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Full Length Article

Spectroscopic ellipsometry characterization of coatings on biaxially anisotropic polymeric substrates

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ABSTRACT

Spectroscopic ellipsometry characterization of coatings on polymeric substrates can be challenging due to the substrate optical anisotropy. We compare four characterization strategies for thin coating layers on anisotropic polymeric substrates with regard to accuracy of the resulting layer thickness and coating optical constants. Each strategy differs in measured data type, model construction, implementation complexity, and inherent capabilities and sensitivity to the coating properties. Best practices and limitations are discussed for each strategy.

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1. Introduction

Polymer substrates are important for many modern applications such as flexible electronics and displays, photovoltaics, food packaging, and medical devices. These substrates typically exhibit anisotropic behaviour, with directional-dependent optical constants. Such properties significantly increase the complexity of optical characterization.

Traditional spectroscopic ellipsometry (SE) measurements provide two parameters (Ψ, Δ) related to the polarization change occurring when light interacts with the sample. This basic measurement assumes no cross-polarization between electric fields oriented parallel to the plane of incidence (E_p) and those oriented perpendicular to the plane of incidence (E_s) and can be written in terms of the reflection (or transmission) coefficients for the corresponding orientations as [1]:

$$\tan(\Psi)e^{i\Delta} = \frac{\tilde{r}_p}{\tilde{r}_s} = \frac{E_{p,out}E_{s,in}}{E_{p,in}E_{s,out}} \quad (1)$$

Thus, SE is limited to isotropic materials and anisotropic samples specifically aligned such that their optical axes coincide parallel or perpendicular to the ellipsometer plane of incidence [2].

For anisotropic samples, generalized SE (g-SE) and Mueller matrix SE (MM-SE) measurements can account for the cross-polarization between *p*- and *s*-orientations [2–4]. If the detected light beam also witnesses a reduction of polarization, termed depolarization, then only MM-SE measurements can fully describe the sample optical response. MM-SE data are reported as the normalized elements of a 4 × 4 sample matrix, given as:

$$\mathbf{M}_{sample} = \begin{bmatrix} 1 & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \quad (2)$$

When light enters an anisotropic substrate, cross-polarization may occur as the *p*- and *s*-waves are no longer independent. The light traveling through the substrate is split into the ordinary and extraordinary beams with different phase velocities as shown as beams “2” and “3” for the first transmitted beam in Fig. 1. This leads to a substantial retardance effect in the ellipsometric data when they are collected together. Similar retardance effects are measured in the reflected data when the ordinary and extraordinary rays reflect from the back-surface and are detected during measurement, as shown for beams “4” and “5”. This retardance effect becomes stronger as the path length increases and results in high-frequency interference oscillations for polymer substrates

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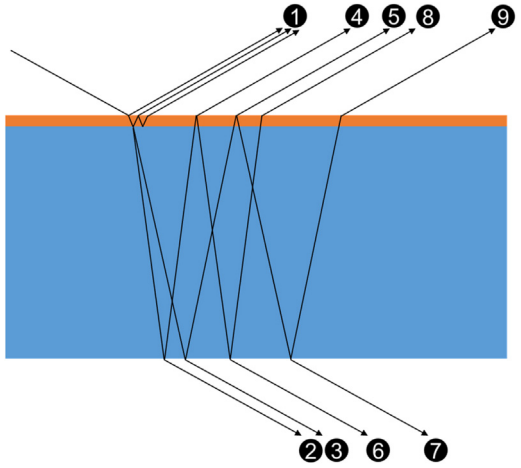

Fig. 1. Light interaction with a coated anisotropic substrate.

measured in transmission or in reflection when backside reflections are present.

However, anisotropic substrates can be approximated by simple isotropic optical constants when the anisotropic effects are minimized. This can be accomplished by detecting only the first surface reflection from the anisotropic substrate, which consists of beam "1" in Fig. 1. Methods to eliminate additional reflections from light that has travelled through the substrate include spatial separation of the beams, index-matching the back surface to suppress the reflection from the back surface, and scattering the light from the back surface by abrading the surface [5]. In the ultraviolet, the polymer substrates become absorbing and the backside reflections are naturally suppressed. This offers special measurement benefits, which are the topic of significant research [6–10]. While only a single reflection is detected, the anisotropic optical properties play a large role in the measured response due to differences between in-plane absorptions in the anisotropic substrates [6,7].

Anisotropic polymer substrates have also been characterized with g-SE and MM-SE where multiple reflections within the anisotropic substrate no longer need to be suppressed [11,12]. These measurements are inherently sensitive to the optical differences between the various orientations and the measured optical response is dominated by the long path-length through the anisotropic substrate.

Our interest in this paper is with regard to coatings on the anisotropic substrate and not the substrate properties themselves. With this in mind, we consider strategies to determine thin film thickness and optical constants on anisotropic polymer substrates giving merit to simplified measurements and modelling, provided the accuracy is not significantly affected.

2. Experimental

A series of Al_2O_3 coatings were prepared on both silicon and 50 μm thick polyethylene terephthalate (PET) substrates using atomic layer deposition (ALD). A primer layer (~80 nm) was present on a single side of the PET substrate, so the Al_2O_3 coatings were deposited on the non-primed surface. The PET was fully characterized using MM-SE methods from a reference sheet [11,12], with the resulting anisotropic optical constants shown in Fig. 2.

SE and MM-SE measurements were acquired from Al_2O_3 coatings with nominal thicknesses of 25, 50, 100, and 150 nm. Measurements were collected with a dual-rotating compensator instrument (Woollam RC2®) at 1000 wavelengths between 192 nm and 1690 nm. Two array-based detectors are used to cover this spectral range, with a Si CCD for wavelengths from 192 nm to 1000 nm and an InGaAs detector array for wavelengths from 1000 nm to 1690 nm.

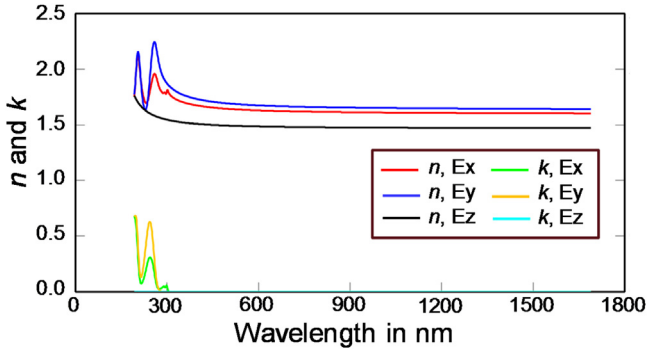

Fig. 2. Anisotropic optical constants determined from reference PET substrate.

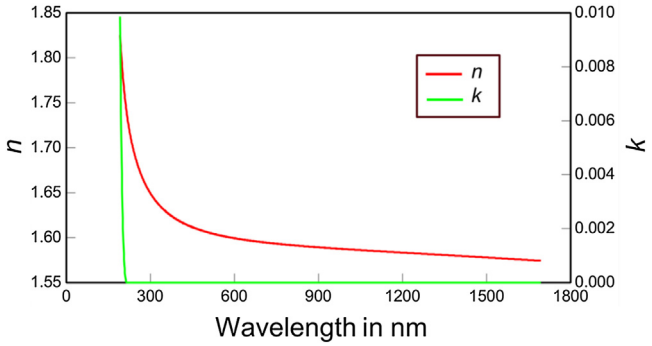

Fig. 3. Optical constants of Al_2O_3 determined from multi-sample analysis of four coatings on silicon.

Measurements were acquired in transmission at angles from 0° to 75° and in reflection at angles from 20° to 75°. As the substrate exhibits biaxial anisotropy, it is important to consider the orientation of the optical axes relative to the ellipsometer frame of reference, which is given by the sample surface, the surface normal, and the plane of incidence. Throughout this study, a sample azimuthal orientation of 0° refers to the situation where sample and ellipsometer reference coordinate system coincide, with the *x*-direction of the PET within the sample surface plane and ellipsometer plane of incidence. Here, the *y*-direction is also in the sample surface plane and perpendicular to the plane of incidence, while the *z*-direction is along the negative sample surface normal. Positive rotations of the sample azimuth coincide with a clock-wise rotation of the sample on the stage, with respect to the positive sample surface normal.

The reference refractive index of Al_2O_3 on Si was modelled using Sellmeier dispersion [13] for transparent wavelengths with Tauc-Lorentz absorption [14] at wavelengths below 215 nm, resulting in optical constants shown in Fig. 3. The index of refraction at wavelength of 633 nm is 1.606 and serves as our reference when studying the films on PET. The Al_2O_3 film thickness on PET substrates differs from those on Si substrates, with values slightly higher on PET. We speculate this is due to faster initial growth on the porous PET surface compared to the smooth Si surface. Thus, the coatings on Si are only used for comparison of refractive index.

Spatially isolating the reflections from front and back surfaces of the polymer substrate significantly simplifies the SE analysis. When only the front reflection is collected, there is minimal cross-polarization between *p*- and *s*- field directions and standard SE measurements contain the primary sample information. Both Strategy #1 and #2 measure data reflected solely from the front-surface. To achieve this, the reverse side of the substrate was abraded with

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