

Plasma polymerization of C₄F₈ thin film on high aspect ratio silicon molds

L. P. Yeo¹, S. L. Poh², Y. C. Lam^{1,2}, Mary B. Chan-Park^{1,2}

¹ Singapore-MIT Alliance, Nanyang Technological University, Singapore 639798

² School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798

Abstract—High aspect ratio polymeric micro-patterns are ubiquitous in many fields ranging from sensors, actuators, optics, fluidics and medical. Second generation PDMS molds are replicated against first generation silicon molds created by deep reactive ion etching. In order to ensure successful demolding, the silicon molds are coated with a thin layer of C₄F₈ plasma polymer to reduce the adhesion force. Peel force and demolding status are used to determine if delamination is successful. Response surface method is employed to provide insights on how changes in coil power, passivating time and gas flow conditions affect plasma polymerization of C₄F₈.

Index Terms— C₄F₈, plasma polymerization, peel force, demolding.

I. INTRODUCTION

POLYMERIC high aspect ratio microstructures (HARMs) are used in many industries including medical [1], sensors and actuators [2], micro-fluidics [3] and optics [4]. The high aspect ratio micro-structured silicon wafers used as first generation molds are fabricated by photolithography and Inductive Coupled Plasma (ICP) Deep Reactive Ion Etching (DRIE) [5] methods. DRIE makes use of alternate etch and passivate steps [6] which uses etchant gas SF₆/O₂ and passivation gas C₄F₈.

UV embossing [7] – [11] is a quick and efficient method which replicates with excellent fidelity high aspect ratio microstructures. A multi-functional acrylate polymer mixture is dispensed over the mold and UV cured in matters of seconds. The hardened resin is then peeled off at

a small angle. To protect the master mold from damage, second generation PolyDimethylsiloxane (PDMS) molds are imprinted from the first generation molds. The success of replicating PDMS molds from the silicon master mold depends on the adhesion force between the master mold and the silicone rubber during the demolding process. Plasma polymerization of C₄F₈ passivation layer deposited on silicon was necessary to allow for ease of demolding PDMS. If the adhesion forces between the silicone rubber and the wafer were too high, the silicone rubber would be stuck in the trenches of the wafer and the mold would be rendered useless for subsequent usage. This was the major challenge to the success of replicating high aspect ratio microstructures. As the aspect ratio increased, it became more difficult to demold with no premature failure.

Plasma polymerization is known to modify material surfaces by the deposition of a thin polymer film which promotes good adhesion between films to substrate [12]. In addition to the capability of providing etching, the DRIE process is also competent of providing polymer passivation [13], [14]. Fluorine containing plasmas are known to decrease surface energy and increase the hydrophobic behavior of surfaces [12]. As such, we selected the DRIE machine to administer the deposition of polymer passivation on silicon wafers after etching. Parameters such as coil power, gas flow and passivation time were found to affect the polymer film thickness.

4-inch <100> orientation, p-type silicon wafers were etched by DRIE. The depths of the trenches etched were greater than 100μm, and the aspect ratios were greater than 10. After etching, a passivation layer was deposited on the silicon master mold and subsequently, silicone rubber replications were made. The 90 Degree Peel test was conducted to determine the peel force and Scanning Electron Microscopy (SEM) was employed to observe the physical topography.

Manuscript received November 9, 2004. This work was supported in part by the Singapore MIT Alliance and A-STAR (Singapore) grant (Project No. 022 107 0004).

L. P. Yeo is with the Singapore MIT Alliance (phone: 65- 67904273; fax: 65- 8627215; e-mail: ps7701328h@ntu.edu.sg).

S. L. Poh graduated from the School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798, Singapore in 2004 June. She is currently working as a process engineer in Ness Display Co Ltd (email: rachelp@nessdisplay.com)

Y. C. Lam is with the School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798, Singapore (e-mail: myclam@ntu.edu.sg).

Mary B. Chan-Park is with the School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798, Singapore (e-mail: mbechan@ntu.edu.sg).

II. EXPERIMENTAL

A. Photomask

The photo-mask pattern consisted of repetitive 2000 μm long channels. The 10 μm -wide dark field lines were separated by 80 μm -wide light field lines.

B. Photolithography

Silicon wafers were cleaned by immersing them in Piranha solution (15:1(v/v) 96wt% H_2SO_4 : H_2O_2) at 120 $^\circ\text{C}$ for 20 min. After the process, the wafers were then rinsed in de-ionized water for 15 min. The acid- cleaned wafers were then placed in the spin dryer to blow dry using compressed nitrogen gas. Lastly, the wafers were placed in the oven for 3 hours at a temperature of 200 $^\circ\text{C}$.

Each wafer was baked at 150 $^\circ\text{C}$ for 5 min to remove the moisture content. Hexamethyldisilazane (HMDS) was spin-coated onto the hot wafer to promote adhesion between the wafer and the photoresist. This was performed at 2000 rpm, which was held for 30sec. The coated wafer was baked for 5 min at 150 $^\circ\text{C}$ and allowed to cool down gradually. The positive photoresist and the developer used were Az 9260cp and Az@ 421k from Clariant. 100mm diameter <100> p type silicon wafers (475 $\mu\text{m} \pm 25\mu\text{m}$) thick were used as substrates. Az 9260cp was spin-coated onto the cooled wafer at 2000rpm for 60sec. The coated wafer was placed on a well- leveled hotplate at room temperature for 10 min. After that the temperature of the hotplate was increased to 110 $^\circ\text{C}$ for 5 min to solidify the photoresist. Lastly the wafer was cooled down gradually.

The photoresist was exposed at a UV power of 9.3 mg/sec for 30s using the J500-IR/VIS Mask Aligner from Optical Associates Inc. (Milpitas, California). The samples were developed at room temperature for around 2 min. Following the development, the patterned wafer was rinsed in the de-ionized water and then spun dry using the spin coater.

C. Deep Reactive Ion Etching

The wafers were etched using a Surface Technology Systems Multiplex Inductive Coupled Plasma (made by Redwood) Machine. The equipment had two independent 13.56 MHz radio frequency (RF) power source. The coil around the etching chamber was used to create plasma, while the platen coil was connected to the wafer electrode to control the RF bias potential of the wafer with respect to the plasma. Backside helium pressurization was used to provide sufficient heat transfer between the wafers to the electrode to maintain a constant wafer temperature.

When the wafer was placed in the machine, it was clamped by a set of eight alumina fingers to the electrode. Alternate etch and passivation steps of 14s and 8 s were used. The gases used for the etching process were SF_6 and O_2 , while the gas used for passivation was C_4F_8 . The flow rates of the SF_6 , O_2 and C_4F_8 were 130 standard cubic centimeters per minute (sccm), 13 sccm and 100 sccm

respectively. The pressure in the chamber was maintained at 36 mTorr and the APC angle was set to 75%. The platen power used was 110 W and the coil power was 800 W. The DRIE had an approximate etch rate of 2.5 $\mu\text{m}/\text{min}$ and the required etching time was 60 min so as to achieve 150 μm trench depth.

After etching the wafers, the microstructures on the wafer were examined using an optical microscope. Subsequently, the photoresist on the silicon wafer was stripped by immersing the wafer in acetone, isopropanol (IPA) and de-ionized water for 5 min each respectively. The chamber of the Reactive Ion Etching machine was cleaned with IPA and a sputtering process using Argon gas. The pressure used for the process was 160mTorr and the power required was 300W. The purpose of using argon gas was to further clean the chamber and remove other contaminant gases that might still exist in the chamber. The whole process lasted for 15 min. Subsequently, the etched wafers were loaded into the cleaned chamber and processed under oxygen- based plasma. The removal of the photoresist was processed at a power of 250W and pressure of 120mTorr. The O_2 gas flow was 10 sccm and the time taken to remove the photoresist was 20 min.

The patterned wafer would then undergo a passivation process. The parameters that affected the passivation process were coil power, passivating time and amount of C_4F_8 gas flow.

D. Response Surface Method

The commercial software, Design Expert 6.0 was used to generate the response surfaces. The Box-Behnken Design was used [15] and based on the working range for the coil power, passivation time and C_4F_8 gas flow, 17 sets of parameters were generated by the software (See Table 1). Two responses, namely the peel force and demolding status were investigated. Demolding status is defined as 1 for successful and 0 for failure. An assumption was made such that the interaction effects between replications are insignificant. Runs 8, 11, 12, 14 and 15 are similar and hence only 1 set of data was generated for all the five runs.

E. Silicone Rubber Replication

The microstructured silicon dioxide wafer was stiffened by attaching it to a glass plate with double-sided tape. 2mm thick TEFLON was attached to the glass plate that acted as a divider. Silicone rubber was made from Silastics J RTV silicone rubber, a two-part, room temperature cure silicone rubber supplied by Dow Corning (Midland, MI). It was prepared by mixing the resin and hardener in a 10:1 weight ratio at room temperature. The mixture was thoroughly mixed by the electronic stirrer for about 5 mins at 200 rpm. It was degassed in vacuum at 22 $^\circ\text{C}$ for 5 to 7 minutes to remove the trapped air. Subsequently, the rubber mixture was poured over the silicon wafer. The wafer with the rubber mixture on it was placed in the vacuum chamber to further degas until the air bubbles disappeared. A PET film

was then placed over the degassed rubber mixture carefully so that demolding will be made simpler after thermal curing. Once this was completed, another glass plate was placed on top of the PET film and the whole sample was clamped with clips and placed in the oven at 65°C for 16 hours.

F. 90 Degree Peel Test

After the silicone rubber was cured, the 90° Degree Peel tests [16] were performed using an Instron Machine. The dimensions of the silicone rubber were 50mm × 110mm × 2mm. Peeling was carried out with a 100N load cell at a peel speed of 25 mm/min. The purpose of conducting the peel test was to obtain the peel strength required for demolding.

G. Surface Topology

Scanning Electron Microscopy (SEM) from JEOL JSM-5600 was used to observe the physical topography of the etched wafers and the silicone rubber replications. All samples were sputtered in Au for 200s at 120mA.

III. RESULTS & DISCUSSION

A. Wafer Etching

The silicon wafer was etched with the various DRIE parameters described. The dimensions of the silicon mold were within the tolerance of $\pm 5\mu\text{m}$ and were hence acceptable. Figure 1 shows the SEM micrograph of a typical silicon wafer mold. The aspect ratios of the silicon wafer molds ranged from 11 to 13. The slight difference in aspect ratio was due to fluctuations in etching rate. The aspect ratios of all runs were considered to be fairly consistent and was expected to have little effect on the responses.

B. Peel Force and Demolding Status

The optimal conditions for the passivated layer should produce a low peel force for successful replicated silicone rubber. Table 2 shows the averaged peel force at each run. For unsuccessful runs, only 1 data point was recorded. Demolding was considered successful if five silicone rubber replications could be successfully detached from the mold (no breakage of trenches should occur). Figures 2 and 3 show the peel force and demolding status as a function of coil power, passivation time and gas flow. The R^2 for the predicted quadratic models of peel force and demolding status based on the software are 0.867, and 0.882.

For fluorine containing systems, surface reactions, etching and plasma polymerization can occur simultaneously. The gas flow and operating conditions determine the dominant mode of reaction [12, 13]. In general, higher CF_x/F ratio enhances polymerization while lower CF_x/F ratio promotes surface reactions and etching. Higher plasma power is known to create more fragmentation of the C_4F_8 monomers [13] – [16]. The increased dissociation of CF_x radicals give rise to higher polymer deposition and it becomes easier to demold.

However with maximum power, F atoms increase more than the CF_x radicals. Therefore the F atoms tend to sputter the polymer surface hence leading to decreased deposition rate. In addition, recombination of radicals tends to occur, giving rise to less plasma polymerization. Peel force varies almost inversely proportional to time. When passivating time is increased, more deposition takes place hence peel force required decreases. When gas flow is increased, the density of reacting ions also increases. However at high gas flow, ion energy decreases and radical density increases [15]. More F atoms are present and polymer etching takes place. Figure 4 shows a typical SEM micrograph of a failed run whereby the silicone rubber replications broke in the mold. Figure 5 shows a typical SEM micrograph of successful replicated rubbers.

IV. CONCLUSIONS

As the aspect ratio of silicon wafers increased, it is important to determine an optimal set of passivation parameters such that the silicone rubber replicated from the master mold could demold successfully without leaving any residue behind. This paper provides insights as to how changes in parameters affected the peel demolding results. Further work will be carried out to determine the actual thickness of the plasma polymer and also to characterize the amount of fluorine transfer from mold to replicate. Low fluorine content was necessary to minimize the contamination of the second generation molds.

ACKNOWLEDGMENT

This research was supported by an A-STAR (Singapore) grant (Project No. 022 107 0004). L. P. Yeo acknowledges the financial sponsorship of the Singapore-MIT Alliance in the form of a research scholarship. The advice and fruitful discussions of SMA Fellow Professor David Hardt of MIT are gratefully acknowledged.

REFERENCES

- [1] E. Ostuni, K. Ravi, C. D. Chen, D. E. Ingber and G. M. Whitesides, "Patterning Mammalian Cells using Elastomeric Membranes," *Langmuir*, vol. 16, pp. 7811- 7819, 2000.
- [2] S. Gaspar, M. Mosbach, L. Wallman, T. Laurell, E. Cosregi and W. Schumann, "A Method for the Design and study of Enzyme Microstructures Formed by a Means of a flow through microdispenser," *Analytical Chemistry*, vol. 73, no. 17, pp. 4254 – 4261, 2001.
- [3] D. L. Pugmire, E. A. Waddell, R. Haasch R, M. J. Tarlov, E. L. Locascio, "Surface Characterization of Laser-Ablated Polymers used for Microfluidics," *Analytical Chemistry*, vol. 74, pp. 871 – 878, 2002.
- [4] M. T. Gale, "Replication," in *Micro-optics: elements, systems and application*, H. P. Herzig, Ed. *Taylor and Francis, London*, 1997
- [5] J. K. Bhardwaj and H. Ashraf, "Advanced silicon etching using high density plasmas" *Proceedings of the SPIE*. vol. 2639, pp. 224 – 233, 1995.
- [6] F. Lärmer and L. A. Schilp, 1992 A Method for anisotropically etching silicon German Patent No. DE4241045.
- [7] M. Bender, M. Otto, B. Hadam, B. Vratzov, B. Spangenberg, H. Kurz, "Fabrication of Nanostructured using a UV- based imprint technique," *Microelectronic Engineering*, vol. 53, pp. 233 – 236, 2000.

- [8] M. Otto, M. Bender, B. Hadam, B. Spangenberg, H. Kurz, "Characterization and application of a UV based imprint technique," *Microelectronic Engineering*, vol. 57 - 58, pp. 361 - 366, 2001.
- [9] F. P. Shartsman, "Holographic optical elements by dry photopolymer embossing," *Proceedings of SPIE*. vol. 1461, pp. 313 - 320, 1991.
- [10] F. P. Shartsman, "Dry photopolymer embossing," *Proceedings of SPIE*. vol. 1507, pp. 383 - 391, 1991.
- [11] M. B. Chan-Park and W. K. Neo, "Ultraviolet Embossing for patterning high aspect ratio polymeric microstructures," *Microsystem Technologies*, vol. 9(6-7), pp. 501, 2003.
- [12] C.M. Chan in: *Polymer Surface Modification and Characterization*. 1st Ed. Carl Hanser Verlag, 1994, ch. 6.
- [13] R. d'Agostino, "Plasma Polymerization of Fluorocarbons," in: *Plasma Deposition, Treatment, and Etching of Polymers*, R. d'Agostino, Ed. New York: Academic Press, 1990
- [14] R. d'Agostino, F. Cramarossa, V. Colaprico and R. d'Ettore, "Mechanisms of etching and polymerization in radio frequency discharges of CF_4-H_2 , $CF_4-C_2F_4$, $C_2F_6-H_2$, $C_3F_8-H_2$ " *Journal of Applied Physics*, vol. 54(3), pp. 1284-1288, 1989.
- [15] M.A. Blauw, T. Zijlstra and E. van der Drift, "Balancing the etching and passivation in time multiplexed deep dry etching of silicon," *Journal of Vacuum Science and Technology, B*, vol. 19, no. 6, pp. 2930 -2934, 2001.
- [16] W. J. Dauksher, S. B. Clemens, D. J. Resnick, K.H. Smith, P.J.S. Mangat, S. Rauf, P.L. G. Ventzek, V. Arunachalam, B.N. Ramamurthi, H. Ashraf, L. Lea, S. Hall, I.R. Johnston, J. Hopkins, J.J. Bhardwaj, "Deep silicon etch modeling for fabrication of 200-mm SCAPEL masks," *Microelectronic Engineering*, vol. 57 - 58, pp. 607 - 612, 2001.
- [17] D. C. Montgomery, *Design and Analysis of Experiments*. 3rd Ed, John Wiley & Sons Ltd, 1991, ch. 11.

TABLE 1
THREE VARIABLE BOX-BEHNEK DESIGN

Run	Coil Power (W)	Passivating Time (s)	Gas Flow (sccm)
1	300	10	65
2	200	10	10
3	300	600	65
4	200	600	120
5	200	600	10
6	300	305	10
7	100	600	65
8	200	305	65
9	100	10	65
10	300	305	120
11	200	305	65
12	200	305	65
13	200	10	120
14	200	305	65
15	200	305	65
16	100	305	10
17	100	305	120

- [18] ASTM Designation: D 6862-03 Standard Test Method for 90 Degree Peel Resistance of Adhesives.

TABLE 2
AVERAGE PEEL FORCE FOR ALL RUNS

Run	Average Peel Force (N)	Variation
1	6.04	N.S. ¹
2	4.49	N.S.
3	3.55	±1.389
4	2.01	±0.559
5	3.10	N.S.
6	4.29	N.S.
7	4.34	±0.395
8	2.97	±0.748
9	4.21	N.S.
10	7.22	±0.833
11	2.97	±0.748
12	2.97	±0.748
13	4.09	N.S.
14	2.97	±0.748
15	2.97	±0.748
16	3.72	N.S.
17	4.37	N.S.

¹ N.S. represents unsuccessful runs in that the silicone rubber broke inside the wafer after the 1st peel attempt

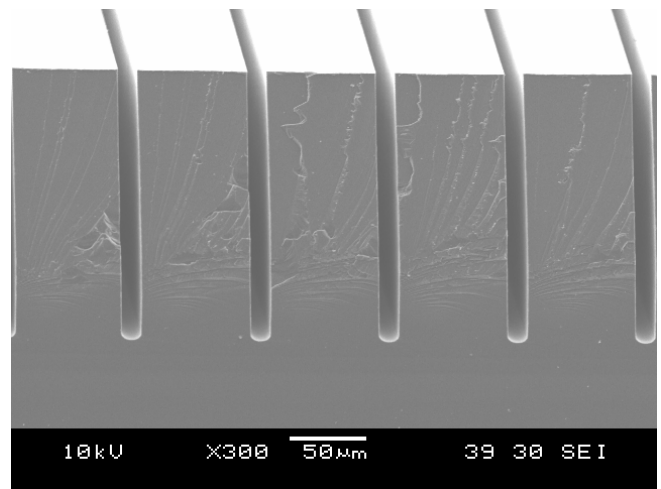
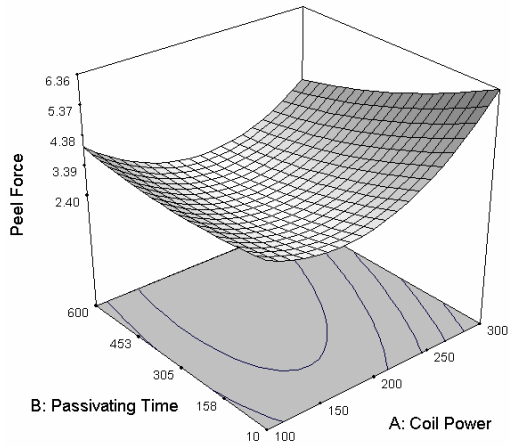
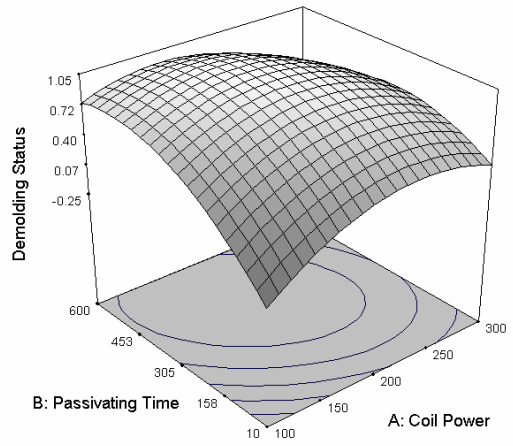


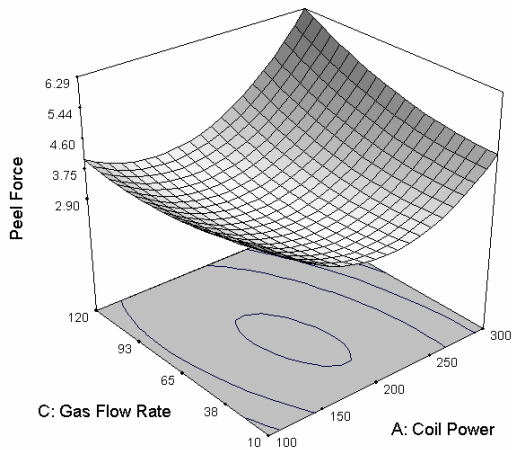
Fig. 1. Scanning Electron Microscopy Micrograph showing a cross-sectional view of an etched wafer with aspect ratio approximately equals to 12.



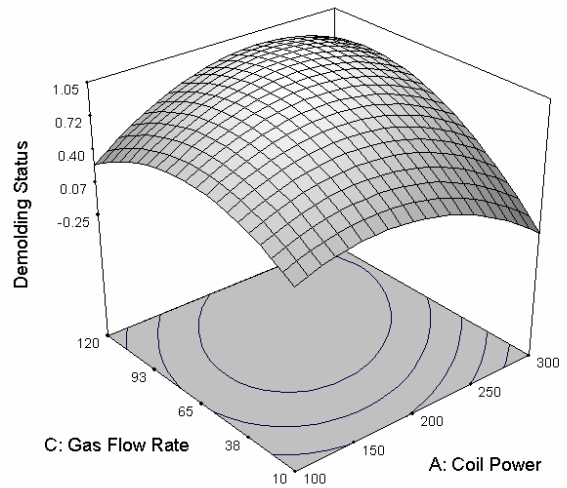
(a)



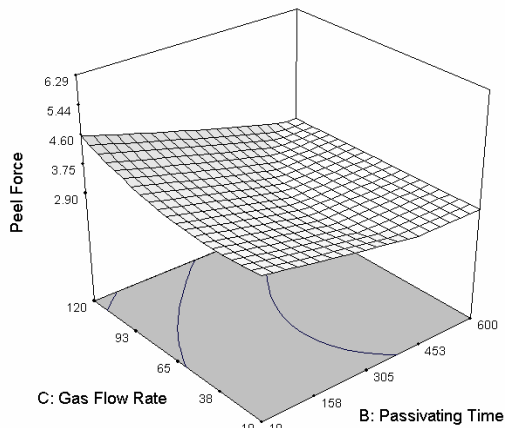
(a)



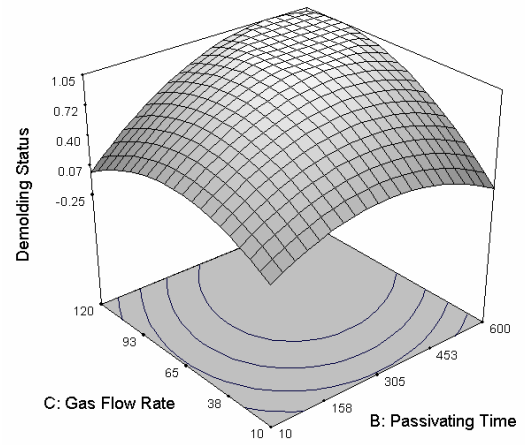
(b)



(b)



(c)



(c)

Fig. 2. 3D Contour response surface plot of peel force dependence on (a) coil power and passivating time at gas flow rate of 65 sccm (b) coil power and gas flow rate at passivating time 305s (c) passivating time and gas flow rate at coil power 200W

Fig. 3. 3D Contour response surface plot of demolding status dependence on (a) coil power and passivating time at gas flow rate of 65 sccm (b) coil power and gas flow rate at passivating time 305s (c) passivating time and gas flow rate at coil power 200W

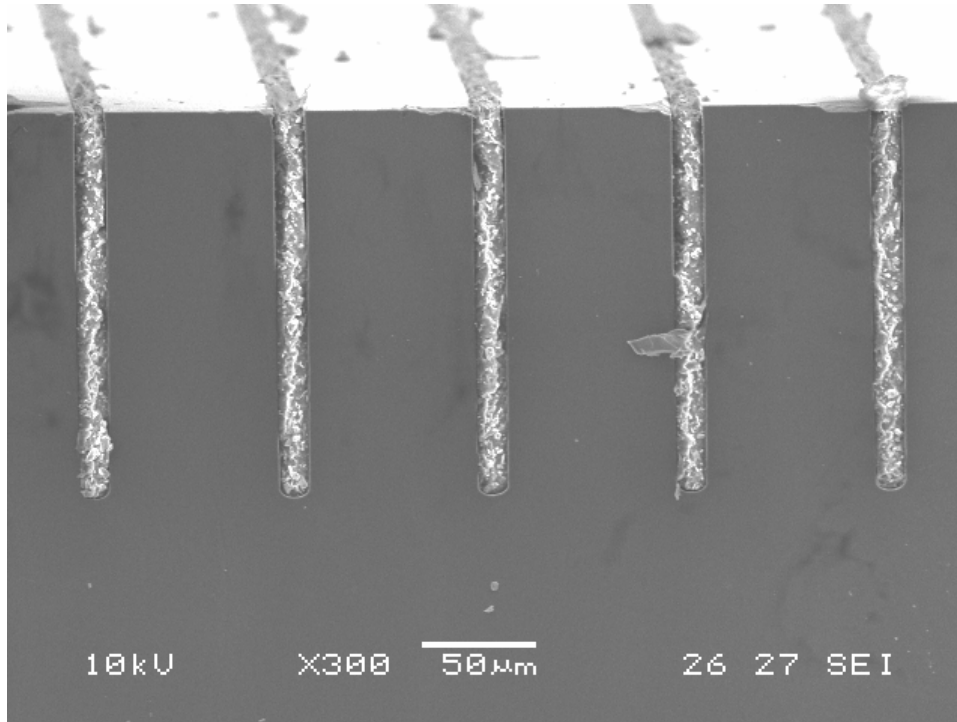


Fig. 4. Scanning Electron Microscopy Micrograph showing a cross-sectional view of a broken silicone rubber remaining in silicon wafer trench

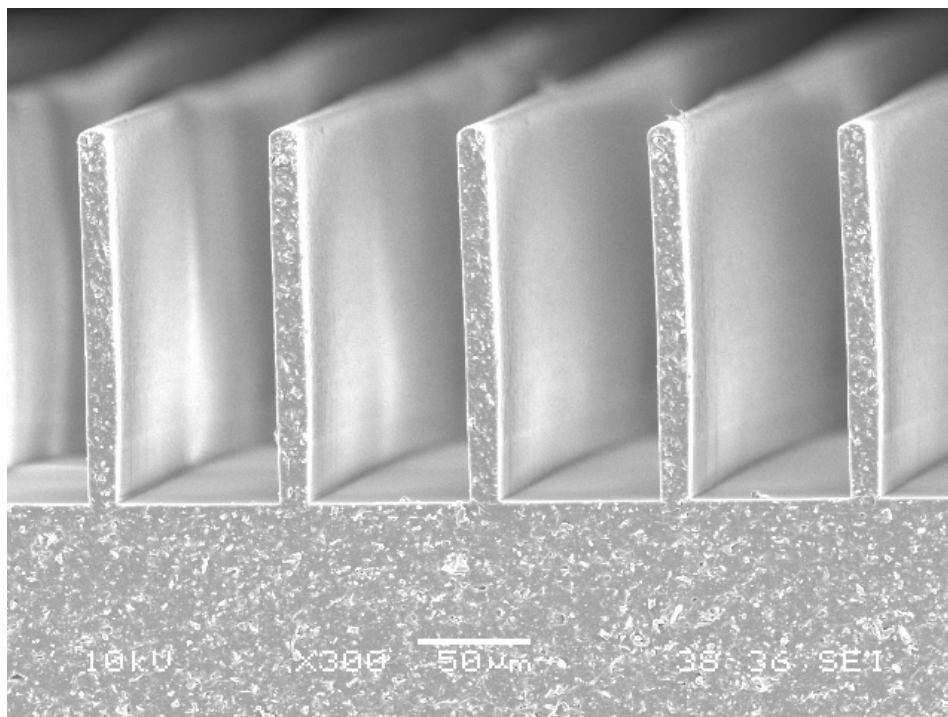


Fig. 5. Scanning Electron Microscopy Micrograph showing a cross-sectional view of a successfully replicated silicone rubber microstructure