion bombardment. However a passivating gas such as oxygen is commonly added to enhance anisotropy. A thin layer of SiO_xF_y measured to be between 0.5 and 2 nm was formed on the sidewalls during the process. Another method for maintaining high anisotropy is to protect sidewalls by passivation. A fine polymer layer based on fluorocarbon chemistries is deposited on the sidewalls during the process, which inhibits spontaneous chemical etching. Deep etching of silicon using this method has reported interesting results and is actually widely used in industry to produce different kinds of MEMS. Sidewalls are first passivated by a polymer during the deposition step and both the polymer and silicon are then etched from the base of the trench during the etching step. Accurate control of anisotropy is achieved by a fine balance between etching and deposition. Trenches of $5\text{ }\mu\text{m}$ wide have been perfectly etched down to a $100\text{ }\mu\text{m}$ depth at an acceptable etch rate ($<3\text{ }\mu\text{m/min}$) [114]. But we found no data about deep etching of narrow trenches ($<500\text{ nm}$) with an aspect ratio of more than 1:10. Contamination of silicon by the polymer and roughness observed on the

profiles due to the alternating steps of deposition and etching were found to be the main problems in the sidewall polymeric passivation method. In this chapter, clean nanotrenches with an aspect ratio of approximately 1:10 have been successfully fabricated using the modified polymeric passivation method.

Experimental

A vertical anisotropic etching of silicon was carried out in a deep reactive ion etcher (Oxford, Plasmalab 100 ICP RIE) using a chromium layer as the mask. The following parameters were used for deep etching of silicon with submicron feature size: 75 sccm of SF_6 for 3 seconds, 50 sccm of C_4F_8 for 2 seconds, 30 mTorr chamber pressure, an ICP power of 500 W (25% of that for standard etching), and an RIE power of 30 W (twice of that for standard etching). The substrate was then placed in ambient air at 600 °C for 5 minutes to remove the residual fluorocarbon polymer during deep reactive ion etch process.

Figure 5.4 (a-b) ~10 nm thick fluorocarbon polymer deposited around the nanoholes during silicon etching, (c-d) removal of the fluorocarbon polymer by baking inside a furnace at 600 °C for 5 minutes, (e-f) cross-section view of deep silicon holes etched using a Bosch process with

modified power and pulses durations (inset shows minimal mask under-cutting during the etching process).

Results and Discussions

A vertical anisotropic etching of silicon was carried out in a deep reactive ion etcher. In fluorine-based etching chemistries a degree of anisotropy could be obtained by the formation of a passivating reaction layer on the vertical surfaces, which prevents the otherwise spontaneous reaction between silicon and atomic fluorine. Figure 5.4 (a-b) shows the top view of an etched silicon substrate, where the deposited fluorocarbon polymer of 10-20 nm thick can be clearly seen in the picture. As the polymer was continuously deposited during etching, the process was tuned to avoid filling the trenches entirely with polymer, as this would prohibit further silicon etching. The passivation layer was removed after silicon etching by burning the residual polymer in a furnace at high temperature as illustrated in Figure 5.4 (c-d). The removal of the fluorocarbon polymer ensures a clean and uniform deposition of parylene inside the deep and narrow silicon trenches. The sidewall profile of the deep silicon etch was observed after the silicon substrate was cleaved, as illustrated in Figure 5.4 (e-f). The independent control of the plasma density, ion energy, etching and passivation time in conjunction with low-pressure operation made it possible to perform deep nano-feature etching in silicon. The lower pressure reduces collisions in the plasma sheath and therefore improves the ions bombardment directionality. Additionally, high density plasma sources, such as an inductively coupled plasma, allow for selective control by offering the ability to independently control the ion flux and ion energy through varying the power of the plasma source (ICP) and the substrate holder (RIE). By reducing the ICP power to 25%

of the typical power for a standard etching process, the amount of reactant ions, neutrals, and etching product species were significantly reduced, thus lowering the etching rates, both in lateral and vertical directions. On the other hand, increasing the RIE power to twice that of a standard etching process could enhance the ion bombardment energy, which eventually leads to a higher etching rate in the vertical direction. The etching time was set at 3 s, instead of a standard etching time of 8 s, to ensure the integrity of the sidewall protection and avoid isotropic etching. In addition, the deposition time was set to 2 s, instead of a standard deposition time of 4 s, to avoid an unnecessarily thick polymer film for the passivation layer. The complete etch process comprised 100 cycles of etching and deposition steps.

5.1.3 Nanomolding

Nanomolding entails the preparation of a variety of micro- and nanomaterials of a desired morphology using a prepared template. If the templates that are used have cylindrical pores of uniform diameter, monodisperse nanocylinders of the desired material could be obtained within the voids of the template material. Depending on the operating parameters, these nanocylinders may be solid (nanofibrils) or hollow (nanotubules). The nanostructures can be freed from the template and protrude from the surface like the bristles of a brush. This method has been used to prepare both nanotubules and nanofibrils composed of conductive polymers [115], metals [116], semiconductors [117], and other materials.

Experimental

A parylene vapor deposition was carried out using a vacuum deposition system (Specialty Coating Systems, Inc., PDS 2010). The parylene was vaporized from its solid dimer form by heating under vacuum at 175 °C. The process was followed by pyrolysis (cleaving) of the gaseous form of the dimer into a monomer by using a high temperature tube furnace at 690 °C. The polymerization of the gaseous monomer occurs at room temperature 25 °C and the parylene deposits as a polymer onto the substrate in the vacuum chamber at 20 mTorr. Finally, the substrate was dry etched using XeF₂ gas in a vacuum chamber at a pressure of 0.3 Torr to obtain a thin transparent polymer film with a nanopillar structure.

Results and Discussions

Parylene has a Young's Modulus of approximately 2.8 GPa [79] and is hydrophobic, thus it serves as a good first approximation for the keratin setae found on gecko lamellae. A gecko seta was reported to have a stiffness in the range of 1-15 GPa [13]. Parylene was deposited at room temperature with vapor deposition equipment that controls the coating rate and the ultimate film thickness. After the parylene deposition process, parylene nanostructures were released from the silicon mold using XeF₂ gas, as illustrated in Figure 5.5 (a-b). Dry etching of silicon was preferred for simplicity in the experiment to avoid lateral collapse or stiction between neighboring hairs due to capillary forces, which may arise when wet etching procedures are carried out.

Figure 5.5 SEM pictures of (a) densely packed nanofibrils structure at 15° angle, (b) enlarged view of (a), inset shows free standing parylene nanofibrils structure.

5.2 Nanoscopic Adhesive Properties

Experimental

The adhesive force of an individual nanofibril was measured using an atomic force microscope (Veeco Instruments, Inc., Multimode PicoForce SPM) in contact mode in air at room temperature. Measurements were conducted under ambient conditions (23 °C, 80% air humidity). A tipless silicon cantilever CSG11 series with a spring constant of 0.058 N/m was obtained from NTI Instruments. The silicon cantilever has dimensions of $250 \pm 5 \mu\text{m}$ in length, $35 \pm 3 \mu\text{m}$ in width, $1 \pm 0.3 \mu\text{m}$ in thickness, and was supplied with a high reflective gold coating on its backside surface. The cantilever was kept stationary and the sample was slowly brought into contact with the cantilever at a forward velocity of 969 nm/s and subsequently retracted at a reverse velocity of 969 nm/s. The sample's vertical displacement was predetermined to pass through a distance of 1 μm .

The backside of the flexible nanostructured polymeric surface was glued with an epoxy resin to a magnetic sample plate of an Atomic Force Microscope (AFM). The

sample was handled with extreme care as slight contamination to the nanofibrils structure by the fluid resin could affect the mechanical behavior and properties of the specimen. A tipless silicon cantilever was used in order to optimize the area of contact between sample and the cantilever surface. Cantilever deflections were recorded and transformed into force values, according to the calibration results of the cantilever spring constant, and finally plotted as a force-displacement curve. The absolute values of the pull-off force plotted in the force-displacement curve represent the spontaneous detachment of the cantilever and sample and thus the adhesive force established during contact [118].

Results and Discussions

Figure 5.6a presents the unique saw-tooth pattern in a force-displacement AFM characterization of a nanofibrillar surface. It clearly indicates the interaction of individual nanofibrils with the cantilever surface. The tracing and retracing curves correspond to the sample's movement towards and away from the cantilever tip, respectively. The individual step of the saw-tooth pattern relates to the adhesive force of individual nanofibril and its magnitude varies according to how complex the nanostructures arrays were arranged and interact with the opposing surface. Despite this fact, the last step of the saw-tooth pattern in the force-displacement curve indicates the adhesion force of an individual nanofibril without any interference from the other fibrils. Adhesion force measurements were conducted at 10 different locations with 10 values of adhesion data collected at each point and the result is plotted in Figure 5.6b. The mean adhesion forces of a single nanofibril or artificial “nanohair” range from 0.91 ± 0.34 nN to 1.35 ± 0.37

nN, which is about an order of magnitude lower than that of a single natural nanohair (11.8 ± 2.2 nN) [119].

Figure 5.6 (a) AFM characterization of the adhesive properties of parylene nanostructures, (b) Mean adhesive force of individual nanofibril or artificial “nanohair” at 10 different locations (indicated by sample A, B, and so on).

The reduction of the measured adhesive force of artificial “nanohair” could be attributed to the elastic leaf-like plate at the tip of a natural nanohair which is able to deform to follow the surface roughness profile and is not incorporated into our artificial structures. It is essential that a good contact is made between the surfaces when optimizing the adhesion between two solid bodies. Small interfacial gaps, due to surface asperities or dust particles, will strongly influence the adhesion because attractive surface forces decrease rapidly with increasing separation. If the nanofibrils were to be made of materials having sufficiently low elastic modulus, the force required to flatten the asperities on fibrils’ top surface will be less than the surface attractive force and good intimate contact could be obtained. However, this requires compromises from other factors such as the hair density and aspect ratio of the nanofibrils structure. As shown in

Figure 5.7, it is apparent that the unnecessarily high aspect-ratios of fibrils (approximately 60 nm wide and 2 μm long) without the support of hard materials could lead to the collapse of the nanofibrils structure. Further, the appropriate choice of fibrils' surface chemistry is important for preventing the aggregation of nanofibrils. The presence of water molecules in the environment could assist the formation of capillary forces between fibrils and it is essential to employ hydrophobic materials for this application. When all these factors are considered the fabricated nanofibrils were found not clustering together, even after repeated adhesion experiments.

Figure 5.7 Bunching of nanofibrils due to the unnecessarily high aspect-ratios and too compliant fibrils.

A simple model based on Johnson-Kendall-Roberts (JKR) contact adhesion theory [55] is used to compare the theoretical and experimental adhesion values of a single nanofibril. Assuming the fibrils tips are spherical in shape, the JKR theory for a sphere contacting a flat cantilever surface predicts a pull-off force of $F_{JKR} = (3/2) \cdot \gamma \cdot \pi \cdot R_s$, where R_s is the radius of the sphere and γ is the interfacial surface energy per unit area.

The interfacial surface energy can be approximated by the following expression:

$\gamma = 2\sqrt{\gamma_1\gamma_2}$, where γ_1 and γ_2 are the surface energy of the two bodies in contact [20].

The surface energy of native silicon dioxide is $\approx 120 \text{ mJ m}^{-2}$ [120] and that of polymer is averaged to be 30 mJ m^{-2} [121]. The estimate puts the adhesive force for a single fibril to be about 70 nN, which is significantly larger than the measured adhesion values. The low experimental adhesion values could be due to surface roughness. The theoretical calculation assumed interaction between two atomically smooth surfaces and zero separation distance between the sphere and the flat surface. In actual circumstances the asperities on cantilever surface and the unevenness of fibrils top surface may reduce the area of intimate contact. It was found that relatively small surface roughness is sufficient to reduce the adhesion to a very small value, between 100 to 1000 times smaller than the theoretical values [64]. The high modulus of the fibrils' material also makes the adhesion much more sensitive to surface roughness. The influence is accentuated by the fact that as the bodies are separated the adhesion at the points of intimate contact are broken sequentially instead of simultaneously. All these factors may contribute to the reduction of adhesion forces measured experimentally.

5.3 Macroscopic Adhesive Properties

In order to assess the adhesion of the synthetic surface on a macroscopic scale, a series of experiments was carried out with a 100 mm^2 flexible nanostructured parylene film and a smooth microscope glass, used as the substrate. The sample was pressed against the substrate with a preloading force of 1 N to initiate the attachment process. The substrate

was then turned upside down and vibrated repeatedly to observe the firmness of the synthetic surface sticking onto the substrate. The adhesion experiments were carried out in three different environments to examine the primary mechanism of adhesion exhibited by the synthetic surface. They consisted of normal, ionized, and vacuum environments. In the ionized environment, the ions neutralize and conduct the charges away from the synthetic surface. Hence, the surface would simply fall off the glass substrate if the underlying mechanism of the adhesion were electrostatic forces. Encouragingly the parylene film incorporating the nanofibrillar structure was able to adhere firmly on the substrate in the ionizing environment, suggesting that electrostatic forces are not responsible for adhesion. Despite this experimental result, it should be noted that electrostatic effects could possibly enhance adhesion even if another mechanism is operating [8]. The subsequent adhesion test in a vacuum also eliminated the “miniature suction cups” hypothesis since the synthetic surface was still able to adhere in the vacuum environment.

In addition to the above hypotheses, interlocking of the nanofibrils to substrate surface irregularities could be another possible adhesive mechanism. However, measurement results of the substrate roughness showed that the nanoscopic irregularities were not large enough for the nanostructures to interlock with, thus microinterlocking mechanism cannot have a significant role in the adhesion. As shown in Figure 5.8, the average and root mean square surface roughness of the glass substrate used in our experiments were 40.44 nm and 47.21 nm, respectively. It could be therefore deduced that the macroscopic results confirmed that the fundamental mechanism of the fabricated

synthetic surface's adhesion was based on intermolecular forces, consisting of van der Waals and capillary forces.

Figure 5.8 Surface topography of smooth glass substrate

The adhesive property of the nanostructured parylene film was further characterized by measuring its carrying capacity by attaching a weight to the adhesive pad with a string. All nanofibrils arrays attached simultaneously could theoretically generate ≈ 1 N of adhesive force. The whole 100 mm^2 adhesive pad was found to support an object weighing approximately 70 g. This corresponds to about 70% of the nanofibrils arrays attached to the substrate. The adhesive force of nanofibrils arrays can be improved by changing the types of polymer material and increasing the density of fibrils arrays. By adopting the fabrication technique demonstrated in this report, it is possible to prepare fibrils array in a large area using a wide range of materials which can be deposited by various template-based deposition methods [122].

Despite the success described above, further experiments using a rough substrate were rather disappointing as the nanostructured surface failed to demonstrate any useful adhesive properties, even when a much larger preloading force was applied. The lack of adhesion was associated with the shape of the ends of the nanofibrils and the compliance of the membrane-nanofibrils system, which was insufficient to deform elastically to make good contact between the nanofibrils and the substrate. Although the flexible membrane can assist the nanofibrils in overcoming the terrain of rough surfaces by modulating the fibrils' height and the inter-fibrils distance (see Figure 5.9), the terminal shape and flatness of the nanofibrils still play an important role in the adhesion, as suggested by Persson [68]. These findings point to the need for future integration of compliant plates at the tip of nanofibrillar structures.

Figure 5.9 (a) SEM picture of modulated height and inter-fibrils distance due to a deflected supporting parylene membrane.

Figure 5.10 (a) Contact angle of water droplets on bare parylene film (70°), (b) contact angle of water droplets on nanostructured parylene film (155°).

5.4 Self-cleaning Effect

Adsorption of water molecules takes place on all matters when they are exposed to and hence immersed in the atmosphere. All too frequently adsorbed water is seen to be problematic, but one could identify its potential benefits by understanding the fundamental adhesive behavior of nano-surfaces separated by the water boundary layer and developing an understanding of the mechanisms that describe the interactions observed at the microscopic and mesoscopic scale. The self-cleaning yet adhesive property of both setal and synthetic nanostructures is one such example. The “dry” self-cleaning effect of biological gecko foot-hairs has been previously discussed by Hansen and Autumn [18]. The self-cleaning characteristic of synthetic nanostructures can be correlated to the presence of an adsorbed water layer on the substrate and the super-hydrophobic property of the adhesive surface. While water droplets wetted well on the unpatterned parylene film, as seen in Figure 5.10a, spherically shaped water droplets were observed on the nanostructured surface as shown in Figure 5.10b, indicating an

increased hydrophobic behavior at the scale of the droplet. Water does not intrude into the valleys between nanostructures because of the interplay between surface tension forces acting on the droplet, and the forces between the droplet and the top of the nanostructured fibrils that make up the surface. The apparent reduction in the affinity of the nanostructures to water molecules is determined by the geometry. The same geometric effect reduces the attraction force between particulate contaminants and the nanostructures. The particulate interacts with both the substrate and the nanostructured surface through the water boundary layers, but the adsorbed water layer on the substrate exhibits a stronger adhesion force, causing the nanostructured surface to be easily cleaned from contaminants.

Figure 5.11 Proposed cleaning mechanism: (1) nanostructured surface was contaminated by particulates of 5 μm in diameter, (2) thin layer of water attracts the particulates to the substrates, (3) nanostructured surface is cleaned from particulate contaminants. Two optical images showing the nanostructured surface before (A) and after (B) stepping onto a wetted mica surface. The nanofibrillar structures cannot be clearly seen in the images due to the limited resolution of the optical microscope.

Figure 5.11b shows the “wet” self-cleaning effect of synthetic nanostructures occurring on specifically wet and hydrophilic surfaces. The sample could be cleaned almost completely from particulate contaminants by using either a water droplet rolling over the surface or attaching wetted mica to the nanostructured surface, resembling a little more closely how the gecko’s foot interacts with opposing substrates. At the scale of particulates, this phenomena describes a “self-cleaning” action, however, the relatively weak interaction of force between particulates and nanostructures does not indicate weak total adhesion between the nanostructures and the substrate. There exists a large number of “active nanohairs” functioning together in summing up to create strong intermolecular forces with the substrate and therefore producing excellent overall adhesion.

5.5 Summary

A novel approach combining colloidal lithography, silicon etching, and nanomolding technology is proposed to fabricate flexible polymer surfaces with a high aspect-ratio nanofibrillar structured surface. The approach reported here offers several advantages over methods introduced earlier in the effort of replicating the structure of gecko foot-hairs: (i) a parallel process with the possibility to process large areas, which is especially important for developing technological applications, (ii) no lateral collapse of synthetic hairs, which is essential for having effective adhesion to the opposing surfaces, and (iii) direct integration of a flexible film to enhance the conformity of a nanofibrillar structure to the underlying substrate topography. However, the use of silicon as sacrificial substrate is less satisfactory in terms of wafer consumptions and in order to reduce the process cost, a nanoimprint approach or another low cost substrate instead of silicon could be

considered. Using AFM, the nanofabricated structures produce some useful adhesive properties and a saw-tooth force-displacement curve was obtained to elucidate the interaction of each single nanofibril with a tipless cantilever surface. The synthetic surface was capable of adhering to a smooth glass substrate and exhibited a contaminant-free characteristic similar to the setal nanostructures.

In Chapter 6, the fabrication of a hierarchical microstructure that mimics the setae and branched structures protruding from the setae will be discussed, so as to bring the results one step closer to the creation of a true biologically- inspired adhesive structure.

CHAPTER 6

Fabrication of Hierarchical Microfibrils Structure

In this chapter, two fabrication techniques will be introduced to construct hierarchical microstructures that mimic the structure of gecko setae and spatula. The first method employs a combination of conventional lithography, stamping/contact printing, and reactive ion etching to produce a hierarchical microfibrils structure on a solid substrate. The second method combines photolithography and self-ordered porous alumina to create high aspect-ratio microporous alumina. It is subsequently bonded with ultra-thin nanoporous alumina by surface forces to form a hierarchical porous alumina template. The template is then infiltrated by the desired materials and chemically etched to obtain a hierarchical microfibrils structure on a flexible substrate.

6.1 Artificial Hierarchical Gecko Foot-Hairs

The artificial gecko foot hairs in general include arrays of tiny elastic structures that are capable of deforming and making close contact with the surface at different length scales. Numerous publications have been dedicated to realizing this concept with various fabrication techniques and materials [12-16]. However, the artificial structures that have been developed so far do not accurately derive the morphology of the natural gecko foot-hairs. The multi-branched setae in geckos are highly evolved to attain the most efficient adhesion on randomly rough surfaces. The small and thin fibrils conform to the surface irregularities and make many points of contact on uneven surfaces. The smaller fibrils

have thinner and more flexible shafts which may stick together and impair adhesive efficiency and this could be the reason why the long and thick fibrils are frequently observed at the base of smaller fibrils in most geckos' species. The setae are present to provide the rigidity to the adhesive fibrillar structures.

A schematic diagram of artificial hierarchical gecko foot-hairs, which have been developed in this study, is shown in Figure 6.1. An ensemble of high aspect-ratio microfibrils (5-10 μm wide and 70-100 μm long) protrudes from a flexible membrane (50-70 μm thick), resembling the setae arrays and gecko lamellae. Densely packed nanofibrils (0.01-0.2 μm wide and 1-2 μm long) are incorporated at the tip of each microfibril to mimic the gecko spatulas. The thin leaf-like pads at the tip of gecko spatulas, as described by Persson [68], are not integrated in the artificial adhesive system since the adhesion is reported to be shape-insensitive at the nanometer length scale [59].

Figure 6.1 Schematic diagram of artificial hierarchical gecko foot-hairs supported by flexible membrane.

In the following sections, two different methods that hold the potential to meet the challenge in fabricating hierarchical structures, as shown in Figure 6.1, will be discussed. The first method combines conventional lithography, contact printing, and reactive ion etching to produce hierarchical structures on a solid substrate. The second method using anodic porous alumina template was developed to overcome the drawbacks of the former, such as the limited aspect ratio of nanofibrils and the use of a solid substrate to support the hierarchical structures, both of which have been said to cause a significant reduction in adhesion [53].

6.2 Nanoparticles Lithography by Stamping/Contact Printing

Contact printing is an easy and efficient way of producing patterns of self-assembled monolayers (SAM) with sub-micrometer lateral dimensions [123]. An elastomer stamp, usually made from polydimethylsiloxane (PDMS), is used to transfer the ‘ink’ to the surface of the substrate by contact printing. When the stamp is lifted from the surface, a patterned deposit of ink defined by the stamp structure is produced on the surface of the substrate. We use the flexibility of the contact printing method to deposit a monolayer of colloidal nanoparticles on the top surface of microfibrillar structures that were previously fabricated using conventional lithography. By using the colloidal particles as the shadow mask, nanofibrillar structures could be produced at the tip of each microfibril by reactive ion etching with an oxygen plasma. A similar method was previously adopted to fabricate periodic submicron diamond cylinder arrays using two dimensional particle arrays [124]. This approach has considerable advantages in terms of cost, efficiency, and scaling viability. The following sections describe in detail the fabrication process and

experimental results to create artificial gecko foot-hairs incorporating the setae and the spatulas in one design.

Figure 6.2 shows a schematic illustration of the fabrication procedure developed for creating hierarchical microstructures. The process started with the formation of high aspect ratio microstructures using conventional lithography. Colloidal monolayers were then selectively deposited on the top surface of microstructures using stamping/contact printing. The colloidal nanoparticles serve as shadow masks during reactive ion etching in an oxygen plasma to produce the nanofibrils structures.

Figure 6.2 Schematic diagram of fabrication process of hierarchical microfibrils structure using nanoparticles lithography and contact printing.

6.2.1 Conventional Lithography

Experimental

A silicon wafer is used as a substrate and cleaned using piranha solution (mixture of H_2O_2 and H_2SO_4), dried with dry nitrogen, and heated on a contact hot plate at 110°C for 20 minutes to dehydrate. SU-8 2050 (MicroChem) was then spun on top of silicon wafer at 2000 rpm to obtain a $70\text{ }\mu\text{m}$ thick photoresist. The resist was then exposed to a UV light with a power density of $10\text{ mW}/\text{cm}^2$ for 70 seconds. The post-baking was performed on a hot plate at 50°C for 10 mins and 95°C for 30 mins to selectively cross-link the exposed portions of the resist. The resist was then developed with SU-8 Developer (MicroChem) using a spin coater. While the wafer was spun at a speed of 500 rpm for 30 seconds, SU-8 developer was dropped continuously on top of the resist using a pipette. After that, the wafer was spun-dry at 500 rpm for another 30 seconds to remove the left-over solvent or unwanted resist. This developing step was repeated four-times until the microstructure was fully developed. The microstructure was then blown-dry with gentle dry N_2 to ensure that there was no developer left.

Figure 6.3 Microstructures with aspect ratio of 1:15; (a) $10\text{ }\mu\text{m}$ gap; (b) $25\text{ }\mu\text{m}$ gap

Results and Discussions

High aspect-ratio (1:15) microfibrils have been successfully fabricated using a conventional photolithography, as shown in Figure 6.3. The microfibrils have dimensions of 5 μm in diameter and 72 μm in length. SU-8, an epoxy based negative photoresist, was used as the structural material because of its potential to provide high aspect-ratio microstructures. The method described to produce a highly anisotropic profile in a thick photoresist has overcome a number of challenges. First, underexposure is a common problem. With thick photoresist, getting enough energy to the base of the resist can be difficult or time-consuming. If there is not enough energy to drive the crosslinking reaction at the base, the photoresist will remain unexposed and subsequent development will lift the entire structure from the substrate. Second, aligning a mask to an underlying feature can be challenging with thick photoresist. An uneven photoresist surface provides uneven contact during exposure. Sections of the substrate not in contact with the mask will not resolve small features. The solution to these two problems was to: (1) extend the soft-baking time so as to remove more solvent from the photoresist. Longer exposure time is also required in order to ensure the UV-energy reaches the base of photoresist. (2) use hard-contact between mask and photoresist. An edge bead removal process was employed to remove a thicker resist on the edges after spin coating process and to achieve a good contact between the resist and the mask.

Figure 6.4 Challenges in fabricating high aspect ratio microfibrils: (a) lift-off, (b) collapse, (c-d) stiction.

Figure 6.4 shows some problems that occur during the fabrication process. When the resist is underexposed (40 seconds exposure time), all the microfibrils are lifted-off from the wafer surface, as depicted in Figure 6.4a. A collapsing problem was also encountered during the experiment when the developing time or method was incorrect. Developing the SU-8 resist by immersing and stirring it inside developer bath may cause the structures to collapse, as shown in Figure 6.4b. A stiction problem, as shown in Figure 6.4 (c-d), was observed when the developer was not completely removed after the microstructure was fully developed. As the distance between two fibrils was small,

capillary forces may be induced by the left-over developer and cause the fibrils to stick to each other.

6.2.2 Colloidal / Nanoparticles Deposition

Experimental

Flat sheets of PDMS were prepared by spreading a layer of Sylgard 184 (PDMS : cross-linker ratio = 10 : 1), of a thickness of 4 mm on a glass substrate and curing at 60 °C for 2 hours. The PDMS sheet was immersed inside a polycation solution (poly-diallyl-dimethyl-amonium-chloride) for 20 mins and rinsed by DI (deionized) water. Immersion of PDMS into a polycation solution was carried out twice and followed by blow-drying with a stream of N₂ gas. The microfibrils were then brought into conformal contact with PDMS for 2 mins and rinsed with DI water. The contact areas, which are the topmost part of microfibrils, then possess positive charges as they adsorb charges from PDMS stamps during contact. The patterned microstructures were immersed in a colloidal bath (Duke Scientific, SiO₂, 0.47 $\mu\text{m} \pm 0.03 \mu\text{m}$, 4 % in aqueous suspension) upside down for 1 hour. The sample was then removed from the bath of colloids and the excess suspension was carefully rinsed from the surface to obtain a monolayer of nanoparticles on top of the microstructures.

Results and Discussions

Colloidal particles in an aqueous suspension usually have ionic charges that are uniformly distributed over their surfaces. Contact printing was carried out to investigate

the adsorption selectivity of colloidal particles onto substrates when the surfaces of substrate are treated chemically. The patterned microstructures, bearing cationic regions on their top layer, were supported upside down in colloidal suspension to avoid the nonspecific sedimentation induced by gravity. Figure 6.5a shows the plan view of a microfibril (5 μm in diameter and 80 μm in height) with colloid SiO_2 particles deposited selectively on the top surface of the microfibrils. Without contact printing, the colloidal particles were distributed both on the top and surrounding sidewall of microfibril, as seen in Figure 6.5b. The quality of the pattern and the resolution of the printed features are dictated by the ink concentration, the procedure of inking of the stamp and the printing conditions, including the surface chemistry of the substrate [125].

Figure 6.5 Colloidal particles adsorption phenomena on surfaces: (a) with contact printing; (b) without contact printing.

A two-stage mechanism of colloidal assembly is proposed to explain the selective monolayers formation. During the first stage, patterned colloidal deposition driven by long-range electrostatic forces occurs. Short-range forces, such as hydrogen bonding and van der Waals forces, do not contribute in attracting the spheres to or driving the spheres

away over micron distances. Negatively charged particles in the vicinity of the positively charged regions, which in this case are the topmost layers of microfibrils, undergo attraction and attach to the substrate. Particles in the vicinity of the neutral region, which are the sidewalls and the base, may be weakly attracted to or repelled from the substrates. The second stage of colloidal assembly corresponds to the rearrangement of particles that occurs during drying. This process is suspected to originate from attractive capillary forces appearing between particles partially immersed in a liquid layer.

It is therefore concluded that long-range electrostatic forces are considered to have significant advantages as compared to non-specific interactions induced by gravity or short range interactions such as hydrogen or covalent bond. As a contact printing method allows selective definition of chemical functionality and thus surface charge over large areas, the electrostatic forces can be easily manipulated to induce the localized colloidal deposition. An additional in-plane ordering of the adsorbed particles can be further initiated by the lateral immersion capillary forces that originate from the wetting/dewetting properties of a patterned substrate and colloidal particles [126]. The deposition of colloids on patterned ionic monolayers is, therefore, a simple and convenient route to directing the colloidal assembly into ordered, complex structures of large arrays.

Despite the advantages of the simple approach described, a lack of controllable surface regularity, such as spacing and uniformity of distribution, becomes a major drawback of this approach. In addition to that, many particles stick to the polymer surface before reaching the ordered regions and form many small groups consisting of several particles. This pattern spacing problem, however, could be overcome by adjusting the

NaCl content in the aqueous polycation solution [127]. As the NaCl concentration increased, the interparticle spacing tended to decrease, suggesting that a larger amount of colloidal adsorption occurred in the presence of a higher salt content. The surface charge density can be adjusted by varying the salt concentration of polycation solutions, thus permitting the tuning of the spacing between colloids. This finding may be correlated to the series of experiments carried out by Denkov et al. [128] who was trying to understand several factors affecting the array formation such as, particle size, particle concentration, electrolyte concentration, water evaporation rate, and presence of surfactants. The addition of NaCl in the aqueous polycation solution was proposed to increase the number of Na^+ ions adsorbed on the substrates, which in this case is the PDMS stamp. The positive charges on PDMS stamps will eventually be transferred to the top layer of microfibrils during contact printing which indirectly controls the amount of negatively charged particles adsorbed on the surface.

6.2.3 Nanoparticles Lithography

Experimental

A dry etching process was carried out with an oxygen plasma in a reactive ion etcher (RIE 600 W, Torr International). Oxygen ions, which are accelerated by the RF generator (13.56 MHz), attacked the top layer of SU-8 microfibrils that is not protected by the SiO_2 particles. The operating oxygen pressure ranged from 20-24 mTorr and the corresponding flow rate was 20 sccm (standard cubic centimeters per minute). The etching was conducted at a constant power of 100 W for 15 minutes.

Results and Discussions

Following the contact printing process, reactive ion etching process with an oxygen plasma was carried out to produce the nanofibrils array. The simplest plasma reactors may consist of opposed parallel plate electrodes in a chamber that can be maintained at low pressure, typically ranging from 0.01 to 1 Torr. When a high frequency voltage (13.6 MHz) is applied between the electrodes, current flows forming a plasma, which emits a characteristic glow. At low pressure and high frequency, a discharge in pure oxygen produces oxygen atoms and ions. Substrate material on the electrode surfaces, which in this case is the microfibrils, is exposed to reactive neutral and charged species. Some of these species combine with the substrate and form volatile products that evaporate, etching the substrate.

To achieve directional and high aspect ratio resist etching, the process was conducted under plasma conditions with low oxygen atom concentrations (flow rate of 20 sccm) and at low pressure (20 mTorr). The gas phase concentration of oxygen must be low relative to the flux of ions to avoid undercutting by a purely chemical reaction [129]. In low pressure plasmas, ion bombardment flux stimulates the vertical etch rate of polymer surfaces by oxygen. The lower pressure favors not only higher ion energy, but also leads to a proportional decrease in the concentration of neutral etchants while the relative rate of energetic ion-enhanced etching increases. The action of neutral gas-solid reactions, stimulated or directed by ion bombardment, eventually brings about anisotropic features of plasma etching. It is worth mentioning that although high energetic ions can increase directionality during etching, selectivity of the target relative to the mask always

decreases with increasing ion energy. Ion energies far above the threshold are thus undesirable.

Besides the pressure effect, the RF excitation frequency also alters the key discharge characteristics that have an important influence on the plasma chemistry and etching [130]. The frequency can change the spatial distributions of species and electrical fields across the discharge. It also affects the minimum voltage that is required to start and operate a plasma and the energy with which ions bombard surfaces. In addition to that, frequency determines whether the energy and concentrations of species are constant in time, or whether they oscillate during a period of the applied field.

Figure 6.6 SU-8 nanofibrils structure with 15 minutes etching time (~ 250 nm wide and $1 \mu\text{m}$ long)

Figure 6.7 Hierarchical microstructures on solid silicon substrate, showing nanofibrils structure on top of microfibril: (a-c) before, and (d) after discarding the nanoparticles in NaOH.

Other than the two factors mentioned above, it is revealed that etching time is one of the important factors affecting the aspect ratio of the fibrils. Figure 6.6 shows the SEM images of SU-8 nanostructures patterned by reactive ion etching process through masks consisting of SiO₂ nanoparticles. Although we have yet to show good control over placement or distribution of particles on substrates, we have demonstrated a versatile and cost-effective method for the formation of nanofibrils array at the tip of microfibrils, as shown in Figure 6.7. In terms of uniformity, there is no significant variation of etching across the substrates. The selectivity of SU-8 resist relative to the SiO₂ particles can be considered high as the SiO₂ particles seem not to be etched away after etching for 15

mins. While anisotropic, straight-wall, and small features sizes can be achieved in the experiment, the surface quality after etching was found to be very poor. The finished surface is found to be very rough and covered with cones or spikes. This may be caused by several factors that contribute during the etching process, such as: high energetic ions bombardment, temperature effects, variations in etchant species, etc.

Figure 6.8 (a) Slender fibrils and (b) Collapse of nanofibrillar structures due to the excessive lateral etching.

Although the fabrication method described above is capable of producing hierarchical microstructures, the length of the nanofibrils is restricted by their resistance to lateral etching in an oxygen plasma environment. As the etching time was increased, it was observed that the diameter of the nanofibrils was getting thinner (Figure 6.8a) and it eventually caused the complete etching of the whole nanostructures (Figure 6.8b). In order to overcome this problem, the second fabrication method using anodic porous alumina templates is adopted and will be discussed in more detail in the subsequent section.

6.3 Anodic Porous Alumina Template

Herein, we demonstrate the simple but widely applicable anodic aluminum oxide (AAO) assisted nanofabrication of two-level hierarchical fibrils array on a flexible substrate over a large area. The central idea of our approach is to fabricate two or more alumina membranes, each containing high aspect ratio micro- and nanopores, and bond them together using surface forces. To prepare the microporous alumina, we used a conventional lithography method for selectively closing part of the channels of an ordered array on an AAO film. The pores structure in the exposed area was subsequently etched away in order to create a custom-patterned microchannel array. In the preparation and manipulation of the thin nanoporous anodic film, great care needs to be exercised as AAO is a brittle ceramic film grown on soft aluminum metal. The key aspect of the nanofabrication process described here is that one could control the aspect ratios of the micro and nanoporous templates independently before integrating the two together. Following the formation of the hierarchical porous template, a polymer solution was spun on its surface to fill the channels. An ensemble of hierarchical microstructures protruding from a surface can be obtained after dissolving the template in a wet etchant solution.

Anodic porous alumina, which is formed by the anodic oxidation of aluminum has attracted much interest as a starting material for the fabrication of several kinds of functional devices, such as photonic [131], electronic [132], and magnetic devices [133], due to its naturally occurring nanometer-order channel array structure with a high aspect ratio. One of the numerous advantages of this material is the ability to control its pore width and pore length over a wide range from a few up to several hundreds of nm. The width depends directly on the anodization voltage, the length on the anodization time.

Based on a two-step replicating process, a self-ordered porous alumina membrane with 100 nm interpore distance was synthesized by Masuda and Fukuda in 1995 [134]. This discovery was a breakthrough in the preparation of two dimensional polydomain porous alumina structures with a very narrow size distribution and extremely high aspect ratios. Numerous other groups, not mentioned here specifically, have also contributed to an improvement of porous alumina structures.

6.3.1 Electrochemistry and Pores Formation Mechanism

The spontaneous reaction leading to the formation of aluminum oxide in air can be ascribed to the large negative Gibb's free energy changes [135],

If aluminum is electrochemically anodized, an oxide grows at the anode electrode [136],

and hydrogen evolves at the cathode,

The current density passing across the oxide film can be written as [136],

$$j = j_a + j_c + j_e \quad (6.5)$$

where j_a , j_c , and j_e are the anion-contributing, cation-contributing, and electron-contributing current densities, respectively. Since the electronic conductivity in the aluminum oxide is very low, the ionic current density ($j_i = j_a + j_c$) is the predominant

mode to transport the charges. The relationship between the ionic current, j_i , and the electric field, E_f , can be expressed in terms of the Guntherschultze-Betz equation,

$$j_i = j_0 \exp(\beta E_f) \quad (6.6)$$

where both j_0 and β are temperature- and metal-dependent parameters. For the aluminum oxide, the electric field E_f , j_0 , and β are in the range of 10^6 to 10^7 V/cm, 1×10^{-16} to 3×10^{-2} mA/cm² and 1×10^{-7} to 5.1×10^{-6} cm/V, respectively [137]. Based on the Guntherschultze-Betz equation, the rate-limiting steps of the film formation are determined by the ionic transport either at the metal/oxide interface, within the bulk oxide or at the oxide/electrolyte interface [138]. Nowadays, it is generally accepted that the oxides simultaneously grow at both interfaces, e.g., at the metal/oxide interface by Al^{3+} transport and at the oxide/electrolyte interface by oxygen ion transport [139].

Two types of anodic films can be produced depending on several factors, in particular the electrolyte solution. They are barrier-type films and porous-type films. Barrier-type films can be formed in completely insoluble electrolytes such as neutral boric acid, ammonium borate, tartrate, and ammonium tetraborate in ethylene glycol. Porous-type films can be created in slightly soluble electrolytes such as sulfuric, phosphoric, chromic, and oxalic acid [138]. Both the barrier- and the porous-type alumina consist of an inner oxide of high purity alumina and an outer oxide layer comprised of alumina which has incorporated anions [140]. The schematic diagram of both anodic films is shown in Figure 6.9.

Figure 6.9 Schematic diagram for barrier-type alumina and porous-type alumina.

In this chapter, we will focus our attention on the second type of anodic films, which is porous-type alumina. The film thickness in the porous-type alumina is dependent upon the anodizing time, current density, and electrolytes. As the temperature increases, the corresponding current density also increases. This does not mean that a higher current density increases the film thickness since the rate of complex dissolution at the electrolyte/oxide interface increases, too. If the temperature is too high so that the rate of dissolution is faster than that of oxide formation, the film even vanishes, resulting in electropolishing of aluminum [138]. The thickness of the thin barrier layer at the bottom of the porous structure is only dependent on the anodizing voltage, regardless of anodizing time.

Figure 6.10 Current density curve corresponding to the pore formation at the beginning of anodization. (1) Formation of barrier oxide on the entire area. (2) Local field distributions caused by surface fluctuations. (3) Creation of pores by field-enhanced or/and temperature-enhanced dissolution. (4) Stable pore growth.

The current density profile, as shown in Figure 6.10, reflects the formation of porous-type alumina [138]. The current density j decreases rapidly at the beginning of the oxide formation (segment 1) and passes through a minimum value (segment 2) before increasing to arrive at a maximum value (segment 3). Subsequently it slightly decreases again and remains at a steady current density (segment 4). The pore formation mechanism, corresponding to the four segments of Figure 6.10 (left), is shown schematically in Figure 6.10 (right). The barrier film, which consists of non-conductive oxide, initially covers the entire surface of the aluminum (segment 1). The electric field is focused locally on fluctuations of the surface (segment 2). This leads to field-enhanced or/and temperature-enhanced dissolution in the formed oxide and thus to the growth of pores (segment 3). Since some pores begin to stop growing due to competition among the pores, the current decreases again (segment 4). Finally, j_p maintains an equilibrated state and the pores grow in a stable manner. However, it is often observed that during the

stable pore growth, the current density continues to decrease slightly. This is due to diffusion limits in the long pore channels.

6.3.2 Anodization Set-up and Fabrication Process

Figure 6.11 shows an apparatus of our electrochemical experiments. The electrochemical cell consists of a two-electrode system, i.e. the graphite rods as the counter electrode and Al foil acting as the working electrode. The Al foil is bonded to the glass slide by using nail polish, which also serves as a protective layer so that the back surface of Al foil is not exposed to the electrolyte during anodization process. A magnetic stir bar is used to stir the electrolytes vigorously. For cooling the apparatus, a high precision thermoregulator cooling bath (Huber, Polystat K6-2) equipped with external temperature sensor and circulation tubes is used. The anodization process is conducted in an enclosed area to maintain the concentration of electrolytes.

Figure 6.11 Schematic diagram of the apparatus used for the anodization.

The fabrication procedure of the binary hierarchical microstructures is schematically shown in Figure 6.12. It combines photolithography and self-assembly porous alumina to create high aspect-ratio microporous alumina (Figure 6.12f). The microporous template is subsequently bonded with ultra-thin nanoporous alumina (Figure 6.12j) by capillary and van der Waals forces to form hierarchical porous alumina template (Figure 6.12k). The template is then infiltrated by the desired materials and chemically etched to obtain hierarchical microfibrils structure on flexible substrate (Figure 6.12m).

Figure 6.12 Schematic diagram of fabrication process of binary hierarchical structure: (a) First-step long anodization; (b) Concave-textured pattern surface after removal of the porous alumina layer; (c) Second-step long anodization; (d) Sputter Au layer and coat photoresist AZ7220 for micropatterning; (e) Pattern transfer from the photoresist to the Au layer; (f) Separation of alumina from aluminum substrate; (g) Second short anodization; (h) Infiltration of PMMA; (i) Separation of alumina from aluminum substrate; (j) Selective etch of barrier layer; (k) Bonding two porous membranes; (l) UV-Ozone treatment; (m) Infiltrate a desired material into the template, which was subsequently etched away to obtain hierarchical polymeric structures on flexible membrane.

6.3.3 Experimental

Detailed description of the first anodization process of aluminum have already been published [131, 134, 135, 141-146]. The following specific conditions were applied in our experiments: an aluminum sheet (99.999% purity, $30 \times 20 \times 0.5$ mm) was first degreased in acetone and annealed in nitrogen ambient at $400\text{ }^{\circ}\text{C}$ to remove mechanical stresses and to recrystallize the samples. Subsequently, the substrate was electropolished under a constant current condition of $100\text{ mA}\cdot\text{cm}^{-2}$ below $10\text{ }^{\circ}\text{C}$ for 4 min in a mixed solution of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ to obtain a mirror surface. Note that caution is needed when perchloric acid/ethanol is used due to its explosiveness at moderate temperatures. The first anodization was conducted in 0.3 M oxalic acid solution at $25\text{ }^{\circ}\text{C}$ under a constant voltage of 40 V using a direct current source for 6 h. The electrolyte solution was stirred vigorously using a magnetic stirrer in order to accelerate the diffusion of the heat that evolved from the sample. This treatment is important to prevent the increasing localized temperature and to maintain the stable growth of the anodic oxide layer. The first porous alumina layer was then removed in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at $60\text{ }^{\circ}\text{C}$. Following this step, two porous alumina membranes were prepared under different anodization conditions. One was anodized at $25\text{ }^{\circ}\text{C}$ for 8 h to obtain a thick porous alumina membrane and another was anodized at $2\text{ }^{\circ}\text{C}$ for 10-30 min dependent upon the desired thickness.

In order to prepare high aspect-ratio microporous alumina template, a $0.15\text{ }\mu\text{m}$ thick Au layer was first sputtered on the surface to block the pores and improve the surface flatness. A photolithography process was then used to define the pattern of micropores. A positive photoresist (Clariant, AZ7220) was spun on the Au-coated alumina substrate and

a potassium iodide based etch solution was used to transfer the patterned resist to the Au layer. The exposed area of the porous alumina was then etched down with a chemical etching in an aqueous 5 wt% phosphoric acid solution. And finally, the alumina layers were separated from the Al substrate in the mixture solution of saturated CuSO_4 and HCl. The freestanding thin nanoporous alumina template was prepared by placing 0.1 ml poly(methyl methacrylate) or PMMA solution (5 wt% in anisole, molecular weight: 950,000) on the top side of the template membrane ($\approx 1 \text{ cm}^2$ surface area) and heating up the polymer solution above its glass transition temperature at 120°C for 1 h. Selective removal of the barrier layer and a pore widening treatment were performed by etching in 5 wt% phosphoric acid solution for 45 m after separation from the Al substrate in the erosive CuCl_2 based solution. The thin alumina-PMMA membrane was subsequently wetted with deionized water and placed on top of the microporous alumina template. The PMMA was then removed using UV-Ozone cleaning system (SAMCO, UV-300H) prior to depositing a desired polymeric material into the hierarchical microporous template. To prove the fabrication concept, we used a more concentrated PMMA (10 wt% in anisole) as the synthetic fibrils material. The material was placed on the top surface of the template, spun at 3000 rpm for 30 s, and heated up in the oven at 120°C for 1 h. The whole template was then dissolved in phosphoric acid solution to free the fibrils that had been deposited within the pores.

6.3.4 Results and discussions

Self-ordered alumina by two-step anodization

At the beginning of anodization, pores are randomly created on the surface and the initial pore arrangement is very irregular, as shown in Figure 6.13a. However, due to the repulsive forces between neighboring pores during the long-anodization, self-organization occurs. After the first-anodization step and removal of the first-alumina layers, patterns that are replicas of the hexagonal pore array are preserved on the fresh aluminum surface. This allows the preparation of pores with a high regularity by a subsequent second anodization under the same conditions as the first anodization. As a result, hexagonally close-packed arrays are obtained at the interface between the porous alumina layer and the aluminum substrate, as shown in Figure 6.13 (b-d). From this figure, an almost ideally hexagonal cell configuration with a cell size of approximately 100 nm was observed. During the anodization, the electrolyte should be vigorously stirred to effectively remove the hydrogen bubbles and local heat on the surface, and to allow a homogenous diffusion of anions into pore channels. The local heat causes an inhomogenous electric field distribution at the bottom, leading to local electrical breakdown of the oxide. In fact, cracks and rupture of the oxide film are generated if porous alumina is formed without temperature control, as shown in Figure 6.14.

Figure 6.13 (a) Irregular arrays of pores. (b-c) Hexagonally ordered arrays of pores. (d) Cross-sectional view of porous alumina

Figure 6.14 Cracks of oxide layer due to heat localization.

In addition to the temperature dependence, there are a number of factors that could influence the self-ordering of pores during anodization. Aluminum has to be of a high purity ($\geq 99.99\%$). Anodization of aluminum having impurities could lead to defects because impurities have a different volume expansion coefficient and chemical properties from aluminum. Furthermore, the type and concentration of the electrolyte for a given potential has to be selected properly to obtain self-ordered pore growth. In general, the anodization of aluminum is carried out in sulfuric acid in low potential ranges (5-40 V), oxalic acid is used for the medium potential ranges (30-120 V), and phosphoric acid for high potential ranges (80-200 V) [142]. This restriction is due to the conductivity of the electrolyte. For example, if aluminum is anodized in sulfuric acid at a high potential, breakdown of the oxide layer could take place very often because the electrolyte has a very high conductivity.

High aspect-ratio microporous alumina template

High aspect ratio microstructures were conventionally fabricated using techniques like deep reactive ion etching or X-ray lithography. By exploiting the built-in anisotropy of nanoporous alumina membrane, such structures can be achieved with sub-micrometer precision using photolithography and isotropic wet etching, as described in this thesis. The result of the micropatterning process is shown in Figure 6.15, where an anisotropic profile can be clearly seen. The pores are about 70 μm long and 10 μm in diameter. A highly anisotropic etch can be expected here as the etchant penetrates into the pores and etching occurs at the whole oxide/solution interface due to the high density of pores of the alumina. By dissolving only half a pore wall, the pores structure in the opened

window of the Au layer can be completely removed. In order to achieve steep side-walls, it is essential that the etching process is slow enough for the etchant to penetrate deep into the pores. Both the etchant concentration and the etching time are the key factors that determine the profile of the microporous structures. The structure begins to undercut with extended etching time, as shown in Figure 6.16a. Conversely, etching time that is too short causes an inhomogeneous penetration of the etchant into the pores, resulting in tapered pores as shown in Figure 6.16b.

Figure 6.15 Highly anisotropic microporous alumina template

Figure 6.16 (a) Undercut due to the too long period of etching time (b) Tapered microporous alumina due to the non-homogenous penetration of the etchant solution into the pores

Ultra-thin nanoporous alumina template

While a freestanding thick alumina membrane ($>30\ \mu\text{m}$) is simple to be prepared, it is not so straightforward to prepare a thin membrane with a thickness in the sub-micrometer range. Due to the handling difficulty, the reported thinnest free-standing alumina is 120-150 nm in thickness [147]. Prior to selective etching of aluminum in copper (II) chloride solution, it is essential that one infiltrates polymer into the pores to act as a supporting layer. In our experiment, PMMA was coated onto the alumina surface and heated above its glass transition temperature so that it can easily move into the pores. After cooling down to room temperature, the sample was immersed into the erosive CuCl_2 solution and within few minutes the $\sim 200\ \mu\text{m}$ thick aluminum was completely removed. The $\sim 0.5\ \mu\text{m}$ alumina was found floating on the surface and still intact with the thin PMMA film.

Hierarchical microporous alumina template

The alumina-PMMA membrane was subsequently rinsed with deionized water and carefully transferred onto the top surface of microporous alumina membrane, which had been prepared previously. Figure 6.17 shows that both surfaces adhered closely by means of van der Waals bonding when the water dries out. Such a technique of bonding alumina with another surface using van der Waals interaction has been previously employed to produce nanodot arrays using alumina templates as masks [148, 149]. Utilizing a combination of ultraviolet light, a high concentration of ozone, and controlled heating, the PMMA was stripped from the bonded template to obtain a clean porous template, as shown in Figure 6.17 (inset).

Figure 6.17 Intimate contact between two membranes (inset shows clean nanoporous alumina template after UV-Ozone treatment).

Formation of hierarchical microfibrils

The final fabrication step involves the infiltration of a solution of the desired material into the pores of alumina membranes. Here we used low-viscosity polymeric solutions (10 wt% PMMA) to fill the pores. PMMA, a thermoplastic material, has a Young's modulus of approximately 2400 MPa [150]. The relatively low processing temperature and low shrinkage properties make PMMA easy to process in casting and molding. Other prominent physical properties of PMMA, such as good mechanical strength and dimensional stability, along with high tensile and flexural strength, also provide a reasonably good approximation to the material properties of natural gecko foot-hairs. Under optimum conditions, PMMA flows into the pores by capillary action, creeps along the inner pore walls and fills them, resulting in fibril structures. As discussed in the experimental section, the alumina membrane was dissolved away to expose the polymeric fibrils prepared in the pores. This fibrils preparation method is applicable to any polymer that can be dissolved in a solvent that does not attack the template membrane. Water soluble polymers might not be suitable for this application as the polymeric fibrils would dissolve in the aqueous solutions used to dissolve the template. Figure 6.18 shows SEM images of hierarchical microstructures composed of PMMA after dissolving the alumina membrane in phosphoric acid solutions. An ensemble of hierarchical microfibrils that protrude from a surface like arrays of gecko foot-hairs is obtained. The lengths of these microfibrils show that they spanned the complete thickness ($\approx 70\text{ }\mu\text{m}$) of the template membrane. The diameter of the fibrils is about $10\text{ }\mu\text{m}$, as determined by the opening diameter of the Au transfer layer. At the tip of these fibrils, closely packed arrays of smaller and thinner fibrils are observed. The fibrils diameter reflects the pores diameter

(≈ 60 nm) of the template, and the fibrils length is equivalent to the thickness (≈ 0.5 μm) of this template.

Figure 6.18 SEM micrographs of: (a) hierarchical microfibers array featuring ≈ 10 μm wide and ≈ 70 μm long microfibers, each branches into ≈ 60 nm wide and ≈ 0.5 μm long nanofibrils array; (b-c) magnified top view and (d) oblique view of the nanofibrils array.

To test the adhesive properties of the hierarchical structures on a macroscopic scale, a 1 cm^2 sample of PMMA membrane containing micro- and nanostructures was pressed against a microscope glass slide with a preload force of 1 N. Rather discouragingly, this resulted in a very small adhesive force of $\approx 0.01\text{ N}$, indicating that a very small amount of nanostructures were in actual contact with the substrate. This could be due to the over densely-packed arrangement of nanostructures, which was inherent in the fabrication

technique using alumina membrane. Naturally occurring self-organized alumina membrane, in general, has very high density of pores with very small interpore distance. In order to overcome this problem, a more sophisticated technology, involving prepatterning of the substrate surface, can be adopted [151]. With this prepatterning method, it is possible to control the interfibril spacing and therefore minimize the clumping effect between fibrils.

The complex hierarchical structures in gecko provide a rich source of inspirations for physical sciences and industrial applications. The fabrication technique developed in this thesis should be of general value for creating synthetic gecko fibrils attachment systems in engineering. While the technique does not incorporate all the design complexities found in nature, it should be emphasized that the aim of this study was to develop simple method that overcome the challenge of fabricating hierarchical structures. Many other important aspects, such as the selection of synthetic materials, the integration of compliant layer on the nanofibrils tips, and the fabrication of slanted setae from the backing surface, have to be considered to optimize the compliance level of fibrillar structures to produce functional synthetic structures.

6.3.5 Superhydrophobic Effect of Double Roughness Structures

Another application, considered to be of significant technological impact, is to make “self-cleaning surfaces” by using hierarchical fibrillar structures – like gecko’s feet that remain clean despite their surroundings. Such surfaces have distinctive superhydrophobic characteristics; that is, water droplets form spheres with very little adhesion to the surface and roll off very quickly even at small inclinations, due to roughness on the micro- and

nanometer scales. Water droplets as well as dirt particles only lie on the tips of these structures and develop low adhesion forces to such rough surfaces.

Figure 6.19 Equilibrium water contact angle on: (a) non-patterned PMMA surface, (b) nanostructured PMMA surface, and (c) hierarchical microstructured PMMA surface

In the present study, we determined the wetting property of three types of surfaces. All samples are made of polymer, have the same surface chemistry, allowing the comparison of the effect of different micro- and nanostructure geometries on water repellency and self-cleaning. Figure 6.19 shows the equilibrium water contact angle on these surfaces. It can be seen that the measured contact angles of the non-patterned PMMA surface is the lowest of all surfaces presented here. The water contact angle was measured to be about 70° (Figure 6.19a). The second specimen was prepared from a $\approx 0.5 \mu\text{m}$ thick alumina membrane, resulting in $\approx 60 \text{ nm}$ wide fibrillar structures with interfibril spacing of $\approx 100 \text{ nm}$. Figure 6.19b shows the water contact angle of $\approx 85^\circ$ on the patterned surface, a mere $\approx 15^\circ$ increment from that on the non-patterned; in view of the fact that the nanostructures are closely packed on the surface and there is very little air enclosed

between the structures. The third specimen, which is our hierarchical fibrils array (Figure 6.18), has a combination of micro- and nanostructures on different length scales. On this surface, the water droplet is almost spherical with contact angle of $\approx 150^\circ$ (Figure 6.19c). It appears that the presence of microstructures on the surface lead to a considerable reduction of the contact area between the surface and the water droplets, resulting in the amplification of the apparent contact angle. This finding is in good accordance with the calculations of Patankar [152] who proposed the significance of double-roughness structures to mimic “self-cleaning” surfaces found on the lotus leaves. However, for such a high aspect ratio hierarchical structure (Figure 6.18), the slender microfibrils array alone is indeed sufficient to cause amplification of the contact angle, i.e. the fine scale fibrils array does not contribute a substantial role in causing superhydrophobicity. Similarly, the nanostructured PMMA surface in Figure 6.19b also can be an excellent water repellent surface if the periodic spacing of the fibrils array is properly arranged, as previously shown in Figure 5.10b. The double-roughness structure becomes important when one must develop “self-cleaning” surfaces without the ability to fabricate high aspect ratio structures. The fabrication technique presented in this chapter can effectively be used to fabricate such double-roughness (hierarchical) structures.

6.4 Summary

Two fabrication methods, nanoparticles lithography by contact printing and anodic porous alumina based technique, have been developed to produce a hierarchical fibrils array, mimicking the micro and nanostructure of gecko foot-hairs. The latter was found to

be a more viable approach in meeting the challenge due to its cost-effective process and simple experimental setup.

Although we have artificially created the binary-branched gecko setae and overcome the challenge of replicating the hierarchical pattern in gecko foot-hairs, more detailed studies are needed to help optimize their compliance level and adhesive properties. In addition, two factors have yet to be incorporated in the design of our artificial structures; future work will pursue these issues. First, the gecko foot-hairs are built at an inclined angle other than 90° to the backing surface and second, at a much smaller scale, there exist triangular-shaped compliant pads at the tips of gecko spatulae. Both have been reported to have considerable influences on the adhesion strength of “hairy” attachment structures [68].

CHAPTER 7

Conclusions

7.1 Summary and Conclusions

Geckos have evolved specialized adhesive tissues with densely-packed tiny fibrillar structures that allow them to manoeuvre on vertical walls and ceilings. The attachment mechanism of gecko is robust enough to function on unknown rough surfaces and also easily releasable upon animal movement. But what is the true nature of the force underlying the remarkable adhesion of geckos' hairy attachment systems? Is the self-cleaning mechanism inherent in geckos to keep their feet clean, allowing them to attach and detach their feet repeatedly during locomotion? What technology would be appropriate to manufacture the hairy structures in large scale? How do the synthetic hairs perform in terms of the adhesion strength as compared to the natural hairs? What is the significance of the hierarchical structure of gecko foot-hairs to the overall adhesion? These questions have motivated the present investigation on the adhesion mechanism of gecko foot-hairs, the fabrication effort of synthetic gecko foot-hairs, and the mechanics of adhesion in fibrillar structures.

Chapter 3 deals with the mechanics of fibrils-substrate adhesion and separation. The influence of peeling action, in particular the position and the orientation of the applied load was studied in correlation to the detachment effectiveness of fibrillar structures. In addition, the anti-bunching condition and contact of fibrillar structures and rough substrate were discussed. The anti-bunching condition was found to be well adopted in

the natural and synthetic gecko foot-hairs to avoid the problem of matting between neighboring hairs. A simple model using springs array system was then used to understand the significance of hierarchical pattern in geckos. The “soft-and-stiff-fibril” behavior in the hierarchical structure appears to have enabled the geckos to switch between a strong adhesion and an effective detachment during locomotion.

In Chapter 4, the characterization of the terminal element of gecko foot-hairs using AFM was discussed to reveal the most dominant force in geckos’ adhesion. The experimental results show that the force between gecko spatula and an AFM cantilever exhibits behavior consistent with an adsorbed surface water layer. Reducing the relative humidity of the environment results in a decrease of adhesion force and vice versa. When the gecko setae were completely submerged in water, the adhesion force vanishes as the capillary force does not exist in the liquid environment.

In Chapter 5, the combination of colloidal nanolithography, deep-silicon etching, and nanomolding was discussed. The fabrication approach allows manufacturing of high aspect-ratio nanofibrillar structures on a flexible membrane in a large area. With a preloading force of 1 N, the 1 cm^2 synthetic gecko foot-hairs are capable of supporting an object weighing 70 g, which corresponds to about 70% of the nanofibrils arrays attached to the substrate. In addition, the surface inherits the in-use, self-cleaning property of the setal nanostructures found in gecko lamellae. Further adhesion experiments using a rough substrate were rather disappointing as the nanostructured surface failed to demonstrate any useful adhesive properties, even when a much larger preloading force was applied. In order to solve this problem, the fabrication of hierarchical synthetic gecko foot-hairs was proposed to closely imitate the structure of setae and spatula in geckos.

Chapter 6 deals with the synthesis of ultra-thin nanoporous alumina and high aspect-ratio microporous alumina. Bonding the two membranes together using capillary and van der Waals forces allows the preparation of hierarchical porous structure. Filling the porous structure with suitable material, such as PMMA, allows the hierarchical synthetic gecko foot-hairs to be fabricated. By adopting the fabrication technique demonstrated in this thesis, it is possible to prepare hierarchical fibrils array in a large area using a wide range of materials which can be deposited by various template-based deposition methods. At the present stage, the fabricated hierarchical structures, however, yet to exhibit any useful adhesive properties and more detailed study in the selection of material and geometry for the synthetic structures will be required to optimize its adhesive properties.

7.2 Outlook

The following research ideas are proposed for future research directions:

Adhesion tests have previously been performed on a single spatula using AFM and on an isolated seta using piezoresistive cantilever. It has been well reported that the initial preloading force, relative humidity, surface's hydrophobicity, and pulling direction of external force would determine the adhesion strength of gecko foot-hairs. However, the detailed characterization work has so far been limited to the individual gecko seta and spatula, and not yet been conducted on a large scale of setae array or a macroscopic attachment pad. Although numerous modeling works [81, 153, 154] have been reported to address this issue, many important aspects of the problem may not be easily captured using theoretical modeling and could only be realized when the characterization work is performed.

It is still an open question what materials would be best to replace the β -keratin used in gecko foot-hairs. We have currently implemented a variety of polymers, such as parylene, SU-8 (epoxy-based photosensitive polymer), and poly(methyl methacrylate), to synthesize the artificial gecko foot-hairs. The material properties of these polymers, though not identical, do not deviate far from that of keratinous setae in terms of their elastic modulus and surface hydrophobicity. The major concern is the durability of such polymeric materials, which may limit the number of successful re-attachments. Further work on searching a suitable material that resembles keratinous material will be needed to improve the resistance of synthetic hairs to the frequent attachment and detachment cycles.

The construction of man-made adhesives based on fiber array systems appears to be an attractive alternative to the usual pressure sensitive adhesives. We have successfully fabricated a single level and hierarchical fibrillar structures on flexible membrane over a large area. The effective elastic modulus of the fibrillar structures can be very small, which is of fundamental importance for adhesion on smooth and rough substrates. To enhance their compliance level, one should consider constructing the fibrillar structures oriented at an angle other than 90° to the backing. At a much smaller scale, a very important means by which geckos attain a large amount of contact compliance is through the thin plate-like spatulas found at their ends. Incorporating these thin structures would greatly enhance the adhesion strength of synthetic hairs. Moreover, it would increase the versatility of synthetic hairs to adhere on substrates of various surface profiles.

The adhesion and detachment mechanics of geckos have been addressed using simplified models, where the thin fibrils of adhesive microstructures are modeled as

linear springs array. While not all the complexities can be captured in our simple models, it is worthwhile to break a complex problem into smaller, more comprehensible sub-problems that can be further understood using simple mechanics principles. Many other important aspects of the problem, such as viscoelasticity and large nonlinear deformation of the fibrils have not been taken into account. Much further work will be needed to advance the current understanding of bio-adhesion mechanisms. The studies on such problems should be of interest not only to the mechanics community but also to a variety of other disciplines including materials science, biology, and nanotechnology.

7.3 List of Presentations and Publications

1. US Patent filed by Institute of Bioengineering and Nanotechnology (IBN): Victor Samper, Dong Kee Yi, Tanu Suryadi Kustandi, "The method of fabricating branched micro and nanostructures", 2004. Application no: 20060131265.*
2. Tanu Suryadi Kustandi, Dong Kee Yi, Victor Samper, and Wan Sing Ng, "Fabrication of branched synthetic setae structure", *International SBE Conference on Bioengineering and Nanotechnology*, pp. 29, Biopolis, Singapore, 26-29 September 2004.
3. Wanxin Sun, Tanu Suryadi Kustandi, Victor Samper, and Pavel Neuzil, "Understanding the gecko's adhesion force and the self-cleaning mechanism", *International SBE Conference on Bioengineering and Nanotechnology*, pp.28, Biopolis, Singapore, 26-29 September 2004.

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* A/P Ng Wan Sing is not included as potential inventor for this patent application due to IBN internal policy.

4. Wanxin Sun, Pavel Neuzil, Tanu Suryadi Kustandi, Sharon Oh, and Victor D. Samper, "The nature of the gecko lizard adhesive force", *Biophysical Journal*, 89: L14-L17, 2005.
5. Tanu Suryadi Kustandi, Victor Samper, Wan Sing Ng, "Mimicking gecko nanostructures", *Proceedings of Eurosensors XIX*, TP72, Barcelona, Spain, 11-14 September 2005.
6. Tanu Suryadi Kustandi, "Biologically inspired adhesive nanostructures", awarded first runner-up in the Andrew Fraser Prize 2005 (IMechE Singapore Branch) for excellence in postgraduate research.
7. Tanu Suryadi Kustandi, Victor Samper, Dong Kee Yi, Wan Sing Ng, Pavel Neuzil, and Wanxin Sun, " Self-assembled nanoparticles based fabrication of gecko foot-hairs inspired polymer nanofibers", *Advanced Functional Mateterial*, 17: 2211-2218, 2007.
8. Tanu Suryadi Kustandi, Victor Samper, Wan Sing Ng, "Mimicking gecko hierarchical micro and nanostructures", *Proceedings of Nanotech Insight '07*, pp. 40-42, Luxor, Egypt, 10-17 March 2007.
9. Tanu Suryadi Kustandi, Victor Samper, Wan Sing Ng, "Fabricating gecko-like hierarchical fibrils array using bonded porous alumina template", *Journal of Micromechanics and Microengineering*, 17: N75-N81, 2007.

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Appendix A Specifications and Properties of Parylene

Extracted from http://www.scscoatings.com/parylene_knowledge/specifications.cfm)

I. Introduction

Parylene is the generic name for members of a unique polymer series. The basic member of the series, called Parylene N, is poly-para-xylylene, a completely linear, highly crystalline material.

Parylene C, the second commercially available member of the series, is produced from the same monomer modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. The structures are shown in Figure A.1.

Figure A.1 Chemical structures of Parylene N, C, and D

Parylene D, the third member of the series, is produced from the same monomer modified by the substitution of the chlorine atom for two of the aromatic hydrogens. Parylene D is similar in properties to Parylene C with the added ability to withstand higher use temperatures.

Parylene N is a primary dielectric, exhibiting a very low dissipation factor, high dielectric strength, and a dielectric constant invariant with frequency. This form has the highest penetrating power of all the Parylenes. Parylene C has a useful combination of electrical and physical properties plus a very low permeability to moisture and other corrosive gases. Along with its ability to provide a true pinhole free conformal insulation, Parylene C is the material of choice for coating critical electronic assemblies.

II. The Deposition Process

The Parylene polymers are deposited from the vapor phase by a process which in some respects resembles vacuum metallizing. Unlike vacuum metallization, however, which is conducted at pressures of 10^{-5} torr or below, the Parylenes are formed at around 0.1 torr. Under these conditions the mean free path of the gas molecules in the deposition chamber is in the order of 0.1 cm. Therefore, unlike vacuum metallizing, the deposition is not line of sight, and all sides of an object to be encapsulated are uniformly impinged by the gaseous monomer. This is responsible for the truly conformal nature of coating.

Figure A.2 Parylene Deposition Process

The process consists of three distinct steps as outlined in Figure A.2 for Parylene N. The first step is vaporization of the solid dimer at approximately 150° C. The second step is the quantitative cleavage (pyrolysis) of the dimer at the two methylene-methylene bonds at about 680° C to yield the stable monomeric diradical, para-xylylene. Finally, the monomer enters the room temperature deposition chamber where it simultaneously adsorbs and polymerizes on the substrate. No liquid phase has ever been isolated and the substrate temperature never rises more than a few degrees above ambient. A necessary fourth component in this system is the mechanical vacuum pump and associated protective traps.

The equipment can be modified to meet the requirements or configuration of the items to be coated. Present coating chambers vary in size from 23 cm in diameter and 31

cm long to a 85 cm high hemi-cylindrical unit. One particular configuration, 45 cm in diameter and 60 cm high, was designed specifically for circuit boards and can accommodate up to two hundred 12 cm wide by 16 cm long boards. The process is inherently simple and can be conducted with a minimum of supervision.

Compared with vacuum metallizing, deposition rates are fast, especially for Parylene C, which is normally deposited at about 0.2 mils/hr. The deposition rate of Parylene N is somewhat slower. Kinetic studies have established that this rate is directly proportional to the square of the monomer concentration and inversely proportional to the absolute temperature.

III. Properties

The electrical and mechanical properties of Parylene N, C and D are discussed below. These properties are compared to those reported for other conformal coating materials such as epoxides, silicones, and urethanes.

A. Electrical Properties

The electrical properties of Parylene N, C, and D are shown in Table A.1.

Table A.1 Parylene Electrical Properties

Properties (1)	Parylene N	Parylene C	Parylene D	Epoxides (2)	Silicones (2)	Urethanes (2)
Dielectric Strength, dc volts/mil short time, 1 mil films ^a	7,000	5,600	5,500	-	-	-
corrected to 1/8 in	630	500	490	400-500	550	450-500
Volume Resistivity, ohm-cm, 23 °C, 50% RH ^b	1.4X10 ¹⁷	8.8X10 ¹⁶	1.2X10 ¹⁷	10 ¹² -10 ¹⁷	10 ¹⁵	10 ¹¹ -10 ¹⁵
Surface Resistivity, ohms, 23 °C, 50% RH ^b	10 ¹³	10 ¹⁴	10 ¹⁶	10 ¹³	10 ¹³	10 ¹⁴
Dielectric Constant ^c						
60 Hz	2.65	3.15	2.84	3.5-5.0	2.7-3.1	5.3-7.8
1 KHz	2.65	3.10	2.82	3.5-4.5	2.6-2.7	5.4-7.6
1 MHz	2.65	2.95	2.80	3.3-4.0	2.6-2.7	4.2-5.2
Dissipation Factor ^c						
60 Hz	0.0002	0.020	0.004	0.002-0.01	0.001-0.007	0.015-0.05
1 KHz	0.0002	0.019	0.003	0.002-0.02	0.001-0.005	0.04-0.06
1 MHz	0.0006	0.013	0.002	0.03-0.05	0.001-0.002	0.05-0.07

^a ASTM D 149^b ASTM D 257, 1 in² mercury electrodes^c ASTM D 150, 1 in² mercury electrodes

(1) Properties measured on Parylene films, 0.001 in thick.

(2) Properties and methods as reported in *Modern Plastics Encyclopedia*, issue for 1968, Vol. 45/No. 1A, McGraw Hill, New York, 1967.

(International Conversion Chart, Page 12)

B. Physical and Mechanical Properties

Physical and mechanical properties of the Parylenes are summarized in Table A.2. Because of their high molecular weight (~500,000) and because the melting temperatures and crystallinity are high, the Parylenes cannot be formed by conventional methods such as extrusion or molding. Solubility in organic or other media, except at temperatures above 175° C, is so low that they cannot be formed by casting.

Table A.2 Parylene Physical and Mechanical Properties

Properties (1)	Method	Parylene N (2)	Parylene C	Parylene D	Epoxides (3)	Silicones (3)	Urethanes (3)
- Secant (Young's) Modulus (psi)	1	350,000	400,000	380,000	350,000	900	1,000-10,000
- Tensile Strength (psi)	2	6,000-11,000	10,000	11,000	4,000-13,000	800-1,000	175-10,000
- Yield Strength (psi)	2	6,100	8,000	9,000	-	-	-
- Elongation to Break (%)	2	20-250	200	10	3-6	100	100-1,000
- Yield Elongation (%)	2	2.5	2.9	3.0	-	-	-
- Density (g/cm ³)	3	1.10-1.12	1.289	1.418	1.11-1.40	1.05-1.23	1.10-2.50
- Index of Refraction (n ₀ ²³)	4	1.661	1.639	1.669	1.55-1.61	1.43	1.50-1.60
- Water Absorption (% after 24 hrs)	5	----- Less than 0.1 -----			0.08-0.15	0.12 (7 days)	0.02-1.50
- Rockwell Hardness	6	R85	R80	R80	M80-M110	40-45 (Shore A)	10A-25D (Shore)
- Coefficient of Friction Static Dynamic	7	0.25 0.25	0.29 0.29	0.33 0.31	-	-	-

Test Methods:

1. ASTM D 882 at 1% strain
2. ASTM D 882 at 10% strain, min.
3. ASTM D 1505
4. Abbe Refractometer
5. ASTM D 570
6. ASTM D 785
7. ASTM D 1894

(1) Properties measured on Parylene films, 0.001-0.003 in thick except where specified.

(2) Properties depend somewhat on deposition conditions.

(3) Properties and methods as reported in *Modern Plastics Encyclopedia*, issue for 1968, Vol. 45/No. 1A, McGraw Hill, New York, 1967. Modulus values are for tensile modulus.

(International Conversion Chart, Page 12)

Appendix B Properties of PMMA

Extracted from http://www.io.tudelft.nl/research/dfs/idemat/Onl_db/Id123p.htm.

Table B.1 PMMA Properties

Property	Min	Max	Unit
Price	2.16	2.67	EURO
Young's modulus	1800	3100	MPa
Shear modulus	1700	1700	MPa
Tensile strength	48	76	MPa
Elongation	2	10	%
Compressive strength	83	124	MPa
Creep strength			
Fatigue	11	12	MPa
Bending strength	120	148	MPa
Hardness	85	105	Rockwell
Impact strength	0.16	0.27	J/cm
Yield strength			
Thermal expansion	50	90	e-6/K
Thermal conductivity	0.167	0.25	W/m.K
Specific heat	1466	1466	J/kg.K
Melting temperature			
Glass temperature	105	105	?C
Service temperature	-40	90	?C
Density	1170	1200	kg/m ³
Resistivity	1E+19		Ohm.mm ² /m
Breakdown potential	16	30	kV/mm
Electrochemical potential			
Dielectric loss factor	0.04	0.06	
Friction coefficient	0.54	0.54	
Refraction index	1.492	1.492	
Thickness	0.6	6.3	mm
Shrinkage	0.3	0.8	%
Water absorption	0.3	0.4	%