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Scratch resistance and durability enhancement of bulk heterojunction organic photovoltaics using ultra-thin alumina layers

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ABSTRACT

Atomic layer deposition (ALD) was studied for ultra-thin (≤ 100 nm) barrier coating deposition onto organic photovoltaics (OPVs) to enhance device lifetime. Herein, we report the first known investigation of the mechanical characteristics of AlO_x encapsulated OPVs using nanoindentation and scratch testing with deposition temperature as a tunable parameter. The higher organic content in the AlO_x film, grown at lower temperatures, enhanced the interfacial bonding at the AlO_x–OPV interface and provided modulus and hardness performance exceeding that of a common polymer encapsulant. Furthermore, AlO_x's organic content impeded fracture propagation, confirming the durability enhancement associated with this approach.

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1. Introduction

The recent proliferation of organic photovoltaic (OPV) research has been driven by the promise of low-cost, lightweight, flexible devices for off-grid power generation capabilities incorporated into textiles, robotics, buildings, and vehicles [1,2]. Core research efforts are directed at improving device efficiency, lifetime, and processability. While improved device efficiency and processing efforts have explored novel low-band gap polymers [3], new device architectures [4], and unique substrate designs [1,2], device lifetime studies have focused on diverse encapsulation approaches in an effort to mitigate atmosphere-induced device degradation. These degradation mechanisms rely on water or molecular oxygen diffusion into the solar cell structure leading to metal oxidation, photo-oxidation of organic constituents, and electrode etching. The reader is referred to several detailed reviews on this subject for further insight [5,6]. In addition to environmental degradation, mechanically driven device failure may originate from adhesion or cohesive failure within the multi-layered structure caused by residual stresses from device fabrication, thermal expansion mismatch, or layer shrinkage [7]. In particular, organic–inorganic interfaces, including polymer substrates encapsulated by an inorganic film, possess low adhesion strength [8], making the interface highly susceptible to failure. Consequently, selective processing of a suitable barrier layer remains a challenge but is essential for effective OPV commercialization.

An ideal environmental barrier coating serves two distinct functions: reducing atmosphere diffusion and providing protection of the underlying soft device from mechanical abrasion. The selected barrier layer must also be compatible with the OPV surface to maintain device longevity. Additionally, the real-world fabrication of OPV modules by advanced printing technology [9,10] adds additional constraints of a simple, consistent process with large area capacity. Furthermore, the barrier coating itself must be slightly flexible to maintain roll processing compatibility. Early OPV encapsulation protocols featured purely inorganic or polymer thin films, which suffered from through-film pinholes and high atmosphere permeability, respectively [11]. To overcome these challenges, new encapsulation approaches have included polymer nanocomposites [12,13] and the deposition of organic–inorganic bilayers [14,15]. These approaches show favorable performance, but they require complex multi-step processing and significantly increase the packaging weight of a laminated cell structure. Alternatively, organic–inorganic hybrid encapsulation approaches are also being examined, with atomic layer deposition (ALD) in particular showing exceptional promise due to its versatility [16]. ALD is a vacuum-based deposition technique consisting of sequential pulses of vaporized organometallic and oxidative precursors, which undergo self-limiting reactions that promote layer-by-layer film growth. ALD also affords precise control over nanoscale film thickness while being adaptable to thin film growth on unique structures such as mesoporous films and structurally

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integrated devices for which conventional encapsulation technology has limited applicability. ALD encapsulation of OPVs was first examined on pentacene:C_{60} bilayer devices [17] with subsequent reports addressing the poly(3-hexylthiophene):6,6-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction (BHJ) system [18–20]. These later reports revealed significant lifetime enhancement using AlO_x coatings with film thicknesses ranging from 10–200 nm. While most papers favor a deposition temperature of 140–150 °C for AlO_x film development [18–20], Clark et al. [20] recently found that reducing the ALD processing temperature to 100 °C preserves intrinsic device performance while simultaneously enhancing device lifetime. This result was attributed to the increased organic nature of the AlO_x coating providing a more robust interface.

In addition to lifetime extension, the encapsulation layer provides mechanical protection of the underlying soft device. Mechanical characteristics of particular importance are the indentation hardness and abrasion resistance of the encapsulating layer. Recently published studies have explored the mechanical performance of AlO_x films deposited by ALD on hard substrates including Si wafers or glass substrates [21–25]. The selected substrate, however, along with ALD processing temperature strongly influence both AlO_x film growth [26] and observed mechanical behavior [21], particularly for deposition on soft, polymer substrates such as OPV devices. In addition, traditional organic–inorganic interfaces suffer from inherent surface energy mismatch and weak interfacial bonding leading to poor interfacial adhesion strength. Kim et al. [8] recently demonstrated a two-fold increase in the adhesion strength of SiN_x–polymer interface through surface modification. As ALD processing temperature directly affects the organic content of the AlO_x film and therefore, the hydrophobic OPV–AlO_x interfacial bonding strength, selective processing will drastically influence both observed mechanical behavior and ultimate device reliability. This contribution presents a comprehensive study on AlO_x film mechanical characterization as deposited on OPV surfaces to address the multi-functional nature of such films and examine ALD processing temperature effects on film durability.

2. Experimental section

2.1. Device fabrication

OPV surfaces were fabricated as described in detail elsewhere [27]. In summary, ITO substrates (Delta Technologies, $10\Omega\square^{-1}$) were ultrasonically degreased in successive solvent baths of detergent solution, water, hexane, isopropanol, acetone, and methanol before UV–ozone treatment (20 min each). A hole transport interlayer blend of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) (PEDOT:PSS, Clevios® P, Hereaus) was filtered and spin cast at 3500 rpm for 45 s before baking on a hot plate (160 °C, 20 min). In a nitrogen glove box, a 5:3 wt% P3HT:PCBM (Rieke Metals, Inc. and American Dye Source) dispersion in chlorobenzene (24 mg/mL) prepared the day before, was then filtered and spin cast at 1500 rpm for 45 s before annealing (160 °C, 8 min). OPV or cleaned glass substrates (Fisher Scientific) were then placed in the ALD deposition chamber (Cambridge Nanotech Savannah 100). Glass substrates were air plasma treated (Harrick Plasma PDC-32 G, 10.5 W, 15 min) and partially masked with Kapton tape for AlO_x film thickness assessment by profilometry (KLA Tencor P15). An automated recipe alternatively pulsed trimethylaluminum (Strem Chemicals) and water precursors for 0.015 ms with a 30 s purge time between pulses for 999 cycles, yielding approximately 95 nm thick AlO_x films, while the ALD processing temperature was varied between 100–150 °C.

2.2. Characterization

X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) was performed with a monochromatic Al K_α radiation source (1486.6 eV), operating at 12 kV and 10 mA, while scanning electron microscopy (SEM, FEI Quanta) images were collected using an operating voltage of 15 kV. Tapping mode atomic force microscopy (AFM, Dimension Instruments Dimension 3100) images were collected using silicon tips (Nanosensors PPP-NCHR) operating at 0.5 Hz.

2.3. Mechanical performance

Nanoindentation (MTS Nanoindenter XP) experiments consisted of a diamond Berkovich indenter penetrating a sample under a surface normal load, allowing construction of load–displacement (P–h) curves. Reduced modulus (E_r) and hardness (H) profiles were then derived from these curves, where the projected contact area (A_p) is a function of penetration depth and indenter geometry. Briefly, reduced modulus profiles are extracted from sample stiffness fluctuations during unloading ($\sim dP/dh$) over the projected contact area while hardness profiles are gleaned from the ratio of maximum load (P_{max}) to residual indentation area (A_r). Further details regarding explicit derivation of these parameters may be found elsewhere [21]. In this work, the continuous stiffness measurement (CSM) technique facilitated continuous evaluation of elastic properties as a function of indentation depth by oscillating the indenter during probing. Nanoindentation was performed at a constant strain rate of $0.1\ s^{-1}$, and a CSM oscillation amplitude of 2 nm at 45 Hz. A contact stiffness of 100 N/m was used to identify surface contact.

Nanoindenter scratch tests consisted of three indenter line scans across the same length. During the second scan, a linearly increasing surface normal load is applied to the indenter tip as the indenter tracks across the surface, resulting in abrasive damage while the first and last scan record surface topology before and after surface abrasion. A 5 mN maximum load and 100 μm scratch distance were used for all tests.

3. Results and discussion

3.1. Surface characterization

AlO_x coated OPV and glass substrates were examined by XPS, AFM, and SEM. As was observed previously [20], lowering the ALD processing temperature resulted in increased organic character of the AlO_x films ($AlO_{1.7}C_{0.6}$ and $AlO_{1.6}C_{0.4}$ for films deposited at 100 and 150 °C respectively as determined by XPS). While increased organic content would be expected to reduce the film's impact hardness, improved interfacial compatibility with the P3HT-rich OPV surface is also anticipated. Tapping mode AFM imaging further revealed the 3D island growth mechanism characteristic of ALD-based AlO_x growth on highly hydrophobic surfaces (Fig. 1) and consistent with previous results [20]. This 3D structured growth was further confirmed by SEM imaging (not shown). While the AlO_x encapsulated OPVs were characterized by slight roughness variability with processing temperature ($r_{RMS}=2.29$ nm and 1.71 nm for 100 °C and 150 °C respectively), another AlO_x film grown at 100 °C under identical conditions on an OPV surface yielded $r_{RMS}=1.70$ nm [20], suggesting that this discrepancy is attributable to intrinsic process variability (e.g. chamber pressure, gas flow rates). Most importantly, the 3D growth mechanism only introduces minimal surface roughness and therefore will not appreciably affect measured mechanical behavior of the multi-layered thin films.