

Growth of phenylene vinylene thin films via surface polymerization by ion-assisted deposition

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Abstract

Surface polymerization by ion-assisted deposition was used to grow phenylene vinylene films (SPIAD-PPV) using the evaporation of 2-methoxy-5-(2'-ethylhexyloxy)-1,4-bis((4',4''-bisstyryl) benzene) (MEH-OPV5) and the simultaneous deposition of non-mass-selected 10–200 eV thiophene or acetylene ions. Images recorded by scanning electron microscopy showed differences in SPIAD-PPV film morphology versus evaporated MEH-OPV5 that indicated changes in the underlying chemical structure. Spectroscopic differences between MEH-OPV5 and SPIAD-PPV films suggested preferential attack of vinylene groups and/or hydrocarbon side chains. A possible explanation for the changes in morphology and electronic structure was cross-linking at vinylene sites of adjacent MEH-OPV5 molecules which could lead to changes in molecular packing. Although morphological and electronic differences were seen for SPIAD-PPV films, these films still showed valence bands characteristic of phenylene vinylenes.

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1. Introduction

Poly(phenylene vinylene)s (PPVs) are commonly used as electron donor materials in optoelectronic applications due to enhanced charge carrier transport of the conjugated system [1–4]. Changing the degree and functionality of substitution along the PPV backbone has resulted in variation of charge carrier transport [5,6]. Phenylene vinylene oligomers can be used as model systems for phenylene vinylene polymers, allowing for vapor-phase deposition and *in situ* characterization. A five ring PPV oligomer, 2-methoxy-5-(2'-ethylhexyloxy)-1,4-bis((4',4''-bisstyryl) benzene) (MEH-OPV5), and C₆₀ have been shown to act as an electron donor/acceptor pair in a photovoltaic device, displaying power conversion efficiencies of up to 2.2% [7,8].

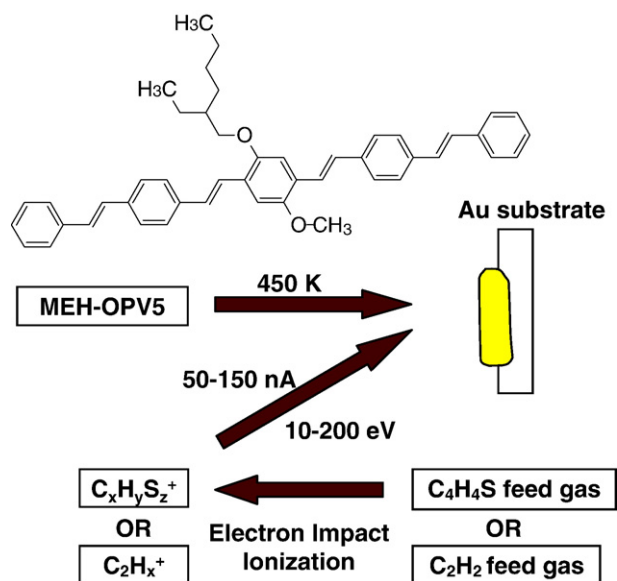
Atomic ions with keV energies have been used to modify the electronic structure of conducting polymer films [9]. Ion-surface modification with hyperthermal (1–500 eV) kinetic energies has

been used to deposit thin films, chemically functionalize surfaces, create interfacial structures on the order of microns and nanometers, and modify the phases of interfaces [10,11]. For example, hyperthermal hydrocarbon ions energies have been used for deposition of carbonaceous films [10,12] while hyperthermal CF₃⁺ and C₃F₅⁺ have been shown to chemically modify polystyrene films [11,13]. Hyperthermal polyatomic ions have also been used to impart functional groups to polymer films [12] and ion-etch semiconductor surfaces [14]. Polymeric thin films have been formed by 10 eV protons that selectively break C–H bonds and cross-link adsorbed organic molecules [15–17].

Surface polymerization by ion-assisted deposition (SPIAD) is a method by which polymer films are grown by the simultaneous deposition of hyperthermal ions and thermally evaporated neutrals (see Scheme 1). SPIAD was found previously to grow thin polythiophene films with a shifted valence band [18–20]. For example, ultraviolet photoelectron spectroscopy showed differences in valence band structure and energy level alignment between evaporated terthiophene films and polythiophene films produced via SPIAD [21]. Control of

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Scheme 1. Surface polymerization by ion-assisted deposition (SPIAD) of thermally evaporated MEH-OPV5 neutrals and non-mass-selected 10–200 eV thiophene ions ($C_xH_yS_z^+$) or acetylene ions ($C_2H_x^+$).

film morphology in SPIAD was achieved by variation of ion:neutral ratio and ion energy [22].

This paper examines changes in the morphology and electronic structure of phenylene vinylene films prepared by SPIAD using the evaporation of MEH-OPV5 and the simultaneous deposition of various ions with hyperthermal kinetic energies. Images recorded by scanning electron microscopy of films grown by simultaneous deposition of hyperthermal thiophene (or acetylene) ions and thermally evaporated MEH-OPV5 (shown in Scheme 1) displayed changes in morphology of these films, referred to here as SPIAD-PPV, that indicate changes in their underlying chemical structure. These changes in chemical bonding of SPIAD-PPV films are compared with evaporated MEH-OPV5 films by X-ray and ultraviolet photoelectron spectroscopy as well as electron energy loss spectroscopy.

2. Experimental details

2.1. Preparation of substrates

100 nm gold films were deposited on silicon wafers (Wafer World, Inc., Si (100), p-type, boron-doped). Gold substrates were ultrasonicated in acetone and isopropanol prior to being introduced into the vacuum chamber where they were sputtered with 500 eV He^+ ions for 1 h. The substrate work function was verified by UPS prior to film deposition.

2.2. Deposition method

Surface polymerization by ion-assisted deposition (SPIAD) was realized by simultaneous deposition of 10–200 eV, non-mass-selected thiophene or acetylene ions and thermally evaporated MEH-OPV5 neutrals. Ion beams were formed by

electron impact ionization of thiophene or acetylene gas fed directly into a sputter ion gun. The ion beam energy was adjusted to the lowest setting (500 eV), and the sample was positively biased to achieve ion energies in the range of 10–200 eV. Fragmentation of thiophene ions by standard 70 eV electron impact ionization energy has been shown to give ~65% intact thiophene ions, $C_4H_4S^+$, and approximately equal amounts of $C_3H_3^+$, CHS^+ , and $C_2H_2S^+$. Fragmentation of acetylene ions has been shown to give ~97% $C_2H_x^+$ ($x=0, 1, 2$) and ~3% CH_x^+ ($x=0$ and 1) (webbook.nist.gov/chemistry). The ion source used here was expected to give similar fragmentation of ions. SPIAD-PPV films were grown using a constant MEH-OPV5 fluence of 3×10^{13} neutrals/cm². An ion current of 100 nA $C_xH_yS_z^+$ was used to give an ion fluence of 6×10^{14} ions/cm² and an ion:neutral ratio of ~19:1 for thiophene ion SPIAD-PPV film deposition. An ion current of 20 nA $C_2H_x^+$ was used to give an ion fluence of 1×10^{14} ions/cm² and an ion:neutral ratio of ~4:1 for acetylene ion SPIAD-PPV film deposition.

2.3. Instrumentation and analysis methods

X-ray photoelectron spectroscopy (XPS) was performed using a monochromatic Al $K\alpha$ X-ray source (15 keV, 25 mA emission current, model VSW MX10 with 700 mm Rowland circle monochromator, VSW Ltd., Macclesfield, UK) and a concentric hemispherical analyzer (150 mm, Model Class 150, VSW Ltd.) with multichannel detector operating in constant energy analyzer mode [13]. The spectrometer was calibrated to the Au $4f_{7/2}$ peak at 83.95 eV binding energy. Ultraviolet photoelectron spectroscopy (UPS) was used to probe the valence band of the thin films and was performed using a helium discharge lamp (Model UV 10, Thermo VG Scientific) operating in He(II) mode ($h\nu=40.8$ eV). During UPS analysis, samples were biased –6 eV relative to ground [21]. The UPS spectrum was calibrated by the Fermi level of a He^+ ion sputter-cleaned gold substrate at 0 eV binding energy. An electron flood gun (Model FRA-2X1, Kimball Physics) and the concentric hemispherical analyzer mentioned above were used to accomplish electron energy loss spectroscopy (EELS) with an electron beam energy of 500 eV. The morphologies of the thin films were characterized by scanning electron microscopy (SEM) using a variable pressure scanning electron microscope (Model S-3000N, Hitachi) with a tungsten electron source operating at 3 keV electron energy.

3. Results

3.1. X-ray photoelectron spectroscopy (XPS)

The S $2p$ and C $1s$ core levels for simultaneous deposition of 200 eV thiophene ions and thermally evaporated MEH-OPV5 neutrals (thiophene ion SPIAD-PPV) at an ion:neutral ratio of ~19:1 are compared in Fig. 1 to films of evaporated MEH-OPV5 neutrals alone. XPS confirmed incorporation of thiophene and MEH-OPV5 species into SPIAD-PPV films by the presence of S $2p$ and O $1s$ peaks at 164.0 eV and 533.0 eV, respectively. The elemental composition of films grown by thiophene ion SPIAD

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