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Effect of Thermal and Deposition Processes on Surface Morphology, Crystallinity, and Adhesion of Parylene-C

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Neural interface devices have been developed for neural science and neuroprosthetics applications to record and stimulate neural signals. Chemical-vapor-deposited Parylene-C films were studied as an encapsulation material for such an implantable device. The surface morphology of an implant affects its biocompatibility; thus, the Parylene-C surface morphology was investigated as a function of the precursor sublimation rate by atomic force microscopy. We found that high precursor sublimation rates resulted in slightly higher root-mean-square surface roughnesses (from 5.78 to 9.53 nm for deposition rates from 0.015 to 0.08 g/min). The crystallinity affects the physical properties of semicrystalline polymers, and various heat treatments were found to modify the crystallinity of Parylene-C films, as assessed by X-ray diffraction (XRD). The XRD peak at $2\theta = \sim 14.5^\circ$ increased in intensity and decreased in full width at half maximum with increasing annealing temperature, indicating an increase in film crystallinity. Poor adhesion would compromise the protection offered by Parylene-C coatings. The adhesion between Parylene-C and silicon, amorphous silicon carbide, and boron silicate glass substrates were evaluated using the standard tape adhesion test from the American Society for Testing and Materials (ASTM) in an attempt to minimize the occurrence of delamination failures. The tape adhesion tests indicated strong adhesion for all the as-deposited Parylene films with the application of an adhesion promoter (Silquest A-174[®] silane). However, annealing the deposited films at temperatures from 85 to 150°C in air for 20 min reduced film adhesion, and also the adhesion testing procedure used significantly affects the results obtained. Supporting evidence suggested that the thermal stress generated in the films weakened the adhesive force. We concluded that

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the Parylene-C film properties (surface morphology, crystallinity, and adhesion) changed during deposition and thermal annealing, suggesting that the Parylene-C film properties can be tailored and that, with care, failure due to film delamination can be avoided.

1. Introduction

Parylene films were deposited using the Gorham chemical vapor deposition (CVD) method, whereby the di-para-xylene precursor was sublimed and pyrolyzed into reactive monomers, followed by a process of free-radical polymerization to form Parylene films. CVD Parylene films have been reported to be conformal, pinhole-free, and to also have a low dielectric constant ($\epsilon \sim 3$). Therefore, they are excellent materials for encapsulation and dielectric insulation. Parylene films with different functional groups have been extensively studied as encapsulation materials for biomedical or microelectronic applications; examples include stents, pacemakers, microelectronics, capacitive sensors, and solder joints.⁽¹⁻⁷⁾ Among the Parylene variants, Parylene-N and -C are currently approved by the Food and Drug Administration (FDA) as class VI polymers, allowing them to be used in biomedical devices.⁽⁸⁾

A fully integrated, wireless neural interface device is being developed to restore functions to patients with neurological disorders,⁽⁹⁾ and Parylene-C was studied as a conformal, hermetic, and biocompatible encapsulation layer for the device.⁽¹⁰⁾ In this work, we studied variables that affect the application of Parylene-C to the neural interface device. First, we explored the effect of deposition conditions on the surface morphology of Parylene-C films. Second, we investigated the effect of various heat treatments performed after deposition on the crystallinity and adhesion properties of Parylene-C.

The surface properties of a biomedical device affect its interactions with biological molecules and the resulting immune responses. Depending on the application of an implant, various surface modification techniques of Parylene have been proposed to improve the biocompatibility of an encapsulated implant.^(8,11-13) The surface roughness is also an important factor that affects the biocompatibility of a Parylene-encapsulated implant and was thus investigated as a function of dimer sublimation rate in this work.

The stress-induced cracking of Parylene material after several months of implantation has been reported.⁽¹⁴⁾ Oxidative degradation, including thermal and photooxidation, has been reported to cause failures in Parylene films.^(15,16) Shaw *et al.* have suggested that annealing films directly after Parylene deposition would result in a film that is more resistant to oxidation.⁽¹⁷⁾ Greater oxidation resistance might result in the increased lifetime of Parylene-encapsulated devices. Parylene was deposited through free-radical polymerization; thus, annealing the film directly after film deposition has been postulated to terminate the free radicals buried in the film through reactions with other radicals at polymer chain ends rather than with the available oxygen.⁽¹⁷⁾ Additionally, annealing at 150°C, which is above the glass transition temperature (35–80°C for

Parylene-C⁽¹⁸⁾, allows the segmental motion of the polymer chains. The segmental motion during thermal treatment allows the polymer chains to form crystalline domains in an amorphous matrix, increasing the degree of film crystallinity, and consequently modifying the film's mechanical properties. The degree of crystallinity affects the physical properties of semicrystalline polymers, such as mechanical properties⁽⁶⁾ and electrical properties (dielectric loss).⁽¹⁸⁾ Tailoring the degree of crystallinity (through the deposition parameters or subsequent annealing processes) may further enhance the mechanical robustness of a Parylene-encapsulated device. Increasing the toughness of the encapsulation material of an implant minimizes the chance of damage during the surgical implantation procedure. Understanding the relationships between the film fabrication process and the resulting properties will also allow films to be engineered for specific applications in the future.

Parylene films generally have poor adhesion to inorganic surfaces; therefore, applying an adhesion promoter or a plasma treatment prior to Parylene deposition is often required to ensure strong adhesion.⁽¹⁹⁻²³⁾ Different substrates and silanization procedures for adhesion promotion may result in different degrees of adhesion force due to surface property variations. Because of the diversity of materials in our neural interface device, we measured the adhesion between Parylene and various substrate materials that are used in the device. Although the steam sterilization method is commonly applied to a Parylene-encapsulated implant, the effect of thermal treatments on the adhesion of deposited Parylene films has not been investigated. In this paper we report on the adhesion between Parylene and the substrate materials of silicon (Si), boron silicate glass (BSG), and hydrogenated amorphous silicon carbide (a-SiC_x:H) after various heat treatments. The results suggest that adhesion with silicon substrates is reduced after 20 min thermal treatment at a temperature higher than 85°C, and the reduction of adhesion may be due to thermal stress.

2. Experimental Details

A silanization adhesion promotion process using Silquest A-174[®] silane (GE Silicones, WV, USA) was performed on all the test substrates before Parylene-C deposition. Silquest A-174[®] silane was mixed with isopropyl alcohol (IPA) and deionized water (DI) with a volume ratio of silane: IPA: DI of 1:100:100. The solution mixture was then stirred for more than 2.5 h, allowing the silane to hydrolyze. The procedure for applying the adhesion promoter started with submerging the substrates in pure IPA for 10 min and then rinsing them in DI for another 10 min. This procedure should result in the presence of hydroxyl groups on the substrate surface. The substrates were then soaked in the silane solution for 30 min, dried in air for 30 min, and then rinsed in IPA for 5 min to remove the excess silane that had not adhered to the surface. Covalent bonds formed between the silanol groups and the hydroxyl-terminated surfaces after 30 min in a 115°C oven. Parylene-C films were then deposited using a LabTop[®] 3000 Deposition System (Para Tech Coating, Inc., CA, USA) using Parylene-C dimers acquired from Cookson Electronics Equipment, USA. This system comprises five main units: a vaporizer, a pyrolysis furnace, a deposition chamber, a cold trap, and a rotary

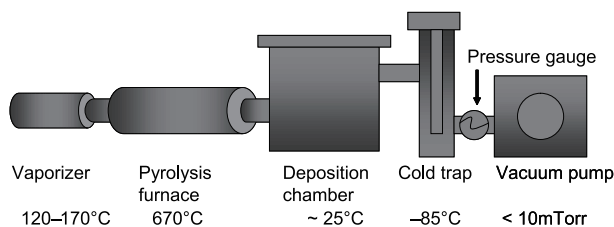


Fig. 1. Schematic structure of the Parylene deposition system.

vane vacuum pump (Fig. 1). The dimer powder was sublimed into a dimer vapor in the vaporizer at 120–170°C and was subsequently pyrolyzed into reactive monomers in the pyrolysis furnace at 670°C. Monomers polymerized via free-radical polymerization into linear polymer chains in the deposition chamber at room temperature. The film thickness was controlled by the quantity of dimer loaded into the vaporizer. Depending on the polymerization temperature (room temperature) and the sample location in the deposition chamber, variations in the coating thickness were observed; however, a film thickness of $1.0 \pm 0.15 \mu\text{m}$ per gram of dimer was typically acquired in our system. In this study, 3.1 g of dimer was used to obtain the film thickness of $\sim 3 \mu\text{m}$ required in our neural interface device.

The monomer vapor that does not polymerize on the substrate surface condenses in the cold trap (-85°C). The vacuum pump is used to maintain a base pressure of less than 10 mTorr, and a pressure gauge is installed between the cold trap and the pump to monitor the pressure during deposition. Because of the location of the pressure gauge, the pressure indicated by the gauge does not represent the pressure inside the deposition chamber, but the gauge can be used to estimate the pressure and monitor the sublimation rate based on the time between the pressure increase and decrease.

In order to investigate the relationship between the surface morphology and the deposition conditions of Parylene-C, samples were deposited at three different dimer sublimation rates (controlled by the vaporizer temperature). The dimer quantity was fixed at 3.1 g, while the sublimation temperature was ramped up from 120 to 170°C to control the sublimation rate. The film thickness was kept approximately constant. The three different deposition rates were designated as FAST (~ 40 min), STD (~ 100 min), and SLOW (~ 190 min), and the pressure (mTorr) and vaporizer temperature ($^\circ\text{C}$) for these conditions are plotted versus time (min) in Fig. 2. Assuming that the sublimation rate is constant during the deposition, the sublimation rates were estimated to be approximately 0.08, 0.03, and 0.015 g/min for the FAST, STD, and SLOW conditions, respectively. The surface morphologies of the Parylene-C films were obtained by atomic force microscopy (AFM) (Dimension3000, Digital Instruments, Veeco Metrology Group) in the tapping mode using etched Si tips with a nominal tip radius of 5–10 nm. The scan rate is 1.489 Hz.

Crystallinity was assessed using an X-ray diffraction system (XRD; Philips MRD X'pert), and the scans were performed with 2θ set in the range of 10 – 20° . The XRD spectra shown in each figure or table were collected within 1 h to minimize the variation resulting from X-ray beam intensity. The size of the crystalline domains, t , was estimated using Scherrer's formula, given as follows:⁽²⁴⁾

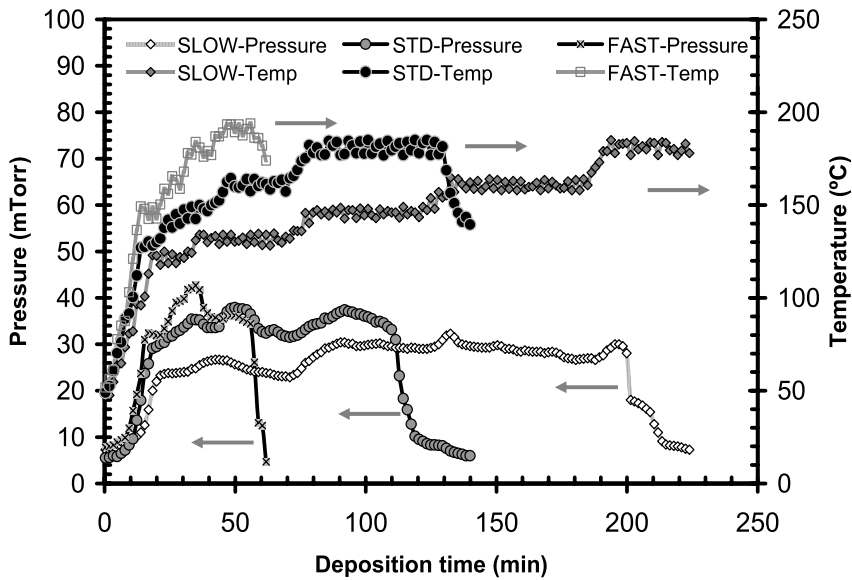


Fig. 2. Deposition time versus vapor pressure and vaporizer temperature. The deposition time was estimated from the pressure curve as shown in the above plots. FAST, STD, and SLOW denote the conditions with deposition times of approximately 40, 100, and 190 min, respectively.

$$t = \frac{0.9\lambda}{B \cos \theta_B} ,$$

where λ is the wavelength of the X-ray beam, 1.5406 Å; B is the full width at half maximum (FWHM) on the 2θ scale (radians); and θ_B is the Bragg angle. A 90° peel test was used to evaluate the tensile strength of the Parylene-C film. A 20 μm Parylene-C film was deposited on a silicon substrate and diced into 5 mm strips for the tensile strength tests. The tensile strength of the film was obtained from a strain-stress curve using a custom-made tool setup described elsewhere.⁽²⁵⁾ Parylene-C films were deposited on the three different substrate materials used in our neural interface device (Si, a-SiC_x:H, and BSG.), followed by various thermal treatments before the adhesion tests. For the tape adhesion test, Parylene films were crosscut into a 10×10 grid pattern with a 1 mm pitch, followed by the application and peeling of Scotch tape (#810, 3M Corp.), following a procedure conforming to the ASTM D3359B standard. Two testing procedures, procedures A and B, were used. For procedure A: (1) make a 10×10 grid pattern, (2) submit the film to thermal treatment at 120°C for 20 min, and (3) perform the tape adhesion test. For procedure B: (1) submit the film to thermal treatment at 120°C for 20 min, (2) make a 10×10 grid pattern, and (3) perform the tape adhesion test.

The adhesion score was classified into six grades, where the best adhesion is graded 5B (no grid pattern removed) and the poorest is 0B (> 65% of the grid pattern removed). Thermal treatments included testing at three temperatures (85, 120, and 150°C) in air

for 20 min and at 85°C / 85% RH for 20 days. In order to investigate the long-term stability and encapsulation properties of annealed Parylene-C films, leakage current and adhesion tests were performed after thermal treatments. Leakage current tests were carried out using an interdigitated electrode structure (IDE). The IDE fabrication method is described elsewhere.⁽²⁶⁾ The IDE chips were deposited with 4.5- μm -thick Parylene-C films, and the deposited chips were placed in test vials as shown in Fig. 3. The test vials were kept dry during the first 3 days and then filled with saline solution provided no short circuit was observed. The samples were then kept in 37°C saline for the remainder of the test period. A 5 V direct current (DC) was applied continuously to the test structures during the leakage current testing period.

3. Results and Discussion

3.1 Effect of dimer sublimation rate on surface morphology

Surface morphology affects the biocompatibility of an implantable device, and was therefore investigated as a function of deposition conditions by AFM. Previous work has suggested that the deposition pressure should be less than 100 mTorr for obtaining high-quality dense films,^(27,28) and a kinetic model for Parylene surface roughening has also been reported.⁽²⁹⁾

The relationship between the surface morphology and the deposition conditions of Parylene-C was studied. The pressure and vaporizer temperature for samples deposited at three different dimer sublimation rates (designated as FAST, STD, and SLOW), described in the experimental details, are plotted versus time (min) in Fig. 2.

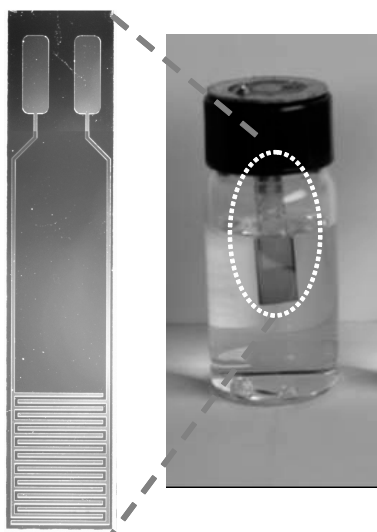


Fig. 3. IDE test structure and the test vial. The IDE is submerged in 37°C saline solution and exposed to a 5 V DC bias during leakage current testing.

The AFM image for the FAST condition (film thickness 3.2 μm) is shown in Fig. 4 and conforms to a typical hillock surface morphology. The root-mean-square (RMS) roughness values of the films deposited under the FAST, STD, and SLOW deposition conditions were calculated from the AFM data to be 9.53, 7.05, and 5.78 nm, respectively. These results indicate that a slightly rougher surface occurs at a higher sublimation rate under the conditions investigated. The increase in roughness may be attributed to the increases in deposition pressure and deposition rate. These results suggest that when increasing the sublimation rate (to increase the film thickness or production throughput), one should be aware of the effect on surface roughness due to the process change. The surface roughness needs to be taken into account for applications, *e.g.*, for implant encapsulation or as a lubricious coating.

3.2 Effect of thermal treatments on film crystallinity

The XRD spectra of the as-deposited and annealed films are presented in Fig. 5, and all show a peak at $2\theta = \sim 14.5^\circ$. Murthy and Kim have proposed a molecular packing model for Parylene-C crystals,⁽³⁰⁾ and the peak has been suggested to correspond to the (020) crystal plane.^(18,31) The interplanar spacing (d -spacing), relative crystalline fraction, and the crystallite size for various heat treatment temperatures were obtained from the XRD spectra and are reported in Table 1.

The decrease in d -spacing with increasing temperature suggests that more ordered polymeric chains are formed when annealing temperature increases, or that the film was under compressive stress in the direction normal to the substrate surface. If this results

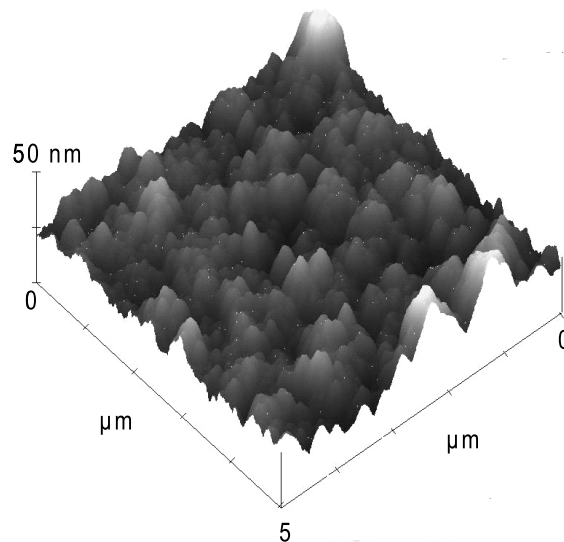


Fig. 4. AFM micrograph of Parylene deposited at the FAST sublimation rate. The RMS roughness is calculated to be 9.53 nm.

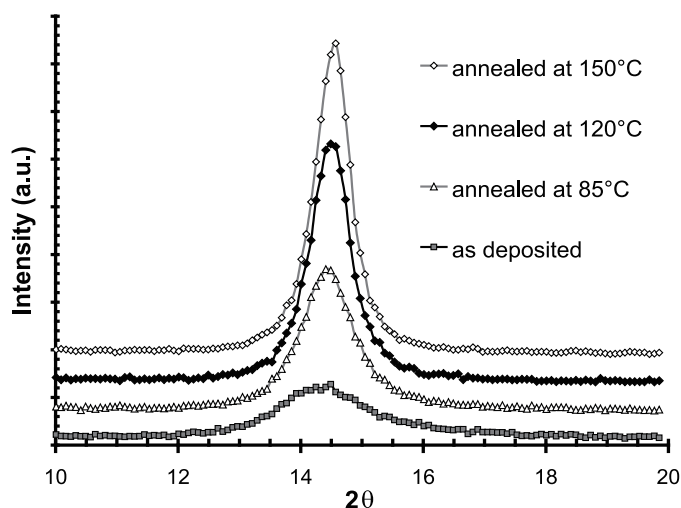


Fig. 5. XRD spectra of 3 μm Parylene films before and after thermal treatment. The peak height increases with increasing annealing temperature, while the peak FWHM is observed to decrease with increasing temperature.

Table 1

XRD results from sample deposited under STD condition with thickness 2.7 μm after different heat treatments for 20 min.

Sample condition	Peak position 2θ	d -spacing (\AA)	Relative peak height	FWHM ($^{\circ}2\theta$)	Crystallite size (\AA)
As-deposited	14.29	6.19	1	1.45	55.2
Annealed at 85 $^{\circ}\text{C}$	14.45	6.12	2.49	0.96	83.4
Annealed at 120 $^{\circ}\text{C}$	14.51	6.10	4.57	0.74	108.2
Annealed at 150 $^{\circ}\text{C}$	14.57	6.07	5.74	0.7	114.4

from increased order, it may be due to the greater energy available for chain motion and crystallization. The intensity of a Bragg peak is a function of the number of unit cells, N (crystallite concentration), and the maximum intensity at a Bragg peak is proportional to F^2N^2 , where F denotes the structure factor. Thus, as a reasonable approximation, the square root of peak intensity increases linearly with N , or the crystallite concentration in the Parylene-C polymer.

In addition to the increased XRD intensity that occurred with increased annealing temperature, the reduction of FWHM was also observed, suggesting an increase in crystallite size. The broadening of the peak (FWHM) in crystalline materials is generally attributed to two factors: smaller crystallite size and greater variation of d -spacing (*e.g.*, resulting from nonuniform strain).⁽²⁴⁾ The size of crystallite domains was estimated from

Scherrer's formula and the results are listed in Table 1. The reported crystallite sizes are considered to be approximate due to a number of error mechanisms resulting from the Scherrer method. Because polymer segmental motion is a function of temperature, whether there is sufficient segmental motion to achieve a certain degree of crystallinity depends on the thermal energy available. The square root of the ratio of the increase in peak intensity to crystallite size was plotted as a function of the annealing temperature (Fig. 6), and a linear relationship is shown. The lines of best fit suggest that the increase in crystallite concentration (intensity) may be mainly caused by the increase in crystallite size.

The time-temperature effect was also demonstrated. Comparing a sample treated at 85°C for 20 days with a sample treated at 85°C for 20 min, a mere ~20% peak intensity increase was observed, whereas a sample treated at 150°C for 20 min exhibited a ~200% peak intensity increase compared with a sample treated at 85°C for 20 min. Furthermore, as shown in Fig. 7, two samples, A and B, were annealed at 150°C for 20 min. Sample B then underwent further treatment at 85°C and 85% RH in an environment-controlled chamber for 20 days. The close overlap of the two plots suggests that no crystallinity change occurs during the further 20 days of treatment at 85°C, which was much lower than the initial annealing temperature (150°C). These observations suggest that the temperature plays a more important role than the time duration of the treatment. The kinetics of the crystallization reaction may be relatively quick compared with the annealing time; therefore, the crystallization reaction is completed even during the brief 20 min of annealing.

The dimer sublimation temperature and polymerization temperature have been reported to affect the crystallinity of as-deposited films.⁽³¹⁾ For the three sublimation rates used in this experiment, only slight differences in crystallinity were observed,

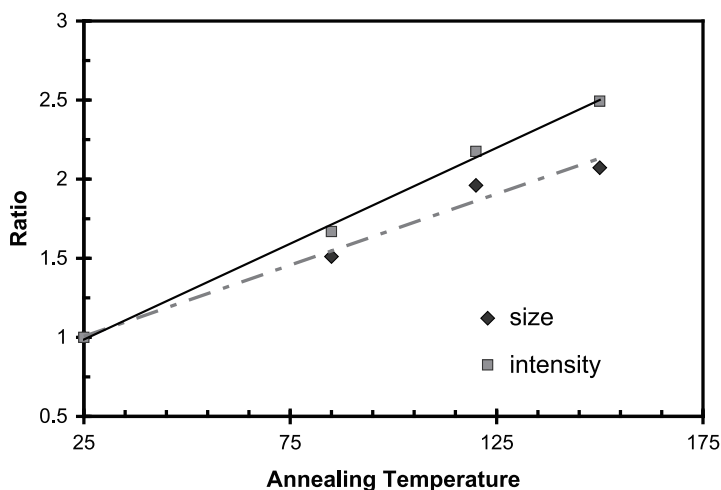


Fig. 6 Square root of ratio of increase in peak intensity to crystallite size plotted as a function of annealing temperature. Note that the sample at 25°C signifies the unannealed film.

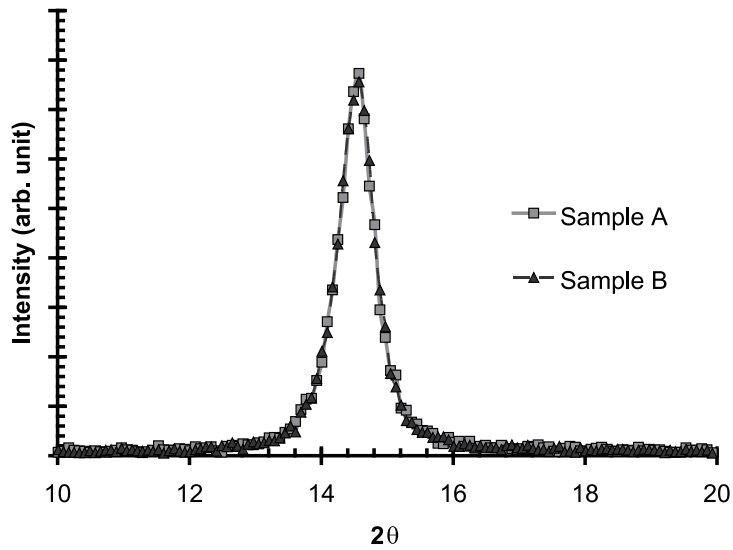


Fig. 7. XRD spectra of two samples after different thermal treatments. Samples A and B were both annealed at 150°C for 20 min, but sample B was additionally annealed at 85°C / 85% RH for 20 days.

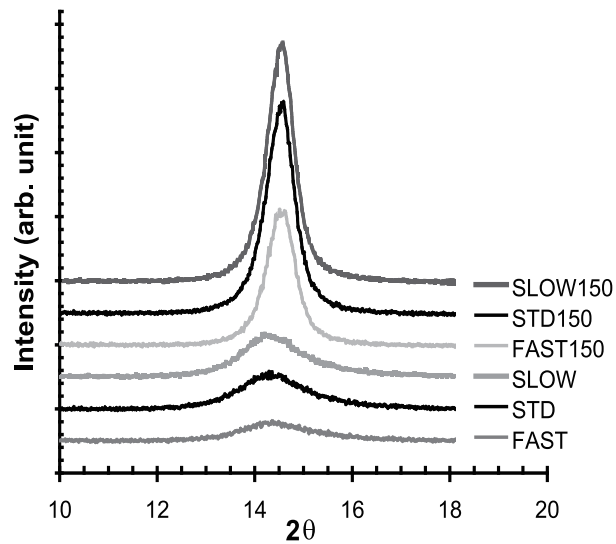


Fig. 8. X-ray diffraction spectra of Parylene thin films as-deposited and after annealing. The samples deposited at different sublimation rates are shown. FAST, STD, and SLOW indicate the samples deposited at the rates given in Fig. 2. "150" indicates that the samples were annealed at 150°C for 20 min. The annealed samples show significantly higher peak intensities and lower FWHMs than the unannealed peaks in all cases.

and the changes were not as significant as those induced by thermal annealing (Fig. 8). Annealing the film at 150°C for 20 min increased the peak XRD intensity 6–8-fold, while decreasing the sublimation rate (from 0.08 to 0.015 g/min) increased the peak intensity only about 2.5-fold.

The degree of crystallinity generally affects the mechanical properties of semicrystalline polymers, such as the elastic modulus and/or Poisson's ratio,⁽⁷⁾ and can result in inconsistent device performance. The effects of annealing on the mechanical properties of deposited films were tested. The tensile strength of a 20- μm -thick Parylene sample was evaluated before and after thermal annealing at 150°C, and the results showed that the samples have approximately 30% greater tensile strength than the as-deposited films (from an average of 51.5 MPa for as-deposited films to 66.7 MPa for annealed films). These preliminary studies suggest that thermal treatments may be used to tailor the crystallinity for further investigations of mechanical strength. The optimization of the crystallinity may yield a film with greater mechanical robustness that can withstand the surgical implantation procedure and satisfy the encapsulation properties required for our neural interface device.

Furthermore, the temperature-dependent behavior indicates that thermal annealing at temperatures higher than the device operation temperature may allow constant Parylene-C crystallinity to be maintained throughout the device operation period. For example, Parylene-based diaphragms for capacitive sensors may require consistent mechanical properties (*e.g.*, modulus) throughout their operation period,^(8,32) which can be achieved by annealing at temperatures higher than the operating temperature. Furthermore, crystallinity affects the device's electrical properties (dielectric loss) and optical anisotropy (birefringence).⁽¹⁸⁾ Therefore, tailoring the degree of crystallinity through the deposition conditions or subsequent annealing processes may help further optimize a Parylene film property of interest. Understanding the relationships between the film fabrication process and the resulting properties will allow Parylene films to be engineered for specific applications.

3.3 Effects of thermal treatment on film adhesion

Parylene has been widely investigated for numerous sensor and electronic device applications, and adhesion failure between Parylene and the substrate is the main cause of failure for these devices. A biomedical coating must be able to withstand sterilization; thus, the adhesion of Parylene to the substrate after 2 h at 120°C in 100% RH was investigated to determine if the films are compatible with steam sterilization. The results from the ASTM tape adhesion test on the as-deposited samples were consistently good (5B) upon the application of the adhesion promoter. However, a reduction in adhesion was observed after 120°C annealing for 2 h, with films achieving a grade of 0B (> 65% of the grid peeled off).

It is important to note that the testing procedure had a large effect on the results of adhesion testing. Figures 9(a) and 9(b) show images of an a-SiC_x:H sample that was coated with Parylene, and the adhesion was tested by both procedure A (Fig. 9(a)) and procedure B (Fig. 9(b)), described in the experimental details. The results for adhesion tests after various thermal treatments are presented in Table 2, and clearly show that

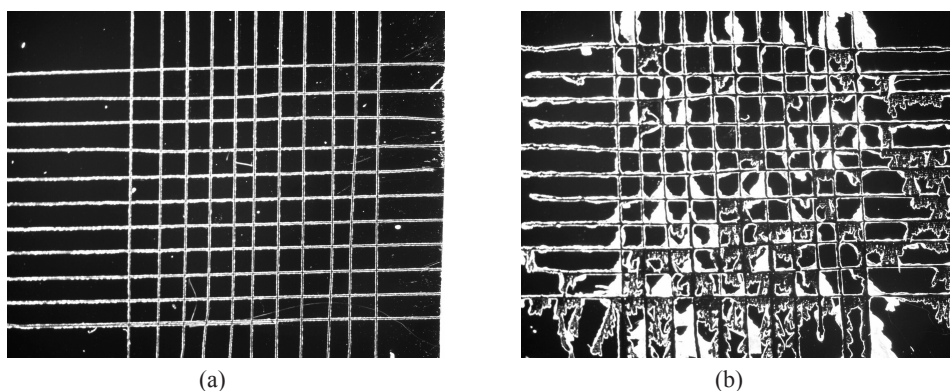


Fig. 9. Optical images showing an adhesion result of 5B using procedure A and an adhesion result of 0B using procedure B (described in experimental details) after the same thermal treatment. The grid size is 1 mm².

Table 2

Thermal treatment conditions versus tape adhesion grade. The adhesion results for grid patterns generated before (procedure A) and after thermal treatment (procedure B) are listed as p-A and p-B, respectively, in the test conditions. Grading conforms to the ASTM 3359B standard.

Test conditions		85°C 20 min		120°C 20 min		150°C 20 min	
		p-A	p-B	p-A	p-B	p-A	p-B
Film thickness 3±0.3 μm	Si	5B	4-5B	5B	0-3B	2-4B	0B
	a-SiC _x :H	—	—	5B	0B	—	—
	BSG	—	—	5B	5B	5B	4-5B
0.38±0.03 μm	Si	—	—	5B	5B	5B	5B

significantly better adhesion is measured using procedure A. The grading differences that arose from the different testing procedures were also observed for silicon substrates.

Two factors that could contribute to the adhesion failure are discussed: adhesion promoter degradation and film stress. Silquest A-174[®] silane is a gamma-substituted silane, which can generally withstand short-term process conditions of 350°C and long-term continuous exposure to 160°C; thus, the annealing temperature is unlikely to cause the degradation of the silane primer.

Large thin-film stress generally results in film cracking or delamination from the substrate; therefore, film stress was investigated in our previously reported work.⁽¹⁰⁾ After heat treatment, the as-deposited film had a tensile stress of approximately 1.56 MPa, and a thermal treatment (150°C for 20 min in air) resulted in a small tensile stress increase (8–15 MPa) measured by the wafer curvature method.⁽¹⁰⁾ The slight increase may be due to the increase in crystallinity after annealing, which causes the film to contract. Parylene-C has a linear coefficient of thermal expansion of 3.5×10⁻⁵ /K at 25°C, which is more than one order of magnitude higher than that of the silicon substrate of 2.6

$\times 10^{-6}$ /K.⁽¹⁸⁾ Thus, a likely explanation for the adhesion failure is that the high stress induced during thermal treatment broke the bonds at the Parylene-substrate interface (to relieve the stress), resulting in poor adhesion after cooling to room temperature. Little residual stress was observed after annealing due to the relaxation and the broken bonds at the substrate-film interface. Furthermore, the film stress may be reduced when the film is cut into discontinuous patterns; the magnitude of the stress at high temperatures was reduced by using a small pattern size, resulting better measured adhesion using procedure A.

In contrast to Si and a-SiC_x:H, the ~ 3 - μm -thick films deposited on BSG substrates have good adhesion even after annealing at 150°C for 20 min and evaluation using procedure B. Note that no difference in adhesion among the three types of substrates could be distinguished in the as-deposited state, because all films scored a grade of 5B on the tape test. This indicates that the thermal annealing process and the tape adhesion test using procedure B may be a way of distinguishing between relative adhesion forces.

Although the effects of temperature on Parylene film have been investigated,⁽¹⁶⁾ adhesion failure was not reported because free-standing films were studied. The majority of device applications using Parylene combine it with silicon-based devices; therefore, the adhesion between Parylene and its substrate is critical. The reduction in adhesion force is affected by thermal stress, which may depend on the pattern size (*e.g.*, 1 mm² in our experiment), the Parylene film thickness, and the temperatures to which the film is exposed. Film stress is proportional to film thickness; therefore, we compared the adhesion of a thinner Parylene coating (0.38 μm) with our standard ~ 3 - μm -thick film. The tests indicated good adhesion (5B) on the thin Parylene-C-coated Si substrates after heat treatments of 120 and 150°C for 20 min (Table 2). The tape adhesion test results also suggested that the adhesion of the 3- μm -thick Parylene-C film was not degraded by heat treatment at temperatures lower than 75°C. These results indicate that care should be taken in processes that involve elevated temperatures after Parylene deposition; for example, steam sterilization for implantable devices is generally carried out at 121°C, and photoresist curing processes used for patterning Parylene on sensor applications may require a soft baking temperature higher than 90°C. Because thermal stress decreases the Parylene adhesion on a silicon-based device, a low-temperature alternative (*e.g.*, ethylene oxide) should be used for sterilization. Furthermore, if an annealing process is used to modify the physical properties (*e.g.*, modulus or dielectric loss) of Parylene after deposition, or if the device operation involves exposure to a temperature that causes a reduction of adhesion, other treatments such as mechanical anchoring⁽²¹⁾ or the further improvement of adhesion promoters need to be considered.

3.4 Leakage current test on thermally treated samples

We have shown that the as-deposited Parylene-C film provides long-term stability in 37°C physiological saline environment, suggesting its suitability as a dielectric encapsulation layer for neural interface devices.⁽¹⁰⁾ In order to further explore the effect of thermal annealing on the Parylene encapsulation properties in a physiological environment, Parylene-C-coated IDEs were annealed before being subjected to leakage current testing. Results from the leakage current tests are presented in Fig. 10, where the current (A) passing through the encapsulated device is measured as a function of time (days).

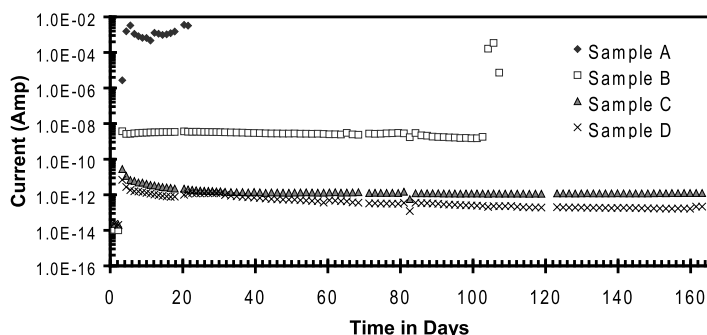


Fig. 10. Leakage current of IDE samples after 150°C / 20 min thermal treatment. The Parylene thickness of these samples was estimated to be 4.5 μm . Sample A failed at the beginning of the test, which may be due to sample preparation failure. Sample B had a higher initial leakage current than samples C and D, suggesting a weak point in the Parylene-C encapsulation layer of sample B generated during the preparation of the test vial.

The adhesion was expected to degrade after annealing at 150°C for 20 min, which may impair the encapsulation properties.

Although the four IDE samples were prepared by exactly the same procedure, sample A failed in the leakage current test immediately after saline was added to the vial. The early failure may be due to damage to the encapsulation film in the electrode area during sample preparation. However, samples B, C, and D exhibited low leakage current for longer than 100 days. A likely explanation for this is that, as long as the mechanical integrity of the encapsulation layer is maintained, it continues to encapsulate the IDE structure despite its reduced adhesion. However, these IDEs may still be more susceptible to damage than unannealed samples, since damage could potentially propagate at the film-substrate interface.

The leakage current test results indicate that there was no cracking or other defect generated on the Parylene-C film after annealing, which suggests that using an annealing process to tailor the material properties should not compromise film integrity. These results also indicate that, if the adhesion can be optimized to withstand the thermal stress, Parylene-C can be steam sterilized or undergo a thermal process while maintaining its encapsulation capability.

4. Conclusions

The surface morphology of Parylene films deposited by chemical vapor deposition is affected by the sublimation/growth rate, with faster growth rates yielding rougher films. The surface roughness change needs to be taken into account if one tries to increase the production throughput by increasing the sublimation rate. We observed that crystallinity increased with annealing temperature. Crystallinity may significantly affect the mechanical properties of semicrystalline polymers such as elastic modulus and Poisson's

ratio; thus, our work provides a method of tailoring the crystallinity of Parylene films for the further investigation of mechanical or physical properties in the future.

In order to investigate whether steam sterilization is compatible with a Parylene-C-encapsulated implantable device, the effects of heat treatments on the adhesion and integrity of Parylene-C films were also investigated. The heat treatments ($> 85^{\circ}\text{C}$) reduced the adhesion of Parylene films to silicon substrates, which we suggest is caused by thermal stress. The results of the adhesion tests after thermal treatment suggest that the substrate surface properties and thermal stress affect the film adhesion to the substrate, and that the testing procedure affects the thermal stress and thus has a great impact on the results obtained. Although adhesion was compromised by the annealing process, thermal treatments at 150°C for 20 min did not degrade the Parylene-C film, as determined by the leakage current tests conducted in saline solution at 37°C over 165 days. These results indicate that, if the adhesion can be optimized to withstand the thermal stress, Parylene-C can undergo a thermal process while maintaining its integrity to protect a Parylene-C encapsulated device *in vivo*.

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