Surface Imaging of Cold DC Magnetized Air Plasma Treated Poly(dimethyl siloxane) Surfaces

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The surface morphology of poly(dimethyl siloxane) surfaces treated with cold dc magnetized air plasma had been investigated via scanning electron microscopy. The treatment parameters involved in the study were sample-cathode distance, discharge power, and discharge pressure. The plasma treated PDMS surfaces exhibit a variety of surface structures ranging from cracked film morphology to the presence of disordered buckling and aligned, corrugation depending on the treatment parameter studied.

Keywords—*surface modification, plasma treatment, air plasma, poly(dimethyl siloxane), scanning electron microscopy, EDX analysis*

1. INTRODUCTION

Surface property studies of radiation-treated poly(dimethyl siloxane) (PDMS) surfaces had been a subject of growing interest throughout the years due to the limitless applications of the engineered PDMS surfaces in biomedicine (Rhee *et al.*, 2008) and microfluidic devices (Ren, Bachman, Sims, Li & Allbritton, 2001). PDMS is an elastomer that is characterized to have low glass transition temperature, high oxidative and chemical resistance, optical transparency and chemical inertness (Hillborg & Gedde, 1999). By exposing the elastomeric surface to radiative sources such as plasma, flame and UV light, the physiochemical properties of the PDMS surface can be modified depending on the treatment parameters.

Physical topographical changes of elastomeric surfaces, brought upon by different surface treatment techniques, include the spontaneous formation of complex and ordered surface structures. Bowden, Brittain, Evans, Hutchinson and Whitesides (1998) were one of the first to report that a corrugated surface with micrometer width and peak-to-trough distance were produced simply by depositing metallic thin films onto elastomeric substrates via electron beam evaporation. Chua, Ng and Li (2000) meanwhile reproduced similar disorganized waves via oxygen plasma treatment; waves were brought upon by the buckling of a thin brittle silica-like layer which is formed during the treatment. Different patterning process like photolithography (Tsougeni, Boulousis, Gogodiles & Tserepi,

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2008) and helicon plasma (Gogodiles et al., 2008) were eventually introduced for producing ordered polymer diffraction gratings, and optical sensors.

This study reports similar stochastic patterning and semi-patterning achieved simultaneously by subjecting the PDMS samples through a low power cold dc magnetized air plasma treatment. By just experimenting on how the samples are placed inside the chamber, a corrugated PDMS surface morphology can be achieved. The study however is without complications as there occurred competing mechanisms between cathode sputter deposition and polymer surface modification involved and so the study is led to explore the actual surface morphological changes involved after the plasma treatment process.

2. METHODOLOGY

PDMS samples were prepared by solution casting. A 10:1 Sylgard-184 elastomer base – curing agent (by mass) was mixed and then poured onto a Plexiglas mold with specific dimensions (10.16 cm X 2.54 cm X 0.10 cm). The substrates were cured for a week before the samples were removed from the mold and cut into the specific dimension. The samples were then washed by soap-water solution, rinsed by running tap water and then distilled water and blow-dried by nitrogen gas. The samples were cut into specific dimensions (1 cm X 1 cm X 0.1 cm) and were then mounted on the DP vacuum chamber collimator where it is subjected to a magnetized DC air plasma treatment with base pressures in orders of millitorr.

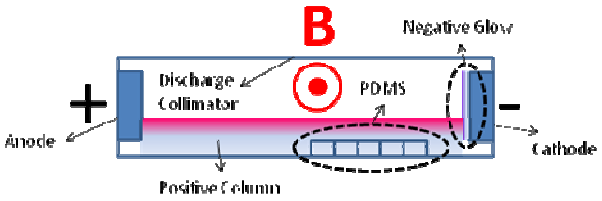

Figure 1. **DC magnetized air plasma treatment of PDMS. Transverse magnetic field was applied across the discharge in order to intensify the positive column of the air plasma having contact with the PDMS.**

The samples were subjected to different treatment parameters such as varying discharge power (10.6, 15.0 and 21.6 watts), pressure (40, 70 and 100 milliTorr), and sample-cathode distance (1, 3 and 5 centimeters). All treatments were subjected to 10 minutes exposure time A base treatment setting (21.6 W, 40 mTorr, 1 cm below cathode) had been set as a comparative basis for the evaluation of different discharge treatment parameters; one parameter was varied while the others were maintained constant. After the discharge treatment, the vacuum system was equilibrated to atmospheric pressure. The samples were blow dried with nitrogen gas before they were stored in air-filled vials. Samples that were characterized under a scanning electron microscope were put in wax paper envelopes to avoid scratches caused by friction.

The JEOL JSM-5310 scanning electron microscope was used to view the surface morphology of the polymer. Samples scanned with the SEM were sputter coated with gold for 30 seconds under 20-30 mA before it was mounted in the stage of the microscope. All of the samples were viewed upon a 15 kV accelerating voltage. Energy dispersive X-ray (EDX) microanalysis was also performed on the samples for the detection of aluminum thin film traces deposited on the plasma treated PDMS surface. Elemental composition of aluminum was compared with the substrate's composition such as Si, C and O.

3. RESULTS AND DISCUSSION

SEM micrographs of an untreated PDMS sample were shown to have a smooth surface (Figure 2.a-c) despite series of surface preparation anomalies. Dirt and other adhering contaminants were observed on the gold coating, and underneath the gold coating as seen from Figure 2.a. The PDMS surface suffered from beam damage as vividly seen on the square mark shown on Figure 2.a and Figure 2.c. This is due to the overexposure of the sample surface to the electron gun which is configured to have high emissive power. Several areas of the untreated PDMS sample suffer from scratches underneath the gold coating as shown in Figure 2.c. This was brought upon by improper handling, mold imperfections and storage of the untreated sample on rough surfaces.

Figure 2. **SEM Micrographs of untreated PDMS samples at a) 1000X b) 3500X and c) 7500X**

At a base discharge setting of 21.6 W power, 40 mtorr discharge pressure and 5 cm sample-cathode distance, a planar film morphology with multiple cracks (Figure 3 – 5, g – i) was formed. Less cracks was seen at 3 cm sample cathode distance (Figure 3.d - f). The micrographs observed were possibly artifacts caused by metal coating deposition. These could occur during the plasma treatment where aluminum, the cathode material, was unintentionally sputter deposited onto the sample surface, and during the sample preparation stage for SEM imaging. Formation of cracks may be due to the low adherence of the gold coating on the polymer and apparently, less cracks was observed at the samples with less sample-cathode distance.

As the sample-cathode distance was decreased to 1 cm, the disordered, wrinkled corrugation, whose widths in the order of micrometers, became apparent as shown in Figure 3.a – c. Bowden *et al.* (1998) and Chua *et al.* (2000) also observed the wrinkled structures despite differences in experimental setups.

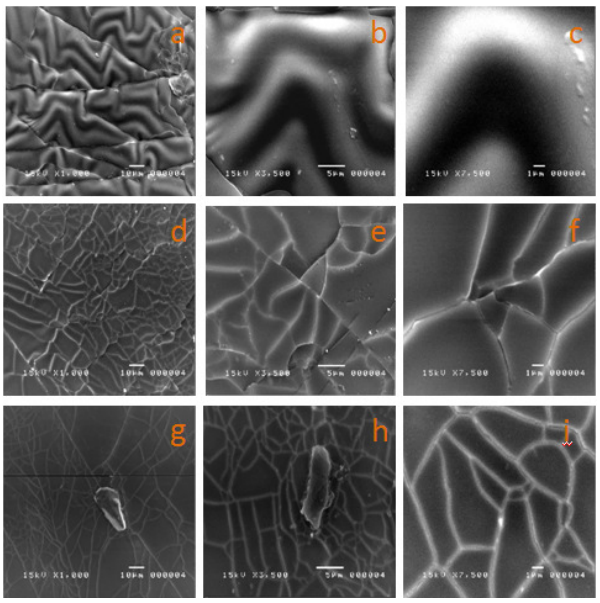

Figure 3. **SEM Micrographs of air plasma-treated PDMS samples subjected at increasing sample-cathode distance. The micrographs represent plasma-treated PDMS surfaces with a distance from the cathode of 1 cm at a) 1000X b) 3500X and c) 7500X, 3 cm at d) 1000X e) 3500X and f) 7500X, and 5 cm at g) 1000X h) 3500X and i) 7500X.**

On the other hand, increasing the discharge pressure lessened the number of interconnected cracks on the sample surface (Figure 4.d – f). However, increasing the pressure to 100 mTorr resulted into a nearly aligned corrugation on the PDMS surface as shown in Figure 4.g – i. The gold film must have covered the undulations that were intended to be observable at lower pressures, since surface corrugation observed at 100 mTorr was barely observed. Crack formation at lower pressures may have been caused by thermal mismatch between the deposited gold film and the substrate surface during sample preparation step for SEM imaging.

Finally, decreasing the discharge power of the processing plasma resulted to a more visible nearly aligned corrugated patterns present on the PDMS as observed in Figure 5.a – f. The corrugation became more predominant at higher discharge power by comparing Figure 5.b and Figure 5.e, with the exception to the sample treated at 21.6 W. The result is in agreement with the results of Chua *et al.* (2000) which indicated that the periodicities and the peak-to-trough distances increases at higher discharge power.

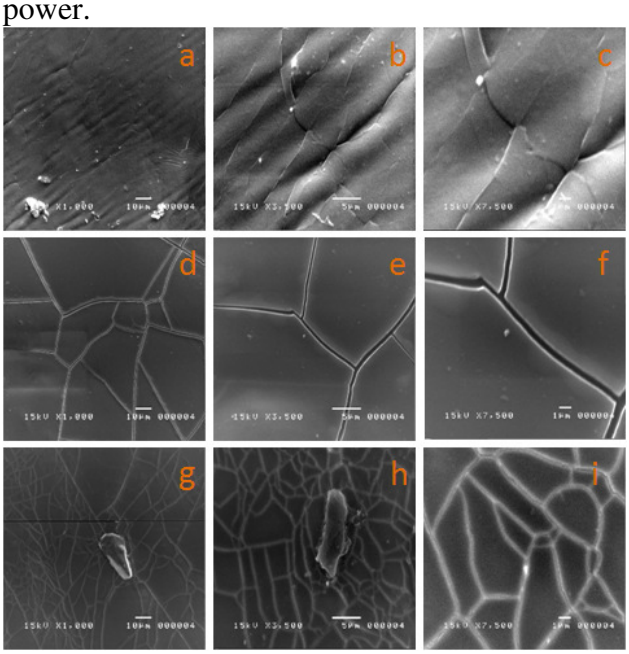

Figure 4. **SEM Micrographs of air plasma-treated PDMS samples subjected at increasing discharge pressures. The micrographs represent plasma-treated PDMS surfaces with discharge pressure of 100 mTorr at a) 1000X b) 3500X and c) 7500X, 70 mTorr at d) 1000X e) 3500X and f) 7500X, and 40 mTorr at g) 1000X h) 3500X and i) 7500X. The sample cathode distance is 5 cm.**

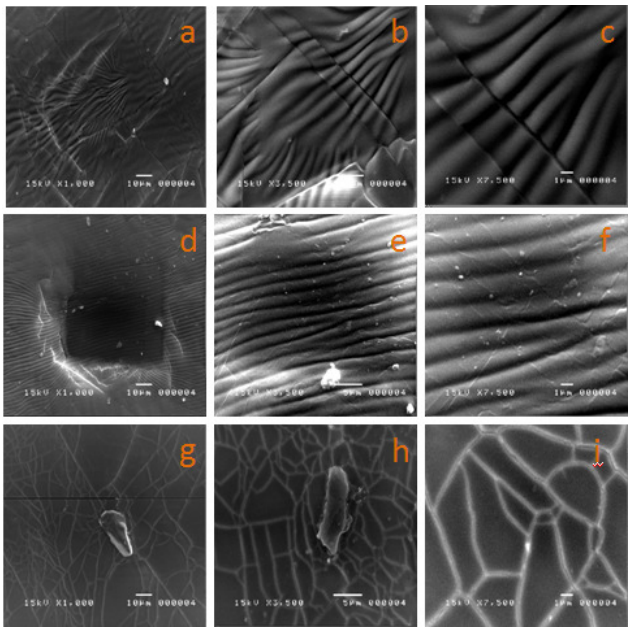

Figure 5. **SEM Micrographs of air plasma-treated PDMS samples subjected at increasing discharge power. The micrographs represent plasma-treated PDMS surfaces with discharge power of 10.6 W at a) 1000X b) 3500X and c) 7500X, 15.0 W at d) 1000X e) 3500X and f) 7500X, and 21.6 W at g) 1000X h) 3500X and i) 7500X. The sample-cathode distance of the samples is 5 cm.**

Changes in the elemental composition of the substrate at different treatment parameters as shown in Table 2 cannot be a direct consequence of magnetized plasma treatment, since the PDMS substrates used in the study were bulk specimens. The variations of the elemental composition of the substrate, not including the relative elemental composition of hydrogen and gold, are caused by how the PDMS is synthesized. During the curing stage, the curing agent is not well-dispersed in the base polymer. Effects of plasma treatment on the relative composition of the sample might have been negligible, since the impinging ions produced from a dc source could only affect the surface and not penetrate to the bulk material.

Table 1.
EDX Elemental Analysis of Aluminum Traces

Plasma Parameter		% Al
Untreated		-0.05
Varying sample-cathode distance (cm) (21.6 W, 40 mTorr, 10 min)	1	0.31
	3	-
	5	0.41
Varying Power (W) (40 mTorr, 10 min, 5 cm)	10.6	0.20
	15.0	0.18
	21.6	0.41
Varying Pressure (mTorr) (21.6 W, 10 min, 5 cm)	40	0.41
	70	0.05
	100	0.03

Table 2.
EDX Elemental Analysis of the PDMS Substrate

Plasma Parameter		% Si	% O	% C
Untreated		45.56	24.61	29.87
Varying sample-cathode distance (cm) (21.6 W, 40 mTorr, 10 min)	1	36.52	33.78	29.39
	3	-	-	-
	5	38.14	25.78	35.67
Varying Power (W) (40 mTorr, 10 min, 5 cm)	10.6	39.87	26.34	33.59
	15.0	39.23	26.15	34.44
	21.6	38.14	25.78	35.67
Varying Pressure (mTorr) (21.6 W, 10 min, 5 cm)	40	38.14	25.78	35.67
	70	28.65	27.15	44.16
	100	38.75	25.83	35.4

The observed surface morphology of the plasma treated PDMS surfaces under different treatment parameters could be superficial; their visibility solely depends on the thickness of the sputter deposited gold thin film coatings. The visible corrugations have heights that bypassed the gold thin film thickness. Nearly aligned corrugations must have existed with the base discharge setting; thick gold coating must have constrained or even have buried the corrugation.

The formation of corrugated surfaces via plasma treatment was brought upon by buckling between the thin brittle silica-like surface layer formed via discharge contact, and the soft PDMS underlayer (Chua *et al.*, 2000). The buckling observed was different from buckling observed in thin film delamination since the silica-like surface was attached on the PDMS underlayer. When subjected to a temperature difference caused by the transfer of energy from the charged gas to the PDMS surface, thermal mismatch between the sandwich layers caused the formation of compressive stresses on the film surface. Compressive stresses increase during quenching by air purging. Buckling then occurs to relieve the built-in stress. The cause of the alignment at different sample-cathode distance in a magnetized plasma source is still unknown and is yet to be investigated in further studies.

The difference in coefficient of thermal expansion is the cause of metallic thin film crack formation on the PDMS surface after plasma treatment. Mattox (1998) explained that coatings on polymer surfaces experience crack formation during rapid cooling which occurs after coating. In the context of the study, this is brought upon by the difference of thermal expansion coefficient between hard coatings (metals, ceramic) and its silica-like thin film surface layer. Conditions which led to predominant microcracking are yet to be investigated.

Cracks observed on the PDMS surface may be complementarily caused by poor adhesion of the gold film to the polymer surface. The samples had aged long enough after plasma treatment which caused the surface to revert back to its hydrophobic state. Poor adhesion of the gold coating leads to thin film delamination which upon minute surface expansion due to heat would create cracks. Charging on the cracks as seen on the micrographs with surface cracks implies that the PDMS surface was exposed.

4. CONCLUSION

The surface morphology of cold DC magnetized air plasma treated PDMS had been investigated in terms of varying sample-cathode distance, discharge pressure and discharge power. Cracked island films and corrugation were the two types of surface morphologies observed on different plasma treated PDMS surfaces. Cracks brought upon by gold deposition was observed on samples with high discharge power, and low discharge pressure surface waves were observed on samples treated with low discharge power and low discharge pressure, where sputter deposition is

higher. Corrugation was observed at high sample-cathode distance, high discharge pressure and lower discharge power where sputter deposition is minimal. It was possible that the corrugation exist under the gold thin film. Thick metal coating must have also buried the developed corrugated surfaces, which subsequently brought upon cracking in the process.

It is highly suggested that more trial parameters needs to be instilled in further studies to have a better analysis on the dependence of plasma parameters of the treatment configuration on the resulting thin film morphology. So far, not much trend can be derived from a small number of samples tested for one type of parameter. Also the substrate thickness must be lessened up to the 100 nm range to make the relative elemental composition of the substrate significant, if a more in-depth EDX analysis would be pursued.

However, it is best recommended to use more appropriate methods for surface characterization apart from EDX analysis. Most researchers use X-ray photoelectron spectroscopy and X-ray diffraction to determine the elemental and chemical composition of the plasma-treated surface. Surface morphology investigation of the plasma-treated PDMS surface is more detailed when atomic force microscopy is enforced. The advantage of AFM over SEM imaging is that surface morphology investigation of non-metallic samples can be done without the need for metal coatings. Furthermore, more information can be obtained using AFM such as periodicities, peak-to-trough distances and other details which quantitatively described the patterned surface. Lastly, ellipsometry studies can elucidate the refractive index of the plasma-treated surface.

The study had also described how alignment of the corrugation changes with increasing sample-cathode distance. Samples near the negative glow (1 cm sample cathode distance) tend to developed disorganized surface wrinkage while samples exposed to the positive column (5 cm sample-cathode distance) attained nearly aligned linear corrugations. The conditions for the increasing alignment of waves need further investigation. This is to welcome the possibility of patterning polymers via plasma treatment without necessarily inputting high discharge power, thereby decreasing energy generation costs in plasma surface modification of elastomers.

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