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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 [15,16], and cell sorting and manipulation using dielectrophoresis (DEP) [17–22] and electro-osmosis [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

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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, and 100 µm) and characteristic dimension D (10, 20, 30, 40, 80 and 160 µm) as detailed in Table 1. Cylindrical posts with varying characteristic dimension as detailed before but with a set height of 300 µm 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 min 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 h 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^3/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 min, and further to the temperature of 1000 °C, where it has held for 75 min before cooling down naturally. Due to system limitation, the temperature could not be increased beyond 1000 °C.

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 µm 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 µm for lateral and 1.8 µm 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.

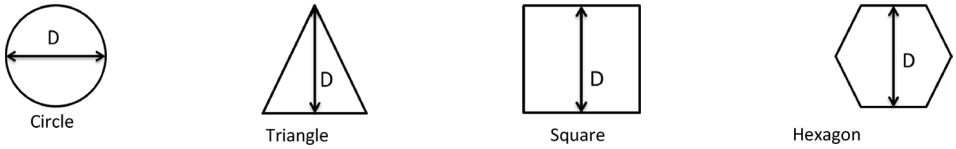
2.4. Data analysis

The percentage shrinkage was calculated using Eq. (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.

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

A surface area ratio (SAR) was defined using Eq. (2). SAR is necessary since neither the characteristic dimension D or height H are

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	
Nominal Height, H (µm)	10, 50, 100, 300
Characteristic Dimension, D (µm)	10, 20, 30, 40, 80, 160
Pyrolysis	
Temperature (°C)	650, 900 and 1150
Atmosphere	Nitrogen(760 Torr) and Vacuum (-762 Torr)
Heating Rate (°C/min)	2, 5, 10
Dwell Time (hours)	0,1.15, 6, 12