A Micro/Nano-Fabricated Gecko-Inspired Reversible Adhesive

A Dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials

by

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March 2006
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by

Michael Thomas Northen
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This manuscript is dedicated to my loving parents Tom and Cheri, for with their gentle guidance and unfaltering support I was able to make a journey longer than I ever imagined. I’d also like to thank my brother Trent for being amazing enough that it has always been okay to follow in his footsteps.

For making this body of work possible, and enticing me to do a PhD in the first place, I would like to thank my advisor and friend Professor Kimberly Turner. Also there have been many friends and colleagues that without their help I would not have been able to traverse this path, or at least wouldn’t have had so much fun in the process. A few key people I would like to thank are Alicia Soliz, for all her love and support; Tellef Tellefson and Laurent Pelletier, for just being darn good friends; Michael Requa, Marco Aimi and Emily Parker, for always being there as friends and colleagues; Masa Rao and Brian Thibeault, for their extensive processing advice; and Jim and Robin Cooper for being friends and helping me along at critical points in this journey. I’d also like to recognize all the staff and faculty at UCSB, in particular the Materials and Mechanical Engineering Departments, for making this institution such a dynamic and supportive environment, where creativity and innovation can flourish.
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ABSTRACT

A Micro/Nano-Fabricated Gecko-Inspired Reversible Adhesive

by

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The gecko adhesive has been of scientific interest for over two millennia, ever since Aristotle observed a gecko running up and down a tree. Since then, advances in optical and electron microscopy have provided increased information on the structure of the pad of the gecko’s foot, for it is the structure that leads to the adhesion and not the chemistry. Each toe contains many ridges, or scanners, displaying arrays of ~100 μm long, ~5 μm wide setae, each branching into hundreds of smaller fibers called spatulae, ~200 nm across and 5 nm thick. The combination of the setal flexibility and the nanoscale compliance of the spatulae creates a large amount of intimate surface contact, enhancing van der Waals interactions, and promoting adhesion.

In this work, an adhesive—inspired by the gecko—was micro/nanofabricated. There were two main thrusts in this work. The first was to show the importance of the hierarchical structure on the performance of the gecko adhesive, and the future need to for multiple levels of compliance in synthetic dry adhesives. The second thrust was to create a surface with controllable adhesion. While the adhesion
properties of the gecko are of great scientific interest, it is the ability to switch adhesion on and off that provides the technological driving force for mimicking the gecko system.

The microscale setae of the gecko have been replicated by microfabricating flexible silicon dioxide freestanding structures ~100 μm long and ~10 μm wide. These structures were coated with aligned vertical polymeric nanorods ~4 μm tall and ~200 nm in diameter, analogous to the gecko spatulae. Testing of the synthetic structures shows that the multi-scale system provides a 5-fold increase in adhesion over nanorods alone, demonstrating the need for a hierarchical structure. To create a switchable adhesive, the silicon dioxide microstructures were replaced with nickel micro-paddles. When the nickel structures were placed in a magnetic field, a conformation change was induced, rotating the paddles away from an adherent surface, and adhesion was reduced by a factor of 40. This is the first demonstration of a surface displaying reversible and controllable adhesion.
# TABLE OF CONTENTS

I. Introduction ............................................................................................................. 1

II. Background ............................................................................................................ 2
   A. Biological Adhesion .......................................................................................... 2
      1. Overview ..................................................................................................... 2
      2. Adhesion Mechanics .................................................................................. 9
      3. Adhesion forces ....................................................................................... 13
   B. MEMS Fabrication Techniques ................................................................. 20
      1. Photolithography ....................................................................................... 20
      2. Wet etching ............................................................................................. 21
      3. Dry Etching ............................................................................................. 22
      4. Electron Beam Deposition ...................................................................... 23
      5. Sputtering ............................................................................................... 23
   C. Micro/Nanotribology ...................................................................................... 24
      1. Nanoindentation ....................................................................................... 24
      2. Wyko Optical Profilometer ..................................................................... 26

III. Detailed Micro/Nanofabrication ..................................................................... 29
   A. Silicon Dioxide Platforms Supported by Single Crystal Silicon Pillars ................................................................. 29
   B. Multi-Scale Integrated Structures ........................................................... 34
   C. Nickel Multi-Scale Integrated Structures .............................................. 37

IV. Single High Aspect Pillar Support Structures ............................................... 44
   A. Introduction .................................................................................................. 45
B. Experimental ................................................................................... 46
   1. Fabrication................................................................................... 46
   2. Equipment ................................................................................... 47
C. Results and Discussion ..................................................................... 48
   1. Characterization .......................................................................... 49
   2. Future Work ................................................................................ 53
D. Conclusions ..................................................................................... 53
E. Acknowledgments........................................................................... 54
F. Figures............................................................................................. 55

V. A batch fabricated biomimetic dry adhesive ....................................... 63
   A. Introduction ..................................................................................... 64
   B. Fabrication ....................................................................................... 66
   C. Experimental ................................................................................... 69
   D. Results and Discussion .................................................................... 70
   E. Summary .......................................................................................... 75
   F. Figures............................................................................................. 76

VI. Batch Fabrication and Characterization of Nanostructures for Enhanced Adhesion 84
   A. Introduction ..................................................................................... 85
   B. Experimental ................................................................................... 87
      1. Fabrication................................................................................... 87
      2. Characterization .......................................................................... 88
   C. Results and Discussion .................................................................... 89
LIST OF FIGURES

Figure II-1 Dude, a male Tokay Gecko (Gekko Gecko) sticking to a wall surface
(Image by Jeff Clark, www.jeffclarkphotography.com) ........................................ 2

Figure II-2 Gecko hierarchical adhesive system. Electron micrographs of: A. the
terminal spatular structure, scale bar 500 nm; B. the heavily branched spatular end of a setal stalk, scale bar 10 μm; C. setae extending from a lamellae surface, scale bar 20 μm. D. setal array showing the branched structures of the setae, scale bar 100 μm. .................................................................................................................. 4

Figure II-3 Images of Dude, a Tokay Gecko, on a glass surfaces. Note the orientation of the toes relative to Dude’s leg and body orientation on the glass surface. .......................................................................................................................................................... 5

Figure II-4 Image of Dude the Gecko peeling his tarsus from the surface (Image by Jeff Clark).................................................................................................................................................. 8

Figure II-5 Illustration of the contact splitting phenomenon in nature. Plot shows that as the animal’s mass increases then so does the necessary density of termini in the adhesion system. Figure from reference (27).................................................. 17

Figure II-6 Diagram of the parallel plate sensing mechanism in the Hysitron™ nanoindenter system................................................................................................................................. 25

Figure II-7 Interference microscope design for the Wyko NT1100 optical profiler. 27

Figure II-8 Fringing pattern see on a tilted surface (top). Illustration of the intensity versus height for interfering light on a tilted surface. ......................................................... 28
Figure III-1  Electron micrographs of SHARPS structures showing the silicon
dioxide platform supported by a single crystal silicon pillar. Right image offers
a magnified view of the pillar. Scale bars are 20 μm and 10 μm left and right
respectively. ........................................................................................................ 30

Figure III-2  SHARPS fabrication process flow schematic. .............................. 31

Figure III-3  Electron micrograph of the organic looking polymeric nanorods,
‘organorods,’ scale bar 10 μm. .................................................................................. 35

Figure III-4  Electron micrographs of SHARPS structures coated with organorods.
Scale bars are 20 μm and 5 μm, left and right respectively. ............................... 36

Figure III-5  (Top) Optical images of a water droplet on untreated (left) and treated
(right) organorod surfaces. (Bottom) Corresponding electron micrographs of
the structure, scale bars 2 μm. .................................................................................. 37

Figure III-6  Electron micrographs of released organorod coated nickel paddle
structures. Opposing paddles coated with organorods scale bar 20 μm (top).
Magnified view with dimensions of organorods, scale bar 2 μm (bottom-left).
Array of paddles, scale bar 100 μm (bottom-right). ............................................. 42

Figure IV-1  Electron micrographs of various SHARPS structures (From Top and
Left to Right) Square topped array, round top, slotted square, slotted round,
branched finger, branched fine finger, radial meander, serpentine. ................. 56

Figure IV-2  SHARPS fabrication process flow. ....................................................... 56

Figure IV-3  Optical micrographs showing pillar geometry along the long axis.
(From left to right) Hexagonal, triangular, square, octagonal. ......................... 57

Figure IV-4  SHARPS structure with modified pillar geometry along the long axis. 57
Figure IV-5  (Top) surface profile taken in a Veeco Wyko N1100 of the structure in the bottom left image. (Bottom left) SHARPS structure after sputtering a half micrometer of titanium. (Bottom right) same structure after sputtering ~5 μm of titanium. ................................................................. 58

Figure IV-6  Nanoindenter bending stiffness experimental data and theoretical plot originating at the center of the SHARPS platform. (Top) Diamond cross section (Bottom) Square cross section. ................................................................. 59

Figure IV-7  (Top) before and after images of a probe pushing laterally on the structure. (Bottom left) Superposition of images illustrating deformation distance: distance between blue and yellow lines. (Bottom right) Schematic representation of 3-dimensional deformation. ........................................ 60

Figure IV-8  SHARPS structures after sputtering ~5 μm titanium....................... 60

Figure IV-9  Comparison of adhesion vs. applied normal force between a polyamide bead and the substrate or a radial meander SHARPS structure. ....................... 61

Figure V-1  Electron micrographs of silicon dioxide platforms supported by single slender pillars and coated with polymeric organorods. The structures are batch fabricated using standard bulk micro fabrication techniques requiring only a single lithography step. a, Array of four-fingered platform structures. Scale bar, 200 μm. b, Profile view of a organorod coated silicon dioxide platform supported by a single crystal silicon pillar. Scale bar, 20 μm. c, Magnified view of the multi-scale system. Scale bar, 20 μm. The integration of the ~200 nm diameter organorods with the 150 μm platform structures provides enhanced
surface conformation. d, High resolution electron micrograph of the edge of an organorod coated finger. Scale bar, 5 µm. ................................................................. 77

Figure V-2 Silicon dioxide platform supported by a single high-aspect-ratio pillar etched out of single crystal silicon using a modified micro fabrication technique. Scale bar 50 µm. ............................................................................... 78

Figure V-3 Organic looking polymeric nanorods, “organorods”, fabricated utilizing the instability of a dielectric in a large electric field. The ~100 nm features were achieved using a bilayer to reduce the interfacial energy, thus reducing the instability wavelength and corresponding feature size. Scale bars, 10 and 2 µm, left and right respectively. ............................................................................................. 78

Figure V-4 Comparison of hydrophilic and hydrophobic surfaces. a, (top) Water droplet partially wetting a hydrophilic organorod surface with a contact angle of 42.5° ± 2 (top). (bottom) Electron micrograph of ~120 nm diameter organic looking nanorods, “organorods”. Scale bar, 5 µm. b, (top) Water droplet resting on top of the highly-hydrophobic organorod surface with a contact angle of 145° ± 2. (bottom) Electron micrograph shows the increased diameter of the organorods to ~350 nm from the fluorocarbon hydrophobic coating applied through plasma deposition. Scale bar, 5 µm. ................................................................. 79

Figure V-5 Typical nanoindenter adhesion test results for a organorod covered structure indented with a semi-rough 3.175 diameter spherical aluminum tip. The plot represents a typical load vs. displacement curve illustrating loading, unloading, and pull-off adhesion................................................................. 80
Figure V-6  Nanoindenter adhesion testing results and theoretical models for hydrophilic polymeric surfaces. Test surfaces were indented with a semi-rough 3.175 diameter spherical aluminum tip. Increased normal loads created more surface contact between the spherical tip and surfaces increasing adhesion. The organorod morphology enhanced surface adhesion over the solid photoresist surface. Adhesion was further enhanced by integration of organorods with flexible silicon dioxide platforms, large data scatter was a by-product of testing meso-scale adhesion with a rough surface. a, van der Waals and b, Johnson-Kendal-Roberts (JKR) adhesion models predicting the collective adhesion of organorods over a given contact area, predicted by JKR contact mechanics for a sphere and flat surface. c and d, Modified van der Waals adhesion accounting for increased contact area attributed to conformation of platform “fingers” to the test sphere; c, two fingers. d, four fingers. The saturation point corresponds to complete finger attachment, in the case of four fingers (d) this value nicely bounds the experimental data.

Figure V-7  Nanoindenter adhesion testing results and theoretical models for hydrophobic polymeric surfaces. Surface adhesion between the sphere and test surfaces is enhanced by a hydrophobic coating on the organorods. The coating increases the size from ~120 nm to ~350 nm and reduces the surface energy. a, van der Waals interaction energy model predicts an increase in adhesion with the larger organorods, but fails to capture the trend of the hydrophobic organorods. b, van der Waals and c, JKR models compensating for an increased radius of curvature- determined by scanning electron microscopy- of
organorods squashed during indentation show better agreement with experimental data. d, Reduction of the interaction distance, $d_o$, from 0.165 nm to 0.09 nm in the van der Waals model. e, Combining the modified van der Waals models for hydrophobic organorods ($d_o=0.09$ nm) and the compliant platform model with 1 finger, excellent agreement with the meso-scale adhesion test is seen. Note the terminus of dotted line represents 1 complete finger adhesion.

Figure V-8  Scanning electron micrographs showing squashed organorods in the central portion of a structure. Scale bars, 20 and 10 μm, left and right respectively.

Figure VI-1  Scanning electron micrographs of the organorod morphology, scale bars 5 μm and 1 μm, left and right respectively.

Figure VI-2  Schematic of the organorod growth mechanism. A bias is applied between oxygen plasma and the substrate, creating an electric field gradient, which acting on the dielectric polymer draws it in the direction of the gradient.

Figure VI-3  Schematic of the nanoindenter test setup. The sphere represents the 3.175 mm aluminum sphere which is fixed to a shank fitted into the nanoindenter transducer. When the sphere is pressed into the platform structures a loading and unloading curve is produced. At the bottom of this curve there is a sudden jump from a negative force value to zero. This jump is indicative of pull-off associated with adhesion, and correspondingly taken to be the adhesive force.
Figure VI-4  Nanoindenter test data plotted against analytical van der Waals (vdw) predictions. The circles represent a smooth polymer surface without modification. The squares represent a hydrophilic organorod surface on a solid substrate. The triangles represent a hydrophobic organorod surface on a solid substrate. Curve a represents a simple vdw model based on the number of organorods contacting the test surface, the radius of curvature of the organorod tips, and using a cut-off distance of 0.165 nm. The number of contacts is estimated by knowing the density of organorods and calculating the contact area of the indenter tip using JKR contact mechanics. Curve b is identical to curve a, but with a reduced cut-off distance in the vdw equation of 0.09 nm. 

Figure VII-1  Multiscale integrated compliant structures (MICS). Portion of a 2,500 array of MICS (top), scale bar 500 μm. Individual MICS (middle), scale bar 50 μm. Central portion of a platform showing organorod integration (bottom), scale bar 10 μm. ..........................................................110

Figure VII-2  Scanning electron micrograph of organic looking polymeric nanorods (“organorods”) on the central portion of a platform, scale bars 5 μm and 2 μm, top and bottom respectively. ..........................................................110

Figure VII-3  Adhesion strength versus applied normal load between a 5 mm diameter aluminum flat punch and a smooth photoresist surface (triangles); a surface of vertically aligned photoresist organorods (diamonds); and a surface of arrayed multiscale integrated compliant structures consisting of silicon dioxide platforms coated with organorods (squares). .............................................111
Figure VII-4  Comparison of repeated adhesion between a organorod surface on solid substrate (diamonds) and a organorod surface on compliant structures (squares). ........................................................................................................... 112

Figure VIII-1 – Electron micrographs of synthetic structures (left) and the analogous gecko structures (right), samples from a Tokay Gecko (*Gekko Gecko*). (A) Paddle surface coated with evenly spaced uncondensed aligned vertical polymer nanorods (left) and the branched terminus of a seta into spatulae (right), same magnification and scale bar 10 μm. (B) Freestanding nickel cantilevers and paddles coated with nanorods (left) and an array of setae (right), same magnification and scale bar 50 μm. (C) Low angle view of cantilevers showing upwards bending of the structures relative to the solid substrate (left) and a profile view of curving setal stalks (right), same magnification and scale bar 50 μm. (D) Lower magnification view of a portion of the synthetic array (left) and the setal array (right), scale bars 500 μm (left) and 200 μm (right). 123

Figure VIII-2 - Stereomicrographs of the adhesive: (A) in the ‘ON’ state, no applied magnetic field, with the adhesive paddles facing vertically; and (B) in the ‘OFF’ state, with an applied magnetic field rotating the paddles sideways, concealing the adhesive faces. Scale bars, 100 μm................................................. 124

Figure VIII-3 – Schematic of the adhesion test apparatus. A laser interferometer monitors the deflection of a glass cantilever spring as a piezo actuator moves a 5 mm glass flat punch into and away from the test surface. The interaction forces are calculated by relating the stiffness and deflection of the cantilever upon contact with the surface................................................................. 125
Figure VIII-4 - Adhesion results showing the on/off behavior of the structures without and with an applied magnetic field, respectively. The insets represent actual adhesion data, where in the ‘ON’ state distinctive pull-off events were observed (top) and in the ‘OFF’ state no pull-off events were observed (bottom). Strength values were obtained by dividing the interaction force by the contact area of the paddles. In the ‘ON’ state, the devices showed an initial increase in adhesion with preload force, characteristic of increased surface contact with applied load (likely a result of slight misalignment between the 5 mm flat punch and test surface). Error bars represent 10 data sets at a specified displacement with no emission of outliers................................. 125

Figure IX-1  Electron micrographs of a double paddle configuration. The paddles are bending out of the base plane. By opposing each other the two paddles create a squeezing action, transforming a pure normal force into a combined normal and lateral force, enhancing a frictional component......................... 131

Figure IX-2  Electron micrograph of a branched fingers bending out of plane. The branch fingers enhance the beams bending while providing surface area for adhesion............................................................................................................. 133

Figure IX-3  Electron micrographs of eight fingered branched platform structures coated with aligned vertical nanorods. The fingers are bending up out of the plane of the center support. Scale bars, in descending order, of 20, 100, 200 and 1000 μm.................................................................................................................. 135
I. Introduction

As a courtesy to the reader, a brief introduction of how to best navigate this thesis is given. For the general reader, the background information on the gecko, found in chapter II, may be quite interesting and important to understanding the research presented here. Also particular attention should be paid to the Chapters V and VIII, as these high impact journal publications highlight the significant findings in this research. As can be seen throughout this thesis, most work was focused on the development of micro/nanofabrication techniques for mimicking the hierarchical structure of the gecko adhesive.

Several new fabrication and characterization techniques were developed throughout the course of this work, leading to four journal publications and three conference proceedings. As a matter of completeness the journal publications and one conference proceeding has been included as chapters in this thesis. However, the reader may find the introductions, background and methods sections in each paper too brief, such is the nature of these publications. Therefore two important chapters have been added to the beginning of the document:

Chapter II. A chapter giving a basic overview of the inspiration of the gecko adhesive system, the techniques used to create an analogue, and the methods employed to characterize the system.
Chapter III. A detailed chapter on the fabrication process, with extended commentary not found in the publications. While the background information on the gecko is important, this body of work was focused on developing new fabrication techniques for creating a hierarchical and reversible gecko inspired adhesive.

II. Background

A. Biological Adhesion Equation Chapter 2 Section 1

1. Overview

Figure II-1 Dude, a male Tokay Gecko (Gekko Gecko) sticking to a wall surface (Image by Jeff Clark, www.jeffclarkphotography.com).
The fine hair adhesive motif is found throughout nature in a variety of insects and lizards (1-8). While flies, beetles, crickets, spiders and anoles all make use of highly branched terminal structures to scale and stick to about any surface, the gecko is the largest animal to employ such a clinging motif. A Tokay Gecko (*Gekko Gecko*, Fig. II-1) weighs up to 300 grams and is able to run up, and down, vertical surfaces and across inverted surfaces (2). Not only does the gecko have the largest mass, it also has the most refined nanostructure, Fig. II-2. This is no coincidence as the structures with more branches produce more adhesion (discussed in detail in section 2 on adhesion mechanics).
Figure II-2  Gecko hierarchical adhesive system. Electron micrographs of:

A. the terminal spatular structure, scale bar 500 nm;  B. the heavily branched spatular end of a setal stalk, scale bar 10 μm;  C. setae extending from a lamellae surface, scale bar 20 μm.  D. setal array showing the branched structures of the setae, scale bar 100 μm.

The gecko adhesive is a multi-scale hierarchical structure composed of β-keratin (3). While the nanostructures at the final termini of the system are of significant interest presently in the scientific community, it is the entire gecko system responsible for the amazing sticking ability of the gecko. The gecko has four feet, each containing five digits, Fig. II-3. The toes themselves are very flexible, able to roll up and away from a surface—important for the release mechanism. Within each toe are rows of imbricated lamellae supported by blood sinuses in the pad of the tarsus – which act as a sort of hydraulic suspension. The lamellae contain rows of thin slender fibers, called setae, approximately 130 μm in length and 20 μm in diameter (2), Fig. II-2. The terminus of each seta branches into thousands of smaller fibers, or spatular stalks. At the end of each of these stalks the structures flatten out into a flat 200 nm wide and 5 nm thick pad, or spatula (1, 2, 6, 9).
Figure II-3  Images of Dude, a Tokay Gecko, on a glass surfaces. Note the orientation of the toes relative to Dude’s leg and body orientation on the glass surface.

As with any adhesive, in order for the adhesive to work it has to come into contact with the adhering surface. For an ideally smooth surface making contact is relatively straight forward. However, the gecko does not have the luxury of ideal surfaces in nature. Imagine a gecko running up a tree trunk trying to maximize contact with the tree. The first thing the gecko is able to do is bend its legs, adjusting for the curvature of the trunk, putting the pads into contact with the surface. Depending on the surface, the toes are then able to bend and wrap around any centimeter scale roughness. Next the blood sinuses in the pad are able to deform to millimeter scale roughness in the surface. The setae are then able to bend and nestle into milli- to micro-scale roughness, which then puts the spatulas into contact with the surface. The thin, compliant spatulas are then able to conform to nanoscale
roughness and make intimate contact with the surface. As will be discussed in the
adhesion mechanics section, this intimate contact is necessary to enhance the van der
Waals interactions responsible for adhesion.

Although in literature, and in this document, this phenomenon of a gecko
sticking to a surface will be called “adhesion,” in fact it is a combination of friction
and adhesion, arguably the more important contributor being friction. Observing a
gecko, immediately one becomes aware of the directionality of the toes and feet, and
how their orientation can change depending on the orientation of the gecko and
surface. While on a vertical surface a gecko tends to have a greater number of toes
point upwards, and toes on opposing legs tend to face away from each other. The
toes facing upwards tend to create a friction in an optimal direction for the gecko
(creating friction on the spatulas by dragging them along a surface instead of peeling
them away from the surface). Meanwhile the toes on opposing legs, by pointing
away from each other, tend to induce a squeezing action, again creating a frictional
component in the system. On an inverted surface the gecko relies on this squeezing
action.

To understand this concept imagine for a second holding a balloon with one
hand. If you simply take a rigid flat hand and press it against a balloon and pull
away, there should be no ‘adhesion,’ the non-compliant situation. Now take a limp
hand and allow it to wrap around the balloon and pull away – probably a slight sense
of adhesion, but the balloon is left behind. Now, place a hand around the balloon
and squeeze slightly. The balloon should easily be manipulated. The gecko uses a
similar strategy, employing friction via a squeezing action, to enhance its ability to stick to surfaces.

Prior work in this area has focused solely on fabricating nanostructured surfaces \((10-13)\). However, it is clear that the hierarchical nature of the gecko adhesive serves many other purposes as well – e.g. enhancing surface conformation and inducing a frictional component. In this work, efforts have been focused on creating the first two levels of the hierarchical structure. That is creating an analogue to the spatular/setal structure by integrating similar nano/micro-scale structures.

The gecko adhesive system may open the door for a variety of new adhesives with niche applications, i.e. tape for high vacuum environments and highly reusable tape. However, the system is of real interest because it presents the opportunity for creating an adhesive that can stick and then be caused to unstick. Thus, it is important to understand a bit about the unsticking mechanism of the gecko.
To unstick its foot from a surface the gecko uses a peeling action, starting from the tip of the toe and rolling inwards, Fig. II-4. From a macroscale understanding of how tape works, peeling is much easier than trying to pull off the entire piece of tape at the same time. However there is more to the story with the gecko. The specific shape of the spatulas and the setae allow for maximum adhesion (actually a combination of adhesion and friction) when the pull-off force is directed at a $30^\circ$ angle from the surface (6, 14, 15). This angle is the point where both the frictional force and adhesion forces are highest; the frictional force due to the larger component of lateral force, but with still enough normal force to maintain contact; and the adhesion force due to the geometry of the spatula creating a compressive force at the base of the stalk inhibiting crack initiation (14). As the pull-off angle
moves above 30° the adhesion (and friction) decreases rapidly facilitating the removal of the pad from the surface.

2. Adhesion Mechanics

In order to mimic the biological adhesive system, it is helpful to understand a little bit more about fundamental adhesion mechanics. In this section a brief and concise overview of a few of the fundamental theories, as well as a few specialized theories, applicable to the multiple contact adhesion phenomenon is presented.

The simplest relevant case to consider is a sphere contacting a flat surface. Hertz found that a sphere contacting a flat, smooth surface (assuming the materials to be homogeneous and isotropic) has a contact area of (16):

\[ A_c = \pi \left( \frac{RF_n}{K} \right)^{\frac{2}{3}}, \quad (\text{II.1}) \]

where \( R \) is the radius of the sphere, \( F_n \) is the normal force and \( K \) is the effective elastic modulus.

\[ \frac{1}{K} = \frac{3}{4} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right), \quad (\text{II.2}) \]
where \(E_i\) and \(\nu_i\) are the Young’s moduli and Poisson ratios of the two materials respectively.

In this case Hertz assumes that the sphere is pushed into the surface, deforms, and then when the force is removed returns back to original configuration without hysteresis. While this theory explains the contact mechanics it does not predict adhesion between the sphere and the flat surface.

Johnson-Kendall-Roberts considered the surface energies of the contacting surfaces and found that the contact area increases due to a reduction in interfacial energy (17-19):

\[
A_c = \pi \left[ \frac{R}{K} \left( F_n + 6\pi R + \sqrt{12\pi \gamma RF_n + (6\pi \gamma R)^2} \right) \right]^{\frac{2}{3}},
\]

where \(\gamma\) is the interfacial energy and responsible for the mechanism of adhesion.

The interesting outcome is that in the absence of a normal force there is still a contact area and an adhesive force. The radius of contact is given by:

\[
a_o = \left( \frac{12\pi \gamma R^2}{K} \right)^{\frac{1}{2}}.
\]

And the pull-off force, or magnitude of adhesion is:

\[
F_{JKR} = 3\pi \gamma R.
\]
The Derjaguin-Muller-Toporov Model (20-22) is a variation of the JKR Model of above and also takes into account long range forces. The attractive force is approximated by Leonard-Jones potentials. The model also considers that surfaces in contact deform due to attractive forces, calculated using a Hertzian approach.

Modifying the JKT model accordingly a new pull-off force is derived:

$$F_{DMT} = 4\pi\gamma R,$$  \hspace{1cm} (II.6)

for the case of an undeformable flat surface and considering both surfaces to have equal surface energies.

This gives a radius of contact with no normal load of:

$$a_0 = \left(\frac{4\pi\gamma R^2}{2K}\right)^{\frac{1}{3}}.$$  \hspace{1cm} (II.7)

As it turns out in some instances it is better to use the JKR method and in other cases to use the DMT method. To determine whether or not to use JKR or DMT Derjaguin introduced a dimensionless number:

$$\beta = \frac{64}{3\pi} \left[ \frac{\gamma^2 R}{\pi K s^2} \right]^{\frac{1}{3}},$$  \hspace{1cm} (II.8)

where $s$ is the separation between the two solids with strongest attraction. If $\beta$ is much greater than unity then the JKR model is valid.
A helpful way to interpret adhesion is the change in surface energy associated with separation of two surfaces, described by the Dupré equation (23):

\[ W_a = \gamma_1 + \gamma_2 - \gamma_{12}, \]  

(II.9)

where \( W_a \) is the work of adhesion, \( \gamma_1 \) and \( \gamma_2 \) are the surface energies of the contacting surfaces, and \( \gamma_{12} \) is the interfacial energy associated with the two surfaces. This concept is revisited in chapter V.

From the above, it is clear that adhesion is related to the amount of contact area between surfaces. A few general rules can be made about adhesion accordingly.

1. Adhesion increases with decreasing surface roughness.
2. Soft, flexible and conformal surfaces increase adhesion.
3. Deformable surfaces conform to surface roughness making intimate contact and enhancing adhesion.
4. Surface conformation can also be enhanced by increasing the normal loading force (24).

Thus far nothing has been said about the actual interactions responsible for adhesion. In the case of the multiple contact biological system, the interaction forces and role of forces is still a debated question. Strong evidence suggests that van der Waals forces are operative (10). Other evidence suggests that humidity plays a significant role (25). However, the introduction of water between two surfaces (due
to a more humid atmosphere) can introduce capillary forces, but may also affect the van der Waals interactions (23).

3. Adhesion forces

a) Van der Waals Forces

Considered a short-range molecular interaction force, van der Waals forces arise from temporarily induced dipoles between two neutral molecules. The momentary shift in the electron cloud of one molecule induces the shift of a neighboring molecule’s cloud of electrons. The two dipoles then attract each other. These London dispersion forces operate over a short range, typically <10 nm, and can be described using a Leonard-Jones potential $\psi(d)$ (23):

$$\psi(d) = \psi_o \left[ \left( \frac{d^*}{d} \right)^{12} - \left( \frac{d^*}{d} \right)^6 \right], \quad (II.10)$$

where $\psi_o$ is the strength of the interaction, $d^*$ the range of the interaction and $d$ the distance of the two molecules. The positive portion of the equation denotes the repulsive energy associated with two molecules not being able to penetrate each other. The force is very strong, but also very short ranged.
Using Derjaguin approximation (21) a force relationship for a sphere on a flat surface can be developed (26):

\[ F(d) = \frac{AR}{3} \left( \frac{1}{d^2} - \frac{d_0^6}{d^8} \right), \quad \text{(II.11)} \]

where \( A \) is the Hamaker Constant, \( R \) the radius of the sphere, \( d_0 \) is a characteristic interaction distance, and \( d \) is the distance between sphere and surface.

**b) Capillary Forces**

Capillary forces are a result of the interaction of a wetting fluid with a surface. In capillary action a wetting agent is pulled up a capillary. This force can also act between two surfaces when a wetting agent is present. If one of the surfaces is not wettable by the liquid, capillary forces are not relevant. A brief treatise will be given to the relation between capillary forces and a sphere contacting a flat surface.

Taking the Laplace pressure:

\[ \Delta p = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right), \quad \text{(II.12)} \]

The force is then:

\[ F = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) A, \quad \text{(II.13)} \]
where $r_1$ and $r_2$ are the curvatures of the hyperbolic paraboloid produced by the meniscus about a sphere. For the case of the sphere and flat Scherge and Gorb (26) have derived the relation:

$$F = 2\pi \gamma R \left( \cos \theta_1 + \cos \theta_2 \right), \quad \text{(II.14)}$$

where $\theta_1$ are the contact-angles. If the two surfaces are made of identical materials then these angles will be equal. Also for the case of $r_2 \gg r_1$ the Laplace pressure reduces to:

$$\Delta p = \frac{\gamma}{r_1} \quad \text{(II.15)}$$

This then leads to the approximation, for hydrophilic surfaces ($\theta \sim 1$, $\cos \theta \sim 1$), of:

$$F = 4\pi \gamma R \quad \text{(II.16)}$$

It is noted that this relationship does not hold for increasingly rough surfaces. In the case of rough surfaces asperities act like local spheres causing a reduction in the large meniscus radius rendering the assumption $r_2 \gg r_1$ invalid. Also, capillary forces dominate when large smooth surfaces are in contact in the presence of atmosphere. Van der Waals interactions become significant when a sharp probe penetrates the liquid interface and allows for short range interactions.
c) Contact Splitting

The concept of contact splitting in the gecko adhesive system offers a direct explanation for the increase in adhesion observed when many small contacts are made as opposed to one large contact. A theory developed by Arzt et al. (27) shows how the size of the final termini of an animal’s contacts is inversely related to the mass of the animal, Fig. II-5. For example, the largest animal to use this adhesion system, the Tokay Gecko, also has the smallest termini, ~200 nm. Whereas a fly has termini of order 2 μm.
Figure II-5  Illustration of the contact splitting phenomenon in nature. Plot shows that as the animal’s mass increases then so does the necessary density of termini in the adhesion system. Figure from reference (27).

The basic concept of contact splitting is that adhesion decreases linearly with the radius of contact, while the number of contacts increases by the square of the radius, or a higher packing density. This means that the net increase in adhesion per unit area is the square root of the number of contacts in the total contact area. This can accordingly modify the JKR model above so that:
This concept of contact splitting offers an explanation for the fine terminal structure of the fine hair attachment system. There is however much more to the structure of the adhesive system. The fine hairs are located at the end of long, 130 μm, slender, 20 μm, setal stalks. These stalks are attached to the foot of the gecko via an undulated surface cushioned by blood sinuses. In view of contact mechanics, this hierarchical system seems to aid in increasing surface contact with non-ideal surfaces.

In the case of rough surfaces, it is no longer possible to assume that a single large contact will make perfect contact with a surface. In addition it is not possible to assume that if a large contact is split into many smaller contacts they will all make contact. For a rough surface it becomes very important to consider the roughness and the ability of the two surfaces to make intimate contact. Thus, the mechanical properties of the underlying substrate become important. If one substrate is highly compliant then the surfaces will mate better and adhesion will be increased (28). The long slender setae aid in surface conformation increasing contact area without increasing the repulsive push-off force. This push-off force can be modeled as an elastic restoring force (29):

\[
F_{adhesion} = F_{attraction} - F_{elastic} \tag{II.18}
\]
The concept of reducing the elastic restoring force and enhancing surface conformation was a driving force for the work presented here. This work was the first effort to create a hierarchical structure; the first work to integrate two different scales of structures (micro and nano) for enhanced adhesion.

**d) Summary**

The adhesion mechanics of the fine hair adhesive system relies on a large number of weak, short-range interactions to create a large amount of adhesion. The fundamental interaction seems to be a van der Waals force, while it may still be possible that water plays a role through other effects. Using JKR contact mechanics, it is possible to demonstrate the improved adhesion due to contact splitting. Just as important as the contact mechanics at the nanoscale is the compliance of the surface at the micro and mesoscales.
B. MEMS Fabrication Techniques

The crux of the doctoral work presented here is the implementation and innovation of MEMS (microelectromechanical systems) processing techniques. However this thesis is aimed at a broader audience as much of the work relates to mimicking a biological system. It is therefore important to establish a baseline of processing knowledge so as to not inhibit the flow of this document with cumbersome descriptions of standard fabrication techniques. This section will give a brief and to the point fundamental overview of the core MEMS processing techniques.

1. Photolithography

Arguably the most important technological innovation of this age, photolithography, has brought about the computer revolution, and subsequently the internet. Simply put, photolithography is the transfer of a pattern into a photoactive polymer. This photoactive polymer then acts as a protective shield for the underlying layer, allowing for selective degradation, or coating, of the material below. Very large scale integration (VLSI) technology uses photolithography to densely pattern wafers with transistors and interconnects. In fact, the density of this packing is what dictates the speed and efficiency of computer chips. Refined
photolithography has allowed for smaller minimum feature sizes (MFS) and correspondingly smaller, faster and cheaper computer chips.

The two basic forms of photolithography are contact and projection lithography. Both techniques are used in this work. Contact lithography uses a chrome/quartz mask defined with the desired pattern, outsourced for about $1,000. A wafer spin coated with a photoactive is brought into contact with this mask and irradiated with UV light. The UV light either serves to degrade the photopolymer (positive resist) or to cross link it (negative resist). The wafer can then be washed in a developer to remove unwanted resist, leaving exposed vias in the polymer coating.

As the name implies, projection lithography does not bring the wafer and mask into contact, but instead projects the pattern on the substrate. This is typically done in a stepper tool which projects the pattern with UV light, then moves to a new location projecting again. In this manner the pattern is stepped across a wafer. Since the pattern is being projected there is a refined control of the focal plane of the image. Additionally steppers usually operate at a 5X reduction in size. This means that if a feature size is 5 μm at the mask level it will be reduced to 1 μm in the resist. As a result of these factors, projection lithography offers enhanced feature resolution over contact lithography.

2. Wet etching
Chemically etching materials in a reactive liquid medium has been in use for centuries, and in recent decades has become quite prevalent in semiconductor and MEMS processing. Samples are simply placed in a solution containing a reactive species with the material that is to be removed. Wet etching is generally isotropic as the solution conformably contacts the entire surface. There are a few exceptions to this where chemicals will selectively etch along certain crystallographic planes. In this work, wet etching will be used to remove thin metal layers difficult to remove by other means.

3. Dry Etching

Reactive ion etching (RIE), also commonly referred to as dry etching, is the hallmark of MEMS processing. As the name implies RIE uses reactive ions (and free radicals) generated in a plasma to chemically and mechanically remove material from a surface. The chemical removal of material is performed by appropriately selecting species that are chemically reactive with the substrate. Mechanical etching is accomplished by applying a bias between the plasma and the substrate. Ions are then accelerated in this electric field gradient toward the substrate, removing material. This electric field gradient is of particular importance in this work and relates directly to one of the major innovations produced in this body of work. Because of the directed nature of the ions bombarding the surface, an anisotropic
etch pattern is produced. This allows for the fabrication of high aspect ratio structures with near vertical etch profiles.

4. Electron Beam Deposition

Electron beam evaporation, or e-beam deposition, is a method for depositing material evenly across a surface with nanometer precision. Samples to be coated are placed in high vacuum facing a crucible containing the material to be deposited. The material, generally a metal (nickel, titanium, gold in this work), in the crucible is then ablated using an electron beam. The material deposits evenly (due to the vacuum and a long mean free path) on the sample surface. The thickness is monitored by measuring the resonance change of a quartz crystal positioned next to the sample. When the desired thickness is reached the electron beam is turned off.

5. Sputtering

Another deposition technique, sputtering offers wider materials selection, better step coverage and improved adhesion over e-beam lithography. Instead of evaporating material, as in e-beam deposition, the source material is bombarded with high energy ions effectively knocking off material which then travels to the sample surface and adheres. The positive ions, generally argon, are created in plasma and directed toward a ring of source material using a negative bias.
C. Micro/Nanotribology

1. Nanoindentation

Indentation testing has long been one of the most important materials characterization techniques. Standard indentation involves indenting a sample with a known force, \( P \), using a tip of particular geometry. After the indentation, the area of the residual indent, \( A \), is measured, and the hardness of the material can be calculated using the relationship \( H = \frac{P}{A} \).

Nanoindentation, as the name implies, uses a much smaller and sharper tip typically in the sub-micrometer regime. While this allows the tip to probe a much smaller volume of material, assessing the size of the indent becomes unreasonable. To circum-indent this problem instrumentation has been developed to record displacement along with load. Once a characteristic penetration versus load function has been established for a particular tip, load versus displacement data can be analyzed to determine the hardness and modulus of a test surface.

Decreasing the size of the tip also means decreasing the penetration depth and load. To detect these small forces and displacements a high resolution transducer must be used. MTS and Hysitron both make commercially available nanoindenters, with the key difference between them the transduction method. MTS uses an inductor to apply a force and measure the displacement of the tip. Hysitron, the system here at UCSB, utilizes a movable parallel plate capacitor strategy. The Hysitron Triboindenter was utilized for all the nanoindentation described in this document.
The fundamental workings of the parallel plate transducer in the Hysitron Triboindenter is a movable plate mounted between two fixed plates, Fig. II-6. To detect movement, alternating currents 180 degrees out of phase are applied between the fixed plates and the center plate. Any small increment in movement is then detected by measuring the change in voltage between the respective plates. To move the tip downwards, applying a load, a DC bias is applied between the lower plate and the movable plate. This bias draws the plate down and by knowing the applied voltage and the spring constant of the movable plate, the force can be determined.

Figure II-6  Diagram of the parallel plate sensing mechanism in the Hysitron™ nanoindenter system.

A reasonable amount of development has been done on using nanoindentation to measure material properties. However, the use of a nanoindenter to probe the mechanical properties of micromechanical devices has been virtually unexplored. Some of the first work done and still unpublished is presented here in the appendix.
2. Wyko Optical Profilometer

In this work a variety of three dimensional structures has been fabricated. These structures predominantly consist of 10-200 micrometer platforms supported by a single pillar. While the in-plane shape of the platforms is well defined by the lithography and easily seen through optical microscopy, the out-of-plane shape of the platforms is more illusive. Given the flexibility of the platforms, contact surface profilometry is not possible. Scanning electron microscopy (SEM) provides an excellent means of visualizing the structures, Fig. II-2, but is a time consuming process and offers little quantitative information. To quickly and quantitatively measure the curvature of the platforms, as well as deposition height and etch depths, an optical profiling methodology was employed.

The Wyko NT110 optical profiling system combines optical microscopy with interferometry to produce accurate vertical measurements of surfaces with micrometer lateral resolution. The system consists of an optical microscope, a vertical optical scanning system, a Mirau interferometer and CCD detector array, Fig. II-7.
Figure II-7 Interference microscope design for the Wyko NT1100 optical profiler.

The basic theory of operation is that a white light beam is focused onto a surface. Prior to reaching the surface, half of the beam is split and focused on an interferometer. The other half of the light reflects off of the surface and onto the interferometer. When the sample is in focus, the path length between the two beams is zero and the intensity is at a maximum. When the sample is moved away from the optics, a series of dark and light interference fringes are passed while the intensity decreases. Another way to conceptualize the fringe effect is to consider a flat sample tilted relative to the optical projection, Fig. II-8. The tilted surface will
create an alternating dark and light fringing pattern, with the maximum intensity located in the middle.

![Fringing pattern on a tilted surface](image)

**Figure II-8 Fringing pattern seen on a tilted surface (top). Illustration of the intensity versus height for interfering light on a tilted surface.**

So when the intensity is a maximum, the microscope is focused on the surface. By then focusing the interference pattern on a CCD it is possible to collect the intensity of each individual pixel. The optical system is then scanned vertically relative to the sample. Through calibration of the motor it is then possible to determine the height of each maxima of each pixel creating a map of the surface. Thus the resolution is limited by the optical resolution and the CCD pixel size.
III. Detailed Micro/Nanofabrication

As the main thrust of the work presented here was to use micro/nano-fabrication techniques to mimic a biological system, and although already published, a more thorough treatise of the fabrication processes used is given here. In addition, commentary on the various techniques is given, including motivation, limitations and future directions for development. The chapter is broken up into three sections, representing the three major advancements in fabrication development. Although the final process flow seems logical and straightforward, this work has been a path of discovery, pioneering new areas of fabrication techniques.

A. Silicon Dioxide Platforms Supported by Single Crystal Silicon Pillars

The initial concept driving the development of these structures was to create a micro-mirror. While conventional micromirrors utilize four springs, in two different planes, to allow for three dimensional mirror rotation, these structures were designed to have a single spring in the middle of the mirror. By placing the spring in the middle of the mirror, and making it flexible enough, three dimensions of rotation would be achieved through a greatly simplified fabrication scheme. Additionally, the location of the pillar directly below the mirror would allow for greater mirror density, desirable in many applications – e.g. projectors. Unfortunately, or fortunately, about this time, the micro-mirror problem was “solved” and commercial products became available, reducing the driving force for fundamental research.
Nonetheless these structures would find a purpose integrated into a hierarchical adhesive system.

The fabrication of centrally supported released platforms, also called single high aspect ratio pillar support structures (SHARPS), was accomplished using a single photolithographic step, a single oxidation, and two deep reactive ion etches (DRIE). The structures, Figure III-1, were fabricated with silicon dioxide platforms with thicknesses varying from 150 nm to 2 μm (see chapter IV, also the paper titled *Single High Aspect Ratio Pillar Support Structures*).

![Figure III-1](image)

**Figure III-1** Electron micrographs of SHARPS structures showing the silicon dioxide platform supported by a single crystal silicon pillar. Right image offers a magnified view of the pillar. Scale bars are 20 μm and 10 μm left and right respectively.

Fabrication begins with oxidation of a silicon wafer, Fig. III-2. Generally (100) n-doped 100 mm wafers were used. In one case a heavily p-doped (111) was used, in a failed attempt at a fringing field actuation mechanism. Using (111) wafers
is discouraged due to the cleaving direction, not orthogonal, making die separation challenging.

Figure III-2 SHARPS fabrication process flow schematic.

Wafers were oxidized in the Tystar™ furnace in the MEMS cleanroom on the second floor of Engineering II. Oxidation times were calculated using the Stanford website: [http://www.lelandstanfordjunior.com/grovedeal.html](http://www.lelandstanfordjunior.com/grovedeal.html). Using this calculator based on the Deal-Grove Oxidation Model, an oxide thickness of 2 μm takes 15 hours 15 minutes and 30 seconds using the wetox2 recipe in tube 2 of the furnace. This thickness was then verified using the Filmetrics white light reflection dielectric characterization tool in the nanofabrication facility.

The oxidized wafers were then coated with Shipley SPR 220-7 photoresist (PR). Prior to resist application, the wafers were soaked HMDS (hexamethyldisiloxane). The HMDS acts as a wetting promoter for the PR on the silicon dioxide wafers by forming a thin layer. The compound is a type of amphiphile that binds nicely to the oxide surface and allows the PR to evenly wet the surface. After soaking the wafers with HMDS for 30 seconds, the wafer was spun at a speed of 3,500 RPM (3.5 kRPM). A large puddle of SPR 220-7 PR was then immediately placed in the center.
of the wafer, approximately 4 cm in diameter, and the wafer was spun again at 3.5 kRPM for 30 seconds. Here it was found useful to ramp the acceleration of the spinner, to avoid edge bounce and to reduce the required amount of PR for complete wafer coverage. The wafer was then removed from the chuck and placed on a hot plate at 95°C for 60 seconds. (This process should apply an approximately 7 μm thick layer of PR.)

The PR was next patterned using projection lithography. Wafers were placed in the GCA AutoStep 200 i-line wafer stepper on the 100 mm wafer chuck. The desired mask was then loaded and aligned. However, since this is a single step process, alignment is not a critical issue. The i-line stepper was then programmed with a given step size and exposure time. An exposure time of 3.75 seconds was used. After exposure the wafers were allowed 10 minutes for the photoreaction mechanism to complete before any further processing was performed. Premature placement of the wafers on a hotplate, for a post exposure bake, would cause a strange reaction in the PR. However, in this work, a post exposure bake was not used and processing proceeded directly to development. Wafers were developed in MF-701 developer. Generally, for this portion of work, developing proceeded until it was visually apparent that the unwanted resist had been washed away. However, as rule of thumb, a developing time of 90” is sufficient (no harm was seen in extending this time to 120”). After developing, the wafers were hard-baked at 110°C for 90”.

The PR pattern was then transferred into the underlying silicon dioxide. Initially the pattern was transferred into oxide using the #3 reactive ion etcher in the
nanofabrication facility. Etching of 2 μm of oxide would take over an hour and a half, with cleaning of the chamber required in between. Fortunately, the cleanroom acquired a Panasonic E640 inductively coupled plasma (ICP) system. Using this system it was possible to reduce the etch time to 14 minutes, while at the same time yielding near perfect sidewall verticality. After the PR pattern was transferred into the oxide, the PR was removed using an ultrasonic acetone bath, followed by isopropanol and a DI water rinse.

The crux of this particular process was then to extend the oxide pattern into the silicon and undercut the silicon dioxide structures by performing an extended release etch. The 4 inch wafer could be placed into the Plasma Therm DRIE ICP etch tool in the nanofabrication facility. The tool is dedicated to running the Bosch™ process. The Bosch™ process is a method for etching high-aspect-ratio features into silicon. The method is to cycle between an aggressive etch step, with SF₆ plasma, and a passivation step using polymeric deposition, C₄F₈ plasma. Although the SF₆ etch is an isotropic etchant, the directionality from the ion bombardment in the chamber gives slight preferentiality to removal of material normal to the ion bombardment. The passivation step, however, has no directionality and evenly coats all surfaces. Thus, by cycling the two, a net removal occurs in the vertical direction. By tailoring the etch and passivation times, more vertical and smoother sidewalls can be achieved, or faster and more aggressive etches can be performed. For this work the standard process was run to create the initial trenches. However, after the trenches were created, the passivation step was turned off and a sustained SF₆ isotropic etch performed. By tailoring the duration of the isotropic etch, it was possible to control
the amount of undercutting of the silicon dioxide platforms until only a single slender silicon pillar was left supporting the platforms, Fig. III-1. It was also found that the shape of the platforms ultimately affected the pillar shape, see chapter IV, opening up the possibility for anisotropic pillar shapes and mechanical properties.

**B. Multi-Scale Integrated Structures**

The silicon dioxide platforms opened up a very interesting 3-dimensional design space in microfabrication. However, the structures needed an application to drive the research. It was about this time that the gecko adhesive was starting to become of interest in the scientific and engineering communities. As discussed in the following chapters, it was clear that all the research aimed at mimicking the system was focused on the nanostructures, and NOT on the hierarchical structure. This hierarchical structure included flexible microstructures, Fig. II-2. After initial testing of the SHARPS structures, no adhesion was observed. Clearly, just as the nanostructures would require integration with microstructures to mimic the system, the converse was also true. Thus it was clear that the silicon dioxide platforms would need to be coated with a nanostructured surface.

Creating nanostructured surfaces presented quite a challenge, after all this was (and is) what most of the research towards mimicking the system was focused. Now the challenge was to create these structures on flexible platforms. A variety of techniques were tried, including: titania grass on the platforms (too stiff),
electrodeposition in porous alumina and polycarbonate matrices, nanosphere lithography, and metal thin-film destabilization, to name a few of the more promising attempts. After a substantial amount of work, and failed attempts, the solution turned out to be quite serendipitous.

Fabrication of the Multi Scale Integrated Structures (MICS) followed the same process flow of the SHARPS, except for one major change. Just as with the SHARPS, silicon dioxide platforms were formed by etching trenches and

**Figure III-3**  Electron micrograph of the organic looking polymeric nanorods, ‘organorods,’ scale bar 10 μm.
undercutting the platforms. However, after platform formation (without having removed the photoresist) an additional reactive ion etch was performed in the Panasonic ICP tool. The wafers were loaded into the etch chamber and exposed to an oxygen plasma at 40 sccm, 1 Pa and 300 W bias for 10 minutes. After which the photoresist was transformed into arrays of vertically aligned nanorods, Fig. III-3. The nanorods were not perfectly cylindrical and were more organic looking nanorods, thus dubbed ‘organorods’—much to the chagrin of organic chemists all around the world. In fact, conferring with polymer experts, with experience with this photoresist, the growth mechanism is not exactly certain. The proposed one, discussed in chapter VI, is that the dielectric polymer, when placed in an electric field gradient, is acted on by a force in the normal direction to the wafer. In addition, the oxygen plasma serves to reduce the surface tension of the resist (the stabilizing mechanism), allowing the field gradient force to dominate and for nanorods to grow in the vertical direction. It is also presumed that the reactivity of the oxygen deteriorates the nanorods, giving them the less uniform structure.

**Figure III-4**  Electron micrographs of SHARPS structures coated with organorods. Scale bars are 20 µm and 5 µm, left and right respectively.
Post organorod growth modification was achieved by fluorocarbon deposition using the passivation step in the PlasmaTherm dedicated Bosch process tool. Running a 9 second deposition would deposit roughly 30 nm of fluorocarbon on the surface of the organorods. The hydrophobic coating switched the organorod surface from hydrophilic to highly-hydrophobic with a contact angle of 154°.

![Figure III-5](image)

**Figure III-5**  (Top) Optical images of a water droplet on untreated (left) and treated (right) organorod surfaces. (Bottom) Corresponding electron micrographs of the structure, scale bars 2 μm.

C. Nickel Multi-Scale Integrated Structures

Comparing the β-Keratin, E ~ 5 GPa, system found in the gecko to the silicon one, E ~ 150 GPa, presented here. There is a glaring difference in the material properties. So one would ask, is the silicon the right material system to use? Just as the gecko has relatively few structural materials to choose from (β-Keratin is used
for everything from the sticky pads to the eye spectacle) there are few engineering materials that have the processing capabilities for creating functional microstructures at the micro and nano-scale. The processibility of silicon allows freedom in the structures that can be created and what other materials can be incorporated. The ultimate goal of this research was not to create another tape, or glue, but instead to create a new type of adhesive with controllable stickiness. The ability to switch adhesion on and off is what allows the gecko to run up, down and across walls. In order to accomplish this, the silicon system above was extended to include activated platforms capable of reversible conformational changes. To achieve this, the silicon platforms were replaced with ferromagnetic nickel paddles. This required an entire new process to be developed.

Silicon (100) wafers were prepped with HMDS, allowing the wafers to soak for 15 seconds and then spinning at 4 kRPM for 15 seconds. Following this, an image reversal photoresist (AZ 5214-IR) was spun onto the wafers at 4 kRPM for 30 seconds. The wafer was then placed on a hotplate at 105°C for 60”. Photolithography was performed in the Karl-Suss MA-BA-6 mask/ bond aligner (MA6) with an exposure time of 5”. Proceeding exposure the wafers were baked at 115°C for 120” before a 60” flood exposure was performed in the MA6. The wafers were then developed in MF-701 developer for 120”. After a 120” dionized water rinse, the wafers were dried and descumed in an oxygen plasma (the Plasma Etching Systems PE-IIA) for 60” – to better promote metal adhesion in the subsequent step.

Next nickel was deposited into the vias created in the PR. Electrodeposited nickel on silicon develops large amounts of stress. This stress can cause
delamination of the PR/nickel during the evaporation, causing the protective resist to peel up and nickel to deposit in unwanted areas. The maximum thickness of evaporated nickel was found to be 200 nm. For the evaporated nickel devices reported here, thicknesses were maintained at 150 nm. After nickel evaporation across the entire wafer in the CHA Muti-Wafer Metal Evaporator (electron beam evaporator #4 in the nanofabrication facility) the photoresist was removed, lifting off nickel not deposited through the vias. This was achieved through an ultrasonic acetone bath for a time of 10 minutes (till the resist was completely lifted off).

For thicker nickel structures, an electrochemical deposition from solution technique was implemented. Electrodeposited nickel does not develop stress during deposition. However, in order to plate nickel, it was first necessary to plate the silicon wafer with a highly conductive seed layer. This conductive layer made it possible to transfer charge from the potentiostat probe across the entire wafer. Thus, before the photoresist was patterned, gold or platinum was evaporated across the entire bare silicon wafer at thicknesses of 25 or 50 nm, respectively. After seed layer deposition, a 25 nm layer of PECVD silicon dioxide was deposited to inhibit nickel undergrowth during electrodeposition. Then the wafer was patterned resist as above. Next the wafer was placed in a nickel electrodeposition bath composed of 200 g/L nickel sulfate, 5 g/L nickel chloride, 25 g/L boric acid, and 3 g/L saccharin (to sweeten the results). To facilitate uniform deposition across the wafer, and save money, a counter electrode was fabricated by coating a 100 mm silicon wafer with 150 nm of platinum. The two wafers were then placed facing each other in a wafer storage box at a distance of 5 slots apart. The bath was circulated by placing the
wafer box on top of a magnetic stirring plate and a magnetic stir bar was placed in the bottom of the container. Using galvanostatic deposition, the current was regulated; values varied from 40 – 100 mA, and electrodeposition proceeded for 15-45 minutes. The thickness of the deposited nickel was ultimately limited by the depth of the vias through the photoresist, determined by the original thickness of the photoresist. After deposition, the wafers were placed in an ultrasonic acetone bath, removing the photoresist and leaving nickel structures atop a thin layer of gold or platinum. Next the gold or platinum was removed. The gold was removed using a proprietary wet etch.

Although the electrodeposited nickel did not have the stress issues of evaporated nickel, achieving thickness across the entire 100 mm wafer proved to be non-trivial. The addition of wetting agents and mixing aided the uniformity; ~30% variance across 100 mm. However, achieving the precise uniformity of the evaporated nickel is unlikely, even in an industrial environment.

Following nickel deposition and definition on the silicon surface, another layer of photoresist was patterned on the surface in direct correlation with the nickel structures. Just as in the SHARPS and MICS processes, a 7 μm layer of photoresist (SPR 220-7) was spun on at 3.5 kRPM. The resist was baked at 95°C for 60” and patterned using contact lithography with an exposure of 20 seconds in the Suss MA6 contact alignment system. After exposure, the wafers were developed (MF-701 developer) for 90”, rinsed with deionized water and blown dry with nitrogen.

For the thicker electrodeposited nickel samples, similar deep etching and releasing as with the SHARPS and MICS could be performed. Etch times, as with
all this work, varied greatly depending on the geometry of the structures. Typically a deep etch time of 25 minutes was used and extended SF₆ release etches varied from 15 minutes to 45 minutes, longer times were required for higher density structures. Proceeding platform formation, the photoresist was then transformed into organorods by placing the samples in the Panasonic ICP with oxygen plasma as previously described. Additional processing could then be executed to coat the structures with a fluorocarbon. Typically the fluorocarbon coating was found to enhance adhesion.

For the thinner, and more uniform evaporated nickel samples, a deep etch and release could be performed to create the nickel platforms. However, upon organorod growth, the force required to grow organorods would also act on the flexible platforms permanently deforming them into an undesirable state. Unfortunately, thinner platforms also mean more compliant platforms. The more compliant the structures the more conformation they are capable of, subsequently enhancing adhesion. From an optimization standpoint, this presented a dead end. Fortunately, however, there was a simple solution. It was found that organorod growth could be performed prior to the final releasing of the structures. This innovation proved to be essential to this work and will allow for further optimization and development.
Figure III-6  Electron micrographs of released organorod coated nickel paddle structures. Opposing paddles coated with organorods scale bar 20 μm (top). Magnified view with dimensions of organorods, scale bar 2 μm (bottom-left). Array of paddles, scale bar 100 μm (bottom-right).
To create thin flexible platforms, the platform pattern was deep etched into the silicon and a partial undercut was performed. This partial undercut etched away the bulk of undesired silicon, but left a support for the thin platforms. Organorod growth was then performed as above. The samples were then transferred back to the PlasmaTherm system to complete the undercut etch and release the flexible platforms. While in the system, the fluorocarbon coating could also be applied.
IV. Single High Aspect Pillar Support Structures

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This paper describes the realization of a new three dimensional dry processing technique used to create structures supported by a single high aspect ratio support. This process allows for the creation of submicron single crystal silicon features, with tight geometric control, attached to much larger (10-200μm) silicon dioxide platforms. These single high aspect-ratio pillar support structures, or SHARPS, lend themselves to testing of submicron features and open new avenues of device design. One application for SHARPS as a passive adhesive is also investigated. The unique geometry created by SHARPS structures allows the structures to conform to non-planar or rough surfaces.
A. Introduction

For several decades researchers have been extending IC fabrication techniques into the rapidly growing field of micro electro mechanical systems (MEMS). Through a variety of processing techniques, the MEMS community has been able to carve microdevices out of bulk materials or build them up layer by layer. Each innovation in fabrication is added to the design toolbox furthering the capabilities of the MEMS community as a whole. Also helping further device innovation is an increased understanding of microscale phenomenon, specifically dynamics and micromechanics. Micromechanical testing is not new to the MEMS community (30-38), however, little work has been done to test the mechanics of refined three-dimensional geometries at the micron size. Here the ability to create refined high-aspect-ratio geometries at the micron and submicron size is reported. The fabrication techniques described add yet another tool to the MEMS fabrication toolbox and allow for new opportunities in testing.

The emergence of microsensors has come about due to increased microfabrication abilities and gain in understanding of microscale mechanics. Sensors for location determination, chemical sensors, mass sensors, pressure sensors, inertial sensors, are among the most common thus far (39-52). Significant developments in microscale sensors have enjoyed significant interest because they possess important properties, including high sensitivity and the ability to be
fabricated in large arrays of thousands to millions. However, there still exists a question in the deployment of these arrays. Adhesion of sensor arrays is one area necessary for many applications that require the deployment of microdevices. In addition chip-scale recognition and adhesion systems will be of great interest for use in fabrication, self-assembling microdevices and immerging miniature aerospace applications. The idea of micromechanical Velcro was laid out over a decade ago by Han et al. (53)). In the work the idea of recognition and mechanical interlocking on two separate chips was introduced. In this paper, the initial steps to create a more universal chip-scale microadhesive are discussed.

**B. Experimental**

1. Fabrication

A number of different single high aspect ratio support (SHARPS) structures have been produced, Figure 1. They all follow the same fundamental process flow, shown in Figure 2. Fabrication begins by growing 2 μm of oxide on a 4 inch silicon wafer in the (100) orientation. The top SHARPS platform is then defined in the photoresist using an I-Line stepper. This pattern is then transferred into the oxide through ICP reactive ion etching using CHF₃ chemistry. The remaining photoresist is stripped
from the wafer and the oxide is then used as a mask in etching the silicon below. This is accomplished by placing the wafer in a PlasmaTherm ICP etcher and performing a modified Bosch etch process, in which the plasma gas is cycled between a reactive etching chemistry, SF$_6$, and a polymer producing species, C$_4$F$_8$, producing high aspect vertical trenches. The duration of each etch or passivation step can be modified to control the vertical profile of each trench, the extreme of this being a sustained SF$_6$ where the silicon is nearly isotropically etched. By controlling these parameters it is possible to create silicon dioxide platforms supported in a single point by a silicon pillar, Figure 1.

2. Equipment

Single crystal silicon wafers 100 mm in diameter in the (100) orientation were used for all processing. Silicon dioxide was grown to a thickness of 2 μm using the wet oxidation process at 1050 C in a Tystar Tytan Furnace (Tystar Corporation, Torrance, California). Standard stepper lithography was carried out using a GCA Mann 5x I-line stepper (Hampton, New Hampshire). The photoresist pattern was transferred into the oxide using a Panasonic E640-ICP dry etching system using CHF$_3$ chemistry (Panasonic Factory Solutions, Osaka, Japan). The deep etching and release was carried out using a modified Bosch Process in a PlasmaTherm 770 ICP reactive ion etcher (Plasmatherm, North St. Petersburg, Florida). In the case where
titanium was deposited, DC reactive sputtering was used using an Endeavor 3000 cluster sputter tool (Sputter Films, Santa Barbara, CA). Titanium was transformed into titania through ICP etching of the samples in Cl₂/Ar.

Scanning electron micrographs were taken in a S2400 Hitachi scanning electron microscope (Hitachi Instruments Inc., San Jose, California) or on a FEI XL40 Serion FEG Digital Scanning Microscope (FEI, Hillsboro, Oregon). Surface profilometry was performed with Wyko NT100 Optical Profiler (Veeco, Woodbury, New York). Nanoindentation and adhesion experiments were performed in a Hysitron Triboindenter (Hysitron Inc., Minneapolis, Minnesota).

**C. C. Results and Discussion**

As seen in Figure 1, a variety of different SHARPS structures have been fabricated. The structures have top platforms varying in size from 10 to 200 μm and pillar diameters from 0.5-10 μm, and heights from 5 to 40 μm. It should be noted that the extents of dimensions are not limiting, with the exception of the pillar diameter. This dimension is not immediately defined by the oxide mask. However, extending the notion of pattern transfer from the planar oxide into the 3-dimensionally etched silicon a variety of pillar geometries have been produced: round, triangular, square, hexagonal and octagonal pillars, Figure 3. In addition to
altering the radial geometry of the pillar the shape along the long axis has been
controlled, though to a lesser degree, by creating a bend along the long axis of the
pillar, Figure 4.

The planar shape of the top platform is easily controlled. This shape is directly
controlled by the resist pattern and gives the designer great flexibility. A variety of
different shapes including platforms, slotted platforms, serpentes of different
varieties, branched fingers and radial meanders have been produced, see Figure 1.
As can be seen in Figure 1 the platforms stay remarkably planar over large distances,
\( \sim 50 \text{ nm height change over } 40 \mu \text{m} \). The planarity of the platform was disrupted by
DC reactive ion sputtering of titanium on the top surface. This served to curl the
platform upwards due to a stress gradient. With increased thickness of titanium
there was an increase in the radius of curvature of the platforms, shown in Figure 5.

1. Characterization

Characterization of the structures created has primarily been carried out using
scanning electron microscopy. The electron micrographs give us detailed
information on the structures created, including shape and dimensions. This
information is invaluable when trying to correlate data from other tests, specifically
nanoindentation testing. Preliminary micromechanical testing has been performed
using a nanoindenter to apply a force at a specific location on the top platform. By monitoring the force versus displacement the bending mechanics predicted from simple bending beam theory correlated with indentation distances far from the center, Equation 1 and Figure 6.

\[
\frac{1}{K} = \frac{4L^3}{E_{SO}bw^3} + \frac{3Lh^2}{E_{SO}a^3}
\]  

[IV.1]

Where b is the thickness of the top surface, w is the total width of support arms, L is the distance from the center to the point load, a is the pillar size and h is the height of the pillar. Moving closer to the center of the structure the theoretical and experimental stiffnesses deviated. This is quite easily explained by the significance of other bending modes, specifically lateral displacement of the platform and off axis bending, as the tip moves closer to center. Off axis bending may be a result of the diamond shape of the pillar, bending about the diagonal as opposed to the orthogonal. Since this is the direction of maximum stiffness the structure may concede to the less stiff off axis modes. This is illustrated in Figure 6, where the top plot shows the diamond shape and the bottom plot shows the square shape, the latter more accurately capturing the bending mechanics closer to the center.

Qualitatively these structures have been found to be quite robust. Although more compelling in video form, a few snapshots of pushing on one of the structures in a probe station are shown, Figure 7. In the figure the structures bend a large amount
before ultimately failing, depicted in Figure 7. Also, while pushing on the platform fingers large amounts of elastic deformation are observed with the fingers deforming in every direction and then snapping back into place.

Characterization of the surface topology of the supported platforms was carried out using a Wyko Profiler. Using the light interferometer system quantitative surface plots of the silicon dioxide platforms with and without titanium sputtered on the surface were obtained, Figure 5. In looking at the electron micrographs there is a dramatic change in curvature of the top platform with the addition of the sputtered titanium. Whereas the initial platform was flat an addition of approximately a half micron of titanium causes the 80 micrometer structure to rise 7 μm on either side. With the addition of approximately 5 μm the edges rise up 23.5 μm. In the latter structure it appears as though the structure has come under some self-limiting condition where the titanium on fingers are interacting with each other. Looking to alternative structures deflections could be further increased by choosing different platform geometries, Figure 8. Here two structures with a radial meander platform geometry are shown, wherein four radial spokes serpentine outward from the center.

The use of the nanoindenter to measure adhesion between SHARPS structures and a 1.5 mm diameter polyamide sphere is reported. In this experiment a polyamide sphere was glued to the tip of a nanoindenter probe. The device was placed in the indenter and the indenter tip pressed against SHARPS devices and the
solid substrate. Initial efforts were made comparing a radial meander SHARPS structure array and the substrate, both covered with 5 µm of titanium under a thin layer of titania. The nanoindenter was operated in displacement control and recorded the load vs. displacement. Initially a plot would show a no load versus displacement until the sphere came into contact with the surface. There would then be a positive increase in the load with further displacement. Upon retraction the load curve would fall below zero to a critical point when it would then return to the origin. The minimum load value is taken to be the maximum adhesive force. The maximum adhesion was found to be highly dependent upon the maximum positive load value, Figure 9. In the case of the SHARPS structures, the indenter tip would have to travel much further to achieve significant positive normal forces. This ultimately limited the maximum force applied to the SHARPS structures, as the instrument has a 5 micrometer maximum travel limitation. However looking at the trend in figure 10 it appears that there is a significant increase in adhesion with the structures as opposed to the solid substrate. This increase in adhesion can be attributed to an increase in contact area. Any adhesive system is going to have an overall increase in adhesion when there is more contact area. In the case of these structures they are more capable of conforming to the spherical morphology than a solid substrate.
2. Future Work

Future work on this project will entail continued development of novel processing to fabricate new SHARPS structures. Helping guide the development of new structures will be new and refined characterization techniques. Initial work in indentation and adhesion testing has been discussed. Further development of these techniques to make robust test methodologies is needed. These techniques may include continued development of nanoindentation test techniques and integrated manipulation and SEM systems. With improved fabrication and testing techniques, the integration of the SHARPS structures into a working device will be explored. Of particular interest is the use of the SHARPS structure as a chip-scale microadhesive. To this end, investigations of integration and reliability will be explored.

D. Conclusions

SHARPS structures consisting of a silicon dioxide platform supported by a single support have been fabricated. The structures were created through a unique process which allows three dimensional control with only a single lithographic step. Platform geometry can be designed to control the geometry of the support pillar about the radial and long axis. Subsequent processing was used to further enhance...
the structure of the platform. Here sputtered titanium was used to alter the curvature of the platform and enhance adhesive properties. The adhesive properties were measured using a modified nanoindentation set-up. It was shown that the SHARPS structures can offer improved adhesion for non-planar surfaces.

E. Acknowledgments

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F. Figures
Figure IV-1  Electron micrographs of various SHARPS structures (From Top and Left to Right) Square topped array, round top, slotted square, slotted round, branched finger, branched fine finger, radial meander, serpentine.

Figure IV-2  SHARPS fabrication process flow.
Figure IV-3  Optical micrographs showing pillar geometry along the long axis. (From left to right) Hexagonal, triangular, square, octagonal.

Figure IV-4  SHARPS structure with modified pillar geometry along the long axis.
Figure IV-5  (Top) surface profile taken in a Veeco Wyko N1100 of the structure in the bottom left image. (Bottom left) SHARPS structure after sputtering a half micrometer of titanium. (Bottom right) same structure after sputtering ~5 μm of titanium.
Figure IV-6  Nanoindenter bending stiffness experimental data and theoretical plot originating at the center of the SHARPS platform. (Top) Diamond cross section (Bottom) Square cross section.
Figure IV-7  (Top) before and after images of a probe pushing laterally on the structure.  (Bottom left) Superposition of images illustrating deformation distance: distance between blue and yellow lines. (Bottom right) Schematic representation of 3-dimensional deformation.

Figure IV-8  SHARPS structures after sputtering ~5 μm titanium.
Figure IV-9  Comparison of adhesion vs. applied normal force between a polyamide bead and the substrate or a radial meander SHARPS structure.
V. A batch fabricated biomimetic dry adhesive

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The fine hair adhesive system found in nature is capable of reversibly adhering to just about any surface. This dry adhesive, best demonstrated in the pad of the gecko, makes use of a multilevel conformal structure to greatly increase inelastic surface contact, enhancing short range interactions and producing significant amounts of attractive forces. Recent work has attempted to reproduce and test the terminal sub-micrometer “hairs” of the system. Here we report the first batch fabricated multi-scale conformal system to mimic nature’s dry adhesive. The approach makes use of massively parallel MEMS processing technology to produce 20-150 µm platforms, supported by single slender pillars, and coated with ~2 µm long, ~200 nm diameter, organic looking polymer nanorods, or “organorods.” To characterize the structures a new meso-scale nanoindenter adhesion test technique has been developed. Experiments indicate significantly improved adhesion with the multi-scale
system. Additional processing caused a hydrophilic to hydrophobic transformation of the surface and testing indicated further improvement in adhesion.

A. Introduction

Used by insects and lizards (including flies, crickets, beetles, spiders, geckos and anoles) to climb wet or dry, vertical and even inverted surfaces, the fine hair adhesive system is an excellent example of convergent evolution in biology(1-4, 6-8, 54). Recently, much work has been done to better understand the science of the sticking of this fine-hair adhesive motif (6-8, 15, 55-57). Experimental evidence has shown that the adhesion is primarily due to short-range weak van der Waals interactions between the fine hairs on the adhering surface and the target surface(7). In order for these “weak” forces to become significant the adhesive surface must create a large amount of intimate surface contact to the binding surface. In the case of the Gekko gecko, that can weigh up to 300 grams, this is achieved by a multilevel conformal system consisting of toes containing blood sinuses supporting rows of imbricated lamellae with densely packed keratinous setae approximately 100 µm in length, which split into finer 200 nm in diameter bristles (2). Each element of the system, from the toe to the terminal bristles, provides another scale of surface conformation, from the centimeter meso-scale (toe) down to the nano-scale.
(bristles). This inelastic surface conformation allows the gecko’s foot to create a large amount of surface contact, without introducing repulsive restoring force from the surface, producing a significant amount of surface adhesion through short-range interactions \((15)\).

Prior work has focused on mimicking the terminal bristle component of the adhesive by fabricating arrays of polymeric nanorods on solid substrate\((7, 11, 58)\). While individual nanorods demonstrated expected amounts of adhesion, larger arrays failed to produce larger amounts of adhesion – unless removed from the substrate and placed on a compliant backing\((11)\), showing the need for multi-scale compliance. Additionally, the arrays of nanorods showed reduced adhesion with use, due to bunching and contamination\((11)\), suggesting the reason for the super-hydrophobic nature of the gecko pad.

In the last two decades the emerging field of microelectromechanical systems (MEMS) has created a variety of micro-devices. These devices offer distinct advantages due to their small size, particularly in sensing. Microsensors have been developed for location determination, chemical sensing, mass sensing, pressure sensing, and inertial sensing\((42, 44-48, 51, 52)\). One key issue is how to deploy these micro-devices. The ability to incorporate an adhesive into the fabrication process and have that adhesive stick to virtually any surface, in any environment, offers a significant technological advancement. Another key aspect in both micro- and nano-devices is the integration into complete device architectures. As device architectures are miniaturized and span multiple disciplines (biology, integrated circuits, MEMS, etc...) new strategies for assembly and integration will be needed.
The ability to pattern an adhesive with potentially sub-micrometer precision for chip recognition or self-assembly strategies will be a valuable tool.

**B. Fabrication**

In this work, a chip-scale batch fabricated multi-scale conformal system has been produced. The microelectromechanical systems (MEMS)-based approach allows for batch fabrication and chip integration of the adhesive. The multi-scale structures consist of arrays of organic-looking photoresist nanorods, “organorods”, approximately 2 μm tall and 50-200 nm in diameter, atop photolithographically defined 2 μm thick silicon dioxide platforms 100-150 μm on a side (Fig. 1). The platforms of varying geometries are supported by single high-aspect-ratio pillars down to 1 μm in diameter and heights up to ~50 μm (Fig. 2). The structures are fabricated out of 4-inch single crystal silicon wafers in the (100) orientation using standard bulk micromachining techniques. Using a wet oxidation process at 1100°C 2 μm of silicon dioxide is grown on the silicon wafer. To define the top platform geometry standard stepper photolithography in an i-line stepper is performed using a positive resist, Shipley SPR 220-7. The resist is then used as an etch mask in an ICP etcher with CHF$_3$ chemistry to vertically etch through the silicon dioxide to the silicon. The exposed silicon is 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. Directly following the deep etch an extended SF$_6$ etch is used to isotropically etch the silicon. Since the reactive etch is significantly more selective to the silicon than the silicon dioxide (or photoresist) the platforms are undercut from all direction leaving behind only a single pillar in the middle (Fig. 2). By controlling the duration of the release it is possible to control the final size of the pillars supporting the platforms(59).

Following the platform and pillar fabrication, the photoresist surface (Shipley SPR 220-7, primarily composed of a diazoquinone ester and a phenolic novolak resin) of the platforms is transformed into organorods by placing it into an oxygen plasma with a 100 W bias for 5 minutes (Fig. 3), for a 3 cm x 3 cm piece. Organorods have also been uniformly fabricated across a 100 mm silicon wafer with good uniformity. The bias creates an electric field gradient, which acting on the dielectric polymer induces a force large enough to overcome surface tension, causing the growth of vertical polymeric columns. Estimating the electric field across the photoresist to be 100 V/µm, a column size of around 1 µm is predicted(60), much larger than the 50-150 nm organorods. The reduced geometry of the organorods may be attributed to a bilayer of photoresist and hexamethyldisilazane (HMDS) decreasing the interfacial energy and shrinking the instability wavelength(61).

The use of a plasma induced electric field offers several advantages over a parallel plate induced field. Using a plasma to create the electric field requires no second electrode, and subsequently no precise gap control between the two plates.
From a fabrication standpoint plasma induced nanorod growth utilizes already established processing infrastructure. Adopted from the IC community, and available on most research campuses, plasma etching systems are convenient and established processing tools.

The most striking difference between the plasma grown nanorods in this work and the parallel plate grown nanorods done by Schäffer et al. is the reduced time it takes to form the nanostructures – 15 minutes versus 18 hours, respectively. In essence the plasma method offers a greatly accelerated growth mechanism; similar initial morphologies are seen before the formation of the organorods. A possible explanation for the greatly reduced formation time can be understood by examining the growth mechanism. Growth is caused by the electric field gradient exerting a force on the dielectric polymer. When this force exceeds the restoring force created by the surface tension of the polymer surface an undulated surface begins to appear and then transform into the polymeric pillars seen in figure 3 and ref (4). In the plasma growth method the oxygen plasma serves to reduce the surface tension of the photoresist by breaking C-H bonds at the surface and leaving dangling –OH bonds. These dangling bonds reduce the surface tension, leaving the dielectric force to dominate over the restoring force, and organorods are formed.

To change the organorod surface from hydrophilic to hydrophobic the samples are placed in a CF$_4$ plasma for 30 seconds. This creates a fluorocarbon coating, increasing their size to ~350 nm, and altering their surface chemistry. The fluorocarbon coating leaves a -CF$_3$ terminated surface, greatly reducing the surface energy. Combining this coating with the morphology of the organorod surface
creates a lotus leaf effect(62), making the surface highly-hydrophobic with a water contact angle of $145^\circ \pm 2$ (Fig. 4).

**C. Experimental**

Adhesion testing was performed using a Hysiton Triboindenter® with a 3.175 mm spherical aluminum tip (RMS roughness of 0.5 µm over a 200 µm square). This non-ideal aluminum tip was chosen to better simulate an actual working environment for the adhesive, e.g. sensor deployment on an aircraft. To simulate a meso-scale adhesion incident, the “rough” tip was pressed into the test surfaces and withdrawn orthogonally from the surface at a constant rate. Operating in displacement control, load versus displacement data was collected and analyzed from the nanoindenter to determine adhesion. Adhering surfaces would produce a distinctive pull-off behavior, where the unloading curve would make a sudden jump (Fig. 5). The adhesive force was taken to be the difference between the minimum value right before pull-off and the next stabilized point (the instrumentation requires a finite time to stabilize after the sudden pull-off event).

To the authors’ knowledge, this is the first time a test measuring orthogonal adhesion on the tens of micrometer to millimeter scale has been performed. Refinement of the technique will hopefully bring about a universal mesoscale adhesion test. The orthogonal test technique measures the pure adhesive component of force, offering the opportunity for better standardization of adhesion testing. In
contrast, lateral force measurements include a frictional force difficult to decouple from the adhesive force. The common peel test, while useful for an industrial standard for tapes, also introduces variables again difficult to decouple from adhesion, e.g. rate and the effect of the support medium.

D. Results and Discussion

The adhesive force was found to significantly depend on the maximum applied normal load (Fig. 6-7). This dependence is likely 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. With hard flat substrates (e.g. silicon) clean loading and unloading curves were produced with no apparent adhesion. The photoresist surfaces demonstrated little adhesion (Fig. 6). In contrast, the organorod coated surfaces demonstrated much higher adhesion strengths (Fig. 6). Combining the organorods with the compliant pillar structures offered a significant increase in adhesion (Fig. 6), suggesting that the compliant structures aid in increasing the surface contact area. Initially it was anticipated that the pillar would allow the entire structure to rotate aiding in surface conformation. However, with the millimeter scale of the aluminum sphere used in testing only one structure is likely being tested and the compliance of the platform fingers are likely the dominant mechanism of conformal enhancement. As the aluminum sphere
contacts the platform, the radial extending fingers are able to bend up and contact the aluminum surface. This produces a near linear increase in adhesion with normal load. At some point, however, the finger (or fingers) is completely in contact and can provide no further adhesion. Adhesion then becomes solely dependent on squashing the organorods in the center of the structure (Fig. 8), and little increase in adhesion is seen thereafter.

To better mimic the structure and properties of the gecko tarsus a conformal hydrophobic fluorocarbon coating was deposited on the organorods. With the addition of the coating contact angle measurements show a change from hydrophilic, $42.5^\circ \pm 2$, to highly-hydrophobic, $145^\circ \pm 2$ (compared to $160.9^\circ \pm 1.4$ for the gecko (7)), behavior with the fluorocarbon coating (Fig. 4). This change from hydrophilic to hydrophobic behavior is significant not only in better mimicking the gecko adhesive structure, but may also shed new light on the purpose of the hydrophobic property. By testing the artificial adhesive before and after the addition of the hydrophobic coating, a comparison between hydrophilic and hydrophobic surface adhesion can be made. While with a gecko, it would be non-trivial to change the hydrophobic nature to perform a similar experiment. Surprisingly, adding a hydrophobic coating to the organorod surface improved adhesion (Fig. 8). As will be discussed later, this result may be associated with other factors than just the change in surface composition, e.g. increased organorod size. Adhesion was further increased when the hydrophobic organorods were combined with the compliant platform structures. Improved adhesion with the platforms may be a result of two mechanisms; one that the fingers are improving meso-scale surface
conformation and the other because the fingers are able to bend out of plane changing the adhesion vector to include a transverse component

Although the adhesion mechanism between the rough aluminum sphere and the organorod coated surfaces is quite complex – and many basic theoretical aspects of adhesion not fully understood – a simplified approach was taken to explain the experimental adhesion measurements. Two simple models based on Johnson-Kendall-Roberts (JKR) contact adhesion theory(63) and van der Waals interaction forces(64) were used to capture the basic trend in adhesion seen. JKR theory for a sphere contacting a flat surface predicts a pull-off force of $F = \frac{3}{2} RW$, where $R$ is the radius of the sphere and $W$ is the work of adhesion, taken to be $\sqrt{\gamma_{Al} \gamma_{polymer}}$, where $\gamma_{Al} = 500 \text{ mJ/m}^2$ and $\gamma_{polymer} = 35 \text{ mJ/m}^2 (65, 66)$. For the organorod surface the radius of curvature of the rods is considered to be very small compared to the sphere (making the organorods the spherical contact surface and the aluminum sphere a flat surface) and the adhesion force estimated to be: $F_{JKR} = \frac{n}{3} R_0 W$, where $R_0$ is the diameter of the organorods (determined using scanning electron microscopy), and $n$ is the number of organorods in contact with the surface – equal to the surface density of organorods multiplied by the contact area (determined using JKR contact mechanics for a sphere contacting a flat surface(63) and verified using scanning electron microscopy).

Alternately, considering only the van der Waals contribution, the force is taken to be $F_{vdW} = HR_0/6d_0^2$, where $H$ is the Hamaker constant (estimated to be $H = 2.1 \times 10^{-21} \text{ W} = 2.8 \times 10^{-19} \text{ J}(64)$, $R_0$ is the diameter of the organorods and $d_0$ is a characteristic cut-off distance equal to $0.165 \text{ nm}(64)$. As can be seen in Figure 6, the
JKR method tends toward the upper limit of values obtained in the rough aluminum sphere adhesion test (overestimate of actual number of organorods contributing to adhesion), while the van der Waals method tends toward the lower limit (not accounting for other interaction forces, e.g. capillary forces).

Increased adhesion with the compliant platforms (Fig. 6) can be attributed to greater surface contact as a result of enhanced surface conformation, primarily due to the flexible platform fingers. The additional contact area of the fingers was assumed to increase linearly with applied load and included in the van der Waals model from above. The new model, for the case of 2 and 4 fingers adhering, was compared with the experimental data for the organorod covered flexible platforms (Fig. 6). Although there is a considerable amount of scatter, due in part to the nature of this “real life” rough sphere test, there is good agreement between the predicted adhesion for all four fingers in contact and the maximum measured adhesion strengths. This also helps to understand the origin of much of the scatter. On every successive indent it is possible that not all the platform fingers are making contact – especially considering the roughness of the indenter tip. While this introduces a variance in the data and makes modeling tricky, from an application standpoint larger arrays will produce a conglomerate adhesive strength.

Addition of the hydrophobic coating to the organorod surface increased adhesion. It was expected that the decrease in surface energy with the hydrophobic coating would reduce the adhesion. The hydrophobic coating on the organorods increased the diameter of the organorods and changed the surface composition. Considering these two factors the van der Waals model was modified, with $R_o = 350$
nm and $\gamma_{\text{polymer}} = 19 \text{ mJ/m}^2(65, 66)$, and plotted against the experimental data (Fig. 7). While the model predicts a slight increase in adhesion over the smaller organorods, it greatly underestimates the adhesion of the hydrophobic organorods. Further investigation using scanning electron microscopy revealed that the hydrophobic organorods tended to change conformation under applied pressure effectively changing their radius of curvature. Both JKR and van der Waals models were modified to account for the increased size of the organorods (Fig. 7, lines b and c).

While the JKR model offered a better prediction, both models failed to capture the experimental data trend. Upon examination the van der Waals equation has a strong dependence on $d_o$, the estimated cut-off distance – basically determining the range of interaction of van der Waals forces. Reducing the cut-off distance, $d_o$, from 0.165 nm to 0.09 nm the van der Waals model better represents the experimental data (Fig. 7 line d). This suggests that the hydrophobic coating may enhance the van der Waals adhesive force by decreasing the surface to surface interaction distance.

A composite model for the hydrophobic organorods on the flexible platforms was made by accounting for the compliant fingers in the van der Waals hydrophobic organorod model, with $d_o=0.09$ nm. Comparing this model with the experimental data, excellent agreement is seen (Fig. 7, line e). The slight lag in the experimental curve can be attributed to the delay in finger attachment (the sphere must press into the center of the platform before it becomes sufficiently close to interact with the
extended fingers). Note that the highest adhesion attainable experimentally, 462 μN, corresponds to 1 complete finger attachment (the end of line e in figure 7) and a predicted adhesion of 485 μN.

Some simple models to explain a complex adhesion phenomenon have been presented. Although simple, the models do show reasonable agreement with the empirical data, although the testing was initially designed to produce only relative adhesion strengths between the biomimetic adhesives and a rough aluminum sphere. The rough sphere testing introduces a significant amount of scatter to the data making analytical comparisons tenuous. However, the relative improvement in adhesion with the hydrophobic surface over the hydrophilic surface is an intriguing result. To ascertain the mechanism of this adhesion improvement, and to support the validity of the testing, the nanoindenter testing should be repeated with a smooth and more ideal indenter surface – e.g. a polished flat punch tip. This would certainly help to eliminate much of the scatter and remove the adhesion strength dependence on applied load, as is seen with the spherical tip.

**E. Summary**

Arrays of flexible silicon dioxide platforms supported by single high-aspect-ratio silicon pillars have been fabricated. These platforms, when coated with polymeric organorods, show a significant increase in adhesion over solid organorod covered substrates. Further improvement in adhesion is measured with the addition of a
highly-hydrophobic organorod surface – possibly enhancing van der Waals interactions. This indicates that the super-hydrophobic nature of the gecko pad may serve to improve adhesion, instead of just aiding in self cleaning and wear characteristics. Future work on the synthetic adhesive will focus on optimization of the structure, more ideal testing for theoretical purposes, and scaling up fabrication for macro-scale testing and device integration.

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**F. Figures**
Figure V-1  Electron micrographs of silicon dioxide platforms supported by single slender pillars and coated with polymeric organorods. The structures are batch fabricated using standard bulk micro fabrication techniques requiring only a single lithography step.  a, Array of four-fingered platform structures. Scale bar, 200 µm.  b, Profile view of a organorod coated silicon dioxide platform supported by a single crystal silicon pillar. Scale bar, 20 µm.  c, Magnified view of the multi-scale system. Scale bar, 20 µm.  The integration of the ~200 nm diameter organorods with the 150 µm platform structures provides enhanced surface conformation.  d, High resolution electron micrograph of the edge of an organorod coated finger. Scale bar, 5 µm.
Figure V-2  Silicon dioxide platform supported by a single high-aspect-ratio pillar etched out of single crystal silicon using a modified micro fabrication technique. Scale bar 50 μm.

Figure V-3  Organic looking polymeric nanorods, “organorods”, fabricated utilizing the instability of a dielectric in a large electric field. The ~100 nm features were achieved using a bilayer to reduce the interfacial energy, thus reducing the instability wavelength and corresponding feature size. Scale bars, 10 and 2 μm, left and right respectively.
Figure V-4  Comparison of hydrophilic and hydrophobic surfaces.  a, (top) Water droplet partially wetting a hydrophilic organorod surface with a contact angle of 42.5° ± 2 (top).  (bottom) Electron micrograph of ~120 nm diameter organic looking nanorods, “organorods”. Scale bar, 5 µm.  b, (top) Water droplet resting on top of the highly-hydrophobic organorod surface with a contact angle of 145° ± 2.  (bottom) Electron micrograph shows the increased diameter of the organorods to ~350 nm from the fluorocarbon hydrophobic coating applied through plasma deposition. Scale bar, 5 µm.
Figure V-5  Typical nanoindenter adhesion test results for a organorod covered structure indented with a semi-rough 3.175 diameter spherical aluminum tip. The plot represents a typical load vs. displacement curve illustrating loading, unloading, and pull-off adhesion.
Figure V-6  Nanoindenter adhesion testing results and theoretical models for hydrophilic polymeric surfaces. Test surfaces were indented with a semi-rough 3.175 diameter spherical aluminum tip. Increased normal loads created more surface contact between the spherical tip and surfaces increasing adhesion. The organorod morphology enhanced surface adhesion over the solid photoresist surface. Adhesion was further enhanced by integration of organorods with flexible silicon dioxide platforms, large data scatter was a bi-product of testing meso-scale adhesion with a rough surface. a, van der Waals and b, Johnson-Kendal-Roberts (JKR) adhesion models predicting the collective adhesion of organorods over a given contact area, predicted by JKR contact mechanics for a sphere and flat surface. c and d, Modified van der Waals adhesion accounting for increased contact area attributed to
conformation of platform “fingers” to the test sphere; c, two fingers. d, four fingers. The saturation point corresponds to complete finger attachment, in the case of four fingers (d) this value nicely bounds the experimental data.

Figure V-7  Nanoindenter adhesion testing results and theoretical models for hydrophobic polymeric surfaces. Surface adhesion between the sphere and test surfaces is enhanced by a hydrophobic coating on the organorods. The coating increases the size from ~120 nm to ~350nm and reduces the surface energy. a, van der Waals interaction energy model predicts an increase in adhesion with the larger organorods, but fails to capture the trend of the hydrophobic organorods. b, van der Waals and c, JKR models compensating
for an increased radius of curvature—determined by scanning electron microscopy—of organorods squashed during indentation show better agreement with experimental data. d, Reduction of the interaction distance, $d_o$, from 0.165 nm to 0.09 nm in the van der Waals model. e, Combining the modified van der Waals models for hydrophobic organorods ($d_o=0.09$ nm) and the compliant platform model with 1 finger, excellent agreement with the meso-scale adhesion test is seen. Note the terminus of dotted line represents 1 complete finger adhesion.

Figure V-8  Scanning electron micrographs showing squashed organorods in the central portion of a structure. Scale bars, 20 and 10 μm, left and right respectively.
VI. Batch Fabrication and Characterization of Nanostructures for Enhanced Adhesion

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This paper describes the realization and characterization of nanofabricated organic looking polymer nanorods, “organorods,” for use in a biomimetic adhesion system. The adhesion system is inspired by the fine hair adhesive motif found in nature and best exemplified by the gecko. The meso- to nano-structure of the gecko’s foot is designed to maximize inelastic surface contact to enhance van der Waals interactions. In this work fabrication and characterization of nanostructures has been performed for inclusion in a multi-scale system mimicking the natural adhesive using cleanroom based processing techniques. The system consists of flexible silicon dioxide platforms, supported by a single silicon pillar, coated with ~200 nm in diameter and ~4 μm tall polymeric organorods. The organorod surface is altered between hydrophilic and highly-hydrophobic. The adhesive properties between the artificial surface
and a 3.175 mm aluminum sphere are measured in a modified nanoindenter. Initial results indicate improved adhesion with the hydrophobic surface over the hydrophilic, further corroborating van der Waals interactions to be the operative force of adhesion and suggesting a reduced cut-off distance in the van der Waals theory.

A. Introduction

The emergence of microsensors has come about due to increased microfabrication abilities and gain in understanding of microscale mechanics. Sensors for chemical, mass, pressure, and inertial sensing are among the most common thus far (42, 47, 51, 52). Significant developments in microscale sensors have enjoyed interest because they possess important properties, including high sensitivity and the ability to be fabricated in large arrays of thousands to millions. However, there still exists a question in the deployment of these arrays. Adhesion of sensor arrays is one area necessary for many applications that require the deployment of microdevices. In addition chip-scale recognition and adhesion systems will be of great interest for use in fabrication, self-assembling microdevices and immersing miniature aerospace applications.

Found in nature, and best demonstrated in the pad of the gecko’s foot, the fine hair adhesive system is an excellent example of convergent evolution in biology(1-4, 6-8, 54). Researchers have puzzled over the phenomenon back all the
way till the days of Aristotle. Recently much work has been done to better understand the mechanism behind the adhesion (6-8, 15, 56, 67), and convincing data has shown that the adhesion is primarily due to short-range weak van der Waals interactions between the fine hairs on the adhering surface and the external surface(7). In order for these weak interaction forces to become significant a large amount of inelastic surface contact must be made between the surfaces. If the adhesive were to elastically conform to the surface then there would be a repulsive force present from the strain in the material. To avoid this the gecko has a multilevel conformation structure which allows for a large amount of surface contact with out creating a repulsive force. The multi-level structure consists of toes containing blood sinuses supporting rows of imbricated lamellae of densely packed keratinous setae, approximately 100 µm in length and 20 µm in diameter, which then split into finer 200 nm in diameter bristles (2).

Previous work in this area has focused on creating the final terminal bristles(7, 11, 12, 58). While individual nanorods demonstrated expected amounts of adhesion, larger arrays failed to produce larger amounts of adhesion – unless removed from the substrate and placed on a compliant backing(11). This illuminates the need for a multi-level conformation scheme. Additionally, due to processing constraints, prior work has not fully duplicated the nano-structure, done so by any mass production means, or emulated the super-hydrophobic nature of the gecko pad (until now only thought to aid in self-cleaning of the surface). In this paper a new fabrication technique to produce, in a massively parallel fashion, sub-micrometer polymeric organorods will be discussed. To test the relative
functionality of the nanostructures an adhesion test technique utilizing nanoindenter instrumentation will be described and results compared with a simple analytical adhesion model.

**B. Experimental**

1. Fabrication

For incorporation into the multi-scale system a compatible nanorod fabrication technique was developed to create 50-150 nm diameter and ~4 μm tall organorods (Fig. 1). The process is compatible with standard microelectromechanical fabrication utilizing a modified reactive ion etch (RIE) process. To create the organic looking nanorods a 4 inch silicon wafer is first soaked with HMDS for 30 seconds and spun ‘dry’ at 3500 rpm. The wafer is then coated with photoresist (Shipley™ SPR 220-7, a diazoquinone ester and a phenolic novolak resin resist) spinning at 3500 rpm and baking at 95°C for 90 seconds. The wafer is then placed into an inductively coupled plasma (ICP) reactive ion etcher using an oxygen plasma with an applied bias between the sample and the plasma (Fig. 2). For the nanorods tested in this paper a RF power of 300 W, an oxygen flow rate of 40 sccm and a 10 minute growth time is used to coat a 4 inch wafer. Further transformation of the hydrophilic organorods to a highly-hydrophobic surface is achieved by placing the
sample in a fluorine plasma. The fluorine deposits a conformal coating on the organorods creating a Teflon® like surface.

2. Characterization

A Hysitron Triboindenter™ is used to measure adhesion between the test surfaces and a 3.175 mm diameter aluminum sphere (see schematic Fig. 2). In this experiment the aluminum sphere is glued to the tip of a nanoindenter probe. The device is placed in the indenter and the indenter tip pressed against the test surfaces. The nanoindenter is operated in displacement control and records the load vs. displacement. To determine the adhesion the loading and unloading curve is analyzed extracting the minimum normal load, taken to be the maximum adhesion. In the case of no adhesion this value is zero or a positive number. In the case of an adhesion event the number would be negative, representing a pulling force on the retracting tip.

Silicon wafers were coated with three different surfaces and tested with the nanoindenter. The first surface was a simple photoresist surface with no other modifications, the next a hydrophilic organorod surface, and the third a hydrophobic organorod surface.

The contact angle of the hydrophilic and hydrophobic surfaces were measured by placing a drop of water on the test surfaces and taking a picture through a
magnifying glass using a Canon A95 digital camera. The high resolution images were then magnified and printed, where lines could be drawn to measure the angle with a protractor. The organorod surface was found to initially have a hydrophilic surface with a contact angle of $42.5^\circ \pm 2$. After the fluorocarbon treatment the surface became highly-hydrophobic with a contact angle of $145^\circ \pm 2$ (compared to $160.9^\circ \pm 1.4$ for the gecko (7)),

C. Results and Discussion

The organorod formation may best be explained by the interaction of the dielectric polymer and the electric field gradient. Schäffer et al. [ref. 20] observed a similar phenomenon when they placed a polymer in an electric field created by two parallel plates. They postulated that the dielectric polymer experienced a force created by the electric field gradient. This force would then be accentuated by an instability wavelength ultimately determining the size of the pillars(60). While qualitatively this explanation fits, the pillars formed using the plasma growth method produced much smaller dimensions. This suggests that the plasma growth method may have other benefits in addition to the ease of alignment and growth. Two factors may be contributing to the reduced geometry of $\sim$50-150 nm the organorods (Fig. 1). One a bilayer of photoresist and hexamethyldisilazane (HMDS) may reduce the interfacial energy, shrinking the instability wavelength(61), and decreasing the final
pillar size. Secondly, the oxygen ions may reduce the surface energy of the polymer, decreasing the surface force opposing the electric field force, and further reducing the size.

Adhesion values were obtained by observing loading and unloading curves in the indenter testing described previously and visually represented in figure 3. Initially a plot shows a no load versus displacement until the sphere comes into contact with the surface. There is then a positive increase in the load with further displacement. Upon retraction the load curve falls below zero to a critical point, where it suddenly jumps back up to zero load. The minimum load value is taken to be the maximum adhesive force. The maximum adhesion was found to be highly dependent upon the maximum positive load value in the case of the organorod surfaces, but not for the smooth photoresist surface, Figure 4. This increase in adhesion with load is due to a greater number of organorods coming into contact with the indentation tip. The flexible organorods offer little restoring force and the net adhesion is much higher. Whereas the solid photoresist surfaces produces an elastic restoring force, repulsing the indenter tip and reducing the adhesion.

To better understand and verify the adhesion data taken in the nanoindenter a basic analytical treatise was given to the system considering van der Waals (vdw) interactions, where the force between a sphere and a flat surface is taken to be 

\[ F_{vdW} = \frac{HR_o}{6d_o^2} \]

where \( H \) is the Hamaker constant (estimated to be \( H = 2.1 \times 10^{-21} \) W = 2.8x10\(^{-19}\) J), \( R_o \) is the diameter of the organorods, \( d_o \) is a characteristic cut-off distance, and \( W \) is the work of adhesion. The Hamaker constant is estimated to be \( H = 2.1 \times 10^{-21} \) W [ref. 22]. The cut-off distance was initially estimated to be 0.165
nm(64), but was then reduced as will be discussed. The work of adhesion, W, was taken to be \( \sqrt{\gamma_{\text{Al}} \gamma_{\text{polymer}}} \), where \( \gamma_{\text{Al}} = 500 \text{ mJ/m}^2 \) and \( \gamma_{\text{polymer}} = 35 \text{ mJ/m}^2 \) and 19 mJ/m², for the hydrophilic and hydrophobic respectively. In this system the radius of the terminus of the organorods is taken to be much smaller than that off the aluminum sphere. In this manner the tips of the organorods are taken to be many small spheres contacting a flat surface, the aluminum indenter tip. The radius of the organorods was taken to be 200 nm for the hydrophilic and 350 nm for the hydrophobic. The number of organorods in contact was estimated using JKR contact theory(68). The contact theory was used to estimate the radius of contact between the spherical aluminum tip and the organorod surface. This of course requires the elastic modulus of the organorod surface to be known. By indenting and measuring the contact radius at different indent loads it was possible to adjust the equation appropriately. The radius indent and density of organorods was measured in a scanning electron microscope, which also allowed for verification of the number of organorods that contacted the sphere. Using the density, and contact radius as a function of load, the number of organorods in contact at any given load could be determined. For example at a contact load of 10 mN approximately 1200 organorods were estimated to be in contact. Then knowing the number of organorods in contact it is possible to determine the total adhesion based on the van der Waals expression above.

Plotting the predicted adhesion force against applied load there is reasonable agreement between the organorod surface and the van der Waals prediction of above (Fig. 4 curve a), note that this test was meant to simulate a “real life” adhesion situation by using a rough indenter tip and scattered data is to be expected. When the
organorods are given a hydrophobic coating there is an unpredicted increase in adhesion. The vdw force equation is highly dependent on the characteristic cut-off distance, which is indicative of the interaction distance between the two surfaces. It may be possible that the hydrophobic coating brings the two surfaces into more intimate contact, reducing the cut-off distance. To test this, the model was modified with different cut-off distances, $d_0$. A $d_0$ equal to 0.09 nm, instead of 0.165 nm, yielded a much better prediction of the empirical data (Fig. 4 curve b). Unfortunately there is a great deal of scatter due to the testing procedure. Considering the potential scientific merits of this find a more ideal test will be performed to test influence of the hydrophobic coating on adhesion.

**D. Conclusions**

A massively parallel fabrication technique for producing ~200 nm diameter, ~4 um tall polymeric pillars has been developed. The technique is compatible with “dry” cleanroom processing and allows for inclusion into a multi-scale system mimicking natures fine hair adhesive(69). The nanostructures have been tested using a novel nanoindenter adhesion test to confirming their enhancement of adhesion over a smooth surface. Adhesion was further increased by the addition of a hydrophobic coating. This increase in adhesion is attributed to more intimate surface interaction due to a reduced van der Waals interaction distance.
E. Acknowledgments and Correspondence

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F. Figures

Figure VI-1 Scanning electron micrographs of the organorod morphology, scale bars 5 μm and 1 μm, left and right respectively.
Figure VI-2  Schematic of the organorod growth mechanism. A bias is applied between oxygen plasma and the substrate, creating an electric field gradient, which acting on the dielectric polymer draws it in the direction of the gradient.
Figure VI-3  Schematic of the nanoindenter test setup. The sphere represents the 3.175 mm aluminum sphere which is fixed to a shank fitted into the nanoindenter transducer. When the sphere is pressed into the platform structures a loading and unloading curve is produced. At the bottom of this curve there is a sudden jump from a negative force value to zero. This jump is indicative of pull-off associated with adhesion, and correspondingly taken to be the adhesive force.
Figure VI-4 Nanoindenter test data plotted against analytical van der Waals (vdw) predictions. The circles represent a smooth polymer surface without modification. The squares represent a hydrophilic organorod surface on a solid substrate. The triangles represent a hydrophobic organorod surface on a solid substrate. Curve a represents a simple vdw model based on the number of organorods contacting the test surface, the radius of curvature of the organorod tips, and using a cut-off distance of 0.165 nm. The number of contacts is estimated by knowing the density of organorods and calculating the contact area of the indenter tip using JKR contact mechanics. Curve b is identical to curve a, but with a reduced cut-off distance in the vdw equation of 0.09 nm.
VII. Meso-Scale Adhesion Testing of Integrated Micro- and Nano-Scale Structures

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Many insects and lizards display the amazing ability to climb and stick to just about any surface. Recent research has honed in on these systems to better understand how they work(6, 7, 15, 70), particularly on how fine sub-micron hairs enhance van der Waals, or other short-range interactions. Provided enough intimate surface contact these “weak” forces can add up to produce significant amounts of adhesion. Additionally, the attractive interaction must be much larger than repulsive forces, due to elastic deformation, for the adhesive to be effective. To achieve this, nature has created a hierarchal structure to conform over a range of size scales(2). In previous work, microfabrication techniques were used to create a synthetic dry adhesive modeled after the fine hair adhesive motif found in nature(71). The artificial structure consists of a silicon dioxide platform, covered with organic looking polymeric nanorods (“organorods”), and supported by a single
single-crystal silicon pillar. The Multiscale Integrated Compliant Structures (MICS) offer three levels of surface compliance: (1) the organorods on the surface (also necessary for enhancing surface adhesion), (2) the fingers of the platforms, and (3) the flexibility of slendör silicon pillar supporting the platform. In this work large arrays, 1cm x 1cm, have been batch fabricated across an entire 10 cm wafer. Additionally, to characterize mesoscale adhesion, a nanoindentation adhesion test technique was extended to measure the adhesion between the microfabricated samples and a rough 5 mm diameter aluminum flat punch. Results indicate improved adhesion with the integration of the nano- and micro-structures. The multi-scale structures also demonstrated improved wear characteristics over solid supported organorods.

**Keywords:** adhesion, nanorod, nanoindenter, 3-D, MEMS, gecko, dry-adhesive
**A. Introduction**

In the emerging field of biomimetics, the ever growing knowledge base of biology is brought together with the rapidly developing ability to measure and manipulate properties at very small length scales. Since the time of Aristotle, scientists have been fascinated by the gecko’s ability to scale virtually any surface, and under completely different environmental conditions(2, 6). In the last hundred years scientists have speculated that the adhesion force in the gecko pad is a result of suction, secretions or capillary forces. Recently Autumn et al. performed a series of experiments giving convincing evidence that van der Waals interactions are the dominant interaction force (6).

An excellent example of convergent evolution, the gecko has developed highly refined 200 nm protrusions to maximize van der Waals interactions (2, 6, 7). However, for this surface contact to be effective there needs to be a minimum amount of repulsive force from the surface. To achieve this, the fine hair adhesive motif has a multi-scale compliant structure designed to conform to varying levels of surface roughness.

The largest scale of conformation, in the case of the gecko, is the gecko itself with a body and legs able to move in and around tens of centimeter size objects. Moving down in size scale are the toes with the ability to wrap around curved
surfaces. Within these toes there are blood sinuses acting as a hydraulic suspension, deforming with little elastic response to millimeter scale roughness. These sinuses support rows of imbricated lamellae composed of rows of keratinous setae 30-130 μm in length and approximately 20 μm in diameter(2). These slender setae can deform to micrometer scale roughness, and offer the densely packed array of fibers necessary to maintain large amounts of surface contact. The terminus of the setae subdivide into 200 nm diameter spatulae, capable of achieving the last level of surface intimacy necessary for van der Waals forces to become significant.

Prior work has succeeded in replicating the final terminal structure of the spatulae, but centimeter scale testing resulted in negligible adhesion(11). The low values of adhesion were attributed to reduced surface conformation across multiple length scales, and to the inability of the surface interface to absorb energy and arrest interfacial crack growth. Additionally, it was seen that the hydrophilic nanorods would adhere to each other reducing wear characteristics.

The emergence of the field microelectromechanical systems (MEMS) over the last three decades has brought with it a variety of microsensors and transducers(42, 44-48, 50, 52, 72). One of the many challenges still remaining in the microsensors field is the deployment and placement of microdevices. The development of a technique to microfabricate an adhesive, capable of sticking to virtually any surface, could greatly enhance the potential for “fly on the wall” distributed sensing.

In previous work the authors have used microprocessing techniques to create novel micro- and nano-structures mimicking the hierarchal structure of the
gecko(71). Here, this fabrication technique has been extended to create larger 1 cm x 1 cm arrays and a new testing methodology has been implemented to measure mesoscale adhesion characteristics of the system. The processing technique is fully compatible with standard microprocessing, requires only a single lithographic step, and uses only dry etch techniques. The structures produced follow a similar motif to the fine hair adhesive in nature by creating multiple levels of compliance. The Multiscale Integrated Compliant Structures (MICS) consist of a single single-crystal silicon piller supporting a silicon dioxide platform coated by polymeric organorods (Fig. 1). The silicon pillars can have high aspect ratios and diameters as small as 1 μm. The silicon dioxide platforms are 1 μm thick and consist of four radial meandering fingers extending 50 μm from a central square platform. Atop these platforms are arrays of vertically aligned ~250 nm diameter, ~4 μm tall organorods composed of positive photoresist (Fig. 2). Combining these three structures an analogous system to the fine hair adhesive is created mimicking the multiple levels of compliance on a chip. The first level of compliance, like the toe of a gecko, is the small size of the chips that can be produced, allowing the chip itself to fit within centimeter scale roughness. The next level of compliance is the flexible silicon pillars, allowing the entire platforms to rotate, accommodating sub-millimeter scale roughness. The fingers of the oxide platforms allow for conformation to tens to hundreds of micron size features. And finally to maximize surface area contact, and enhance van der Waals interactions, are 250 nanometer diameter organorods.
B. Fabrication

The MICS structures were fabricated using a single lithographic step and multiple etch process\(^{(59, 71)}\). Single crystal silicon wafers in the (100) orientation were used for all fabrication. Wafers were first coated with 1\(\mu\)m of thermal oxide using a wet oxidation process at 1150\(^{\circ}\)C. Positive photoresist (Shipley\textsuperscript{TM} SPR220-7) was spun on the wafers to a thickness of 7\(\mu\)m. The top platforms were then patterned in the resist using projection lithography. This pattern was then transferred into the underlying oxide using an inductively coupled plasma (ICP) etch with CHF\(_3\) chemistry defining the platforms in the silicon dioxide. Deep reactive ion etching, using the Bosch process, was then used to extend the oxide pattern vertically \(\sim\)35 \(\mu\)m into the bulk silicon. Subsequent to the extension etch an extended isotropic SF6 etch is run, undercutting the silicon dioxide, and creating oxide platforms supported by a single silicon pillar (Fig. 1).

To create the polymer organorods, the photoresist coated structures were placed in an inductively coupled oxygen plasma. By controlling the oxygen pressure, RF bias, and time the photoresist surface was transformed into first a roughened morphology and then into a coating of organorods\(^{(71)}\) (Fig. 2). Different organorod morphologies were observed by adjusting the various growth parameters. In this work better spacing and isolation of the organorods was achieved by increasing the RF bias and growth time than in previous work. Additionally,
uniform coatings of organorods have been created over a complete 100 mm wafer, with and without structures. As can be seen in Figure 1, incomplete coverage was seen on the platform fingers as a result of previous degradation of the photoresist during the silicon dioxide and silicon etch steps. As will be discussed momentarily, this incomplete coating may have a significant impact on the adhesion strength of the system.

Using this fabrication method, 100 mm wafers have been created with 80 separate 10 mm x 10 mm arrays of 2,500 platforms, each containing ~50,000 organorods. The process technique is true batch fabrication allowing for simultaneous creation of 200,000 platforms and ten billion organorods. This massively parallel approach highlights the potential of this fabrication technique for future low cost device implementation.

**C. Experimental**

Previous testing of artificial fine hair dry adhesives has focused on measuring the adhesion of individual nanorods\(^{(7, 11, 12)}\). Scaling of individual nanorod adhesion greatly overestimates the adhesion of larger scale (50\(\mu\)m) adhesion testing \((11)\). This suggests the need to develop alternate test techniques for measuring the meso-scale adhesion of these systems. Additionally, a rough surface was desired to test the MICS in a simulated application environment, e.g. an aircraft wing. To
accomplish these testing requirements a Hysitron Triboindenter™ was retrofitted with 5 mm aluminum flat punch tip. The tip was fabricated using a stock indenter shaft and a 5 mm aluminum puck (RMS roughness of 2.5 μm). To bring the two components into registration the puck was placed on the sample stage, with a drop of glue on the top surface, and the shaft was fitted into the Triboindenter™ transducer. By performing a standard load controlled indent, the tip was brought into contact with the puck and allowed to rest there while the glue dried.

Operating the nanoindenter in displacement control, the flat punch tip was brought into contact with the test surfaces and withdrawn at a constant rate recording the normal force and displacement. Upon unloading an adhesion event would cause a negative normal load. The maximum negative force was taken to be a measurement of adhesion. Repeated tests were performed in the same location to assess wear characteristics of the structures.

**D. Result and Discussion**

Previous testing used a spherical tip geometry with a diameter of ~3mm(71). While the spherical geometry avoids the requirement for near perfect tip sample registration, the spherical tip produced several complications in testing. The spherical geometry, even at scales as large as 3 mm, would only contact a single platform structure, making it difficult to ascertain the conglomerate effects of arrays
of structures. Additionally, the tip added strong normal load dependence to adhesion (more indentation force would increase the surface contact area and subsequent adhesion). The incorporation of the 5 mm flat punch into the testing aimed to alleviate these two complications.

Using the aluminum flat punch, adhesion testing was performed on three test surfaces including: photoresist coated silicon wafers, organorod coated wafers, and arrays of MICS on a silicon substrate (Fig. 3). The photoresist surface showed very little adhesion with the average adhesion strength of 0.1 Pa. The organorod surface demonstrated improved adhesion strength of 6.5 Pa. Integrating the pillar supported platforms with the organorods enhanced adhesion by more than a factor of three to 21.8 Pa. No significant dependence was seen on the maximum positive applied normal load.

Upon repeated adhesion tests in the same location, the MICS demonstrated no reduction in adhesion by the fifth iteration. Whereas the adhesion to the organorod surface decreased nearly to zero by the fifth indent (Fig. 4). The diminished adhesion is likely a result of damage to the organorod surface by the indenting puck. Individual organorods are either pushed down to the surface where they remain, are permanently deformed moving them out of the contact zone, or condense into clumps of organorods. The integration of the flexible platforms may improve wear by flexing before a critical load is placed on the organorods, causing non-recoverable damage. This behavior is not unlike that of the gecko, where the long
shafts of the setae can bend before the nanoscopic spatulae receive an excessive load.

The experimental values of adhesion strength for the MICS of ~20 Pa is much lower than those reported for the gecko, *Gekko gecko*, of ~100 kPa (6, 73). Although there is much work left to be done to rival nature, there are several significant testing differences that account for the orders of magnitude difference in adhesion strength. The first major difference is that the MICS adhesion was measured in a normal direction to the surface. While in the gecko testing, adhesion was measured in a direction parallel to the surface, likely creating a composite adhesion and friction force. Autumn et al. did show that adhesion in the transverse direction was over a factor of 30 times greater than in the normal direction. By measuring the force of a single 20 μm seta, on an atomically smooth surface, normal adhesion strengths of 3 kPa were measured (6). Additionally, based on transverse adhesion measurements, a 10 fold reduction in adhesion can be expected for macro-scale testing (or whole gecko pad tests) (6, 11). Taking this into account, a normal adhesion measurement between a smooth surface and an entire gecko pad may yield adhesion values around 300 Pa. This leaves only an order of magnitude difference in adhesion without taking onto account the reduced adhesion expected on a rough surface.

Diminished performance of the artificial adhesive can be attributed to the incomplete organorod coverage on the platform fingers. The ends of the fingers offer the highest compliance of the structure, providing the potential for improved surface contact. However, without the organorod coating van der Waals interactions
are greatly reduced, along with the subsequent adhesion strength. Improved adhesion is expected with refined processing to produce complete coverage.

The difficulty comparing values here clearly presents the need for a standardized test technique for adhesion on the millimeter size scale. For now it may be best to perform experiments on standardized samples to determine relative adhesion strengths. In this work, the photoresist surface was used as a baseline and relative improvements were shown with each additional level of compliance: first with the organorods and then with combination of organorods and flexible platforms.

Future work will focus on enhancing adhesion through modification of the three key design components. These components are the silicon support pillar, the silicon dioxide platform, and the organorod surface. The aspect ratio of the silicon pillar can be modified to assess an optimum height and shape for adhesion. The pattern of the silicon dioxide platform can be modified to further enhance surface compliance while maintaining structural stability. Also the spacing between individual platforms can be reduced to offer larger surface contact area. Perhaps, most importantly, the height, size, spacing, and material of the organorods can be modified to optimize adhesion.

E. Conclusion
Multi-scale Integrated Compliant Structures (MICS) have been fabricated with aligned vertical photoresist organorods coating lithographically defined flexible silicon dioxide fingers supported by a single silicon pillar. The MICS have been produced using batch fabrication techniques creating 10 mm x 10 mm arrays across an entire 100 mm wafer.

To measure adhesion a new test technique has been developed. The technique employs nanoindenter instrumentation to measure the pull-off force between a 5 mm diameter aluminum flat punch and test surfaces. Appreciable increases in adhesion are observed with the integration of the multiple scales of compliant structures. Additionally, the MICS offer enhanced wear characteristics with sustainable adhesion over repeated testing.

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F. Figures
Figure VII-1  Multiscale integrated compliant structures (MICS). Portion of a 2,500 array of MICS (top), scale bar 500 μm. Individual MICS (middle), scale bar 50 μm. Central portion of a platform showing organorod integration (bottom), scale bar 10 μm.

Figure VII-2  Scanning electron micrograph of organic looking polymeric nanorods (“organorods”) on the central portion of a platform, scale bars 5 μm and 2 μm, top and bottom respectively.
Figure VII-3  Adhesion strength versus applied normal load between a 5 mm diameter aluminum flat punch and a smooth photoresist surface (triangles); a surface of vertically aligned photoresist organorods (diamonds); and a surface of arrayed multiscale integrated compliant structures consisting of silicon dioxide platforms coated with organorods (squares).
Figure VII-4  Comparison of repeated adhesion between a organorod surface on solid substrate (diamonds) and a organorod surface on compliant structures (squares).
VIII. A bio-inspired reversible adhesive

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Geckos, as well as many insects, have evolved a robust reversible adhesion mechanism, enabling them to traverse rough, smooth, vertical or inverted surfaces. Here we report the fabrication and demonstration of a synthetic reversible adhesive composed of flexible nickel paddles coated by aligned vertical polymeric nanorods. When subjected to a magnetic field, the nickel paddles undergo a reversible conformational change, greatly reducing the contact area, and decreasing adhesion by a factor of 40. Such controllable adhesion may impact technologies ranging from ubiquitous latching systems to high-tech applications such as microrobotics.
The mechanism of adhesion in the gecko has been of scientific interest since Aristotle (74). Since then scientific investigations have revealed much about the construction of the pad in the gecko’s foot (5, 9, 75-77). Most recently there has been an intensifying scientific investigation into the fundamental physics of the adhesive, isolating van der Waals as the primary source of adhesion (6, 10), with additional evidence that humidity may also play an important role (25, 78). Van der Waals interactions produce weak and short-range forces, therefore the gecko must create a large amount of intimate surface contact to have enough adhesion to hang from a vertical or inverted surface. The gecko accomplishes this with a highly compliant pad structure, which allows it to conform to surfaces, without creating a large amount of elastic repulsive force (29). This ability to comply to a wide range of surfaces, from the curvature of a tree branch to micro- and nano-scale roughness of bark, is a result of a multi-scale compliant structure (26, 28, 79, 80). The hierarchical structure consists of 200 nm wide, 5 nm thick spatulas at the ends of ~100 μm long, ~5 μm diameter setae (5, 75, 76, 81). The fine and thin spatulas conform to nanoscale roughness of a surface, enhancing the van der Waals forces and increasing adhesion through a contact splitting phenomenon (27). The setae provide the next level of surface compliance by bending to conform to micro- and millimeter scale roughness. Without the compliance of the setal stalks, the spatulae would not come into contact with even the most moderately rough surface, greatly affecting the adhesive properties. There is evidence that the hierarchical structure may serve another purpose than enhancing adhesion – to reduce adhesion (6, 14, 82). As interesting as the gecko adhesion mechanism is, if the gecko were unable to
release a surface, it would not be possible to take the next step. The nano/micro-

scale components integrated into a hierarchical attachment/detachment structure
allows the gecko to control adhesion at the nano-scale through macroscopic muscle
movements (10, 14, 29).

Previously, a bio-inspired synthetic system enhancing adhesion utilizing a

hierarchical structure was fabricated and tested (83). The system consisted of
aligned vertical nanorods coating thin silicon dioxide platforms. The nanorods
provided sufficient short-distance interactions to provide adhesion and the platform
provided the bulk scale conformity necessary to adhere to rough or contoured
surfaces. The combination of both structures provided increased adhesion over either
isolated component. However, unlike the gecko, the system did not provide a
mechanism for decreasing adhesion. This attribute is critical to any application of
such a biomimetic system.

Here we report a new biomimetic system which provides a mechanism for
decreasing adhesion using a magnetic field to actuate nickel cantilevers. The nickel
beams, when placed in a magnetic field, reorient themselves so that the terminal pad
of the structure, responsible for adhesion, rotates to face away from an adhering
surface, Fig. 2. This conformational change effectively switches off the structure’s
ability to adhere by drastically reducing the available adhesive area.

Further development of reversible adhesive systems will lead to a new class
of materials, able to stick and unstick controllably. These controllable adhesives
may find applications ranging from everyday consumer products; such as a non-
mechanical car door latching and sealing system; to improving manufacturing
techniques with the ability to grip just about any surface; to high-tech niche
applications, e.g. microrobotics. Just as this adhesive motif enables creatures such
as beetles, spiders, and geckos to climb up and over objects, controlled adhesion will
enable small scale robots to surmount obstacles of all sizes – allowing for the
exploration of environments inhospitable or inaccessible to man, e.g. the surface of
mars or the inside of a burning building.

Fabrication of the multi-scale structures required the integration of two different
processing modalities. The nickel platform microstructures were
photolithographically defined and etched using standard microfabrication reactive
ion etching. The vertically aligned polymeric nanostructures were created through a
stochastic growth method. Both methods employ batch fabrication techniques and
are scalable to production quantities.

Released 150 nm thick and 130 μm long nickel structures, coated with aligned
vertical arrays of stiff polymeric nanorods ~200 nm in diameter and ~3 μm tall, were
fabricated using a combination of compatible massively parallel fabrication
techniques. The fabrication process began by coating blank 4-inch (100) silicon
wafers with a 1.4 μm thick layer of image reversal photoresist (AZ 5214). The
negative image of the desired platforms was then transferred into the resist across the
entire wafer using a Karl Suss MA6 contact aligner. After developing, a 150 nm
thick nickel layer was electron beam evaporated onto the entire wafer. The
photoresist was then removed, via an ultrasonic acetone bath, lifting off the excess
nickel. The wafer was cleaned and dried and a 7 μm layer of photoresist was spun onto the wafer surface (Shipley SPR 220-7). The positive pattern of the platforms was then transferred into the resist, aligned with the nickel platforms below. The resist and nickel pattern was transferred into the exposed silicon alternating between a highly reactive mostly isotropic SF$_6$ etch and a C$_4$F$_8$ passivation deposition (the Bosch process) effectively etching vertically into the silicon. After etching approximately 30 μm into the silicon, a sustained SF$_6$ etch was performed to undercut the nickel/photoresist platforms. The released platforms were then placed in oxygen plasma with an applied bias between wafer and plasma, creating ~200 nm diameter nanorods, orthogonally to the surface, with an aspect ratio of ~15, Fig. 1.

The structures were characterized using a home-built adhesion test apparatus (Basalt II), Fig. 3 (84). The basic operating principle of the system is similar to an atomic force microscope, but implemented on a larger scale: the deflection of a glass spring is monitored, using laser interferometry, to determine the forces applied to the spring tip. This tip was a glass flat punch of 5 mm diameter. In order to ensure proper alignment between the tip and the sample, the tip was attached to the cantilever with high-strength glue while in intimate contact with the sample stage.

Test samples were placed on the micropositioning stage and moved to near contact with the spring tip. The tip was then lowered using a piezo electric actuator, and proper alignment was ensured through a horizontally oriented stereomicroscope. Actuation of the probe and data collection was performed using an automated National Instruments LabView™ program. Through calibration of the cantilever
(spring constant, $k=137.1 \text{ N/m}$) it was possible to determine the interaction forces between the flat punch tip and the test surface. Upon withdrawal from the surface, adhesion produced a characteristic pull-off event, evident in a negative dip of the force-displacement curve. The reversible adhesive was tested with and without Neodymium Iron Boron (Nd$_2$Fe$_{14}$B) rare earth metal magnet below the silicon chip.

While the gecko setae and spatulae are composed of $\beta$-keratin, here a combination of photoresist, silicon and nickel was used to create a 3-dimensional structure actuated through the application of a magnetic field. The photoresist ($E = 6.2 \pm 0.2 \text{ GPa}$) is transformed into 200 nm diameter 3 $\mu$m tall nanorods, analogous to the $\beta$-keratin [$E = 1-15 \text{ GPa} (13)$], spatulae of the gecko. These nanorods coat the thin nickel beams and act to enhance adhesion through contact splitting and nanoscale roughness conformation – thus acting as the active portion of the adhesive. The 150 nm thick nickel beams aid in surface conformation (just as the setae in the gecko) and as a deactivation mechanism for the adhesive. The stress mismatch between the photoresist and nickel causes the cantilevers to bend away from the surface. The upwards bend of these beams gives added compliance to a rough test surface by allowing individual cantilevers to bend and conform long before the test surface makes contact with the rigid adhesive substrate. In addition, the upwards bending of the beams isolates the active portion of the adhesive from the substrate.

With the active portion of the adhesive isolated, the properties of the adhesive could then be controlled by actuating the platforms. High-aspect-ratio ferromagnetic
structures have been shown to rotate within a magnetic field to align their long axis with the magnetic field vector (85). When the structures were placed on top of a permanent magnet the paddles were observed to rotate about their long axis, Fig. 2. This rotation is attributed to the preferential alignment of the long axis of the width of the pad in the magnetic field. In order to rotate the paddles in given direction, the stress inducing photoresist was offset on the paddles causing a slight pre-rotation, Fig. 4. The large rotation induced by the magnetic field causes the paddles to turn sideways, concealing the active portion of the adhesive from the test surface, Fig. 2.

Adhesion testing of the structures, without an applied magnetic field, produced unloading curves with a characteristic pull-off event shown in figure 4 (upper inset). The pull-off force was observed to vary with the maximum applied normal load (due to slight misalignments between the flat punch and the test surface) until a saturation adhesion strength of ~14 Pa was observed (obtained by dividing the adhesion force by the projected area of all pad surfaces), Fig. 4. It should be noted that this is a purely adhesive measurement testing in the normal pull-off direction, whereas reported values for the gecko test in the transverse frictional direction (86), making comparisons between the two systems tenuous.

Alignment issues, surface inconsistencies and unknown probe geometries have presented difficulties in quantification of this new class of bio-inspired non-pressure-sensitive-adhesives. One suggested metric is to simply divide the adhesion force by the maximum preload force, \( \mu' = \frac{F_{\text{adhesion}}}{F_{\text{preload}}} \) (86). In this system the maximum \( \mu' \) value was found to be 1.47 +/- 0.4, occurring at the minimum pre-load with an
observable pull-off event (limited by the noise level of the instrumentation). This value offers a substantial increase from previous synthetic work with μ’ values of 0.125 (83) and 0.06 (11), but still falls short of the gecko with μ’ = 8 to 16 (86).

In contrast to the adhesion seen in a rest state, the application of a magnetic field to the structures produced a catastrophic loss of adhesion, Fig. 4. The minimum negative force detected was 0.37 +/- 0.28 Pa (compared with 14 Pa without a magnetic field). For no tests on the structures with an applied magnetic field was there an observable pull-off incident. This complete reduction in adhesion is attributed to the concealing of the nanorod-coated platforms from the test probe. Subjected to a magnetic field, the platforms rotate to align themselves with the magnetic field lines. The rotation leaves the edge of the platforms facing in the normal direction and the “sticky” face to the side. Thus when a surface approaches from the normal direction it only contacts the edges of the platforms. Since the edges of the platforms provide very little surface area, and have no nanorod coating, very little adhesion is produced – less than the noise in the instrumentation.

Additionally, a decrease in surface compliance was seen in the structures with an applied magnetic field. The twisting of the cantilevers increases the second moment of area of the structures, relative to the indenting tip, increasing the stiffness and consequently reducing the compliance of the system. Ultimately, the sideways turned paddles will contact the underlying substrate and statically block an adhering surface from contacting the support substrate – completely turning off adhesion.
In this paper, a novel approach has been presented for creating a synthetic analogue to the gecko adhesive system. The hierarchical system is composed of aligned vertical nanorods coating flexible micron scale cantilever paddles. The paddles, composed of nickel, rotate when subjected to a magnetic field. This rotation conceals the nanostructures on the paddle surface and greatly reduces the available surface area for adhesion. Testing of the system showed reversible adhesion behavior switching from a μ’ value ($F_{\text{adhesion}}/F_{\text{preload}}$) of 1.47 +/- 0.4 (largest reported value for a biomimetic system to date (86)) to less than the noise level in the instrumentation. Thus an active hierarchical structure has been fabricated and demonstrated to display controlled and reversible adhesion. Further development of switchable adhesives will find applications ranging from everyday consumer products such as latching and fastening systems; to high-tech applications, such as enabling microrobotics to explore extraterrestrial surfaces or harsh climates otherwise not accessible to man.
Figures
Figure VIII-1 – Electron micrographs of synthetic structures (left) and the analogous gecko structures (right), samples from a Tokay Gecko (*Gekko Gecko*). (A) Paddle surface coated with evenly spaced uncondensed aligned vertical polymer nanorods (left) and the branched terminus of a seta into spatulae (right), same magnification and scale bar 10 μm. (B) Freestanding nickel cantilevers and paddles coated with nanorods (left) and an array of setae (right), same magnification and scale bar 50 μm. (C) Low angle view of cantilevers showing upwards bending of the structures relative to the solid substrate (left) and a profile view of curving setal stalks (right), same magnification and scale bar 50 μm. (D) Lower magnification view of a portion of the synthetic array (left) and the setal array (right), scale bars 500 μm (left) and 200 μm (right).
Figure VIII-2 - Stereomicrographs of the adhesive: (A) in the ‘ON’ state, no applied magnetic field, with the adhesive paddles facing vertically; and (B) in the ‘OFF’ state, with an applied magnetic field rotating the paddles sideways, concealing the adhesive faces. Scale bars, 100 μm.
Figure VIII-3 – Schematic of the adhesion test apparatus. A laser interferometer monitors the deflection of a glass cantilever spring as a piezo actuator moves a 5 mm glass flat punch into and away from the test surface. The interaction forces are calculated by relating the stiffness and deflection of the cantilever upon contact with the surface.

Figure VIII-4 - Adhesion results showing the on/off behavior of the structures without and with an applied magnetic field, respectively. The insets represent actual adhesion data, where in the ‘ON’ state distinctive pull-off events were observed (top) and in the ‘OFF’ state no pull-off events were observed (bottom). Strength values were obtained by dividing the interaction force by the contact area of the paddles. In the ‘ON’ state, the devices showed an initial increase in adhesion with preload force, characteristic of increased surface contact with applied load (likely a result of slight misalignment between
the 5 mm flat punch and test surface). Error bars represent 10 data sets at a specified displacement with no emission of outliers.
IX. Concluding Remarks and Future Work

In this thesis, novel fabrication strategies have been presented and implemented to create a bio-inspired adhesive system. Characterization techniques developed to qualify the biomimetic structures, indicate that the hierarchical system found in nature may serve two purposes. One, the hierarchical structure enhances surface compliance, increasing the surface contact area, and subsequently increasing adhesion. Second, the hierarchical structure may be necessary for a detachment mechanism.

In the first instance, a hierarchical system (nanostructures atop microstructures) was shown to enhance adhesion, over a one component system (nanostructures or microstructures). This enhancement is attributed to the microstructures bending to allow for more surface contact, while the nanostructures provided the short range interactions necessary for adhesion. In addition, the platforms, when bent, change the orientation of the pull-off force, translating some of the normal pull-off force into a shear frictional force.

While the dry sticking properties of these biological systems are of great interest, it is the combination of sticking and unsticking that may provide the greatest technological impact. Here again it was shown that mimicking the hierarchical structure of gecko is beneficial. To illustrate this point, compare the force required to separate two blocks, with a piece of double sided Scotch™ tape between them; with the force required to peel a piece of tape off of a flat surface. Clearly peeling
facilitates the removal of the tape. The peeling action deforms the tape backing, which, for the confines of this discussion, represents another level of hierarchy in that system. In this work, unlike with tape, a surface was created that is controlled to switch adhesive properties. This was accomplished through creating flexible micrometer scale paddles that can undergo a conformational change. The paddles, made of nickel, change orientation when a magnetic field is applied. In the ‘on’ state, the paddles face up, presenting a sticky nanorod surface. In the presence of a magnetic field, the paddles rotate to face to the side, presenting a single thin edge. The adhesion change was found to be some 40 fold. While this is not the exact mechanism of the gecko, it does demonstrate the use of hierarchy to create a release mechanism.

While a proof of principle has been developed for a reversible adhesive, further work will need to be done to create a working prototype. Future work will need to focus on extending the underlying design principles presented here. While this work has rapidly developed a new research area, there is now much work to be done to optimize individual components of the system and intelligently integrate them into an overall system.

The obvious place to start optimizing is at the beginning, in this case that would be where the adhesive first makes contact – the nanorods. While the nanorods are the right overall length and width, have an ideal modulus (6 GPa compared with 1-15 GPa for the gecko), and are spaced without condensation, refinement of the tip geometry will significantly enhance adhesion. The work of Arzt et al. has shown that tip geometry can play a significant role in the adhesive properties (87). The
gecko, as well as other creatures using this adhesive motif, has flat spatulas at the end of the nanorods. The spatulas are approximately 200 nm in width and 5 nm thick. The ultra-thin spatulas are able to easily deform to the contact surface, making intimate contact and greatly enhancing the van der Waals interactions – remember the attraction scales with the inverse square distance. Further development of the nanorod structure to include flat thin tips will greatly enhance the adhesion of the surface.

Further enhancing the adhesion in the spatulas is the direction of applied force. The gecko achieves maximum adhesion when the pull-off force is at a 30° angle from the setal stalk to the surface. It is at this angle that both the frictional component of adhesion and the normal component are at a maximum (88). The prior is due to optimum combination of applied normal load maximizing the frictional component, and the latter due to a compressive force at the base of the spatula arresting crack initiation. The important lesson is that the appropriate force must be applied to the macro structure to cause the microstructure to exert the optimum force on the nanostructure. This will require a systems engineering approach to design microstructures capable of transmitting loads intelligently to the nanostructures. Preliminary work has been done to create 3-dimensional microstructures with built in curvature, Figs. IX-1. When the structures are contacted, the load causes the structures to bend, creating a pre-stress similar to the pre-loaded setae in the gecko. This pre-stress induces a resolved lateral force as well as a normal force. While the gecko uses a squeezing action to enhance adhesion through the incorporation of a frictional force, these structures now induce a frictional force, passively and at the
microscale. In figure IX-1 two sets of opposing paddles bend towards each other. In this configuration, when a surface makes contact with the paddles, the paddles will bend down and away from each other—creating a component of lateral force between the surface and the paddle face.
Figure IX-1 Electron micrographs of a double paddle configuration. The paddles are bending out of the base plane. By opposing each other the two
paddles create a squeezing action, transforming a pure normal force into a combined normal and lateral force, enhancing a frictional component.

While the paddles presented in figure IX-1 induce a lateral force component and should aid in adhesion, they clearly are not an optimized surface for adhesion. To maximize adhesion, the contact area between two surfaces should be maximized. In the case of the hierarchical structures this requires increasing the active area of the adhesive, the presented nanorod coated surface. While in chapter VIII a reversible adhesive was presented, the overall adhesion strength is quite low. The primary method of improving this adhesion is to create structures with a greater contact area. Again, with the lithographic processing employed here, this should be no problem. It is simply a matter of better designing an optimal microstructure to increase contact area. In figure IX-2 an example of this presented. Instead of having a long beam supporting a single paddle, a thin beam extends with paddles radiating along the length. In this manner, the beam maintains its flexibility while the presented contact area is increased. While two opposing paddles produce a bilateral squeezing force, more complex shapes may produce alternative adhesion forces. Again using the robustness of photolithography creative designs may be implemented to further enhance adhesion, Fig. IX-3.
Figure IX-2  Electron micrograph of a branched fingers bending out of plane. The branch fingers enhance the beams bending while providing surface area for adhesion.

There may be many other approaches to improving adhesion. These approaches will be enabled through the extension of a simple and robust fabrication process. The process based on photolithography will enable improved design of the microstructure. At the same time additional processing steps may be added to incorporate new levels of sophistication. One obvious place for the next level of innovation is creating the next level of hierarchy, moving from the micro-scale to the milli-scale. This will be the last gap to close between the state of art in robotics and this new class of bio-inspired adhesives.
Figure IX-3  Electron micrographs of eight fingered branched platform structures coated with aligned vertical nanorods. The fingers are bending up out of the plane of the center support. Scale bars, in descending order, of 20, 100, 200 and 1000 μm.
X. References


137
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Appendix

A.1 Micromechanical Nanoindenter Testing

To qualify the micromechanical testing used in this work, initial tests were performed on more standard MEMS shapes. Though not immediately applicable to this project, the work described in this section was one of the first explorations of the use of nanoindentation instrumentation for the characterization of micromechanical structures and has not been published elsewhere. Tested were a fixed-fixed cantilever, a fixed-free cantilever and in-plane resonator.

Operating in load control, a desired load function was programmed, Fig. A-1, for a 5 μm 60° conical indenter tip to deflect the center portion of a fixed-fixed beam,
Fig. A-2. The beam deflected a maximum of 525 nm, with a force of just over 11 μm. To extract a more accurate spring force the data was fit with a linear curve fit to determine a spring constant of 20.9 N/m.

Figure A-1 A typical load-control function showing the ramp rate of the load.
Figure A-2 Schematic of a nanoindenter tip pressing against the center portion of a fixed-fixed beam (top). A load vs. deflection curve for the indenting tip, the slope of the line represents the spring constant of the beam (bottom).

This spring constant value can be compared with an analytical calculation of the beam. Using standard beam theory the applied normal force can be related to the deflection, and relating the two the spring constant is obtained.

\[
K_{TH} = \frac{P}{\delta} = \frac{192EI}{L^3} = \frac{16Et^3b}{L^3} \quad (A.1)
\]

Where \( P \) is the load, \( \delta \) is the deflection, \( K_{TH} \) is the spring constant, and \( L \) is the length. \( I \) is the moment of inertia about the bending axis described in terms of
thickness, t, and width, b. Estimated values can then be taken to be t = 2\( \mu \)m, b = 5\( \mu \)m, E = 150 GPa, and L = 150 \( \mu \)m. This gives an estimated spring constant of 28.4 N/m. While in the nanoindenter experiment a value of 20.9 N/m was obtained.

Several factors may effect the analytical approximation. The beam may have slightly different geometries due to microfabrication error. The material properties of the polysilicon beam may vary from those used. And likely the largest contribution may be from the boundary conditions on the actual beam. The analytical model assumes fixed conditions, while the actual structure may have a less-fixed make-up due to undercutting of the supports during microfabrication (this issue will be discussed momentarily).

To make another empirical comparison a laser Doppler vibrometer was used to measure the frequency response of the beam. The idea was then that the resonance value could be compared with an analytical value to see if the error corresponds to that of the nanoindenter. Using the vibrometer the resonance was found to be 650 kHz. While the resonance of the ideal beam can be calculated by:

\[
\frac{1}{2\pi} \sqrt{\frac{K_{TH}}{m_{eff}}} = \frac{1}{2\pi} \sqrt{\frac{K_{TH}}{\rho V(0.23)}}
\] (A.2)

Calculating the volume using the length, width and thickness, the theoretical resonance is found to be 947 Hz. Comparing this with the experimental value a deviation of a factor of 1.46 is found. Whereas the square root deviation (frequency
is related to the square root of the spring constant) between calculated spring constant and that of the nanoindenter experiment gives a factor of 1.17 difference.

While this experiment gives far from conclusive evidence of the accuracy of the two test techniques, it does give some initial proof of principle of the nanoindentation measurement technique.

Similar to the above experiment a test was performed on a fixed-free cantilever. The cantilever was placed in the nanoindenter and the end of the cantilever displaced by the indenter tip. Again monitoring the force versus displacement it was possible to determine the spring constant of the beam, Fig. A-3. Unfortunately the flexible nature of the cantilever eluded the sensitivity of the indenter. While the spring constant was estimated to be 1.5 N/m this cannot be stated conclusively.
Figure A-3  Indentation schematic of a nanoindenter tip pressing against the end of a cantilever (top). Nanoindenter force versus displacement data for a typical experiment (bottom). Note the large amount of scatter in the data corresponding to the sensitivity limit of the tool.

As a fix to this problem the experiment was repeated, however this time the indenter tip was pressed into the middle of the beam instead of the end, Fig. A-4. This effectively increased the stiffness of the beam by a factor of 8 and moved the spring constant within the sensitivity of the instrumentation, Fig. A-4. Using this data a spring constant of 7.3 N/m was determined. Dividing by a factor of eight the spring constant of the entire beam can be estimated to be 0.9 N/m.
Figure A-4 Schematic of the indentation of the central portion of the beam (top). Nanoindenter data of the force versus displacement for the mid-beam
indent (bottom), the slope of the curve yields a spring constant of 7.3 N/m for the halfway point of the beam.

To give a more accurate spring constant and resonant frequency prediction a model was constructed in ANSYS, Fig. A-5. This model predicts a spring constant of 1.3 N/m and a resonance at 68.3 kHz. Again using a laser vibrometer the resonance of the structure was measured to be 50.8 kHz. Comparing the empirical values with the finite element model values the resonance varies by a factor of 1.3, while the square root of the spring constant varies by a factor of 1.2. Thus using the nanoindenter it is possible to corroborate data taken using the laser vibrometer.
Figure A-5 Finite element model of a cantilever made in Ansys. Note the quasi fixed boundary condition where the undercutting of the beam support has been taken into account.

Having qualified this test methodology on simple structures where it was simple to build an analytical or numerical model, the characterization technique was then extended to more complex structures. For application to the platform pillar structures highlighted in this work please refer to the paper *Single High Aspect Ratio Pillar Support Structures* in chapter IV.

An even more complex structure used as a high sensitivity mass sensor. The sensor makes use of parametric resonance to detect small changes in the resonance
frequency, which can then be related to a mass shift. The device is explained in
great detail in ref (89). Thorough characterization of the device was desirable and
measurements of the spring constant out-of-plane and in-plane were made. The in-
plane measurement was the first of its kind. The device consists of a backbone
connected to two springs at either end of the device, Fig. A-6. In the middle portion
of the device along the backbone there are a series of non-interdigitated comb
fingers. Using the scanning probe microscopy of the nanoindenter high resolution
images of these fingers can be taken, Fig. A-6. These images also allow for exact
placement of the nanoindenter tip, a nice feature of using the actual tip for imaging.

Figure A-6  Optical image of the non-interdigitated comb drive oscillator
obtained in the nanoindenter (left). Scanning probe image (SPM) obtained
using the 5 \( \mu \)m cone tip in the nanoindenter imaging the non-interdigitated portion of the comb fingers (right).

The out-of-plane mode of flexure was tested by placing the indenter tip on the backbone of the structure and performing a load-controlled indent. Interpreting the slope of the indent to be the spring constant of the structure a value of 12.5 N/m was determined. Given this particular device’s primary operation mode, the in-plane spring constant of the structure was of particular interest. To ascertain this another functionality of the nanoindenter was explored.

Originally designed for scratch testing, making a lateral movement of the tip with a constant normal load, the nanoindenter is equipped with a 2-dimensional transducer able to move and sense in the orthogonal and transverse directions. Making use of the transverse translocation feature lateral spring constant measurements were performed.

Instead of placing the indenter tip on the backbone of the structure the tip was placed within in a slot of the backbone. A desired load function must then be supplied to the transducer. This load function must include both a normal load component and a lateral displacement component, Fig. A-7. The normal load is typically held constant while a lateral displacement is applied to the tip.
Figure A- 7  Typical load function for performing a lateral compliance test.
The normal load is ramped to a specified value (top) to then remain constant while a lateral displacement is applied (bottom).

While the transducer is applying a normal load and moving transversely, the normal displacement and transverse load is monitored. The outputted data then contains all four of these data sets plotted against time, Fig A-8. In order to determine the lateral spring constant of the device the slope of the lateral load versus displacement can be determined. Here care must be taken to only analyze the lateral data while the normal load and displacement is constant. As can be seen in figure A-8, the normal load and displacement rises and drops with a periodicity corresponding
to the spacing of the backbone of the device, thus adding another force component as the tip rises. While the normal force is constant there is only the lateral force component. Relating this lateral force to the lateral displacement, over the constant force region, a spring constant of 9 N/m was determined for the device.

Figure A- 8 Outputted data versus time for a typical lateral force test:
Normal force (top-left), (top-right) Normal displacement, (bottom-left) Lateral force, (bottom-right) Lateral displacement. The slope of the lateral force versus lateral displacement for the constant normal force section was taken to be the lateral spring constant of the device.