Chemical Vapor Deposition of Functional and Conformal Polymer Thin Films for the Formation and Modification of Nanostructures

By

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Abstract

Autonomous mini- and microscale devices require the miniaturization of component devices such as on board integrated circuits (ICs) and electrochemical power sources. A paradigm shift to micro/nanostructured 3D geometries can enable high device performance within a small areal footprint. Fabrication of such devices requires processes to form structures in a material of interest and subsequently modify the structure with additional functional materials. This thesis explores the chemical vapor deposition (CVD) of polymer thin films to enable both the formation and modification of nanostructures. The CVD method allows for simultaneous polymer synthesis and thin film formation. The broad range of applications studied in this thesis all benefit from the single-step, in-situ control of the final polymer functionality and thin film properties enabled by the CVD of polymers. The first portion of this thesis studies the formation of nanostructures for ICs via the directed self-assembly (DSA) of block copolymers (BCPs). Initiated CVD (iCVD) is used to form cross-linked poly(divinyl benzene) (pDVB) films that control the orientation of self-assembled BCPs. The cross-linking mechanism of pDVB is first ascertained to form durable films. In-situ chemical modification of iCVD pDVB is then used to tune the final orientation of the self-assembled BCP film. A conformal iCVD pDVB film is then integrated into existing DSA processes to yield a nano-template that could be used to fabricate nanostructured ICs. The second portion of this thesis studies the modification of nanostructures by active and supporting materials used in electrochemical power systems. The iCVD process is used to develop conformal, solid polymer electrolytes, a supporting material for solid state lithium ion batteries. Out of several multi-vinyl cyclic chemistries, poly(tetravinyltetramethylcyclotetrasiloxane) (pV4D4) films displayed the highest ionic conductivity ($10^{-7}$ S cm$^{-1}$) and high conformality. Active materials for supercapacitors were developed using the oxidative chemical vapor deposition (oCVD) of conductive polymers. The oCVD process was used to control the crystallographic texture of poly(3,4-ethylenedioxythiophene) (PEDOT) thin films. Edge-on texture maximized the pseudocapacitative charge storage of this material. Conformal PEDOT thin films on microstructured current collectors enabled higher energy densities in a high power, asymmetric supercapacitor.

Thesis Supervisor: Karen K. Gleason

Title: Associate Provost and Professor of Chemical Engineering
Dedicated to my mother, Dr. Janaki Moni, grandmother, Vedam Moni, and grandfather, V.S. Moni, for their unwavering support and unconditional love

In memory of my great-grandfather, S. Venkateswaran, D.Sc. Chemistry
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Table of Contents

Abstract ................................................................................................................................. 3

Acknowledgements .............................................................................................................. 7

List of Figures ..................................................................................................................... 13

List of Charts ...................................................................................................................... 19

List of Tables ...................................................................................................................... 20

Chapter 1 Introduction ....................................................................................................... 21

1.1 Chemical Vapor Deposition of Polymer Films ............................................................ 21

1.1.1 Initiated Chemical Vapor Deposition ..................................................................... 22

1.1.2 Oxidative Chemical Vapor Deposition .................................................................. 23

1.1.3 Controlling Conformality ...................................................................................... 24

1.2 Formation of nanostructures for integrated circuits .................................................. 26

1.2.1 Block Copolymers ................................................................................................. 27

1.2.2 Directed Self-Assembly ......................................................................................... 28

1.3 Modification of nanostructures for electrochemical power sources ....................... 31

1.3.1 Lithium ion batteries .............................................................................................. 32

1.3.2 Supercapacitors ..................................................................................................... 34

1.4 References .................................................................................................................. 36

Chapter 2 Growth rate and cross-linking kinetics of poly(divinyl benzene) thin films formed via initiated chemical vapor deposition ......................................................... 41

2.1 Abstract ....................................................................................................................... 41

2.2 Introduction ................................................................................................................ 41

2.3 Background ................................................................................................................. 44

2.4 Experimental Section ............................................................................................... 47

2.4.1 Synthesis of polymer films .................................................................................. 47
Chapter 3 Ultrathin and conformal initiated chemical vapor deposited (iCVD) layers of systematically varied surface energy for controlling the directed self-assembly of block copolymers.

3.1 Abstract

3.2 Introduction

3.3 Experimental

3.3.1 iCVD Film Preparation

3.3.2 Reference PS film Treatment

3.3.3 Film Characterization

3.3.4 Commensurability test

3.3.5 DSA Sample Preparation

3.4 Results and Discussion

3.4.1 Film Chemical Structure

3.4.2 Film Surface Energy and Wetting Behavior

3.4.3 Block copolymer wetting preference

3.4.4 Integration in DSA process

3.5 Conclusions
Chapter 4 Conformal Solid Polymer Electrolytes for Three-Dimensional Lithium Ion Batteries

4.1 Abstract .......................................................................................................................... 91
4.2 Introduction ..................................................................................................................... 92
4.3 Experimental .................................................................................................................. 94
  4.3.1 Materials .................................................................................................................. 94
  4.3.2 Solution Lithiation .................................................................................................... 94
  4.3.3 Characterization ....................................................................................................... 94
  4.3.4 Half Cell Testing ...................................................................................................... 95
4.4 Results and Discussion ................................................................................................. 96
  4.4.1 Ionic Conductivity by Chemistry ........................................................................... 96
  4.4.2 Film Morphology – Comparison between siloxanes .............................................. 98
  4.4.3 Film Mechanical Integrity ....................................................................................... 100
  4.4.4 Assessing conformality .......................................................................................... 102
  4.4.5 Electrochemical Lithiation of Thick Films .............................................................. 105
  4.4.6 Comparison with other solid electrolytes .............................................................. 107
4.5 Conclusion .................................................................................................................... 108
4.6 References .................................................................................................................... 109

Chapter 5 Crystallographic Texture and Electrochemical Performance in Vapor-Deposited Poly(3,4-Ethylenedioxythiophene) Thin Films for High-Rate Electrochemical Energy Storage

5.1 Abstract .......................................................................................................................... 113
5.2 Introduction .................................................................................................................... 113
5.3 Experimental methods ................................................................................................. 117
  5.3.1 PEDOT Film Synthesis ........................................................................................... 117
5.3.2 Electrode Preparation ................................................................. 118
5.3.3 Electrochemical Characterization .............................................. 118
5.3.4 PEDOT Film Characterization .................................................. 119
5.3.5 Full Cell Assembly ................................................................. 119
5.4 Results and discussion .............................................................. 120
5.4.1 Thin Film Texture ................................................................. 120
5.4.2 Electrochemical Performance .................................................... 123
5.4.3 Long-term electrochemical performance .................................. 126
5.4.4 oCVD PEDOT|MoS₂ Full-Cell Prototype ............................. 129
5.5 Conclusion ................................................................................. 132
5.6 References ................................................................................. 133

Chapter 6 Conclusions and Future Directions ...................................... 139
6.1 Summary .................................................................................. 139
6.1.1 Formation of nanostructures ................................................ 139
6.1.2 Modification of nanostructures .............................................. 140
6.2 Future Outlook ........................................................................ 142
6.2.1 Integrated Circuit Fabrication ................................................... 142
6.2.2 Electrochemical Devices ......................................................... 142
6.3 References ................................................................................. 144

Appendix A: Supplemental For Chapter 3 .............................................. 145
Appendix B: Supplemental For Chapter 4 .............................................. 147
Appendix C: Supplemental For Chapter 5 .............................................. 151
Appendix D: Permissions for Reprints ............................................... 159
List of Figures

**Figure 1-1.** Diagram of iCVD reactor. Monomer and initiator vapors are metered into the reactor. The filament array decomposes the initiator into free radicals which impinge and react with surface adsorbed monomer molecules. Reprinted with permission from Advanced Materials Interfaces, 2014, 1, 14000117. Copyright 2014, John Wiley & Sons. ................................................................. 23

**Figure 1-2.** Diagram of oCVD reactor. Monomer vapors are metered into chamber and adsorb on substrate. Solid oxidant is evaporated inside the chamber with vapors directed toward substrate. Reprinted with permission from Advanced Materials Interfaces, 2014, 1, 14000117. Copyright 2014, John Wiley & Sons. ............................................................................................................ 24

**Figure 1-3.** Intel device architectures for 22 nm node. (a) FinFET with 60 nm transistor Fin pitch (b) Interconnects with 80 nm pitch. (a, b) Reproduced with permission from IEEE International Electron Devices Meeting, 15-17 Dec. 2014; 2014; pp 3.7.1-3.7.3. Copyright 2014 IEEE..... 26

**Figure 1-4.** (a) Schematic of di-block copolymer. Linear chain of “A” molecules is covalently ended linked with linear chain of “B” molecules. (b, left) Theoretical phase diagram for microphase segregation of di-block copolymers and corresponding microphase ordered structured. (b) reprinted with permission from Soft Matter, 2013, 9, 630128. Copyright 2013 Royal Society of Chemistry.................................................................................................................................. 28

**Figure 1-5.** Schematics of (a) graphoepitaxy, where a topographical pattern to direct assembly is formed and (b) chemoepitaxy, where chemical patterns direct BCP self assembly. (a) Reproduced with permission from Journal of Materials Chemistry C 2013, 1 (6), 1192-1196. Copyright 2013 Royal Society of Chemistry. (b) Reproduced with permission from Macromolecules 2011, 44 (7), 1876-1885. Copyright 2011 American Chemical Society ............................................................... 30

**Figure 1-6.** Ragone plot comparing specific power and specific energy of several electrochemical energy storage devices. Reproduced with permission from Nat. Mater. 2008, 7, 845-854. Copyright 2008 Springer Nature.......................................................... 32

**Figure 1-7.** Schematic of (a) Thin film battery with high power density and (b) 3D battery with high energy and power density in small areal footprint. Reproduced with permission from MRS Bull. 2011, 36 (07), 523-531. Copyright 2011 Cambridge University Press. .................................................... 33

**Figure 2-1.** Series 1: Constant DVB partial pressure and T_{filament}=270 °C. Deposition rate dependence on stage temperature ................................................................. 50

**Figure 2-2.** Series 2: Constant P_{M/P_{sa}} (DVB surface concentration) and P_{I} (TBPO partial pressure). Deposition rate as a function of stage temperature and filament temperature. Filament temperatures are 200 °C(●), 220 °C(■), 240 °C(▲). Grey box highlights slope of regime II used to calculate apparent activation energy (~85 kJ/mol). ............................................................................. 51

**Figure 2-3.** Transmission FTIR spectra of iCVD pDVB (top) and DVB monomer (bottom). Peaks found mainly in the polymer spectra are methyl (filled in circle), and methylene (filled in diamond). Vinyl stretch at 903 cm⁻¹ highlighted in gray, para- vibration at 837 cm⁻¹ highlighted in orange, meta- vibration at 795 cm⁻¹ highlighted in blue. The areas under these peaks were used to calculate the pendant vinyl bond conversion. ......................................................................... 53
Figure 2-4. Pendant vinyl bond conversion as a function of substrate stage temperature and filament temperature for deposition series 2. (left) 200 °C(●) and (right) 220 °C(●), 240 °C(▲). The left (Ln(fraction conversion) and right (fraction conversion) axes apply to both plots. 58

Figure 2-5. Pendant vinyl bond conversion as a function of deposition rate and filament temperature [200 °C(●), 220 °C(●), 240 °C(▲)]. 59

Figure 2-6. iCVD pDVB film roughness as a function of (a) deposition rate and filament temperature [200 °C(●), 220 °C(●), 240 °C(▲)]. (b) Box and whisker plots depicting spread in film roughness as a function of filament temperature. Mean roughness (■) and outliers (♦) indicated on plot. Measurements area was 2μm x 2μm. 61

Figure 3-1: Diagram of iCVD reactor based on a schematic from Jayan et al. 70

Figure 3-2. (a) Low wavenumber ATR-FTIR spectra of p(DVB) grown at different filament currents. Vinyl stretches highlighted in gray. Ether stretch highlighted in blue. T-butyl skeletal vibration highlighted in orange (b) ATR-FTIR C-H stretch region of p(DVB) grown at different filament currents. CH₃ sp³ peaks highlighted in orange. CH₂ sp³ peaks highlighted in blue. 76

Figure 3-3. (a) Transmission FTIR of pS standard and iCVD pS at filament temperatures of 210 °C and 330 °C. CH sp² highlighted in pink. CH₃ sp³ peaks highlighted in orange. CH₂ sp³ peaks highlighted in blue. Mono-substituted benzene peaks in gray. (b) FTIR Peak area ratio of CH₃:CH₂ (▲), CH₃:Aromatic (●), and CH₂:Aromatic (♦) for Omnic reference and iCVD synthesized pS (c) ATR FTIR of Pike Technologies pS standard film as received (black) and after 2 hour TBPO treatment with filament at 330 °C (red). CH₃ sp³ peaks highlighted in gray. 79

Figure 3-4. (a) Static contact angle of diiodomethane (●) and water (●) as function of filament temperature (b) Polar(●), dispersive(●), and total (▲) surface tension of pDVB as function of filament temperature. 81

Figure 3-5: Representative AFM images of PS-b-PMMA thin films self-assembled on a PMMA preferential surface (top) and a PS preferential surface (bottom). PMMA-b-PS film thickness increases from 1.5L₀ to 2L₀ from left to right where L₀ ~ 40 nm. At 1.75L₀, PMMA preference produces islands whereas PS preference produces holes. 83

Figure 3-6. Wetting behavior of PS-b-PMMA films on iCVD pDVB substrates. BCP film thicknesses of 1.5L₀, 1.75L₀, and 2.0L₀ (across) were spin cast on ~12 nm thick iCVD pDVB films grown at 5 different filament temperatures (down). L₀ ~ 40 nm. The 50 μm X 50 μm top-down optical micrograph are shown on the left-side. The right-side shows 2 μm X 2 μm top-down SEMs. The blue-to-red color continuum at the bottom demonstrates the difference in wetting behavior between pDVB films grown at different filament temperatures from PMMA preferential to non-preferential (NP) to PS preferential. 85

Figure 3-7. (a) Schematic of HSQ (green) template on silicon with conformal iCVD pDVB coating (beige). (b) 45° -tilted cross-sectional SEM image of HSQ template coated with iCVD pDVB demonstrating coating conformality. HSQ regions highlighted in green. iCVD pDVB coating highlighted in yellow. Yellow dots delineate interface between template and polymer film. Schematics of PS-b-PMMA self assembly with non-preferential bottom wall and (c) PMMA sidewall preference (light-red color) and (d) PS side wall preference (light blue color). PMMA domains shown in blue, PS domains shown in red. SEM images of self-assembled PS-b-PMMA
(L₀ = 25nm) in HSQ template coated with iCVD pDVB grown at (c) Tᵣ=210 °C with PMMA sidewall preference and (f) Tᵣ=240 °C with PS sidewall preference. Insets are enlarged views with PMMA domains highlighted in blue and PS domains highlighted in red.

**Figure 4-1.** (a) Solution lithiation scheme. The iCVD polymer film is grown on an ITO/Glass slide. (1) Soaking slide in 1 M LiClO₄ in propylene carbonate (PC) for 3 days (2) Rinse in PC (3) Anneal at 110 °C in an argon filled glovebox (b) Chemical structures of siloxane and silazane monomers used (c) Ionic conductivity of poly(siloxane) and poly(silazane) films as determined by EIS. Adapted with permission from *Macromolecules* 2015, 48 (15), 5222-5229. Copyright 2015, American Chemical Society.

**Figure 4-2.** AFM images of 30 nm thick iCVD pV3D3 film on silicon wafer (a) before (Rₘs=1.29 nm) and (b) after lithiation (Rₘs=4.26 nm). AFM images of 25 nm iCVD PV4D4 film on silicon wafer (c) before (Rₘs=0.67 nm) and (d) after lithiation (Rₘs=2.92 nm). Rₘs is root-mean-square roughness. Reproduced with permission from *Macromolecules* 2015, 48 (15), 5222-5229. Copyright 2015, American Chemical Society.

**Figure 4-3.** (a) Sample preparation scheme. Silver nanowires were dispersed on a TEM grid and then (1) coated with iCVD pV4D4 (orange outline) and (2) lithiated via solution soaking (blue outline). (b,c) TEM images of a 10 nm iCVD pV4D4 coating (b) as deposited and (c) after solution lithiation. (d,e) iCVD pV4D4 film thickness distribution as obtained from TEM imaging of (d) as deposited iCVD pV4D4 (11.5 nm ± 2.6 nm) and (e) solution lithiated iCVD pV4D4 (12.6 nm ± 3.2 nm). To obtain the data for each condition, 11 wires were chosen at random from different locations of the grid and 30 measurements were taken on each wire. (b, c, d, e) Reproduced with permission from *Mater. Horiz.* 2015, 2 (3), 309-314. Copyright 2015 Royal Society of Chemistry.

**Figure 4-4:** (a) Sample preparation scheme for Si Nanowire imaging. Nanowire array is (1) coated with iCVD pV4D4 and (2) sonicated in isopropanol and dispersed on a TEM grid for imaging. SEM images of (b) as received Si nanowire array and (c) iCVD pV4D4 coated nanowire array. TEM images of Si nanowire array(d) as received and (e) coated with iCVD pV4D4. The iCVD coating is highlighted in light purple. Si nanowire arrays were provided Dr. Ahmed Al-Obeidi of Professor Carl V. Thompson’s group at MIT. (b-c) Reproduced with from *Beilstein J. Nanotechnology* 2017, 8, 723-735 under a Creative Commons 4.0 License.

**Figure 4-5.** Schematic of three-electrode setup used for half-cell testing of iCVD pV4D4 on a mesocarbon microbead (MCMB) slurry anode. Stainless steel substrate used as current collector. Image courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles).

**Figure 4-6.** (a) Cyclic voltammetry of 400 nm iCVD pV4D4 on MCMB after 1, 25, and 50 galvanostatic cycles. Inset shows CV of bare carbon for comparison. (b) Half-cell capacity as a function of conditioning cycles. Currents of 0.5 μA, 1.0 μA, and 5.0 μA correspond to C/1000, C/500, and C/100 respectively. (c) Impedance spectra of carbon only (gray), half-cell after conditioning (black-dashed), and half-cell after 50 G/V cycles. Ionic conductivity of pV4D4 is 1.2*10⁻⁷ S/cm and 3.2*10⁻⁷ S/cm after conditioning and 50 cycles respectively. (d) Half-cell capacity at higher rates. Solid line is C/20, dashed line is C/10. Figure courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles).
Figure 5-1. Schematic of (a) Doped PEDOT crystal structure. Anion dopants occupy the (020) plane between the thiophene planes (b) Face-on crystallite orientation with (0k0) planes parallel to substrate (c) Edge-on crystallite orientation with (h00) planes parallel to substrate.

Figure 5-2. (a) X-Ray Diffraction Spectra of oCVD PEDOT grown T_{stage} = 65 °C, 100 °C, 150 °C, 175 °C, and 250 °C. The peaks corresponding to the (100) and (020) planes occur at 20 equal to 7° and 26° respectively. (b) Peak area ratio of 7° to 26°. The increase in the ratio with T_{stage} indicates an increase in the edge-on orientation of the crystallites.

Figure 5-3. (a) Cyclic voltammograms of Face-On and Edge-On oCVD PEDOT cycled from 2 to 4.2 V vs. Li/Li⁺ at a sweep rate of 10 mV s⁻¹. Galvanostatic profiles of (b) Face-On and (c) Edge-On oCVD PEDOT from 2 to 4.2 vs Li/Li⁺ at current densities of 0.1, 1.0, and 10 mA cm⁻². (d) Specific capacities and capacitances of Face-On and Edge-On oCVD PEDOT as a function of a current density from 0.1 to 10 mA cm⁻².

Figure 5-4. (a) Chemical structure of PEDOT with α and β carbons labelled. (b) Raman spectra of films as-deposited (dashed) and after long-term cycling (solid) for (top) Edge-On and (bottom) Face-On oCVD PEDOT. (c) Peak area ratio of oxidized to neutral Cα,β stretch of Face-On and Edge-On oCVD PEDOT. Gray column is for as-deposited films. Black column is after long-term cycling.

Figure 5-5. (a) Nyquist plots of the impedance spectra for (top) Edge-On and (bottom) Face-On oCVD PEDOT before (solid) and after (dashed) long-term galvanostatic cycling. Inset is the equivalent circuit used for fitting. Where R_{CT} is the charge-transfer-resistance. (b) Cycle stability from galvanostatic cycling at a 1 mA cm⁻² current density of Edge-On (red, solid line) and Face-On (blue, dashed line) oCVD PEDOT. The stability conferred by edge-on dominance is evident by both methods of comparison.

Figure 5-6. (a) Cyclic voltammograms at sweep rates of 10, 20, 50, and 100 mV s⁻¹ and (b) galvanostatic cycling at current densities of 0.1, 1, and 10 mA cm⁻² of an Edge-On oCVD PEDOT|MoS₂ asymmetric device from 3 to -1 V. (c) Charge-discharge profiles of the device are pseudo-linear. (d) Device characteristics of the asymmetric cell are depicted in a Ragone plot.

Figure A-1. (Left) AFM images and (Right) AFM line scans and corresponding roughness values of pDVB grown at varying filament temperatures.

Figure A-2. High wavenumber transmission mode FTIR data and individual Voigt fitted peaks for polystyrene (a) reference from Omnic (b) iCVD grown at 225 C (c) iCVD grown at 330 C.

Figure B-1. (a) Representation of the experimental configuration used for electrochemical impedance spectroscopy. Impedance of the (b) unlihiated and (c) lithiated 25 nm pV4D4 films. The data were taken in the frequency range from 100 kHz to 100 Hz using a 10 mV (RMS) potential. The circuits for equivalent circuit fitting are shown. The semi-circles in (c) are indicative of ionic conduction. The solid curves were obtained from data fitting and used to determine R_p. Cartoon insets in (b) and (c) propose the pV4D4 structure before and after lithiation respectively. Blue and red spheres represent Si and O atoms respectively. In (b) and (c) the geometric markers indicate different positions on the sample. Reproduced with permission from Mater. Horiz. 2015, 2 (3), 309-314. Copyright 2015 Royal Society of Chemistry.
Figure B-2. (a) AFM image of the surface of pV4D3 film after lithiation. (b) SEM image of particle that appears as “white” feature on AFM scan. (c) Energy dispersive spectrum (EDS) of particle showing a strong chlorine signal (d) EDS on the surface adjacent to the particle showing no chlorine signal. This confirms that the particles observed in the AFM are precipitated LiClO4. Reproduced with permission from Macromolecules 2015, 48 (15), 5222-5229. Copyright 2015, American Chemical Society.

Figure B-3. Fitting circuit used for EIS of carbon/pV4D4 half cell

Figure B-4. Galvanostatic cycling of MCMB slurry on stainless steel only. Cycles at C/20 and C/10 shown. Approximate capacity is 270 mAh/g. Image courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles).

Figure C-1. Cyclic voltammograms of Face-On oCVD PEDOT cycled from 2 to 4, 4.2, and 4.4 V vs. Li/Li+ at a sweep rate of 10 mV s⁻¹.

Figure C-2. Cyclic voltammograms of Edge-On oCVD PEDOT cycled from 2 to 4, 4.2, and 4.4 V vs. Li/Li+ at a sweep rate of 10 mV s⁻¹.

Figure C-3. Cyclic voltammogram of commercially purchased PEDOT:PSS coated on stainless steel cycled from 2 to 4.2 V vs. Li/Li+ at a sweep rate of 10 mV s⁻¹. The areal current scale (−150, 150 μA cm⁻²) is used for comparison with oCVD PEDOT. Inset shows voltammogram in smaller range of areal currents. PEDOT:PSS is essentially electrochemically inactive in this potential window, unlike oCVD PEDOT.

Figure C-4. EDS spectra of oCVD PEDOT films on stainless steel as-deposited (dashed line) and after long term cycling (solid line) at stage temperatures of A) 100 °C (Face-On) and B) 175 °C (Edge-On).

Figure C-5. Deconvolution and fit of Raman spectra of (a) Face-On (100 °C) – As Deposited, (b) Face-On (100 °C) – long-term cycled, (c) Edge-On (175 °C) – As Deposited, and (d) Edge-On (175 °C) – Long-term cycled oCVD PEDOT films.

Figure C-6. (a) Cyclic voltammetry and (b) galvanostatic cycling of EPD MoS2 electrodes cycled in 1M LiClO4 EC:DMC with Li counter and reference electrodes in a three-electrode cell. Galvanostatic cycling shows high capacities at current densities up to 5 mA cm⁻² due to the high density of defects in the MoS2 nanocrystals and semi-metallic conduction of the 1T phase. The native oxide on the Ni foam current collector may also contribute to the high capacities observed.

Figure C-7. (a) Representative galvanostatic profiles of positive oCVD PEDOT and negative EPD MoS2 electrodes (blue) used to determine the operating voltage of the full cell. (b) Corresponding voltage ranges of charge-discharge in the full cell device. The voltages listed are with respect to MoS2 as the counter electrode. Due to the overcapacity of MoS2 electrode in the full cell, the upper voltage was limited to 3 V.

Figure C-8. Gravimetric Ragone plot comparing the oCVD PEDOT|MoS2 asymmetric device with PEDOT-based devices. The pairing of PEDOT with MoS2 increases the maximum voltage of the full cell to 3 V and results in a 1.4x increase in energy compared to devices with aqueous electrolytes (upper voltage limit 1.8 V). The power densities of the oCVD PEDOT|MoS2 device are also markedly higher than the comparison devices that utilize PEDOT:PSS (≈10³ W kg⁻¹).
This difference may be due to the higher electronic and ionic conductivities offered by oCVD PEDOT.
List of Charts

Chart 2-1. Structures of (a) TBPO Initiator (b) DVB Monomer (combined isomers) (c) pDVB with both reacted and unreacted pendant vinyl bonds. Tert-butoxy moieties from the initiator serve as end groups.................................................................................................................................. 43

Chart 3-1. (a) Structure of poly(styrene-b-methylmethacrylate). PS block in red, PMMA block in blue (b) structure of divinyl benzene monomer, which is a mixture of para- and meta- isomers (c) α scission of TBPO to form t-butoxy radicals (d) β scission of t-butoxy radical to form methyl radical and acetone........................................................................................................................ 71

Chart 3-2: Potential reactions with methyl radical: (a) Chain initiation by methyl reaction with the first vinyl moiety of DVB (b) Chain branching by reaction with a pendant vinyl bond (c) Two-step abstraction of aromatic hydrogen and methyl substitution (d) Two-step abstraction of backbone hydrogen and methyl substitution................................................................. 77

Chart 3-3. (a) Structure of styrene monomer (b) Structure of iCVD polymerized polystyrene with partially methylated backbone and t-butox end groups. Postulated structure of iCVD pDVB based on FTIR analysis of pS at (c) low filament temperatures (d) high filament temperatures. .......... 80
List of Tables

Table 2-1. Summary of gas phase and surface processes and the dependence of rate constants on associated activation energies and temperatures in the iCVD process. .................................................. 44

Table 2-2. Series 1: Deposition constant monomer partial pressure and stage temperature variation. ........................................................................................................................................ 47

Table 2-3. Series 2: Deposition conditions for constant \( P_{DVB}/P_{Sat} \) (0.30) and stage temperature variation ........................................................................................................................................ 48

Table 2-4. Composition of technical grade DVB used in this work ........................................................................................................................................ 54

Table 2-5. Potential initiation and propagation reactions for the pendant vinyl bond at the film surface and within the bulk film ........................................................................................................................................ 56

Table 3-1. Infrared spectral peak assignments used in this work. Compiled from references 12, 15, 19-21 ............................................................................................................................................... 75

Table A-1. Area under pS FTIR peaks resolved and fitted assuming Voigt distribution from Figure A-2. ............................................................................................................................................ 146

Table C-1. Deconvolution and fit parameters of Raman spectra of oCVD PEDOT films from Figure C-5 assuming Gaussian peaks. AD = As Deposited films. LT= Long term cycled films. ........................................................................................................................................ 153

Table C-2. Fit parameters for impedance spectroscopy of oCVD PEDOT films. AD = As Deposited films. LT= Long term cycled films. ........................................................................................................................................ 154

Table C-3. oCVD PEDOT|MoS\(_2\) on Ni Foam full cell gravimetric energy and power as a function of current density. ........................................................................................................................................ 156

Table C-4. Values used in comparison Ragone plot of PEDOT(A-CNT)| A-Graphene device. 4 ........................................................................................................................................................................................................ 156

Table C-5. Values used in comparison Ragone plot of PEDOT(A-CNT)| A-CNT device. 5 ........................................................................................................................................................................................................ 157
Chapter 1 Introduction

Autonomous mini- and microscale devices for sensing, actuation, and communication require the miniaturization of component devices such as on board integrated circuits (ICs) and electrochemical power sources.\textsuperscript{1-3} The areal footprint of such component devices becomes critical given that high performance must be maintained without substantially increasing the device size. Traditional methods and materials to form macroscopic component devices do not always translate to high performance microscopic component devices. Most often, the limiting factor is the use of planar or two-dimensional (2D) architectures. A paradigm shift to three-dimensional (3D) geometries, where the device architecture is extended in the height dimension, can remove the limits associated with 2D geometries. Using micro or nano-structured architectures ensures that these 3D geometries reduce the areal footprint with minimal increase in the component device height.\textsuperscript{1-4} The integration of micro/nanostructures into devices requires two separate but equally important processes. First is the formation of the structure, which requires some kind of nanoscale template. This step is particularly important when designing on board ICs for mini and micro devices. Second is the modification of these structures with materials needed for the device to function. With respect to electrochemical energy storage, these materials include solid electrolytes and electrode materials. This thesis investigates the chemical vapor deposition of polymer thin films to enable both the formation and modification of nanostructures.

1.1 Chemical Vapor Deposition of Polymer Films

Chemical vapor deposition (CVD) is a solvent-free process that proceeds by the introduction of gas phase precursors into a vacuum chamber where they subsequently adsorb, react, and form a thin film on the substrate surface of interest. In the context of polymers, CVD allows the polymer chemistry and thin film properties to be controlled in a single process.\textsuperscript{5-6} Thin films of insoluble materials, such as conjugated or cross-linked polymers, can be made since polymer synthesis and film formation occur simultaneously. Conformal polymer coatings on high-aspect ratio structures are possible since there are no surface tension or de-wetting effects.\textsuperscript{7} Depending on the type of
polymer CVD process used, additional parameters such as chemical structure, morphology, or crystallographic texture can also be controlled in-situ. Facile control of these properties while retaining coating conformality is essential for both the formation and modification of micro/nanostructures.

Several forms of polymer CVD have been developed to date and can be separated based on their reaction mechanism and/or material class formed. The most established form is parylene CVD, which proceeds via the pyrolysis and self-polymerization of 2,2-paracyclophane derivatives. A broader range of chemistries is accessible via initiated chemical vapor deposition (iCVD), which has translated liquid-phase free-radical polymerization to the vapor phase. Thin films of step-growth polymers, such as polyamides, polyesters, and polyureas, can be synthesized using molecular layer deposition (MLD). Conjugated polymers, such as polyaniline, polypyrrole, and polythiophenes, can be synthesized using oxidative chemical vapor deposition (oCVD). Out of these various types of polymer CVD, the materials formed by iCVD and oCVD were most relevant for this thesis. Sections 1.1.1 and 1.1.2 provide a brief overview of these processes. Section 1.1.3 defines film conformality and how process conditions control the overall film conformality.

1.1.1 Initiated Chemical Vapor Deposition

Initiated chemical vapor deposition (iCVD) proceeds via free-radical polymerization of a monomer and initiator to form chain-growth polymer films. Monomers typically have at least one reactive, polymerizable moiety, such as an acrylate, methacrylate, or vinyl group. To form crosslinked thin films, two or more reactive moieties are needed per monomer molecule. Primarily peroxide based initiators are used given their modest decomposition temperatures. A schematic of an iCVD chamber is shown in Figure 1-1. Vapors of the monomer(s) and initiator are metered into a vacuum chamber. Monomer molecules adsorb on a near room temperature substrate (15-50 °C). A heated filament array (200-350 °C) decomposes the peroxide initiator into alkoxy free radicals. These radicals collide with the surface adsorbed monomers and react with the polymerizable moiety.
**Figure 1-1.** Diagram of iCVD reactor. Monomer and initiator vapors are metered into the reactor. The filament array decomposes the initiator into free radicals which impinge and react with surface adsorbed monomer molecules. Reprinted with permission from Advanced Materials Interfaces, 2014, 1, 14000117. Copyright 2014, John Wiley & Sons.

### 1.1.2 Oxidative Chemical Vapor Deposition

Oxidative chemical vapor deposition (oCVD) proceeds via step-growth polymerization to form conjugated polymer thin films. Backbone conjugation, or alternating double and single bonds, imparts electron conducting or semi-conducting properties to the polymer. A schematic of an oCVD chamber is shown in **Figure 1-2**. Monomer vapors are metered into a vacuum chamber where they adsorb on the substrate of interest. A solid oxidant, most often iron(III) chloride (FeCl₃), is thermally evaporated with the resulting vapors impinging on the substrate. The combination of monomer and oxidant commences step-growth polymerization, where dimers and trimers combine until the final film made up of n-mers is formed. Much like solution oxidative polymerization, excess chlorine ions dope the growing polymer film yielding a p-type conducting or semi-conducting film.
Figure 1-2. Diagram of oCVD reactor. Monomer vapors are metered into chamber and adsorb on substrate. Solid oxidant is evaporated inside the chamber with vapors directed toward substrate. Reprinted with permission from Advanced Materials Interfaces, 2014, 1, 14000117. Copyright 2014, John Wiley & Sons.

1.1.3 Controlling Conformality

Depending on the conditions used, a CVD process can vary from extremely conformal to extremely non-conformal (planarization). Therefore, it is important to know what factors enable conformal film deposition and how these are related to the deposition conditions used.

Thin film depositions on well-defined micron-sized trench structures are often used to study the process’ conformality. When studying the conformality on a trench structure, step coverage (SC) and side-wall coverage (SWC) are the most important properties to assess. SC and SWC are defined in Equation 1-1 and Equation 1-2 respectively,

**Equation 1-1**

\[ SC = \frac{t_{\text{bottom}}}{t_{\text{flat}}} \]

**Equation 1-2**

\[ SWC = \frac{t_{\text{side}}}{t_{\text{flat}}} \]
Where $t_{\text{bottom}}$, $t_{\text{side}}$, and $t_{\text{flat}}$ are the film thicknesses at the bottom of trench, side wall of a trench, and flat surface at the top of a trench, respectively. For perfect conformality, SC and SWC should be unity, where any deviation indicates some degree of non conformality. Several theoretical models regarding conformal depositions of parylene-CVD and iCVD in high aspect ratio structures have been published elsewhere. However all systems share a common dependence on the sticking probability, $\Gamma$, or the probability that a gas molecule will chemisorb on a surface. In CVD reactions, film conformality improves as reactant sticking probabilities decreases since this enables gas diffusion deeper into high aspect ratio structures. In general, increasing $\theta$ and/or reducing $R$ results in a reduced $\Gamma$. In order to develop process optimization strategies for deposition process having more than one gas phase reactant, it is important to determine which species has the $\Gamma$ which controls the degree of conformality.

In iCVD, clusters of unreacted monomers adsorb on the substrate and quickly polymerize upon the impingement of an initiator radical. The initiator radicals are quite volatile and are expected to have negligible adsorption on the bare surface. Additionally, once a monomer undergoes polymerization, it is no longer a site for initiator chemisorption. Therefore, the number surface sites available for the initiator is directly related to the monomer fractional surface coverage given by $P_m/P_{\text{sat}}$ where $P_m$ is the partial pressure of the monomer in the chamber and $P_{\text{sat}}$ is the monomer’s saturation pressure under the given deposition conditions. Operating at lower $P_m/P_{\text{sat}}$ values thus reduces the sticking probability of the initiator radical yielding highly conformal films.

Theoretical models devoted solely to oCVD have yet to be developed. Qualitative experimental evidence suggests that the oxidant sticking coefficient is the limiting factor. The low volatility of the oxidant would result in high sticking coefficient values. Once a molecule lands on the substrate, the likelihood of desorption is low. Furthermore, the evaporation of a solid oxidant is a line-of-sight process that does not necessarily yield even coverage on all surfaces. Thus at moderate substrate temperatures ($80 \, ^{\circ}\text{C}$) and chamber pressures (150 mTorr), solid oxidants form non-conformal films. One approach to improve conformality is to use liquid oxidants, like Br$_2$ or VOCl$_3$, whose vapors are metered into the chamber. Another approach is to reduce the
monomer surface concentration by reducing the chamber pressure. Decreasing the chamber pressure to 50 mTorr enabled conformal poly(3,4-ethylenedioxythiophene) coatings on vertically aligned carbon nanotube arrays.22-23

1.2 Formation of nanostructures for integrated circuits

The integrated circuit industry has already incorporated nanostructured 3D geometries in commercial systems. Fin field-effect transistors (FinFETs), as seen in Figure 1-3a, have multiple gates on a single device, which enables more processing power within a smaller areal footprint. Maintaining a smaller areal footprint can also be achieved by increasing the volumetric processing power. In this case, integrated circuits on several silicon wafers are stacked and electrically connected with vertical interconnect accesses (VIAs) so the overall structure behaves like a single device. An example of these interconnects is shown in Figure 1-3b.

![Figure 1-3](image_url)

**Figure 1-3.** Intel device architectures for 22 nm node. (a) FinFET with 60 nm transistor Fin pitch (b) Interconnects with 80 nm pitch. (a, b) Reproduced with permission from IEEE International Electron Devices Meeting, 15-17 Dec. 2014; 2014; pp 3.7.1-3.7.3.24 Copyright 2014 IEEE.

Intel first introduced the 22-nm node, featuring the FinFET and interconnects similar in geometry to those seen in Figure 1-3, in 2011. The transistor fins and interconnects have pitches of 60 nm and 80 nm respectively, which are produced by 193 nm immersion photolithography, the industry standard. By 2018, the introduction of the 10-nm node will reduce the fin and interconnect pitches to 34 nm and 52 nm respectively. Beyond the 10-nm node, 193 nm immersion lithography
no longer produces features of the required size and spacing to increase the areal density of transistors. Anticipating this event, new strategies to form nanostructures at these smaller feature sizes have been studied extensively. In this regard, there were two main contenders: extreme ultraviolet (EUV) lithography and directed-self assembly (DSA) of block copolymers (BCPs). EUV lithography requires the adaptation of existing photolithography techniques for 13.5 nm wavelength light. The process is significantly more expensive than its predecessor and requires the development of new lenses, resists, and photomasks compatible with this wavelength. A cheaper alternative is the DSA of BCPs, where a block copolymer thin film self-assembles into nanostructures of the desired length-scale. These block copolymer nanostructures serve as a template for the final IC pattern required.

1.2.1 Block Copolymers

Di-block copolymers are the simplest molecules amongst the various molecular geometries of BCPs. A di-block copolymer is formed by covalently end linking two linear polymer chains of different chemistry (Figure 1-4a). Within the full chain, these areas of distinct chemistry are referred to as “blocks.” For a general case, the two blocks are labelled as “A” and “B.” The difference in chemistry between the two blocks drives segregation. As macro-phase segregation is prevented by the covalent linkage, micro and nano-phase segregation occur instead. In a bulk material, the free energy of this system ($\Delta G_{\text{mix}}$) is governed by Equation 1-3, where $k_B$ is the Boltzmann constant, $T$ is temperature, $\chi_{AB}$ is the Flory-Huggins interaction parameter, $N_i$ is the number of monomers in block “i”, and $f_i$ is the fraction of the full chain made up of block “i.”

$$\Delta G_{\text{mix}} = k_B T \left( f_A f_B \chi_{AB} + \frac{1}{N_A} \ln f_A + \frac{1}{N_B} \ln f_B \right)$$

Bates et al. constructed a theoretical phase diagram based on this free energy to determine what type of self-assembled structure would occur given the total chain length, the Flory-Huggins interaction parameter, and the polymer composition (Figure 1-4b, c). Out of these structures, cylindrical and lamellar geometries have the greatest applicability to patterning for integrated circuits. Henceforth in this thesis, any mention of block copolymers specifically refers to di-block copolymers unless otherwise stated.
Figure 1-4. (a) Schematic of di-block copolymer. Linear chain of “A” molecules is covalently ended linked with linear chain of “B” molecules. (b, left) Theoretical phase diagram for microphase segregation of di-block copolymers and corresponding microphase ordered structured. (b) reprinted with permission from Soft Matter, 2013, 9, 630128 . Copyright 2013 Royal Society of Chemistry.

1.2.2 Directed Self-Assembly

Block copolymer thin films do not readily form patterns that can immediately be used in an integrated circuit. Interfacial energies between the block copolymer and the substrate and surface energies alter the orientation of the self assembled pattern with respect to the substrate. The film then self assembles to minimize these interface and surface energies. For example, lamellar forming film assemble to that the block with the lowest interface energy wets the substrate and the block with the lowest surface energy covers the surface. This results in a layered structure where the desired pattern is parallel to the structure. Pattern transfer of the nanodomains cannot occur in this case. To facilitate pattern transfer, both blocks must wet the surface and the substrate, resulting in a perpendicular orientation. Once films of desirable pattern orientation are formed, small areas of local alignment are forming a structure analogous to a polycrystalline material. However, long
range alignment with low defectivity is needed to form patterns that the IC industry can actually use.

Directed self-assembly (DSA) is a strategy to control the orientation and alignment of block copolymer thin films so that patterns useful to the IC industry are formed. Interfacial wetting layers sandwiched between the block copolymer film and substrate can control the pattern orientation at the substrate/film interface. Topcoats can be employed in a similar fashion to control pattern orientation at the film surface. Long range alignment is then controlled by providing a “road map” for self-assembly to follow. This “road map” is formed by larger scale patterns formed by traditional lithographic techniques. Two overarching methods are used: graphoepitaxy and chemoepitaxy. A schematic of graphoepitaxy is shown in Figure 1-5a. A topographical pattern, such as a trench, is used to physically constrain self-assembly. Ideally, the bottom of the trench would be non-preferential to both blocks while the sidewalls were preferential to a certain block. This enables perpendicular orientation and long-range alignment. Chemoepitaxy can yield a similar result by using chemical constraints. As seen in Figure 1-5b, alternating strips of preferential and non-preferential wetting are formed without physical topography. Areas with preferential strips force a particular chemical domain of the block to nucleate there. The remaining domains line up appropriately in the non preferential strip.
Several factors impede the large-scale implementation of BCP-DSA. In particular, interfacial wetting layers require several constraints to be met before they are useable. The ideal wetting layer is ultra-thin, ultra-smooth, and solvent resistant. Moreover, the chemistry of the wetting layer must be controlled to yield the desired pattern orientation. End grafted brushes form durable wetting layers but require appropriately activated substrate surfaces. Cross-linked polymer thin films remain durable without a covalent linkage to the substrate. However, multiple synthesis and processing steps are needed to form a cross-linked thin film. Furthermore, the chemistry must be re-developed for each type of wetting behavior required.

Chapter 2 and Chapter 3 of this thesis explore iCVD as a technique to form crosslinked interfacial wetting layers for BCP-DSA. Ultra-crosslinked thin films can be formed with iCVD in a single step. Poly(divinyl benzene) (pDVB) films were developed to control the orientation of poly(styrene-b-methylmethacrylate) (PS-b-PMMA). Chapter 2 is a kinetic study of iCVD from DVB to determine what processes control the degree-of-crosslinking and the film roughness.
Using this information to guide deposition parameters, Chapter 3 focuses on the chemical structure modification of pDVB during growth. The change in chemical structure shows a significant impact on block copolymer wetting, ranging from non-preferential to completely PS preferential films. The films were then incorporated into a graphoepitaxial template to yield block copolymer nanopatterns with perpendicular orientation and long range alignment.

1.3 Modification of nanostructures for electrochemical power sources

The design of electrochemical power sources usually forces a compromise between energy density (how much energy the device stores) and power density (how quickly the energy is delivered). A Ragone plot visually demonstrates this trade-off. As seen in Figure 1-6, high power density capacitors store a relatively small amount of energy. On the other end, batteries store a great deal of energy but have low densities. Supercapacitors fall in an intermediate space, where power density is reasonable and energy density is modest. Modified micro and nanostructures can improve the energy and power densities of both batteries and supercapacitors. The specific needs for lithium ion batteries and supercapacitors are explored further in sections 1.3.1 and 1.3.2 respectively. Conformal coatings of active and/or supporting materials is key to implementing modified micro/nanostructures in these devices.
Amongst the various types of rechargeable batteries, those using lithium-based chemistries deliver the highest energy and power densities. Within the various sub-types (e.g. lithium-sulfur, lithium-air), lithium ion batteries are the most ubiquitous. The compromise between energy and power densities in planar lithium ion batteries occurs because design factors that enhance energy density diminish power density and vice versa. In the case of device energy storage, two important factors to consider are the specific capacities of the active materials (anode and cathode) and then amount of active material used. In a given pair of active materials, simply increasing the amount of material used increases the overall amount of energy stored. For power density, electrical and ionic charge transport are the limiting factors. Cathode active materials (e.g. transition metal oxides, polyanions) suffer from low ionic and electrical conductivity. The short ion transport times needed for high power density can be achieved by reducing the thickness (i.e. diffusion distance) of the cathode material. To facilitate electrical charge transfer to the current collector, conductive binders such as Super P or carbon black are mixed in with the cathode active material.
The combination of these two efforts to improve the power density reduces the overall energy density. Three-dimensional electrode architectures increase the surface to volume ratio of active materials. Figure 1-7 illustrates the difference between conventional planar geometries and 3D geometries. Ionic transport distances within the cathode active material are shortened without having to reduce the overall amount of material used. The high surface area of both electrodes combined with the shorter inter-electrode distances reduces the overall ohmic resistance of the cell. 1,3,42

**Figure 1-7.** Schematic of (a) Thin film battery with high power density and (b) 3D battery with high energy and power density in small areal footprint. Reproduced with permission from *MRS Bull.* 2011, 36 (07), 523-531. Copyright 2011 Cambridge University Press.

Several materials and process developments are required to create viable full cell assembles with 3D electrode architectures. Most notable is the development of conformal, solid electrolytes. Existing planar lithium ion batteries use liquid electrolytes to facilitate ion transport between the electrodes. Typically, a lithium containing salt (e.g. LiClO4, LiPF6) is dissolved in an organic solvent (e.g. ethylene carbonate, dimethyl carbonate) to form the liquid electrolyte. A porous, polymer separator is soaked in the liquid electrolyte and then sandwiched between the two electrodes. This set-up prevents electronic shorts while maintaining ionic transport between the two electrodes. The thickness of the polymer separator sets the minimum inter-electrode spacing. This is on the order of hundreds of microns. The interelectrode spacing in a 3D battery must several
orders of magnitude smaller to maintain a high surface to volume ratio within a small areal footprint. Thus, the polymer separator/liquid electrolyte combination cannot be used in a 3D battery. This requires the development of solid electrolytes, a new class of materials that can simultaneously serve as electrical charge separators and ion transport media. These materials must be mechanically durable, electrically insulating, ionically conductive, and stable against high electric fields. Additionally, new processes are needed to conformally coat the 3D electrode structure with the solid electrolyte. A uniform solid electrolyte film thickness over all surfaces ensures constant inter-electrode ionic transport lengths.

Chapter 4 of this thesis studies the use of cross-linked, ultra-thin iCVD films as solid electrolytes. The films are rendered ionically conductive by soaking in a liquid electrolyte solution (lithiation). Thin films of multi-vinyl cyclic siloxanes and silazanes were compared to determine the influence of ring chemistry and ring size on the ionic conductivity. Out of these chemistries, a 25 nm thick layers of poly(tetravinyltetramethylcyclotetrasiloxane) (pV4D4) demonstrated the highest ionic conductivities (approaching $10^{-7}$ S cm$^{-1}$). The film durability after lithiation and coating conformality were analyzed with electron microscopy studies on silver nanowires and silicon nanowire arrays respectively. Galvanostatic cycling with incremental increases in the charge/discharge rate enables ionic conductivities exceeding $10^{-7}$ S cm$^{-1}$ in 400 nm thick pV4D4 films.

1.3.2 Supercapacitors

The overall structure of a supercapacitor is similar to a Li ion battery, where a positive and negative electrode are separated by an electrolyte. The charge storage mechanisms employed in supercapacitors fall into two overarching categories: electrical double layer capacitance (EDLC) and pseudocapacitance. In EDLC, a charge is stored in a Helmholtz layer that forms at the electrode/electrolyte interface.$^{43-44}$ For this to occur, the electrode material must be an electrical conductor. High power densities are therefore enabled by facile electron transport and the fast formation/dissolution of these Helmholtz layers. Incorporating nanostructured carbon electrodes increases the surface area where charge can be stored, and therefore the energy density. Pseudocapacitive charge storage occurs via a Faradaic process between the electrode and ions in the electrolyte.$^{45-46}$ These processes are similar to what occurs in Li ion batteries: redox reactions
and ion intercalation. This leads to significantly higher energy storage than ELDC. Several factors differentiate pseudocapacitive materials from battery electrodes. Bulk pseudocapacitors do not phase change (i.e. crystal structure change) when ions are inserted and removed from its structure. Furthermore, ion diffusion within the material occurs quickly and is not the limiting process. Therefore, with respect to ion transport, significantly faster charge/discharge rates are now possible.

ELDC materials and pseudocapacitive materials are complementary rather than rivals. Composite electrodes that combine these two types of materials can maximize energy and power density. ELDC materials are primarily high surface area carbons (e.g. activated charcoal, aligned graphene flakes, aligned carbon nanotubes). A broader array of materials has been studied for pseudocapacitive charge storage, including transition metal hydroxides, transition metal oxides, and conductive polymers. Out of these materials, conductive polymers are of significant interest since they exhibit high ionic and electrical conductivities. To successfully combine the benefits of ELDC and pseudocapacitance, the conductive polymer must be combined with carbon electrode in such a way that the high surface area is maintained. This necessitates conformal coverage of the pseudocapacitive conductive polymer. Previous studies poly(3,4 ethylenedioxythiophene) (PEDOT) ultrathin films synthesized by oxidative chemical vapor deposition (oCVD) demonstrated that highly conformal films enveloped individual carbon nanotubes (CNTs) in an array of vertically aligned CNTs. Increasing the film thickness from 3 nm to 10 nm showed substantial increases in energy density without a reduction in power density. Further increases in energy density are possible if the film thickness increases to several hundred nanometers. At these length scales, the diffusion time for an ion to travel through the film plays a larger role in both the final power and energy densities achievable. Facile ion conduction enables high power densities by the swift movement of ions from the film/substrate interface to the film/electrolyte interface. Additionally, it enables a larger amount of charge to enter the film in a given time period, thus increasing energy density.

Chapter 5 of this thesis examines the role of thin film texture on the electrochemical properties of oCVD PEDOT. The oCVD process generates semi-crystalline films of Cl-doped PEDOT, which assembles in an orthorhombic structure with the π-π stack along the b-axis. Depending on the substrate and deposition conditions used, films will align so that the π-π stack
is either perpendicular (edge-on) or parallel (face-on) to the substrate normal. First, an x-ray diffraction study shows that the dominant film texture can be controlled using the substrate temperature during growth. Operating at temperatures significantly higher than the glass-transition temperature of PEDOT enables a transition from face-on dominance to edge-on dominance. The impact of crystal texture is studied both in the initial electrochemical properties and after long term cycling. Raman spectroscopy before and after long term cycling determines that irreversible oxidation is the cause of degraded performance. The edge-on films show less oxidation and maintain high ionic conductivities (~10^{-6} \text{ S cm}^{-1}) even after long term cycling. A proof-of-concept Li-ion supercapacitor, which operates over a wide potential window, is demonstrated by pairing edge-on oCVD PEDOT with a molybdenum disulfide (MoS_2) anode.

1.4 References


Chapter 2  Growth rate and cross-linking kinetics of poly(divinyl benzene) thin films formed via initiated chemical vapor deposition

A version of this chapter has been submitted to Langmuir for publication. It is currently under review

2.1 Abstract

Initiated chemical vapor deposition (iCVD) allows for the formation of highly cross-linked, polymer thin films on a variety of substrates. Here we study the impact of substrate stage temperature and filament temperature on the deposition and crosslinking characteristics of iCVD from divinyl benzene (DVB). Maintaining a constant monomer surface concentration reveals that deposition rates upwards of 15 nm/min can be achieved at substrate stage temperatures of 50 °C. The degree-of-crosslinking is limited by the rate of initiation of the pendant vinyl bonds. At a filament temperature of 200 °C, the pendant vinyl bond conversion is highly sensitive to the surface concentration of initiator radicals. A significant decrease of the pendant vinyl bond conversion is observed with increasing stage temperatures. At higher filament temperatures, the pendant vinyl bond conversion appears to plateau at approximately 50%. However, faster deposition rates yield lower conversion. This trade-off is mitigated by increasing the filament temperature to increase initiator radical production. A higher flux of initiator radicals toward the surface at a constant deposition rate increases the rate of initiation of pendant vinyl bonds and therefore their overall conversion. At a deposition rate of ~7 nm/min, an increase in the filament temperature from 200 °C to 240 °C results in an 18% increase in the pendant vinyl bond conversion.

2.2 Introduction

Thin films of cross-linked polymer networks fabricated by initiated chemical vapor deposition (iCVD) have utility in a broad variety of applications including 1) integrated circuit fabrication1-2 2) surface energy modification 3-4 3) ablator materials for nuclear fusion5-7 4) electrochemical power systems8-10. Conventional solution synthesis techniques require multiple steps to form cross-linked polymer films adhered to substrates. Usually a polymer with incorporated cross-linkable moieties is first synthesized and then either spin or dip coated on the substrate of interest.
A curing step, such as a thermal anneal, UV exposure, or electron beam exposure, is required to activate the cross-linking reaction to form the final crosslinked thin film. However, iCVD permits the single-step formation of a broad library of cross-linked polymer thin films. During the iCVD process, monomer, crosslinker, and initiator vapors are fed into a low-pressure reactor containing the substrate of interest. A hot filament array thermally cracks the initiator to form radicals. A free-radical polymerization takes place on the substrate surface and results in the formation of the crosslinked polymer thin film in a single step.

iCVD cross-linkers have multiple polymerizable moieties (acrylate, methacrylate, or vinyl) on a single monomer unit. Maximizing the reaction of these moieties during film synthesis is key to the functionality of the cross-linked film. For example, Zhao et al. found that unreacted vinyl groups in iCVD poly(divinyl benzene) (pDVB) films oxidized over time and reduced the films' hydrophobicity. The majority of iCVD kinetic studies have focused on mono-functional acrylates and methacrylates, which polymerize swiftly via the free-radical mechanism. By contrast, the majority of cross-linking chemistries used in iCVD are multi-vinyl based. This is significant as the free-radical propagation rate constant for the vinyl groups is typically orders of magnitude lower than for acrylates. Complete reaction of pendant vinyl groups in multi-vinyl monomers becomes more difficult. Only two studies were found by the authors that specifically studied the degree-of-crosslinking in multivinyl chemistries. Petruczok et al. studied the impact of monomer flow rates on the degree-of-crosslinking in the copolymer poly(4-vinyl pyridine-co-divinyl benzene). This work used DVB as a cross-linking agent for poly(4-vinyl pyridine) and then examined the subsequent impact of DVB content on the film properties. The conversion of the pendant vinyl bond was used to determine the extent of cross-linking both in pDVB homopolymer films. An elastic modulus of ~5 GPa was obtained through nanoindentation measurements of the pDVB, indicating a cross-linked film. Coclite et al. examined the cross-linking of hexavinyldisiloxane (HVDSO), a linear monomer with six vinyl groups, in the iCVD process by determining the percentage of unreacted vinyl bonds within the film as a function of substrate temperature. They found that higher temperatures reduced the percentage of unreacted vinyl bonds, indicating that cross-linking of HVDSO is a kinetically limited process. Tape tests of a film with 3% conversion of all vinyl bonds showed severe delamination to a film with 95% conversion.
The work presented here uses iCVD of DVB with initiator di-tert-butyl peroxide (TBPO, Chart 2-1a), as a model system to understand both the growth rate and crosslinking kinetics of cyclic multivinyl chemistries. DVB is the simplest of the cyclic multivinyl chemistries used in iCVD. Commercially available DVB is a mixture of meta and para isomers, as shown in Chart 2-1b. The first vinyl bond polymerizes to form a poly(styrene) derivative, with pendant vinyl bonds. Reaction of these pendant vinyl bonds results in a cross-linked structure. Chart 2-1c presents the structure of iCVD pDVB with both unreacted and reacted pendant vinyl bonds. The effects temperature (filament and substrate stage) are the primary focus of this work. We first study the temperature dependence of the deposition rate and identify regimes were a specific sub-process is rate limiting. Next, we ascertain the pendant vinyl bond conversion using FTIR spectroscopy of the pDVB films. In the previously described iCVD studies, increased vinyl bond conversion resulted in improved mechanical properties associated with higher degrees of crosslinking. Therefore, we focus on the mechanism of pendant vinyl bond conversion and the associated limiting processes as a function of temperature and deposition rate. Finally, the dependence of the film morphology on temperature and deposition rate is investigated.

**Chart 2-1.** Structures of (a) TBPO Initiator (b) DVB Monomer (combined isomers) (c) pDVB with both reacted and unreacted pendant vinyl bonds. Tert-butoxy moieties from the initiator serve as end groups.

\[ \text{A)} \quad (\text{H}_3\text{C})_2\text{CO} \quad \text{OC(CH}_3\text{)}_2 \]

\[ \text{B)} \]

\[ \text{C)} \quad (\text{H}_3\text{C})_2\text{CO} \quad \text{OC(CH}_3\text{)}_2 \]

Pendant vinyl bond

Reacted vinyl bond
2.3 Background

Table 2-1. Summary of gas phase and surface processes and the dependence of rate constants on
associated activation energies and temperatures in the iCVD process.

<table>
<thead>
<tr>
<th>Process Group</th>
<th>Reaction</th>
<th>Rate Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator Decomp.</td>
<td>$I_{(g)} \rightarrow 2R^*_{in(g)}$</td>
<td>$k_d \propto \exp \left(-\frac{E_d}{RT_{filament}}\right)$</td>
</tr>
<tr>
<td>Gas Transport</td>
<td>$M_{(g,bulk)} \rightarrow M_{(g,surf)}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^<em>_{in(g,bulk)} \rightarrow R^</em>_{in(g,surf)}$</td>
<td></td>
</tr>
<tr>
<td>Monomer Adsorption</td>
<td>$M_{(g,surf)} \rightarrow M_{(ad)}$</td>
<td></td>
</tr>
<tr>
<td>Polymerization</td>
<td>$R^<em><em>{in(g,surf)} + M</em>{(ad)} \rightarrow RM^</em>_{1(ad)}$</td>
<td>$k_i \propto \exp \left(-\frac{E_i}{RT_{stage}}\right)$</td>
</tr>
<tr>
<td>Reactions</td>
<td>$M^<em><em>{n(ad)} + M</em>{(ad)} \rightarrow M^</em>_{n+1(ad)}$</td>
<td>$k_p \propto \exp \left(-\frac{E_p}{RT_{stage}}\right)$</td>
</tr>
<tr>
<td></td>
<td>$M^<em>_{n(ad)} + M^</em><em>{m(ad)} \rightarrow M</em>{n+m(ad)}$</td>
<td>$k_t \propto \exp \left(-\frac{E_t}{RT_{stage}}\right)$</td>
</tr>
<tr>
<td></td>
<td>$M^<em>_{n(ad)} + M^</em><em>{in(g)} \rightarrow M</em>{n(ad)}$</td>
<td></td>
</tr>
</tbody>
</table>

The iCVD process has the same primary reaction steps as conventional solution phase free-
radical polymerization: initiator decomposition, primary initiation, propagation, and termination.
In addition, two more steps are required for iCVD to successfully proceed: gas transport of reactant
molecules to the substrate and the subsequent adsorption of monomer molecules on the substrate
surface. For a monovinyl species, these processes can be grouped as 1) initiator decomposition
2) gas transport 3) monomer adsorption and 4) polymerization reactions, as presented in Table 2-
1. Each process group has the potential to be deposition rate limiting. Determining the temperature
dependence of the deposition rate ($R_{dep}$) in these regimes requires relating these processes to the
rate of polymerization ($R_{poly}$). Previous studies found that $R_{poly}$ was proportional to $R_{dep}$, which
allows us to simultaneously consider the effect on both rates. A general rate of polymerization is given by Equation 2-1. A combined rate constant ($k_{rxn}$) and stoichiometric coefficient ($n_{rxn}$) includes the potential effects from the chemical reactions and rate constants (Table 2-1). These include the rate constants for initiator dissociation ($k_d$), primary initiation ($k_i$), propagation ($k_p$), and termination ($k_t$). The superscripts “a” and “b” are the reaction order with respect to the monomer and initiator concentrations respectively.

Equation 2-1

$$R_p = \frac{1}{n_{rxn}} * k_{rxn}[M]^a[I]^b$$

Initiator decomposition occurs in the gas phase due to the proximity of the hot filament. Therefore, [$I]=P_i$, or the initiator partial pressure in the chamber. As initiator decomposition is a gas phase process, it has an Arrhenius dependence on the filament temperature. If “b”, the reaction order with respect to initiator concentration, is greater than zero, the dissociation rate constant factors into the combined rate constant. With all other factors held constant, $R_p$ and therefore the deposition rate should increase with filament temperature. However, once the filament temperature is sufficiently high, initiator decomposition is no longer rate limiting. At these high filament temperatures, the initiator is in excess and the film growth rate becomes insensitive to further increases in filament temperature. The chemical reactions involving the monomer occur at the substrate surface. Therefore, [$M]= [M]_{ads}$, or the concentration of adsorbed monomer. Previous iCVD studies have used the Brunauer-Emmett-Teller (BET) theory for multilayer adsorption to determine $[M]_{ads}$. The BET equation utilizes the monomer saturation pressure ($P_{Sat}$) as a function of temperature, which can be approximated by the Clausius-Claperyon relationship. The adsorbed monomer concentration is proportional to the total adsorbed volume, $V_{ads}$, as given in Equation 2-2. The total adsorbed volume is proportional to the volume of a monolayer ($V_m$), the BET constant ($c$), the monomer partial pressure during deposition ($P_M$), $P_{Sat}$. The temperature dependencies of $c$ and $P_{Sat}$ are given by Equation 2-3 and Equation 2-4 respectively, where $\Delta H_{ads}$ is the enthalpy of adsorption, $\Delta H_{vap}$ is the enthalpy of vaporization, and $T_{stage}$ is the stage temperature.

Equation 2-2 $[M]_{ads} \propto V_{ads} = \lim_{P_M \rightarrow 0} \frac{V_{ml}c\left(P_M\right)}{P_{Sat}} \propto c\left(P_M\right)$

Equation 2-3 $c \propto \exp\left[\frac{\Delta H_{ads} + \Delta H_{vap}}{RT_{stage}}\right]$
Equation 2-4 \[ P_{\text{Sat}} \propto \exp \left( -\frac{\Delta H_{\text{vap}}}{RT_{\text{stage}}} \right) \]

By combining Equation 2-2 through Equation 2-4, we can express \([M]_{\text{ads}}\) as given in Equation 2-5. From this equation, we see that the surface adsorbed monomer concentration can be changed either by changing \(P_m\), the monomer partial pressure, or \(T_{\text{stage}}\) (or some combination thereof).

Equation 2-5 \[ [M]_{\text{ads}} \propto P_m \exp \left[ \frac{\Delta H_{\text{ads}} + 2\Delta H_{\text{vap}}}{RT_{\text{stage}}} \right] \]

In the absence of gas transport limitations (i.e. in the surface-reaction limited regime), the deposition rate is given by Equation 2-6. Factoring in the relevant expressions for \([M]_{\text{ads}}\) and \([I]\) into this equation yields Equation 2-7, where \(A_{\text{rxn}}\) and \(E_{\text{rxn}}\) are the combined frequency factor and activation energy associated with \(k_{\text{rxn}}\). When \(P_m\) and \(P_i\) are held constant and stage temperature is varied, the apparent activation energy of the deposition (\(E_A\)) of the deposition is given by Equation 2-8.

Equation 2-6 \[ R_{\text{dep}} \propto k_{\text{rxn}} [M]_{\text{ads}} [I]^b \]

Equation 2-7 \[ R_{\text{dep}} \propto P_m^a \times P_i^b \times A_{\text{rxn}} \times \exp \left( \frac{-E_{\text{rxn}}}{RT_{\text{stage}}} \right) \times \exp \left( \frac{a(\Delta H_{\text{ads}} + 2\Delta H_{\text{vap}})}{RT_{\text{stage}}} \right) \]

Equation 2-8 \[ E_A = E_{\text{rxn}} - a(\Delta H_{\text{ads}} + 2\Delta H_{\text{vap}}) \]

The enthalpy of adsorption is a negative (exothermic) quantity whereas the enthalpy of vaporization is a positive (endothermic) quantity. When \(2a\Delta H_{\text{vap}} > (E_{\text{rxn}} - a\Delta H_{\text{ads}})\), a negative apparent activation energy is observed (i.e. deposition rate decreases with increasing stage temperature). This effect has been observed in previous iCVD studies of acrylates and methacrylates. This was attributed to the relatively fast propagation rates of these monomers resulting in a low \(E_{\text{rxn}}\).\textsuperscript{14-15, 23} By contrast, styrene and its derivatives can have over a 10-fold reduction in propagation rate.\textsuperscript{16, 24-26} The impact of stage temperature on the deposition rate for iCVD from styrene derivatives can determine what effect, if any, the reduced propagation rates cause on the deposition rate.
2.4 Experimental Section

2.4.1 Synthesis of polymer films

Divinyl benzene (DVB, 80%) and di-tert-butyl peroxide (TBPO, 98%) were purchased from Sigma-Aldrich and used without any further purification. Argon gas (100%) was purchased from Airgas and used without any further purification. All depositions occurred in a custom built iCVD chamber described elsewhere. Films were grown on 100 mm Si wafers (WRS Materials). The chamber pressure was controlled using a throttling butterfly valve (MKS Instruments) and substrate temperature controlled using a stage chiller (Thermo-Fisher). Precursor vapors was delivered to the chamber using mass flow controllers (MKS Instruments). A Chromaloy O (Goodfellow) filament array was heated to crack the TBPO peroxide bond. Film growth and thickness were monitored in situ using a 633 nm HeNe Laser (JDS Uniphase).

Detailed experimental conditions of the variable $P_{DVB}/P_{Sat}$ series are given in Table 2-2. For these depositions, the filament temperature, chamber pressure, TBPO flow rate, and DVB flow rate were held constant. Stage temperature was varied from 15 °C to 30 °C in 5° increments. The change in stage temperature induced a change in in the saturation pressures of both TBPO and DVB. The impact on their respective $P/P_{sat}$ values is also given in Table 2-2. Films were grown to a thickness of ~150 nm as determined by in-situ laser interferometry.

Table 2-2. Series 1: Deposition constant monomer partial pressure and stage temperature variation.

<table>
<thead>
<tr>
<th>$T_{Filament}$ °C</th>
<th>$P_{chamber}$ mTorr</th>
<th>$TBPO$ Flow SCCM</th>
<th>$DVB$ Flow SCCM</th>
<th>Stage Temperature °C</th>
<th>DVB $P/P_{Sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>270</td>
<td>400</td>
<td>3.2</td>
<td>0.8</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

47
Details of the deposition conditions used for the constant $P_{\text{DVB}}/P_{\text{Sat}}$ are given in Table 2-3. The chamber pressure (800 mTorr) and TBPO flow rate (2 SCCM) were constant for all depositions. The flow rate of DVB for a given stage temperature was adjusted based on the Clausius-Clapeyron equation to ensure a constant $P_{\text{DVB}}/P_{\text{Sat}}$ of 0.30. An argon patch was introduced to maintain a constant total flow rate of 4.4 standard cubic centimeters per minute (SCCM). The stage temperature was varied from 25 °C to 50 °C in 5° increments. The entire series was repeated at three different filament temperatures: 200 °C, 220 °C, and 240 °C. Each deposition lasted for 90 minutes.

<table>
<thead>
<tr>
<th>TFilament °C</th>
<th>Pchamber mTorr</th>
<th>TBPO Flow SCCM</th>
<th>DVB Flow SCCM</th>
<th>Ar Flow SCCM</th>
<th>Stage Temperature °C</th>
<th>DVB P/P_{Sat}</th>
</tr>
</thead>
<tbody>
<tr>
<td>200, 220, 240</td>
<td>800</td>
<td>2</td>
<td>0.5</td>
<td>1.9</td>
<td>25</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>1.7</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.4</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.4</td>
<td>1.0</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
<td>0.5</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
<td>0.0</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

2.4.2 Film Characterization

Ex-situ film thicknesses were determined using a J.A. Woollam variable angle spectroscopic ellipsometer at incident angles of 65°, 70°, and 75°. The data were fit to a Cauchy-Urbach isotropic model using WVASE32 modelling software (J.A. Woollam). Fourier transform infrared (FTIR) spectra were obtained using a Thermo-Fisher Nicolet iS50 Spectrometer. The DVB monomer and iCVD pDVB films were measured in transmission mode with a liquid N$_2$ cooled mercury cadmium telluride (MCT-A) detector. The spectra were averaged over 256 scans. The DVB monomer was measured in a liquid cell with KBr windows and constant pathlength of 15 μm (Pike technologies). The area of the vinyl bond peak at 903 cm$^{-1}$ was determined using the software program Omnic (Thermo-Fisher). The roughness of pDVB films on Si wafers was
measured using a Veeco Dimension 3100 atomic force microscope (AFM) in tapping mode over a 2μm x 2μm area with 512 points per line and lines per scan.

2.5 Results and Discussion

2.5.1 Deposition Rate Characteristics

The iCVD pDVB depositions in Series 1 replicates the experimental set-up used in previous iCVD studies of other monomer chemistries. The total flow rate and chamber pressure are held constant to avoid any convoluting effects of variation in gas residence time in the iCVD chamber. A constant filament temperature ensures the dissociation rate constant of TBPO is constant for all depositions. The initiator and monomer flow rates are held constant, yielding the same partial pressures, \( P_i \) and \( P_M \) respectively, for each deposition. The effect of stage temperature is presented in Figure 2-1, which depicts an Arrhenius plot of the deposition rate vs. stage temperature. Usually, activation energies can only be extracted from plots of rate vs. temperature when the relevant monomer and initiator concentrations are held constant. In the case of series 1, the initiator concentration \( (P_i) \) was held constant, but the variation in \( T_{\text{stage}} \) changed the adsorbed monomer concentration. However the monomer partial pressure \( (P_M) \) was held constant so the only change in \( [M]_{\text{ads}} \) is due to \( T_{\text{stage}} \). In this special case, the slope in Figure 2-1 can be used to calculate an apparent activation energy of -29 kJ/mol. Based on Equation 2-8, this indicates that \( 2a\Delta H_{\text{vap}} > (E_{\text{rxn}} - a\Delta H_{\text{ads}}) \), where the magnitude of vaporization enthalpy of DVB is sufficiently large to offset the combined activation energy of the chemical reaction and enthalpy of adsorption.
To understand the impact of stage temperature alone on the reaction kinetics, the relevant monomer and initiator concentrations must be held constant. In Series 2, we continue to hold the total flow rate and chamber pressure constant for all depositions. The flow rate and therefore partial pressure of TBPO ([I]) are held constant for all depositions. Maintaining a constant monomer surface concentration as a function of substrate stage temperature is more difficult to achieve given that [M]$_{ads}$ is a function of $T_{stage}$. If we assume the enthalpies of adsorption and vaporization are similar in magnitude (i.e. BET constant is not strongly temperature dependent), the adsorbed monomer concentration can be estimated by the quantity $PM/PSat$, or the ratio of the monomer partial pressure to its saturation pressure at a given stage temperature. The change in saturation pressure as a function stage temperature can be calculated from Equation 2-4. The partial pressure of DVB ($P_M$) is then adjusted so that the quantity $P_M/PSat$ remains constant for all depositions. The monomer partial pressure is calculated from Equation 2-9, where $P_{chamber}$, $U_M$, and $U_{tot}$ are the total chamber pressure, monomer flow rate, and total flow rate respectively.

**Equation 2-9** \[ P_M = P_{chamber} \times \frac{U_M}{U_{tot}} \]

Coclite and Ozaydin-Inc et al. adjusted $P_M$ to compensate for the change in $P_{Sat}$ with $T_{stage}$ by changing the total chamber pressure for each condition while holding the monomer flow rate and
total flow rate constant. In these experiments, the deposition rate was observed to increase with stage temperature, suggesting that the monomer concentration was not changing significantly as a function of temperature. However, the change in total pressure did cause the initiator partial pressure to change for each stage temperature. If $b$, the reaction order for the initiator concentration, is greater than zero, then the enhanced deposition rate observed could be due to the larger initiator partial pressures. Instead, we control $P_m/P_{sat}$ via the DVB:Ar flow ratio as opposed to the total chamber pressure for series 2. This ensures the partial pressure of TBPO is constant for all depositions. The series is repeated at three different filament temperatures to ascertain what effects, if any, the dissociation rate constant has on the deposition rate.

Figure 2-2. Series 2: Constant $P_m/P_{sat}$ (DVB surface concentration) and $P_I$ (TBPO partial pressure). Deposition rate as a function of stage temperature and filament temperature. Filament temperatures are 200 °C (○), 220 °C (■), 240 °C (▲). Grey box highlights slope of regime II used to calculate apparent activation energy (~85 kJ/mol).

Figure 2-2 depicts the dependence of the natural logarithm of deposition rate on substrate stage temperature when $P_m/P_{sat}$ is held constant (Series 2). The deposition rate is observed to increase with increasing $T_{stage}$. This supports our assumption that $P_m/P_{sat}$ is a reasonable measure of
monomer surface concentration and that when held constant, the chemical reaction kinetics limit
the process. The rate of polymerization should depend on the combined rate constant, \( k_{rxn} \).
Equation 2-8 then simplifies to \( E_A = E_{rxn} \). The data in Figure 2-2 can be divided into two regimes
based on the change in slope with respect to substrate stage temperature. In regime I, which occurs
at deposition rates below 2 nm/min, increases in the deposition rate are seen both with increasing
filament temperature and substrate stage temperature. In regime II, which occurs at deposition
rates above 2 nm/min, faster deposition rates are only seen with respect to substrate stage
temperature. Additionally, the transition from regime I to regime II occurs at a lower substrate
stage temperature at higher filament temperatures.

The enhanced deposition rates with respect to filament temperature observed in regime 1
suggests that the \( k_{rxn} \) does have some dependence on \( k_d \), the dissociation rate constant.\(^{16}\) However,
the very slow deposition rates in this regime make it difficult to draw any definitive conclusions
from the data. Quantitative analysis of iCVD kinetics is possible at faster deposition rates, such
as a range observed in regime II.\(^{14,19,23}\) The average calculated apparent activation energy from
Figure 2-2 in regime II is \( 85 \pm 12 \) kJ/mol. In this regime, the deposition rate is essentially
independent of \( k_d \). This type of behavior is observed when there is a high concentration of primary
initiating radicals. The rate of polymerization is independent of the initiator concentration and is
given by Equation 2-10, where \( k_{tp} \) is the rate constant for primary termination.\(^{16}\) The combined
activation energy for this system is then calculated by Equation 2-11, where \( E_i \), \( E_p \), and \( E_{tp} \) are the
activation energies associated with initiation, propagation, and primary termination respectively.

**Equation 2-10**

\[
R_p \approx \frac{k_i}{k_{tp}} \frac{k_p}{k_{tp}} [M]^2
\]

**Equation 2-11**

\[
E_{rxn} = E_i + E_p - E_{tp}
\]

\( E_i \) can be approximated by the activation energy of an alkoxy radical (RO\(^*\)) reacting
with a double bond (CH\(_2\)=CH-R). This energy is \( \sim 68 \) kJ/mol on average.\(^{30}\) \( E_p \) can be approximated
by the activation energy a propagating styryl radical. This energy is \( \sim 30 \) kJ/mol.\(^{16,25,31}\) Finally,
\( E_{tp} \) is assumed to have a similar value to \( E_i \) of styrene (8 kJ/mol).\(^{16}\) With these values, we estimate
\( E_{rxn} \approx 90 \) kJ/mol, which falls within the range of experimental apparent activation energies
determined from Figure 2-2. This supports our hypothesis that the rate of polymerization in regime
II is given by Equation 2-10. The second order dependence on monomer concentration is in good agreement with previous iCVD studies.14-15

2.5.2 Calculation of Pendant Vinyl Bond Conversion

The transmission FTIR spectra the DVB monomer and an a representative iCVD pDVB film are presented in Figure 2-3. The meta and para-substituted benzene vibrations from 700 – 850 cm\(^{-1}\) are present in both the monomer and polymer spectra, indicating the ring structure remained intact after the iCVD process. The reduction in the vinyl peaks from 900 – 1000 cm\(^{-1}\) coupled with the emergence of the methylene peak at 2930 cm\(^{-1}\) in the polymer spectrum confirms polymerization was successful. We note the emergence of methyl peaks at 2870 cm\(^{-1}\) and 2960 cm\(^{-1}\). These can originate from the ethylvinyl benzene (EVB) impurities in technical grade DVB, the t-butyl component of the initiator radical, and backbone methylation during the iCVD process.32 The lack of a strong ether peak at ~1100 cm\(^{-1}\) suggests that the number of t-butoxy moieties incorporated in the structure is relatively low. The aforementioned spectral characteristics were observed in all spectra collected of the iCVD pDVB films.

![FTIR Spectra](image)

**Figure 2-3.** Transmission FTIR spectra of iCVD pDVB (top) and DVB monomer (bottom). Peaks found mainly in the polymer spectra are methyl (filled in circle), and methylene (filled in diamond). Vinyl stretch at 903 cm\(^{-1}\) highlighted in gray, para- vibration at 837 cm\(^{-1}\) highlighted in orange, meta- vibration at 795 cm\(^{-1}\) highlighted in blue. The areas under these peaks were used to calculate the pendant vinyl bond conversion.
The fraction of pendant vinyl bonds that have reacted, or the pendant vinyl bond conversion, can be determined using the FTIR spectra of the monomer and polymer. Typical methods compare the areal intensities of the aromatic vibrations to vinyl vibrations. When technical grade DVB is used, the effects of impurities in the monomer must also be accounted for in any analysis. The most significant impurity is EVB, which is made up of meta and para isomers. The certificate of analysis from Sigma-Aldrich informs us of the specific composition of the technical grade DVB used in this work. These values are enumerated in Table 2-4.

Table 2-4. Composition of technical grade DVB used in this work

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Variable</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-DVB</td>
<td>(x_{meta,DVB})</td>
<td>0.56</td>
</tr>
<tr>
<td>p-DVB</td>
<td>(x_{para,DVB})</td>
<td>0.25</td>
</tr>
<tr>
<td>m-EVB + p-EVB</td>
<td>(x_{meta,EVB} + x_{para,EVB})</td>
<td>0.18</td>
</tr>
</tbody>
</table>

We follow the same procedure as Petručzok and Yang et al. to calculate the pendant vinyl bond conversion while accounting for the EVB content. The meta, para, and vinyl vibrations occurring at 795 cm\(^{-1}\), 837 cm\(^{-1}\), and 903 cm\(^{-1}\) in the FTIR spectra are used to quantify conversion. These peaks are indicated in Figure 2-3, which shows the FTIR spectra of DVB and iCVD pDVB. The reduction in the vinyl peak at 903 cm\(^{-1}\) is indicative of polymerization of the primary bond and unreacted pendant vinyl bonds. The Beer-Lambert equation relates the absorbance of a given vibrational peak, \(A\), to the molar absorptivity, \(\varepsilon\), path length, \(l\), and mole fraction, \(x\). This is given by Equation 2-12.

**Equation 2-12**  \[ A = \varepsilon lx \]

The molar absorptivity ratio of meta- and para- disubstituted benzenes is then calculated using Equation 2-13, where the subscript “mon” refers to values measured in the monomer and the mole fractions are from Table 2-4.
Equation 2-13
\[
\frac{\varepsilon_{meta}}{\varepsilon_{para}} = \frac{\left(\frac{A_{meta}}{A_{para}}\right)_{mon}}{\left(\frac{A_{meta}}{A_{para}}\right)_{mon}} = \frac{\left(\frac{X_{para,DVB} + X_{para,EVB} A_{meta}}{X_{meta,DVB} + X_{meta,EVB} A_{para}}\right)_{mon}}{\left(\frac{X_{para,DVB} + X_{para,EVB} A_{meta}}{X_{meta,DVB} + X_{meta,EVB} A_{para}}\right)_{mon}}
\]

Exact fractions for m-EVB and p-EVB were not provided. If we assume the mole fraction ratio of m-DVB to p-DVB is approximately equal to the mole fraction ratio of m-EVB to p-EVB, we can estimate \(X_{meta,EVB} = 0.12\) and \(X_{para,EVB} = 0.06\). From the monomer FTIR spectrum, we calculate \(A_{meta}/A_{para} = 1.21\). Substituting these values and those in Table 2-4 into Equation 2-13 results in \(\varepsilon_{meta}/\varepsilon_{para} = 0.56\). The mole fraction ratio of meta to para disubstituted benzenes in the polymer is then calculated by Equation 2-14, where the subscript “poly” refers to the polymer.

Equation 2-14
\[
\frac{X_{meta}}{X_{para}}_{poly} = \frac{\varepsilon_{para}}{\varepsilon_{meta}} \cdot \frac{\left(\frac{A_{meta}}{A_{para}}\right)_{poly}}{\left(\frac{A_{meta}}{A_{para}}\right)_{poly}} = \frac{1}{0.56} \left(\frac{A_{meta}}{A_{para}}\right)_{poly}
\]

The mole fraction of m-DVB in the polymer film, \((X_{meta,DVB})_{poly}\), can be calculated using Equation 2-15.

Equation 2-15
\[
(X_{meta,DVB})_{poly} = \left(1 - \frac{1}{\frac{1}{0.56} \left(\frac{A_{meta}}{A_{para}}\right)_{poly} + 1}\right) \left(X_{meta,DVB} + X_{para,DVB}\right)_{mon}
\]

The final equation they obtained for the fraction of pendant vinyl bonds converted is given by Equation 2-16. The full derivation of this equation can be found in the 2013 Macromolecules publication by Petruiczok and Yang et al. 17

Equation 2-16
\[
Frac.\ Converted = 1 - \left(2 \cdot \frac{\left(\frac{A_{vinyl}}{A_{meta}}\right)_{poly}}{\left(\frac{A_{vinyl}}{A_{meta}}\right)_{mon}} \cdot \frac{(X_{meta,DVB})_{poly}}{(X_{meta,DVB})_{mon}}\right)
\]
2.5.3 Mechanism of Pendant Vinyl Bond Conversion

The crosslinking reaction could occur both at the growing pDVB film surface or within the bulk polymer film already formed. To fully understand the impact of iCVD process parameters on the pendant vinyl bond conversion, new reaction processes in addition to those in Table 2-1 must be considered. The potential iCVD cross-linking reaction routes summarized in Table 2-5 were adapted from Tobita and coworkers’ study in solution phase crosslinking.

Table 2-5. Potential initiation and propagation reactions for the pendant vinyl bond at the film surface and within the bulk film

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pendant Vinyl Initiation (Surface)</td>
<td>$R_{in}^<em>(g) + M_{n,pen(surf)} \rightarrow M_{n,pen(surf)}^</em>$</td>
</tr>
<tr>
<td>Pendant Vinyl Propagation (Surface)</td>
<td>$M_{n,pen(surf)} + M_{m,pen(surf)} \rightarrow M_{n+m,pen(surf)}^*$</td>
</tr>
<tr>
<td>Pendant Vinyl Initiation (Bulk)</td>
<td>$R_{in(ad)} \rightarrow R_{in(bulk)}^*$</td>
</tr>
<tr>
<td></td>
<td>$R_{in(bulk)}^* + M_{n,pen(s)} \rightarrow M_{n,pen(s)}^*$</td>
</tr>
<tr>
<td>Pendant Vinyl Bond Propagation (Bulk)</td>
<td>$M_{n,pen(bulk)}^* + M_{m,pen(bulk)} \rightarrow M_{n+m,pen(bulk)}^*$</td>
</tr>
</tbody>
</table>

For both the surface and bulk limited reactions, initiation occurs via a radical attacking the pendant vinyl bond of a pre-existing polymer. Propagation occurs when an activated pendant vinyl group reacts with another pendant vinyl group. The first major difference is in initiation. For crosslinking within the bulk, an initiator radical must diffuse from the surface into the bulk to initiate a pendant vinyl bond. The second is the difference in physical constraints. The propagation reaction requires some degree of mobility of the pendant vinyl group such as bond rotation about the C-C single bond or changes in the polymer chain conformation. The bulk film has physical constraints in all directions whereas the film surface imposes fewer physical constraints. At temperatures below the glass transition temperature, polymer chains in the bulk film are effectively frozen in place, making any reaction in the bulk highly unlikely. Sanetra et al. found the glass transition temperature of poly(styrene-co-divinyl benzene) increased from 102 °C at 5 wt% DVB to 133 °C.
at 20 wt% DVB\textsuperscript{41}. Given the present work uses pure pDVB films and the film temperature during growth does not exceed 50 °C, it is reasonable to assume the growing iCVD pDVB films are well below their glass transition temperature preventing reaction in the bulk. Therefore, it is likely that the cross-linking reaction is limited to the surface.

Studying the impact of filament and substrate stage temperatures can elucidate the limiting deposition sub-process for cross-linking during growth. Figure 2-4 depicts the calculated pendant vinyl bond conversion as a function of inverse stage temperature for deposition series 2. At the lowest filament temperature, 200 °C (Figure 2-4(left)), the conversion of the pendant vinyl bond decreases rapidly as stage temperature is elevated. This indicates that the reaction of the pendant vinyl bond is strongly dependent on the surface concentration of one of the participating species. It also supports our hypothesis that cross-linking is limited to the film surface. Whereas the surface concentration of DVB was held near constant for all experiments, the surface concentration of initiator radicals was not held constant. The initiator radical surface concentration, \([R^*]_{\text{ads}}\), is proportional to the ratio of \(P_R\) and \(P_{R,\text{Sat}}\), the respective partial and saturation pressures of the initiating radical. An increase in stage temperature increases the saturation pressure of \(R^*\). At constant \(P_R\), an increase in \(P_{R,\text{Sat}}\) would result in a reduced surface concentration of the initiator radicals. Whereas the reaction of the primary vinyl bond for series 2 is relatively insensitive to the gas-phase and surface concentrations of initiating radicals, the conversion of the pendant vinyl bond very much depends on the surface concentration of initiating radicals at the lowest filament temperature. Therefore, there is a non-zero reaction order with respect to t-butoxy radical concentration for the cross-linking reaction.
Figure 2-4. Pendant vinyl bond conversion as a function of substrate stage temperature and filament temperature for deposition series 2. (left) 200 °C(●) and (right) 220 °C(■), 240 °C(▲). The left (Ln(fraction conversion)) and right (fraction conversion) axes apply to both plots.

At the higher filament temperatures (Figure 2-4(right)), the pendant vinyl bond conversion is no longer has a strong dependence on stage temperature. Instead, the conversion appears to plateau. A significantly larger number of t-butoxy radicals are produced at high filament temperatures due the enhanced dissociation rate constant. The reaction order appears to be approaching zero with respect to the initiator radical surface concentration. Of note are the slightly higher conversion levels at a filament temperature of 240 °C vs. 220 °C. This behavior can be explained using the kinetic theory of gases. The container wall collision rate, ν, denotes the number of molecules that strike a unit of area per unit of time. From Equation 2-17, this quantity is related to the number of gas molecules, N, occupying a volume, V, the mass of the molecule, m, and the gas temperature, $T_{gas}$.  

\[ \nu = \frac{N}{4V} \sqrt{\frac{8k_BT_{gas}}{\pi m}} \]  

Equation 2-17
At higher filament temperatures, a larger number of free-radicals are formed and higher gas temperatures are obtained. Thus, at a fixed stage temperature, increasing the filament temperature increases the container wall collision rate. Since initiation occurs when a gas-phase t-butoxy molecule collides with a surface-bound pendant vinyl bond, the higher collision rate of elevated filament temperatures results in increased pendant vinyl bond conversion.

![Graph showing the relationship between filament temperature and pendant vinyl bond conversion](image)

**Figure 2-5.** Pendant vinyl bond conversion as a function of deposition rate and filament temperature [200 °C(●), 220 °C(■), 240 °C(▲)].

The deposition rate is another important factor to consider in the conversion of the pendant vinyl bonds. **Figure 2-5** shows that the pendant vinyl bond conversion decreases as the deposition rate increases. Faster deposition rates cause a given surface layer to become part of the bulk film more quickly as the next layer of DVB monomer adsorbs and reacts to form a polymer film. This trend further supports our assertion that cross-linking is limited to the growing film surface. The reaction of pendant vinyl bonds is effectively quenched once the surface layer is covered with new layers of polymer. These unreacted pendant vinyl bonds are now part of the bulk film and cannot react to cross-link as previously described. This imposes a compromise between deposition rate and pendant vinyl bond conversion. However, **Figure 2-5** also shows that at a given deposition
rate, higher conversion levels are possible at higher filament temperatures. This is most clearly illustrated at a deposition rate of \( \sim 7 \) nm/min. The conversion fraction increases from 0.44 at 200 °C to 0.52 at 240 °C. The deposition rate describes the time an arbitrary monolayer of pDVB spends at the surface, \( t_s \). This quantity can be calculated using Equation 2-18, where \( h_{ml} \) is the height of the pDVB monolayer. The total areal dose of radicals, \( N_{R/A} \), impinging on the film surface layer can be calculated as a function of deposition rate as given by Equation 2-19.

**Equation 2-18**

\[
ts_s = \frac{h_{ml}}{R_{dep}}
\]

**Equation 2-19**

\[
\frac{N_{R}}{A} = v \cdot t_s = v \cdot \frac{h_{ml}}{R_{dep}}
\]

When the collision rate is fixed (i.e. filament temperature), slower deposition rates increase \( t_s \) thereby increasing the total areal dose of initiating radicals that collide with the surface and initiate pendant vinyl groups. Faster deposition rates result in a lower total areal dose and lower conversion of the pendant vinyl bonds. If the deposition rate is fixed instead, the higher collision rate at elevated filament temperatures increases the total areal dose of initiating radicals and therefore the conversion of the pendant vinyl. Conversion could be due to either true cross-links being formed or increased rates of primary initiation and termination by t-butoxy radicals. The lack of a strong ether peak in all FTIR spectra suggests that true cross-links are being formed at higher filament temperatures. Therefore, operating at higher filament temperatures could reduce the compromise between fast deposition rates and high degrees of cross-linking.

### 2.5.4 Film Morphology

The iCVD pDVB films are relatively smooth, with all the root mean square roughness values falling under 1 nm, as seen in Figure 2-6. The majority of the roughness values fall in the range of 0.3 nm to 0.7 nm. There appears to be a slight increase in roughness at faster deposition rates and elevated filament temperatures (Figure 2-6a). Other iCVD polymer film chemistries and inorganic hot-wire CVD films demonstrate substantial changes in surface morphology, especially with respect to filament temperature.\(^{23,43-45}\) In Figure 2-6b, we evaluate the spread of roughness values as a function of filament temperature. For each filament temperature, the mean roughness falls in the range of 0.47 nm to 0.56 nm, with an average roughness of 0.51 nm for all filament
temperatures. The spread in data for each filament temperature is on the order of 0.2 nm, or ~40% of the mean. The comparatively large spread with respect to the mean indicates the roughness of iCVD pDVB films is not significantly impacted by filament temperature in the range evaluated in this work.

Figure 2-6. iCVD pDVB film roughness as a function of (a) deposition rate and filament temperature [200 ºC(●), 220 ºC(■), 240 ºC(▲)]. (b) Box and whisker plots depicting spread in film roughness as a function of filament temperature. Mean roughness (■) and outliers (○) indicated on plot. Measurements area was 2µm x 2µm.
2.6 Conclusion

This study investigated the impact of substrate stage temperature and filament temperature on the growth rate, pendant vinyl bond conversion and film morphology of iCVD from divinyl benzene. Maintaining $P_{pm}/P_{Sat}$ of DVB as a function of stage temperature yields faster deposition rates at higher stage temperatures. Deposition rates greater than 2 nm/min appear to be insensitive to the filament temperature, suggesting a zero-order dependence on the initiator concentration and second order dependence on the monomer concentration. Whereas the deposition rate depends on the reaction of the primary vinyl bond, cross-linking is determined by the reaction of the pendant vinyl bond. Significantly lower fractions of pendant vinyl bond conversion are observed at increasing stage temperatures at a filament temperature of 200 °C, indicating the t-butoxy surface concentration strongly affects the degree of crosslinking. This effect is reduced at higher filament temperatures. Faster deposition rates also result in lower fractions of pendant vinyl bond conversion, supporting our hypothesis that the cross-linking reactions are limited to the growing film surface. Increased filament temperatures may allow for a greater degree of cross-linking without sacrificing deposition rate. While this study only studied divinyl benzene, the principles of cross-linking gleaned from this study can be extended to the iCVD from other cyclic multivinyl chemistries.

2.7 References


Chapter 3  Ultrathin and conformal initiated chemical vapor deposited (iCVD) layers of systematically varied surface energy for controlling the directed self-assembly of block co-polymers.
This work was done in conjunction with Professor Paul Nealey’s research group at the University of Chicago.

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3.1 Abstract

Directed self-assembly (DSA) of block copolymer (BCP) thin films is a promising approach to enable next generation patterning at increasingly smaller length scales. DSA utilizes interfacial wetting layers to force the BCP domains to self-assemble with the desired orientation with respect to the substrate. Here, we demonstrate that initiated chemical vapor deposited (iCVD) polydivinylbenzene (pDVB) ultra-thin films can direct the self-assembly of poly(styrene-block-methylmethacrylate) (PS-b-PMMA). We found that methyl radicals formed at increased filament temperatures during the iCVD processes result in backbone methylation of pDVB. By tuning the degree of backbone methylation, we systematically changed the wetting properties of iCVD p(DVB) from slight PMMA preference to complete PS preference. Additionally, we utilize the conformal nature of the iCVD to form a wetting layer over a topographical line and space pattern which is subsequently used to produce self-assembled BCP films with both perpendicular orientation and long range alignment.

3.2 Introduction

Block copolymer (BCP) thin films has been extensively studied for next generation lithography given their ability to self-assemble into periodic patterns of the requisite length scale for the future of the semiconductor industry. Directed self-assembly (DSA) is a strategy to ensure that the patterns formed from self-assembled BCP thin films have the appropriate orientation with respect
to the substrate and long-range pattern order for use in nanofabrication\textsuperscript{1-3}. Long-range pattern order can be controlled by larger, more easily patterned, topographical templates generated by traditional lithographic techniques. Controlling the orientation with respect to the substrate requires careful interfacial energy control to ensure wetting by the appropriate block(s) for an application. Achieving the perpendicular orientation of the BCP requires a non-preferential wetting layer, which has an equal interfacial energy with each block. Without this layer, preferential wetting of the substrate by the lower interfacial energy block ensues, resulting in the parallel self-assembled orientation\textsuperscript{4}.

To control orientation, interfacial wetting layers are sandwiched between the substrate and the BCP thin film. For example, the patterning of long range lines requires lamellae forming poly(styrene)-block-poly(methylmethacrylate) (PS-b-PMMA) to be perpendicularly oriented to the substrate, such that both the PS and PMMA blocks wet the substrate. In a graphoepitaxial template, both non-preferential wetting and preferential wetting are needed to ensure perpendicular orientation of domains and long range axial alignment respectively\textsuperscript{5}. Usually, sidewall wetting is dictated by the preference of the template material, such as hydrogen silesquioxane (HSQ). If all template surfaces were modified with a non-preferential coating, the BCP self-assembles into lamellae perpendicular to the template axis. Therefore, conventional DSA requires the non-preferential interfacial wetting layer cover only the bottom wall while minimizing coverage of the sidewall to ensure parallel alignment of lamellae with respect to the template axis.

Careful control of the wetting layer's chemistry is paramount to ensuring the appropriate BCP wetting properties. However, durability of these layers is equally important as they will be exposed to solvents and sonication several times during the DSA process. To achieve this, the first generation of wetting layers were polymer brushes directly grafted to the substrate\textsuperscript{6}. However, this process can only modify oxide surfaces and requires fine control of the brush polydispersity for uniform layer thickness. The development of cross-linked polymer mats has allowed use of a greater variety of substrates. In this case, the cross-linked polymer mats are generated by first synthesizing a random copolymer containing both BCP monomers and crosslink-able constituents on the back bone. After film casting, a thermal anneal activates the cross-linking reaction\textsuperscript{7}. Like its predecessor, this technique requires development of a unique polymer chemistry for each wetting scenario (preferential or non-preferential). More recently, the development of
organosilicate layers has simplified wetting control of PS-b-PMMA\(^8-9\). In this case, the same starting material is spun cast on the substrate and the resulting wetting properties are controlled by the cure temperature of the organosilicate film. A range of wetting behaviors from complete PMMA preference to mostly non-preferential with slight PS preference was achieved.

Here we present the application of cross-linked poly(divinyl benzene) (pDVB) ultra-thin films, formed via a single-step initiated chemical vapor deposition (iCVD) process, as wetting layers with tunable preference for PS-b-PMMA. iCVD is an adaptation of conventional, solution radical chain polymerization which allows for simultaneous polymer synthesis and thin film formation by using vapor phase precursors\(^{10-11}\). The solvent-less nature of this technique enables formation of cross-linked polymer thin films of several multi-vinyl cross-linking chemistries (e.g. pDVB, poly(ethylene glycol diacrylate), poly(cyclic-siloxanes)) that are inaccessible via traditional solution routes\(^{12-15}\). Additionally, iCVD process can be scaled up to allow many wafers to be coated in a single run. The process occurs as depicted in Figure 3-1. In short, monomer and initiator vapors are metered into a vacuum chamber where monomer molecules adsorb onto a room-temperature substrate. A heated filament array cracks the labile bond of the initiator (e.g. di-tert-butylperoxide) and the resulting gaseous radicals collide with adsorbed monomers to initiate polymerization. Polymer chain growth and cross-linking occurs simultaneously during film growth.

One major difference between iCVD and traditional solution cast layers is its ability to form incredibly conformal films, where the film thickness is uniform over complex features\(^{16}\). This may initially seem problematic given the need for different wetting characteristics for the sidewall and bottom wall. However, the wetting preference of a polymer film is not limited to discrete values of PMMA, PS, or non-preferential preference only. Instead, it exists in a continuum where the wetting layers have mixed character between non-preferential and complete preference for a particular block. Therefore, even if the same material coats the sidewall and bottom wall, the self-assembling BCP can essentially be tricked into seeing a preferential sidewall and a non-preferential bottom wall. Conformal interfacial wetting layer film coverage is now essential for high quality self-assembly.
The chemical structures of PS-b-PMMA BCP and the DVB monomer are presented in Chart 3-1a and 1b respectively. Given the similarity in structure between styrene and DVB, where DVB has an additional vinyl bond compared to styrene, it can be expected that pDVB films should form cross linked mats favoring styrene wetting. However, the types of radical species present during deposition have a major impact on the final film structure and wetting properties. Ozaydin-Ince et al. found that at filament temperatures lower than 250 °C, t-butoxy radicals are primarily formed via the α-scission of TBPO, as seen in Chart 3-1c. At filament temperatures greater than 250 °C, t-butoxy radicals further decompose into methyl radicals and acetone via a β-scission reaction, as seen in Chart 3-1d. Here we demonstrate that varying the chamber methyl radical concentration by changing the deposition filament temperature results in varying degrees of backbone methylation of the pDVB film. By increasing the degree of backbone methylation, iCVD pDVB films wetting properties transition from slight PMMA preference to complete PS
preference. We also show the successful integration of iCVD pDVB films into the DSA process by coating the line and space patterns defined by e-beam lithography of HSQ to induce both perpendicular orientation and long-range alignment of lamellae PS-b-PMMA. Furthermore, we demonstrate the ability to switch between PMMA and PS preferential sidewalls to easily alter the order of self-assembled domains within the HSQ patterns.

**Chart 3-1.** (a) Structure of poly(styrene-b-methylmethacrylate). PS block in red, PMMA block in blue (b) structure of divinyl benzene monomer, which is a mixture of para- and meta- isomers (c) α scission of TBPO to form t-butoxy radicals (d) β scission of t-butoxy radical to form methyl radical and acetone

3.3 Experimental

3.3.1 iCVD Film Preparation.

Divinyl benzene monomer (DVB, 80%), styrene (99%), and di-tert-butyl peroxide (TBPO, 98%) were purchased from Sigma-Aldrich and Argon gas (100%) from Airgas and used without any further purification. All polymer film depositions occurred in a custom built initiated chemical vapor deposition (iCVD) chamber described elsewhere. The chamber pressure was controlled
using a throttling butterfly valve (MKS Instruments) and substrate temperature controlled using a stage chiller (Thermo-Fisher). Precursor vapors was delivered to the chamber using mass flow controllers (MKS Instruments). A Chromaloy O (Goodfellow) filament array was heated to crack the TBPO peroxide bond. Film growth and thickness were monitored in situ using a 633 nm HeNe Laser (JDS Uniphase).

Approximately ~12 nm thick poly(divinyl benzene) (pDVB) films were deposited on 100 mm Si wafers (WRS Materials) and custom prepared DSA samples. The chamber pressure and substrate temperature were maintained at 150 mTorr and 37 °C respectively for all depositions. DVB was heated to 40 °C and delivered to the reactor at 0.5 standard cubic centimeters per minute (sccm). TBPO and an Argon patch were delivered at room temperature to the reactor at 2 sccm each using individual mass flow controllers. pDVB films were grown at five filament temperatures between 210 °C and 330 °C in increments of 30 °C resulting in five conditions to be analyzed.

Approximately 200 nm thick polystyrene (PS) films were deposited on 100 mm Si wafers. The chamber pressure and substrate temperature were maintained at 600 mTorr and 25 °C respectively for all depositions. Styrene was heated to 30 °C and delivered to the reactor at 3.0 standard cubic centimeters per minute (sccm). TBPO was delivered at room temperature to the reactor at 2 sccm. Filament temperatures of 225 °C and 330 °C were used respectively.

3.3.2 Reference PS film Treatment.

55 μm polystyrene standard films were purchased from Pike technologies. The films were treated in the aforementioned iCVD chamber at a chamber pressure and substrate temperature of 1 Torr and 25 °C respectively. The films were exposed to 2.7 sccm of TBPO decomposed at a filament temperature of 330 °C for two hours.

3.3.3 Film Characterization.

Ex Situ iCVD polymer film thicknesses were determined using a J.A. Woollam M-2000 variable angle spectroscopic ellipsometer (VASE) at incident angles of 65°, 70°, and 75° over five positions on the Si wafer. The data were fit to a Cauchy-Urbach isotropic model using WVASE32 modeling software (J.A. Woollam) and averaged over the five positions. The standard deviation of thickness for a given pDVB batch was less than 1 nm across a 100 mm wafer. Fourier transform infrared
(FTIR) spectra were obtained using a Thermo-Fisher Nicolet iS50 Spectrometer. The DVB monomer, iCVD pDVB films, as received Pike standard PS film, and TBPO treated Pike standard PS film were measured in attenuated total reflection (ATR) mode using a variGATR accessory (Harrick Sci.) at 65° with a germanium crystal and a liquid N₂ cooled mercury cadmium telluride (MCT-A) detector. iCVD PS film spectra were measured in transmission mode using the MCT-A detector. All spectra were averaged over 256 scans. A reference PS spectra was obtained from the Omnic (Thermo-Fisher) software library. Analysis of all FTIR spectra was done using Omnic. The alkane residue peaks (3100 cm⁻¹ to 2800 cm⁻¹) of the PS spectra were resolved and fitted assuming a Voigt distribution. The surface energy of pDVB films was determined by sessile drop contact angle measurements performed on a Ramé-Hart model 500 goniometer equipped with an automatic dispenser. The contact angles of three 6 μL droplets of deionized water (VWR) and diiodomethane (Sigma-Aldrich) were measured on samples of each filament condition. The surface energy, assuming a harmonic mean, was calculated using Drop Advanced software (Ramé-Hart). The roughness of pDVB films on Si wafers was measured using a Veeco Dimension 3100 atomic force microscope (AFM) in tapping mode over a 5μm x 5μm area with 512 points per line and lines per scan. The root mean square roughness was 0.32 nm or less for all depositions (Figure A-1). Resistance to toluene was determined by measuring the film thickness with VASE of a 2 cm x 2 cm sample before and after 5 minutes of sonication in toluene at 25 °C. Films showed less than 1 nm of thickness lost.

3.3.4 Commensurability test.

74 kg/mol (37k-37k) PS-b-PMMA with a lamellae domain spacing (L₀) of 40nm was purchased from Polymer Source Inc. and used without further purification. BCP films with thicknesses of 1.5 L₀, 1.75 L₀, and 2.0 L₀ were spun cast from a 2 wt% BCP in toluene solution on pDVB coated Si pieces from each filament temperature condition and a reference Si piece. Self-assembly was induced by annealing the samples for 20 hours at 170 °C in a nitrogen filled glovebox. Optical microscopy (OM) of each temperature-BCP thickness condition was performed with a Carl Zeiss Axio Imager A1m. Determination of hole vs. island was done using a Digital Instrument Nanoscope IIIA AFM in tapping mode over a 20μm x 20μm area. Samples were further imaged using a LEO 1550VP field emission scanning electron microscope (SEM) to determine whether
samples with no topographical features displayed commensurate preferential wetting or non-preferential wetting.

3.3.5 DSA Sample Preparation.

60 nm thick HSQ film was spun cast on Si substrates with XR-1541 (Dow Corning). Line and space e-beam patterns with a 275 nm trench width on a 350 nm pitch were obtained after exposure in a JEOL 9300 system with an area dose of 1,400 µC cm\(^{-2}\). Development was done using MF-CD-26 (Dow Chemical) at 50 deg C for 2 minutes. The samples were rinsed with deionized water and then isopropanol. Compressed nitrogen gas was used to dry the sample. After deposition of iCVD pDVB, 44 kg/mol PS-b-PMMA (22k-22k) with an \(L_0\) of 25 nm obtained from Polymer Source Inc. was back-filled into the pattern via spin casting. The sample was then annealed for 20 minutes at 250 °C in a nitrogen filled glovebox and then imaged using a SEM.

3.4 Results and Discussion

3.4.1 Film Chemical Structure

Fourier transform infrared spectroscopy (FTIR) was used to confirm the polymerization of pDVB and analyze the impact of filament temperature on the final polymer structure. Table 3-1 summarizes all peak assignments used in this analysis. In Figure 3-2a, the successful polymerization and crosslinking of pDVB is confirmed by the complete elimination of the vinyl stretch peak at 990 cm\(^{-1}\) and reduction of the vinyl peak at 903 cm\(^{-1}\) in the FTIR spectra of pDVB. The DVB monomer used was an isomeric mix of para-substituted DVB (\(p\)-DVB) and meta-substituted DVB (\(m\)-DVB) which results in three di-substituted benzene peaks from 850 cm\(^{-1}\) to 710 cm\(^{-1}\) in the monomer spectrum. These three peaks are retained in the polymer spectra, indicating retention of the di-substituted benzene structure. Two new peaks at 1105 cm\(^{-1}\) (blue highlight) and 1230 cm\(^{-1}\) (orange highlight) indicate the ether stretch and t-butyl skeletal vibration of t-butoxy groups incorporated within the pDVB structure. Minimal change is observed in the peak strengths as a function of the deposition filament temperature, suggesting that the t-butoxy content does not change significantly with filament temperature. However, in Figure 3-2b, blue highlighted sp\(^3\) methylene C-H stretch peaks at 2930 cm\(^{-1}\) and 2850 cm\(^{-1}\) respectively consistently decrease in strength while orange highlighted sp\(^3\) methyl C-H stretch peaks at 2964 cm\(^{-1}\) and 2874
cm\(^{-1}\) consistently increase in strength. This indicates that methyl content in the film increases with filament temperature. If we assume t-butoxy content in the iCVD pDVB films is relatively constant, the increase in methyl content must come from lone methyl radicals generated during the \(\beta\)-scission reaction. The increasing methyl content with filament temperature also corresponds with the increased frequency of the \(\beta\)-scission reaction as filament temperature increases.

**Table 3-1.** Infrared spectral peak assignments used in this work. Compiled from references \(^{12, 15}\) [9-21]

<table>
<thead>
<tr>
<th>Approximate Wavenumber (cm(^{-1}))</th>
<th>Characteristic Group</th>
</tr>
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<tbody>
<tr>
<td>3027</td>
<td>arom. sp(^2) CH</td>
</tr>
<tr>
<td>2964</td>
<td>asym. sp(^3) CH(_3)</td>
</tr>
<tr>
<td>2930</td>
<td>asym. sp(^3) CH(_2)</td>
</tr>
<tr>
<td>2874</td>
<td>sym sp(^3) CH(_3)</td>
</tr>
<tr>
<td>2850</td>
<td>sym sp(^3) CH(_2)</td>
</tr>
<tr>
<td>1230</td>
<td>-C(C)(_3)</td>
</tr>
<tr>
<td>1105</td>
<td>C-O-C</td>
</tr>
<tr>
<td>990</td>
<td>vinyl</td>
</tr>
<tr>
<td>903</td>
<td>vinyl</td>
</tr>
<tr>
<td>848</td>
<td>para di-substituted benzene</td>
</tr>
<tr>
<td>801</td>
<td>meta di-substituted benzene</td>
</tr>
<tr>
<td>761</td>
<td>mono-substituted benzene</td>
</tr>
<tr>
<td>710</td>
<td>meta di-substituted benzene</td>
</tr>
<tr>
<td>700</td>
<td>mono-substituted benzene</td>
</tr>
</tbody>
</table>
Reaction with a vinyl group or vinyl radical in the growing free radical chain is one means for additional methyl groups to incorporate into the pDVB structure. As a direct participant in the iCVD chain growth process, methyl radicals could act as either initiating or terminating species. Reaction with first of two vinyl bonds the DVB monomer would produce a methyl end group and initiate chain growth of the main polymer backbone (see Chart 3-2a). Reaction with the second unreacted vinyl group of a DVB unit already incorporated into a chain, would produce a pendent
methyl group and a vinyl radical. The vinyl radical could either undergo further chain growth to produce a branching chain or be terminated by another methyl radical (Chart 3-2b).

Alternatively or additionally, substitution of a methyl group onto the pDVB chain could occur by a two step sequence where first a methyl radical abstracts a hydrogen atom from the benzene ring (Chart 3-2c) or from the methylene bridge of the polymer backbone (Chart 3-2d) and then a second methyl radical reacts with newly created radical site to produce the methyl group substitution.

**Chart 3-2**: Potential reactions with methyl radical: (a) Chain initiation by methyl reaction with the first vinyl moiety of DVB (b) Chain branching by reaction with a pendant vinyl bond (c) Two-step abstraction of aromatic hydrogen and methyl substitution (d) Two-step abstraction of backbone hydrogen and methyl substitution

![Diagram of potential reactions](chart-3-2.png)
The addition of a methyl radical to a vinyl bond (primary or pendant) as seen in Chart 3-2a,b is unlikely. Ozaydin-Ince et al. concluded that even with the presence of methyl radicals, only t-butoxy radicals were active initiators given since the activation energy of initiation remained constant as filament temperature increased\(^\text{13}\). If methyl initiation did occur, their kinetic study would have revealed a second activation energy corresponding to methyl initiation at higher filament temperatures before the mass transport regime was achieved. Therefore, we focused on determining whether the reactions in Chart 3-2c,d occurred. Unfortunately, Figure 3-2 does not readily differentiate between these two possible mechanisms for methyl incorporation. The ATR-FTIR spectra has limited ability to be quantitatively analyzed, given its sensitivity to sample microscopic contact area with the Ge crystal\(^\text{22}\). Qualitative analysis is also hindered by the overlap of the multiple aromatic FTIR multi-substituted benzene peaks from a large number of isomeric forms. The DVB monomer is a mixture of its meta and para isomers and these give rise to multitude of isomeric bonding configurations possible for the crosslinked iCVD pDVB film.

As a model system for exploring the chemistry of methyl radicals in the iCVD process, depositions were performed with styrene as the monomer (Chart 3-3a). The resulting iCVD polystyrene (PS) films have many fewer vibrational bands than the pDVB films and hence fewer overlapping peaks. Thick films (200 nm) were grown to allow use of quantitative analysis of transmission mode FTIR spectra at filament temperatures of 225 °C and 330 °C. Figure 3-3a shows the transmission FTIR spectra of the relative thick iCVD films compared on a PS standard in the Omnic library. The methyl asymmetric C-H stretch is highlighted in orange and is only present in the iCVD synthesized films. In gray, the two peaks at 700 and 760 are a ring out-of-plane deformation and out-of-plane vibration, respectively, for a mono-substituted benzene species\(^\text{20}\). No additional peaks in region of 900 cm\(^{-1}\) to 710 cm\(^{-1}\) in the iCVD spectra indicates no substitution onto the benzene ring. With this information, we assume the aromatic hydrogen content to be constant and proportional to the area of the sp\(^{2}\) C-H peak highlighted in pink. We can then quantitatively assess each spectrum by comparing peak area ratios as given by Equation 3-1.

**Equation 3-1**

\[
m : n = \frac{A_m}{A_n}
\]
where m and n are the peaks of interest and $A_m$ and $A_n$ are the areas under peaks m and n respectively. The symmetric and asymmetric CH$_2$ stretches at 2850 and 2930 cm$^{-1}$, respectively; the symmetric and asymmetric CH$_3$ stretch at 2874 and 2964 cm$^{-1}$, respectively; and the aromatic CH stretch at 3027 cm$^{-1}$ were resolved and fit using assuming a Voigt distribution (Figure A-2). The areas under each fitted peak are listed in Table A-1. For quantitative analysis, only the peaks at 3027, 2964, and 2930 cm$^{-1}$ henceforth referred to as aromatic, CH$_3$ and CH$_2$ were used due to their minimal overlap in area. The peak area ratios were determined for each spectra using these three peaks and Equation 3-1 and are summarized in Figure 3-3b. The CH$_3$:Aromatic ratio sees a large increase between the reference sample and iCVD pS grown at 225 °C. A modest increase in the ratio at 330 °C confirms that methyl content does indeed increase with filament temperature. The CH$_2$:Aromatic ratio sees a large decrease between the reference sample and iCVD pS grown at 225 °C and a further decrease in methylene content as filament temperature increases. A corresponding increase in CH$_3$:CH$_2$ ratio confirms that methyl groups are indeed replacing hydrogens on methylene groups. The mechanism of replacement likely occurs through abstraction of hydrogen by an initial methyl radical and the reaction with a second methyl radical to form the methylated backbone. Indeed, previous studies have shown that methyl radicals generated from the decomposition of TBPO can abstract hydrogen from the Si-H bond$^{23-24}$.

**Figure 3-3.** (a) Transmission FTIR of pS standard and iCVD pS at filament temperatures of 210 °C and 330 °C. CH sp$^2$ highlighted in pink. CH$_3$ sp$^3$ peaks highlighted in orange. CH$_2$ sp$^3$ peaks highlighted in blue. Mono-substituted benzene peaks in gray. (b) FTIR Peak area ratio of CH$_3$:CH$_2$ (▲), CH$_3$:Aromatic (●), and CH$_2$:Aromatic (●) for Omnic reference and iCVD synthesized pS (c) ATR FTIR of Pike Technologies pS standard film as received (black) and after 2 hour TBPO treatment with filament at 330 °C (red). CH$_3$ sp$^3$ peaks highlighted in gray.
To test the abstraction hypothesis, reference polystyrene samples from Pike technologies were exposed to TBPO vapor at a filament temperature of 330 °C. Figure 3-3c shows the ATR FTIR spectra of a treated sample compared to the as received sample. The spectra are indistinguishable except for the emergence of an asymmetric methyl stretch in the TBPO treated spectrum, highlighted in gray. Since no other species were also introduced to the reactor, these new methyl groups must have been introduced via an abstraction/substitution reaction. From this information, we postulate the styrene polymerized via iCVD has the same polymeric structure as a copolymer of styrene and \( \beta \)-methyl styrene as seen in Chart 3-3b. As filament temperature increases, the \( \beta \) -methyl styrene content increases while styrene content decreases. We can then extrapolate the structure of iCVD pDVB at low filament temperatures to that of Chart 3-3c which then gradually shifts to the methylated structure seen in Chart 3-3d at high filament temperatures. T-butoxy end groups are present for all of these structures given that it is the only reactive group capable of vinyl bond initiation.

**Chart 3-3.** (a) Structure of styrene monomer (b) Structure of iCVD polymerized polystyrene with partially methylated backbone and t-butoxy end groups. Postulated structure of iCVD pDVB based on FTIR analysis of pS at (c) low filament temperatures (d) high filament temperatures.
3.4.2 Film Surface Energy and Wetting Behavior

The static contact angles (SCA) of deionized water and diiodomethane were measured for each pDVB film using the sessile drop technique. As seen in Figure 3-4a, the water SCA remains at approximately 97° for all pDVB films. Correspondingly, the polar component of the surface energy remains largely invariable, as seen in Figure 3-4b. The ether linkages formed by t-butoxy initiation is the primary source of the polar surface energy. This supports the previous assertion that t-butoxy content is relatively constant with respect to filament temperature. The impact of increased backbone methylation is seen most clearly by the increase in the diiodomethane SCA from 39.7° to 45.8° as filament temperature increases. This increase in methyl groups results in a lowering of the dispersive component of surface energy yielding a decrease in overall surface energy from 42.7 mN/m to 39.9 mN/m as the filament temperature during deposition increases from 210 °C to 330 °C.

![Figure 3-4a](image)

![Figure 3-4b](image)

**Figure 3-4.** (a) Static contact angle of diiodomethane (■) and water (●) as function of filament temperature (b) Polar (●), dispersive (●), and total (▲) surface tension of pDVB as function of filament temperature.
3.4.3 Block copolymer wetting preference

When a BCP thin film is annealed to induce self-assembly, the film thickness and substrate wetting characteristics and surface free energy determine both the orientation of domains with respect to the substrate and the order in which they are layered. In the case of PS-b-PMMA thermally annealed at 170°C, PS preferentially wets the free interface due to its slightly lower free surface energy. At these conditions, however, a non-preferential substrate can still induce perpendicularly oriented domains in thin films due to the entropic penalty associated with parallel orientation. By contrast, if the substrate is also preferential, only parallel-oriented domains are seen, where the free surface is always the lower surface energy PS domain while the domain at the BCP film/substrate interface is dependent on the substrate wetting properties. In this parallel domain orientation, the proportionality between film thickness and BCP domain spacing, $L_0$, and substrate wetting determine film strain and therefore commensurability. A film with no strain is commensurate in thickness and has no topographical differences before and after annealing. However, an incommensurate film relieves strain during the anneal by forming a hole/island morphology with a step height of $L_0$. Therefore, the substrate wetting preference can be determined by observing the BCP film morphology after self-assembly for a particular film thickness. Figure 3-5 shows representative AFM images of the morphology of self-assembled symmetric PS-b-PMMA films of three different thicknesses self-assembled on substrates with PMMA (top) and PS (bottom) wetting preference. The PS preferential substrate produces commensurate films when the BCP film thickness is $2L_0$ whereas a PMMA preferential substrate produces commensurate films with thicknesses of $1.5L_0$, as evidenced by the flat topography. A bicontinuous morphology, where there are an equal number of holes and islands, is produced at $2L_0$ and $1.5L_0$ for PMMA and PS preference respectively. Additional information regarding substrate wetting properties is obtained when the BCP film thickness is $1.75L_0$. A BCP film on a PS preferential substrate experiences tension, which is relieved during self-assembly by forming islands of height $L_0$. The same film on a PMMA preferential substrate experiences compression, which is relieved during self-assembly by forming holes of depth $L_0$. 

82
Figure 3-5: Representative AFM images of PS-b-PMMA thin films self-assembled on a PMMA preferential surface (top) and a PS preferential surface (bottom). PMMA-b-PS film thickness increases from 1.5$L_0$ to 2$L_0$ from left to right where $L_0 \sim 40$ nm. At 1.75$L_0$, PMMA preference produces islands whereas PS preference produces holes.

Figure 3-6(left) presents top-down optical microscope images of PS-b-PMMA (37k-37k, $L_0 = 40$ nm) films after self assembly on ~12 nm thick iCVD pDVB films. A silicon wafer serves as a PMMA-wetting reference. For a PS-b-PMMA film thickness of 1.5$L_0$, a gradual change from a flat surface to a bicontinuous structure occurs as the filament temperature increases. As the filament temperature increases to about 270 °C, PS-b-PMMA films of 1.75$L_0$ thickness form islands, as confirmed by AFM. This corresponds to increasing PS preference of pDVB films as filament temperature increases. The 2$L_0$ PS-b-PMMA films remain flat for all filament temperatures, indicating some degree of either non-preferential or PS preference for all pDVB films. SEM images in Figure 3-6(right) reveal whether the flat optical images correspond to a commensurate parallel orientation or non-preferential perpendicular orientation of the BCP film. At the lowest filament temperature of 210 °C, the PS-b-PMMA film with thickness of 1.5$L_0$, the domains are primarily parallel to the substrate with no bicontinuous topography, indicating PMMA preference of the iCVD surface. However, at PS-b-PMMA film thicknesses of 1.75$L_0$ and 2.0$L_0$, the domains are perpendicularly oriented, indicating a non-preferential character. Therefore, for the iCVD film grown at this lowest filament temperature, we can characterize the wetting behavior of this pDVB film as mostly non-preferential with slight PMMA preference. An increase of
filament temperature to 240 °C produces perpendicular orientations at PS-b-PMMA film thicknesses of 1.5L₀ and 1.75 L₀ while having a parallel orientation at a thickness of 2L₀. This pDVB film is therefore mostly non-preferential with slight PS preference. A visual representation of the wetting transition with temperature is shown in Figure 6(bottom). As the filament temperature continues to increase, pDVB film wetting becomes less non-preferential and more PS preferential. At the highest filament temperature, 330 °C, the pDVB film becomes completely PS preferential. We attribute this transition to the increasing presence of methyl groups on the pDVB backbone, whose interaction with the PMMA block is energetically unfavorable thus resulting in increased PS preferential wetting.
Figure 3-6. Wetting behavior of PS-b-PMMA films on iCVD pDVB substrates. BCP film thicknesses of 1.5 $L_0$, 1.75 $L_0$, and 2.0$L_0$ (across) were spin cast on ~12 nm thick iCVD pDVB films grown at 5 different filament temperatures (down). $L_0$ ~ 40 nm. The 50 µm X 50 µm top-down optical micrograph are shown on the left-side. The right-side shows 2 µm X 2 µm top-down SEMs. The blue-to-red color continuum at the bottom demonstrates the difference in wetting behavior between pDVB films grown at different filament temperatures from PMMA preferential to non-preferential (NP) to PS preferential.
3.4.4 Integration in DSA process

To demonstrate that iCVD wetting layers can be integrated into the DSA process, iCVD pDVB films grown at filament temperatures of 210 °C and 240 °C were deposited onto HSQ line and space topographical patterns. The trenches were then backfilled with PS-b-PMMA (22k-22k, L₀=25nm). Figure 3-7a shows a schematic of a conformal pDVB coating on an HSQ line and space template. An initial trench width of 275 nm was reduced to ~250 nm by a 12 nm thick, conformal pDVB film. This final width is symmetrically commensurate with the L₀ of the lower molecular weight PS-b-PMMA. Figure 3-7b shows a corresponding cross-sectional SEM image of the HSQ template coated with an iCVD pDVB film. Coating conformality is confirmed by examining the interface between the pDVB film (highlighted in yellow) and HSQ template (highlighted in green), indicated by the yellow dotted line. Furthermore, the very low roughness of the pDVB film is also visually confirmed. The root mean square roughness of pDVB films grown at all filament temperatures was less than 0.32 nm (see Figure S1).

After backfilling with PS-b-PMMA and annealing the samples, BCP films perpendicularly oriented with respect to the bottom wall are expected. If the pDVB films were truly non-preferential, the pattern would be perpendicular to the sidewalls as well. Preferential sidewalls induce parallel pattern alignment. Furthermore, sidewall preference also controls the order of PS and PMMA lines within the trench. For instance, Figure 3-7c shows the expected BCP self-assembled structure assuming a non-preferential bottom wall and PMMA preferential sidewall. During self-assembly, the PMMA blocks preferentially nucleate at the sidewall, resulting in a structure with six ~12.5 nm wide PS lines interspersed with five ~12.5 nm PMMA lines. Approximately 6 nm wide PMMA domains separate the sidewalls from the PS domains. However, if the sidewall is PS preferential, the ordering of blocks changes to that of Figure 3-7d. The structure now has six ~12.5 nm wide PMMA lines interspersed with five ~12.5 nm wide PS lines. The sidewalls are now separated from the PMMA domains by ~6 nm wide PS domains. The commensurability test revealed that pDVB grown at filament temperatures of 210 °C and 240 °C were mostly non-preferential in character. This results in the perpendicular self-assembly of PS-b-PMMA within the HSQ patterns coated with pDVB, as seen in Figure 3-7e,f. Pattern alignment parallel to the sidewall confirms the pDVB films are not completely non-preferential in character. The ordering of domain lines, colorized in the figure insets, demonstrate PMMA and PS sidewall
preference for pDVB grown at 210 °C and 240 °C respectively. The slight PMMA preference of the pDVB film grown at 210 °C, as demonstrated in Figure 3-6, enables sidewall wetting by PMMA domains. Likewise, the slight PS preference of the pDVB film grown at 240 °C allows the change to PS wetting of the sidewall. These results establish two key benefits of iCVD pDVB wetting layers for DSA: First, a single process forms both a non-preferential bottom wall for perpendicular assembly of BCPs and a preferential sidewall to force parallel domain alignment. Second, by only changing the deposition filament temperature, the sidewall preference can easily switch from PMMA to PS while maintaining a non-preferential bottom wall.
Figure 3-7. (a) Schematic of HSQ (green) template on silicon with conformal iCVD pDVB coating (beige). (b) 45°-tiled cross-sectional SEM image of HSQ template coated with iCVD pDVB demonstrating coating conformality. HSQ regions highlighted in green. iCVD pDVB coating highlighted in yellow. Yellow dots delineate interface between template and polymer film. Schematics of PS-b-PMMA self assembly with non-preferential bottom wall and (c) PMMA sidewall preference (light-red color) and (d) PS side wall preference (light blue color). PMMA domains shown in blue, PS domains shown in red. SEM images of self-assembled PS-b-PMMA (L₀ = 25nm) in HSQ template coated with iCVD pDVB grown at (e) Tᵢ=210 °C with PMMA sidewall preference and (f) Tᵢ=240 °C with PS sidewall preference. Insets are enlarged views with PMMA domains highlighted in blue and PS domains highlighted in red.
3.5 Conclusions

iCVD was used to deposit ultra-thin films of pDVB for use as an interfacial wetting layer to control the self-assembly orientation of PS-b-PMMA thin films. Increasing the iCVD deposition filament temperature promotes beta-scission of the initiator thus resulting in higher methyl radical concentrations during the deposition. FTIR analysis of both pDVB and PS thin films demonstrates increased methylation of the chain backbone with filament temperature which in turn leads to a reduction of the film surface energy. This surface energy change can be exploited to alter the wetting behavior of pDVB films from mostly non-preferential with slight PMMA preference all the way to complete PS wetting preference. The pDVB films proved robust to the solvents and annealing temperatures used in the subsequent DSA processes. The conformality of pDVB films over a trench topography allowed coated graphoepitaxy patterns yielding BCP patterns perpendicularly oriented with the substrate and parallel oriented with the topographical pattern axis. The preference of the BCP for the sidewall of the coated pattern could be switched by simply altering the filament temperature used to deposit the iCVD coating.

3.6 References

Chapter 4  Conformal Solid Polymer Electrolytes for Three-Dimensional Lithium Ion Batteries

This work was done in conjunction with Prof. Bruce Dunn’s research group at the University of California, Los Angeles

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4.1 Abstract

The realization of solid state, three-dimensional lithium ion batteries requires the development of nanoscale, conformal, solid electrolytes. Here we study the initiated chemical vapor deposition (iCVD) from cyclic siloxane and cyclic silazane monomers to form conformal, solid polymer electrolytes. The films are good electrical insulators that can be rendered room temperature ionic conductors by soaking in a liquid electrolyte system. Out of the chemistries studied, 25 nm thick poly(tetravinyltetramethylcyclotetrasiloxane) (pV4D4) films displayed the highest ionic conductivity (approaching $10^{-7} \text{ S cm}^{-1}$) and retention of Li ions after soaking. Electron microscopy studies demonstrate minimal swelling after lithiation, indicating good mechanical stability. Images of iCVD pV4D4 on high aspect ratio (> 50) Si nanowire arrays demonstrate the process is highly conformal. Finally, electrochemically lithiating the film via galvanostatic charge-discharge
cycles renders even thick pV4D4 films (400 nm) ionic conductors, with conductivity values exceeding $10^{-7}$ S cm$^{-1}$.

4.2 Introduction

Microelectromechanical systems (MEMS) have established high-volume markets for multiple commercial products over the past 20 years and possess further potential for widespread application in sensors, microfluidics, wireless communications, and optics. However, MEMS devices require miniaturized or microbatteries with higher areal energy densities (>100 J cm$^{-2}$) than current planar lithium-ion (Li$^+$) batteries can provide (<5 J cm$^{-2}$). Three-dimensional or 3D battery architectures comprising of high surface area, nonplanar electrode structures (e.g., interdigitated rods, cylinder, plates, and microporous networks) instead of the traditional planar electrodes can address this challenge by increasing areal energy density, while also maintaining the short ion-transport distances necessary for high power densities. A key obstacle to the development of such 3D battery architectures is the synthesis of a suitable electrolyte, which must be conformal, pinhole-free, electronically insulating, and ionically conducting. Unlike liquid electrolytes, conformal, solid-state polymer electrolytes that uniformly “shrink-wrap” nonplanar electrode structures can minimize the volume devoted to the electrochemically inactive electrolyte and thus increase energy density to levels suitable for powering autonomous MEMS devices. Liquid electrolytes further suffer from surface tension and dewetting effects, which lead to “soft” shorts that can create undesirable current shunting pathways in a battery. Finally, solid-state electrolytes with thicknesses on the nanoscale can provide significantly shorter ionic transport times compared to their micron scale or liquid state counterparts. The need for nanoscale thickness uniformity and conformality over the complex geometries of 3D battery electrodes has presented one of the most significant design challenges for the realization of 3D batteries.

The most commonly explored polymeric electrolyte is poly-(ethylene oxide) (PEO, [-{(O-CH$_2$-CH$_2$)}$_n$]). PEO and its cyclic variants are known to chelate ions like Li$^+$. However, PEO is crystalline at room temperature and the segmental motion of the –C–O–C– linkages that facilitate Li$^+$ transport only occurs in amorphous phase, resulting in improved ionic conductivity at elevated temperatures (>60 °C). Conjugating siloxane segments to PEO is reported to increase ionic conductivity and impart improved mechanical and electrochemical stability.
Si–O–Si– bonds in the siloxane moieties are more ionic than –C–O–C– bonds leading to a more negative charge on the oxygen atom that can chelate Li+. The flexible nature and associated free volume of the siloxane linkages further facilitate ionic transport. Moreover, multivinyl cyclic siloxanes can form an electrically insulating, cross-linked network structure, with the potential for the ring structures in the monomer to stack and form built-in channels for Li+ transport. A similar phenomenon is plausible with multivinyl cyclic silazanes, which contain Si-N-Si bonds. However, current bulk synthesis techniques are not suitable for growing conformal poly(siloxane) or poly(silazane) thin films.

In this work, we use initiated chemical vapor deposition (iCVD) to form conformal poly(cyclic siloxane) and poly(cyclic silazane) thin films. The iCVD process directly converts gas phase monomers into solid films through polymerization of the vinyl bonds. One of the primary benefits of iCVD is the ability to retain all non-vinyl organic moieties present in the monomer. In the case of monomers used in this study, the siloxane or silazane ring structure of the monomer is retained while reaction of the four vinyl groups results in a highly cross-linked network. The monomer and a thermally labile initiator flow into a reaction chamber, wherein thermal energy from heated filaments generates initiator radicals, which react with adsorbed monomer on a cooled substrate, forming a polymer film. The resulting polymer films are capable of uniformly covering such structures as arrays of high-aspect-ratio nanowires which could serve as 3D electrodes. In this work, we compare the performance of poly(cyclic siloxane) and poly(cyclic silazane) thin films (10 nm – 50 nm) as ionic conductors. The as deposited films were infused with Li ions by soaking the films in a lithium salt solution. The best ionic conductivity values (>10⁻⁸ S cm⁻¹) were obtained for poly(tetravinyltetramethyl cyclictetrasiloxane) (pV4D4) and the remainder of the work focused on this chemistry. We demonstrate that film swelling after lithiation is minimal and that Si nanowire arrays with aspect ratios >50 can be conformally coated with ultrasmooth pV4D4 using the iCVD process. Finally, we show that even thick films of pV4D4 (>400 nm) can be successfully lithiated using electrochemical methods and display even higher conductivities (>10⁻⁷ S cm⁻¹) than their solution soaked, ultrathin film counterparts. Even though these values of ionic conductivity are modest compared to liquid electrolytes, the nanoscale diffusion length compensates for this fact by enabling short ionic diffusion times when compared to conventional bulk or microscale polymeric electrolytes. This is illustrated in half-cell testing.
of a carbon anode coated with 400 nm of electrochemically lithiated pV4D4, where galvanostatic cycling at C/20 and C/10 delivered the full, 270 mAh g⁻¹ capacity of the carbon anode.

4.3 Experimental

4.3.1 Materials.

The 10–50 nm thick poly(1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane) (PV3D3), poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcycloctetrasiloxane) (PV4D4), poly(1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane) (PV3N3), and poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcycloctetrasilazane) (PV4N4) films were synthesized using the iCVD method, which is described in detail elsewhere.24-27 The V3D3, V4D4, V3N3, and V4N4 monomers were heated at 70 °C, and their vapors along with vapors of the tert-butyl peroxide initiator (at room temperature) were delivered into the reactor at flow rates of 0.1–0.3 and 1.0 sccm, respectively. The reactor pressure, substrate temperature, and filament temperature were maintained at 200 mTorr, 35 °C, and 280 °C, respectively. These films were deposited on silicon wafers (Wafer World, Inc.) and indium tin oxide (ITO)-coated glass (1 × 2 cm, ~50 Ω, Precision Glass and Optics). The salt and solvent used for solution lithiation, anhydrous lithium perchlorate (LiClO4), and anhydrous propylene carbonate (PC), were purchased from Sigma-Aldrich and used without further purification.

4.3.2 Solution Lithiation.

Unless otherwise stated, Li ions (Li⁺) were introduced into iCVD grown polymer films using the following procedure: Coated substrates were soaked for 3 days in a 1 M solution of LiClO4 in propylene carbonate (PC).28 The soaking process was carried out inside an argon-filled glovebox, with O2 and H2O levels <0.1 ppm. The soaked films were subsequently rinsed with fresh PC and annealed in the glovebox at 110–130 °C for 1 h to remove residual solvent present in the films.

4.3.3 Characterization.

The thicknesses of the iCVD grown polymer films on Si wafers were measured using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam Model M-2000). Measurements were made at three incident angles (65°, 70°, and 75°), and the data were fit to the Cauchy–Urbach
isotropic model using WVASE32 software. The spot size of the VASE beam was 1 x 4 mm. Atomic force microscopy (AFM) images were obtained on a Veeco Dimension 3100 scanning probe microscope operated in tapping mode. Ionic conductivity of these iCVD grown polymer films was determined using electrochemical impedance spectroscopy (EIS). The EIS spectra were collected at room temperature in an argon-filled glovebox with O2 and H2O levels <0.5 ppm using a Solartron 1252 frequency response analyzer at a frequency range of 100 kHz–100 Hz and a 10 mV (rms) potential. Soft but robust contacts to the nanoscale polymer films and ITO substrate were made using hanging mercury (Hg) drop electrodes with contact areas of 0.0707–0.0177 cm2 (corresponding to drops of 3 and 1.5 mm in diameter, respectively). Measurements were taken at different positions on each sample, and the impedance data were fit to equivalent circuits (Scribner). Experimental details about making these measurements were reported previously. 

Transmission electron microscopy (TEM) images of Ag nanowires coated with pV4D4 were obtained by a JEOL 2010 advanced high performance TEM. The TEM samples were prepared by placing a drop of 0.05%Ag nanowires in isopropanol (Sigma-Aldrich) on a Lacey carbon copper TEM grid (Ted Pella) and drying overnight under an incandescent bulb. The grids were coated with pV4D4 via iCVD and lithiated as previously described.

Scanning electron microscopy (SEM) of the ordered Si nanowire arrays were obtained using a Zeiss-Merlin high resolution SEM. TEM samples were prepared by sonicating the arrays in 5 mL of isopropanol and placing a drop of solution on a Lacey carbon copper TEM grid. The samples were dried overnight under an incandescent bulb. TEM images of the as received and iCVD pV4D4 coated Si nanowires were obtained on an FEI Tecnai multipurpose TEM.

4.3.4 Half Cell Testing

Mesocarbon microbead (MCMB) electrodes were prepared by slurry casting on a stainless steel current collector. The slurry was 83 wt% MCMB, 7 wt% carboxymethyl cellulose binder, and 8 wt% graphite, and 2 wt% Ketjen Black in deionized water. After casting, the electrodes were dried at 120 °C. The electrodes were then coated with 400 nm thick iCVD pV4D4 to form a half cell. The iCVD pV4D4 film was not solution lithiated prior to cycling. Cycling took place in a three-neck flask in an Ar-filled glovebox using a Bio-Logic VMP-3 potentiostat. Lithium metal was used as the counter and reference electrodes with 1 M LiPF6 EC:DMC (1:1 by volume) as the
supporting electrolyte. Conditioning cycles, to electrochemically lithiate iCVD pV4D4, were carried out at C/1000, C/500, and C/100 for a total of 10 cycles. After conditioning, the cycles rates were increased to C/20 and C/10. Electrochemical impedance spectroscopy was performed using a Solartron 1252 Frequency Response Analyzer and 1287A Potentiostat Galvanostat and a 10 mV RMS potential and 0 V bias from 1 MHz to 100 mHz. The spectra were fit to an equivalent circuit to determine the charge-transfer resistance of the iCVD pV4D4 layer.

4.4 Results and Discussion

4.4.1 Ionic Conductivity by Chemistry

The as-deposited iCVD polymer films studied here are electrical insulators. The excellent dielectric and mechanical properties of iCVD polymer films derived from the V3D3 monomer have enabled fabrication of flexible field effect transistors. We previously reported the electrical resistivity to be in the range $10^{11}$–$10^{15}$ ohm-cm. Such low electrical conductivity values are an important property for electrolyte materials so that short-circuiting inside a battery is prevented. In contrast, the ionic conductivity values for electrolytes must be high in order to minimize ohmic loss in the battery. Here we use a solution based lithiation process (Figure 4-1a) to dope Li+ into these films and make them ionic conductors. Prior to lithiation, the films are both electronic and ionic insulators. After lithiation they retain their very high electronic resistivity but now exhibit ionic conduction. Figure 4-1c compares the ionic conductivity of the pV3D3, pV4D4, pV3N3, and pV4N4 films measured using electrochemical impedance spectroscopy (EIS). The chemical structure of the monomers used to grow these films is depicted in Figure 4-1b. The characteristic semicircles in the Nyquist plot (Figure B-1) obtained from the EIS measurements were fitted to a Randles equivalent circuit to determine the average ionic resistance (Rp). The ionic conductivity (σ) values in Figure 1b were calculated using Equation 4-1, where the film thickness is averaged from ellipsometry measurements at five positions on the sample and the electrode contact area is defined by the Hg drop size:

**Equation 4-1**

$$
\sigma = \frac{\text{film thickness}}{\text{ionic resistance} \times \text{electrode contact area}}
$$
We observed ionic conductivity in the four polymer films we synthesized. The values range from $\sigma = 10^{-7}$ to $10^{-11}$ S cm$^{-1}$ at room temperature. For a similar film thickness range of 10–50 nm, lithiated siloxane films pV3D3 and pV4D4 show higher conductivities than their silazane counterparts pV3N3 and pV4N4. We hypothesize that oxygen atoms on siloxane rings of the former can provide more favorable binding sites for Li+. This would be consistent with the more ionic nature of the Si–O bond compared to the Si–N bond$^{31}$. In addition, the vibrations of flexible Si–O–Si bonds$^{32}$ have the potential to facilitate a hopping ion transport mechanism, resulting in higher ionic conduction at room temperature.$^{21}$

As the film thickness increases beyond 30–50 nm there is a steady decrease in ionic conductivity. Full lithiation of the thicker film cannot usually be achieved and the unlithiated material does not conduct ions. It is further plausible that as film thickness increases, the roughness and disorder in
ring stacking increase, leading to poor diffusion of Li into the bulk of the films. The highest ionic conductivity obtained in these measurements was just under $10^{-7}$ S/cm for ~25 nm PV4D4. Since the pV3D3 and pV4D4 systems exhibited consistently higher values for ionic conductivity compared to the pV3N3 and pV4N4 systems, the next section focuses only on the polysiloxane chemistries.

4.4.2 Film Morphology – Comparison between siloxanes

The surface morphologies of the 30 nm thick pV3D3 and 25 nm thick pV4D4 films before and after lithiation are compared in Figure 4-2. The as-deposited iCVD films of both types display low surface roughness, having values that are on the same order as the roughness of a typical silicon wafer (~0.5 nm). The as-deposited PV4D4 films are particularly smooth with a root-mean-square roughness ($R_{\text{rms}}$) of ~0.67 nm, averaged over multiple line scans on the sample depicted in Figure 4-2c. The roughness is approximately double for PV3D3 films ($R_{\text{rms}}$ ~ 1.29 nm), as depicted in Figure 4-2a. Surface roughness increases after lithiation for both polymers, with the pV4D4 again displaying approximately roughly half the surface roughness ($R_{\text{rms}}$ = 2.92 nm) as compared to an $R_{\text{rms}}$ = 4.76 nm for pV3D3.
Figure 4-2. AFM images of 30 nm thick iCVD pV3D3 film on silicon wafer (a) before ($R_{\text{rms}} = 1.29$ nm) and (b) after lithiation ($R_{\text{rms}} = 4.26$ nm). AFM images of 25 nm iCVD PV4D4 film on silicon wafer (c) before ($R_{\text{rms}} = 0.67$ nm) and (d) after lithiation ($R_{\text{rms}} = 2.92$ nm). $R_{\text{rms}}$ is root-mean-square roughness. Reproduced with permission from *Macromolecules* 2015, 48 (15), 5222-5229. Copyright 2015, American Chemical Society.

The lithiated samples in Figure 4-2b,d show the appearance of clusters. Energy dispersive X-ray spectroscopy (EDS) indicates that these clusters contain chlorine (Cl), suggesting that they are LiClO$_4$ particles resulting from the lithiation process (Figure B-2). Thus, the increase in surface roughness after lithiation measured by AFM can be attributed to these salt clusters. The number and size of LiClO$_4$ particles is much greater in the lithiated pV3D3 film than the lithiated pV4D4 film. One possible reason is the smaller ring size of pV3D3 reduces the amount of LiClO$_4$.
that can be dissolved into the film. Once the film is removed from solution and dried, excess LiClO₄ precipitates on the surface of the and forms the particles observed by AFM. The inability of the pV3D3 film to retain dissolved LiClO₄ could explain its lower ionic conductivity values compared to pV4D4. This explanation is supported by ICP-MS measurements done by Reeja-Jayan et al. on solution soaked pV4D4 and pV3D3 films. In a comparison of 21 nm films that underwent exactly the same solution lithiation procedure, pV3D3 contained \(5.2 \times 10^{20}\) Li ions per cubic centimeter whereas pV4D4 nearly doubled this value at \(9.85 \times 10^{20}\) Li ions per cubic centimeter.

The remainder of this study focuses on iCVD pV4D4 given it retains more dissolved lithium salt after lithiation than iCVD pV3D3. Before iCVD pV4D4 can be integrated in a practical device, surface salt precipitates must be removed. These can be stress points that lead to shorts. Two approaches have demonstrated the reduction of surface salt precipitates. In the first approach, lithiation proceeds as described previously. After the samples are dried, they are rinsed in ethanol, a volatile solvent. This effectively removes clusters, as seen in AFM imaging. The other approach changes the solvent used during the lithiation procedure. Using a highly volatile solvent like dimethyl carbonate (vapor pressure 18 mmHg) in lieu of propylene carbonate (vapor pressure 0.13 mmHg) leads to faster drying times thus preventing surface salt precipitation.

4.4.3 Film Mechanical Integrity

Device failure could occur if the polymer thin film swells significantly after lithiation. In a completed full cell, solid state device, the swollen film would place additional stresses on the electrode materials. An electrode with a 3D architecture, such as a nanowire array, is more susceptible to fracture especially if the stress on the wire is perpendicular to the wire long axis. Catastrophic failure would occur if the film swells sufficiently to delaminate from the electrode surface. If the film developed tears, the device would then short circuit. Therefore, it is necessary for the solid polymer electrolyte to swell minimally after lithiation.

The effect of the lithiation procedure on the mechanical integrity of the iCVD pV4D4 films was assessed using TEM microscopy. Silver nanowires were dispersed on a TEM grid and then subsequently coated with iCVD pV4D4 and lithiated in solution, as depicted in Figure 4-3. TEM imaging was carried out on the iCVD pV4D4 coated nanowires after deposition (Figure 4-3b) and
after lithiation (Figure 4-3c). Figure 4-3b shows a smooth, conformal iCVD pV4D4 coating around the nanowire. No pinholes are visible at this length scale, suggesting a continuous film. After lithiation (Figure 4-3c), no gaps at the film-wire interface are observed. No deformation of the nanowire suggests any potential swelling of the film does not result in stresses significant enough to result in damage.

Figure 4-3. (a) Sample preparation scheme. Silver nanowires were dispersed on a TEM grid and then (1) coated with iCVD pV4D4 (orange outline) and (2) lithiated via solution soaking (blue outline). (b,c) TEM images of a 10 nm iCVD pV4D4 coating (b) as deposited and (c) after solution lithiation. (d,e) iCVD pV4D4 film thickness distribution as obtained from TEM imaging of (d) as deposited iCVD pV4D4 (11.5 nm ± 2.6 nm) and (e) solution lithiated iCVD pV4D4 (12.6 nm ± 3.2 nm). To obtain the data for each condition, 11 wires were chosen at random from different locations of the grid and 30 measurements were taken on each wire. (b, c, d, e) Reproduced with permission from *Mater. Horiz.* 2015, 2 (3), 309-314. Copyright 2015 Royal Society of Chemistry.
The swelling of the film was quantitatively assessed by taking multiple thickness measurements across several wires for the as deposited and lithiated samples. The data for the as deposited iCVD pV4D4 film are summarized in Figure 4-3d with an average film thickness of 11.5 nm ± 2.6 nm. The thickness standard deviation of the as deposited film corresponds to a 22% variation about the mean on a 3 mm diameter, which is much larger than the 4.5% variation from ellipsometry measurements on a 100 mm diameter reference Si wafer. The normality of the distribution can be evaluated by calculating Pearson’s first coefficient of skewness using Equation 4-2.

\[
\text{Equation 4-2 } \text{skew} = \frac{\text{mode} - \text{mean}}{\text{standard deviation}}
\]

A calculated mode of 12.8 nm results in a skew coefficient of -0.56, indicating a negatively skewed distribution. This suggests a variation in the deposition rate with a significant number of slower than average rates. The iCVD deposition rate is primarily dependent on the monomer surface concentration on the sample, which is a function of sample temperature and the monomer partial pressure in the chamber. In particular, fluctuations of sample temperature can significantly change the monomer surface concentration locally. Temperature fluctuations are minimized when there is good thermal contact between the sample and the temperature controlled stage, like in the case of an Si wafer. However, a TEM grid may not have complete contact with the stage given its tendency to deform and crinkle. This would result in “hot-spots” where the monomer surface concentration is lower than expected and the deposition rate is reduced.

After lithiation (Figure 4-3e), the average thickness increases to 12.6 nm ± 3.2 nm, which corresponds to ~10% change due to swelling. The variation about the mean increases to 25%, or a 3% difference from the as deposited samples. These values significantly lower than other polymer electrolyte systems which can swell over 250% from their original thickness.

### 4.4.4 Assessing conformality

The ability of iCVD pV4D4 to conformally coat nanostructures was studied using periodic silicon nanowire arrays provided by Carl V. Thompson’s group at MIT. The nanowire arrays were imaged with SEM and TEM before and after being coated with iCVD pV4D4. Figure 4-4a shows the TEM sample preparation scheme, where the nanowire array is sonicated in isopropanol and then
dispersed on a TEM grid. This process has the benefit of good thermal contact during deposition combined with facile sample preparation. An SEM image of the as received nanowire array is shown in Figure 4-4b. In-situ measurements determined each individual nanowire was \( \sim 140 \) nm in diameter and \( 8 \) \( \mu \)m in height, corresponding to a 57:1 aspect ratio. The center-to-center spacing of the wires was 350 nm and the spacing in-between wires was 210 nm. The nanowire array was then coated with iCVD pV4D4 and re-imaged (Figure 4-4c). The diameter of the wire increased to approximately 180 nm and the spacing in-between wires decreased to \( \sim 190 \) nm, corresponding to a 20 nm thick film iCVD pV4D4. The measured diameters at the top and the bottom of the nanowire were nearly equal, suggesting perfect conformality. However, given the feature size as compared to the size of the overall area imaged, this particular measurement is unreliable. TEM images of the nanowires enable accurate measurements of the polymer film thickness on an individual nanowire array. Figure 4-4d,e show an Si nanowire as-received and after coating with iCVD pV4D4 respectively. The iCVD coating is highlighted in purple. Measurements along the wire axis yield an average film thickness of 21.8 nm \( \pm 0.7 \) nm, which is in good agreement with the expected diameter based on the SEM images. The 3.2% variation in thickness along the wire length is comparable to the thickness variation seen on a planar silicon wafer. However, measurements at the top of the wire indicate a slightly thicker film of 27.5 nm \( \pm 0.6 \) nm. This corresponds to a side-wall coverage of 0.79 (where unity would indicate perfect conformality). This number is far higher than previously reported values of 0.55 for iCVD coatings on micro-trenches 8 \( \mu \)m in depth and 1 \( \mu \)m in width.\textsuperscript{34-35}
Figure 4-4: (a) Sample preparation scheme for Si Nanowire imaging. Nanowire array is (1) coated with iCVD pV4D4 and (2) sonicated in isopropanol and dispersed on a TEM grid for imaging. SEM images of (b) as received Si nanowire array and (c) iCVD pV4D4 coated nanowire array. TEM images of Si nanowire array(d) as received and (e) coated with iCVD pV4D4. The iCVD coating is highlighted in light purple. Si nanowire arrays were provided Dr. Ahmed Al-Obeidi of Professor Carl V. Thompson’s group at MIT. (b-e) Reproduced with from Beilstein J. Nanotechnology 2017, 8, 723-735 under a Creative Commons 4.0 License.
4.4.5 Electrochemical Lithiation of Thick Films

In a full-cell (cathode+electrolyte+anode), the electrical leakage current must be minimized to reduce the rate of self-discharge. The impact of the leakage current is maximal when the battery is fully charged. This corresponds to ~4 V in a typical Li-ion chemistry (e.g. graphite + lithium cobalt oxide). If the upper limit on the initial leakage current is set at 5 μA, then the required resistance of the electrolyte calculated from Ohm’s law \(V=IR\) is 800,000 Ω. With this value, the required film thickness can be calculated from Equation 4-3. Previous measurements of pV4D4 determined the electrical conductivity to be ~ 5*10^{-11} S/cm.\(^{28}\) An electrode area of 1 cm\(^2\) was used for the half cells. Solving for film thickness yields a minimum value of 400 nm.

\[
\text{Equation 4-3} \quad \text{Resistance} = \frac{1}{\text{electrical conductivity}} \times \frac{\text{film thickness}}{\text{electrode area}}
\]

This poses a problem since lithiation via soaking in solution only penetrates the top 25 nm of the film. As film thickness increases, the ionic conductivity decreases because a smaller volume of the total film is lithiated. This limit can be removed if electrochemical methods are used instead. Equation 4-4, the Nernst-Planck equation, is a modified form of Fick’s law that includes contributions the flux of an ionic species \(j\) from an applied potential.\(^{37}\) Applying a potential while the film is in an electrolyte solution will increase the flux of Li ions into the film.

\[
\text{Equation 4-4} \quad I_j(x) = -D_j \left( \frac{\partial C_j(x)}{\partial x} \right) - \frac{z_j F}{RT} D_j C_j \left( \frac{\partial \phi(x)}{\partial x} \right)
\]

We tested this method using by studying a carbon/pV4D4 half cell in a three-electrode setup, as depicted in Figure 4-5. This enabled cyclic voltammetry (CV), galvanostatic cycling (GV), and electrochemical impedance (EIS) measurements to be taken in one setting. A mesocarbon microbead (MCMB) slurry was coated on half of a 1 cm x 2 cm stainless steel current collector. A 400 nm iCVD pV4D4 layer was deposited on top MCMB anode. A schematic of the final half cell is also seen in Figure 4-5.
Figure 4-5. Schematic of three-electrode setup used for half-cell testing of iCVD pV4D4 on a mesocarbon microbead (MCMB) slurry anode. Stainless steel substrate used as current collector. Image courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles)

The initial CV of the half-cell (Figure 4-6a), shows the elimination of the redox peaks associated with MCMB (Figure 4-6a inset). The pV4D4 layer is essentially an ionic resistor that does not allow charge transfer into the carbon anode. The half-cell is then cycled at very low rates (C/1000, C/500, C/100) to condition the film. Figure 4-6b shows the half-cell capacity slowly increasing with cycling. As more lithium ions are introduced into the structure, charge transfer to the anode is now possible and occurs more easily. CV after multiple cycles shows the redox peaks associated with carbon have now returned (Figure 4-6a). Figure 4-6c shows the impedance spectra of the bare carbon anode, pV4D4 on carbon after conditioning, and pV4D4 on carbon after 50 GV cycles. The charge transfer resistance is nearly negligible in the bare carbon anode and the primary response is that of a resistor. The data for the conditioned and the cycled carbon/pV4D4 half-cell was fit to the circuit in Figure B-3. After conditioning, the ionic conductivity of the 400 nm thick pV4D4 film is 1.2*10^{-7} S/cm. This is an order of magnitude higher than the 35 nm pV4D4 film lithiated via solution soaking. Galvanostatic cycling of the conditioned half-cell at higher C-rates for 40 cycles more than doubles the ionic conductivity to 3.2*10^{-7} S/cm. Finally, Figure 4-6d shows that after electrochemical lithiation of the pV4D4 film, the half-cell now has the charge storage capacity associated with the bare carbon electrode, ~270 mAh/g (Figure B-4). Obtaining
the full capacity is not limited by C-rate, as seen by the C/20 and C/10 plots almost completely overlapping.

Figure 4-6. (a) Cyclic voltammetry of 400 nm iCVD pV4D4 on MCMB after 1, 25, and 50 galvanostatic cycles. Inset shows CV of bare carbon for comparison. (b) Half-cell capacity as a function of conditioning cycles. Currents of 0.5 μA, 1.0 μA, and 5.0 μA correspond to C/1000, C/500, and C/100 respectively. (c) Impedance spectra of carbon only (gray), half-cell after conditioning (black-dashed), and half-cell after 50 GV cycles. Ionic conductivity of pV4D4 is 1.2*10^{-7} S/cm and 3.2*10^{-7} S/cm after conditioning and 50 cycles respectively. (d) Half-cell capacity at higher rates. Solid line is C/20, dashed line is C/10. Figure courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles)

4.4.6 Comparison with other solid electrolytes

There are many film properties that contribute to the overall performance of a solid electrolyte for a 3D electrode architecture. Properties of particular importance when evaluating a
material/process combination are the material’s ionic conductivity and electronic conductivity as well as the range of film thicknesses and conformality produced by the coating process. The characteristic diffusion time of Li ions between electrodes, $\tau$, dictates rate limitations due to the electrolyte. Lower values of $\tau$ enable higher rates of charge and discharge. At a given value of $D_{\text{ion}}$, the ionic diffusion coefficient, the ionic diffusion time increases as the square of $L_{\text{ion}}$, the ionic diffusion length, as described by Equation 4-5. In the case of solid electrolytes films, the ionic diffusion length is the film thickness and the ionic diffusion coefficient is proportional to the ionic conductivity.

\[
\tau = \frac{L_{\text{ion}}^2}{D_{\text{ion}}} 
\]

Galvanostatic conditioning of iCVD pV4D4 films enables room temperature ionic conductivities greater than $10^{-7}$ S cm$^{-1}$ in films that are up to 400 nm thick. This value is an order of magnitude greater than solution prepared poly(ethylene oxide) electrolyte films 70 $\mu$m in thickness. Sputtered lithium phosphorous oxynitride (LiPON) thin films have demonstrated ionic conductivities in the $10^{-7}$ cm$^{-1}$ range as well, enabling a direct comparison with pV4D4 with respect to ionic conductivity. The LiPON film thickness was greater than 1 micron, or a minimum 2.5-fold increase in $L_{\text{ion}}$ with respect to the conditioned 400 nm thick pV4D4 films. The iCVD pV4D4 film then has at least a 11-fold reduction in the ionic diffusion time compared to LiPON. Furthermore, the iCVD method generates a much more conformal coating compared to sputtering.

4.5 Conclusion

The iCVD method was used to form conformal thin film electrolytes that can be used in Li ion batteries with three-dimensional electrode architectures. Poly(cyclic siloxanes) and poly(cyclic silazanes) were investigated given their ring systems could act as permanent conduction channels for Li ions. Impedance spectra of solution lithiated films revealed that the siloxane based chemistries were better Li ion conductors than their silazane counterparts. Retention of dissolved LiClO$_4$ within the iCVD films was higher in pV4D4 than pV3D3 as evidenced by the precipitation of salt clusters at the polymer surface after lithiation. This is attributed to the larger ring size of
pV4D4, which can more easily contain Li+ and its counter-anion. The highly conformal nature of the iCVD process was confirmed via electron micrographs of a 20 nm pV4D4 film on ordered Si nanowire arrays with an aspect ratio greater than 50. Finally, galvanostatic conditioning enables complete lithiation of much thicker iCVD pV4D4 films. Even higher ionic conductivities (>10⁻⁷ S/cm) than the ultrathin films are observed by using this method. The reduced ionic diffusion time compared to other solid electrolytes combined with its highly conformal nature makes iCVD pV4D4 a promising candidate to enable 3D Li ion batteries.

4.6 References


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Chapter 5  Crystallographic Texture and Electrochemical Performance in Vapor-Deposited Poly(3,4-Ethyleneoxythiophene) Thin Films for High-Rate Electrochemical Energy Storage

The work in this chapter was done in conjunction with Prof. Bruce Dunn’s group at the University of California, Los Angeles. A version of this chapter will be submitted for publication.

5.1 Abstract

The oxidative chemical vapor deposition (oCVD) of poly(3,4-ethylenedioxythiophene) (PEDOT) has previously been demonstrated for electrochemical energy storage applications. In this work, we rationally design the thin-film crystallographic texture of oCVD PEDOT for high-rate performance and cycle life. The stage temperature during deposition was used to change the dominant crystallographic texture of the oCVD PEDOT film. By operating significantly above the glass-transition temperature of PEDOT, the film reorganizes during growth to an edge-on structure. In this case, the π-π stack is perpendicular to the substrate surface. The alternative dominant texture is face-on dominance, where the π-π stack is parallel to the substrate surface. Edge-on dominance facilitates the doping and dedoping of the oCVD PEDOT film with anions during electrochemical cycling. Higher specific capacities for edge-on dominant films compared to face-on dominant films are observed for a given charge/discharge rate. Furthermore, Raman spectroscopy demonstrates that edge-on dominant films are less susceptible to oxidative damage after long-term cycling. This also enables edge-on dominant films to maintain lower charge-transfer resistances compared to identically cycled face-on films. Edge-on OCVD PEDOT is paired with molybdenum disulfide to demonstrate crystallographically textured PEDOT in asymmetric devices for high-rate electrochemical energy storage.

5.2 Introduction

High-rate electrochemical energy storage devices are of considerable research interest due to the growing electric vehicle market and the increased demand for load-leveling of renewable energy resources. Asymmetric energy storage cells, which are broadly defined as every combination of positive and negative electrodes which are different from one another, are an
interesting direction for high-rate energy storage.\textsuperscript{2-3} Such asymmetric cells enable one to use the desired combination of positive and negative pseudocapacitive electrode materials and thus improve overall device performance. Asymmetric cells which utilize pseudocapacitive materials are particularly promising as they store energy via Faradaic processes and exhibit fast ion diffusion which maintains the power densities needed for high-rate applications.\textsuperscript{4}

The energy and power density of asymmetric devices based on pseudocapacitive materials are ultimately determined by the difference in the chemical potentials of the active materials as this defines the working voltage. However, with the relative dearth of available pseudocapacitive materials, the rational selection of suitable electrode materials for asymmetric devices is limited. The overwhelming majority of asymmetric devices reported in literature are aqueous systems based on pseudocapacitive RuO\textsubscript{2}\textsuperscript{5-9} and MnO\textsubscript{2}.\textsuperscript{10-18} Transition metal hydroxides (including Co(OH)\textsubscript{2} and Ni(OH)\textsubscript{2})\textsuperscript{6,8,17,19-20} and, most recently, MXenes\textsuperscript{7,11,20} have also been demonstrated in asymmetric full cells. A wider range of chemistries can be accessed through the use of non-aqueous electrolyte, and the wider electrochemical stability window of the commonly employed organic solvents can enable the use of materials with higher redox potentials. However, non-aqueous systems have thus far been limited to hybrid devices that pair a pseudocapacitive electrode material with a carbon-based electrode that stores charge in the electric double-layer.\textsuperscript{3}

Nanosized molybdenum disulfide (MoS\textsubscript{2}) is a pseudocapacitive material that intercalates/deintercalates Li\textsuperscript{+} from 1 – 3 V vs. Li/Li\textsuperscript{+} and is a promising negative electrode in an asymmetric device. Conjugated polymers are another class of pseudocapacitive materials with charge storage occurring via redox reactions with a dopant anion (e.g. Cl\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-} or ClO\textsubscript{4}\textsuperscript{-}) along the polymer backbone.\textsuperscript{21-22} Of these materials, poly(3,4-ethylenedioxythiophene) (PEDOT) is particularly attractive due to its electrochemical stability,\textsuperscript{23} and its ability to dope/dedope (between neutral and p-type) from 2 – 4 V vs. Li/Li\textsuperscript{+}\textsuperscript{24-25} making it a promising positive electrode to pair with MoS\textsubscript{2}. The use of active materials in an asymmetric device that independently undergo redox reactions with cations or anions has previously been referred to as a Daniell-type cell\textsuperscript{26-27} or dual-ion battery.\textsuperscript{28-29} The electronic conductivities of both MoS\textsubscript{2} (>500 S cm\textsuperscript{-1} in the semi-metallic 1T phase) and PEDOT (10 to >3000 S cm\textsuperscript{-1} depending on the synthesis route and dopant used)\textsuperscript{23,30-32} obviate the need for conductive additives and make these pseudocapacitive materials particularly well-suited for high-rate applications. However, the electrochemical properties of PEDOT
including its specific capacity depend heavily on its synthesis method and rational material design is required for energy storage applications.

The chemical synthesis of PEDOT is often coupled with the polymerization of poly(styrene sulfonate) (PSS) to yield a water-soluble dispersion that can be used for solution processing (e.g. spin/dip coating applications). However, PEDOT:PSS shows no redox activity from 2 – 4 V vs. Li/Li+. PEDOT doped with smaller anions does show electrochemical activity in this potential range, but the insoluble polymer formed during conventional solution synthesis requires the formation of macroscopic, pellet-electrodes. The relatively low surface-area-to-volume ratio of a pellet impedes the diffusion of anions into the active material. This results in low specific capacities of ~30 mAh g⁻¹. Electropolymerized thin-films of PEDOT that have a higher surface-area-to-volume ratio demonstrate higher capacities of ~40 mAh g⁻¹, and indicate that film thickness and deposition method are important considerations for improving energy storage in PEDOT. To achieve a high mass-loading of active material while exploiting the higher capacities demonstrated in thin films, micro or nano-structured current collectors must be used. Certain three-dimensional (3D) architectures enable higher power and energy densities than are accessible by a planar film. Utilizing the available surface area of these current collectors requires a conformal coating of PEDOT.

Conformal PEDOT thin films have been synthesized via oxidative chemical vapor deposition (oCVD), a solvent-less process where EDOT and oxidant (e.g. FeCl₃) vapors are introduced into a vacuum chamber, adsorb onto the substrate surface of interest, and react to form a thin film. Doping of the polymer by chlorine anions in-situ results in electronically conductive, p-type polymer thin films. The potential of oCVD PEDOT in energy storage applications has been demonstrated in hybrid devices consisting of positive electrodes of oCVD PEDOT deposited onto high surface area, aligned CNT and carbon-based negative electrodes of aligned graphene flakes or aligned CNTs. The use of ultra-thin oCVD PEDOT films (3-10 nm) in these studies ensured that the diffusion of dopant anions did not limit device performance and resulted in high energy and power densities up to 177 Wh kg⁻¹ (113 Wh L⁻¹) and 233 kW kg⁻¹ (149 kW L⁻¹). However, in order to achieve higher total energy, increased active material loading in the form of thicker PEDOT films (e.g. ~200 nm) is required, and retaining the ease of doping/dedoping becomes important to maintain high power densities. Tailoring the crystallographic texture of the thin films offers a unique opportunity to facilitate the diffusion of
dopant into and out of the polymer film. If the plane of ion conduction is perpendicular to the film surface-normal, anion diffusion occurs along the direction of the applied electric field. Furthermore, the plane of ion conduction is more easily accessed by the electrolyte, rather than being obscured by the polymer structure.

In order to determine the optimal film crystallographic texture, the crystal structure of doped PEDOT must be understood. Figure 5-1a shows the orthorhombic structure of doped PEDOT, where the conjugated backbone is parallel to the c-axis. The crystal is formed by π-π stacking of the polymer chains along the b-axis, where anion dopants reside in the (020) plane. In PEDOT films formed via oCVD, two dominant crystal textures are observed. Crystallites can have a face-on orientation, where the (0k0) planes are parallel to the substrate (Figure 5-1) or an edge-on orientation, where the (h00) planes are parallel to the substrate (Figure 5-1c). Controlling the orientation of the PEDOT crystallite with respect to the substrate enables optimization of material properties for a given application. For instance, oCVD PEDOT films with face-on dominance enables the 2D confinement of electrons resulting in in-plane electrical conductivities exceeding 3500 S/cm. Meanwhile, edge-on dominance permits 3D conduction to occur at the expense of in-plane electrical conductivity (< 500 S/cm).

Figure 5-1. Schematic of (a) Doped PEDOT crystal structure. Anion dopants occupy the (020) plane between the thiophene planes (b) Face-on crystallite orientation with (0k0) planes parallel to substrate (c) Edge-on crystallite orientation with (h00) planes parallel to substrate.
In this work, we study the impact of crystallographic texture on the electrochemical properties of oCVD PEDOT thin films. Volumetric charge storage occurs when anions (e.g. Cl\(^-\), PF\(_6^-\), or ClO\(_4^-\)) are inserted and removed the (020) planes during charge/discharge of the oCVD PEDOT. We hypothesize that edge-on dominance facilitates anion diffusion because the direction of the applied electric field (normal to substrate) is parallel to the anion dopant plane. We start by investigating stage temperature during deposition as a means of controlling the dominant film crystal texture. After identifying appropriate conditions to yield face-on and edge-on dominant films respectively, the effects of crystal texture on the electrochemical properties of oCVD PEDOT are studied. The degradation mechanism of these materials is determined using Raman spectroscopy and electrical impedance spectroscopy of the oCVD PEDOT films before and after 500 galvanostatic charge-discharge cycles. After identifying the optimal crystal texture, the benefits of the conformal deposition process are realized by coating oCVD PEDOT onto 3D nickel foam current collectors. These oCVD PEDOT electrodes are paired with molybdenum disulfide (MoS\(_2\)) electrodes to demonstrate high-power asymmetric devices free of conductive additives.

5.3 Experimental methods

5.3.1 PEDOT Film Synthesis

The oxidant, iron (III) chloride (FeCl\(_3\), 97%), and monomer, 3,4 ethylenedioxythiophene (EDOT, 97%), were purchased from Sigma-Aldrich and used without further purification. All PEDOT film depositions were performed in a custom-built oxidative chemical vapor deposition (oCVD) chamber described elsewhere.\(^4\) A dry pump (Edwards, iQDP40 with a QMB mechanical booster) was used to achieve vacuum levels of approximately 20 mTorr as measured by an absolute capacitance manometer (MKS Instruments). A turbomolecular pump (Pfeiffer Vacuum, HiPace 300C) was used to achieve higher vacuum levels of 1-2 mTorr. A low temperature evaporation (LTE) point source (Kurt J. Lesker) was used to sublime the oxidant. A custom-designed infrared substrate stage heater was used to achieve the higher stage temperatures used in the work.

Oxidative chemical vapor deposition (oCVD) was used to deposit poly(3,4 ethylenedioxythiophene) (PEDOT) films onto Si wafer (WRS Materials), stainless steel (Type
316, McMaster Carr), and Ni foam (<20% porosity, 80 μm thick, MTI Corporation) substrates. The chamber pressure and LTE point source temperature were 1 mTorr and 230 °C respectively. EDOT was heated to 160 °C to facilitate evaporation and the resulting vapors were delivered to the reactor using a needle-valve. PEDOT films were grown on Si wafers at stage temperatures of 65 °C, 100 °C, 150 °C, and 175 °C to study the temperature dependence of film texture. Films on stainless steel for electrochemical characterization were only grown at stage temperatures of 100 °C and 175 °C. Films on Ni foam used in the PEDOT|MoS₂ asymmetric devices were grown only at a stage temperature of 175 °C. All oCVD PEDOT films were ~200 to 300 nm in thickness. All samples were immediately rinsed in methanol after deposition and dried with a compressed air gun.

5.3.2 Electrode Preparation

oCVD PEDOT samples on stainless steel and Ni foam were electrochemically cycled without further modification. PEDOT:PSS electrodes were drop-cast onto stainless steel substrates from a commercial PEDOT:PSS dispersion (Sigma-Aldrich). The substrates were oxygen plasma cleaned prior to deposition in order to improve the wetting of the current collector. PEDOT:PSS electrodes were allowed to dry in air overnight and in a 120 °C vacuum oven for at least 2 h.

5.3.3 Electrochemical Characterization

Battery grade lithium hexafluorophosphate (LiPF₆, Sigma Aldrich), lithium perchlorate (LiClO₄, Sigma-Aldrich), anhydrous ethylene carbonate (EC, Sigma-Aldrich), and anhydrous dimethyl carbonate (DMC, Sigma-Aldrich) were stored in an Ar-filled glove box (less than 1 ppm O₂/H₂O).

Electrochemical characterization was carried out in a flooded three-electrode cell in an Ar-filled glovebox using a Bio-Logic VMP-3 potentiostat. Lithium metal was used as counter and reference electrodes with 1M LiPF₆ EC:DMC (1:1 by volume) as the supporting electrolyte. Specific capacities were calculated from film thicknesses measured via AFM and assuming a density of ~1 g cm⁻³ for doped PEDOT.⁴⁶ Electrochemical impedance spectroscopy was performed on the potentiostat using a 10 mV RMS potential and 0 V bias from 1 MHz to 100 mHz. Impedance
spectra were fit to an equivalent circuit to determine the series and charge-transfer resistances of the electrodes.

5.3.4 PEDOT Film Characterization

*Ex situ* oCVD PEDOT film thicknesses on Si wafers were determined using a Veeco Dimension 3100 atomic force microscope to measure step height differences. X-ray diffraction (XRD) measurements were taken using a Bruker D8 Discover with GADDS with CuKα radiation (λ=0.15418 nm). An X-ray beam of 40 kV and 40 mA probed the surface at a fixed omega angle of 5° to reduce saturation by the primary beam. For higher-intensity measurements, we used a fiber-optic moncapillary collimator (0.3 mm diameter). The detector was placed 18.61 cm away from the sample. A Vantec2000 2D detector was used at a fixed 2θ angle of 20° which allowed a range of 2θ (0° to 40°) measurements to be collected simultaneously. The Bruker software program Diffrac.Eva was used to analyze the data. For each sample, the 2D data were integrated in a slice defined by 2θ = [4°, 30°] and γ = [240°, 300°]. The resulting 1D spectrum was baseline corrected and noise filtered. The areas of the peaks at 2θ approximately equal to 7° and 26° were calculated using the software’s peak-area tool.

The following measurements were taken of as-deposited and long-term cycled oCVD PEDOT on stainless steel. Raman spectroscopy was carried out using a Renishaw Invia Reflex Micro Raman at an excitation wavelength of 785 nm. Deconvolution and fitting of peaks from 1400 cm⁻¹ to 1500 cm⁻¹ was carried out using Renishaw’s WiRE 4.4 software. Energy-dispersive X-ray spectroscopy (EDS) was carried out in a Zeiss Merlin High-resolution SEM with an EDAX accessory.

5.3.5 Full Cell Assembly

MoS₂ electrodes were prepared through electrophoretic deposition (EPD) onto Ni foam from a 1 mg mL⁻¹ dispersion of MoS₂ nanoparticles in acetone. MoS₂ nanoparticles were synthesized through the sulfurization of MoO₂ nanoparticles described elsewhere.⁴⁷ Electrophoretic deposition was carried out using a 50 V cm⁻¹ electric field for 30 s with a platinum counter electrode resulting in mass loadings ~60 μg cm⁻². Electrodes were rinsed with acetone and dried in a 120 °C vacuum oven for at least 2 h. MoS₂ electrodes were conditioned in three-electrode half-cells at a 2C rate (based on theoretical specific capacity of 167 mAh g⁻¹) from 0.8 to 3V vs.
Li/Li\textsuperscript{+} for 10 cycles to ensure conversion of the MoS\textsubscript{2} from the semiconducting 2H to the semi-metallic 1T phase prior to full cell assembly.

PEDOT|MoS\textsubscript{2} asymmetric devices were assembled in 2032 coin cells with glass fiber separator (Whatman GF/C, 260 µm thick). 1M LiClO\textsubscript{4} EC:DMC was used as the supporting electrolyte to avoid side reactions with the Ni foam current collector at high potentials. Energy and power densities of the PEDOT|MoS\textsubscript{2} asymmetric device were calculated from full-cell discharge from 3 to 0 V.

5.4 Results and discussion

5.4.1 Thin Film Texture

The crystallographic film texture describes the dominant orientation of PEDOT crystallites with respect to the substrate and is determined using x-ray diffraction (XRD). Two major XRD reflections for doped PEDOT occur at 2\(\theta\) approximately equal to 7\(^\circ\) and to 26\(^\circ\), which correspond to the (100) and (020) planes respectively. These peaks have been previously used to determine the preferred orientation of crystallites in oCVD PEDOT thin films.\textsuperscript{30} In the standard one-dimensional Bragg-Brentano geometry, a reflection is only detected when the given crystal plane is parallel to the substrate. Figure 5-2a presents the XRD spectra of oCVD PEDOT grown onto Si wafer utilizing stage temperatures ranging from 65 °C to 175 °C, while all other process conditions were fixed. At the lowest temperature, 65 °C, the (020) reflection at 26° is significantly stronger than the (100) reflection at 7°, revealing that the PEDOT crystallites primarily exhibit the face-on orientation. As the stage temperature increases, the appearance and increase in intensity of the 7° peak coupled with a decrease in the 26° peak indicates the formation of edge-on crystallites. The relative change in face-on to edge-on orientation can be quantified by taking the ratio of the area under the (100) peak to the (020) peak, \(A_{(100)}/A_{(020)}\). The temperature dependence of this ratio is shown in Figure 5-2b. The positive trend confirms the increase in edge-on dominance with increasing stage temperature. We attribute this behavior to the balance of interfacial and surface energies of the film. The substrate-PEDOT interfacial energy is minimized in the face-on configuration due to favorable interactions between the oxygen atoms in the (010) plane and the native oxide on the Si wafer. By contrast, the surface energy is minimized in the edge-on configuration, where the carbon-hydrogen bonds are exposed but oxygen atoms are buried. We hypothesize the film crystallites initially grow in the face-on orientation but transition
to the edge-on orientation via surface reorganization as the film thickness increases. The conformational changes needed to facilitate reorganization occur when the polymer thin-film is heated above its $T_g$, the glass-transition temperature.\textsuperscript{48} Differential scanning calorimetry measurements by Lakshmi et al. determined the $T_g$ of PEDOT grown via oxidative polymerization is approximately 102 °C.\textsuperscript{49} Growth at 65 °C is well below this value and accordingly, there are minimal edge-on crystallites. Increasing the stage temperature to 100 °C yields a slight increase in the number of edge-on crystallites, which suggests the $T_g$ of these oCVD PEDOT films is near the reported literature value. The continuous increase in $A_{(100)}/A_{(020)}$ at stage temperatures well above the glass-transition temperature confirms that the mechanism of face-on to edge-on growth is surface reorganization \textit{in-situ}. To assess the impact of crystallographic texture on the electrochemical properties of the PEDOT films, a comparison between oCVD PEDOT grown at 65 °C (face-on) and at 175 °C (edge-on dominant) would be ideal. However, the film grown at 65 °C was found to be unstable in electrolyte and was therefore unsuitable for analysis. Instead, we compared the electrochemical properties of oCVD PEDOT grown at 100 °C, which is face-on dominant, to that grown at 175 °C. Henceforth, references to “Face-On” and “Edge-On” oCVD PEDOT correspond to films grown at 100 °C and 175 °C respectively.
Figure 5-2. (a) X-Ray Diffraction Spectra of oCVD PEDOT grown $T_{\text{Stage}} = 65 \, ^{\circ}\text{C}, 100 \, ^{\circ}\text{C}, 150 \, ^{\circ}\text{C}, 175 \, ^{\circ}\text{C}, \text{and} 250 \, ^{\circ}\text{C}$. The peaks corresponding to the (100) and (020) planes occur at $2\theta$ equal to $7^\circ$ and $26^\circ$ respectively. (b) Peak area ratio of $7^\circ$ to $26^\circ$. The increase in the ratio with $T_{\text{stage}}$ indicates an increase in the edge-on orientation of the crystallites.
5.4.2 Electrochemical Performance

The electrochemical performance of oCVD PEDOT thin films were assessed using cyclic voltammetry (CV) and galvanostatic cycling (GV). CV of Face-On and Edge-On oCVD PEDOT shows that the conductive polymer is electrochemically active from 2 to 4.2 V vs. Li/Li⁺ (Figure 5-3a). Electrochemical stability was also demonstrated up to 4.4 V vs. Li/Li⁺ as indicated by the absence of a drastic increase in oxidative current at higher potentials (Figure C-1 and Figure C-2). By comparison, PEDOT:PSS displays little to no electrochemical activity in this region as seen in Figure C-3. We attribute the difference in the electrochemical activity of PEDOT:PSS in this potential range to the mobility of dopant anions within the film- polystyrene sulfonate dopants are large, bulky macromolecules that cannot easily be extracted from the PEDOT matrix. In comparison, the Cl⁻ dopant in oCVD PEDOT introduced during synthesis are small anions that are more easily inserted and extracted from the PEDOT matrix. For example, oCVD PEDOT can undergo dopant exchange when exposed to a strong acid in solution, and chlorine anion dopants introduced during the deposition process can be successfully exchanged with bromine and sulfate anions respectively. This same effect can also be achieved electrochemically when an electrolyte solution is combined with an applied potential. Energy dispersive X-ray spectroscopy (EDS) measurements show that the chlorine signal in the as-deposited film is eliminated and replaced with phosphorus and fluorine signals in the cycled oCVD PEDOT films (Figure C-4).

Once Cl⁻ is successfully replaced with PF₆⁻ in oCVD PEDOT, subsequent cycles only involve the removal of PF₆⁻ from the anion dopant plane during reduction and its insertion during oxidation. Oxidative doping of PEDOT occurs in a two-step process. Initial oxidation of the film forms polarons (radical-cation) on the PEDOT chain. At higher doping levels, bipolarons (dication) are formed. The UV-vis-NIR absorbances associated with polarons and bipolarons occur at ~900 nm at ~1300 nm respectively. Previous spectrochemical studies of PEDOT correlate the first oxidation peak observed in CV with an increase in absorbance at ~900 nm in the UV-vis-NIR spectra obtained at the same applied voltage. The UV-vis-NIR spectra obtained at the voltage of the second oxidation peak revealed decreased absorbance at ~900 nm and increased absorbance at ~1300 nm. We therefore ascribe the first oxidation peak in the CVs of oCVD PEDOT to polaron formation and the second oxidation peak to bipolaron formation. These reactions remain consistent regardless of growth temperature. However, the current
densities displayed by Edge-On are significantly larger than those of Face-On oCVD PEDOT, even after accounting for the small difference in active material loading. This is particularly apparent in the potential region from 2.6 to 4.2 V vs. Li/Li⁺. Modeling has shown that higher currents observed during CV measurements may be observed in more concentrated electrolyte solutions. Given that the concentration of the electrolyte solution in the three-electrode cell remains constant during electrochemical cycling of oCVD PEDOT, the concentration of PF₆⁻ anions inside the film (i.e. doping level) must be greater for the Edge-On rather than the Face-On film. The ability of the anion to successfully enter the film during the doping process is dependent on access to the anion dopant plane, and face-on dominance hinders whereas edge-on dominance enables access. These differences are also expressed in the current densities observed during the reduction and dedoping of the oCVD PEDOT. The reduction peaks observed on the reverse sweep are due to the elimination of bipolarons and polarons during dedoping.

The effect of edge-on vs face-on dominance on the concentration of PF₆⁻ anions within the film and corresponding energy storage capacity is determined using galvanostatic cycling (GV). Electrochemical cycling of the oCVD PEDOT was performed from 2 to 4.2 vs. Li/Li⁺ using current densities ranging from 0.1 to 10 mA cm⁻². The upper voltage limit was reduced from 4.4 V to 4.2 V vs. Li/Li⁺ in order to eliminate the possibility of electrolyte degradation at higher potentials during cycling (Figure 5-3b,c). The theoretical capacity \( Q_{th} \) for anion doped PEDOT can be calculated using Equation 5-1, where \( M_w \) is the molecular weight of a single EDOT mer, \( n \) is the fraction of EDOT mers that are associated with an anion, and \( F \) is Faraday’s constant in mAh mol⁻¹. If every EDOT mer is associated with one PF₆⁻ anion, then \( n \) is equal to unity. This corresponds to a theoretical capacity of 191.2 mAh g⁻¹.

\[
\text{Equation 5-1} \quad Q_{th} = \frac{nF}{M_w}
\]

The approximate doping level of the film, can then be calculated using Equation 5-2, where \( Q_{exp} \) is the experimentally determined specific capacity of PEDOT.

\[
\text{Equation 5-2} \quad n = \frac{Q_{exp}}{191.2 \text{ mAh g}^{-1}}
\]
Regardless of the applied current density, the Edge-On films maintain higher specific capacities than the Face-On oCVD PEDOT films (Figure 5-3d). At a current density of 0.1 mA cm\(^{-2}\), Edge-On demonstrates a capacity of 178.9 mAh g\(^{-1}\), while Face-On oCVD PEDOT demonstrates a capacity of 75.8 mAh g\(^{-1}\). From Equation 5-2, the fraction of EDOT mers associated with a PF\(_6^\) anion are found to be 0.94 and 0.40 for Edge-On and Face-On oCVD PEDOT,
respectively. This validates our previous assertion that edge-on dominance enables higher levels of doping within the film.

At a current density of 10 mA cm\(^{-2}\) the experimentally measured specific capacities for Edge-On and Face-On oCVD PEDOT were 93.8 mAh g\(^{-1}\) and 39.5 mAh g\(^{-1}\), respectively. This corresponds to PF\(_6\)\(^-\) levels that are 52% of the values calculated at 0.1 mA cm\(^{-2}\). The same relative decrease in doping level regardless of edge-on vs. face-on dominance suggests that the mobility of PF\(_6\) anions within oCVD PEDOT ultimately limits the capacity at very high rates.

### 5.4.3 Long-term electrochemical performance

Conductive polymers are susceptible to chemical degradation during long-term cycling due to expansions and contractions in the crystal lattice caused by the changing concentration of anions within the film. This can eventually lead to scission of the polymer chains through irreversible oxidation.\(^22\text{-}23\) We hypothesize that an edge-on dominant crystallite orientation could mitigate these effects with its more easily accessed ion channels. The oCVD PEDOT films were cycled at 1 mA cm\(^{-2}\) over 500 galvanostatic charge-discharge cycles to elucidate the effect of dominant crystallite orientation on long-term cycling performance. Raman spectroscopy of the oCVD PEDOT films before and after long-term cycling reveals the changes in the polymer chemical structure caused by extensive cycling. The degree of oxidation in the film is determined by studying the scattering associated with the \(\alpha\) and \(\beta\) carbons in the thiophene ring. Figure 5-4a highlights the locations of these carbons on the ring. Two major vibrational modes are present in the region from 1300 cm\(^{-1}\) to 1500 cm\(^{-1}\): the \(C_\beta-C_\beta\) stretch at \(~1360\) cm\(^{-1}\) and the \(C_\alpha-C_\beta\) stretch at \(~1430\) cm\(^{-1}\). In situ spectroscopic studies demonstrated that the symmetric \(C_\alpha-C_\beta\) stretch shifts to higher wavenumbers as an increasingly positive voltage is applied.\(^56\text{-}57\), \(^59\) Two types of \(C_\alpha-C_\beta\) stretches contribute to the overall peak measure- stretches at 1414 cm\(^{-1}\) and 1445 cm\(^{-1}\) correspond to the neutral and highly oxidized structures respectively.\(^59\) Figure 5-4b presents the Raman spectra of the oCVD PEDOT films before and after long-term cycling. In the as-deposited films, the symmetric \(C_\alpha-C_\beta\) stretch is located at approximately 1425 cm\(^{-1}\), confirming a partially oxidatively-doped structure. After long-term cycling, the symmetric \(C_\alpha-C_\beta\) stretch in the Face-On samples blue shifts by approximately 9 cm\(^{-1}\) whereas the Edge-On oCVD PEDOT sample only shifts by 3 cm\(^{-1}\). Deconvolution of the peaks in the 1300-1500 cm\(^{-1}\) region enables a quantitative
analysis of the change in oxidation. The spectra were fit to the Cβ-Cβ stretch at ~1360 cm⁻¹ and the two Cα-Cβ stretches corresponding to the neutral and oxidized structures. The results of the deconvolution and fitting are presented in Figure C-5 and Table C-1. The relative number of oxidized to neutral structures is given by the ratio of $A_{1445}$ to $A_{1414}$, where $A_i$ corresponds to the area under fitted peak centered at wavenumber ‘$i$’. The calculated ratio as a function of stage temperature is given in Figure 5-4c. In the as-deposited films, a higher value of $A_{1445}:A_{1414}$ indicates high levels of doping during growth, which is beneficial for high electronic conductivity. Edge-On shows a higher degree of doping during growth compared to Face-On oCVD PEDOT, which is in good agreement with previous studies of oCVD PEDOT. After electrochemical cycling and the return of the oCVD PEDOT films to their original open circuit potential, the doping level should return to the value of the as-deposited films. Any increase observed in $A_{1445}:A_{1414}$ corresponds to the degradation of the polymer structure through irreversible oxidation. After long-term cycling, Face-On demonstrates a large increase in $A_{1445}:A_{1414}$ (0.28 to 0.97) whereas Edge-On oCVD PEDOT remains stable at 0.56 before and after long-term cycling. The anion dopant planes in the face-on dominant films are perpendicular to the applied electric field and this forces the diffusion of anions through instead of parallel to the thiophene plane. In order to accommodate this flux, PEDOT chains must break up to form suitable channels for anion diffusion, resulting in the irreversible oxidation observed through Raman spectroscopy for Face-On oCVD PEDOT.

![Chemical structure of PEDOT with α and β carbons labelled](image)

**Figure 5-4.** (a) Chemical structure of PEDOT with α and β carbons labelled. (b) Raman spectra of films as-deposited (dashed) and after long-term cycling (solid) for (top) Edge-On and (bottom) Face-On oCVD PEDOT. (c) Peak area ratio of oxidized to neutral Cαβ stretch of Face-On and
The scission of PEDOT chains destroys the local lattice and any associated anion dopant planes. The impact of this structural change is evident in the electrochemical impedance spectra of oCVD PEDOT films before and after long-term cycling. Nyquist plots of Face-On and Edge-On oCVD PEDOT show an increased charge-transfer-resistance ($R_{CT}$, equivalent to the diameter of the semi-circle in the high-frequency region) after long-term cycling (Figure 5-5a). The values of $R_{CT}$ were obtained by fitting the impedance spectra to the equivalent circuit shown in the inset figure, and all equivalent circuit fit values are summarized in Table C-2.

Long-term cycling results in the reduction of the specific capacities of the oCVD PEDOT films (Figure 5-5b,c). This suggests that the extent of doping in the PEDOT films decreases with subsequent cycling. The specific capacities are shown to stabilize after ~100 cycles to 71% and 75% of the initial capacity for Face-On and Edge-On oCVD PEDOT, respectively. After 500 cycles, these values plateau to 64% and 67%. Even though roughly the same percentage of initial capacity is retained both crystallographic textures, Edge-On consistently maintains higher absolute values of specific capacity for PF$_6^-$ anion compared to Face-On oCVD PEDOT. These electrochemical results in combination with the degradation studies, highlight the importance of crystallographic texture on the electrochemical properties of Edge-On oCVD PEDOT and its suitability for use in an electrochemical energy storage device.
Figure 5-5. (a) Nyquist plots of the impedance spectra for (top) Edge-On and (bottom) Face-On oCVD PEDOT before (solid) and after (dashed) long-term galvanostatic cycling. Inset is the equivalent circuit used for fitting. Where $R_{CT}$ is the charge-transfer-resistance. (b) Cycle stability from galvanostatic cycling at a 1 mA cm$^{-2}$ current density of Edge-On (red, solid line) and Face-On (blue, dashed line) oCVD PEDOT. The stability conferred by edge-on dominance is evident by both methods of comparison.

5.4.4 oCVD PEDOT|MoS$_2$ Full-Cell Prototype

The oCVD PEDOT|MoS$_2$ asymmetric devices were fabricated to demonstrate the electrochemical properties offered by Edge-On oCVD PEDOT. oCVD PEDOT was deposited onto porous Ni foam at 175 °C to yield Edge-On films on 3D substrates and were paired with MoS$_2$ electrodes fabricated using EPD. The use of thin films (~200 nm of oCVD PEDOT; ~60 μg of MoS$_2$) of active material do not require the use of binder. The elimination of the typically electronically and ionically insulating binder material (e.g. polyvinylidene fluoride) from the electrodes can result in ancillary benefits in the energy and power densities of the device. MoS$_2$ electrodes were electrochemically characterized in a three-electrode cell prior to full-cell fabrication (Figure C-6).
Figure 5-6. (a) Cyclic voltammograms at sweep rates of 10, 20, 50, and 100 mV s\(^{-1}\) and (b) galvanostatic cycling at current densities of 0.1, 1, and 10 mA cm\(^{-2}\) of an Edge-On oCVD PEDOT\textvert MoS\(_2\) asymmetric device from 3 to -1 V. (c) Charge-discharge profiles of the device are pseudo-linear. (d) Device characteristics of the asymmetric cell are depicted in a Ragone plot.

The oCVD PEDOT\textvert MoS\(_2\) asymmetric devices were cycled from 3 to -1 V as determined from three-electrode electrochemical cells (Figure C-7). This voltage range ensures full depth of charge-discharge of the oCVD PEDOT and MoS\(_2\) electrodes. On charging of the oCVD PEDOT\textvert MoS\(_2\) full cell to 3 V, oxidation of the PEDOT with concomitant anion doping occurs while MoS\(_2\) is reduced as lithium is intercalated. On discharge, the reverse processes occur. The use of negative voltages is due to the absence of a reference electrode in transitioning from a three- to two-electrode cell,\(^62\) and the reversal of polarity in similar full cells has not been shown to be
Cyclic voltammograms of an asymmetric device are shown in Figure 5-6a. During charging, the oxidation peak at \(-1\) V is attributed to the formation of polarons in oCVD PEDOT and the lithiation of MoS\(_2\). Bipolarons are formed at higher potentials (~2.5 V) prior to the complete charging of the device. During discharge, the reduction peak at \(-0.8\) V is due to the elimination of bipolarons and the delithiation of MoS\(_2\). Dedoping of the oCVD PEDOT and the elimination of polarons occur at lower potentials (~0.5 V) prior to the complete discharging of the device. GV for the oCVD PEDOT|MoS\(_2\) asymmetric device yields a capacity of 125.4 mAh g\(^{-1}\) (normalized to the total active material loading of the full cell) at a current density of 0.1 mA cm\(^{-2}\) when (Figure 5-6b), indicating that there is good material utilization of both oCVD PEDOT and MoS\(_2\) on the 3D substrate. Figure 5-6c shows the pseudo-linear charge-discharge profiles of the oCVD PEDOT|MoS\(_2\) asymmetric device. The IR drop is negligible at current densities of 0.1 and 1 mA cm\(^{-2}\). At a current density of 10 mA cm\(^{-2}\) the resistance obtained from the IR drop is only \(-40\) \(\Omega\), and complete charge-discharge occurs in less than 3 seconds. The above results are a clear indication that the rational selection of organic and inorganic redox materials can lead to high-rate performance in an asymmetric device.

Device characteristics of the oCVD PEDOT|MoS\(_2\) full cell can be calculated using the peak energy measured from discharge of the device from 3 to 0 V. The energy and power densities of the device using current densities ranging from 0.1 to 10 mA cm\(^{-2}\) are shown in Figure 5-6d. The oCVD PEDOT|MoS\(_2\) full cell demonstrates an energy density of 5 \(\mu\)Wh cm\(^{-2}\) and a power density of 1 mW cm\(^{-2}\) at a practical current density of 1 mA cm\(^{-2}\). While the benchmarking of gravimetric energy and power densities for thin-film full-cells against more practical devices is often inappropriate,\(^64\) it can provide a useful context in the discussion of the prospects of a full-cell chemistry. The oCVD PEDOT|MoS\(_2\) asymmetric device is compared to other PEDOT-based devices\(^{14, 41-42, 65}\) in Figure C-8 and further details can be found in Appendix C (Table C-3 to Table C-5). The comparison of the oCVD PEDOT|MoS\(_2\) asymmetric device to the previously reported oCVD PEDOT hybrid devices is particularly notable. The asymmetric full cell reported here demonstrates comparable gravimetric power densities but lower gravimetric energy densities (46 Wh kg\(^{-1}\) and 175 kW kg\(^{-1}\) at a current density of 10 mA cm\(^{-2}\)) compared to hybrid devices (~175Wh kg\(^{-1}\), ~250 kW kg\(^{-1}\)) comprised of positive electrodes of oCVD PEDOT and carbon-based negative electrodes of aligned graphene flakes or aligned CNTs \(^{41-42}\) However, the similarity
is mainly attributed to the difference in the surface areas of the current collectors used in the experiments (Ni foam $\sim 3 \times 10^{-3}$ m$^2$ g$^{-1}$ vs. aligned carbon nanotubes $\sim 3100$ m$^2$ g$^{-1}$). We estimate that a 200 nm thick Edge-On PEDOT film deposited onto aligned carbon nanotubes, capacity matched to an MoS$_2$ electrode, and utilizing the maximum voltage (3.6 V if oCVD PEDOT is charged up to 4.4 V vs. Li/Li$^+$) could result in an energy density of 188 Wh kg$^{-1}$. While the realization of such a device is ultimately outside the scope of the current work, this significant value highlights the promise of the oCVD PEDOT with tailored crystallographic texture for high-rate electrochemical energy storage applications.

5.5 Conclusion

The crystallographic texture of PEDOT thin films greatly affects its electrochemical performance. Using oxidative chemical deposition allows the formation of conformal PEDOT thin films with controlled crystallographic texture. Surface reorganization from the Face-on to the Edge-on structure is enabled by depositing at temperatures well above the glass-transition temperature of PEDOT. Films with Edge-on dominance, where the anion dopant plane is perpendicular to the substrate, consistently display higher anionic charge storage capacities than Face-on dominant films. Edge-on dominance also reduces the degree of oxidative degradation and minimizes the increase in charge-transfer resistance compared to Face-on dominance after 500 galvanostatic charge-discharge cycles. The pairing of oCVD PEDOT with MoS$_2$ is demonstrated in the fabrication of an asymmetric device. The intrinsic electronic conductivity of both active materials eliminates the need for additional conductive additives. Both the oCVD of PEDOT and the EPD of MoS$_2$ allow attachment of these active materials to nickel foam current collectors without the use of binder. The oCVD PEDOT|MoS$_2$ asymmetric device displays high-rate capability and an energy density of 5 $\mu$Wh cm$^{-2}$ and power density of 1 mW cm$^{-2}$ at a practical current density of 1 mA cm$^{-2}$.
5.6 References


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Chapter 6 Conclusions and Future Directions

6.1 Summary

A paradigm shift from planar device architectures to three-dimensional (3D) architectures allows mini and micro devices to deliver high performance within a small areal footprint. Construction of such architectures requires formation of the 3D scaffold and its subsequent modification with active/supporting materials. In this thesis, chemical vapor deposition (CVD) was investigated to form a broad range of polymeric materials to enable the construction of 3D device architectures. Materials and process development were specifically focused on templates for integrated circuits (ICs) and active/supporting materials for electrochemical energy storage. For each polymer system, this requires understanding the mechanisms that control the polymer functionality (chemical structure, cross-linking, doping level) and thin film properties (conformality, roughness, texture). The optimized polymer films were then integrated with existing techniques for 3D device construction to demonstrate the utility of CVD polymers.

6.1.1 Formation of nanostructures

The directed self assembly (DSA) of block copolymers (BCPs) is a patterning technique to form nanotemplates for integrated circuits. Chapters 2 and 3 of this thesis used initiated chemical vapor deposition (iCVD) from divinyl benzene (DVB) to form crosslinked interfacial wetting layers for graphoepitaxial DSA of BCPs.

Chapter 2 presented a kinetic study of iCVD from DVB that investigated the control mechanism of crosslinking and film roughness. When the monomer surface concentration is held near constant, the growth rate of pDVB increases with substrate temperature. This indicates propagation of the primary vinyl bond is kinetically limited. By contrast, crosslinking, or reaction of the pendant vinyl bond, decreases with substrate temperature. Since the depositions occur well below the glass transition temperature of pDVB, increases in stage temperature do not enable the conformational changes needed for pendant vinyl bond reaction in the film bulk. Instead, the crosslinking reaction is limited to the exposed surface layer. Therefore, a high degree-of-crosslinking requires slower deposition rates to increase the time a given film layer spends at the surface. In the case of film roughness, higher stage temperatures yield rougher films. The
enhanced deposition rates result in greater instability of topographical fluctuations. The glassy state of the deposited film does not permit chain motion to even out these fluctuations. In the context of interfacial wetting layers for BCP-DSA, pDVB films must be grown at very slow deposition rates to form crosslinked and smooth films. These slow rates are easier to achieve when the deposition process is adsorption limited rather than kinetically limited. Substantial decreases in the chamber pressure can yield deposition rates as low as 0.08 nm/min. This is ideal to form ultra-thin, ultra-smooth, and ultra-crosslinked interfacial wetting layers for BCP-DSA.

Chapter 3 used the information gleaned in Chapter 2 as a starting point to form pDVB interfacial wetting layers for DSA of poly(styrene-b-methylmethacrylate) (PS-b-PMMA). The types of gas-phase free-radical species present during growth were used to change the film chemical functionality in lieu of using multiple monomers. This greatly simplified the process as only two precursors (DVB and tert-butyl peroxide (TBPO)) were needed to form films with a range of wetting preference. The relatively high concentration of t-butoxy end groups in iCVD pDVB yield films that are very weakly PMMA preferential. Increasing the filament temperature during growth introduces methyl radicals into the chamber, which abstract and substitute on the pDVB polymer backbone. Depending on the degree of backbone methylation, the wetting preference of iCVD pDVB can be shifted from weakly PS preferential to highly PS preferential. Conformal coatings of weakly preferential iCVD pDVB films on graphoepitaxial line and space templates yield PS-b-PMMA nanotemplates where the pattern in perpendicularly oriented to the substrate normal and have long-range, areal alignment.

6.1.2 Modification of nanostructures

Electrochemical energy storage is an enabling technology for autonomous mini and micro devices. Several methods to form micro and nanostructured electrodes and current collectors have already been developed. These include nickel foams, carbon micro-post arrays, Si nanowire arrays, and align carbon nanotube arrays. Methods to integrate additional active/supporting materials while maintaining the high surface area of these structures were investigated in Chapters 4 and 5.

Chapter 4 used iCVD to form solid, conformal, polymer electrolytes for solid state Li ion batteries. Cross-linked siloxane and silazane polymer chemistries were evaluated as nanoscale ionically conducting and electrically insulating layers. The films were rendered ionically conductive via
lithiation, where the films were soaked in liquid electrolyte and then dried. Out of these chemistries, poly(tetravinyltetramethylcyclotetrasiloxane) (pV4D4) exhibited the highest room temperature ionic conductivities (approaching $10^{-7}$ S cm$^{-1}$) in a 25 nm thick film. Transmission electron microscopy (TEM) studies of pV4D4 films on Ag nanowires determined minimal swelling occurred after lithiation, indicating a mechanically robust system. The conformality of the pV4D4 films on high aspect ratio structures was assessed by coating Si nanowire arrays (aspect ratio > 50). Scanning electron microscopy (SEM) and TEM imaging revealed that a pV4D4 thin film maintained a thickness of ~20 nm down the length of ~8 micron tall Si nanowires. Finally, using electrochemical techniques can render even thick films of pV4D4 ionically conductive. Initial galvanostatic cycles at very low C-rates ($C/1000$) introduce ions into the polymer film via ion migration rather than diffusion. With this method, 400 nm thick pV4D4 films display ionic conductivities greater than $10^{-7}$ S cm$^{-1}$.

Chapter 5 investigated CVD polymers as redox active materials for Li-ion supercapacitors. Oxidative chemical vapor deposition (oCVD) was used to deposit conformal coatings of poly(3,4-ethylenedioxythiophene) (PEDOT), a conductive polymer capable of pseudocapacitive charge storage. The stage temperature during growth was used to change the dominant crystallographic texture of the oCVD PEDOT film. By operating significantly above the glass transition temperature of PEDOT, the film reorganizes during growth to an edge-on structure. In this case, the $\pi$-$\pi$ stack is perpendicular to the substrate surface. The alternative dominant texture is face-on dominance, where the $\pi$-$\pi$ stack is parallel to the substrate surface. Edge-on dominance facilitates the insertion and removal of counter-anions from the oCVD PEDOT film during cycling. Higher specific capacities at a given charge/discharge rate are observed in edge-on dominant films. Furthermore, Raman spectroscopy shows that edge-on dominant films are less susceptible to oxidative damage after long term cycling. This enables edge-on dominant films to maintain ionic conductivities greater than $10^{-6}$ S cm$^{-1}$ after long term cycling, whereas the ionic conductivity of face-on films decreases by an order of magnitude to $10^{-7}$ S cm$^{-1}$ after long term cycling. Finally, a proto-type lithium ion supercapacitor is demonstrated by pairing oCVD PEDOT with a molybdenum disulfide anode.
6.2 Future Outlook

6.2.1 Integrated Circuit Fabrication

Ultra-thin films of iCVD pDVB can control the self-assembly of BCP thin films both at the substrate/BCP-film interface (Chapter 3) and at the BCP film surface. Overall, this is a promising technology and materials system to incorporate in DSA of BCPs. However, as of Fall 2017, the IC-industry plans to use extreme UV (EUV) for future generations of lithography rather than DSA of BCPs. This is in part due to the large defect densities that have persisted in line and space patterns. Commercial FinFET architectures using EUV may be launched as soon as 2019.

DSA of BCPs still has industrial utility for the formation of smaller VIAs by contact-hole shrinkage. Instead of requiring defect-free self assembly over large areas (e.g 300 nm x 10 μm), self assembly is constrained to shallow holes, at most 100 nm in diameter and depth. In the case of asymmetric PS-b-PMMA, ideally two concentric cylinders are assembled inside the hole. The outer cylinder would be PS, which forms a larger domain, and the inner cylinder would be PMMA, which forms the smaller domain. The contact hole can then be shrunk to the size of the PMMA domain. PS sidewall preference is key to enabling this sidewall architecture. Simulations show that as long as the sidewall is strongly PS preferential, the desired self-assembled structure can be achieved even with neutral or PS preferential bottom wall. Efforts are currently underway, in conjunction with the Nealey group at the University of Chicago, to apply iCVD pDVB films for contact hole-shrinkage.

6.2.2 Electrochemical Devices

CVD polymers have utility in electrochemical energy storage devices both as supporting materials (electrolytes) and active materials (pseudocapacitive cathodes). There are several avenues to build on the current body of work.

Solid Polymer Electrolytes

In terms of solid polymer electrolytes, iCVD pV4D4 demonstrated high ionic conductivity, even in thick films. However, the electrical conductivity of this material (10^{-11} S/cm) requires a minimum film thickness of 400 nm to minimize leakage current between the electrodes. Inorganic LASO electrolytes formed by atomic layer deposition (ALD) are far more electrically resistive.
(10^{-15} \text{ S/cm}), requiring a theoretical minimum film thickness of less than 1 nm.\textsuperscript{6} Practically, avoiding pinhole formation due to the volumetric expansion/contraction of electrodes during cycling requires thicker films (tens of nanometers). At these film thicknesses, the room temperature ionic conductivity of these materials drops below 10^{-9} \text{ S/cm}.\textsuperscript{6-7} A hybrid system, where ALD LASO and iCVD pV4D4 are layered, can yield an ultra-thin electrolyte that has high ionic conductivity, low leakage current, and remains pinhole free after cycling. The Gleason group is currently collaborating with the Dunn and Chang groups at the University of California- Los Angeles (UCLA) to realize such an electrolyte system.

**Pseudocapacitive Conductive Polymers**

This thesis demonstrated the importance of oCVD PEDOT film texture to yield optimal pseudocapacitive properties. Stage temperature controls the dominant film texture, but does not ensure that the entire film displays edge-on orientation. This same phenomenon is observed when surface silanization is used as the texture control mechanism.\textsuperscript{8} Since interfacial properties are what affect the initial formation of edge-on vs. face-on crystallites, a new approach could use the interfacial wetting layers developed in Chapter 3. An ultra-thin layer of pDVB (<5 nm thick) would conformally coat all surface features of the current collector and force edge-on crystallite growth. Should this layer be too electrically resistive, semiconducting poly(p-di-ethynylbenzene) films could be used instead. The starting monomer is analogous to DVB, except that the double bonds in vinyl groups have been replaced with triple bonds (ethynyl). The resulting conjugated network has electrical conductivities of \sim 10^{-3} \text{ S/cm}.\textsuperscript{9}

With respect to the PEDOT|MoS\textsubscript{2} full cell, the next logical step would be to coat these pseudocapacitive materials on EDLC materials, such as aligned graphene flakes and aligned carbon nanotube arrays, to form an even more powerful cell. Coatings of oCVD PEDOT on carbon nanotube arrays have already been demonstrated. The electrophoretic deposition of MoS\textsubscript{2} on carbon nanotubes or graphene flakes requires further study to optimize the final coating conformality. Once this is achieved, a supercapacitor with high energy and power density is not far away.
6.3 References


Appendix A: Supplemental For Chapter 3

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![AFM images and AFM line scans and corresponding roughness values](image)

**Figure A-1.** (Left) AFM images and (Right) AFM line scans and corresponding roughness values of pDVB grown at varying filament temperatures.
Figure A-2. High wavenumber transmission mode FTIR data and individual Voigt fitted peaks for polystyrene (a) reference from Omnic (b) iCVD grown at 225 C (c) iCVD grown at 330 C.

Table A-1. Area under pS FTIR peaks resolved and fitted assuming Voigt distribution from Figure A-2.

<table>
<thead>
<tr>
<th></th>
<th>CH Arom.</th>
<th>CH₃ asym</th>
<th>CH₂ asym</th>
<th>CH₃ sym</th>
<th>CH₂ sym</th>
</tr>
</thead>
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<tr>
<td></td>
<td>3027 cm⁻¹</td>
<td>2964 cm⁻¹</td>
<td>2930 cm⁻¹</td>
<td>2874 cm⁻¹</td>
<td>2850 cm⁻¹</td>
</tr>
<tr>
<td>Omnic Ref</td>
<td>21.427</td>
<td>0.000</td>
<td>92.651</td>
<td>0.000</td>
<td>16.056</td>
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<tr>
<td>iCVD 225 C</td>
<td>0.113</td>
<td>0.298</td>
<td>0.324</td>
<td>0.176</td>
<td>0.000</td>
</tr>
<tr>
<td>iCVD 330 C</td>
<td>0.125</td>
<td>0.360</td>
<td>0.356</td>
<td>0.152</td>
<td>0.000</td>
</tr>
</tbody>
</table>
Appendix B: Supplemental For Chapter 4

Figure B-1. (a) Representation of the experimental configuration used for electrochemical impedance spectroscopy. Impedance of the (b) unlithiated and (c) lithiated 25 nm pV4D4 films. The data were taken in the frequency range from 100 kHz to 100 Hz using a 10 mV (RMS) potential. The circuits for equivalent circuit fitting are shown. The semi-circles in (c) are indicative of ionic conduction. The solid curves were obtained from data fitting and used to determine $R_p$. Cartoon insets in (b) and (c) propose the pV4D4 structure before and after lithiation respectively. Blue and red spheres represent Si and O atoms respectively. In (b) and (c) the geometric markers indicate different positions on the sample. Reproduced with permission from Mater. Horiz. 2015, 2 (3), 309-314. Copyright 2015 Royal Society of Chemistry
Figure B-2. (a) AFM image of the surface of pV4D3 film after lithiation. (b) SEM image of particle that appears as “white” feature on AFM scan. (c) Energy dispersive spectrum (EDS) of particle showing a strong chlorine signal (d) EDS on the surface adjacent to the particle showing no chlorine signal. This confirms that the particles observed in the AFM are precipitated LiClO$_4$. Reproduced with permission from *Macromolecules* 2015, 48 (15), 5222-5229. Copyright 2015, American Chemical Society.
Figure B-3. Fitting circuit used for EIS of carbon/pV4D4 half cell

Figure B-4. Galvanostatic cycling of MCMB slurry on stainless steel only. Cycles at C/20 and C/10 shown. Approximate capacity is 270 mAh/g. Image courtesy of Jonathan Lau (Dunn Group, University of California, Los Angeles)

References

Appendix C: Supplemental For Chapter 5

This appendix will be submitted for peer-review publication in conjunction with Chapter 5 as supplemental information.

Electrochemical Characterization of PEDOT

Figure C-1. Cyclic voltammograms of Face-On oCVD PEDOT cycled from 2 to 4, 4.2, and 4.4 V vs. Li/Li\(^+\) at a sweep rate of 10 mV s\(^{-1}\).

Figure C-2. Cyclic voltammograms of Edge-On oCVD PEDOT cycled from 2 to 4, 4.2, and 4.4 V vs. Li/Li\(^+\) at a sweep rate of 10 mV s\(^{-1}\).
Figure C-3. Cyclic voltammogram of commercially purchased PEDOT:PSS coated on stainless steel cycled from 2 to 4.2 V vs. Li/Li⁺ at a sweep rate of 10 mV s⁻¹. The areal current scale (-150, 150 μA cm⁻²) is used for comparison with oCVD PEDOT. Inset shows voltammogram in smaller range of areal currents. PEDOT:PSS is essentially electrochemically inactive in this potential window, unlike oCVD PEDOT.

**(Electro)Chemical Characterization of oCVD PEDOT as deposited and after 500 cycles**

Figure C-4. EDS spectra of oCVD PEDOT films on stainless steel as-deposited (dashed line) and after long term cycling (solid line) at stage temperatures of A) 100 °C (Face-On) and B) 175 °C (Edge-On).
Figure C-5. Deconvolution and fit of Raman spectra of (a) Face-On (100 °C) – As Deposited, (b) Face-On (100 °C) – long-term cycled, (c) Edge-On (175 °C) – As Deposited, and (d) Edge-On (175 °C) – Long-term cycled oCVD PEDOT films.

Table C-1. Deconvolution and fit parameters of Raman spectra of oCVD PEDOT films from Figure C-5 assuming Gaussian peaks. AD = As Deposited films. LT = Long term cycled films.

<table>
<thead>
<tr>
<th>Wave Number (cm⁻¹)</th>
<th>Face-On AD</th>
<th>Face-On LT</th>
<th>Edge-On AD</th>
<th>Edge-On LT</th>
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</thead>
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<tr>
<td>1360 cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>1.89*10⁶</td>
<td>1.50*10⁵</td>
<td>1.81*10⁶</td>
<td>1.26*10⁶</td>
</tr>
<tr>
<td>Height</td>
<td>2.95*10⁴</td>
<td>3.79*10³</td>
<td>2.86*10⁴</td>
<td>2.40*10⁴</td>
</tr>
<tr>
<td>1414 cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>2.40*10⁶</td>
<td>4.17*10⁵</td>
<td>2.50*10⁶</td>
<td>2.41*10⁶</td>
</tr>
<tr>
<td>Height</td>
<td>4.55*10⁴</td>
<td>7.99*10³</td>
<td>4.94*10⁴</td>
<td>4.44*10⁴</td>
</tr>
<tr>
<td>1445 cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>6.73*10⁵</td>
<td>4.04*10⁵</td>
<td>1.42*10⁶</td>
<td>1.39*10⁶</td>
</tr>
<tr>
<td>Height</td>
<td>1.44*10⁴</td>
<td>6.49*10³</td>
<td>2.58*10⁴</td>
<td>1.95*10⁴</td>
</tr>
</tbody>
</table>
Table C-2. Fit parameters for impedance spectroscopy of oCVD PEDOT films. AD = As Deposited films. LT= Long term cycled films.

<table>
<thead>
<tr>
<th></th>
<th>Face-On AD</th>
<th>Face-On LT</th>
<th>Edge-On AD</th>
<th>Edge-On LT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{Series}}$ ($\Omega \text{ cm}^2$)</td>
<td>7.8</td>
<td>7.72</td>
<td>7.8</td>
<td>7.99</td>
</tr>
<tr>
<td>CPE1 ($F \text{s}^{(a-1)}$)</td>
<td>1.14E-04</td>
<td>4.34E-05</td>
<td>4.53E-07</td>
<td>2.58E-04</td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.7969</td>
<td>0.8198</td>
<td>0.7531</td>
<td>0.7081</td>
</tr>
<tr>
<td>$R_{\text{CT}}$ ($\Omega \text{ cm}^2$)</td>
<td>12.5</td>
<td>62.97</td>
<td>9.536</td>
<td>21.07</td>
</tr>
<tr>
<td>CPE2 ($F \text{s}^{(a-1)}$)</td>
<td>3.53E-03</td>
<td>4.16E-03</td>
<td>6.37E-03</td>
<td>6.22E-03</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.8019</td>
<td>0.6913</td>
<td>0.8477</td>
<td>0.7589</td>
</tr>
</tbody>
</table>

EPD MoS$_2$ Electrochemical Characterization

![Graph](image)

Figure C-6. (a) Cyclic voltammetry and (b) galvanostatic cycling of EPD MoS$_2$ electrodes cycled in 1M LiClO$_4$ EC:DMC with Li counter and reference electrodes in a three-electrode cell. Galvanostatic cycling shows high capacities at current densities up to 5 mA cm$^{-2}$ due to the high density of defects in the MoS$_2$ nanocrystals and semi-metallic conduction of the 1T phase.$^1$ The native oxide on the Ni foam current collector may also contribute to the high capacities observed.
Full Cell Operating Voltage Determination

Figure C-7. (a) Representative galvanostatic profiles of positive oCVD PEDOT and negative EPD MoS2 electrodes (blue) used to determine the operating voltage of the full cell. (b) Corresponding voltage ranges of charge-discharge in the full cell device. The voltages listed are with respect to MoS2 as the counter electrode. Due to the overcapacity of MoS2 electrode in the full cell, the upper voltage was limited to 3 V.

Ragone Plot

Figure C-8. Gravimetric Ragone plot comparing the oCVD PEDOT|MoS2 asymmetric device with PEDOT-based devices. The pairing of PEDOT with MoS2 increases the maximum voltage of the full cell to 3 V and results in a 1.4x increase in energy compared to devices with aqueous electrolytes (upper voltage limit 1.8 V).\(^3\) The power densities of the oCVD PEDOT|MoS2 device are also markedly higher than the comparison devices that utilize PEDOT:PSS (~10\(^3\) W kg\(^{-1}\)).\(^6-9\) This difference may be due to the higher electronic and ionic conductivities offered by oCVD PEDOT.
The values used for the oCVD PEDOT|MoS$_2$ device in Figure six are summarized in Table C-3.

**Table C-3.** oCVD PEDOT|MoS$_2$ on Ni Foam full cell gravimetric energy and power as a function of current density.

<table>
<thead>
<tr>
<th>Current Density [mA cm$^{-2}$]</th>
<th>Energy [Wh kg$^{-1}$]</th>
<th>Power [W kg$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>93.1</td>
<td>$1.76 \times 10^3$</td>
</tr>
<tr>
<td>0.2</td>
<td>88.9</td>
<td>$3.61 \times 10^3$</td>
</tr>
<tr>
<td>0.5</td>
<td>82.5</td>
<td>$9.34 \times 10^3$</td>
</tr>
<tr>
<td>1</td>
<td>76.5</td>
<td>$1.90 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>69.6</td>
<td>$3.81 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>58.7</td>
<td>$9.34 \times 10^4$</td>
</tr>
<tr>
<td>10</td>
<td>45.9</td>
<td>$1.75 \times 10^5$</td>
</tr>
</tbody>
</table>

The comparison gravimetric Ragone Plot in Figure C-8 includes data from references that combined PEDOT with a high surface area carbon (e.g. carbon nanotube, graphene oxide, graphene flakes).$^{2-5}$ The plotted values for PEDOT (CNT)| MnO$_2$ (CNT)$^3$ and PEDOT:PSS(reduced-graphene oxide)$^2$ were the numbers reported within the text.

The references to asymmetric devices using oCVD PEDOT on A-CNT contained Ragone plots where the data were measured over a range of current densities.$^{4,5}$ For each reference, three points were selected from the Ragone plot that corresponded to minimum, maximum, and median current density. These correspond to 1) maximum energy 2) maximum power 3) median energy and power. The text did not supply numerical values for all these data points. The numerical values were approximated based on their position in the Ragone plot. The values used in the comparison Ragone plot for the oCVD PEDOT (A-CNT)| A-Graphene are enumerated in Table C-4.

**Table C-4.** Values used in comparison Ragone plot of PEDOT(A-CNT)| A-Graphene device.$^4$

<table>
<thead>
<tr>
<th>Gravimetric Energy Density Wh kg$^{-1}$</th>
<th>Gravimetric Power Density kW kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>176.6</td>
<td>30</td>
</tr>
<tr>
<td>95</td>
<td>140</td>
</tr>
<tr>
<td>54</td>
<td>233</td>
</tr>
</tbody>
</table>
The Ragone plot of the asymmetric device formed by oCVD PEDOT (A-CNT)\(\mid\) A-CNT only reported volumetric energy and power.\(^5\) The text supplied values for maximum volumetric and gravimetric energy (82.8 Wh L\(^{-1}\) and 170.7 Wh kg\(^{-1}\) respectively). The ratio of gravimetric to volumetric energy is then \(\sim 2.06\). The volumetric energy and power of the devices were approximated from the Ragone plot. These values were converted to gravimetric energy and power by multiplying the volumetric values by 2.06. The final values used for this device in the comparison Ragone plot are enumerated in Table C-5.

Table C-5. Values used in comparison Ragone plot of PEDOT\(\mid\)A-CNT device.\(^5\)

<table>
<thead>
<tr>
<th>Volumetric Energy Density Wh L(^{-1})</th>
<th>Volumetric Power Density kW L(^{-1})</th>
<th>Gravimetric Energy Density Wh kg(^{-1})</th>
<th>Gravimetric Power Density kW kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.8</td>
<td>0.6</td>
<td>170.7</td>
<td>1.236</td>
</tr>
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<td>65</td>
<td>2.2</td>
<td>134</td>
<td>4.532</td>
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<tr>
<td>45</td>
<td>19</td>
<td>93</td>
<td>39.14</td>
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</table>

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