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Surface Polymerization by Ion-Assisted Deposition for Polythiophene Film Growth

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Organic cations can induce polymerization of monomers in the liquid phase.[1] Ion−molecule reactions in the gas phase can lead to the formation of large ions, clusters, and even macroscopic particles.[2−4] This communication demonstrates that cationic polymerization can also be induced at the gas−solid interface by hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers. It is shown here that this surface polymerization by ion-assisted deposition (SPIAD) produces films that maintain the monomer's chemical structure.

Oligo- and polythiophenes have been extensively explored as conducting polymers for use in light-emitting diodes, electrochromic devices, field effect transistors, antistatic coatings, sensor films, organic photovoltaics, and recording materials.[5−7] New methods of growing polythiophene films with desired optoelectronic properties are critical to the success of these various applications. A polythiophene film is produced here by SPIAD with 100 eV thiophene ions and terthiophene monomers coincident on Si and indium tin oxide (ITO) substrates held under vacuum. The polythiophene displays fluorescence and Raman spectral features similar to terthiophene films.

Strategies utilizing polyatomic ion deposition display great promise for creation of new types of polythiophene and other classes of conducting polymers. Fluorocarbon and siloxane polymeric films have been deposited directly onto various substrates from mass-selected, gaseous, organic cations with 5−200 eV kinetic energies.[8−12] Mass-selected organic cations (>20 eV)) have been shown to create selective chemical bonds with self-assembled monolayers[13,14] and carbon nanotubes.[15] Ion-assisted deposition from a non-mass-selected source has produced new conducting polymers.[16,17] Atomic ions with 1−100 keV kinetic energies have been used to produce carbonaceous films from gaseous thermal beams of organics.[11,18] Kiloelectronvolt atomic ions have also been utilized to modify polymer films,[11] sometimes with the goal of creating conducting polymers.[19] However, the SPIAD method described here allows more control over film properties than the aforementioned ion-deposition methods and occurs by an unambiguous cationic polymerization mechanism. Furthermore, the polythiophene films produced by SPIAD display an important property of a conducting polymer, fluorescence in the UV/vis region.

SPIAD is performed by combining thiophene ion deposition with simultaneous dosing of α-terthiophene vapor. Beams of mass-selected thiophene ions (60 nA) are produced by electron impact, as previously described.[9,20] The doser[21] is heated resistively to between 300 and 440 K such that the pressure rise due to terthiophene is on the order of ∼5 × 10⁻⁶ Torr. One to 4 h are required to prepare a single thin film of a few square millimeters area by mass-selected ions. Monochromatic X-ray photoelectron spectra (XPS) are recorded at 44 eV of pass energy and normal takeoff angle without air exposure following deposition, as previously described.[9,20] Films are also prepared in a different apparatus by 20 min of non-mass-selected polyatomic ion deposition. This
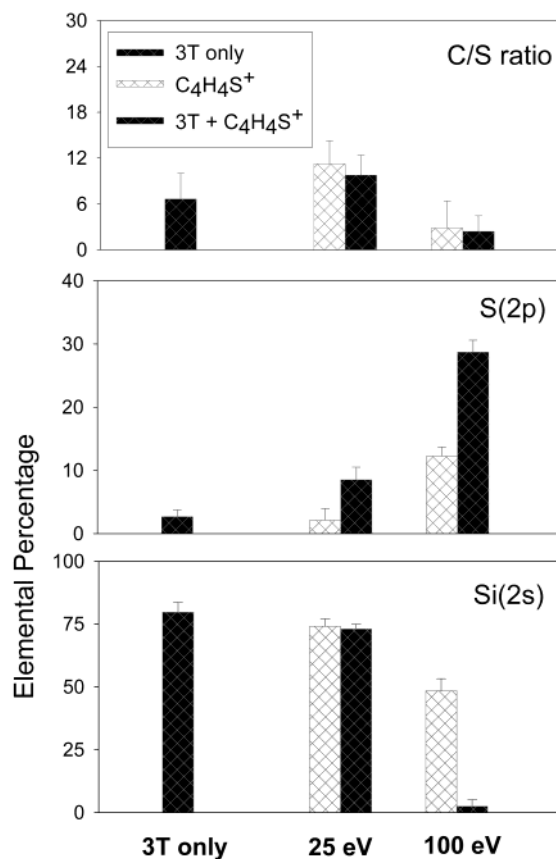

Figure 1. S and Si percentages as well as C/S ratios for films grown on H−Si(100) substrates from 25 and 100 eV $C_4H_4S^+$, surface polymerization by ion-assisted deposition (SPIAD) with 25 and 100 eV $C_4H_4S^+$ and thermal terthiophene (3T) and thermal terthiophene alone. All $C_4H_4S^+$ ions are mass-selected, with fluences of 10^{16} ions/cm².

method uses a broad beam Kaufman ion source (Veeco-CS, 3 cm Ion Source) tuned such that the parent ion $C_4H_4S^+$ constitutes over 60% of the ∼100 nA/cm² total ion current.[22]

The XPS data is reported for deposition on hydrogen-terminated Si substrates.[12] The fluorescence data is recorded for films deposited on transparent ITO-coated glass substrates cleaned in solvents prior to deposition. Fluorescence spectroscopy is performed with 370-nm excitation at 45° off the surface normal, emission collection from the film backside, at 8-nm resolution (SLM Aminco 8000c, Champaign, IL). Raman spectra are recorded with 514.5-nm Ar⁺ laser excitation (Renishaw Ramanscope 2000, Gloucestershire, UK).

Surface polymerization is clearly evidence in the SPIAD films when analyzed by XPS. Figure 1 displays the elemental content by XPS of the top ∼10 nm of films evaporated directly from terthiophene (labeled "3T only"), 25 or 100 eV thiophene ion deposition alone ("$C_4H_4S^+$"), and 25 or 100 eV SPIAD ("3T + $C_4H_4S^+$"). SPIAD leads to a 2- to 3-fold increase in the total S

Scheme 1. Polythiophene Film Formation by SPIAD with 100 eV $C_4H_4S^+$ and Thermal Terthiophene

content in the film compared with only isoenergetic thiophene ions. One hundred electronvolt SPIAD leads to a 10-fold increase in S compared with neutral dosing alone and a 3-fold increase compared with 25 eV SPIAD. The Si content for 100 eV SPIAD is lowest of all, indicating a film thickness >10 nm.

The C/S ratios for terthiophene dosing alone are within error bars of the theoretical value of four, with the mean exceeding this C/S ratio due to contributions from adventitious carbon on the Si substrate. Both direct deposition and SPIAD with 25 eV ions lead to high C/S ratios of ~10 that are indicative of low sulfur content in the deposited film. Both direct deposition and SPIAD with 100 eV ions lead to low C/S ratios of ~3, consistent with polythiophene. Low oxygen content of less than a few percent is due largely to residual oxide and contaminants on the Si surface prior to deposition (data not shown).

SPIAD films deposited at 100 eV display fluorescent spectral features and peak intensities similar to those of films of terthiophene monomers. Terthiophene films display a well-established fluorescence spectrum with two peaks at 448 and 471 nm when excited at 380 nm, but no significant fluorescence at 400 nm.[23] The fluorescence intensity ratios for $I_{\lambda=448\ nm}/I_{\lambda=400\ nm}$ and $I_{471\ nm}/I_{400\ nm}$ are >5 for both mass-selected and non-mass-selected 100 eV SPIAD films. The ITO substrate does not fluoresce here.

Raman spectra of non-mass-selected 100 eV SPIAD films display strong vibrations at 1460 and 1530 cm^{-1} that are also observed in terthiophene films (see Supporting Information).[24,25] These Raman features are strongest for films produced with low ion currents, and they also display weaker vibrations at 690 and 1050 cm^{-1}. High ion currents lead to films with weak Raman lines at 1460 and 1530 cm^{-1} only, which are broadened similar to doped polythiophene.[25] 1530 cm^{-1} is assigned to a C=C antisymmetric stretch, 1460 cm^{-1} to a C=C symmetric stretch, 1050 cm^{-1} to a C−H bend, and 690 cm^{-1} to a C−S−C deformation.[24,25]

The final experimental result is the vacuum stability of the SPIAD polythiophene films. Terthiophene films are not stable under vacuum, unlike the higher-order oligothiophenes.[5] Thus, the terthiophene films prepared by evaporation are rapidly removed from vacuum to prevent sublimation. By contrast the SPIAD films are stable in a vacuum for over 4 h, a period during which pure terthiophene films are observed to completely sublime. Surface polymerization of terthiophene leads to formation of higher-molecular weight, less volatile polythiophene. Scheme 1 portrays one of several classes of feasible polymer structures for SPIAD-produced polythiophene.

These results clearly indicate that SPIAD proceeds by a cation-induced polymerization mechanism. Both mass-selected and non-mass-selected beams of thiophene ions cause surface polymerization of terthiophene. Evidence of a form of polythiophene is the C/S ratio, fluorescence, Raman spectra, and vacuum stability. The monomeric terthiophene unit remains intact for a significant fraction of the polymerization, as indicated by fluorescence and Raman data. Ion-induced surface polymerization of neutrals has been proposed as a growth mechanism of polymer films from plasmas[2,11] and non-mass-selected ion-assisted deposition.[16,19] However, it is difficult to determine film growth mechanisms from such complex, multiparticle environments. For example, pyrolytic formation of radicals can also contribute to surface polymerization with the participation

of radicals.[2,26] The data here shows that ions play a critical role in film growth from non-mass-selected ions, in addition to any radical or photochemically driven processes that may also occur.

These results show that SPIAD should be a viable method for the growth of a wide variety of conducting polymers and other organic thin films. SPIAD should also permit the nanostructuring of these films, since polyatomic ions only interact with the top few nanometers of a surface.[9,11,22,27] The selection of ion structure, energy, and ion/neutral flux ratio will tune between the various deposition, polymerization, surface decomposition, and diffusion processes that collectively control the surface morphology. Furthermore, non-mass-selected ion sources can be used to grow these films on a large scale.

Supporting Information Available: Raman spectra of films grown on ITO substrates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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