Real-time and in-line Optical monitoring of Functional Nano-Layer Deposition on Flexible Polymeric Substrates

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Abstract

The roll-to-roll (r2r) deposition of functional nano-layers onto flexible polymeric substrates leads to the large scale production of multifunctional materials systems. These include the encapsulation (ultra barrier) layers, and Transparent Conductive Oxide (TCO) electrodes, for the low cost production of Flexible Electronic Devices (FEDs), such as flexible OLEDs and OPVs. The performance, efficiency and lifetime of FEDs are affected by the properties of the barrier film/polymer and optical and electrical properties of the TCO electrodes. The determination of the optical properties by real-time and in-situ optical sensing techniques and the correlation to the final properties provide insights towards for the growth mechanisms, whereas their in-line integration onto r2r production methods will boost their low-cost large scale production.

In this work, we focus on the incorporation of in-situ and real-time Spectroscopic Ellipsometry in combination with advanced modeling and analysis techniques, towards the determination of optical and functional properties of polymer substrates and functional nano-layers as a novel method to meet these challenges.

Introduction

One of the state-of-the-art applications of polymer films is the production of Flexible Electronic Devices (FEDs) such as flexible displays & lighting (OLEDs), flexible organic photovoltaic cells (OPVs), which is a radically expanding sector of the modern industry. FEDs are expected to be integrated in several applications in our everyday life. The use of polymer materials towards this direction is motivated by the advantages and the conducting, and light emitting properties of organics (polymers, oligomers) and hybrids (organic–inorganic composites), combined with easy processing, low cost and production flexibility, which are necessary in large scale roll-to-roll (r2r) configurations. The deposition of functional layers (barrier layers, electrodes, Transparent Conductive Oxides-TCO, organic emitters) onto bendable and flexible polymer substrates in new and intelligent production techniques open up the possibility of cost-effective, roll-to-roll processing in high volumes. A major factor for the achievement of the evaluation of properties and uniformity of nanolayers onto polymeric substrates is the integration onto r2r production, real-time and in-situ optical sensing techniques.

This presentation focused on the incorporation of in-situ and real-time Spectroscopic Ellipsometry in combination to advanced modelling and analysis techniques, towards the determination of optical and functional properties of polymer substrates, organic semi-
conductor materials and functional nano-layers (for high barrier and electrode materials) as a novel method to meet these challenges.

**In-Situ and real-time Spectroscopic Ellipsometry**

The optical monitoring of the deposited transparent barrier, TCOs and organic layers is being performed by In-Situ and real-time Spectroscopic Ellipsometry (SE) in a wide spectral region (IR to Vis-fUV). In-situ and real-time SE is a powerful, surface-sensitive optical technique, which allow determination of thickness, bonding structure & configurations, vibrational properties, electronic transitions, stoichiometry, optical anisotropy, deposition rate, growth mechanism of nanolayers. Also SE is a non-destructive technique, allow the direct and simultaneous determination of Real $\varepsilon_1(\omega)$ and Imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, as a function of photon energy $\omega$. SE can be used in a variety of media (vacuum, air, transparent liquids) and does not require special conditions for the measured materials.

**Optical Properties of Materials for the Production of Flexible Electronic Devices**

**i. Anisotropic Polymeric Substrates**

SE in a wide spectral region from the IR to the Vis-fUV has been implemented in order to investigate the optical and electronic properties of the Poly(Ethylene Terephthalate) (PET) and Poly(Ethylene Naphthalate) (PEN) films. The optical response functions of PET and PEN films in the Vis-fUV spectral region (1.5-6.5 eV) measured with the plane of incidence parallel to the Machine Direction. The results showed that the optical absorption of PET and PEN starts at ~4 and ~3 eV, respectively. The dielectric function $\varepsilon(\omega)$ of PET at photon energies above 4 eV, is dominated by four characteristic features at ~4.15 and 4.3 eV, whereas two stronger bands are centered at ~5.0 and 6.3 eV. The $\varepsilon(\omega)$ of PEN shows similar features due to the similarities in the molecular structure between the monomer units of PET and PEN. However, the existence of two phenyl rings in the naphthalene group in PEN, instead of the benzene ring in PET, leads to the significant shift of the characteristic absorption bands to lower energies as well as a characteristic split in all of them. Therefore, we observe an energy shift of peaks I and II to 3.4 and 3.6 eV respectively, although this energy shift is much more pronounced in peaks III and IV, which are appeared at 4.4 and 5.1 eV, respectively, along with a characteristic split in three components.

Also, the optical anisotropy of biaxially stretched PET and PEN films has been extensively investigated by Fourier transform IR spectroscopic ellipsometry (FTIRSE) (900–3500 cm$^{-1}$) and Vis-fUV variable angle SE (1.5–6.5 eV) techniques.

**ii) Barrier Nano-layers**

The use of flexible polymeric substrates will revolutionize the production of organic electronic devices, and it will provide added-value since new applications will be generated.
However, flexible polymeric substrates are characterized by relatively high permeability values for various substances, such as gases or water vapor. This is a major problem, since the permeation of atmospheric O\textsubscript{2} (OTR) and H\textsubscript{2}O (WVTR) through the polymeric substrate into the active layers of the device leads to corrosion and degradation effects, significantly limiting their operation time and stability. In order to achieve the necessary improvements in barrier properties of the polymeric substrates, additional barrier layers have to be used. As barrier layers used materials SiO\textsubscript{x} and AlO\textsubscript{x}, inorganic-organic hybrid polymers, which have shown to provide very good barrier properties.

In-Situ and Real-Time SE in the spectral region 3-6.5 eV has been implemented, in order to investigate the optical response and growth mechanism of SiO\textsubscript{x} nanolayers deposited onto PET, PEN as well as Hybrid (organic-inorganic) substrates. The analysis showed that SiO\textsubscript{x} follows an island type mechanism onto PET substrate and a layer-by-layer growth mechanism onto PEN substrate. SE provided information about the time-dependence of the optical parameters (energy gap, absorption peaks) and of SiO\textsubscript{x} stoichiometry in combination to the effect of the substrate. In addition, In-situ and real monitoring of deposition of SiO\textsubscript{x} nano-layers onto hybrid substrates showed different deposition rates due to the different growth mechanism. SE was used in order to study the uniformity of AlO\textsubscript{x} coating on a web which moved with speed 0.2 m/min. Finally via in-situ SE studied the influence of incorporation of different percentages of SiO\textsubscript{2} nanoparticles in the optical response of hybrid material.

iii) Electrodes and Transparent Conductive Oxides (TCOs)

Transparent Conductive Oxides (TCOs) are an essential part of the FED Technology since they exhibit both large-area electrical contact and optical access in the visible portion of the light spectrum. Zinc oxide (ZnO), which is a wide direct band-gap semiconductor with a hexagonal crystal structure of wurtzite, is a most promising material for the production of the new generation of FEDs, and it has gained great commercial and scientific interest compared with the other TCO films, such as indium tin oxide (ITO). Some of its numerous advantages include the electrical conductivity, its good ultraviolet absorption behaviour, the compatibility with large scale processes, the low cost, abundance, non-toxicity and easy fabrication.

In-situ and real-time SE gives the opportunity of monitoring the growing of ZnO thin films and extracting information about the evolution of their optical parameters, thickness and growth mechanisms. The analysis of real-time spectra using the Tauc-Lorentz model with the two oscillators allowed the calculation of the bulk complex dielectric function $\varepsilon(\omega)$ of the growing film, and to the determination of the complex optical conductivity. The ZnO films have a fundamental gap $E_g$ at $\sim$3.15 eV. The maximum absorption appears at two distinct energy gaps at $E_1 \approx 3.4$ eV due to the presence of the absorption exciton, and at energy $E_2$, which is appeared at $\sim$6.5 eV. Large differences are found between the $\varepsilon(\omega)$ of the initial and final stages of growth. At the initial stages of growth small islands and nano-crystals are presented with a lot of deficiencies are presented, not permitting the excitons to move and reduces the optical response.

iv) Organic Semiconducting materials
The active materials of FEDs are consisted by organic semiconductive layers, for the charge generation and transport that will lead to the light emission and generation of electricity for organic light-emitting devices OLEDs and OPVs, respectively. Therefore, during the past decade, the development of semiconductive organic active materials has become one of the fore most topics in chemistry and applied physics. Due to the variety of organic materials and their physical and chemical properties such as the fluidity of their precursors and their compatibility with a range of foils and other substrates, a large number of new and adapted, fast and direct structuring techniques can be applied.

The usual structure of a FED, consists of an anode such as indium tin oxide (ITO) film, deposited onto a flexible transparent substrate, and followed by two conducting layers, a hole injection layer an electron transport layer, which sandwich the emissive organic layer. The structure is topped with a reflective metal cathode of Mg-Ag alloy or Li-Al.

PEDOT is a low band gap polymer with promising properties for applications such as transparent electrode materials or ElectroChromic devices. It shows a high electrical conductivity (up to 5.50 S/cm) in the doped state and a good thermal and chemical stability. PEDOT-PSS thin films are deposited by spin coating and exhibit anisotropy in optical and electrical properties. SE has been implemented in order to measure dielectric function $\varepsilon(\omega)$ of a PEDOT-PSS thin film grown onto a flexible PEN substrate by spin-coating technique. The analysis of the measured $\varepsilon(\omega)$ by the use of two TL oscillators revealed that the thickness of the PEDOT film is 285 nm, whereas two electronic transitions have been found at ~5.3 and 6.4 eV.

**Up-scaling of Optical Sensing techniques from Lab scale to Large scale r2r Production Processes**

In large scale production of FED via the roll-to-roll technique the quality control of the deposited nano-layers should be provided and it is necessary to integrate the real-time control in all the production steps.

**Conclusions**

Real-time SE in combination to Modelling and Analysis techniques provides accurate results on the optical properties, thickness, stoichiometry, composition, microstructure and density of polymeric substrates, barrier layers, TCOs and organic layers. Also, the correlation of optical properties to intermediate and functional properties, leads to the determination and control the quality of transparent functional layers (barrier, electrodes, etc.) and organic developed onto polymers for flexible electronics applications. Finally in-line SE will play a major role towards the cost-effective Large Scale r2r production of transparent functional layers onto polymeric substrates.

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