Solar Energy Materials & Solar Cells 112 (2013) 144–156

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

In-line spectroscopic ellipsometry for the monitoring of the optical properties and quality of roll-to-roll printed nanolayers for organic photovoltaics

Stergios Logothetidis *, Despoina Georgiou, Argiris Laskarakis, Christos Koidis, Nikolaos Kalfagiannis

Laboratory for Thin Films-Nanosystems and Nanometrology (LTFN), Physics Department, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 1 November 2012
Received in revised form
24 December 2012
Accepted 8 January 2013
Available online 13 February 2013

Keywords:
In-line monitoring
Spectroscopic ellipsometry
Organic electronics
Organic photovoltaics
PEDOT:PSS
Roll-to-roll

ABSTRACT

The fabrication of organic electronics devices onto flexible polymer substrates by roll-to-roll (r2r) processes requires the use of in-line quality control tools for the optimization of the optical and electronic properties of semiconducting, electrodes and barrier layers and their thickness that will achieve the required performance and lifetime of the devices. This paper focuses of the investigation of the optical properties of r2r printed nanolayers for organic photovoltaics, by in-line spectroscopic ellipsometry (SE) in the visible-far ultraviolet spectral region. This is performed by a prototype very fast stand-alone SE unit adapted onto a lab-scale r2r system. First, we test the stability and precision of measurements to validate the optical measurements and the analysis procedure. Afterward, we report on the robust determination of the thickness and optical properties of barrier thin layers (a combination of SiO_x and hybrid polymer bilayers), PEDOT:PSS transparent electrodes and polymer:fullerene (P3HT:PCBM) blends that were gravure printed onto flexible PET substrates in the form of rolls. Finally, we discuss on the effect of the experimental parameters on the optical properties and the quality of the printed nanolayers as determined by the modeling approaches of the in-line measurements.

1. Introduction

One of the main advantages of organic electronics devices (such as organic photovoltaics—OPVs, organic light emitting diodes, organic thin film transistors, sensors, and biosensors) is their capability for low cost fabrication by large area roll-to-roll (r2r) production processes [1–7]. These devices consist of a multilayer stack of soluble organic semiconductors, transparent electrodes and barrier layers deposited by printing process onto flexible polymer substrates (e.g. PolyEthylene Terephthalate—PET and PolyEthylene Naphthalate—PEN) that have the form of rolls with width of some centimeters and length of several meters or even some kilometers [5,7–10].

The organic device nanolayers have initially the form of inks that can be deposited onto the flexible polymer substrates by printing (e.g. inkjet, gravure, screen, etc.) that is followed by curing (e.g thermal treatment and ultraviolet light exposure) [11]. The major factor that affects the functionality of the printed films are the uniformity of composition and thickness [8]. These are controlled by the r2r process experimental parameters such as rolling speed, the curing temperature and the material viscosity. The non-optimum process optimization leads to fluctuations in micro-structure and thickness during the printing process, and consequently to devices with non-reproducible functionality. Therefore, one of the most crucial steps of r2r production processes is the in-situ quality control that will provide robust information on the printed film quality and will ensure the process stability and reproducibility. Process control has been used for years in batch production mainly for the control of dynamic processes, such as reaction kinetics and curing processes [12–15]. However, there are only very few attempts to combine analytical techniques (that are used to lab scale) with pilot and large scale production processes [16–18].

Spectroscopic ellipsometry (SE) is a powerful and robust, non-destructive and surface sensitive optical technique for the determination of the optical properties, thickness, deposition rate and growth mechanisms of a wide range of nanolayers [12,19,20]. Several reports focus on the implementation of SE for in-situ monitoring and investigation of the growth mechanisms of vacuum deposited thin films [21–25]. However, the implementation of SE for the in-line optical monitoring of r2r fabricated nanolayers has not been reported in detail.

In this work, we investigate in detail the optical properties of gravure printed nanolayers for OPVs by in-line SE. These include inorganic silicon oxide (SiO_x) and hybrid barrier layers, Poly(3, 4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and polymer:fullerene blends that are deposited onto flexible polymer substrates (PET). The in-line SE unit has been adapted on

* Corresponding author. Tel.: +30 2310 998 174.
E-mail address: logot@auth.gr (S. Logothetidis).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.01.007

a pilot scale r2r printing system for the determination of the thickness and optical properties of r2r printed nanolayers. The real time analysis of the measured $\langle \varepsilon(\omega) \rangle$ provides accurate information on the stability of the gravure printing process and the homogeneity of the film thickness and composition throughout the printed area. This will demonstrate the potential of SE to be used as a robust in-line technique for r2r large scale fabrication of several flexible organic electronic devices [26,27].

2. Experimental

The flexible polymer substrates are commercially available polyethylene terephthalate (PET) in the form of polymer rolls of thickness of 50 μm that were adapted and integrated between the unwinding and winding rolls of the r2r printing system. The studied nanolayers are given as follows: (a) SiO_x thin films with thickness of 70 nm, which were deposited onto the PET roll by electron beam evaporation, by Amcor [28]. (b) Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films [29–32], of the formulation Clevios™ FET, provided from Heraeus, that has been gravure printed onto PET, (c) multilayer structure that consist of PEDOT:PSS/(hybrid polymer)/SiO_x/PET substrate. The hybrid polymer layer are inorganic–organic hybrid polymers (ORMOCER®) supplied from Fraunhofer-Institut für Silicatforschung (ISC), Germany) [28]. (d) Blend of poly(3-hexylthiophene):(6,6)-phenyl C61 butyric acid methyl ester (P3HT:PCBM) that has been gravure printed onto PET. More details on the preparation conditions are provided below in the respective sections of the manuscript.

The r2r printing process has been performed by a lab scale r2r system from RK Print Coat Instruments Ltd. It has a fully manual configuration and it consists of several gravure printing stations, dryers (one after each printing station) and a corona treatment (see Fig. 1). The gravure printing cylinder has an electromechanically engraved pattern that consists of stripes with a width of 10 mm. The screen has 80 lines/cm and pyramidal cells with nominal volume at 12.7 ml/m^2. After the gravure printing, the printed roll passes in front of two dryers (each one having an effective drying length of 60 cm) to evaporate the solvent. Thermocouples are connected to the pressure chambers of the dryers before the heated air is directed onto the coated roll through nozzles.

The in-line monitoring of thickness, uniformity and optical properties of the printed nanolayers were performed in the vis–UV energy region (3–6.5 eV) by an ultra-fast Multi-Wavelength Phase Modulated Spectroscopic Ellipsometer (SE) from Horiba Jobin Yvon. This unit has been adapted onto the r2r system on a moving stage and the light beam focuses on the moving roll surface with an angle of incidence of 70° at the center of the polymer roll, and at a location between two directional rolls. The light beam is produced by a Xe lamp and after its focusing by mirrors and lenses it passes through the polarizer and the modulator. Afterward, it is focused on the polymer roll surface and it is reflected by an angle of 70° toward the detection head, which consists of the analyzer, the multiwavelength (MWL) unit and the detector. The MWL unit uses a fiber-optic array to split the light beam energy profile in 32 specific photon energies in the range of 3–6.5 eV, for the simultaneous measurements of the $\langle \varepsilon(\omega) \rangle$ values.

The spot of the light beam on the roll is a circle of a diameter of ~2 mm. This size can be reduced by optical adjustments, but this can lead to the reduction of the intensity of the reflected beam at the detector and furthermore to less accurate measurements. At this configuration the plane of incidence is perpendicular to the roll plane and to the rolling direction (see Fig. 1). In order to ensure that the polymer roll is stable and without wrinkles during its rolling, a planarization procedure of the roll takes place before each experiment. In this procedure, a continuous and stable tension is applied along the rolling direction, and a detailed alignment of the roll along the perpendicular direction is established. After the planarization procedure of the polymer roll, the light beam is focused on the polymer roll. Finally, in order to eliminate the effect of any vibrations on the polymer roll, the whole r2r system is placed on an anti-vibration stage. Fig. 1 shows the experimental setup of the small scale r2r system on which the in-line SE unit has been adapted.

The SE unit is equipped with a 32-fiber-optic array detector for the simultaneous measurements of the $\langle \varepsilon(\omega) \rangle$ values at 32 specific photon energies in the range of 3–6.5 eV. The integration time (IT), which is the time for the measurement of one multi-wavelength (MWE) spectrum, was set at 100 ms. If we assume a fast rolling speed of 10 m/min, during one single SE measurement the "scanned" area that corresponds to a full spectrum is a line of a length of ~1.6 cm and width of ~2 mm (the diameter of the light spot). If the rolling speed and the IT are

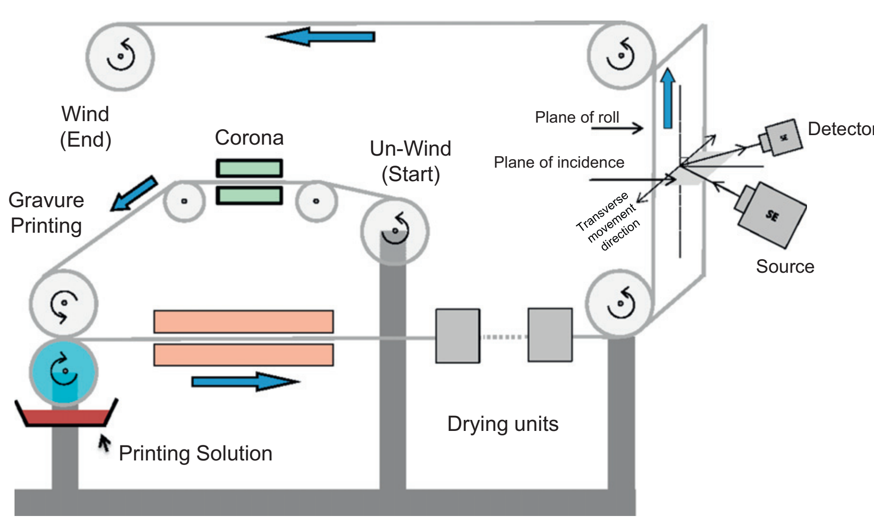

Fig. 1. A simplified configuration of a lab scale r2r system and the adapted in-line SE unit. Several printing and drying units are added in this configuration. The plane of incidence is perpendicular to the plane of the polymer substrate roll.