# Shrinkage of SU-8 microstructures during carbonization

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## Abstract:

SU-8 is a negative photoresist that is widely used as a precursor to carbon in the fabrication of 3D carbon microstructures. These microstructures are used in applications including sensors, manipulators and batteries. The SU-8 structures are usually made using photolithography and heat treated to high temperatures in an inert atmosphere to achieve carbonization. The shrinkage that results during carbonization affects the design of devices where these structures are used. In this work we studied the shrinkage during carbonization. We emphasized the impact of 1) carbonization protocol and 2) geometry and shape of the SU-8 precursor. Using statistical analysis with ANOVA, we concluded that the geometry of the structure, pyrolysis temperature and pyrolysis atmosphere play a major role in determining the shrinkage of the SU-8 structures. We did not observe a statistically-valid impact from changes in dwell times and heating rate. Based on these results, we present a series of relations to help predict the shrinkage of SU-8 microstructures during carbonization, and facilitate the design of carbon 3D microstructures in different fields.

## 1. Introduction:

It is well known that glass-like carbon, widely known as glassy carbon, is an excellent electrode material given its electrochemical stability and biocompatibility [1,2]. Carbon MEMS (C-MEMS) is a set of methods to derive glass-like carbon micro-structures by pyrolysis of patterned organic polymers. In contrast to pyrolyzed photoresist films (PPF) [3,4], C-MEMS emphasizes the derivation of 3D microstructures. Such structures have enabled a myriad of applications such as biosensors [5,6], electrochemical sensors [7–9], fuel cells [10], batteries [11–14], micro capacitors

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[15,16], and cell sorting and manipulation using dielectrophoresis (DEP) [17-22] and electroosmosis [23]. SU-8, a negative photoresist, is a carbon precursor that is widely used in the fabrication of carbon microstructures using the C-MEMS technique. Although other precursors can also be used to make planar films, such as positive tone photoresists like AZ and Shipley products, SU-8 is the material of choice when fabricating high aspect ratio structures with height above 10 µm [24]. Photolithography, or the patterning with light, is a well-established technique to pattern SU-8 since it enables flexibility and reproducibility in dimensions and shapes [25-27]. Once fabricated, the SU-8 microstructures are pyrolyzed, or heat treated in an inert atmosphere, to derive glass-like carbon [28–30]. The resultant glass-like carbon is an excellent electrode material since it is impermeable to gases, extremely inert and electrochemically stable [1,31]. As expected, the SU-8 original shapes shrink during carbonization. This shrinkage has been shown to be reproducible for specific dimensions of the precursor SU-8 structure and the carbonization protocol [32]. Hence, once shrinkage is characterized one may implement a production process. However, there are no guidelines that allow for the *a priori* design of carbon microstructures. To this end, here we focus on elucidating the impact of 1) heating protocol and 2) geometry and shape of the SU-8 precursor on the shrinkage of SU-8 microstructures during carbonization.

SU-8 shrinkage was initially reported when studying films. Previous works reported a slight increase on shrinkage as the temperature increased from 600 to 1000°C [33,34]. The effect of pyrolysis atmosphere was studied by Ranganathan et al, who reported that vacuum produces the least shrinkage, while nitrogen generally produced the most shrinkage. These authors also showed the shrinkage to depend on temperature [35]. The reported studies characterizing shrinkage of SU-8 microstructures are few; although different authors have reported a strong and repeatable dependence of the shrinkage of cylindrical structures on the structure height and aspect ratios of the SU-8 precursor [32,36–39]. Recently, we reported on the importance of degassing on the shrinkage of SU-8 microstructures [40]. We showed how degassing through the top surface of the structure leads to shrinkage in height, while degassing on the lateral surface originates shrinkage in the footprint of the structure. Hence, the relation between the height and lateral surface determines the total shrinkage of the structure. For example, a structure with high aspect ratio will shrink less in height than a structure with lower aspect ratio. Such findings added to the body of knowledge about the impact of degassing on the shrinkage of polymers [41,42].

Here we contribute a methodical study of the shrinkage of SU-8 microstructures during carbonization. We aim at elucidating the dependence of shrinkage on the dimensions and shape of the precursor, as well as pyrolysis conditions. We used statistical analysis based on Analysis of Variance test (ANOVA) with the p-value 0.01 and Tukey's Honest Significant Difference test (HSD) for comparison of shrinkage for multiple parameters. Our goal is to advance the understanding of shrinkage of SU-8 micro-structures and enable a design tool for 3D carbon micro-electrodes. This is important given the number of demonstrated and potential applications of carbon microstructures derived from SU-8.

#### 2. Materials and Methods

#### 2.1 SU-8 Photolithograpy

We fabricated SU-8 (Gersteltec, Switzerland) microstructures of different cross sections (circle, square, triangle and hexagon), nominal height  $H(10, 50, \text{ and } 100 \,\mu\text{m})$  and characteristic dimension D (10, 20, 30, 40, 80 and 160  $\mu\text{m}$ ) as detailed in Table 1. Cylindrical posts with varying characteristic dimension as detailed before but with a set height of 300  $\mu\text{m}$  were also fabricated. The fabrication of all these structures on a silicon/silicon oxide substrate was optimized (data not shown) and detailed in Table 2.

#### 2.2 Pyrolysis

The SU-8 microstructures were pyrolyzed in an inert atmosphere using a quartz tube furnace (TF1400 Across International, New Jersey, USA). The details of the carbonization protocols are summarized in Table 1. The carbonization protocol featured five stages: (i) heating from room temperature to 300°C with a heating rate of 5 °C/min; (ii) a dwell time of 30 minutes at 300 °C to allow for residual oxygen to be evacuated from the chamber; (iii) a temperature ramp from 300 °C to the final temperature with a specific heating rate; (iv) a dwell at the final temperature to complete carbonization; and (v) cooling to room temperature with a cooling rate of 5 °C/min. We varied the heating rates in step (iii) from 2, 5 and 10 °C/min to study the effect of heating ramp on shrinkage. Final temperatures in step (iv) were 600 °C, 900 °C and 1150 °C. In order to study the effect of dwell time, we studied 0, 1.25, 6 and 12 hours at 900 °C. The effect of heating atmosphere was investigated by using vacuum (pressure = -762 torr =-30 in of Hg) or nitrogen atmospheres (760 torr (29.92 in of Hg) at a flow rate of 0.005 m<sup>3</sup>/min in a tube furnace of 140 mm inside

diameter) at 900 °C. In this study we used 900 °C as the pivot final temperature given the wide application of carbon structures obtained at this temperature [37,38,43–45]. We could not study temperatures beyond 1150 °C due to experimental limitations imposed by the thermal stability of the quartz tube. Thermogravimetric analysis (TGA) was conducted for SU-8 posts using a TGA Q5000 system (TA Instruments, Delaware USA). The sample was heated in a nitrogen environment at 5°C/min initially to the temperature of 300°C, where it was held constant for 30 minutes, and further to the temperature of 1000°C, where it has held for 75 minutes before cooling down naturally. Due to system limitation, the temperature could not be increased beyond 1000°C.

Table 1. The geometry section details the different shapes used in this work as well as their dimensions. The pyrolysis section summarizes the values tested for different process variables.

| Parameter                | Value                                     |   |   |                |  |  |  |  |  |  |  |
|--------------------------|---|---|---|----------------|--|--|--|--|--|--|--|
| Geometry                 |   |   |   |                |  |  |  |  |  |  |  |
| Shape                    | D<br>Circle                               | Image: Difference of the second se | D | <b>Hexagon</b> |  |  |  |  |  |  |  |
| Nominal                  | 10, 50, 100, 300                          |   |   |                |  |  |  |  |  |  |  |
| Height, $H(\mu m)$       |   |   |   |                |  |  |  |  |  |  |  |
| Characteristic           |   |   |   |                |  |  |  |  |  |  |  |
| Dimension, D             | 10, 20, 30, 40, 80, 160                   |   |   |                |  |  |  |  |  |  |  |
| (μm)                     |   |   |   |                |  |  |  |  |  |  |  |
| Pyrolysis                |   |   |   |                |  |  |  |  |  |  |  |
| Temperature              | 650, 000 and 1150                         |   |   |                |  |  |  |  |  |  |  |
| (°C)                     | 030, 900 and 1130                         |   |   |                |  |  |  |  |  |  |  |
| Atmosphere               | Nitrogen(760 torr) and Vacuum (-762 torr) |   |   |                |  |  |  |  |  |  |  |
| Heating Rate<br>(°C/min) | 2, 5, 10                                  |   |   |                |  |  |  |  |  |  |  |

| Dwell Time | 0 1 15 6 12   |
|------------|---------------|
| (hours)    | 0,1.13, 0, 12 |

Table 2: Photolithography parameters to fabricate cylindrical posts of SU-8. The first step during spin coating was used to coat the substrate with photoresist. The thickness of the layer was obtained thanks to the speed and spin time used in step 2.

| Height<br>of Post<br>(µm) | Shapes  | Typ<br>e of<br>SU-8 | Spin Coating |                              | Soft                                  |  | PEB*                              | Develop              |                                   |
|---------------------------|---|---------------------|--------------|------------------------------|---------------------------------------|--|-----------------------------------|----------------------|-----------------------------------|
|                           |   |                     | Step         | Speed<br>(rpm <sup>*</sup> ) | Time<br>(s)                           | Bake at<br>95 °C<br>(min)                                    | Exposure<br>(mJ/cm <sup>2</sup> ) | at<br>95 °C<br>(min) | in<br>PGMEA <sup>*</sup><br>(min) |
| 10                        | Cylinders   | GM<br>1060          | 1            | 500<br>2500                  | 5<br>40                               | 30   | 225<br>(Hard<br>contact)          | 20                   | 3                                 |
| 50                        | Cylinders,  | GM<br>1075          | 1            | 500<br>3000                  | 5<br>100                              | . 45   | 165<br>(Hard<br>contact)          | 35                   | 6                                 |
| 50                        | Cylinders,<br>squares,<br>50 triangles<br>and<br>hexagons | GM<br>1075          | 2            | 1700<br>2700                 | 100<br>For<br>edge<br>bead<br>removal | At 90°C<br>for 30<br>min and<br>at<br>130°C<br>for 15<br>min | 200<br>(Soft<br>Contact)          | 25                   | 6                                 |
| 100                       | Cylinders   | GM<br>1075          | 1            | 500<br>1700                  | 5<br>100                              | . 45   | 195<br>(Hard<br>contact)          | 35                   | 8                                 |
| 300                       | Cylinders   | GM<br>1075          | 2            | 300<br>600                   | 50<br>40                              | for 30<br>min and<br>at<br>130°C<br>for 90<br>min            | 200<br>(Hard<br>contact)          | 90                   | 16                                |

\*Notes: rpm= revolutions per minute, PEB= post exposure bake, PGMEA= Propylene glycol methyl ether acetate

# 2.3 Characterization

The characteristic dimension D of the SU-8 and carbon structures were analyzed using optical microscopy (Nikon Eclipse LV100) and the native Nikon NIS Elements BR software. The characteristic dimension was measured at the top surface of the structure. The nominal height H was measured using a surface profilometer (Tencor Alpha Step 200) as the difference between the height of the wafer and the elevation at the center of the structure. The tip radius of the probe of the profilometer was 1.5  $\mu$ m and the resolution of this instrument as reported by the manufacturer was 5 nm in the micron mode. Height was also measured at the edges of the structure and is used for characterizing the sagging behavior of the structure, which is essentially the difference between the structure height at the center and at the edges of the top surface. At least 8 structures were measured for each data point reported in the results section (n=8). The maximum standard deviation from these measurements was 1.5  $\mu$ m for lateral and 1.8  $\mu$ m for height measurements.

Such measurements allowed for the calculation of surface area, volume, and aspect ratio (H/D) for all structures before and after pyrolysis. The surface area was calculated as the sum of the top and the lateral surfaces, which are the only ones available for degassing. Hence, the surface area of the structure that is attached to the substrate was not considered.

# 2.4 Data Analysis

The percentage shrinkage was calculated using Equation 1, where the dimension can either be the height or diameter of the microstructure. The reported data points are the average values of at least 8 measurements. Error is reported as standard deviation.

$$\% Shrinkage = \frac{Dimension \ before \ pyrolysis - Dimension \ after \ pyrolysis}{Dimension \ before \ pyrolysis} * 100$$
(1)

A surface area ratio (SAR) was defined using Equation 2. SAR is necessary since neither the characteristic dimension D or height H are enough to characterize the surface area of a structure.

Furthermore, the *SAR* used here for all microstructures considers the surface area that is available for degassing. Hence, the surface of the structure on direct contact with the substrate was not considered.

$$Surface Area Ratio (SAR) = \frac{Lateral Surface Area}{Top Surface Area}$$
(2)

The factors considered here for the study of shrinkage were the *SAR*, shape of cross section, temperature of pyrolysis, pyrolysis atmosphere, heating rates and dwell times of the pyrolysis process. A statistical analysis based on Analysis of Variance (ANOVA) and Tukey's honest significant difference (HSD) test was performed to determine the impact of each of these factors on shrinkage. The procedure is explained in Supplementary Information. Briefly, ANOVA was used here to determine the contribution of different parameters for shrinkage of the same structure. If results of ANOVA indicated that the considered factor, for example pyrolysis temperature, affected the shrinkage of the posts, then the shrinkage obtained at different temperatures was analyzed using Tukey's HSD. Tukey's method provided the tools to identify which temperature from the analyzed values gave a statistically different shrinkage value.

Three categories of *SAR* were used and one ratio in each category was selected. The categories used were: a low value of *SAR* (<1), representing a short structure; a high *SAR* (>10), representing a tall structure; and an intermediate SAR. For example, the SAR values 0.60, 2.57 and 12.49 were selected in the three categories for the study of dwell time. It is important to note that different shapes did not have the exact same *SAR* values. Hence the closest possible values between them were selected for analysis. For example, structures with cross section of hexagon with the *SAR* value of  $2.15\pm0.84$ , square with *SAR* value of  $1.87\pm1.07$  and circle with *SAR* value of  $1.80\pm0.23$  were grouped together.

## 3. Results and Discussion:

## 3.1 SU-8 Photolithography

The results from the fabrication of SU-8 microstructures are shown in Figure 1 when plotting the designed vs. the fabricated aspect ratio. The structures were fabricated as designed as long as the

aspect ratio (AR) was less than 6. Posts with square cross section were fabricated slightly bigger than fabricated at AR values between 6 and 10. In contrast, circular posts were fabricated slightly smaller than designed in this same range; triangles and hexagons display a significant deviation. At AR>12, the deviation between designed and fabricated is rather significant for hexagons and circles. These fabrication results were obtained using the optimized parameters of Table 2. We increased the values for energy dose delivered to the resist during exposure as well as the baking times after exposure when compared to those recommended by the vendor (Gersteltec, www.gersteltec.ch). Hence, we assumed the SU-8 microstructures fabricated here were fully cross-linked. This is an important assumption since partially cross-linked SU-8 structures have been shown to deform during heat treatment.[46] Further photolithography optimization is necessary for structures with AR>12, but this is out of the scope of this paper. The dimensions of SU-8 microstructures used in the rest of this current work were those of the fabricated structures.



Figure 1. Carbon structures with (a) circular, (b) square, (c) hexagonal and (d) triangular cross section. The base of the structures featured a curved profile due to restricted shrinkage of the SU-8 which remains adhered to the substrate throughout the carbonization process (insert Figure 1 A).

(e) Results for fabricated aspect ratio in comparison to designed aspect ratio for different structures.

## 3.2 Dependence of shrinkage on geometry:

Examples of carbon structures obtained from SU-8 are shown in Figure 1. Note that the shrinkage was not uniform throughout the height of structures. A curvature at the base of all structures resulted due to the fact that the SU-8 structure was well adhered to the substrate, which restricted shrinkage at the base. This curvature exists in the region within 10 um from the substrate and had been reported by us and other authors before [9,43,47]. This curvature is expected to change according to the choice of substrate due to the difference between the coefficient of thermal expansion of the substrate and the morphing material from SU-8 to carbon. This curvature disappears when carbonizing free-standing SU-8 structures[48]. After this curvature, the profile is uniform throughout the height of the structure. Sagging on the top surface was also detected and is discussed below. Connecting wires between structures can be seen in some cases, which result when the gap between structures is small and exposure dose is optimized [49].

# 3.2.1 Effect of Surface Area Ratio (SAR)

The percent shrinkage of the characteristic dimension D for cylinders with respect to the logarithm of *SAR* is shown in Figure 2a. Low values of log (*SAR*) denote structures with low aspect ratio. In this case shrinkage in H (Figure 2b) is considerably higher than shrinkage in D. This is because degassing occurs mostly through the top surface. A similar trend was observed in previous works where a low shrinkage in linewidth and a high shrinkage in thickness was seen for low aspect ratio structures and films [33,50–52] As the *SAR* value increases, the shrinkage in H decreases and the shrinkage in D gradually increases. The solid vertical line marked in Figure 2a-c indicates the SAR value of 1. At this line, the lateral and top surface area are equal. Beyond this, the lateral surface area becomes dominant. As the *SAR* value increases further, the lateral surface area becomes excessively dominant for degassing. Hence, the lateral surface area becomes the preferred path for degassing, which results in a gradual increase of the shrinkage of D. With an increase in *SAR, the* top surface area plays a secondary role in degassing thus resulting in the gradual decrease of shrinkage of H. Curve fitting was employed to derive relations that describe this behavior for Dand H. Equations 3 and 4 offer a quantitative relation between *SAR* and percentage shrinkage in D

and H respectively. For SAR values greater than the studied values, the shrinkage in D is expected to increase gradually and the shrinkage in case of H is expected to decrease gradually.

Based on the trend observed in Figure 2c we hypothesize that shrinkage in D for lower values of log (*SAR*) than those shown here will further reduce, and the shrinkage of H will gradually increase. Such behavior is similar to that seen in the case of thin SU-8 films.[33] These results might differ slightly depending on the SU-8 manufacturer, but the trend reported here is expected to be the same. This expectation is based on previous observations with SU-8 procured from MicroChem [32].

% Shrinkage in 
$$D = (51.28 \pm 1.32) - (16.61 \pm 2.14) * \exp(\frac{\log(SAR)}{-(0.46 \pm 0.07)})$$
 (3)

% Shrinkage in 
$$H = (50.73 \pm 1.88) + (19.98 \pm 2.22) * exp(\frac{\log(SAR)}{-(0.47\pm0.08)})$$
 (4)

#### 3.2.2 Impact of Shape

We characterized the shrinkage in *H* and *D* for the different shapes presented above. Results are presented in Figure 2a and b for *H* and *D* respectively. We also plotted results from Amato et al [37] who characterized the shrinkage of cylinders with 1.4  $\mu$ m diameter and 11  $\mu$ m height.

Tuckey's test analysis for selected shapes (marked by blocks in Figure 2a,b) indicates that the shrinkage for different cross sections does not show a statistically significant difference as long as the *SAR* is similar. Thus, the cross sectional shape was not seen to play a role in determining the shrinkage for posts. Equation 3 for percent shrinkage in D and Equation 4 for percent shrinkage in H are valid for the shapes considered in the range of area ratios plotted in Figure 2.



Figure 2: The effect of shape on shrinkage: a) The plot shows the shrinkage in characteristic dimension D for posts with different cross sections. The blocks show the points that were studied in the statistical analysis. Using statistical analysis using Tuckey's test, it is proved that the shape does not affect the shrinkage significantly as long as the area ratio for different posts is the same. The solid vertical line indicates the SAR = 1 or the value where lateral and top surface area are equal. b) This plot shows the shrinkage in height for different cross sections: hexagons, squares and triangles as superimposed on the graph for shrinkage in height in case of cylinders. The blocks show the points which were studied in the statistical analysis. The shrinkage values for the posts fabricated by Amato et al. [37] are also plotted in the figure. c) The plot shows the variation of diameter and height for the cylindrical posts with respect to the logarithm of *SAR*. The shrinkage in diameter increases with the increase in the ratio and the shrinkage in height decreases with the

increase in ratio. Curve fitted to the diameter has the adjusted R-squared value of 0.95 and the curve fit for the shrinkage in height has the adjusted R-square fit value of 0.90.

#### 3.2.3 Sagging on Top surface of carbon structures

Sagging at the top surface was observed on carbonized structures as shown in Figure 3 a, b, c. Such sagging was not observed in the SU-8 structures. The edges of short carbon posts are seen to protrude compared to the central region of the top surface. The dependence of sagging on the top surface area for different shapes and as percentage of H after pyrolysis (nominal height) for varying log (*SAR*) are plotted in Figure 3 d and e respectively. Height measurements were done with a Tencor Alpha Step 2 featuring a tip radius of 1.5 um and expected resolution of 5 nm in micron mode. Sagging decreases with the top surface area for any given shape, i.e. circles, triangles, squares. Sagging decreases as log(SAR) increases. As *SAR* is proportional to the aspect ratio, sagging decreases with an increasing aspect ratio. We hypothesize that the sagging phenomena occurs due to the residual stresses developed in the sample during degassing. Such phenomena is observed during shrinkage at different instances with polymers [53,54].Residual stresses appear as tensile forces at the surfaces of the structure as it attempts to shrink. Similar behavior is also observed in other polymers during shrinkage [55,56].

For a SAR<1, the top surface area is larger than the lateral surface area and degassing primarily happens through the top surface. Hence, residual stresses will primarily appear at the top surface, resulting in increased sagging at the top surface. For structures with *SAR* >1, degassing primarily happens through the lateral surface area, leading to decreased sagging on the top surface.

In the case of cross sections containing vertices such as squares, hexagons and triangles, we hypothesize that the stress develops at these vertices along with the edges. Because of this, the region near the vertices shrinks at a different rate than the edges and the center of the structure. The center develops sagging, whereas the vertices look protruded compared to the edges. For example, in the case of a post with triangular cross section, the top surface shows three different height levels. As the structure shrinks, the central region develops sagging. The edges also show sagging ( $\sim 1\mu$ m) as compared to the vertices. This indicates that the center, edges and vertices all shrink at different rates. Ongoing work is on characterizing the difference in the shrinkage of vertices and edges to assess their effect on the sagging of shapes other than circles.

An empirical relation to predict the sagging as a percentage of nominal height was obtained using curve fitting and presented here as Equation 5. This equation is valid in the range of *SAR*s studied in this work.

Sagging as a percentage of nominal height = 
$$56.92 * \exp\left(\frac{-\log(SAR)}{0.60}\right) - 21.22$$
 (5)



Figure 3. a-c) Cylindrical posts with height 10  $\mu$ m, 50  $\mu$ m and 100  $\mu$ m after pyrolysis are shown in the figure with corresponding post profile. The inset figures show the height profile measured by the profilometer. The 10  $\mu$ m post shows high sagging at the top whereas negligible sagging is observed at the top of 100  $\mu$ m post. d) The plot shows the sagging obtained for different structures as a function of top surface area. Sagging increases with the increase in top surface area for any given shape. e) The graph shows the sagging caused in the top surface of the posts as a percentage

of the post height. The amount of sagging reduces with the increase in post height as seen in the graph. The observed sagging was similar for posts of different cross sections.

## 3.2 Dependence of shrinkage on pyrolysis conditions:

## 3.2.1 Final Temperature

It is known that carbonization of an organic polymer occurs in several stages [57–60]. For most bulk materials, the initial stage is the dehydration and elimination of halogens below 500° C. Above 500°C, hydrogen, oxygen and nitrogen are eliminated and the coalescence of polymer chains results in volume shrinkage. Above 800°C, pores in the structure gradually disappear and aromatic networks get interconnected. Annealing above the temperature of 1200°C allows for the gradual elimination of any structural defects, the elimination of the last vestiges of hydrogen, and the evolution of any further impurities [32,57,61]. Thus, the primary shrinkage due to degassing of volatile products other than hydrogen compounds happens at temperatures around 600°C. After this temperature, the shrinkage can be attributed to condensation of aromatic chains, pore closing and removal of hydrogen.

The shrinkage that results when heating SU-8 microstructures with different *SAR*s to different final temperatures in the range  $650-1150^{\circ}$ C is shown in Figure 4a and b. Low aspect ratio structures shrink more in their *H* than on their *D*. Shrinkage of both *H* and *D* seems to slightly depend on heating temperature. The ANOVA test for different temperatures proved that the difference between shrinkage at different temperatures was statistically significant. This prompted us to perform the Tuckey's test on the data set to find out which temperature resulted in a different shrinkage. The data points used are enclosed by the rectangles shown in Figure 4a and b. Tuckey's test indicated that the average shrinkage different for all the three temperatures. Hence, shrinkage shows a dependence on final pyrolysis temperature.

The rate of change of shrinkage for selected *SARs* is shown in Figure 4 c. The slopes of the different curves are similar. However, the shrinkage in *H* for *SAR*=0.57 is much higher than shrinkage of *D* of the same structure. As the *SAR* value increases, the shrinkage in *H* and *D* show a similar value. Irrespective of the *SAR* value, the rate of change of shrinkage with respect to temperature is similar for all the considered *SARs*. Thus, the effect of temperature is independent of the *SAR* value. As temperature increases, shrinkage of the structure occurs due to interconnection of aromatic rings and removal of the last vestiges of gases. The slope for the increase in shrinkage from 650°C to

1150°C is around 0.01%/°C. Hence, by knowing the shrinkage at the temperature of 900°C (Equations 3 and 4) and considering the slope of the curve in Figure 4c, the shrinkage at other temperatures in the range 650-1150°C can be predicted. The average increase in shrinkage when using temperatures between 650-1150°C for all *SARs* tested here was 3.45±0.93 % in diameter and 4.92±1.17% in height. The TGA results (fig. 4d) show a rapid weight loss occurring at the temperature of 300°C, where the temperature is held constant for 30 minutes. This can be related to the weight loss occurring due to the complete evaporation of the solvent. The weight loss between 300°C to 600°C can be attributed to the elimination of halogens followed by nitrogen, hydrogen and oxygen as discussed previously. Beyond 600°C, the weight loss becomes gradual to the temperature of 800°C. Beyond this temperature, the weight loss decreases further due to the elimination of hydrogen and the formation of interconnects in the aromatic structure. These results are similar to the results by previous works [34,46,62].

This shows that the increase in shrinkage in diameter and height are comparable and do not depend on the *SAR*. Here we could only test a narrow temperature range and further studies are necessary to characterize shrinkage beyond 1150 °C. Further shrinkage due to degassing is expected above 1150 °C [32,63].



Figure 4: a) The figure shows the diametrical shrinkage in cylindrical posts for the pyrolysis temperature of 650, 900 and  $1150^{\circ}$ C. The blocks indicate the cases which were considered for statistical analysis. b) The shrinkage in height for cylindrical posts pyrolysed at different temperatures is shown in this figure. The blocks indicate the cases which were considered for statistical analysis. c) The plot for percent shrinkage in diameter (a) and percent shrinkage in height (b) with respect to the change in temperature indicates a gradual increase in the shrinkage. The rate of increase in shrinkage or the slope of the graphs, remains same with the change in *SAR* as shown in the figure. d) TGA results showing the weight loss as temperature increases.

#### *3.2.2 Dwell time at final temperature*

Dwell time refers to the time the sample is maintained at the final temperature. We tested different dwell times (0, 75 min, 6 and 12 hours) when carbonizing cylindrical structures at 900 °C. Dwell times do not show a statistically valid change in shrinkage (Figure 5d), indicating that increasing the carbonization time does not have an effect on shrinkage. Previous work by Mardegan et al reported that the increase of dwell time from 1 hour to 4 hours resulted in about 10% higher weight

loss at 800 and 900°C [52]. A corresponding change in dimensions was not observed in our results. Further work is required to draw more conclusions on the effect of dwell time.

## 3.2.3 Heating rate

Three different heating rates were implemented in order to elucidate the dependence of shrinkage on heating rate. Results are shown in Figure 5c when carbonizing cylindrical posts. Tuckey's test concluded that varying the heating rate between 2, 5 and 10 °C/min did not yield a statistically valid impact on shrinkage. Hassan et al reported an increase on shrinkage of around 10% when carbonizing SU-8 polymer at 50 °C/min [64]. We could not replicate this condition due to experimental limitations. Sharma et al reported that an increase on heating rate up to 15° C/min leads to the formation of micropores in the carbon structures. The pore size found at the heating rate of 90°C/min is around 10-15  $\mu$ m[65]. We studied the internal structure of the carbon cylinders by fabricating in-situ cross sections of the different carbon structures obtained from SU-8 using ion milling (Focused Ion Beam, nanoDUET NB5000, Hitachi). We did not observe any micropores in the carbon sample derived at a heating rate of 10 °C/min using electron microscopy at magnification 40k. Further characterization of the different samples using a porosity meter are necessary.

## 3.2.4 Pyrolysis Atmosphere

We hypothesized that shrinkage would depend on the evacuation of byproducts from the sample and the heat transfer coefficient of the atmosphere. The byproducts of carbonization would diffuse from the core of the structure to its surface, and such transport would be enhanced by implementing a low pressure environment in the tube [66]. The ability of the gas to conduct the heat to the sample also plays an important role in formation of byproducts and consequent degassing [67]. Previous studies of the pyrolysis of positive photoresist AZ4430 indicated that the shrinkage in the vacuum environment was less than in nitrogen environment due to presence of traces of oxygen in the furnace environment and that this difference increased with the temperature [35]. Lyons et al. compared the shrinkage of HPR-206 photoresist in pure H<sub>2</sub> and pure N<sub>2</sub> atmospheres. The use of an hydrogen atmosphere resulted in about 10% more shrinkage [51]. Based on the values of thermal conductivity and viscosity for Nitrogen and Hydrogen [68–71], we compared the heat transfer coefficient for Nitrogen and Hydrogen. Hydrogen was found to have higher heat transfer

coefficient than nitrogen resulting into higher amount of heat transferred to the sample. Hydrogen also provides a reducing environment for pyrolysis which results in degassing of more carbonaceous material than with nitrogen atmosphere and results into higher shrinkage [72]. Here, we replicated experiments using nitrogen and vacuum.

The results when characterizing shrinkage for different *SAR*s depending on the tube atmosphere during carbonization are shown in Figure 5a-b. The use of vacuum during carbonization yielded a higher shrinkage than when using a nitrogen atmosphere. This difference is statistically valid as determined using ANOVA. The geometry of the structure still plays a significant role, as shown by the different shrinkage of *D* and *H* in low aspect ratio structures with log(SAR) < 1. The increase in the shrinkage of *D* for a given *SAR* between the two atmospheres is  $5.37 \pm 1.24$  %, whereas the shrinkage in *H* only increases by  $2.26 \pm 0.81$ %. This indicates that a change in pyrolysis atmosphere has a greater effect on the lateral shrinkage compared to the vertical shrinkage.

In the case of a vacuum environment, the pressure is expected to be lower than in the case of nitrogen environment. At low pressure, we expect enhanced diffusion of volatile byproducts. In a study for thermal degradation of polyethylene under vacuum and nitrogen environment with 787 torr (31 inches of Hg) pressure, it was observed that the vacuum produces volatiles which are about ten times heavier, indicating that the volatilization is higher in vacuum environment [73]. The formation of volatile byproducts in vacuum also occurs at a temperature lower than in the case of nitrogen [42,74]. Thus we expect that the formation of volatiles occurs at an earlier stage with a vacuum environment. In case of high pressure in the furnace, the rise in temperature can increase the formation of volatile components. This is evident from the fact that the shrinkage in nitrogen environment increases with increase in temperature.

Due to limitations of our equipment, we are currently unable to vary the nitrogen pressure in the furnace. Therefore, this parameter could not be analyzed here. Other authors reported on the effect of pressure on shrinkage when carbonizing different materials. For example, the pyrolysis of bituminous coal in nitrogen atmosphere at high pressure resulted in a decrease of the yield of volatiles [75]; pyrolysis of biomass chars also show evidence of low degassing at high pressure [76]; while a study on the thermal decomposition of polyethylene showed an evidence for decrease in volatiles with increase in furnace pressure [77]. We thus expect the degassing of SU-8 to be

suppressed as the pressure in the furnace increases. Further studies are necessary in this topic.



Figure 5. a-b) Dependence of shrinkage on pyrolysis atmosphere for the shrinkage in diameter and height of the structure are shown in the figures. The shrinkage for vacuum and nitrogen atmosphere show a similar trend, but the shrinkage in vacuum shows a higher value, especially for diametrical shrinkage. c) The cases selected for statistical analysis for heating rates 2, 5 and 10°C/min is shown in the figure. These heating rates do not show statistically significant effect on the shrinkage. d) The cases selected for statistical analysis for dwell times of 0, 1.15 hours, 6 hours and 12 hours during pyrolysis indicate that the shrinkage does not change with the dwell time.

## 3.2.5 A proposed curve fit to predict shrinkage of SU-8 microstructures

The results show that *SAR* is the most important factor in determining the shrinkage of the SU-8 structure. The final temperature and atmosphere during carbonization also play a role.

Below we report three relations that can help in the design of SU-8 structures that will be carbonized. Equations 6, 7, 8 help calculating the percent of shrinkage in characteristic dimension and height, as well as the total height of the carbon posts when taking sagging into account. These equations apply when using process temperature T between 650 °C to 1150 °C in a nitrogen environment at atmospheric pressure.

% Shrinkage in characteristic dimension D =

$$(51.28 \pm 1.32) - (16.61 \pm 2.14) * exp\left(\frac{\log(SAR)}{-(0.46 \mp 0.07)}\right) - 0.01 * (T - 900^{\circ}C)$$
(6)

% Shrinkage in *H*=

$$(50.73 \mp 1.88) + (19.98 \mp 2.22) * \exp\left(\frac{\log(SAR)}{-(0.47 \mp 0.08)}\right) - 0.01 * (T - 900^{\circ}C)$$
(7)

Sagging of posts as a percentage of nominal height at different temperatures,

Sagging as % of nominal height =

$$56.92 * \exp\left(\frac{-\log(SAR)}{0.60}\right) - 21.22 - 0.01 * (T - 900^{\circ})$$
(8)

For calculations of shrinkage when using vacuum during carbonization, a factor of  $5.37\pm1.24$  % must be taken into account for characteristic dimension (Equation 6); and a factor of  $2.26\pm0.81$ % for height to the total shrinkage in *H* (Equations 7 and 8). For example, if the *SAR* value of the structure is 1.80, the shrinkage in *D* at the temperature of  $650^{\circ}$ C in nitrogen atmosphere can be calculated by Equation 6 as  $39.22\pm3.32$ % and shrinkage in *H* is  $57.37\pm1.98$ % using Equation 7. For a vacuum atmosphere, the corresponding shrinkage in *D* will be  $44.59\pm4.56$ % and shrinkage in *H* will be  $59.63\pm2.79$ %

Equations 6 and 7 were used to calculate the shrinkage of structures presented by Amato et al. [37], Sharma et al.[12] and Lee et al. [47]. Results are shown in Figure 6a. Amato et al. used SU-8 obtained from Microresist GmbH (Berlin, Germany) to fabricate carbon posts of 1.4  $\mu$ m in diameter and 11 $\mu$ m um in height. Carbonization was done at a final temperature of 900°C, a dwell time of 1 hour and a heating ramp of 2°C/min. Lee et al. (Figure 6b) used NANO<sup>TM</sup> SU-8 (MicroChem Corp., Newton, MA) for fabrication of mushroom-like shapes and cylindrical posts with height of 54  $\mu$ m and diameter of 300  $\mu$ m. Carbonization was carried out at 700°C with a dwell time of 30 minutes, and a heating rate of 10°C/min. Sharma et al. (Figure 6c) used a carbonization protocol similar to Amato et al. but with a heating rate of 10°C/min. These authors carbonized cylindrical posts with height 80  $\mu$ m and diameter of 15  $\mu$ m.

In the case of Amato et al our equation is effective in predicting shrinkage of the structures with an error of only around 1%. In the case of structures fabricated by Sharma et al. the shrinkage in the diameter was predicted precisely, but the shrinkage in height shows a difference of 10%. In the case of mushroom-like structures fabricated by Lee et al, we are able to correctly approximate the shrinkage in diameter and height of the mushroom stem but not the shrinkage of the cap. Further work will be required to validate Equations 6-8 in predicting shrinkage of more complex shapes.



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Figure 6. The graph shows the predicted shrinkage using Equations 6, 7 and the shrinkage reported in the work by different authors [12,37,47] a) Posts from work of Amato et al.[37] and the predicted values of shrinkage for the structures show agreement. b) Posts from the work of Lee et al. [47] where the shrinkage in the stem of the mushroom structure shows agreement with the predicted value of shrinkage, but the diameter of the cap shows higher shrinkage than the predicted value, mostly due to higher surface area. For the cylindrical structure, the fitted curve predicts the shrinkage in diameter precisely, but the shrinkage in height observed is lower than the predicted value. c) The shrinkage of the posts fabricated by Sharma et al. [12] have shrinkage in diameter similar to the predicted value, but shrinkage observed in the height is more than the predicted value.

## 4. Conclusions and Future work

In our analysis we established the importance of degassing through surface area as a prime contributor for structural shrinkage. The results show that SAR is the most important factor in the basic shrinkage value for the SU-8 structure. A set of mathematical relations were obtained to calculate shrinkage based on SAR. The equations for curve fitting were successfully validated to predict shrinkage with previously published data. As long as the SAR value remains unchanged, the change in the cross section of the structure did not change shrinkage significantly. The effect of heating protocol on shrinkage was also studied. The final temperature and atmosphere during carbonization also play a role in shrinkage. We did not discern any impact on shrinkage from changes in dwell time and heating rate. Based on our results, we conclude that SAR, pyrolysis temperature and pyrolysis atmosphere are the major factors that affect shrinkage. These results were obtained using silicon substrates and taking the necessary steps to maximize the possibility that SU-8 was fully cross-linked before carbonization. These results will likely not be applicable for partially cross-linked SU-8. The shrinkage trends reported here are expected to be similar when using other substrates, as long as such substrate impedes degassing of the material during carbonization. The work presented here is the first methodical study of SU-8 shrinkage during carbonization and there are still gaps to be addressed. These include studying the impact of pressure, degree of SU-8 cross-linking, and exploring other atmospheres. These are necessary towards designing manufacturing processes that yield carbon structures tailored to specific applications.

Future work will be developing a computational model for shrinkage based on the geometry and the varying surface area available for degassing during pyrolysis. In this model, degassing will be modeled as a mass loss, and heat transfer from the pyrolysis atmosphere will be studied along the surface area of the post. This will enable consideration of different heating protocols. A computational model could also consider the fact that the surface area of the structure available for degassing changes as the structure shrinks during pyrolysis. Such model will also enable further study of the residual stresses built in the structure towards characterizing the sagging behavior throughout the structure.

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