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Self-Cleaning Synthetic Adhesive Surfaces Mimicking Tokay Geckos

Eric D. Branson, Seema Singh, Patrick Johnson, D. Bruce Burckel, Hongyou Fan, Jack E. Houston, and C. Jeffrey Brinker

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Albuquerque, New Mexico 87185

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Eric D. Branson[a], Seema Singh[a], Patrick Johnson[a], D. Bruce Burckel[a], Hongyou Fan[a,d], Jack E. Houston[b], C. Jeffrey Brinker[c,d]

[a]Ceramic Processing and Inorganic Materials Department, Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185-1349

[b]Surface and Interface Sciences Department, Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185-1415

[c]Self-Assembled Materials Department, Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185-1349

[d]Chemical & Nuclear Engineering Department, Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87106

ABSTRACT

A gecko's extraordinary ability to suspend itself from walls and ceilings of varied surface roughness has interested humans for hundreds of years. Many theories and possible explanations describing this phenomenon have been proposed including sticky secretions, microsuckers, and electrostatic forces; however, today it is widely accepted that van der Waals forces play the most important role in this type of dry adhesion. Inarguably, the vital feature that allows a gecko's suspension is the presence of billions

of tiny hairs on the pad of its foot called spatula. These features are small enough to reach within van der Waals distances of any surface (spatula radius ~100 nm); thus, the combined effect of billions of van der Waals interactions is more than sufficient to hold a gecko's weight to surfaces such as smooth ceilings or wet glass.

Two lithographic approaches were used to make hierarchal structures with dimensions similar to the gecko foot dimensions noted above. One approach combined photo-lithography with soft lithography (micro-molding). In this fabrication scheme the fiber feature size, defined by the alumina micromold was 0.2 µm in diameter and 60 µm in height. The second approach followed more conventional photolithography-based patterning. Patterned features with dimensions ~0.3 mm in diameter by 0.5 mm tall were produced. We used interfacial force microscopy employing a parabolic diamond tip with a diameter of 200 nm to measure the surface adhesion of these structures. The measured adhesive forces ranged from 0.3 µN - 0.6 µN, yielding an average bonding stress between 50 N/cm^2 to 100 N/cm^2. By comparison the reported literature value for the average stress of a Tokay gecko foot is 10 N/cm^2.

Acknowledgements

This work was funded by Sandia National Laboratory's Laboratory Directed Research & Development program (LDRD). All coating processes were conducted in the cleanroom facility located at the University of New Mexico's Center for High Technology Materials (CHTM). SEM images were performed at UNM's Center for Micro-Engineering on equipment funded by a NSF New Mexico EPSCoR grant.

Contents

List of Figures

Introduction

Close examination of a gecko foot reveals a remarkable hierarchy of structures (see Figure 1). At the coarsest scale (mm) we see lamellar-like features oriented perpendicular to the direction of motion. The lamellae are composed of arrays of setae, rod-like structures (100 µm long x 4 µm in diameter) that each branch into ~1000 finer fibers (10 µm long x 0.1 µm in diameter), terminating in leaf-like plates called spatula[1]. This design presumably makes the lizard adhesive system elastically compliant/adaptive over the range of length scales needed for locomotion/adhesion on surfaces with varying roughness and surface chemistry. Also, this hierarchical design allows for rapid release that occurs by a successive peeling process. Constructed of beta-keratin, the gecko foot can adhere to both hydrophilic and hydrophobic surfaces varying from rough to smooth. The maximum adhesive force (~450 Newtons) greatly exceeds the necessary force requirements, providing an ample safety margin and allowing the gecko to hang easily from one foot.

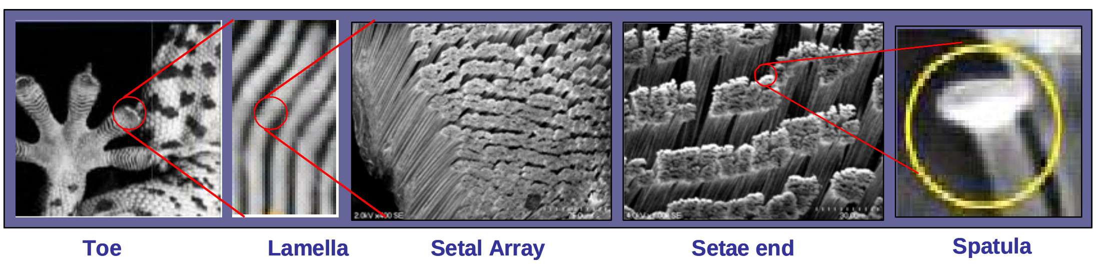

Figure 1 Hierarchical structure of Tokay Gecko feet

A major activity of this project was to devise processing strategies to develop hierarchical surfaces with systematically varying structural features. A second major activity was to quantify adhesive behavior and develop relationships between structure and adhesion. Interfacial force microscopy (IFM) was used to generate force-displacement profiles. The IFM utilizes a unique self-balancing capacitance force sensor. It incorporates force-feedback control to rebalance the sensor thus eliminating the instability encountered in traditional atomic force microscopes. The result is that the probe can be brought into near contact and through contact, providing unambiguous measurements of the attractive and contact forces through this entire range of interrogation[1]. Employing materials fabricated with a wide range of fiber feature sizes, we attempted to establish the relationship between feature size and pull-off force for this new class of synthetic materials.

The evolved aspect ratios present in the gecko foot, 25:1 for setae features and 100:1 for finer fibers, are not attainable by traditional photo-lithographic techniques. The initial approach we took to this problem combined photo-lithography with soft lithography (micro-molding) to create surfaces with systematically varying dimensions, spacings, and aerial densities of both rod-like and fiber-like features, see schematic in Figure 2.

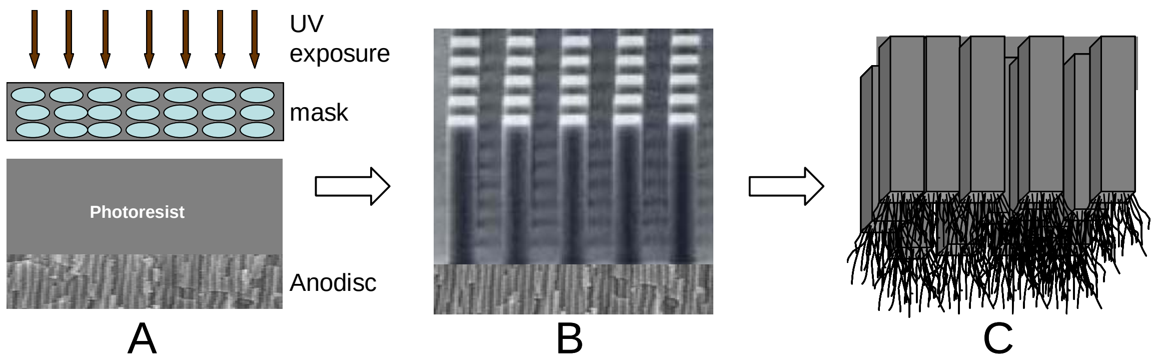

Figure 2 Scheme for fabrication of hierarchical structure A) photolithography of SU-8 coating deposited on and within porous alumina micromold B) platform after UV irradiation & etching, C) after alumina dissolution, showing micro/nano hierarchy

The fabrication process used anodic alumina membranes as micro-molds to define the smaller scale features of the fibers and photo-lithography to define the coarser scale features, corresponding to the rods. We used Whatman® Anodisc inorganic membranes as the mold for the smaller feature sizes. The anodisc provided us with three nominal pore sizes (0.02 µm, 0.1 µm, and 0.2 µm) with an overall thickness of ~60 µm. Initial studies demonstrated that a sodium hydroxide (NaOH) solution was the best option for anodisc removal. This process requirement dictated the type of photoresist to use in the photo-lithography process. Also, since most developers used in photo-lithography are a basic solution, we needed a photoresist that possessed robust chemical properties to withstand the NaOH etching process and not develop away. Furthermore, the aspect ratio requirements for the hierarchical features necessitated using a photoresist with optimal mechanical properties. Due to these combined constraints, we chose to use MicroChem's® Nano SU-8 2000 negative tone photo-resist.

The standard coating process for SU-8 photo-resists consists of the following steps: spin coat, soft bake, expose, post exposure bake, and develop, and is sometimes followed by a hard bake for further cross-linking. The anodisc was placed on the substrate after a fixed period of spin coating to allow the partially solvated SU-8 to wick-up into the membrane by capillary filling producing the smaller feature sizes.

Experimental

Several one inch square silicon substrates were cleaned with Alconox™, rinsed with deionized (DI) water, dried, and plasma cleaned for ten minutes before use. SU-8 was deposited on the substrates and spun at 3,000 rpm. After spinning for a fixed period of time, the anodisc was placed in contact with the SU8. The spinning time was systematically varied in an attempt to control the height of the SU-8 wicking up through the anodisc. Five seconds was found to be the optimal time for complete filling of the anodisc. The samples (substrate + SU8 + anodisc) were then taken through a soft bake step at 90ºC for three minutes. Exposures were done at 365 nm on a Karl Suss mask aligner for 30 seconds through a mask using grid size features of 0.25 mm squares. The post exposure bake step was performed for two minutes at 90ºC. Finally, the samples were developed using a propylene glycol monomethyl ether acetate (PGMEA) solution. The samples then were placed in a 6N NaOH solution and sonicated for ten minutes to remove the anodisc.

Samples where the spin coater was stopped/anodisc dropped in less than five seconds after reaching 3,000 rpm had a skin of photoresist that had developed over the top of the anodisc. This skin prevented NaOH etching of the anodisc mold due to excess wicking of the SU-8. The samples where the anodisc was dropped more than five seconds after reaching 3,000 rpm did not possess this skin and the anodisc was completely etched away. Unfortunately the SU-8 under the anodisc was also completely etched away. This presented two different problems: 1) adhesion issues between the SU-8 and the substrate under the anodisc and 2) a skin layer that needed removal. To remedy the first problem we needed to ensure complete substrate surface dehydration before coating. To do this the substrates were subjected to a piranha etch (two parts sulfuric acid with one part hydrogen peroxide) for five minutes, rinsed with deionized water and dried. They were then heated to 200ºC for fifteen minutes, cooled, spin coated with HMDS (hexamethyldisilazane) at 3,000 rpm, and reheated to 200ºC for 5 minutes. When the substrates had completely cooled they were coated with SU-8 immediately.   Adhesion to the silicon substrate was greatly improved.

The skin layer was far more difficult to overcome, see Figure 3a,b. Three different strategies were investigated to surmount this problem. The first approach was to polish off the skin layer by using 30µm size diamond lapping paste, see Figure 3c,d.

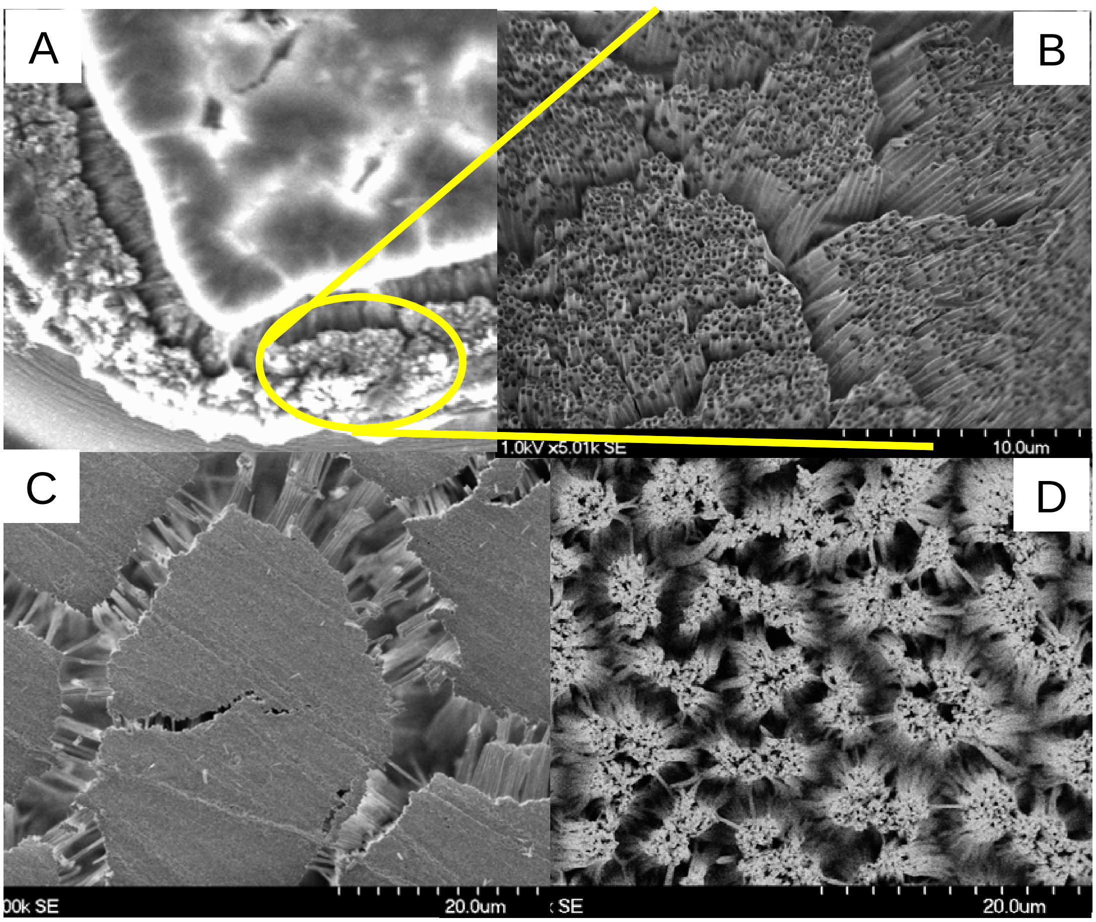

Figure 3: SEM images of synthetic Gecko-like microstructures made by combined photo- and soft-lithography (see Fig 2) A) low magnification image showing small areas of hair-like features on the edge of the patterned 0.25mm squares. B) 5K X magnification of yellow circular region of A showing actual synthetic hairs - 0.2µm in diameter and ~60µm in height C) 2.5K X magnification showing skin layer on top of synthetic hairs after polishing D) 2.5K X magnification showing a small area where the excess SU-8 was polished away leaving hair like features that were clumped together.

The second strategy was to use the PGMEA developer during the coating process to remove the excess SU-8 that had wicked completely through the anodisc. For this method, the substrates were coated with SU-8, spun to 3,000 rpm and stopped after five seconds; the anodisc was then dropped. At this point we re-spun the samples to 3,000 rpm while dropping some of the developer on top of the anodisc in an attempt to wash away the excess SU-8 that resided on top of the anodisc. These two strategies reduced the skin layer but could not eradicate the problem.

A third strategy was investigated briefly and employed a Branson/IPC 8000 Series plasma cleaner in an oxygenated environment at 500W. This ended up being an all or nothing process: either the SU-8 was not touched, or it was removed from throughout the entire sample, and the anodisc fell off.

Due to the irreproducibility issues associated with the skin layer, we developed a second overall approach to achieve gecko-like features. This approach followed more conventional photolithography-based patterning. Initial experiments entailed interferometric lithography to pattern a photoresist coated glass substrate. Standard metal liftoff was performed resulting in a chrome coated mask with arrays of ~0.3 micrometer holes on a ~1.0 micrometer spatial period. These masks were used in two separate schemes: 1) SU-8 resist was spun directly on the glass substrate/mask and exposed from the backside, such that the resist over the hole was exposed and remained upon post exposure bake and develop, 2) the mask was used as a typical contact printing mask to pattern other samples with photoresist. In both cases, patterned features with dimensions ~0.3 mm in diameter by 0.5 mm tall were produced, see Figure 4. The feature height is a function of the resist thickness upon spin, while the diameter is controlled by the mask dimensions.

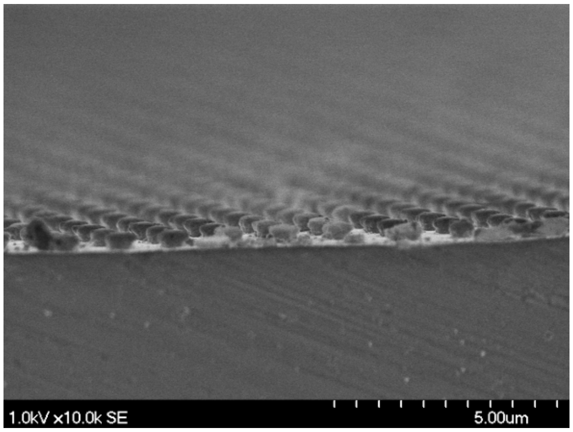

Figure 4: SEM at 10K X magnification showing arrays of features ~0.3µm x 0.5µm made using standard photolithography.

We used IFM to measure surface adhesion on both advancing and retracting surfaces, using a diamond tip with a diameter of 200 nm, see Figure 5. The measured adhesive forces ranged from 0.2 µN (for the photolithography process) - 0.6 µN (for the micromolding process), yielding an average bonding stress between 20 N/cm^2 to 100 N/cm^2. The reported literature value for the average pull off stress of a Tokay gecko foot is 10 N/cm^2, meaning that these artificial constructs are promising for development of dry adhesive systems.

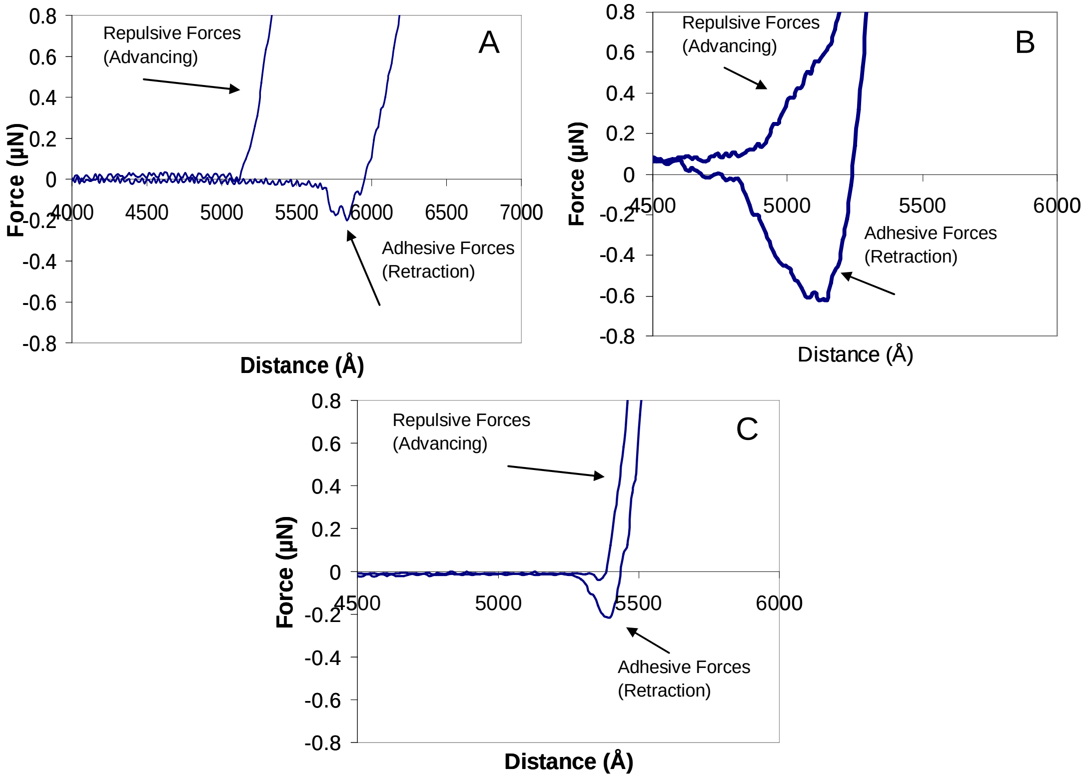

Figure 5. Force profiles of A) skin layer atop hairs B) hairs made by micromolding process, observed attractive forces of 0.6µN. C) hairs made by photolithography process, average attractive force of 0.21µN. All profiles having the same area of 1.0×10^{-9}cm^2 upon pull-off. For the x-axis, zero Å is located an arbitrary distance from the sample surface (~4600Å in this case)

Conclusions

We developed characterization tools, processing skills, and fabrication techniques that led to the development of novel nanostructures with potential to achieve reversible adhesion and high strength to surface area ratios. We were able to fabricate a hierarchical structure using a combination of lithography and micromolding techniques to demonstrate novel structures that may satisfy these demands. The IFM was shown to be a very effective tool for initial quantitative measurements of surface adhesion.

For future research, we would like to avoid the skin layer associated with micromolding, vary the aspect ratio of our nanostructures and decrease the clumping effects characteristic of our nanohairs. By varying the aspect ratios, we will be able to develop relationships between structure and adhesion. Furthermore, we would attempt to fabricate our hairs using materials more biologically similar to Keratin, the biological makeup of natural gecko foot hairs.

References

1. K. Autumn, Y.A. Liang, S.T. Hsieh, W. Zesch, W.P. Chan, T.W. Kenny, R. Fearing, RJ. Full; Nature, 405, p.681, 2000.

2. S.A. Joyce and J.E. Houston, Rev. Sci. Instrum. 62(3) p.710 (1991).

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