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Determining thickness and refractive index from free-standing ultra-thin polymer films with spectroscopic ellipsometry

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ABSTRACT

It is a well-known challenge to determine refractive index (n) from ultra-thin films where the thickness is less than about 10 nm [1,2]. We discovered an interesting exception to this issue while characterizing spectroscopic ellipsometry (SE) data from isotropic, free-standing polymer films. Ellipsometry analysis shows that both thickness and refractive index can be independently determined for free-standing films as thin as 5 nm. Simulations further confirm an orthogonal separation between thickness and index effects on the experimental SE data. Effects of angle of incidence and wavelength on the data and sensitivity are discussed. While others have demonstrated methods to determine refractive index from ultra-thin films [3,4], our analysis provides the first results to demonstrate high-sensitivity to the refractive index from ultra-thin layers.

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1. Introduction

It is difficult, and often considered impossible, to determine both thickness and refractive index from ultra-thin films where the thickness is less than about 10 nm [1–6]. This is primarily due to strong correlation between the thickness (d) and index (n), where variation in either property leads to very similar changes in the measured ellipsometric parameters (Ψ, Δ). There can be significant sensitivity to the optical thickness ($n{\cdot}d$) from changes in the measured phase parameter, Δ, but analysis is generally unable to separate this product and determine index of refraction [1,2].

Various strategies used to determine both thickness and index from ultra-thin protein layers have been reviewed by Arwin [3]. For example, Arwin and Aspnes demonstrated successful determination of both thickness and index from ultra-thin films deposited on substrates that exhibit sharp optical features [4]. These features vanish from the film optical functions at the correct thickness, providing unique determination of both thickness and optical constants. However, this method does not increase the sensitivity to the film optical constants.

While characterizing isotropic, free-standing polymer films, we discovered this special case offers high sensitivity to both thickness and index. Free-standing films have been studied with ellipsometry for decades, with Azzam demonstrating analytical approaches to the solution of this special case [7,8]. Recent interest in free-standing films has concentrated on how their properties may differ from the same materials supported on a substrate [9], but ellipsometry measurements have not been shown for free-standing films in the ultra-thin thickness limit. In this paper, we demonstrate the ability to simultaneously characterize both thickness and refractive index from free-standing films as thin as 5 nm.

2. Theoretical background

Ellipsometry measurements of a thin film with thickness, d, on substrate can be calculated at wavelength, λ, by considering the Fresnel coefficients at each interface for both p- and s- polarized light. For the case of an ambient "0"/thin film "1"/substrate "2", this leads to the following simplified expression [10,11]:

$$\tan(\Psi)e^{i\Delta} = \frac{r_{01p} + r_{12p}e^{-i2\beta}}{1 + r_{01p}r_{12p}e^{-i2\beta}} \times \frac{1 + r_{01s}r_{12s}e^{-i2\beta}}{r_{01s} + r_{12s}e^{-i2\beta}} \quad (1)$$

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where the subscripts on each Fresnel reflection coefficient refer to the interface between the two materials, while β is the film phase thickness, given as:

$$\beta = \frac{2\pi d}{\lambda} n_1 \cos\phi_1 \quad (2)$$

where n_1 and ϕ_1 are the index for the film and the angle the light refracts into this layer, respectively. For free-standing films in an air ambient ($n_0 = 1$), the ellipsometric ratio further reduces to:

$$\tan(\Psi)e^{i\Delta} = \frac{r_p(1 - r_s{}^2 e^{-i2\beta})}{r_s(1 - r_p{}^2 e^{-i2\beta})} \quad (3)$$

where subscripts describing the material interface numbers are omitted as all interfaces will be between ambient and the single free-standing material. When $d/\lambda \ll 1$, β is very small and $e^{-i2\beta} \cong 1 - i2\beta$. This means that, in the ultra-thin film limit:

$$\tan(\Psi)e^{i\Delta} \cong \frac{r_p\left(1 - r_s{}^2 - i2r_s{}^2\beta\right)}{r_s\left(1 - r_p{}^2 - i2r_p{}^2\beta\right)} \quad (4)$$

Thus, in the ultra-thin film limit, Ψ is mostly a function of $r_p\left(1 - r_s{}^2\right)/r_s\left(1 - r_p{}^2\right)$ with only a small contribution from β. Therefore, Ψ is primarily a function of n_1 and ϕ; (through r_p and r_s); and only a very weak function of thickness d (through β). On the other hand, Δ is a function of thickness d (through β), along with ϕ, n_1, and λ (through β, r_p and r_s). The main point here is that Ψ is a sensitive measure of the index for ultra-thin free-standing films, and is largely unaffected by variations in thickness.

3. Experimental

Polymer films of polyvinyl formal with molecular weights of 100,000 (Vinylec E, SPI Supplies, West Chester, PA) and 230,000 (synthesized at LLNL and dubbed 'superformvar') were prepared on silicon substrates and as free-standing films with thicknesses down to 5 nm. The free-standing films were prepared by direct delamination onto metal supports, per methods described by Baxamusa et al. [12], and summarized here. To prepare free-standing films, the layers are first formed by spin-coating onto a silicon substrate pre-treated with polydiallyldimethylammonium chloride PDAC (Sigma-Aldrich St. Louis, MO. Mw ~ 1 × 105–2 × 105 g/mol), and baked for 1 min at 50 °C on a hot plate. The spin-coating proceeds from a solution of 0.25 wt% Vinylec E in ethyl lactate (98%, Sigma Aldrich, St. Louis, MO). The films are then lifted in water from the silicon substrate and mounted on the metal supports. The films are then dried overnight under ambient conditions.

Spectroscopic ellipsometry (SE) measurements were collected with a rotating compensator ellipsometer (Woollam M-2000 instrument) with collimated beam in reflection and a dual-rotating compensator ellipsometer (Woollam RC2 instrument) with focused micro-spot in both reflection and transmission. The free-standing films remain very flat with excellent uniformity over the central area of the metal supports. Fig. 1 shows an example uniformity map from a free-standing superformvar film. The average thickness from the 345 measurement locations is 12.68 nm with a standard deviation of 0.23 nm.

Data analysis was constrained between 210 nm and 900 nm where sufficient signal intensity from the free-standing ultra-thin films could be obtained. A reference silicon wafer was measured to determine the native oxide layer thickness (1.40 nm), using fixed literature values for both silicon substrate and native silicon oxide [13]. The polymer coatings were modelled as a transparent, isotropic material using Sellmeier dispersion [14]. Mueller matrix measurements in transmission showed the in-plane optical constants to be isotropic. In addition, the excellent uniformity resulted in low depolarization, generally less than 1%.

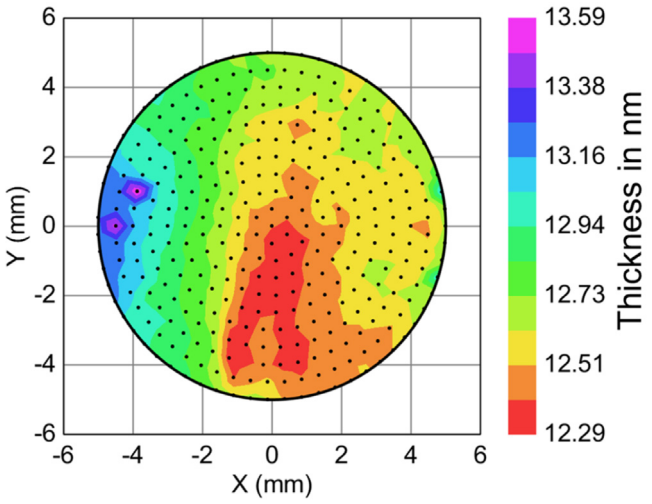

Fig. 1. Thickness uniformity map for free-standing superformvar film.

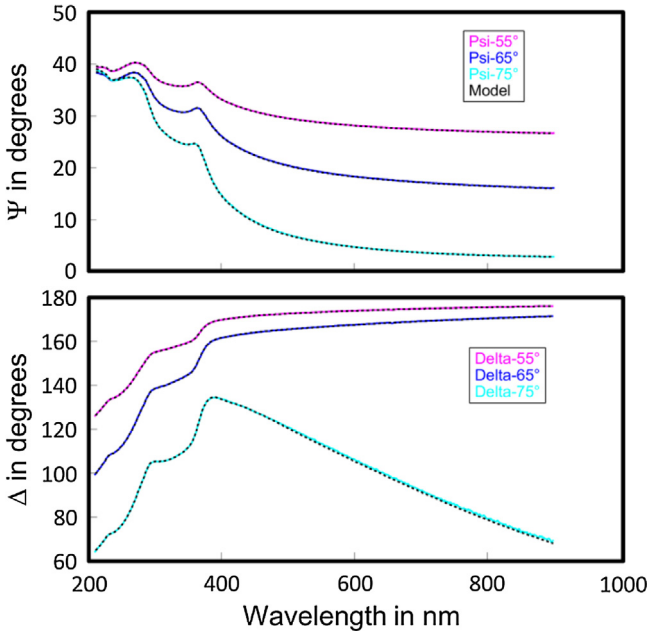

Fig. 2. SE data and corresponding fits for a 5.49 nm thick SF film on 1.40 nm native oxide coated silicon substrate.

4. Results and discussion

4.1. Ultra-thin films on silicon

Experimental SE measurements from an ultra-thin superformvar (SF) film on silicon are shown in Fig. 2. The SF layer was modelled using Sellmeier dispersion, resulting in a thickness of 5.49 ± 0.02 nm. Subject to these model assumptions, there is good confidence in reported thickness. However, the resulting film index of 1.548 ± 0.005 needs further confirmation. In addition to accuracy concerns related to the model assumptions (dispersion equation, free parameters, native oxide thickness, etc.), there is an underlying sensitivity issue for the index of refraction for ultra-thin films on silicon. With the Sellmeier model, the absolute value of cross-correlation between thickness and Sellmeier terms remains <0.37. However, when the refractive index is not restricted to Sellmeier dispersion, the cross-correlation between thickness and index = −0.999. This strong negative correlation, even when fit-

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