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Flexible Mold for Microstructures Replication

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Space debris has been a growing concern in the space exploration sector. To reduce this issue, biomimicry is utilized to create gecko's feet microstructures that can be attached to a gripper or robotic arm of the service spacecraft. However, the production of such microstructures is difficult and expensive which hinders their implementation. The objective of this research is to develop an advanced fabrication process to mass produce gecko's feet microstructure with soft polymer mold. The possibility of using different coating methods using various coating materials are studied. The process of fabricating mold and replicating mold are studied and improved. The method of mass-producing microstructures is verified and the limitations of the method are also studied.

I. Introduction

The existence of space debris can cause significantly adverse effects on mission planning, cost, time, and general moral of space exploration. Although commercial use of space has been growing rapidly, the growth rate can be considerably reduced if the number of space debris is not diminished in future. Resolving this current and future issue of space debris is important for the next generation of space explorers and to utilize our Earth orbits for humankind. Most of all, many current orbital missions have to account for navigating through space debris [1], which could cause catastrophic damages and mission failures to spacecraft that are already in orbit upon impact [2]. Both space debris impact on spacecraft and safe navigation through those take extreme human resources. This research hopes to bring a solution to these problems.

Gecko inspired dry adhesion has brought much attention from researchers due to its remarkable adhesion on various surfaces [3]. The smallest unit of gecko's foot is setae and it can attach to various types of surface until the force exceeds 200 micronewton (μN) parallel to the surface or 20 μN perpendicular to the surface [4]. There are mainly two designs to imitate the gecko setae, i.e. triangular wedges [5] and mushrooms shape [6] [7]. The triangular wedge design requires preload or unload shear force to attach or detach, but the mushrooms shape only needs external force to detach as the tradeoff for no requirement to attach [8]. For fabrication of the artificial setae, mold casting is the most efficient and cost-effective way to mass produce the microstructure. Casting polymer on a metal sheet machine-processed by laser micro-machining [9] or 3D printed gecko setae covered by polytetrafluoroethylene (PTFE) using plasma-enhanced chemical vapor deposition [10] are some flexible ways to mass produce the setae structures. However, the shape of the design for gecko setae is limited by how the metal can be processed by laser micro-machining. For the second method, the PTFE layer generally remains on the mold. In this study, the feasibility of multiple approaches to fabricate the microstructural mold of gecko setae is examined.

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II. Design and Fabrication

This section describes designing, printing, coating and fabricating of the molds. The master molds, which consisted of multiple microstructures, were designed in CATIA and printed with a negative photoresist (IP-Q, Nanoscribe, Germany) using two-photon polymerization (2PP) printing technique with Photonic Professional GT2 (Nanoscribe, Germany). Different coating materials and techniques were applied on the printed master molds. Polydimethylsiloxane (PDMS) was poured and cured on the printed microstructure and the cured PDMS molds were detached.

2.1 Microstructure Design for Gecko Grips

A few design factors were put into consideration for the fabrication of gecko setae, such as resolution of different height, printability of thin and tall structure, and overhanging. As shown in Figure 1 (a), four different structures were designed to examine above; (i) step-structure design with 250×200×250 micrometer (µm) in XYZ direction to study the effects of different shapes and depth on adhesion, (ii) two-wall design with 20×200×250 µm in XYZ direction and 20 µm gap to investigate the effects of distance between structures, (iii) 50 µm thick plane rectangular standard shape for comparison, and (iv) a gecko setae inspired design with a height of 250 µm, consisting a disk with a diameter of 220 µm and thickness of 20 µm and a cylinder with a diameter of 100 µm, for a proof of concept. In addition, tilted four gecko setae structures were designed to see the effect of angles as shown in Figure 1 (b).

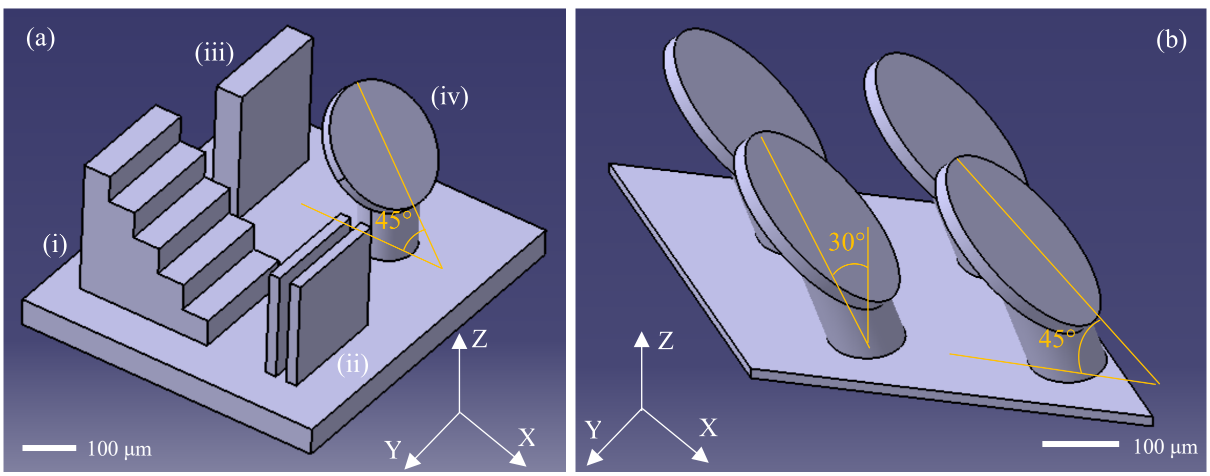

Figure 1. CAD model of a) Multi-design structure panel and b) gecko setae unit panel

2.2 Printing Microstructure Master Mold and Surface Treatment

For the requirement of the design, the microstructure must be flexible and the thinnest feature was 20 µm. Traditional fused deposition modeling (FDM) printing machine which was able to print flexible filament cannot print microstructures due to the limits of filament, step motors and nozzle diameter. Even though mask stereolithography (MSLA) printing machine could print flexible material by curing resin with ultraviolet (UV) light, the resolution was not capable of printing the desired structure. To acquire a flexible microstructure, the rigid master mold printed using 2PP was casted with PDMS to create the negative mold, the negative mold was then used to fabricate the positive mold out of PDMS. In terms of the cost and efficiency, the printing process was time consuming and expensive by comparing with casting molds. A 1 cm by 1 cm area of desired microstructure took about 8 hours to print and the cost of the photoresist was relevantly higher than PDMS in unit volume. Not only the material, but the operation fee of the 2PP machine was expensive. Therefore, to ensure the desired microstructure could be mass produced, fabricating the molds from the printed structure was essential. In addition, a mold with having larger areas could be obtained by casting PDMS on the array consisting of multiple smaller PDMS negative molds.

The microstructure master mold was printed with a negative photoresist in a 2PP machine. A clean silicon wafer with a drop of photoresist in the center was placed inside of the printer. Using the 2PP process, the designed microstructures were printed with 100 mm/s scan speed and 100% laser power. The printed microstructure was developed in 1-methoxy-2-propanol acetate (PGMEA) (Merck, Germany), rinsed with isopropanol and dried with air blower ball. The printed micro-structure was exposed to 405 nm UV light for 30 minutes to fully cure the photoresist.

Below steps describe different master mold surface treatment processes. The following surface treatments had the potential to keep the printed master mold from sticking to the negative mold during the detaching process. Due to the excellent malleability of gold, sputtering a thin gold layer on the printed master mold might help detach the negative mold without destroying the printed master mold. Otherwise, both polyacrylic acid (PAA) and poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) could form an isolated layer when they were dried, and they were soluble in water. Applying PPA or PEDOT: PSS on the printed master with micropipette liquid deposition or spin coating might ensure only the PDMS mold would be detached, and the layers could be washed out with water. However, PAA was much thicker than PEDOT: PSS, so 5% PPA was prepared by diluting 1 gram of PPA with 6 gram of isopropanol to decrease the viscosity of PPA.

A. Gold Sputtering

The micro-structure was placed in a sputter coater (108 Manual, Ted Pella, U.S.) to coat with gold for 30 seconds with 30 milliamps (mA) current and 0.08 millibars Argon gas pressure.

B. Micropipette Liquid Deposition

5 microliters (μL) of 5% PPA were dropped on two multi-design structure panels with PEDOT: PSS dropped on the other two multi-design structure panels. The microstructure was dried at room temperature for 1 hour.

C. Spin Coating

The master mold, covered with 5% PPA, was placed on the spin coater and span for 60 seconds at 2000 RPM. The microstructure was dried at room temperature for 1 hour.

2.3 Fabrication of Negative and Positive Molds

The 2” diameter silicon wafer which carried the printed master mold was placed and locked in an acrylic frame as shown in Figure 2. A cubic hole was surrounded by four pieces of acrylic blocks as Figure 2 (a) shown. The PDMS used in this experiment was Sylgard® 184 and was mixed in a 10:1 ratio of base to curing agent. The printed master molds were place in the center of the cubic hole and the hole was filled with PDMS. The negative mold was acquired by curing PDMS at 90 °C for 12 hours in a vacuum chamber at 700 mmHg. The replicated positive mold was fabricated from the negative mold with the same procedure for pouring and curing the negative mold.

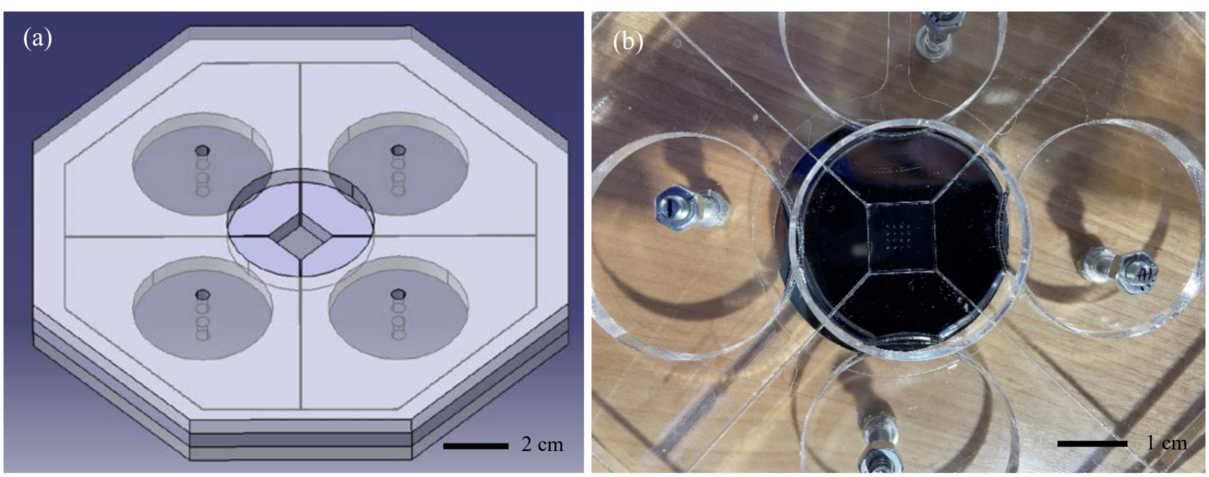

Figure 2. Fabricate a) CAD model for acrylic frame and b) printed master mold with silicon wafer substrate in the acrylic frame

III. Results and Discussion

The quality of printed molds and fabricated PDMS molds were determined with a digital microscope (Dino-Lite Edge, AnMo Electronics Corporation, Taiwan). Various coating methods were examined by inspecting the completeness of the printed molds and PDMS molds, before and after surface treatment and detaching.

3.1 Printing of Master Mold

An 8 by 8 array of multi-design structure panel was printed on a silicon wafer with 1000 micrometer in X and Y direction spacing as seen in Figure 3 (a). The printing quality of four shapes array was acceptable, however, two-walled structure did not maintain constant separation distance when printed. Figure 3 (b) showed the gecko setae unit panel with an array of 19 × 25 (in XY direction) to fit the 1 centimeter by 1 centimeter area of the center of the silicon wafer.

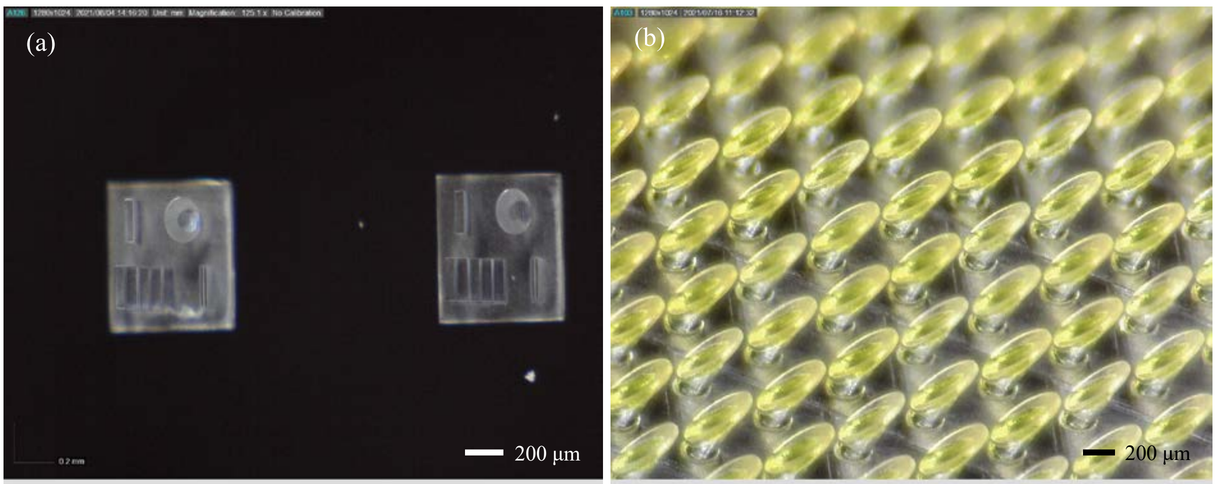

Figure 3. Printed master mold on silicon wafer: a) Multi-design structure panel array and b) gecko setae array

3.2 Surface treatment

Gold sputtering, micropipette liquid deposition and spin coating were applied to the printed master molds. The objective of coating the mold was to isolate the exposed photoresist from cured PDMS, so that the cured PDMS could be separated from the printed microstructure without damaging and sticking.

A. Gold Sputtering

By inspecting the two-wall design thick plane rectangular standard shape, the gold layer seem to fully cover the exposed surface of microstructure as seen in Figure 4.

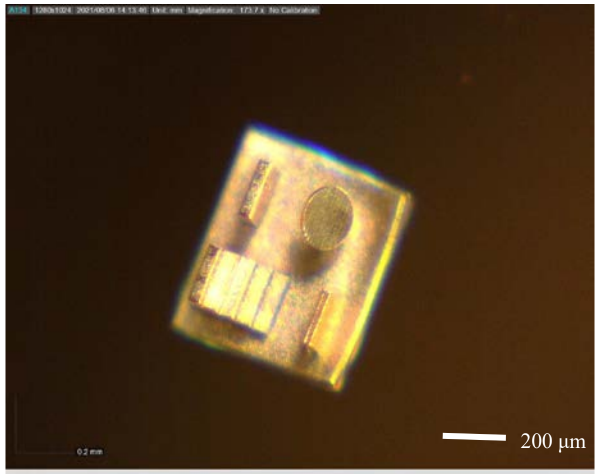

Figure 4. Multi-design structure panel treated with gold sputtering

The exposed surface of the multi-design structure panel was fully covered by gold through the sputtering process. The thickness of the gold could be calculated with equation from Sputter Coating Technical Brief [11].

$$Th = 7.5 \times I \times t \qquad \text{Eq (1)}$$

Where I was 30 mA and t was 30 seconds, which gave a gold layer thickness of 112.5 angstrom.

B. Micropipette Liquid Deposition

The PPA layer fully covered the multi-design structure panel when 5 µL of 5% PPA was dried as shown in Figure 5 (a). Curved PPA layer was formed at the sharp edges of the microstructure. Dried PEDOT: PSS layer in Figure 5 (b) also had the same issue, but the edge of the microstructure was more distinct.

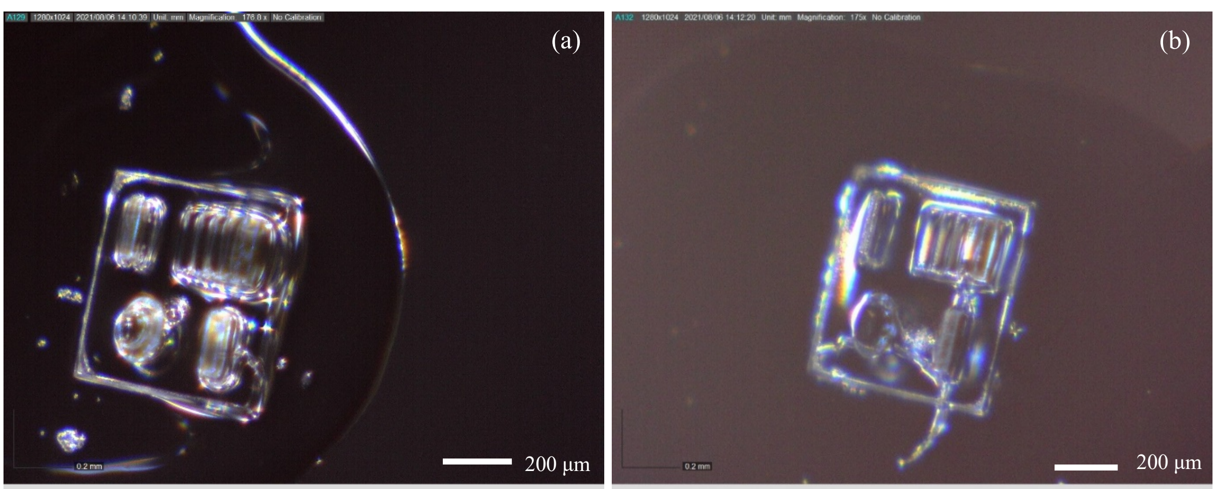

Figure 5. Multi-design structure panel treated with 5 microliter of a) 5% Polyacrylic acid and b) PEDOT: PSS

To obtain a better quality of PPA layer and PEDOT: PSS layer, the excessive liquid, which gathered at the sharp edge of the microstructure, needed to be removed. Therefore, spin coating was introduced to form a uniform layer of PPA and PEDOT: PSS.

C. Spin Coating

The gecko setae array was fully covered by 5% PPA and placed in spin coater to remove the extra solution at 2000 RPM for 60 seconds. When the layer of 5% PPA was dried out, the surface of the gecko setae array in Figure 6 (b) was determined to be fully cover by PPA because it had less yellow hue compared to Figure 3 (b).

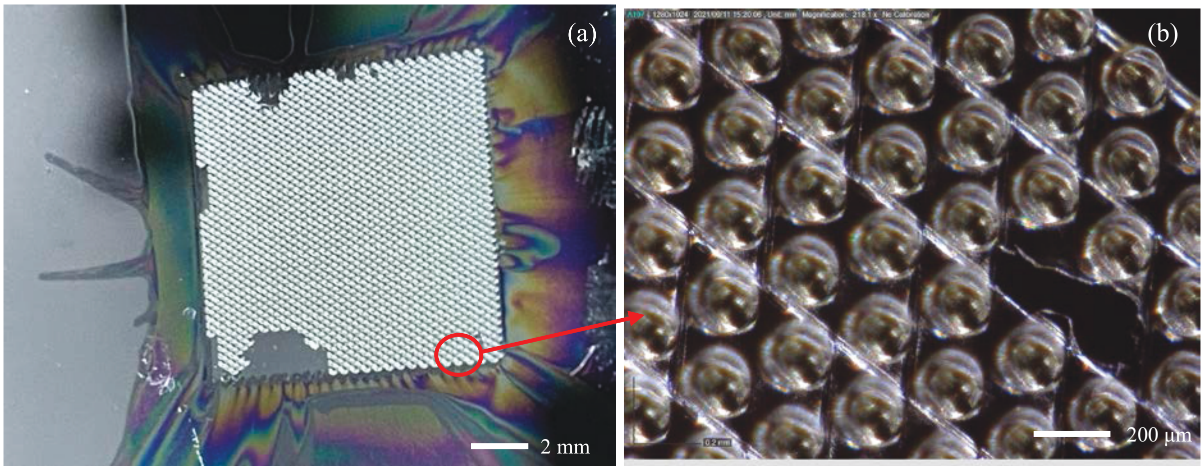

Figure 6. a) Spin-coated gecko setae array and b) zoomed in portion.

3.3 Fabricating Negative PDMS Molds

Negative PDMS molds were fabricated by pouring PDMS onto an acrylic frame, which had printed master molds installed, and detaching after PDMS was cured. A PDMS mold for uncoated master mold was fabricated as a control group. The defects of the negative PDMS molds and printed master molds were inspected with a digital microscope.

A. No Surface Treatment

Without surface treatment on the master mold, the printed structure was stuck in the PDMS negative mold during the demolding process. Only one of the structures in the multi-design structure panel array was separated from the PDMS negative mold with tape, but the demolded structure was not completed. The rest of the structures that had no surface treatment were pull off with tweezers. However, none of the master molds can be separated without damaging the structure. The negative PDMS mold sustained damage when tweezers were utilized. Therefore, the master mold must be treated to achieve demolding without damaging negative mold and master mold.

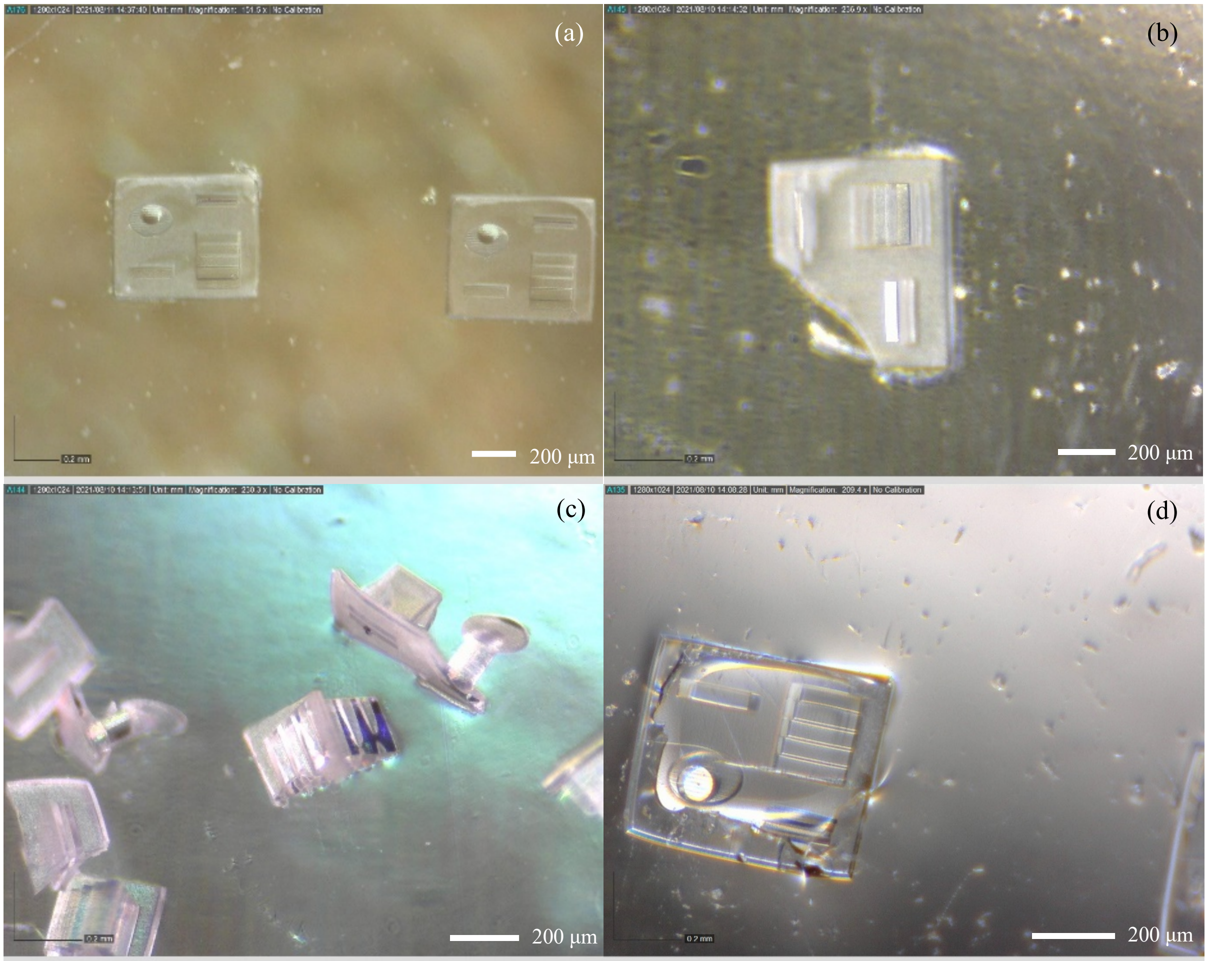

Figure 7. a) Negative PDMS mold with no treatment and trapped master mold b) Master mold separated with tape and c) Master mold separated with tweezer. d) Negative PDMS mold damaged by tweezer

B. Gold Sputtering

The master mold structures that were covered by gold adhered to the PDMS negative mold during the demolding process. The master mold cannot be demolded with tape, and the tape can only peel off most of the gold from the PDMS negative mold surface. Using tweezers cannot demold the entire master mold structures from the PDMS negative mold.

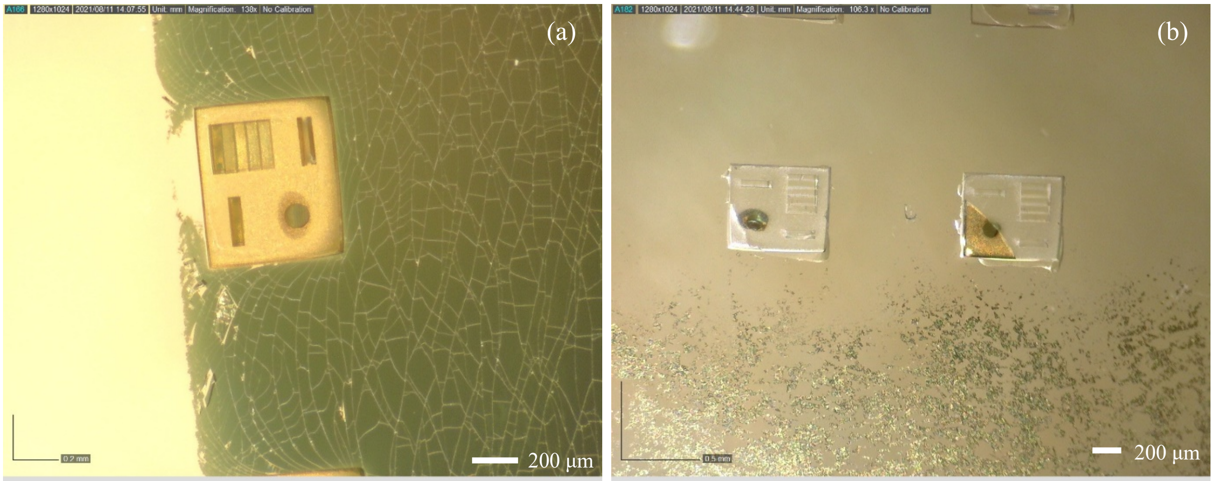

Figure 8. a) Negative PDMS mold with gold-sputtered and trapped master mold b) Master mold separated with tape and tweezer.

C. Micropipette Liquid Deposition

The master mold structure treated with 5 microliter of 5% PPA was demolded from the PDMS negative mold successfully. The master mold structure was demolded in one piece without damage and the quality of the PDMS negative mold was acceptable. Due to the 5% PPA, a uniform layer was not formed as the PDSM negative mold had wrinkles surrounding the microstructure.

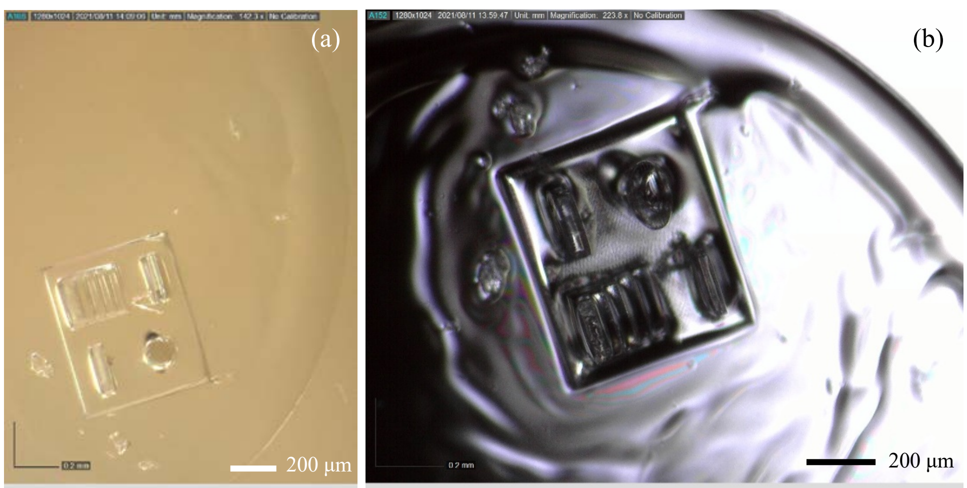

Figure 9. a) Negative PDMS mold with 5% Polyacrylic acid b) Separated master mold.

The master mold structure treated with 5 microliter of PEDOT: PSS was demolded from the PDMS negative mold successfully. The circular panel of the multi-design panel in the master mold structure was damaged during the demolding process, however the broken pieces did not remain in the negative PDMS mold. The surface of the PDMS negative mold that surrounded the microstructure was even by comparing the surface as shown in Figure 9 (a).

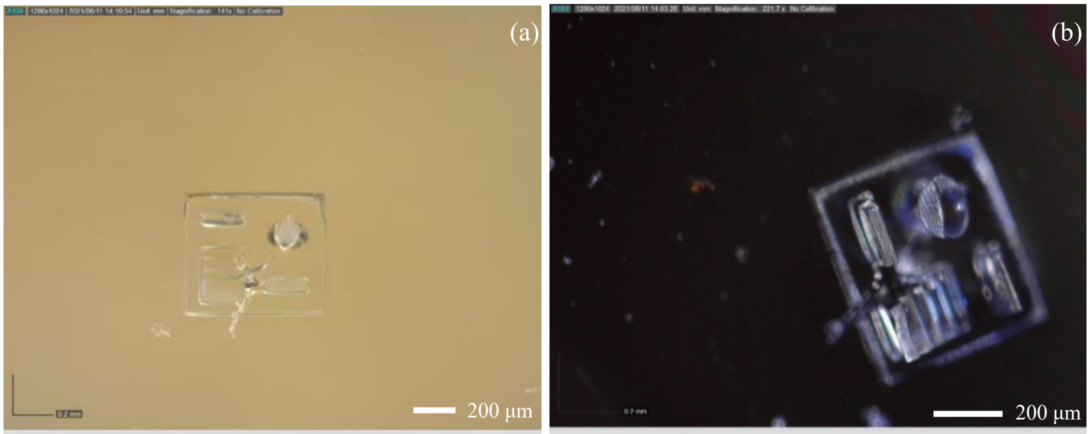

Figure 10. a) Negative PDMS mold with PEDOT: PSS b) Separated master mold.

D. Spin Coating

About 5% of gecko setae array structure was missing during the demolding process as Figure 11 (b) and (d) shown, but most of the printed structure remained on the silicon wafer. Uneven applied force to separate the negative mold might be the reason why most of missing structures occur at the boarder of the master mold, The negative PDMS mold had even surface when the master mold was spin-coated with 5% PPA as Figure 11 (c) shown. There were some minor defects due to the dust in the printed microstructure before casting PDMS. The negative PDMS mold demolded from the microstructure favorably when the master mold was spin-coated with 5% PPA.

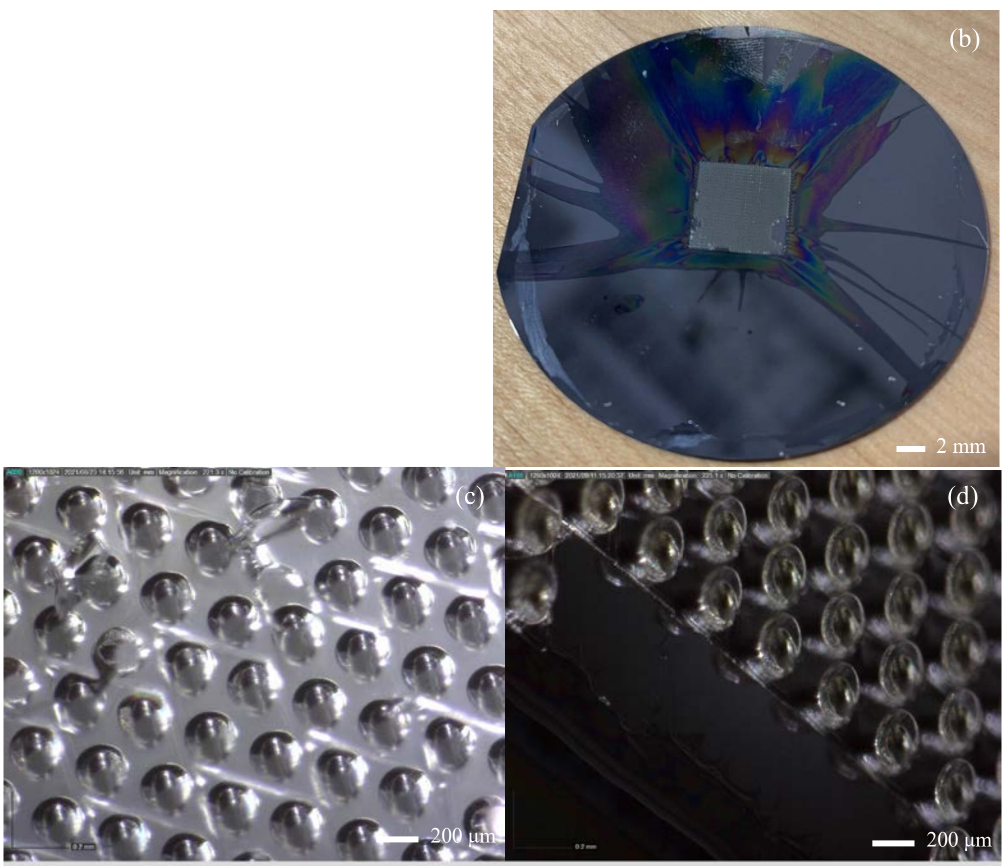

Figure 11. a) Negative PDMS mold before demold b) separated master mold c) microstructure in the negative PDMS mold d) microstructure in the master mold.

3.4 Replicated Positive Mold

The positive mold of multi-design structure and gecko setae array were fabricated by pouring PDMS onto an acrylic frame with negative PDMS mold installed. By analyzing the quality of negative molds, the mold that spin-coated with 5% PPA had the better overall quality. Therefore, applying spin coating on the negative PDMS mold then fabricating the positive mold was a better approach.

The negative PDMS mold for the multi-design structure panel was spin-coated with 5% PPA. Furthermore, PDMS was poured on top of the negative PDMS mold to replicate the positive mold. Nonetheless, outlines of the design were observed and the multi-design structure panel was not fully replicated.

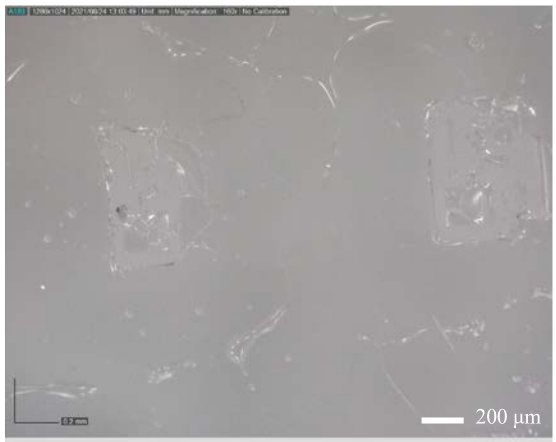

Figure 12. Replicated positive multi-design structure panel PDMS mold.

The surface of the negative PDMS mold containing microstructures were covered by 5% PPA and was degassed at 700 mmHg for 120 seconds. The negative PDMS mold was then spin-coated at 2000 RPM for 60 seconds. PDMS was poured on top of the negative PDMS mold to replicate the positive mold. The replicated positive mold was demolded, though not all the gecko setae could be demolded from the negative mold successfully. Some gecko setae structures were completely stuck in the negative PDMS mold and some gecko setae had broken tips.

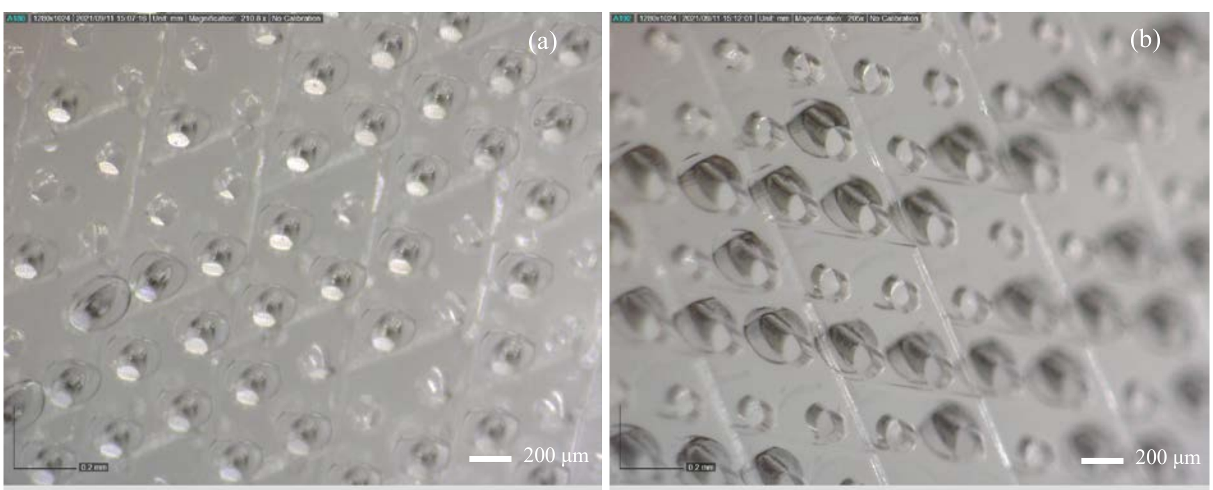

Figure 13. (a) Replicated positive gecko setae array and (b) the pilled off negative PDMS mold.

IV. Conclusion

Acceptable printing quality was achieved which verified the manufacturing possibility. The printed master mold must be treated before casting PDMS to make the negative mold. Gold sputtering does not work well when separating PDMS and printed structure. Micropipette dropping with acid and PEDOT: PSS help demolding the negative mold from the printed positive mold. However, the negative mold that was fabricated from the master mold which was covered by Polyacrylic acid had uneven surface. The master mold treated with PEDOT: PSS was damaged after it was demolded. To obtain a good quality negative mold, the printed master mold was spin-coated with 5% Polyacrylic acid and casted with PDMS. Before spin-coating the negative mold, it was degassed in a vacuum chamber after it was covered by 5% Polyacrylic acid to ensure the microstructure was filled with 5% Polyacrylic acid instead of air. Even though the microstructure in replicated positive mold was not completed, it showed that spin-coating with 5% Polyacrylic acid was a viable approach. Development of non-destructive separation technique is imperative to preserve the molded structure.

V. Future Work

Air bubble may play a significant role in microstructure mold. To eliminate effect of air bubble, instead of degassing the PDMS and other liquid after pouring on the mold, pouring PDMS or other liquid in a vacuum chamber at vacuum state with a device is a better approach. Even spin coating the mold in vacuum state might help improve the results.

ACKNOWLEDGMENT

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References

1. Roberts, L. D. "Addressing the Problem of Orbital Space Debris: Combining International Regulatory and Liability Regimes," *Boston College International and Comparative Law Review* Vol. 15, No. 1, 1992, pp. 51-74.
2. Hobe, S. "Environmental protection in outer space: Where we stand and what is needed to make progress with regard to the problem of space debris," *Indian JL & Tech.* Vol. 8, 2012, p. 1.
3. Autumn, K., Sitti, M., Liang, Y. A., Peattie, A. M., Hansen, W. R., Sponberg, S., Kenny, T. W., Fearing, R., Israelachvili, J. N., and Full, R. J. "Evidence for van der Waals adhesion in gecko setae," *Proceedings of the National Academy of Sciences* Vol. 99, No. 19, 2002, p. 12252.

doi: 10.1073/pnas.192252799

4. Autumn, K., Liang, Y. A., Hsieh, S. T., Zesch, W., Chan, W. P., Kenny, T. W., Fearing, R., and Full, R. J. "Adhesive force of a single gecko foot-hair," *Nature* Vol. 405, No. 6787, 2000, pp. 681-685.

doi: 10.1038/35015073

5. Dadkhah, M., Zhao, Z., Wettels, N., and Spenko, M. "A self-aligning gripper using an electrostatic/gecko-like adhesive," *2016 IEEE/RSJ International Conference on Intelligent Robots and Systems (IROS)*. 2016, pp. 1006-1011.
6. Heepe, L., and Gorb, S. "Biologically Inspired Mushroom-Shaped Adhesive Microstructures," *Annual Review of Materials Research* Vol. 44, 2014.

doi: 10.1146/annurev-matsci-062910-100458

7. Henrey, M., Díaz Téllez, J. P., Wormnes, K., Pambaguian, L., and Menon, C. "Towards the use of mushroom-capped dry adhesives in outer space: Effects of low pressure and temperature on adhesion strength," *Aerospace Science and Technology* Vol. 29, No. 1, 2013, pp. 185-190.

doi: https://doi.org/10.1016/j.ast.2013.03.003

8. Trentlage, C., and Stoll, E. "The applicability of gecko adhesives in a docking mechanism for active debris removal missions," *13th Symposium on Advanced Space Technologies in Robotics and Automation, ASTRA*. 2015.
9. Kim, J.-K., and Varenberg, M. "Biomimetic wall-shaped adhesive microstructure for shear-induced attachment: the effects of pulling angle and preliminary displacement," *Journal of The Royal Society Interface* Vol. 14, No. 137, 2017, p. 20170832.

doi: doi:10.1098/rsif.2017.0832

10. Busche, J. F., Starke, G., Knickmeier, S., and Dietzel, A. "Controllable dry adhesion based on two-photon polymerization and replication molding for space debris removal," *Micro and Nano Engineering* Vol. 7, 2020, p. 100052.

doi: https://doi.org/10.1016/j.mne.2020.100052

11. Limited, Q. T. "Sputter Coating Technical Brief," No. 2, p. 13.