Emergent properties of spatially organized poly(p-xylylene) films fabricated by vapor deposition

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ABSTRACT

A novel bottom-up process to deposit structured poly(p-xylylene) (PPX) polymer films, based on oblique angle vapor deposition polymerization, is introduced. In this process, monomer vapors produced by pyrolysis of chemically functionalized p-xylylene precursors are directed at an oblique angle towards a surface to initiate structured polymer growth. Inclined deposition induces growth of PPX nanofibers leading to a nanostructured surface comprising clusters of ∼100–150 nm diameter nanocolumns. Morphology of these films can be controlled by manipulating the substrate rotation during oblique angle deposition (i.e., helical, chevron and columnar morphology). The morphology of the nanostructured PPX films are characterized by atomic force microscopy and scanning electron microscopy.

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1. Introduction

The ability to control and tune the chemical and physical properties of surfaces has scientific and technological importance in many medical areas including biomedical coatings, biosensing, tissue culture and growth, and biocatalyst supports. Self-assembled monolayers (SAMs) [1,2] and polymer brushes [3] are commonly used for studying chemistry at interfaces under controlled conditions. However, SAMs are limited in terms of the surface density of coupled molecules since they are intrinsically two-dimensional systems. Hence the approaches that increase the surface/volume ratio are of great importance. Three-dimensional functionalized surfaces have been created by polymer brushes [3]. It is possible to assemble many possible combinations of monomers that have desired functional groups. However, a crucial step in order to approach this goal is the formation of structures exhibiting long-range order. Unfortunately, the grafting density of the polymer brushes limits the formation of these structures. A feasible alternative to this problem is to create high-density brushes (or structured polymers) that exhibit different properties from those in the low-density regime due to higher-order interactions between chains (Fig. 1). Recently, the preparation of structured polymers has been explored by sol–gel based templating methods, surface initiated polymerization, dip-pen nanolithograpy and optical lithography

[4–10]. Structured polymer brushes (aspect ratio ∼1:1000) have been developed by porous membrane based methods [8] but these structures require complicated templating processes. On the other hand, lithographically prepared structures have low aspect ratio (∼1:10) and require multiple processing steps and clean room facilities for fabrication [7,9,10].

We recently demonstrated that structured polymers of poly-(p-xylylene) (PPX) can be fabricated by oblique angle deposition method [11–16]. These structures have high aspect ratio (∼1:1000) and the production technique does not require any template, lithography method or a surfactant for deposition. The structured polymer films are conformal to any surface and suitable for industrial applications. Structured PPX offers the possibility of fabricating surfaces exhibiting tunable properties (e.g., hydrophobicity, electrochemistry, chemical reactivity, and surface energy) by systematically varying and controlling the surface chemistry and morphology at the same time.

PPX is a polymeric thin film grown by vapor deposition method using di-p-xylylene (a.k.a [2.2]paracyclophane or parylene) as starting monomer. Di-p-xylylene was first synthesized in 1949 [17] and systematically investigated by Cram and Steinberg from 1951 onward [18]. The planar PPX polymer films have a wide range of usage such as chemical and corrosion resistant coatings, electrical insulators and dry lubricants, moisture barriers, capacitor dielectrics, and anti-friction layers in MEMS [19,20]. We should note that traditionally coated PPX film morphology is different from the structured PPX film. The latter comprises free-standing, slanted, parallel columns containing nanowires. Herein, we reported the

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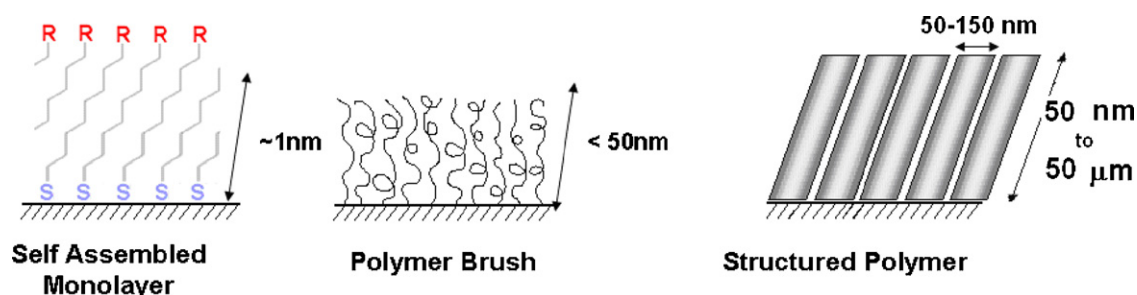*E-mail address:* mdemirel@engr.psu.edu.

Fig. 1. Three ways of studying, controlling and tuning surfaces are self assembled monolayers, polymer brushes and structured polymers.

control of morphology of structured PPX deposition and provided recent results related to deposition of these films. We discussed the advantages of depositing structured PPX films, such as the dielectric and hydrophobic properties.

2. Experimental methods

PPX-Cl planar and nanostructured films are prepared from dichloro-[2.2]paracyclophane (a.k.a. dichloro-di-*p*-xylylene or Parylene Type C; Lot #060514; Parylene Distribution Services Inc.) on native oxide Si wafers using the procedure and instrument described previously [11–16]. Cross sectional images are completed by a scanning electron microscope (JEOL 6700F FE-SEM) images. The samples are prepared by depositing polymer films on silicon substrates and then by cleaving the thin films in liquid nitrogen. The surface analysis is completed by an atomic force microscope (Nanoscope E, Veeco) using silicon-nitride cantilevers in contact mode. The surface area of a structured PPX film is measured using BET (after Brunauer, Emmett and Teller) method by a SA 3100 Surface Area and Pore Size Analyzer (Beckman Coulter, Inc.). Fifty milligrams of PPX-Cl film is analyzed under nitrogen gas. Static con-

tact angles are measured by applying a video microscope interfaced to a computer (FTA-1000) to capture drop images.

3. Results and discussions

Metallic and ceramic structured films using oblique angle physical vapor deposition (PVD) method were first grown in 1959 [13] but, for the first time, structured polymers have been recently deposited by our group using oblique angle vapor deposition polymerization (VDP) [11–16]. VDP starts with a monomer (i.e., xylylene) or a dimer (i.e., paracyclophane), and the monomers are converted to a polymer (poly(*p*-xylylene), PPX) during the growth process by radical polymerization. PVD is different from VDP because the reactive monomer, in VDP, has to search the end of the polymer chain after it is condensed on the surface. For oblique angle VDP deposition, the substrate is tilted with respect to the incident vapor flux, thereby exciting a self-shadowing [21] and nucleation [22,23] processes. Di-chloro-paracyclophane is placed in an evacuated chamber and converted to a reactive vapor of monomers by pyrolysis that forms the PPX-Cl film (Fig. 2A). The deposition rate and the deposition pressure are controlled by the
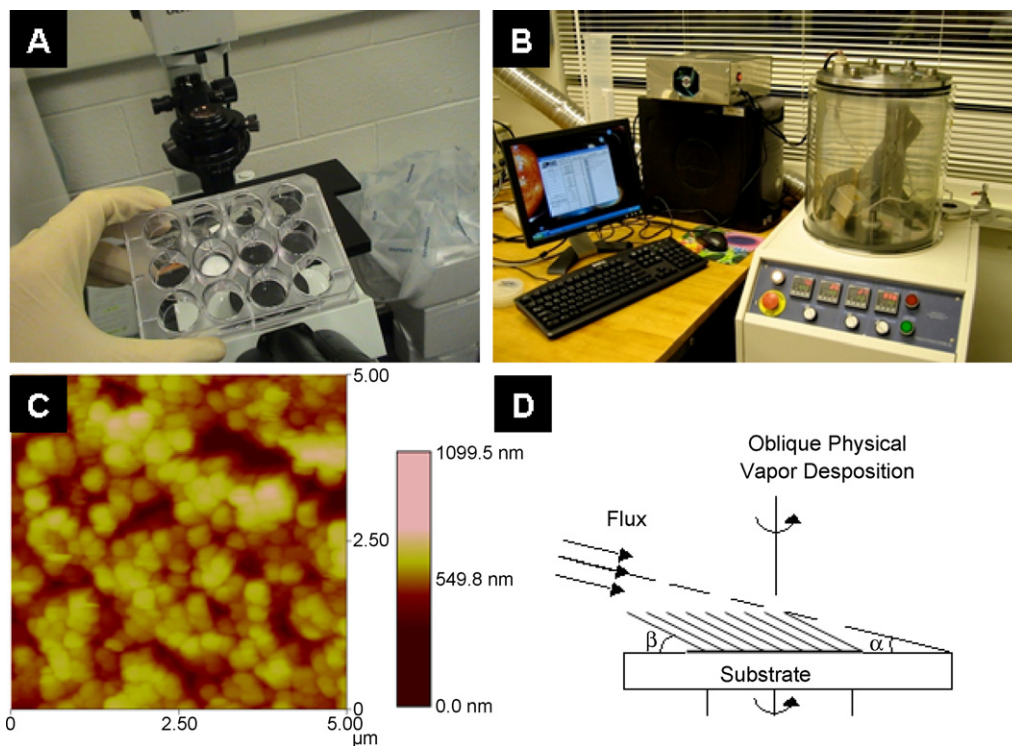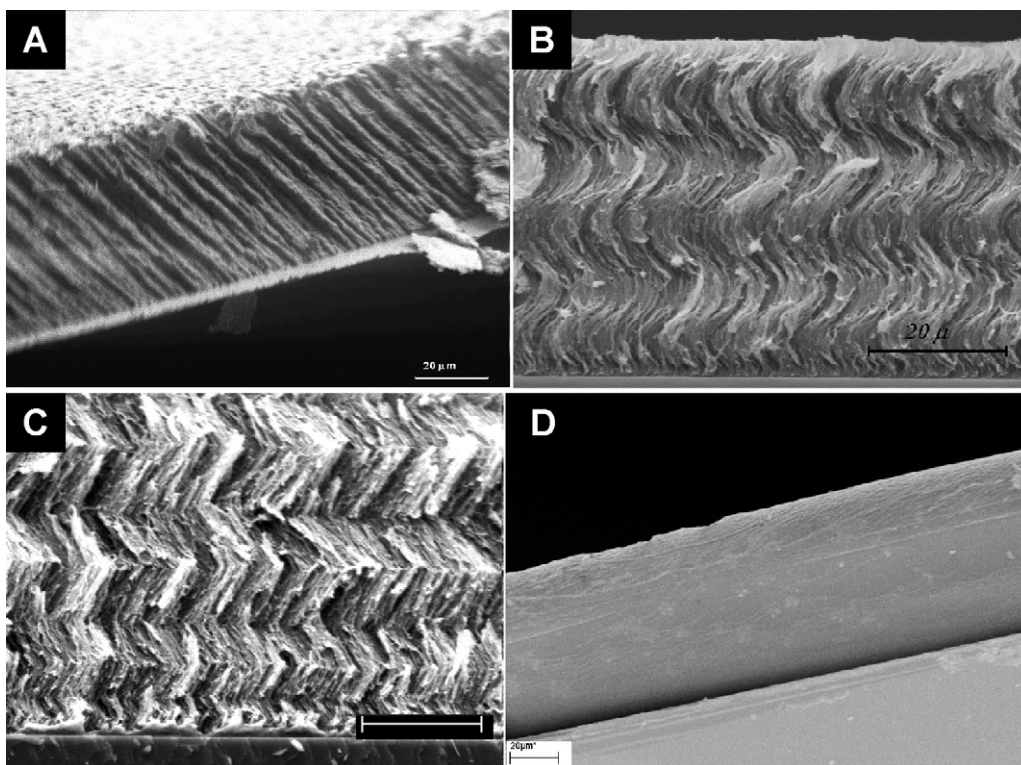

Fig. 2. (A) Structured polymer film coated on a 12-well plate (white-disk) is shown. (B) A computer controlled stepper motor and nozzle assembly are developed to deposit structured PPX. (C) Top-surface AFM image of the same film showing nano-columns approximately 150 nm in diameter (color scale shows the height). (D) A schematic of oblique angle deposition process is shown.

Fig. 3. Cross sectional SEM micrographs of columnar (A) columnar, (B) helical, (C) chevron and (D) planar PPX films. Planar PPX films do not possess nanostructured morphology. Scale bar for all micrographs are 20 μm.

evaporation temperature (150–175 °C) of the dimer and the pyrolysis temperature (600–690 °C). 0.3 g of the dimer is inserted into the vaporizer for each deposition, and the vapor pressure is maintained at approximately ∼10 Torr. The deposition process takes 10 min after the required vacuum level has been achieved. Fig. 2A shows a structured polymer film coated on a 12-well plate (white-disk). Fig. 2B shows a computer controlled stepper motor and nozzle assembly of the oblique angle VDP system. Fig. 2C shows a top-surface atomic force microscopy image of a structured PPX film deposited for 10 min on a silicon substrate. A description of oblique angle deposition process is shown in Fig. 2D. The incident vapor flux

is directed, on average, at an angle α (=10°) to the substrate plane.

Morphology control can be achieved by manipulating the substrate rotation during oblique angle deposition. It is possible to vary the two fundamental axes of rotation (i.e., normal to the substrate and parallel to the substrate) either separately or concurrently in order to obtain a wide variety of morphologies. Cross sectional scanning electron microscopy (SEM) is used to compare the nanostructured PPX films with a planar PPX film (which are conventionally deposited [24] and do not possess nanostructured morphology). Fig. 3 shows SEM cross sectional micrographs of columnar, helical, chevron and planar PPX films. Computerized con-
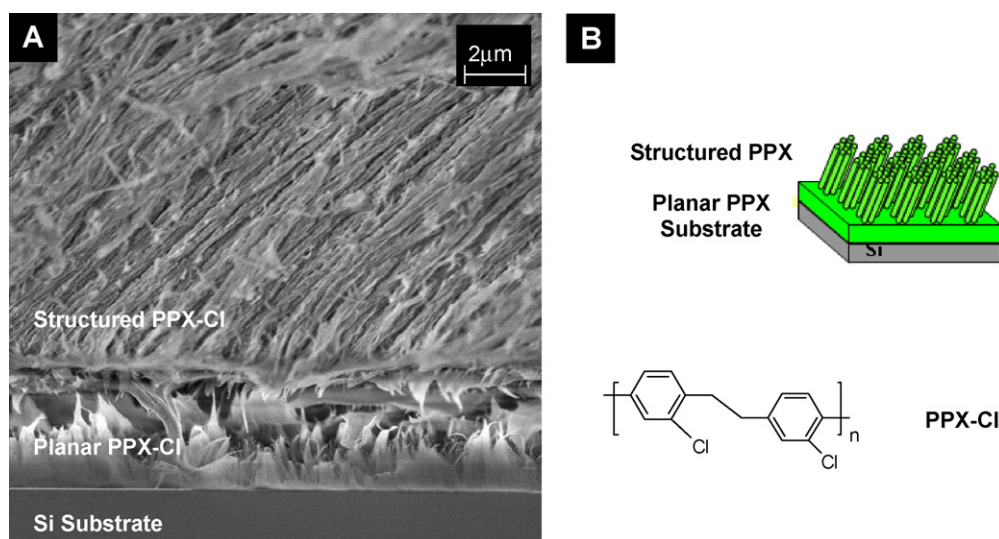
Fig. 4. Two-layer deposition of PPX-Cl film is shown: (A) cross section SEM micrograph of a composite planar-structured polymer film (scale bar 2 μm), (B) Schematic of the two-layer deposition.

trol of substrate rotation introduces a rotation axis normal to the substrate surface φ, in addition to the rotation axis that enables oblique flux incidence angles α. By changing the relative direction of the vapor flux, we can manipulate column growth to engineer the nanostructure of the film. The substrate is kept constant for columnar growth, and it is rotated normal to the surface for helical and chevron growth. The nanowire diameters are approximately 150 nm.

The three major advantages of structured PPX polymers as surface coatings are as follows: (i) Their surface-to-volume ratio is very high, the available surface area increasing by over two orders of magnitude in relation to the bulk material. We have measured the surface area of structured PPX films using a nitrogen adsorption technique. BET results showed that the surface area of a PPX-Cl is 76.9 m^2 (i.e., an increase of 392 times of the geometric area) and has an estimated 50% porosity. (ii) Their chemistry is controllable, and so it is possible to engineer structured PPX from many possible combinations of monomers that have desired functional groups. (iii) They can have varying structure morphology to provide the best possible substrate and coating material for medical devices, for example, columnar, helical and chevron morphology can be obtained by controlling the rotation of the substrate.

Fig. 4A shows a two-layer film which has both planar and structured PPX film. Initially the substrate is kept perpendicular to the vapor flux ($\alpha = 90°$) that forms the planar film layer. Subsequently, the substrate is tilted to an inclined angle ($\alpha = 10°$). Fig. 4B describes the schematic of the two-layer PPX-Cl film which is formed by vapor deposition polymerization. There are many advantages of two-layer PPX film coating such as increased hydrophobicity and decreased dielectric constant. This is especially true for PPX films used nowadays in coatings of surgical instruments, biomedical devices, circuit boards, semiconductors and fiber optics components. PPX is insoluble in most organic solvents up to 150 °C. PPX film increases the lifetime of these devices by providing diffusion barrier to many solvents. A low-k dielectric PPX provides better insulating properties for thermal applications. Halogen derivatives of PPX film are hydrophobic, which provide a non-sticky surface. The hydrophobicity of PPX film increases proportionally to the surface roughness. The nanostructured PPX-Cl film is more hydrophobic ($\theta_w = 120°$) than the planar PPX-Cl film ($\theta_w = 88°$). For contact angle measurements, a sessile water droplet (static contact angle, θ_w) resting on a PPX film surface is measured by a goniometer to assess the relative hydrophobicity of the surface. Additionally, the two-layer PPX film has better dielectric properties than the planar PPX film. Planar PPX film has a dielectric constant of 2.8, whereas the two-layer film has a dielectric constant of 1.4. For dielectric constant measurements, a thin gold layer with a diameter of 0.6 mm is deposited on the film surface by a mask-sputtering method. The capacitance, C, is measured by an impedance analyzer at 100 kHz. The dielectric constant k of the film is calculated by the capacitor formula: $k = C \times t/(k_o \times A)$, where t is the thickness of the two-layer PPX-Cl film, A is the area of the gold electrode, and k_o is the permittivity of free space.

4. Conclusion

In conclusion, a structured polymer PPX film is successfully fabricated by a simple method of oblique angle vapor deposition polymerization. Morphology control is achieved by manipulating the substrate rotation during oblique angle deposition. Helical, columnar and chevron films are deposited and characterized by electron microscopy. Tunable physical properties (i.e., hydrophobicity and dielectric) are obtained by multi-layer PPX deposition. The static contact angle increases from 88° to 120° due to nanoscale surface roughness. The dielectric constant decreases from 2.8 to 1.4 with an estimated porosity of 50% from BET results.

For future studies, we shall systematically vary and control the chemistry (i.e., combinations of monomers that have desired functional groups) and morphology (i.e., helical, columnar, and chevron) at the same time to fabricate coatings exhibiting tunable physical properties (i.e., modulus, hydrophobicity, toughness, porosity, etc...). Structured PPX deposition technology can be a simple and inexpensive method for the functionalization of surfaces for industrial scale applications.

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