Optical and Chemical Properties of Polythiophene Films Produced via Surface Polymerization by Ion-Assisted Deposition

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Polythiophene films are produced via surface polymerization by ion-assisted deposition (SPIAD), in which 55−200 eV thiophene ions and α-terthiophene (3T) neutrals are co-deposited on surfaces. These SPIAD polythiophene films display unique optical properties in their photoluminescence and UV/vis absorption compared with films prepared by either 3T or direct thiophene ion deposition only. The optical properties of SPIAD polythiophene depend on the deposited ion-to-neutral ratio and ion energy. Ion-to-neutral ratios of 1/100 cause a red shift in the photoluminescence of SPIAD films compared with 3T films whereas ratios of ∼1/400 cause a blue shift. Ion energies at 100 eV showed the most enhanced photoluminescence and UV/vis absorption compared with 3T films. Mass spectrometry indicates that a variety of higher molecular weight oligomers with some masses exceeding $[3T]_3$ are formed by SPIAD. UV/vis spectra and X-ray photoelectron spectroscopy support the formation of a distribution of oligomers, while the latter method reveals elemental content consistent with polythiophene.

I. Introduction

Oligo- and polythiophenes are some of the most promising materials among organic conjugated polymers for many applications, including field effect transistors, photovoltaics, light-emitting diodes, antistatic coatings, sensor films, recording materials, rechargeable batteries, and capacitors.[1−7] The intense interest in oligo- and polythiophenes for these applications is due to their high conductivity in the doped and pristine form as well as their high stability with respect to atmospheric exposure.[1,8] Since the synthesis of first-generation polythiophene, a wide variety of polythiophenes have been synthesized and their physical and chemical properties established. The electron conjugation length of polythiophene increases with chain length, typically leading to red shifts in the photoluminescence and UV/vis absorption spectra. This relationship of optical properties, charge mobility, and conductivity to chain length and film structure has driven the development of novel polythiophene films, especially for applications in light-emitting films, photovoltaics, and thin film transistors.

Organic synthesis[9−11]and electrochemical methods[12−14] are the most popular methods of synthesizing new polythiophenes for enhanced processibility, mobility, and optical or electrical properties. However, these methods can be limited by the presence of solvents in the films and difficulty in controlling film morphology.[15]

Vapor-phase deposition can also be used to prepare well-defined conducting polymers of oligothiophenes and related materials. Evaporation of oligomers such as sexithiophene is a straightforward approach to film deposition, but film disordering sets in with increasing film thickness, even when the substrate temperature is controlled.[16] Supersonic molecular beam deposition[17]

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(1) Heeger, A. J. *J. Phys. Chem. B* **2001**, *105*, 8475.

(2) Garnier, F. *J. Chem. Phys.* **1998**, *227*, 253.

(3) Granstrom, M.; Harrison, M. G.; Friend, R. H. Electro-optical polythiophene devices. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999; p 405.

(4) Catellani, M.; Boselli, B.; Luzzati, S.; Tripodi, C. *Thin Solid Films* **2002**, *403−404*, 66.

(5) Pei, J.; Yu, W.; Huang, W.; Heeger, A. *Macromolecules* **2000**, *33*, 2462.

(6) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884.

(7) Schon, J. H.; Dodabalapur, A.; Kloc, C.; Balogg, B. *Science* **2000**, *290*, 963.

(8) Fujimoto, H.; Najashima, U.; Inokuchi, H.; Seki, K.; Cao, Y.; Nakahara, H.; Nakayama, J.; Hoshino, M.; Fukuda, K. *J. Chem. Phys.* **1990**, *92*, 4077.

(9) Leclerc, M.; Faid, K. *Adv. Mater.* **1997**, *9*, 1087.

(10) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(11) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.

(12) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183.

(13) Roncali, J. Advances in the molecular design of functional conjugated polymers. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 311.

(14) Yumoto, Y.; Yoshimura, S. *Synth. Met.* **1986**, *13*, 185.

(15) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141.

(16) Fichou, D.; Ziegler, C. Structure and properties of oligothiophenes in the solid state: Single crystals and thin films. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999; p 185.

(17) Podesta, A.; Toccoli, T.; Milani, P.; Boschetti, A.; Iannotta, S. *Surf. Sci.* **2000**, *464*, L673.

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has been shown to overcome this problem, allowing growth of ordered films of up to 500-nm-thick quaterthiophene. X-ray or electron induced polymerization of condensed thiophene or 3-hexylthiophene films has also been demonstrated.[18-22] Thiophene monomers can be polymerized by plasmas in either pulsed[23] or continuous mode.[24] The plasma method provides very thin, pinhole-free films that can adhere to almost any substrate, but difficulty in controlling monomer fragmentation appears to limit production of films with interesting electronic properties.

There have been various attempts to grow conducting polymers using gaseous ions. Moliton[25] described modification of a polythiophene film using >10 keV atomic ions and further proposed that <1 keV atomic ion-assisted deposition might also be utilized for the production of conducting polymers. Other workers have used polyatomic ion-assisted deposition of tris(8-hydroxyquinoline)aluminum (Alq3) to produce organic thin films for conducting polymers.[26,27] However, all the molecular species pass through the ionization source in these polyatomic ion deposition experiments, preventing direct control of ion fragmentation or ion/neutral ratio. Co-deposition from separate sources of <1 keV ions and neutral species to grow conducting polymer films by ion-assisted deposition has been demonstrated, but only using chemically inactive atomic ion species such as He^+ and Ar^+ or doping ions such as I^+.[28] Finally, optical properties of evaporated films have been thoroughly examined,[16] but the optical properties of only a few of these other vacuum-prepared films have been reported.[17,22,29]

We recently developed surface polymerization by ion-assisted deposition (SPIAD) as a novel method to grow polythiophene films by the co-deposition of hyperthermal thiophene ions and thermal α-terthiophene (3T) neutrals.[30] SPIAD is performed here with a non-mass-selected Kaufman ion source tuned to operate with a minimum of fragmentation, but it can also be performed with a mass-selected ion source. The Kaufman ion source allows rapid film deposition over wide areas, while the mass-selected source permits more selective, albeit slower, film deposition for mechanistic studies. We previously showed that SPIAD can be used to polymerize films with photoluminescence similar to evaporated 3T films,[30] but no new optical properties and no systematic study of ion/neutral ratio were presented. Previous work by our group studied direct polyatomic ion deposition of fluorocarbon, siloxane, amine, and thiophenic organic films.[31-36] We have demonstrated in this previous work that both polyatomic ion structure and kinetic energy can control film chemistry and morphology. Here, we use non-mass-selected SPIAD of polythiophene, demonstrating the ability of thiophene ion energy and ion-to-neutral ratio to control the film's optical properties and chemistry. We characterize these SPIAD polythiophene films by photoluminescence (PL), UV/vis absorption, X-ray photoelectron spectroscopy, desorption ionization on oxidized silicon mass spectrometry, and atomic force microscopy.

II. Experimental Details

A. Polythiophene Film Deposition. Figure 1 depicts the instrument used for SPIAD of polythiophene films, which combines simultaneous deposition of hyperthermal polyatomic ions and thermal neutrals. This instrument is equipped with a broad beam Kaufman ion source (Veeco-CS, 3 cm Ion Source) using degassed thiophene vapor metered by a mass flow controller (MKS, Type 246). Fragmentation of thiophene ions in the source is monitored by an energy analyzer/quadrupole mass spectrometer. Mass spectrometry shows that 65% of the ions emitted from the source are the intact thiophene parent ion, $C_4H_4S^+$, at m/z 84. The remaining ion fraction is due to roughly equal parts m/z 39, 45, and 56 corresponding to $C_3H_3^+$, CHS^+, and $C_2H_2S^+$, respectively. Ion fragmentation is minimized by lowering the electron impact energy of the source to 30 eV for all experiments. The ion current range used for direct ion deposition is 0.1−0.3 mA/cm². A much lower ion current range of 2−8 μA/cm² is used for SPIAD, varied to obtain the desired ion-to-neutral ratio. The ion energy distribution is measured as ~15 eV (fwhm) in the ion energy range from 25 to 200 eV using a Faraday cup detector with a retarding grid and an electron suppressor grid. These measurements find that electron flux on the surface from the ion source is less than 5% of the ion current.

α-Terthiophene (3T) is evaporated onto the substrate from a home-built resistively heated doser[37] at a constant flux of 5 × 10¹⁵ molecules/s·cm² for all experiments. 3T flux is determined by converting the frequency change of a quartz crystal microbalance (STM 100/MF, Sycon) by the following equation:[38,39] $\Delta f = (-2.26 \times 10^{-6}\ \mathrm{cm^2/Hz\ g}) f_o^2 \Delta m$, where Δf is frequency change, Δm is the change in mass per square centimeter, and f_o is the reference frequency (6 MHz). SPIAD films are typically deposited for 10 min, corresponding to ion fluences of 0.7−3 × 10¹⁶/cm² and neutral fluences of ~3 × 10¹⁸/cm².

SPIAD films are kept in a vacuum for several hours to allow any residual, unbound 3T to desorb completely from the surface. All SPIAD films are exposed to air intentionally for about 30 min to match exposure time required for some of the

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(18) Baumgartner, K. M.; Volmer-Uebing, M.; Taborski, J.; Bauerle, P.; Umbach, E. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1488.

(19) Land, T. A.; Hemminger, J. C. *Surf. Sci.* **1992**, *268*, 179.

(20) Raza, H.; Wincott, P. L.; Thornton, G.; Casanova, R.; Rodriguez, A. *Surf. Sci.* **1997**, *390*, 256.

(21) Hernandez, J. E.; Ahn, H.; Whitten, J. E. *J. Phys. Chem. B* **2001**, *105*, 8339.

(22) Ahn, H.; Whitten, J. E. *J. Phys. Chem. B* **2002**, *106*, 11404.

(23) Groenewoud, L. M. H.; Engbers, G. H. M.; Terlingen, J. G. A.; Wormeester, H.; Feijen, J. *Langmuir* **2000**, *16*, 6278.

(24) Kiesow, A.; Heilman, A. *Thin Solid Films* **1999**, *343/344*, 338.

(25) Moliton, A. Ion implantation doping of electroactive polymers and device fabrication. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 589.

(26) Usui, H. *Thin Solid Films* **2000**, *365*, 22.

(27) Kim, J.-Y.; Kim, E.-S.; Choi, J.-H. *J. Appl. Phys.* **2002**, *91*, 1944.

(28) Antony, R.; Moliton, A.; Ratier, B. *Appl. Phys. B* **2000**, *71*, 33.

(29) Iannotta, S.; Toccoli, T.; Biasioli, F.; Boschetti, A.; Ferrari, M. *Appl. Phys. Lett.* **2000**, *76*, 1845.

(30) Tepavcevic, S.; Choi, Y.; Hanley, L. *J. Am. Chem. Soc.* **2003**, *125*, 2396.

(31) Hanley, L.; Sinnott, S. B. *Surf. Sci.* **2002**, *500*, 500.

(32) Wijesundara, M. B. J.; Ji, Y.; Ni, B.; Sinnott, S. B.; Hanley, L. *J. Appl. Phys.* **2000**, *88*, 5004.

(33) Fuoco, E. R.; Hanley, L. *J. Appl. Phys.* **2002**, *92*, 37.

(34) Brookes, P. N.; Fraser, S.; Short, R. D.; Hanley, L.; Fuoco, E.; Roberts, A.; Hutton, S. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *121*, 281.

(35) Hanley, L.; Choi, Y.; Fuoco, E. R.; Akin, F. A.; Wijesundara, M. B. J.; Li, M.; Tikhonov, A.; Schlossman, M. *Nucl. Instr. Methods Phys. Res., Sect. B* **2003**, *203C*, 116.

(36) Choukourov, A.; Biederman, H.; Fuoco, E. R.; Tepavcevic, S.; Hanley, L. Deposition of amine containing films from hyperthermal silazane ions; 16th International Symposium on Plasma Chem., Toramina, Italy, 2003.

(37) Yates, J. T., Jr. *Experimental Innovations in Surface Science. A Guide to Practical Laboratory Methods and Instruments*; Springer-Verlag: New York, 1998; p 198.

(38) Dunham, E. C.; Benson, N. H.; Petelenz, D.; Janata, J. *Anal. Chem.* **1995**, *67*, 267.

(39) Caruso, F.; Serizawa, T.; Furlong, D. N.; Okahata, Y. *Langmuir* **1995**, *11*, 1546.

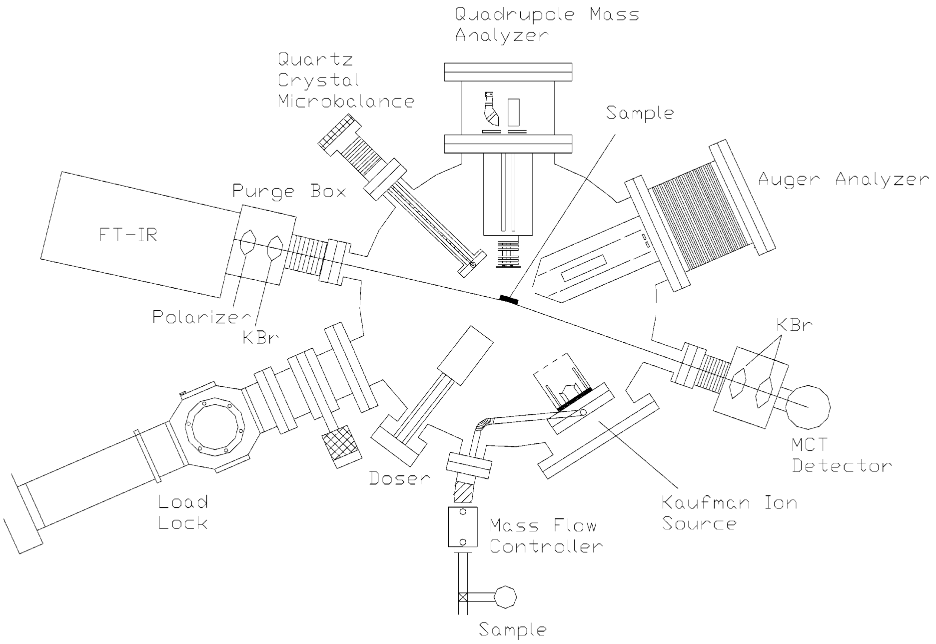

Figure 1. Schematic diagram of surface polymerization by ion-assisted deposition (SPIAD) system with the non-mass-selected Kaufman ion source.

analyses, as required for transfer between instruments. Samples are exposed to air for several hours and approximately 4 days prior to mass spectrometric and UV/vis absorption measurements, respectively.

Films are deposited on indium tin oxide (ITO) coated glass substrates for optical measurements. The ITO substrates are cleaned with methylene chloride, ethanol, and deionized water and then dried in a stream of nitrogen gas. Films are also deposited onto boron-doped Si(100) wafers (380-μm thickness, 76-mm diameter, Atomergic Chemical Corp.) for X-ray photoelectron spectroscopy (XPS). The Si surfaces are prepared by etching with 5% HF solution for 40 s followed by rinsing with deionized water, to remove the native SiO_2 layer and produce a hydrogen-terminated surface. Substrates are held at 300 K during film deposition. Two copper plates on the sample holder can resistively heat the sample substrate, with the temperature measured by a chromel−alumel thermocouple wire inserted in a hole in the sample holder. A copper braid is connected between the back plate and a liquid nitrogen reservoir, allowing cooling of the sample holder to ∼200 K.

B. Optical Characterization by Photoluminescence and UV/Vis Absorption. Photoluminescence (PL) of the films is performed with a fluorescence spectrometer (SLM Aminco 8000C, Champaign, IL) using 390-nm excitation incident at 45° off the surface normal, emission collected from the film backside, at 8-nm resolution. UV/vis absorption is performed with a spectrophotometer (Perkin-Elmer Lambda 14 double beam) modified to focus light into a ∼2-mm spot on the sample surface, with 2-nm resolution and beam normal to the surface.

C. Chemical and Morphological Characterization by X-ray Photoelectron Spectroscopy, Mass Spectrometry, and Atomic Force Microscopy. The apparatus and procedures for XPS were previously described in detail and are only summarized here.[32,35] All XPS data are obtained using a high-resolution monochromatic Al Kα X-ray source (15 keV, 25 mA emission current, VSW Ltd., Macclesfield, Cheshire, U.K., model MX10), 700-mm Rowland circle monochromator (VSW) with a 150-mm concentric hemispherical analyzer (VSW, model Class 150) equipped with a five-channel detector operated at constant energy analyzer mode. Twenty-two electron-volt pass energy is used for high-resolution scans while 44 eV pass energy is used for survey scans. All binding energies are referenced to the C 1s core level photoemission peak of aliphatic/aromatic carbon at 285.0 eV. Peak fitting is performed using the Spectra software with Shirley background and 35:65 Lorentzian:Gaussian product line shape, with corrections for photoionization cross section and analyzer transmission function.

SPIAD films are deposited onto a photo-patterned DIOS chip (Mass Consortium Corp, 3.3 cm × 3.3 cm, 0.5-mm thickness, 1-mm spot diameter) and analyzed with a commercial matrix-assisted laser desorption ionization reflectron time-of-flight mass spectrometer (Voyager-DE PRO 6275, Applied Biosystems) equipped with a N_2 laser at 337 nm. Each mass spectrum is obtained by integrating more than 200 laser shots. DIOS chips are silicon wafers on which a nanostructured oxide layer has been formed. This nanostructured oxide has been shown to enhance desorption of compounds deposited as aqueous solutions, in a process termed desorption ionization on silicon (DIOS).[40−43] DIOS has been applied to the mass spectral analysis of molecular species below ∼5 kDa without addition of the matrix compound usually required in matrix-assisted laser desorption ionization.

Atomic force microscopy of air-exposed SPIAD films is recorded as described previously.[33,35]

All SPIAD films and direct ion deposition films are grown three times for reproducibility except for SPIAD films for XPS and atomic force microscopy where only two films are grown. All work is performed at the University of Illinois at Chicago, except for the UV/vis absorption experiments which are performed at the University of Missouri at St. Louis.

III. Results

A. Optical Properties of SPIAD Polythiophene. Figure 2 shows photoluminescence (PL) spectra of evaporated α-terthiophene (3T) films and SPIAD films formed from co-deposited 100 eV thiophene ions and evaporated 3T at ion-to-neutral ratios of 1/100 and 1/400. The 3T film PL spectra display peaks at 448, 470, and 502 nm as well as a small shoulder at 550 nm. SPIAD films prepared at 1/400 ratio display a blue shift in the PL, with a new peak at 420 nm. By contrast,

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(40) Wei, J.; Buriak, J. M.; Siuzdak, G. *Nature* **1999**, *399*, 243.

(41) Kruse, R. A.; Li, X.; Bohn, P. W.; Sweedler, J. V. *Anal. Chem.* **2001**, *73*, 3639.

(42) Thomas, J. J.; Shen, Z. X.; Crowell, J. E.; Finn, M. G.; Siuzdak, G. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4932.

(43) Shen, Z.; Thomas, J. J.; Averbuj, C.; Broo, K. M.; Engelhard, M.; Crowell, J. E.; Finn, M. G.; Siuzdak, G. *Anal. Chem.* **2001**, *73*, 612.

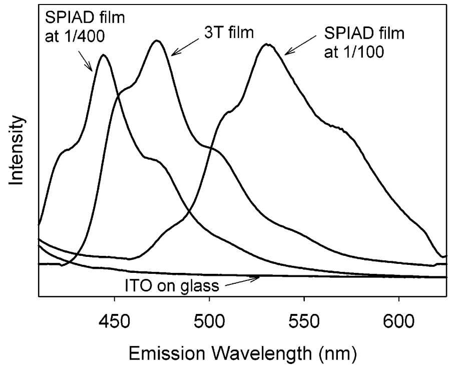

Figure 2. Photoluminescence of a 3T film and several 100 eV SPIAD films prepared at ion-to-neutral ratios of 1/100 and 1/400, all films optically excited at 390 nm.

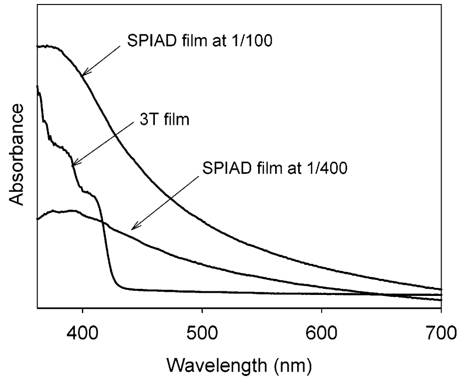

Figure 3. UV/vis absorption of a 3T film and 100 eV SPIAD films at different ion-to-neutral ratios of 1/100 and 1/400.

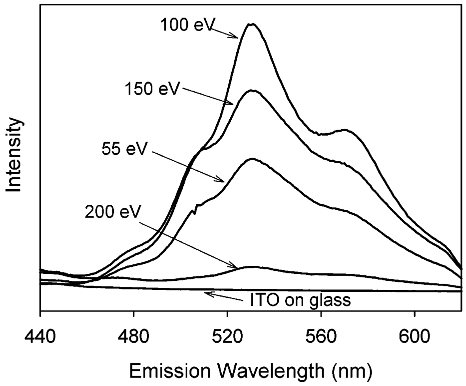

Figure 4. Photoluminescence of SPIAD films at different ion energies of 200, 150, 100, and 55 eV, respectively. 1/100 ion-to-neutral flux ratio is used for all SPIAD films.

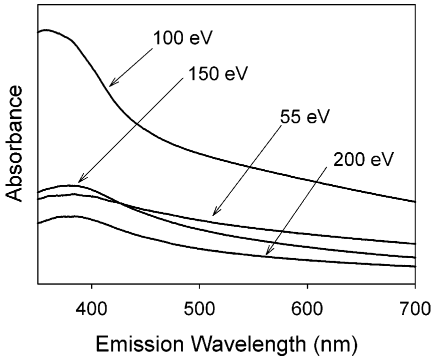

Figure 5. UV/vis absorption spectra of SPIAD films at different ion energies of 200, 150, 100, and 55 eV. 1/100 ion-to-neutral flux ratio is used for all SPIAD films.

Table 1. Comparison of Elemental Composition for Direct Ion-Deposited and SPIAD Films at 1/100 Ion/Neutral Ratios, for Several Ion Energies

	25 eV		100 eV		150 eV	
	direct ion deposition	SPIAD	direct ion deposition	SPIAD	direct ion deposition	SPIAD
C (%)	57	69		71	64	72
S (%)	43	31		29	36	28
C/S ratio	1.3	2.2		2.4	1.8	2.6

SPIAD films prepared at a 1/100 ratio red shift with two new peaks at 535 and 570 nm. The blue and red shifts in PL between SPIAD and 3T films are not due to simple film thickness or substrate annealing affects. However, intensities of the three PL peaks of the 3T film do depend on the substrate temperature during deposition, with the 470- and 502-nm peak intensity increasing with film thickness and the 448-nm peak intensity increasing as the substrate is cooled from 300 to 200 K. This change in 3T PL spectra with substrate temperature during deposition is attributed to molecular orientation and/or film thickness effects, the latter resulting from changes in 3T sticking coefficient. Direct ion-deposited films do not show any PL peak in this spectral region (data not shown).

Figure 3 shows the UV/vis absorption spectra of 3T and SPIAD films at different ion-to-neutral ratios of 1/100 and 1/400. Absorption spectra of SPIAD films at 1/400 and 1/100 ratio are similar to each other, but differ from that of the 3T film. Broad tailing absorption ranging from 400 nm to at least 600 nm is characteristic of the SPIAD films, but 3T films do not absorb to the red of 420 nm. Strong optical absorption of ITO-coated glass begins at wavelengths shorter than 350 nm, only permitting UV/vis absorption measurements from 360 nm. Direct ion-deposited films display only a UV/vis absorption peak from 400 to 500 nm that is very weak compared to the 3T or SPIAD films (data not shown).

The effect of ion energy on the PL spectra of SPIAD films at 1/100 ion-to-neutral ratio is shown in Figure 4. PL intensity varies with ion energy in this order: $100 > 150 \approx 55 \gg 200$ eV, based on the spectra shown in Figure 4 and those of other films prepared under similar conditions. The effect of ion energy on the UV/vis absorption of SPIAD films is shown in Figure 5. The absorption peak at 390 nm in the 200 eV SPIAD film is the lowest of all four films while the 100 eV film displays the strongest absorbance. Furthermore, the UV/vis absorption at 390 nm (Figure 3) correlates with the PL trends for ion energy, indicating the dependence of PL upon the efficiency of excitation at 390 nm.

B. Chemical Content of SPIAD Polythiophene Films. X-ray photoelectron spectroscopy and mass spectrometry are used to analyze the SPIAD films prepared with 100 eV ions and 1/100 ion/neutral ratios, as these films display the most interesting optical properties. Previous work has discussed the direct deposition of thiophene ions,[33] which is only discussed here in comparison with SPIAD.

Table 1. shows that ion energy controls the elemental composition of both SPIAD and direct ion-deposited films. The C/S ratio of the SPIAD films ranges from 2 to 3 while it is <2 for the direct ion-deposited films. There is only a slight difference in the elemental content of direct ion-deposited films between 25 and 150 eV ion

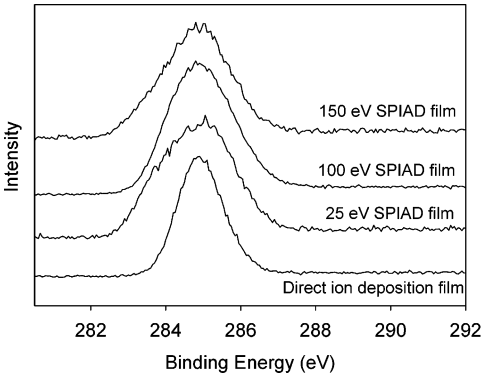

Figure 6. Core level C 1s scans of direct ion-deposited and SPIAD films at different ion energies and ion/neutral ratios of 1/100, measured by XPS.

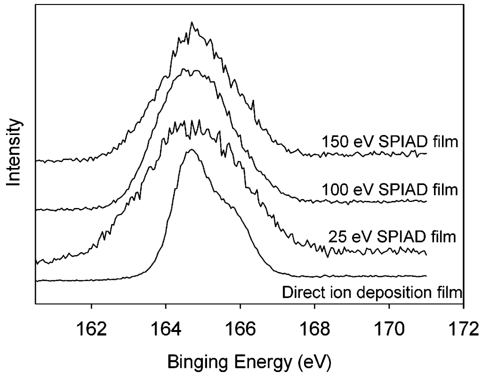

Figure 7. Core level S 2p scans of direct ion-deposited ion and SPIAD films at different ion energies and ion/neutral ratios of 1/100, measured by XPS.

energy, with carbon content slightly lower and sulfur content slightly higher at 25 eV. By contrast, the elemental content of SPIAD films between 25 and ≥100 eV is relatively constant.

Figure 6 shows core level C 1s scans of direct ion-deposited and SPIAD films at different incident ion energies, measured by XPS. The sulfur content does not strongly shift the aliphatic/aromatic C 1s peak at 285.0 eV, in general agreement with measurements on polythiophene and oligothiophene films. However, the core level C 1s scans do show wider peak widths of ~2.0 eV (fwhm) for SPIAD films compared with ~1.7 eV for direct ion-deposited films. The widths of the C 1s and S 2p XPS peaks indicate the presence of multiple species in the SPIAD films, as discussed further below.

Figure 7 shows the core level S 2p scans of direct ion-deposited and SPIAD films at various ion kinetic energies, measured by XPS. Direct ion-deposited films clearly display the $2p_{3/2}$ and $2p_{1/2}$ spin−orbital splitting, with the expected intensity ratio of ~2/1, but this feature is not as clear in the SPIAD film spectra due to peak broadening.

XPS survey scans (data not shown) show no silicon signal and less than 1% of oxygen content when the films are intentionally exposed to air for ~30 min (required for air transfer between instruments prior to XPS analysis). Oxygen content of 100 eV SPIAD films aged for 4 weeks is measured to be ~10%. It is therefore estimated that the oxygen content of the SPIAD films is a few percent at the time of the UV/vis measurements, which are made after several days of air exposure.

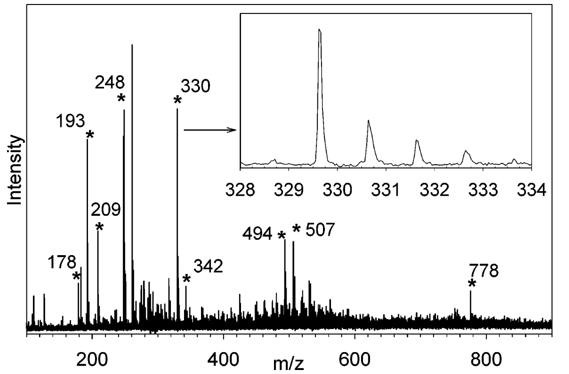

Figure 8. Mass spectra of 100 eV SPIAD film, deposited at an ion-to-neutral ratio of 1/100 on a nanostructured, oxidized silicon surface (DIOS chip).

Table 2. Intensities of M + 1 and M + 2 Peaks Relative to Their Main Peaks M for Mass Spectra of the 100 eV, 1/100 Ion/Neutral Ratio SPIAD Films (i.e., Figure 8), Reported as Average of Several Spectra

	M	M + 1	M + 2	ion
m/*z*	178	179	180	
calc	100		8.8	$[T_2CH]^+$
expt		14.3 ± 2.3	14 ± 8	
m/*z*	193	194	195	
calc	100		8.8	$[T_2C_2H_3]^+$
expt		13.7 ± 3.8	11.7 ± 6.0	
m/*z*	209	210	211	
calc	100		8.8	$[T_2CHS]^+$
expt		16 ± 2	21 ± 5.3	
m/*z*	248	249	250	
calc	100		13.2	$[3T]^+$
expt		60 ± 33	22.5 ± 6.8	
m/*z*	330	331	332	
calc	100		17.6	$[3T]T^+$
expt		40 ± 19	23.7 ± 4.3	
m/*z*	342	343	344	
calc	100		17.6	$[3T]TCH^+$
expt		29.3 ± 9.3	37 ± 5	
m/*z*	494	495	496	
calc	100		26.4	$[3T]_2{}^+$
expt		44 ± 12	40 ± 3.2	
m/*z*	507	508	509	
calc	100		26.4	$[3T]_2CH^+$
expt		58.3 ± 9.1	45 ± 3.3	
m/*z*	778	779	780	
calc	100		39.6	$[3T]_3C_3H_2{}^+$
expt		*a*	51 ± 5.4	

[a] Indicates a very low signal-to-noise ratio. T = C_4H_4S.

Mass spectra of 100 eV SPIAD films at an ion-to-neutral ratio of 1/100 are shown in Figure 8. Peak assignments as well as experimental and calculated relative intensities of M + 2 isotopes for those assigned peaks are displayed in Table 2. Multiple peaks are observed which correspond to polymerization products. The highest mass peak of SPIAD film at 100 eV is seen at *m*/*z* 778 and is assigned as $[3T]_3C_3H_2{}^+$. Other prominent peaks at *m*/*z* 507, 494, 342, 330, and 248 are assigned as $[3T]_2CH^+$, $[3T]_2{}^+$, $[3T]TCH^+$, $[3T]T^+$, and $[3T]^+$, respectively (where T = C_4H_4S). The high experimental M + 2 values are consistent with the expected contributions from ^{34}S isotopes. The fact that the experimental M + 2 isotopic ratios in Table 2 are greater than the calculated values indicates contributions from the M + 1 isotope of protonated ions. For example, M^+ for the $[3T]^+$ ion occurs at *m*/*z* 248, the *m*/*z* 249 ion has contributions from both [3T]H$^+$ and the ^{13}C-containing peak of [3T]$^+$, and the *m*/*z* 250 peak has contributions from both the ^{34}S-containing peak of [3T]$^+$ and the ^{13}C containing peak of [3T]H$^+$. Similar isotopic contributions appear for all of the 3T-containing ions, although with variations in the protonated peak intensity. Dissociation peaks are observed below *m*/*z* 248, which correspond to 3T fragments with attached thiophene ion fragments (see Table 2 for assignments). The 3T film shows only the [3T]$^+$ peaks at *m*/*z* 248, 249, and 250 in the mass spectrum (not shown) with less than 0.1% relative intensity (with respect to *m*/*z* 248) of higher mass peaks, indicating that the SPIAD film mass spectra do not result from photopolymerization during laser desorption. Furthermore, mass spectra of the 3T only film display M + 1 and M + 2 peaks whose intensities are consistent with the ^{13}C and ^{34}S isotopes of the M peak at *m*/*z* 248. Thus, the 3T only film appears to lack the protonated peaks that enhanced M + 1 and M + 2 intensities in the SPIAD films.

C. Structural Characterization of SPIAD Polythiophene. Atomic force microscopy of SPIAD films prepared at 100 eV display random features with a RMS roughness of ∼60 nm (data not shown). 3T only films display randomly oriented grains of several hundred nanometer size, with a RMS roughness of ∼100 nm.[44] Direct ion-deposited films are very smooth, with RMS roughness <1 nm.[35] SPIAD films are strongly adhered to the surface. No information on orientation of the polythiophene chains is available from these experiments.

IV. Discussion

A. Summary of Results. SPIAD using 50−200 eV non-mass-selected thiophene ions and α-terthiophene (3T) neutrals produces polythiophene films that display unique optical and chemical properties. These optical properties are strongly controlled by the thiophene ion kinetic energy and the ion-to-3T neutral ratio. An ion-to-neutral ratio of 1/400 blue shifts the photoluminescence (PL) of the SPIAD film compared with evaporated 3T films, leading to a new peak at 420 nm (Figure 2). An ion-to-neutral ratio of 1/100 red shifts the PL of the SPIAD film, leading to two new peaks at 535 and 570 nm. SPIAD films also display a broad red shift in the UV/vis spectra compared to 3T films (Figure 3). Figures 4 and 5 show that ion kinetic energy controls peak intensities of both PL and UV/vis in the SPIAD film at 1/100 ion-to-neutral ratio. The most intense PL and strongest UV/vis absorption is observed for SPIAD films prepared at 100 eV kinetic energy.

The thiophene ion kinetic energy also controls the film chemistry of the 100 eV SPIAD film (Table 1). Sulfur content of the direct ion-deposited films formed at 25 and 150 eV is ∼40% while sulfur content of the 100 eV SPIAD film is ≤30%, closer to the theoretical value of 25% for polythiophene. Additional chemical analyses of these 100 eV SPIAD films are performed due to their enhanced optical properties. Core level C 1s and S 2p XPS data (Figures 6 and 7) as well as mass spectra (Figure 8 and Table 2) indicate a distribution of species in the 100 eV SPIAD film which includes 3T, 3T dimers, 3T trimers, and adducts of same. Higher molecular weight oligomers such as these display longer electron conjugation lengths,[16] contributing to the red shifts in the PL and UV/vis absorption in the SPIAD films. By contrast, direct ion-deposited films do not display such optical shifts, indicating a lack of extended electron conjugation. Aggregates and/or quenching traps may also contribute to the observed optical effects in the SPIAD films, as described further below.

B. Formation of Higher Molecular Weight Oligomers. The PL of SPIAD film at 1/100 ion-to-neutral ratio and the extended UV/vis absorption is correlated to the formation of oligomers of long conjugation length. Polythiophene as well as higher order oligomers such as 4T, 6T, and 8T[16] display similar PL and UV/vis spectral features to those observed here for SPIAD films prepared at an ion energy of 100 eV and 1/100 ion-to-neutral ratio. The observation of higher molecular weight species such as 3T dimers, 3T trimers, and adducts of same by mass spectrometry supports their presence in the SPIAD films (Figure 8 and Table 2). SPIAD forms a distribution of different oligomers, although the mass spectra cannot be directly converted into the exact mass distribution of those oligomers in the film due to the possibility of fragmentation during desorption or preferential ionization. Furthermore, the exact structure of these higher molecular weight oligomers has not been determined here, and they may not be linear with the normal α−α bonding.

The widths of the C 1s and S 2p XPS peaks also support the presence of multiple oligomers in the SPIAD films (see Figures 6 and 7). A 0.34 eV difference has been observed between the C 1s peaks of carbons α and β to the S atom in polythiophene.[45] This small shift, superimposed over the several different oligomers observed by mass spectrometry in the SPIAD films, leads to the C 1s peak broadening compared with the direct deposited films. A similar effect of multiple species leads to the loss of the resolved spin−orbit splitting of the S 2p peak in the SPIAD films.

UV/vis absorption of 3T films on quartz substrates previously showed four unique peaks in the range of 310−420 nm and an overall spectrum whose shape was symmetric with its PL spectrum,[46] in general agreement with Figures 2 and 3. PL of 100 eV SPIAD films prepared at 1/100 ion-to-neutral ratio displays five peaks while its UV/vis absorption spectra display only one main peak near 380 nm. The complete UV/vis spectra cannot be seen in our experiment due to strong absorption of the ITO-coated glass substrate. However, the PL and UV/vis spectra of the SPIAD film clearly lack the symmetry of the 3T films. These spectral changes from 3T to SPIAD films are further evidence of modification of the 3T electronic structure during ion-induced polymerization. Band gaps of this SPIAD film are 3.2 eV, compared with 3.6 eV of the 3T film, if calculated from the maximum in the UV/vis spectra.[47] The onset of the UV/vis absorption can also be used to

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(44) Tepavcevic, S.; Choi, Y.; Wu, C.; Hanley, L. **2004**, submitted.

(45) Jugnet, Y.; Tourillon, G.; Duc, T. M. *Phys. Rev. Lett.* **1986**, *56*, 1862.

(46) Bosisio, R.; Botta, C.; Colombo, A.; Destri, S.; Porzio, W.; Grilli, E.; Tubino, R.; Bongiovanni, G.; Mura, A.; Di Silvestro, G. *Synth. Met.* **1997**, *87*, 23.

(47) Schroeder, P. G.; France, C. B.; Park, J. B.; Parkinson, B. A. *J. Phys. Chem. B* **2003**, *107*, 2253.

estimate the band gap,[48] which if applied here would indicate an even greater reduction in band gap from 3T to the SPIAD film. The increased UV/vis absorption in the red for the SPIAD films is predominantly attributed to the formation of higher molecular weight oligomers.

C. Changes in Film Organization. SPIAD films formed at 100 eV and 1/400 ion-to-neutral ratio display a blue shift in the PL with a new peak at 420 nm (compared with 3T). Polymerization is also occurring here, but this blue shift cannot be readily explained simply by the formation of higher molecular weight oligomers. Instead, this blue shift is likely caused by competing effects of film organization, such as the formation of aggregates or other supramolecular structures.[46,49] The density of nucleation sites leading to polymerization will be affected by the ion-to-neutral ratio, leading to control of aggregate structure, as has been argued for electron and X-ray induced polymerization of 3-hexylthiophene.[22] Formation of abundant MH^+ peaks in the mass spectra which are not observed in the 3T only films are indicative of free hydrogen content in the films as a result of ion bombardment. Differences in the free hydrogen content might also affect aggregate formation, which in turn will affect the optical properties.

Ion-to-neutral ratio has also been found previously to strongly affect optical properties of conducting polymers formed by ion-assisted deposition.[26−28] Overall, it is clear that ion-to-neutral flux is critical to the appearance of PL spectra, with a high ratio of ions reducing PL. Besides affecting the formation of aggregates, it has been argued that ions form radicals on the surface which behave as quenching traps for PL. Radicals as quenching traps may also be significant in SPIAD polythiophene. Given that aggreates and quenching traps play a role in the SPIAD films that display red-shifted PL, they may also affect the optical properties of the blue-shifted films.

D. Ion Energy Control of Film Structure. Ion energy also affects PL and UV/vis absorption of the SPIAD films, as seen in Figure 4. PL intensity at 535 nm of the 100 eV SPIAD film is much higher than films prepared at other ion energies. The UV/vis absorption of the 100 eV SPIAD film is also several times higher than that of the 200 eV SPIAD film, qualitatively (but not quantitatively) following the trend in PL intensity. The differences in PL intensity and UV/vis absorbance with ion energy are attributed to changes in film structure, including the possible formation of aggregates. Preliminary measurements using a quartz crystal microbalance indicate that these changes in optical properties cannot be attributed to different film thicknesses, as film thickness appears relatively independent of ion energy (results to be published). The 150−200 eV polyatomic ions are more likely to damage or sputter adsorbed 3T films than are $\leq$100 eV ions, thereby reducing the number of undamaged, optically active monomers available for polymerization. Previous reports of organic films deposited by other ion-assisted deposition strategies have found different optimal ion energies than observed here,[26,28] suggesting a dependence upon ion structure.

E. Film Oxidation and Substrate Effects. Previous studies found removal of oxygen impurities as ion energy was increased led to an enhanced PL intensity.[26] Oxygen behaving as a quenching trap in a polythiophene film was also reported by other workers.[50] The effect of oxygen as a quenching trap on PL is less significant here because of the low oxygen content of <1%. However, our studies show a decrease of PL intensity in aged SPIAD film, indicating the adverse effect of oxygen on film optical properties. The delay in measuring UV/vis absorption prevents determination of the oxidation effect, but an effect is expected.

SPIAD films are deposited on H-terminated silicon wafers for XPS and ITO-coated glass for optical measurements. More recent studies have deposited SPIAD films on gold-coated substrates used in a quartz crystal microbalance (results to be published). Deposition has been efficient for all three types of substrates, but a direct comparison is difficult here as the different substrates are utilized to facilitate different methods of film characterization. However, the film thicknesses are in excess of several hundred nanometers, which combined with the hyperthermal ion energies should overcome any effects of substrate upon film structure.

F. Comparison with SPIAD by Mass-Selected Ion Deposition. Simultaneous studies at UIC have utilized mass-selected thiophene ions in SPIAD for polythiophene film growth during simultaneous 3T evaporation,[30] with a full report to be published.[44] Similar surface polymerization is observed at similar, but not identical, ion energies and ion/neutral ratios with both mass-selected and non-mass-selected thiophene ion sources. This indicates that the radicals, photons, and low-energy electrons emanating from the non-mass-selected ion source are not the predominant initiator of polymerization. Nevertheless, either these non-ion events or effects of ion flux must contribute to the SPIAD event, given that nanostructures are readily observed only on the films prepared by mass-selected ion deposition[44] and not here. It is possible that radiative heating, photolysis, radicals, or thiophene ion fragments emitting here from the non-mass-selected ion source destroy the nanostructures observed as forming during mass-selected ion deposition.[44] However, the mass-selected ion studies have shown that the size and distribution of these nanostructures are correlated with the extent of polymerization, in support of arguments made above.

G. Comparison of SPIAD to Wet Methods. Casting or spin-coating of organic films[9−11] and electropolymerization[12−14,51] are the most popular methods of preparing polythiophene films. Variation of the optical properties of such films are typically achieved through changing the chemical structure of the precursor, the conditions of electropolymerization, and/or the liquid deposition parameters.[15] For example, varying the alkyl chain length and applied potential in electropolymerization of poly(alkylthiophene) films shifted the peak in their UV/vis absorbance by ~100 nm, from ~420 to

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(48) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.

(49) Yang, A.; Kuroda, M.; Shiraishi, Y.; Kobayashi, T. *J. Chem. Phys.* **1998**, *109*, 8442.

(50) Kaminorz, Y.; Smela, E.; Inganas, O.; Brehmer, L. *Adv. Mater.* **1988**, *10*, 765.

(51) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.

~520 nm. By comparison, tuning the ion energy and ion/neutral ratio shifts the peak in the UV/vis absorbance of SPIAD polythiophene films by ~20 nm, but the tail in the absorption curve is extended from ~430 nm (for 3T only films) to >600 nm (for SPIAD films). The flexibility of the SPIAD method is yet clearer when it is considered that changing the ion and/or neutral species used in SPIAD will also have a dramatic effect on film optical properties. Furthermore, SPIAD films do not have the entrained solvents known to affect optical properties.[15]

V. Conclusions

Polythiophene films are produced via surface polymerization by ion-assisted deposition, in which 55−200 eV thiophene ions and α-terthiophene (3T) neutrals are co-deposited on surfaces. These SPIAD polythiophene films display unique optical properties in their photoluminescence and UV/vis absorption compared with films prepared by either 3T or direct thiophene ion deposition only. The optical properties of SPIAD polythiophene depend on the ion-to-neutral ratio and ion energy used. Ion-to-neutral ratios of 1/100 cause a red shift in the photoluminescence of SPIAD films compared with 3T films whereas ratios of ~1/400 cause a blue shift. The most enhanced photoluminescence and UV/vis absorption for SPIAD is observed with 100 eV ions, compared with 3T films. Mass spectrometry indicates that a variety of higher molecular weight oligomers with masses up to $[3T]_3$ are formed in SPIAD, but does not reveal whether these oligomers are bonded at carbon atoms α or β to the sulfur atom of the thiophene ring. UV/vis spectra and X-ray photoelectron spectroscopy support the formation of a distribution of oligomers, while the latter method reveals elemental content consistent with polythiophene. The higher molecular weight oligomers formed by SPIAD display longer electron conjugation lengths and are therefore a major contributor to the red shifts in the PL and UV/vis in the SPIAD films. By contrast, direct ion-deposited films do not display such optical shifts, indicating a lack of extended electron conjugation.

The low ion-to-neutral ratios utilized here indicate that the thiophene ions may only serve as initiators or catalysts for surface polymerization, in a type of cationic polymerization.[28] However, this assumes that the sticking coefficients for the thiophene ions and 3T neutrals are similar. Comparisons of 3T adsorption at 300 vs 200 K indicate the sticking coefficient of 3T at 300 K, where the SPIAD films are formed, is probably much lower than unity. By contrast, our previous experience indicates near unity sticking coefficients for hyperthermal ion deposition.[33] Furthermore, it is unclear from the mass spectra whether the thiophene fragments incorporated into many of the oligomers derive from fragmented 3T (indicating ions as catalysts) or the thiophene ion (indicating bi- or termolecular collisions involving ions). Elucidating the role of the ion in the surface polymerization event is the subject of ongoing work.

SPIAD has been demonstrated here for the formation of a novel type of polythiophene film from one distribution of polyatomic ions (~65% $C_4H_4S^+$ and ~35% fragments thereof) and one evaporated oligomer. However, the method is clearly applicable to a wide range of different ions and neutral species and is limited only by the ability to vaporize and ionize candidate reagent species. SPIAD is essentially combinatorial in nature in that the ion energy, ion structure, ion fragment distribution, ion kinetic energy, neutral structure, ion-to-neutral ratio, and substrate temperature can all be varied to create libraries of candidate films which can then be rapidly probed for target properties. This approach is employed here, by first searching across a wide parameter space of ion energy and ion-to-neutral ratios for films with interesting optical properties and then chemically characterizing only the most promising films. Furthermore, SPIAD is a “green” or environmentally sound manufacturing process, in that it uses very small amounts of reagents and essentially no solvents.

The non-mass-selected ion SPIAD method described here can be scaled up to a commercial film growth method by use of larger area ion beams. Furthermore, the relatively high ion current allows rapid film growth. By contrast, the mass-selected ion SPIAD method is most useful for mechanistic and spectroscopic studies of film growth and the cationic polymerization event, as it allows exclusion of fragment ions, radicals, and photons from the source.

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