Processing PDMS Gecko Tape Using Isopore Filters and Silicon Wafer Templates

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Approval Page

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Abstract

Processing PDMS Gecko Tape Using Isopore Filters and Silicon Wafer Templates

By: Boris Luu

Gecko tape was processed through nanomolding involving two types of templates. One template was a Millapore Isopore polycarbonate membrane filter and the other template was an n-type silicon wafer processed to include four different pore diameters. These pore diameters were 20, 40, 80, and 160 microns. AutoCAD was used to design to a mask to be used later during photolithography. Two n-type wafers were sputtered with aluminum, underwent photolithography, and then etched using reactive ion etching. A template was placed into a Petri dish and Sylgard 184 polydimethylsiloxane (PDMS) was poured on the template. Once the PDMS cured, the 1 mm slab of PDMS gecko tape was sliced into 20 mm x 20 mm samples. Micrographs of the gecko tape processed using the Isopore filters revealed hairs that were 5 µm in diameter and 20 µm in height. The hairs were also dispersed, and sporadically oriented; some hairs being erected but most were lying down. Using a thinner Isopore filter will produce PDMS gecko tape with micro-hairs that will stand straight up. About 99% of the micro-hairs of the gecko tape processed using the silicon wafer templates failed to peel out of the pores. The possible causes for the failed peel out were thermal mechanical lock between the PDMS micro-hairs and silicon pores, incorrect application of mold release agent, and the mold release agent, Jerseycote, did not provide an adequate release layer. Improvements on fabricating gecko tape using silicon wafers include freezing PDMS before peeling it off, spin coating the mold release agent, and using SU-8 negative resist to fabricate the pores.

Key words: Materials engineering, gecko adhesion, gecko tape, synthetic setae, PDMS pillars, nanomolding, Isopore filters, silicon wafer templates, biomimicry

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1. Introduction

1.1 Problem Statement

Fabricate a dry adhesive tape containing synthetic gecko feet micro-hairs that adheres to glass by shear at Cal Poly San Luis Obispo, and compare the two different processes used to make them. Once a reliable process is found for fabricating and reproducing “gecko tape,” conduct experiments to observe the effects of hair diameter and hair density on the shear adhesion strength of the gecko tape.

1.2 Theoretical Framework

Real geckos can cling to almost any type of surface using millions of microscopic hair like structures called setae. Each seta branches off into 1000’s of nanoscopic hairs called spatulas. The hierarchical structure gives the gecko’s toes a tremendous surface area, which enables intimate contact with a surface’s topography allowing for huge amounts of Van der Waals interactions to form (Figure 1). All of the Van der Waals interactions add up and generates an adhesive force that enables geckos to cling to surfaces. One toe of a Tokay gecko is able to support eight times the gecko’s weight on glass.

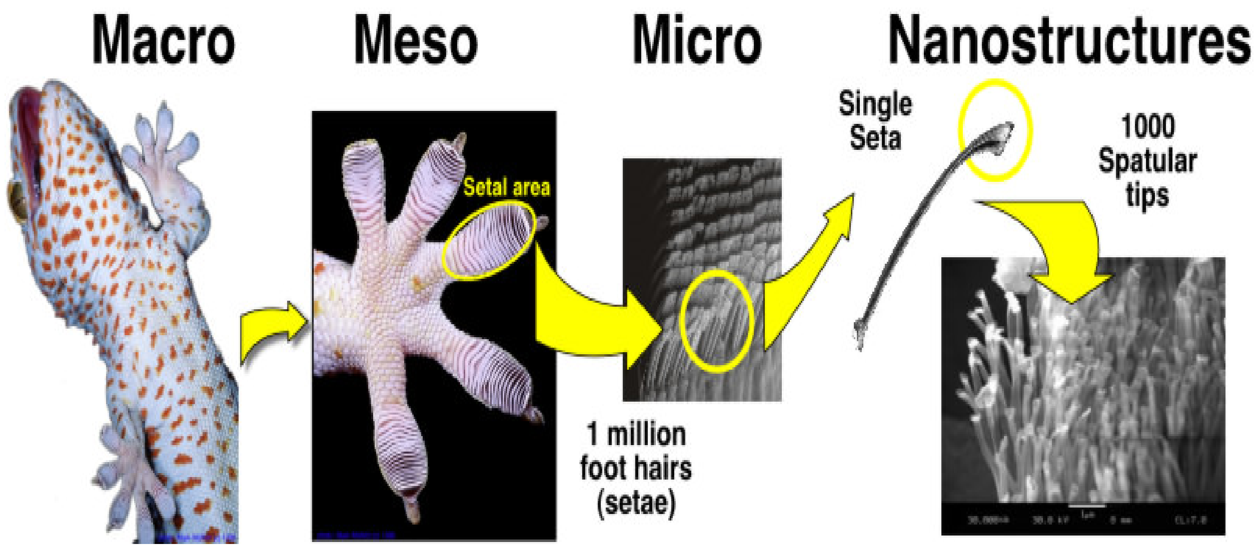


Figure 1: The hierarchical structure of the Tokay gecko’s foot is made apparent as it is scaled down from macroscopic scale to the nanoscopic scale[1].

1.3 Broader Impacts

This project could be made into a lab to help teach people about nanotechnology because generally people believe nanotechnology to be something futuristic and fictional. It could possibly influence students ranging from elementary to undergraduate college level to pursue materials engineering and a career in nanotechnology. The project could help inspire biomedical students and appeal to students working in robotics and lead to innovations in the medical field and robotics. One application in the works

is a new type of bandage that can replace sutures and stables in surgery. A problem that arises through the use of sutures and stable is necrosis caused by tissue damage from puncturing the tissue. A biomedical tape using gecko adhesion would eliminate that problem by attaching tissue together without the need of puncturing it[2]. Another biomedical application of gecko adhesion are drug eluting patches. Applied to robotics, it can let robots scale walls and aid robots used to scan the terrain of different environments such as on other planets[3].

1.4 Stakeholders

Stakeholders with interest in the project include Dr. Chen, Dr. Savage, and Cal Poly's Materials Engineering department. Also future engineering students are stakeholders because this project can be furthered researched at Cal Poly and possibly lead into new senior projects (biomedical, materials).

1.5 Background

One of the leading researchers on synthetic gecko feet microstructures is Professor Fearing of UC Berkeley. This project is based on Professor Fearing's early work with fabricating gecko tape. In one of his paper on fabrication of synthetic gecko feet microstructures, two fabrication techniques were identified. One technique used an atomic force microscope (AFM) to indent a wax surface that would be used as a mold to cast a polymer into gecko tape. A second technique used an Isopore membrane as a template to cast the gecko tape. "Long" synthetic microscopic and nanoscopic hairs were found to have a self-sticking problem due to hydrophobic attraction, so the hairs would clump up together. Since 2002, many gecko tapes have been fabricated. Many were fabricated by casting polymers such as silicone rubber, polyester, polyamide, polycarbonate, and epoxy in either an anodisc or Isopore membrane filter[4]. The sizes of the synthetic gecko setae ranged from 0.1 µm – 5 µm wide and 2 µm – 60 µm in height[5]. Real gecko setae are about 5 µm wide and made of a protein called beta-keratin[6].

In other publications, PDMS gecko tapes were fabricated using photolithography. A positive or a negative mask was designed with CAD. The general procedure involving the use of the negative mask to fabricate silicon mold involved photolithography of a photoresist spun coated on the surface of a silicon wafer, etching the silicon wafers to produce the molds, coating the molds in fluorocarbon release agent, spin casting PDMS onto the mold, letting it cure and then peeling the cured PDMS off the mold. Sizes of gecko setae fabricated this way ranged from 7 µm - 20 µm wide and 20 µm - 100 µm[7].

Seven benchmark of functional properties of the gecko adhesive system were identified by Autumn (MRS Bulletin 2007). They are anisotropic attachment, high pull-off to preload ratio, low detachment force, material independence / Van der Waals adhesion, self-cleaning, anti-self matting, and non-sticky default state. Anisotropic attachment is adhesion initiated by applying a force parallel to the surface in one direction instead of perpendicular to it. High pull-off to preload ratio is requiring a small force to initiate adhesion while sustaining adhesion under higher loads. Low detachment force is requiring a small

amount of force to release the adhesion. Material independence is adhesion due to Van der Waal forces which is dependent on the geometry of gecko feet microstructure and not due to a specific material property. Reusable adhesion even after use on a dirty surface is self-cleaning. Anti-self matting is non-clumping of gecko feet micro-hair. Non-sticky default state is adhesion only when shear force applied. Professor Fearing and his team of researchers at UC Berkeley have achieved all benchmarks except for self-cleaning. Current research is now going towards achieving self cleaning and surface topography independence.

2. Materials and Processing

2.1 Nanomolding and Polydimethlysiloxane (PDMS)

The process used in creating gecko tape is called nanomolding. In nanomolding, a template containing micro to nano size features is used as a mold to cast an uncured polymer. The features used were micron sized pores that enabled fabrication of the micro-hairs of the gecko tape. Two different templates were used. One template was a 20 μm thick Isopore polycarbonate filter purchased from Millipore which contained 5 μm sized pores. The second template was a silicon wafer template which was processed using photolithography.

Dow Corning Sylgard 184 polydimethylsiloxane (PDMS) was chosen for its viscoelastic ability to conform to surface features precisely. A resin to catalyst ratio of 10:1 was chosen and a total volume of about 18 ml of PDMS was used to produce 1 mm thick samples of gecko tape. PDMS is a silicone elastomer containing a siloxane backbone and methyl groups (Figure 2). It is optically transparent, chemically inert, and biocompatible. PDMS thermal properties include low thermal conductivity and high thermal coefficient of expansion. PDMS has a low surface energy and therefore is hydrophobic and impermeable to water. PDMS is also known to swell temporarily when exposed to organic solvents. PDMS is most commonly used in soft lithography, especially in the fabrication of microfluidic devices.

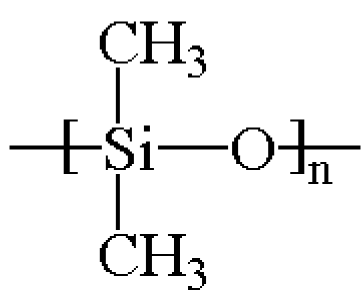


Figure 2: Repeating unit of PDMS, the flexible siloxane backbone combined with methyl groups give PDMS its low surface energy property.

2.2 Silicon Wafer Templates

A 100 mm n-type silicon wafer was patterned and etched to have various sized pores for molding various gecko tapes of different hair diameters. First a mask and a mask design needed to be developed in order to pattern the silicon wafers. Using AutoCAD, a positive mask is designed in order to produce four 20 mm x 20 mm gecko tape samples. Each gecko tape would possess different sized diameter hairs, one 20 μm, one 40 μm, one 80 μm, and one 160 μm (Figure 3). The space between hairs or pitch of the gecko tape was designed to be equal to the diameter of hair, so a gecko tape with 20 μm diameter hairs had a 20 μm pitch.

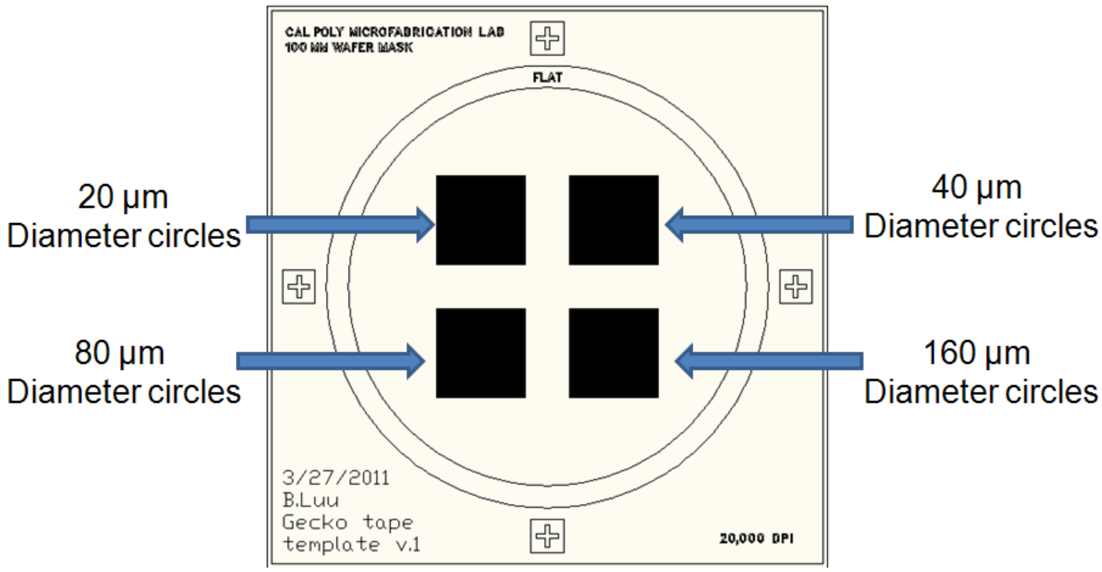


Figure 3: The actual color scheme of the mask is inverted so light only passes through the circles in the four squares.

Two silicon wafers underwent processing in order to produce more samples in one sitting of fabricating gecko tape. Both wafers first underwent pre-sputter cleaning in piranha (sulfuric acid) for 10-15 minutes and in buffed oxide etch (BOE) (hydrofluoric acid) for 2-3 minutes. After a rinse in water and dried with low purity nitrogen, wafers were sputtered using the Torr CrC150 magnetron sputtering system to obtain a 0.2-.03 μm thick aluminum thin film layer. The aluminum layer would be patterned and later act as the physical mask allowing only regions of exposed silicon to be etched.

Using a Laural Spin Coater, 1-2 ml of hexadimethylsilane (HDMS) is first spun coated on the wafers, and then a thin layer of positive photoresist was spun coated onto the wafers. The wafers are placed onto a hotplate at 90℃ to be soft bake for 1 minute and then exposed to UV light from a mercury-arc lamp in the Shipley S1813 aligner. A light integral of 4.7 was found to be adequate in supplying the necessary dose for developing the micron size circles while retaining tolerable resolution (Table I). The wafers are developed in TMAH for 2 minutes only so that the developed circle regions of photoresist are removed and not the aluminum mask. The wafer patterns are inspected under an optical microscope and placed

on a hotplate at 150℃ to be hard bake for 1 minute. The regions of aluminum not covered with photoresist were etched away in Transene type A etchant resulting in circular regions of silicon. The rest of the photoresist is stripped off the wafer using Microposit Remover 1165.

Table I: Measured dimensions of pores of silicon wafer templates

Silicon Wafer Template	Pore diameter (µm)	Actual Pore diameter (µm)	Actual Pitch (µm)	Actual Pore depth (µm)
#1	20	30	10	4.5
	40	55	25	5.4
	80	95	65	5.4
	160	175	145	7.5
#2	20	25	15	5.6
	40	50	30	5.5
	80	90	70	5.6
	160	175	145	5.7

The next step in producing the silicon template was to etch the circular regions of silicon using reactive ion etching (RIE). The wafers were etched for 2 minutes to get around 6 µm deep pores. The depth of the pores was measured using a profilometer. Silicon wafer template #1 showed different depths in the 20 µm diameter and 160 µm diameter pore regions (Table I). The processing the silicon wafer template underwent is illustrated in (Figure 4).

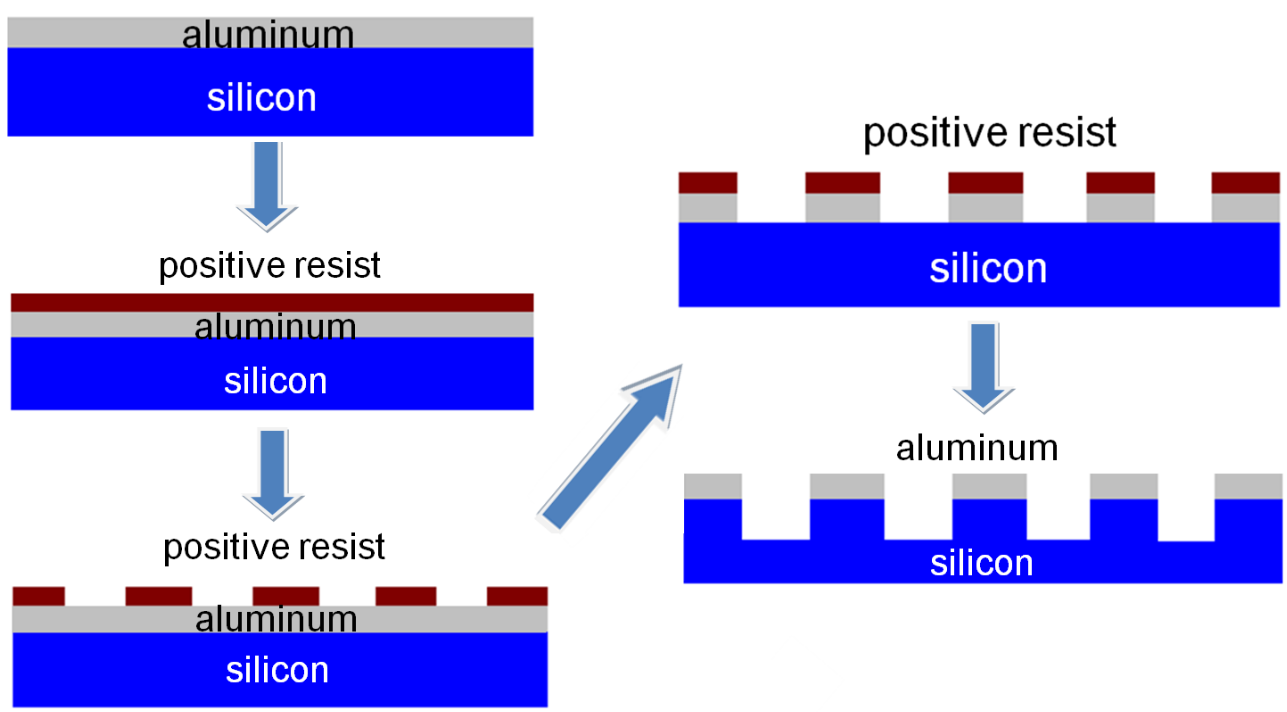


Figure 4: The cross section of the silicon wafer as it is processed to become a template; sputtering aluminum, spin coating the positive photoresist, exposing and developing the photoresist, etching the aluminum, stripping away the photoresist, and finally reactive ion etching the silicon wafer.

2.3 Fabricating Gecko Tape

Making gecko tape with isopore filter

1. Mix 18 ml of Sylgard 184 PDMS in 10:1 resin to catalyst ratio
2. Degas using vacuum chamber until there is no more air bubbles
3. Lay down aluminum foil in 12” diameter petri dish
4. Place clean junk wafer in petri dish
5. Carefully lay down Isopore filter on top silicon wafer
6. Pour PDMS onto center of Isopore filter
7. Cure PDMS in furnace at 70ºC for 1.5 hours
8. Peel PDMS out and cut out eight 20 mm x 20 mm samples with x-acto knife

Making gecko tape with silicon wafer template

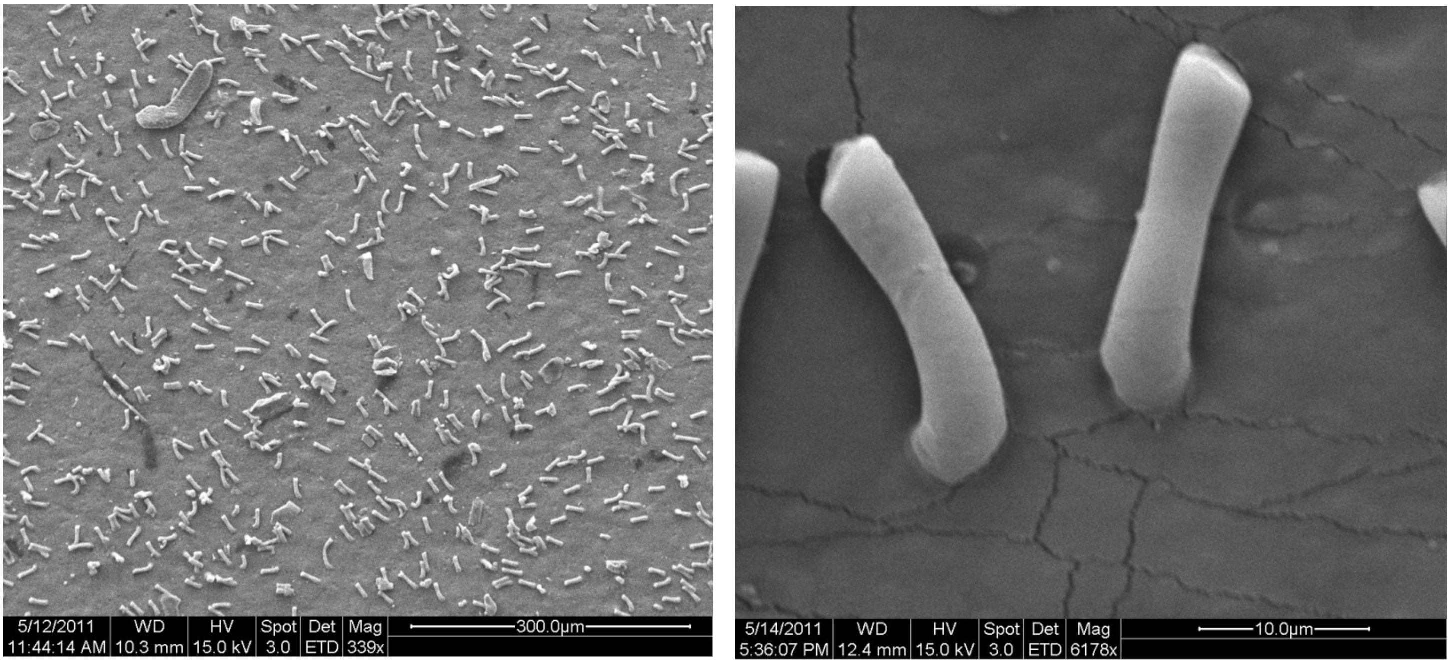
1. Mix 18 ml of Sylgard 184 PDMS in 10:1 resin to catalyst ratio
2. Degas using vacuum chamber until there is no more air bubbles
3. Lay down aluminum foil in 12” diameter petri dish
4. Place silicon wafer template in petri dish
5. Dispense some JerseyCote* onto a paper towel and place over petri dish
6. Place petri dish lid on and wait 2 minutes
7. Take off lid and towel, and Pour PDMS onto center of silicon wafer template
8. Cure PDMS in furnace at 70ºC for 1.5 hours
9. Peel PDMS out and cut out the four 20 mm x 20 mm square with x-acto knife

*Jerseycote is a mold release agent containing isopropanol alcohol and ethanol. The application of Jerseycote in the procedures steps above was to have the vapor of the Jerseycote form a monolayer onto surface the silicon template.

3. Results

3.1 Characterization of Isopore Filter Gecko Tape

The micro-hairs were randomly dispersed and oriented; there was no orderly array (Figure 5A). Majority of the hairs were slanted or prone, and few stood upright. The hairs were characterized to be 5 microns in diameter and 20 microns in diameter and so the aspect ratio is 4 (Figure 5B). Also many hairs were ripped off and remained on the silicon wafer as a thin white residue.

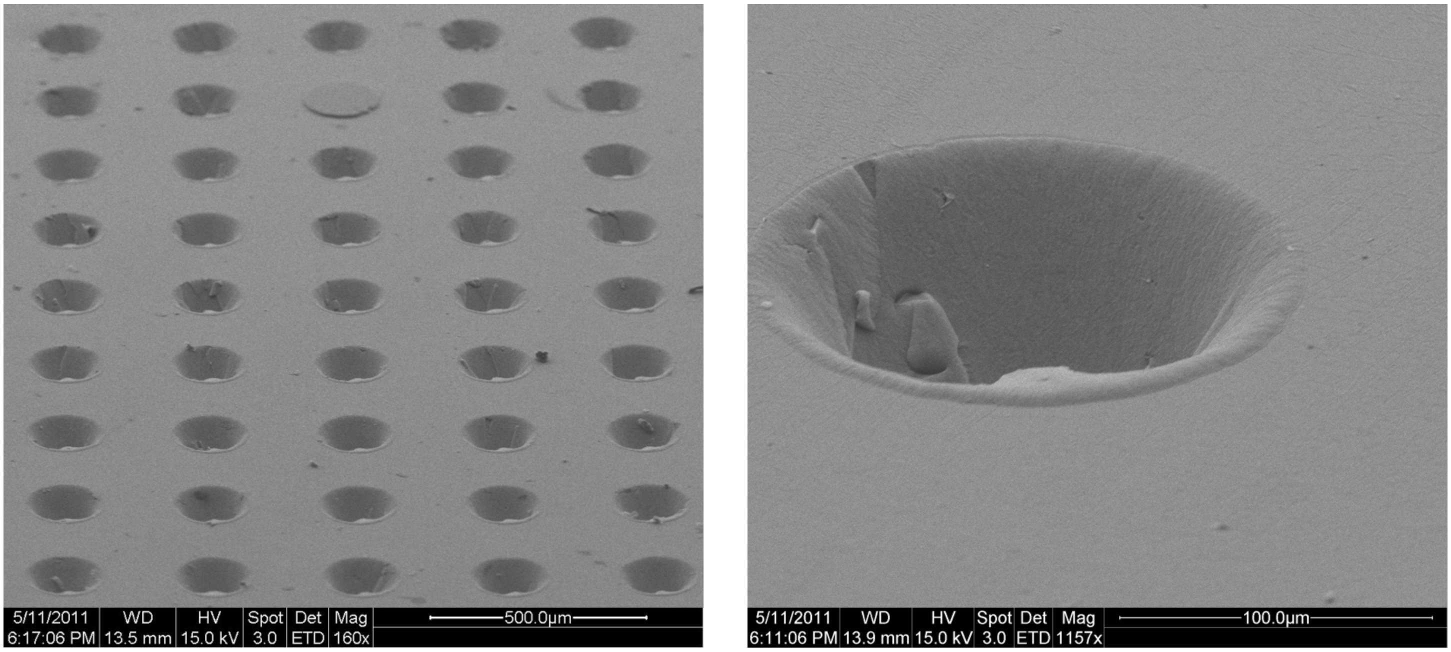


A **B**

Figure 5: A) SEM picture of PDMS micro-hairs processed through nanomolding with isopore filter (339x magnifications) B) Hairs are 5 microns in diameter and 20 microns in height and are laterally collapsed. The cracks are in the gold thin film sputtered on to the gecko tape (6178x magnification).

3.2 Characterization of Silicon Wafer Template Gecko Tape

The vast majority of the hairs were ripped off the tape and remained lodged in the pores of the template (Figure 6A). The hairs did not simply rip in half but up rooted leaving micron sized holes (Figure 6B). This was observed in gecko tapes at all hair diameters. A few hairs peeled out successfully, but the amount was about 1% of the total numbers hairs intended to be produced on a 20 mm x 20 mm area (Figure 7).



A **B**

Figure 6: A) SEM picture of 160 µm diameter hair PDMS gecko tape shows majority of hairs were ripped off (160x magnification). The same type of failure is seen in the 20, 40, and 80 µm diameter hair PDMS gecko tape as well B) SEM picture of 160 micron hole shows micro-hairs were uprooted taking some of the material from the gecko tape (1157x magnification).

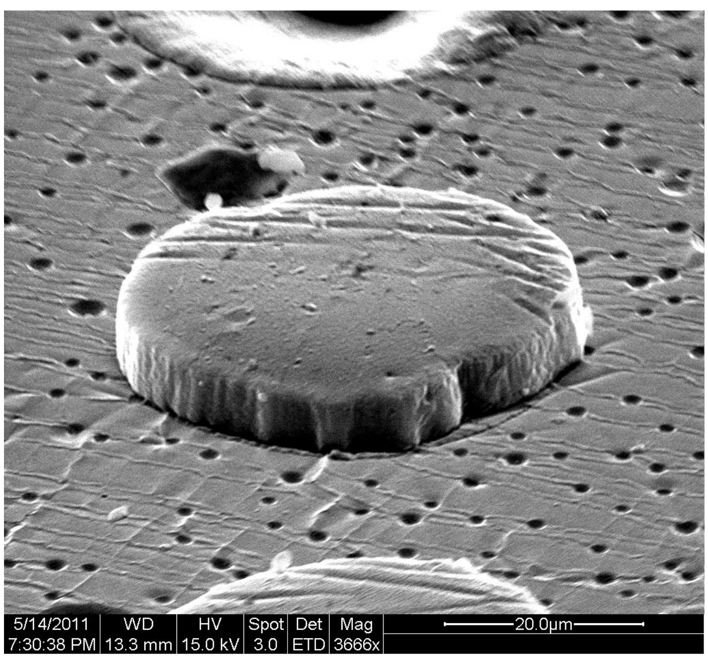


Figure 7: SEM picture of 40 µm PDMS hair that successfully peeled out of silicon wafer pore. The hairs become flatter as the diameter increased.

4. Discussion

4.1 Isopore Filter Gecko Tape

The shear adhesion strength of the gecko tape was weak, evident by its failure to support its own weight during functional testing on glass. The weak adhesion strength may be due to the sporadic orientation and/or the lateral collapse of the micro-hairs. The micro-hairs would not be able to work in unison to provide adhesion if a one way directional shear force is applied because the micro-hairs are sporadically oriented. The lateral collapse of hairs would decrease the amount of hairs able to make contact with the surface and therefore hinder the adhesion strength of the tape. The mechanical properties of PDMS cause micro-hairs with aspect ratios of greater than 3 to laterally collapse and the aspect ratio here was 4[8].

4.2 Silicon Wafer Gecko Tape

The failed peel off of the PDMS micro-hairs from the silicon wafer template could have been caused by a thermal mechanical lock. The PDMS micro-hairs could have expanded enough to the point of pressing up against the pore walls of the silicon template resulting in an increase in friction between the PDMS and silicon. The increase in friction could have caused the force needed to pull the hair out to be greater than the cohesive force of the PDMS, leading the micro-hairs to be lodged in the pores and rip off the PDMS body. PDMS's coefficient of thermal expansion (CTE) is 310 µstrain/K while silicon's CTE is 2.49 µstrain/K, making PDMS's CTE more than 120 times greater than silicon's CTE[9].

Another possible explanation is the adhesion strength between the PDMS hairs and silicon pores was greater than the cohesive force of the PDMS resulting in the failed peel off. In soft lithography, PDMS is known have adhesion issues with the silicon master mold. A mold release agent is often used to silanize the master mold to help the PDMS peel off. A commonly used mold release agent is trichlorosilane, but it is highly dangerous because of its extreme flammability and many health issues associated with its use. The use of the safer mold release agent, Jerseycote, may not have been effective in decreasing the PDMS-silicon adhesion or an ineffective application may have failed to decrease the PDMS-silicon adhesion and ultimately led to the failed peel off of the micro-hairs.

4.3 Improvements on Processing

4.3.1 Using Isopore Filters

The lateral collapse of the mirco-hairs could be mitigated by decreasing the aspect ratio to be below 3. To do so, the height of hairs could be halved by using an Isopore filter that is 10 µm in thickness instead of 20 µm.

4.3.2 Using Silicon Wafer Templates

The thermal mechanical lock problem could be solved by freezing the PDMS gecko tape for a few minutes before peeling it off the silicone template so that the PDMS micro-hairs can shrink and ease the

peel off. Spin coating Jerseycote onto the template or using a dessicator may prove more effective for easier PDMS peel off.

Using SU-8 negative resist in the processing of the silicon wafer templates could make the template processing faster and may be easier for PDMS to peel off. The template would just need to be spun coated with 10-15 μm thick layer of SU-8, exposed to be patterned with circles, and developed to produce the pores. This way eliminates the aluminum sputtering, aluminum etching, stripping off resist, and RIE steps, and make processing of the silicon wafer templates much faster.

5. Conclusions

1. Through the processing of PDMS gecko tape using Isopore filters, majority of micro-hairs collapsed laterally due to possessing an aspect ratio of 4.
2. PDMS gecko tape nanomolded in Isopore filters displayed “weak adhesion” which may be due to random orientation of micro-hairs and/or due to the lateral collapse of most of the micro-hairs.
3. Through the processing of PDMS gecko tape using silicon wafer templates, an estimate of 99% of micro-hairs failed to peel out of template and the possible causes for the failure are
    a. Thermal mechanical lock caused by PDMS’s high CTE and silicon’s low CTE
    b. Ineffective application of mold release agent
    c. Mold release agent failed to ease the adhesion between PDMS and silicon

References

[1] "Biologically Inspired Synthetic Gecko Adhesive ." *Biomimetric Millisytems Lab Department of EECS UC Berkeley*. N.p., n.d. Web. 29 Nov 2010. http://robotics.eecs.berkeley.edu/~ronf/Gecko/index.html

[2] Aleccia, JoNel. "Gecko's sticky secrets inspire new bandages ." *msnbc* n. pag. Web. 29 Nov 2010. http://www.msnbc.msn.com/id/23189028/

[3]"Secrets of the gecko foot help robot climb." *Science Centric* n. pag. Web. 29 Nov 2010.

http://www.sciencecentric.com/news/10082677-secrets-the-gecko-foot-help-robot-climb.html

[4] Sitti, Metin, and Ronald S. Fearing. "Nanomolding Based Fabrication of Synthetic Gecko Foot-Hairs." n. pag. Web. 19 Oct 2010. <citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.126.>

[5] C. Majidi, . "Catalogue of Synthetic Hairs." *Biomimetric Millisystems lab Dept. EECS UC Berkeley*. N.p., 09/02/2004. Web. 19 Oct 2010. http://robotics.eecs.berkeley.edu/~ronf/Gecko/Catalogue/

[6] "Gecko Hair Manufacturing." *NanoRobotics Laboratory*. N.p., n.d. Web. 19 Oct 2010. http://nanolab.me.cmu.edu/projects/geckohair/

[7] Davies, J., S. Haq, T. Hawke, and J.P. Sargent. "A practical approach to the development of a synthetic Gecko tape ." *International Journal Adhesion and Adhesives* 29.4 (2009): 380-390. Web. 29 Nov 2010.

http://www.sciencedirect.com.ezproxy.lib.calpoly.edu/science?

[8] Boesel, L. F., Greiner, C., Arzt, E. and del Campo, A. (2010), Gecko-Inspired Surfaces: A Path to Strong and Reversible Dry Adhesives. Advanced Materials, 22: 2125–2137. doi: 10.1002/adma.200903200

[9] Wang, Wanjun. *Bio-MEMS: technologies and applications*. 137. eBook.