

Parylene-N a Better Candidate for Medical Substrate Coating than Parylene-C

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The biomaterial - tissue interface plays a key role in implant success. The advantage of using parylene-C a class VI FDA approved polymer for implants is well known. Parylene-N and parylene-C thin films deposited via polymer vapor deposition (PVD) on Si(111) were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The surface of parylene - C is smooth, while for parylene - N bundles of fibrils are clearly observed by SEM. XRD showed that parylene-N is more packed than parylene-C thus should withstand better to moisture. The kinetics of the two is different; parylene-C has a greater deposition rate than parylene-N but the last one has a greater penetration to small crevices than parylene-C. Therefore we hypothesize that parylene-N could be more suitable as protective coating for medical instruments (not for implantable devices though) than parylene-C.

Keywords: Parylene - N, Parylene - C, PVD, AFM, SEM, XRD

Parylene group polymers possess many properties that make them suitable for many applications ranging from microelectronics to medical devices industry (parylene-N and parylene-C are both class VI FDA approved polymers) [1]. Unlike conventional liquid coatings, parylene group polymers are deposited onto substrate via gas-phase polymerization deposition (polymer vapour deposition - PVD) to form a thin, transparent film of infinitely controllable thickness [2]. A thin film is defined as a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness [3-4]. The parylene group has unique properties: absolute conformance to substrate topography, pinhole-free coverage even in very thin applications, and the ability to penetrate and coat complex geometric shapes. When deposited as a conformal coating, parylene film resists chemical attack from organic solvents, inorganic reagents, and acids; adheres to plastics, ceramics, glass, and metal; and offers dielectric strength above 5000VDC/mil of coating thickness (1mil = 25.4µm). For example, parylene-C coated semiconductor devices have been shown to be operable after more than 300 days of complete immersion in saline solutions, with no change in measured input bias when compared with dry operation [5]. Parylene-C is the most widely used dimer due to a very low permeability to moisture, chemicals, and corrosive gases. Parylene-C differs from Parylene-N by a single chlorine substitution of aromatic hydrogen [6]. It possesses a lower conformability but the biocompatibility (FDA Class VI) is the best in parylene group. Parylene-N has high dielectric strength; its dielectric constant does not vary with frequency. It is the best selection where greater coating protection is required. Parylene-C and parylene-N can be deposited via PVD (polymer vapor deposition) to thin (1-30 µm) layers which are conformally [7, 8].

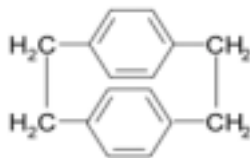


Fig. 1 The dimer di-para-xylylene

Experimental part

Materials and methods

The substrate was Si orientation $\langle 111 \rangle \pm 0.5^\circ$ with B as dopant, double-side polished, (5x21mm²), resistivity 0.7-1.2 Ohm cm, thickness 300µm ± 25µm (MTI, Richmond, CA 94804, USA).

The dimer was di-para-xylylene (fig. 1) as also depicted by [9], from Metal Improvement Company LLC - Parylene Coating Services - Galway Division, Ireland. Polymer vapor deposition onto Si(111) was performed at the same company.

Polymer vapour deposition

The polymer vapour deposition process utilizes the monomer in the vapor phase that enters the deposition chamber where it adsorbs and polymerizes onto the substrate at room temperature (RT). Advantages of PVD are: uniform, smooth, stress-free, pinhole-free, and conformal coating [10]. Parylene deposition began with dimer (di-para-xylylene) vaporization at 100-175°C and 1Torr. Then the gaseous dimer enters the zone where it pyrolyzes at ~680°C and 0.5 Torr. The result is the polymerization as poly-para-xylylene of the monomer (para-xylylene).

X-ray diffraction

The structure of the parylene-N thin film was monitored by X-ray diffraction (XRD) with a D8 DISCOVER (Bruker Axs) diffractometer equipped with a Cu Kα ($\lambda = 1.54060\text{\AA}$) radiation source and a LynxEye OD detector. Data were collected by scanning in grazing incidence diffraction (GID) configuration at grazing angle $\theta = 0.2^\circ$, from 5 to 65° (2θ) with a step size of 0.04° (2θ).

Atomic force microscopy

The topography was studied using an AFM Digital Instruments Nanoscope Veeco with a Si₃N₄ tip in tapping mode. The aims of the study were to observe surface homogeneity and the roughness.

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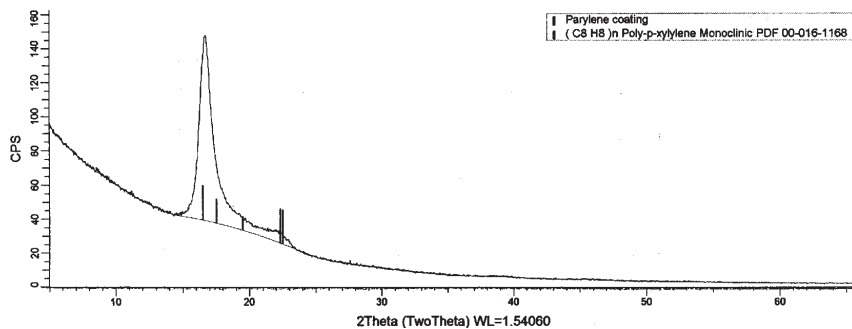


Fig. 2 XRD data for parylene-N showing a phase at room temperature for an as-deposited film

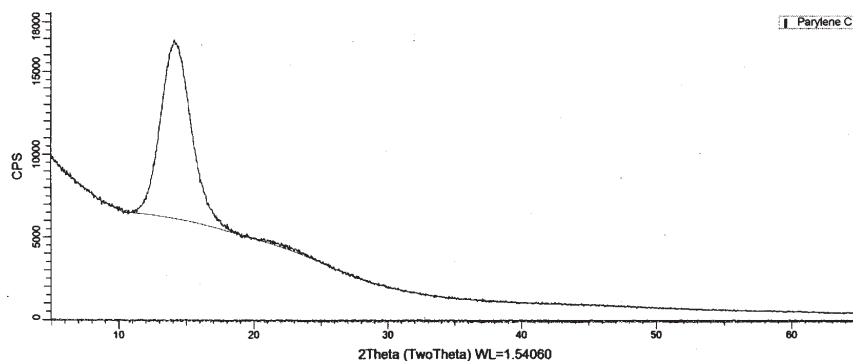


Fig. 3 XRD data for parylene-C at room temperature for an as-deposited film

Scanning electron microscopy

The SEM used for analysis was a FEI Quanta Inspect F and images are obtained using a Everhart - Thornley detector.

Results and discussions

Polymer vapour deposition

The difference in deposition rate between parylene-N and parylene-C (parylene-C deposits faster than parylene-N) [11] could be explained by the structural difference of the two. Parylene-C molecules are less elastic than parylene-N molecules and therefore they bounce around much less than parylene-N molecules. On the opposite, parylene-N molecules are very elastic and therefore they will bounce around many times prior to depositing and polymerizing; that can result in a greater penetration into small openings for the parylene-N than for the parylene-C.

X-ray diffraction

The X-ray diffractogram showed a peak at $2\theta \sim 16.66^\circ$, for interplanar spacing, $d=5.31644\text{\AA}$ having full width at half maximum, $\text{FWHM}=0.963^\circ$ (fig. 2). The peak position is similar to what was reported by G.-R. Yang et al. for parylene-N sample [12]. It was calculated, using Scherrer formula, the mean crystallite size $D=9.26\text{nm}$, and also it was evaluated the degree of crystallinity for the full range of the scan, the parylene-N coating having 87.3% crystallinity

The X-ray diffractogram showed for the parylene-C thin film a peak at $2\theta \sim 14.15^\circ$, for interplanar spacing, $d=6.25527\text{\AA}$ having full width at half maximum, $\text{FWHM}=2.445^\circ$ (fig. 3). It was calculated, using Scherrer formula, the mean crystalite size $D=36.3\text{\AA}$, and also it was evaluated the degree of cristalinity for the full range of the pattern, the parylene-C coating having 78.5% crystallinity.

Atomic force microscopy

The samples were scanned, at first, on a $10 \times 10 \mu\text{m}^2$ then the surface was increased at $30 \times 30 \mu\text{m}^2$, keeping the same region from the sample. The reconstructed images and the statistics are presented in figure 4 - 5.

The parylene-C coating appears to be textured, with a preferred orientation, while the parylene-N coating appears

with dimples uniformly scattered on the scanned surface.

The root mean square roughness (RMS) for parylene-N is greater than for parylene-C. Using this parameter, RMS, is adequate when comparing materials with similar structure, but a faster variation of height in respect with horizontal position may be deceiving.

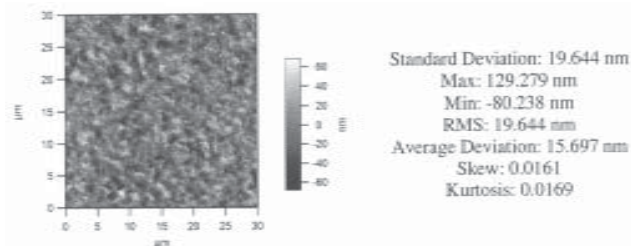


Fig. 4 Topography images of Parylene -C on a $30 \times 30 \mu\text{m}^2$ surface and associated statistics

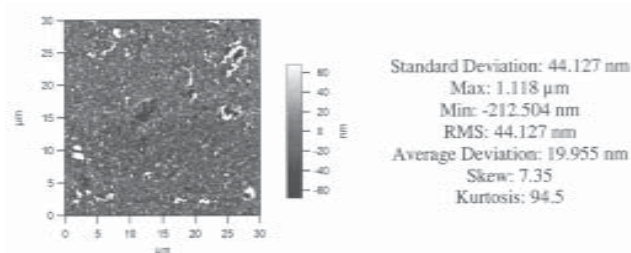


Fig. 5 Topography images of Parylene - N on a $30 \times 30 \mu\text{m}^2$ surface and associated statistics

The skewness, a measure of the departure of surface from symmetry, is positive. A positive value reflects a surface that comprises mainly peaks. For parylene-C the skewness is lower, almost nil, which means an almost equal presence of peaks and valleys on the scanned surface.

The kurtosis reflects the sharpness of the profile peaks, and for parylene-C the peaks are almost blunt, while parylene-N has sharper peaks.

On the parylene-N surface several features, most likely debris are present.

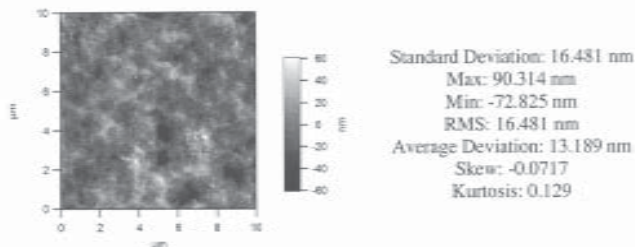


Fig. 6 Topography images of Parylene - C on a 10x10 μm^2 surface and associated statistics

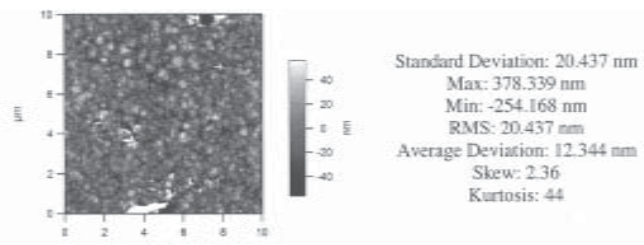


Fig. 7 Topography images of Parylene - N on a 10x10 μm^2 surface and associated statistics

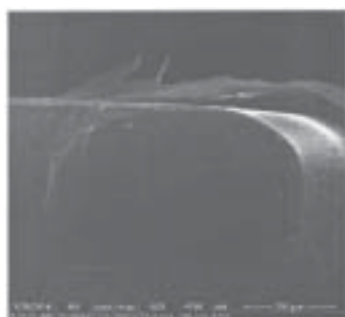


Fig. 8 SEM image of parylene-C - parameters at the bottom of the image

Scanning electron microscopy

SEM images obtained from parylene-C sample revealed an exfoliated area at the edge of the silicon wafer (fig. 8).

There are no signs of cohesive failure, no debris on the wafer; an adhesive failure was also excluded. This aspect was generated by the installation used to perform the deposition since it was not our intention to fully coat the wafer.

The layer thickness on the edge of the exfoliated area was measured at 1.10 μm . The surface appeared smooth with debris (fig. 9).

For parylene - N the surface appears rougher, with protrusions with various heights, figure 10. Higher magnifications revealed fibrils bundling in groups, narrowing at the tip. The measured thickness on the SEM image was around 3 μm , as observed in figure 11.

By SEM analysis parylene-C was found to have a smoother surface than parylene-N that showed bundled fibrils protruding at various heights.

Conclusions

The PVD method employed for film deposition assured high quality layers, with no defects and with the possibility to control layer thickness.

By XRD the interplanar distance was determined for parylene-N at 5.31644 \AA vs. 6.25527 \AA in parylene-C and the crystallite size is 9.26nm in parylene-N vs. 36.3 \AA in parylene-C.

The AFM studies showed a rougher surface for parylene-N, with sharper peaks and a larger number of mountains on the scanned surface, while parylene-C developed a smooth surface with an approximately equal number of valleys and mountains in the scanned area.

By SEM it was observed that parylene-N has, at surface,

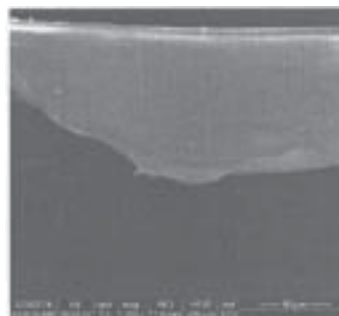


Fig. 9 SEM image of parylene-C, detail on the exfoliated area - parameters at the bottom of the image

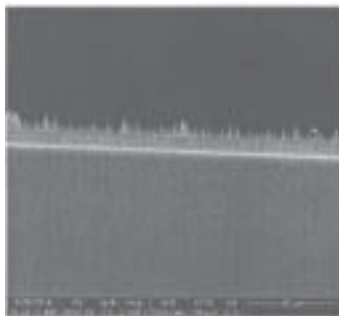


Fig. 10 SEM image on a section of parylene -N

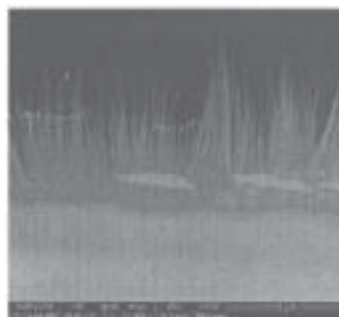


Fig. 11 SEM image showing a magnified protrusion with fibrils - parameters at the bottom of the image

fibril bundles that appeared as dimples on AFM images.

We hypothesize that parylene-N could be a better candidate for medical instrumentation coating than parylene-C since it withstands better to moisture (parylene-N absorbs 6 times less water than parylene-C i.e. 0.01 vs. 0.06 (% /24h) [13]) and it is most effective to penetrating crevices even though parylene-C would be the preferred polymer of the two since it deposits faster than parylene-N [11]. In addition to that parylene-N is more packed than parylene-C (interplanar distance $d=5.31644\text{\AA}$, FWHM = 0.963 \AA° with the mean crystallite size $D=9.26\text{nm}$, 87.3% crystallinity for parylene-N vs. interplanar distance $d=6.25527\text{\AA}$, FWHM = 2.445 \AA° with the mean crystallite size $D=36.3\text{\AA}$, 78.5% crystallinity for parylene-C).

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