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Growth of sculptured polymer submicronwire assemblies by vapor deposition

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Abstract

We have grown helical nanowire assemblies of parylene C, thereby demonstrating that polymeric sculptured thin films (STFs) can be fabricated by a combination of physical and chemical vapor deposition processes. The deposition method is explained in detail and electron micrographs of 200–400 nm size sculptured thin film of parylene are given. The shapes of the submicron and nanowire assemblies can be engineered so that the polymeric STF acts as a template for preferential attachment of biomolecules.

Keywords: Parylene; Nanowires; Chemical and vapor deposition

1. Introduction

According to a recent report by the Royal Society and the Royal Academy of Engineering [1], nanomaterials have structured components with at least one dimension less than 100 nm. Nanomaterials have a relatively large surface area per unit mass in comparison to bulk materials. This fact is commonly held responsible for the higher chemical and biochemical reactivity of nanomaterials as well as for their unusual electrical and mechanical properties. The growth of films comprising arrays and networks of polymer nanowires has, therefore, emerged as an important nanotechnology. This is due, in part, to the potential commercial application of this knowledge for the development of microfluidics and optical devices such as biosensors, as well as prosthetic coatings that would render them more bio-compatible within the body. Such films are mostly grown by electropolymerization [2–4], but reverse templating [5], DNA-templating [6], vapor-liquid-growth [7] and dip-pen nanolithography [8] have also been used. A recent study [9] has demonstrated synthesis of large scale helical carbon nanotubes by pyrolysis.

Sculptured polymer nanowires are expected to simultaneously provide optical functionalities associated with sculptured thin films (STFs) of inorganic materials [10, 11] as well as compatibility with biological materials. Surface to volume ratio is very high in STF films. STFs can be made out of virtually any material and can increase available surface area by over two orders of magnitude. Indeed, it is well-known that cell attachment to substrates and films with large surface area per unit volume is enhanced [12]. The use of organic substrates such as collagen attached to such films would create a biocompatible material for medical implants and biological sensors. Similar bottom-to-top nanotechnology approaches have been studied by several experimental groups, as reviewed recently by Yeates [13].

In this communication, we report progress towards the goal of sculptured polymer nanowire assemblies. The assemblies are not of true nanowires, because the diameters are of the order of 200–400 nm; and it would be more appropriate to call them submicronwires. However, the novel combination of physical and chemical vapor deposition processes devised to grow these assemblies promises that true sculptured polymer nanowire assemblies will soon grown.

2. Experimental

Chiral STFs, comprising assemblies of parallel submicronwire helixes, were grown by a combination of

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physical vapor deposition (PVD) and chemical vapor deposition (CVD) in a commercial parylene reactor. The PDS 2010 equipment (Cookson Electronics) is designed to provide an even, conformal coating to any substrate placed in deposition chamber. Unlike conventional PVD systems such as thermal evaporators or sputtering systems [14], deposition variables such as pressure or deposition rate are indirectly adjusted by varying the vaporizing and pyrolizing temperatures. The type C parylene, which was deposited is the polymer form of the low-molecular-weight dimer of *para*-chloro-xylylene [15]. Polymeric parylene is formed by evaporating a dimer and then pyrolizing the dimer into a monomer precursor for polymer formation. The chemical structure of the parylene C monomer is a benzene ring with two *para*-methylene groups and one chlorine side group, and has the chemical formula of C_8H_7Cl. The amount of this dimer was the only fixed deposition parameter in our initial experiments.

In order to grow STFs on the chosen system, several modifications were made. Parylene flux (monomer) delivered by this system is inherently non-directional, which is not amenable to the formation of STFs [10]; therefore, a nozzle was constructed to provide the requisite directionality. The nozzle has an inlet diameter of 1 in. and an outlet of 0.25 in., which was held approximately 2 in. from the rotating substrate. In addition to enabling directionality, a motor assembly was designed that allowed the substrate to be rotated in two directions in the vacuum environment necessary for shaping the growing submicronwires [10]. This assembly consisted of vacuum stepper motors rated to 10^{-7} Torr and 155 °C internal operating temperature; a motion control box housing micro-stepping drives for each motor; a networking hub that allowed control over both motors in real time; and a power supply. Real-time micro-stepping at rates as high as 50,800 steps/rev was implemented using a laptop computer and control software. The original ‘lid’ to the deposition system was replaced by a modified chamber. The chamber consisted of a 12-in.-diameter cylindrical quartz enclosure with two viton rubber flanges on each end. One end of the quartz enclosure sat on the base-plate of the parylene system. The motor assembly was mounted on a metal plate that served as a top to the 18-in.-high deposition chamber.

The modified deposition assembly, wherein features of both physical vapor deposition (directional evaporation) and chemical vapor deposition (pyrolysis of the parylene dimer, followed by polymerization) have been incorporated, is shown schematically in Fig. 1. The vapor flux is controlled by the evaporation temperature of the dimer and the pyrolyzing temperature. The two temperatures together control the deposition rate and deposition pressure.

Deposition time was measured from when the vaporization temperature reached 150 °C to when the system was manually shut down. Parylene depositions were made for 5, 10, and 15 min with rotation speeds of either 0.167 and 0.025 rps and the incoming flux arriving at an angle θ of 80° with respect to the substrate normal (Fig. 1). Two depositions were done with the substrate perpendicular to the vapor flux ($\theta = 0°$) to serve as control samples. Depositions were done on 7059 Corning Glass and also on silicon to facilitate cross-sectional SEM microscopy. In an attempt to maintain the same vapor pressure during each deposition, five grams of the parylene C dimer were inserted into the vaporizer for

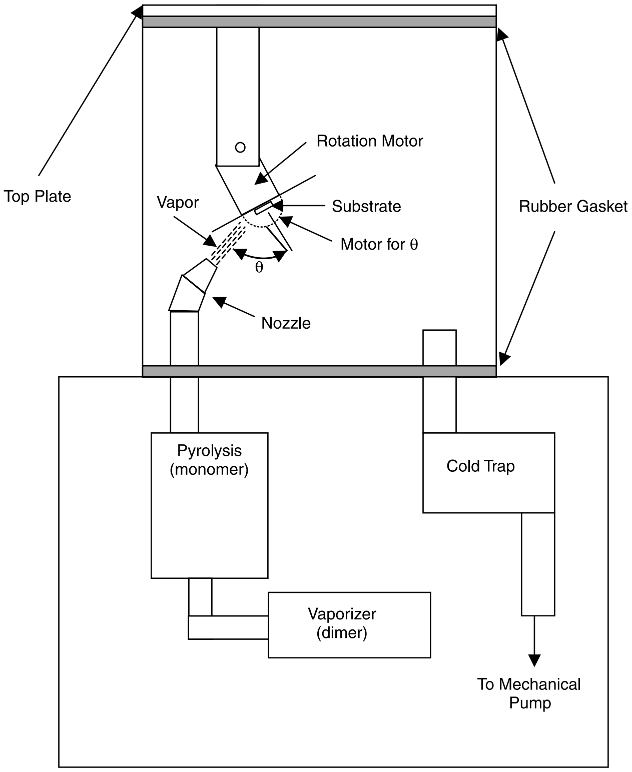

Fig. 1. Schematic of stepper motor and nozzle assembly used with the parylene deposition system. This system combines physical and chemical vapor deposition processes.

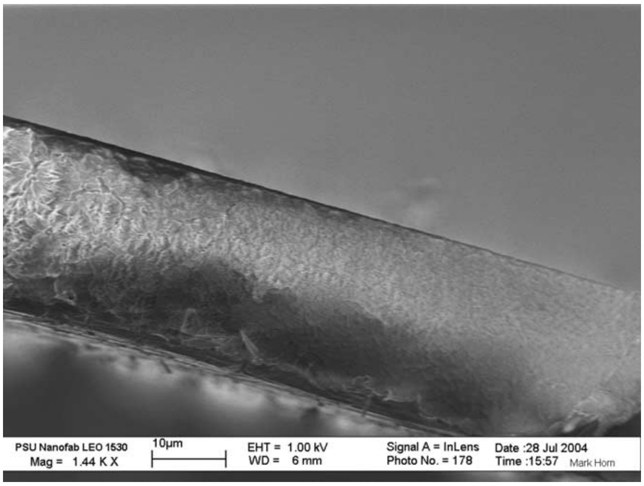

Fig. 2. Cross-section SEM micrograph of a parylene thin film grown normal to the nozzle assembly.

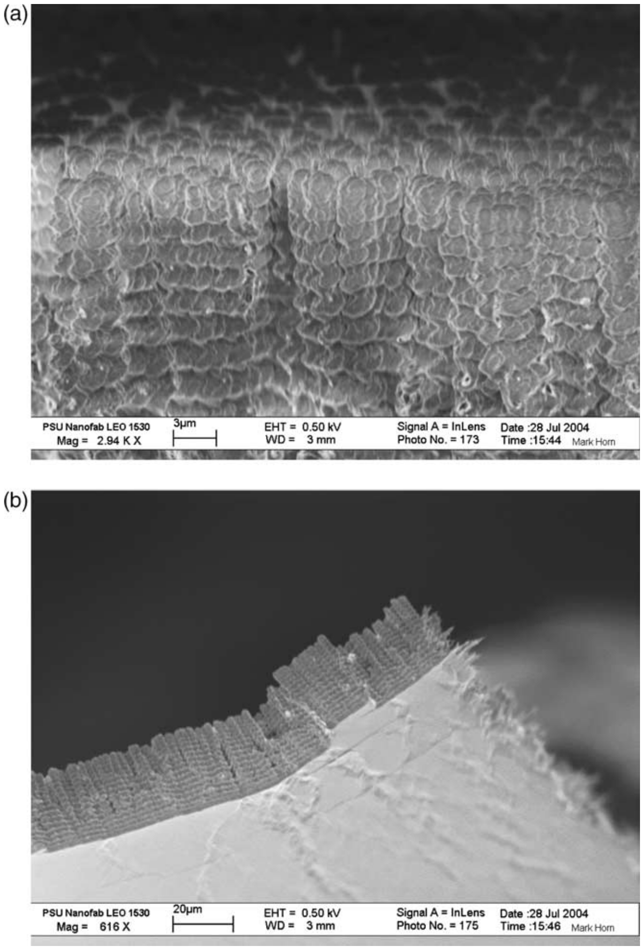

Fig. 3. SEM micrographs of a chiral sculptured thin film of parylene deposited at an angle θ of 80° and a rotation speed of 0.025 rps (1.5 rpm). (a) 2.94K× magnification and (b) 616× magnification.

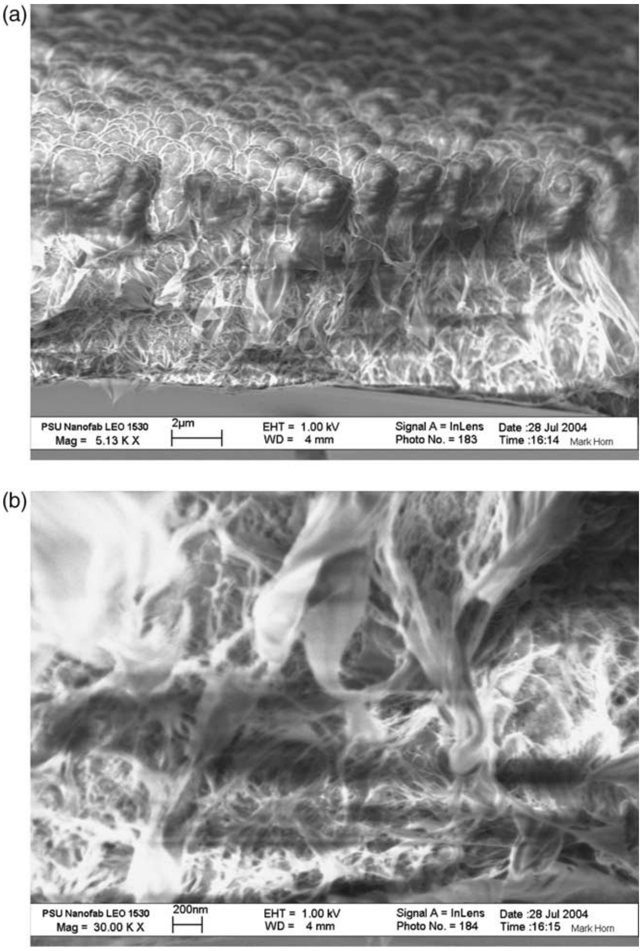

Fig. 4. Cross-section SEM micrographs of a parylene film deposited at an angle θ of 80° and a rotational velocity of 0.167 rps (10 rpm). (a) 5.13 KX magnification and (b) 30 KX magnification. Note the fibrous nature of the film during initial growth (bottom) and the columnar structure near the top.

each deposition. The vapor pressure was approximately 10 Torr during deposition. Deposition thickness for all films varied from 15 to 30 μm, as measured with a surface profilometer, showing no apparent dependence on deposition time.

3. Results and discussion

Before discussing the structure of the polymeric chiral STFs deposited by us, let us mention that the growth of polymeric chiral STFs has been reported by Harris et al. [16] using a three-step replamineform technique: first, a chiral STF of an inorganic material is made using PVD; second, the void regions are filled with a polymer that is cured; and third, the inorganic material is etched out. The result is a polymeric thin film with an array of parallel helical holes. In contrast, we grew polymeric thin films comprising helical submicronwires, by a combination of PVD and CVD.

Fig. 2 shows a cross-section SEM micrograph of a parylene film deposited with the vapor flux incident normally on the rotating substrate. The film lacks nanostructure typical of a dense film deposited at normal incidence [17,18]. It is this lack of porosity that gives parylene its desirable properties as a hermetic coating, but which is obviously deleterious to the growth of chiral STFs, which are necessarily porous. Therefore, we set $\theta \gg 0°$ to grow polymeric chiral STFs.

Fig. 3 shows cross-section SEM micrographs of a chiral STF deposited for ten minutes on a silicon substrate rotating at 0.025 rps. The vapor flux was directed at the substrate with $\theta = 80°$. Fig. 3(a) shows a higher-magnification view of the top of the chiral STF which had fifteen turns and a total thickness of about 30 μm so that the helical submicronwire assemblies have a period of ~ 2 μm per turn. Fig. 3(b) shows a lower-magnification view of a section of the film that had delaminated from the substrate revealing a pin-hole free bottom surface. The parylene depositions produced with θ values greater than 80° appeared to be a frosted white color to the naked eye, which we attribute to

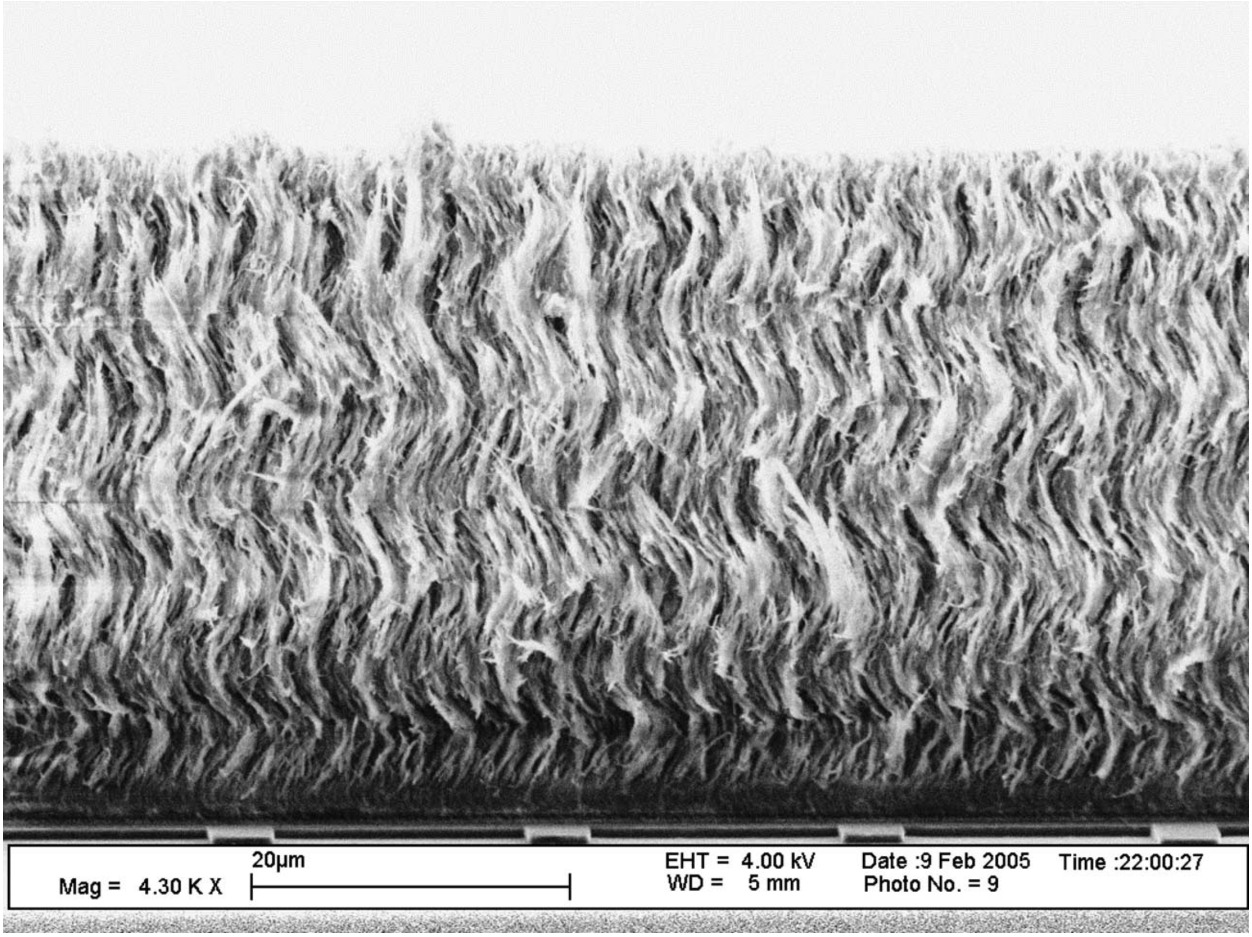

Fig. 5. SEM micrographs of a chiral sculptured thin film of parylene with small diameter size. The helical features are approximately 200 nm.

the topography, whereas the depositions done at normal incidence were transparent.

The films deposited on substrates rotating at 0.167 rps turned out to have a more complex structure, as can be deduced from the cross-section SEM micrographs provided in Fig. 4. These films were initially a network of parylene strands, which eventually coalesced into columns perpendicular to the substrate. The columns in these films lack the distinct structural chirality evident in Fig. 3 for films deposited on more slowly rotating substrates. This observation is consistent with STFs of inorganic materials grown on rotating substrates [19]. The fibrous nanoscale porosity shown in the higher magnification SEM of Fig. 4(b) was unexpected but supports the assertion that the STFs are made of nanoscale strands. Fig. 5 shows a chiral sculptured thin film of parylene with smaller diameter (∼200 nm).

4. Conclusion

Parylene was chosen because of its historical use as a robust polymer both in microelectronic and biological applications. We have grown assemblies of parylene-C submicronwires but other types of parylene such as PPX (*p*-xylylene carboxylic acid) and PPF (pentafluorophnelester-*co*-*p*-xylylene) [20] or other polymers such as polyurethane, and teflon are alternative materials for STF films.

Future work will center on physical and chemical adsorption of proteins on polymeric STFs. Examples of two-dimensional protein patterning in polymers were reported by Shi et al. [21] and reviewed by Blawas et al. [22]. STFs provide optical properties that can be used for highly specific detection of biomolecules. This possibility is all the more attractive because the optical properties of polymeric STFs can be piezoelectrically tuned for lasing as well as polarization-dependent filtering [23,24]. Whereas sculptured submicronwire assemblies would display optical functionalities in the far-infrared regime, sculptured nanowire assemblies would be suitable in the visible regime.

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References

[1] Royal Society and Royal Academy of Engineering. Nanoscience and nanotechnologies: Opportunities and uncertainties, RS Policy Document 19/04; 2004. http://www.nanotec.org.uk/finalReport.htm.
[2] Liang L, Liu J, Windisch CF, Exarhos GJ, Lin YH. Angew Chem Int Ed 2002;41:3665–8.
[3] Huang LM, Wang ZB, Wang HT, Cheng XL, Mitra A, Yan YX. J Mater Chem 2002;12:388–91.
[4] Ramanathan K, Bangar MA, Yun MH, Chen WF, Mulchandani A, Myung NV. Nano Lett 2004;4:1237–9.
[5] Yana X, Liua G, Dickeyb M, Willsonb CG. Polymer 2004;45:8469–74.
[6] Nickels P, Dittmer W, Beyer S, Kotthaus J, Simmel F. Nanotechnology 2004;15:1524–9.
[7] Abramson AR, Kim WC, Huxtable ST, Yan HQ, Wu YY, Majumdar A, et al. J Microelectromech Syst 2004;13:505–13.
[8] Maynor BW, Filocamo SF, Grinstaff MW, Liu J. J Am Chem Soc 2002;124:522–3.
[9] Bajpai V, Dai LM, Ohashi T. J Am Chem Soc 2004;126:5070–1.
[10] Lakhtakia A, Messier R. Sculptured thin films, in nanometer structures: Theory, modeling, and simulation. Bellingham, WA, USA: SPIE Press; 2004. p. 5–44.
[11] Horn MW, Pickett MD, Messier R, Lakhtakia A. J Vac Sci Technol, B 2004;22:3426–30.
[12] Motlagh D, Senyo SE, Desai TA, Russell B. Biomaterials 2003;24:2463–76.
[13] Yeates TO, Padilla JE. Curr Opin Struct Biol 2002;12:464–70.
[14] Mattox D. The foundations of vacuum coating technology. Norwich, NY, USA: Noyes Publications; 2003.
[15] Kramer P, Sharma AK, Hennecke EE, Yasuda H. J Polym Sci, Polym Chem 1984;22:475–91.
[16] Harris KD, Westra KL, Brett MJ. Electrochem Solid State Lett 2001;4:C39–C42.
[17] Lakhtakia A, Messier R. Sculptured thin films: Nanoengineered morphology and optics. Bellingham, WA, USA: SPIE Press; 2005.
[18] Messier R, Venugopal VC, Sunal PD. J Vac Sci Technol 2000;18:1538–45.
[19] Malac M, Egerton RF. J Vac Sci Technol, A 2001;19:158–66.
[20] Lahann J, Langer R. Macromolecules 2002;35:4380–6.
[21] Shi HQ, Tsai WB, Garrison MD, Ferrari S, Ratner BD. Nature 1999;398:593–7.
[22] Blawas AS, Reichert WM. Biomaterials 1998;19:595–609.
[23] Wang F, Lakhtakia A, Messier R. Sens Actuators A-Phys 2002;102:31–5.
[24] Wang F, Lakhtakia A, Messier R. J Modern Opt 2003;50:239–49.