Applied Surface Science 421 (2017) 508–512

Contents lists available at ScienceDirect

Applied Surface Science

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

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

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ARTICLE INFO

Article history:
Received 5 July 2016
Received in revised form 24 August 2016
Accepted 26 August 2016
Available online 27 August 2016

Keywords:
Spectroscopic ellipsometry
Free-standing thin films
Ultrathin film
Index-thickness correlation
Refractive index
Nanometer thickness

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.

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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http://dx.doi.org/10.1016/j.apsusc.2016.08.131
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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%.

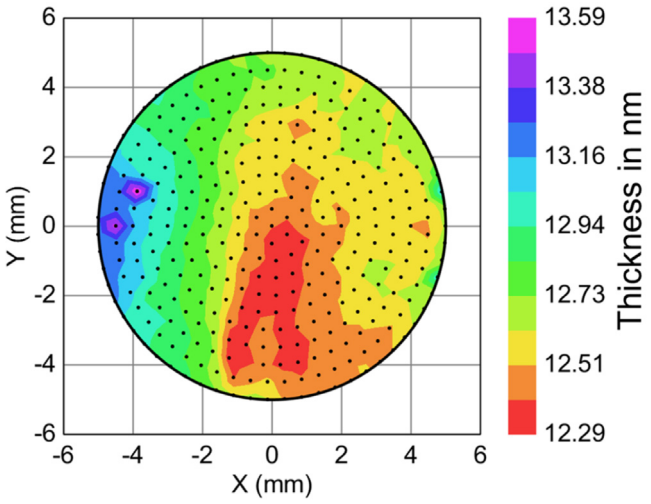

Fig. 1. Thickness uniformity map for free-standing superformvar film.

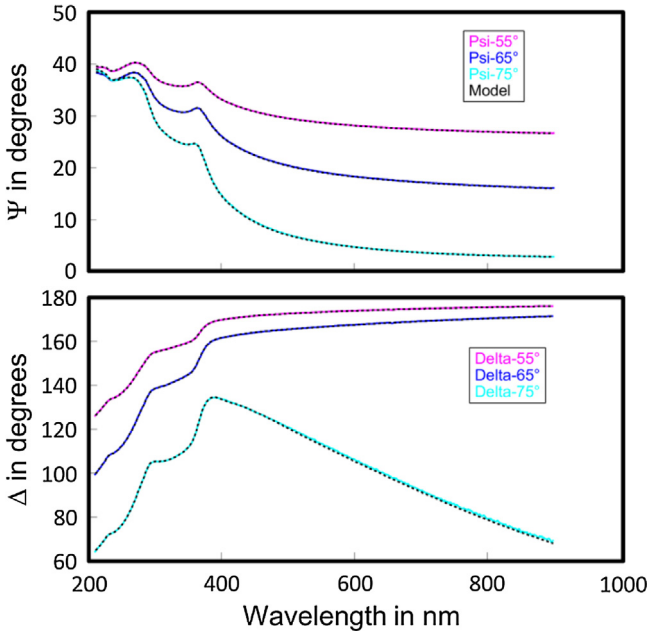

Fig. 2. SE data and corresponding fits for a 5.49 nm thick SF film on 1.40 nm native oxide coated silicon substrate.

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-

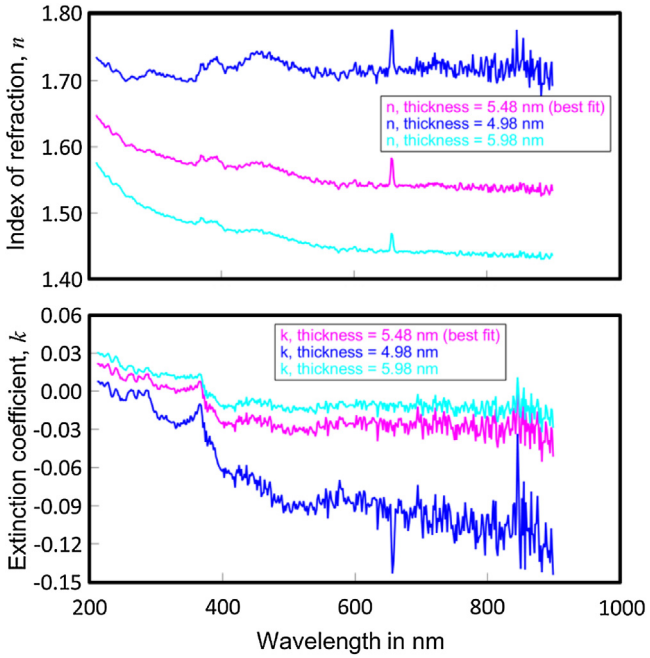

Fig. 3. Direct fit of *n,k* values for ultra-thin film on silicon using the best-fit thickness from Sellmeier model (magenta) as well as adjusted thickness by +/− 0.5 nm (blue, cyan). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

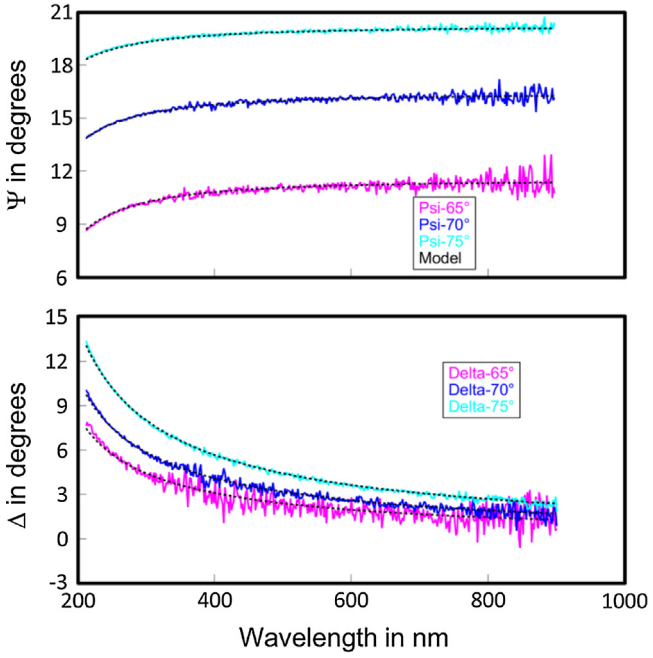

Fig. 4. SE data and corresponding Sellmeier model fit for a 5.30 nm thick SF free-standing film.

ting data from multiple angles of incidence, prevents simultaneous determination of each parameter independently.

The sensitivity to index of refraction can be demonstrated by allowing both index of refraction (*n)* and extinction coefficient (*k)* of the film to vary independently at each wavelength with thickness fixed at the resulting value from the Sellmeier model. Noise in the resulting optical constants (Fig. 3, magenta curves) is a direct result of the low sensitivity. The strong correlation between optical constants and thickness can also be demonstrated by repeating this direct-*nk* fit with the thickness adjusted by ±0.5 nm (Fig. 3, blue and cyan curves). The modified thickness has a large effect on the resulting optical constants. Thus, any error in thickness when characterizing ultra-thin coatings on silicon has a significant impact on the optical constant accuracy. Due to this challenge, it is common to use fixed optical constants and determine only the thickness of ultra-thin layers [1,2].

4.2. Free-standing ultra-thin films

Next, consider SE measurements from the same polymer as a free-standing film. Fig. 4 shows the experimental SE data and corresponding fits for an ultra-thin free-standing SF film. The layer was modelled as a transparent material using Sellmeier dispersion with air as the substrate such that coherent light interaction is calculated within the layer. The layer thickness was found to be 5.30 ± 0.03 nm with an index for 633 nm wavelength light of 1.47638 ± 0.0002, which shows 90% confidence limits that are more than an order of magnitude better than for the SF film on silicon. In addition, there are fewer sources of error, as the substrate (air) is ideal with no additional materials or layers to contend with. Furthermore, the absolute value of cross-correlation between thickness and Sellmeier terms are all <0.02. When the refractive index is not restricted to Sellmeier dispersion, the cross-correlation between thickness and index is nearly zero (=0.078) and signifies that the two parameters are uncorrelated and can both be determined independently.

To test measurement sensitivity, the resulting optical constants are allowed to vary independently at each wavelength with the

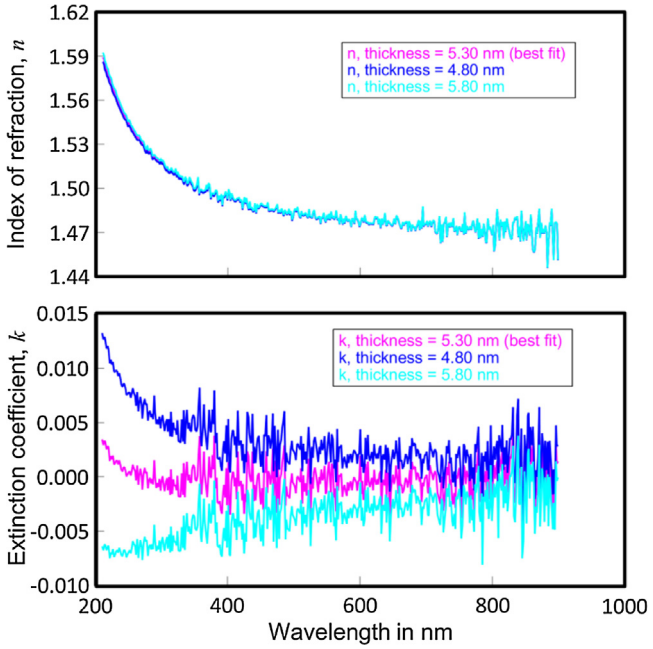

Fig. 5. Direct fit of *n,k* values for ultra-thin free-standing film on silicon using the best-fit thickness (magenta) as well as adjusted thickness by +/− 0.5 nm (blue, cyan). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

thickness fixed at the final result from the Sellmeier model (Fig. 5, magenta curve). While the free-standing SE data appear noisier than the corresponding data for a film on Si, this does not translate into additional noise in *n* and *k*. More importantly, when the thickness is varied by ±0.5 nm (Fig. 5 cyan and blue curves), the resulting optical constants show very little effect. This clearly demonstrates the uncorrelated separation between thickness and index for the free-standing ultra-thin film. Any error in thickness has very small effect on calculated index. There is slight correlation between *k* and

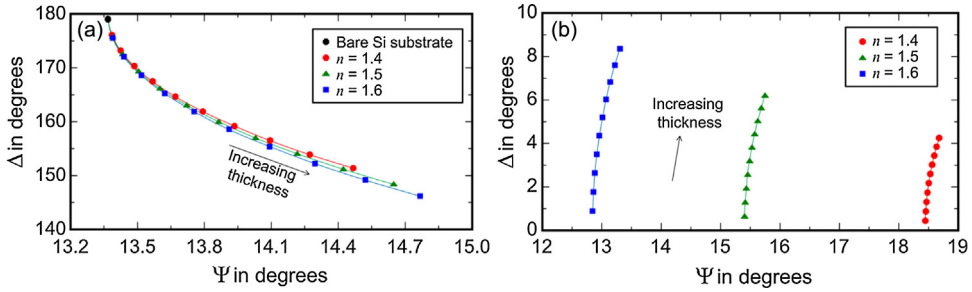

Fig. 6. Simulated Ψ-Δ curves at 70° angle and 633 nm wavelength for (a) ultra-thin films on silicon substrate and (b) free-standing films. The film thickness is varied up to 10 nm with index values of 1.4, 1.5, and 1.6. Fig. 6a is reproduced from reference [1] with permission from Momentum Press.

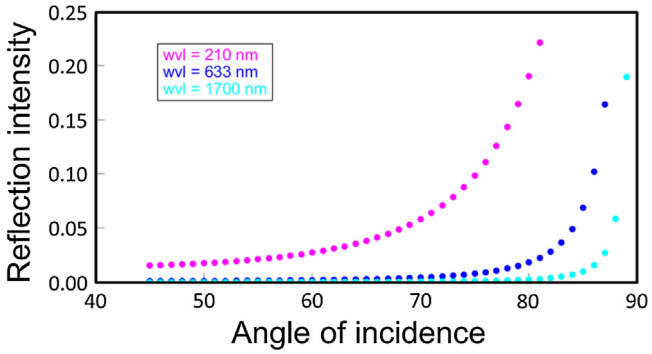

Fig. 7. Reflected unpolarized intensity versus angle of incidence calculated for the 5.3 nm free-standing SF film. Improved signal intensities require either very oblique angles or shorter wavelengths.

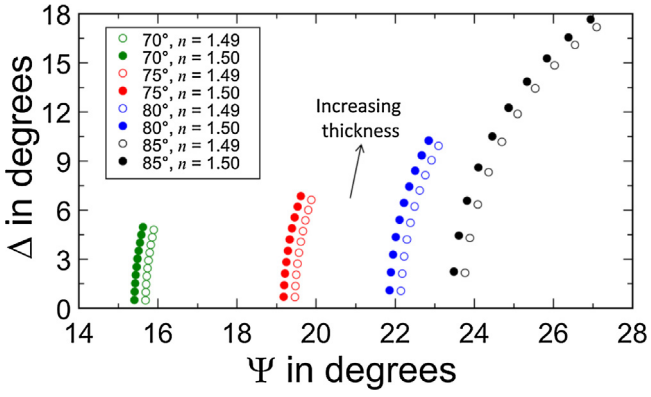

Fig. 8. Simulated Ψ-Δ trajectory at 633 nm wavelength for free-standing films from 1 to 10 nm in 1 nm increments showing increased thickness sensitivity with increasing angle of incidence, while the Ψ-separation for films with index of 1.49 (open circles) to films of index of 1.50 (closed circles) is retained with angle changes.

thickness, such that the best fit results also occur when k is near zero, which was assumed with the Sellmeier model.

4.3. Sensitivity and uniqueness simulations

Measurement sensitivity and thickness-index correlation are often best visualized by examining Ψ-Δ trajectory plots. Fig. 6 shows simulated SE data at 1 nm increments up to 10 nm layer thicknesses for (a) films on the silicon substrate, and (b) free-standing films. Three separate curves are plotted for transparent films with refractive index of 1.4, 1.5, and 1.6; which is a common index range for many organic materials. In Fig. 6a, the curve separation gradually increases, but still remains minimal even as the thickness approaches 10 nm. Thus, sensitivity to index of refraction, *n*, depends on the film thickness and separation in Ψ for films on silicon substrates. Without a substrate, the measured data show unique sensitivity to both thickness and index (Fig. 6b). The underlying reason for this is an orthogonal separation between the data effects due to changes in thickness and changes in index. Unlike the trajectories in Fig. 6a, there is now clear separation between the Ψ-Δ trajectories plotted for films with different index. Specifically, the film index produces a clear shift on the measured Ψ values, while thickness variations continue to primarily affect Δ for such ultra-thin layers.

While there is a clear benefit to measuring free-standing films, there are also obstacles. First is the obvious challenge of sample preparation for such free-standing films with ultra-thin thickness. Second is the challenge of collecting adequate signal from such layers in reflection. Fig. 7 shows the reflected unpolarized intensity calculated for the 5.3 nm free-standing film versus angle of incidence. The reflected intensity is very low until glancing angles of incidence. At 80°, the reflected intensity at 210 nm, 633 nm, and 1700 nm wavelengths is 19%, 1.8%, and 0.25%, respectively. It is clear that measurement signal improves with shorter wavelength and with increasingly oblique angles.

This leads to a question of whether oblique angles of incidence still maintain sensitivity to both thickness and index. Fig. 8 shows simulated Ψ-Δ trajectories at 633 nm wavelength for free-standing films with index of 1.49 and 1.50. It is clear that the index-thickness variations remain orthogonal, such that both can be uniquely determined. The sensitivity to thickness increases at oblique angles while retaining similar index sensitivity.

To significantly increase signal-to-noise, transmitted SE measurements were collected through the free-standing films. Unfortunately, the orthogonal separation between thickness and index is lost for the transmitted SE measurement and the data lack sensitivity to the film index. This is confirmed by considering the simulation in Fig. 9 where angle-dependent Ψ curves for the reflected and transmitted SE data are shown for a 5 nm film with index of 1.40 and 1.50. The shift in Ψ is quite evident for reflected SE data, while the transmitted Ψ data remain mostly close to 45° regardless of index of refraction.

4.4. Free-standing polymer index trends

The properties of nanometer-scale polymer films are of interest, as their mechanical, dielectric, and thermal properties may all be significantly different from the bulk (thick-film) polymer properties [15,16]. Measuring the refractive index for ultra-thin films was extremely challenging before now. With the methods described in this paper, we measured a series of Superformvar and Vinylec E free-standing layers to determine accurate refractive index and show that the index decreases as the layer thickness decreases below about 20 nm. This is demonstrated in Fig. 10 for the complete series of measurements.

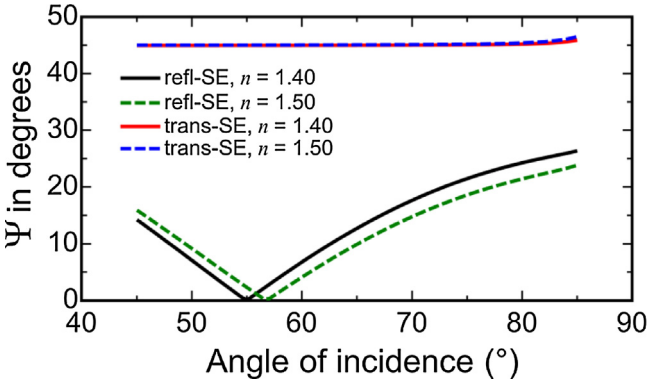

Fig. 9. Simulated SE data in reflection and transmission for a 5 nm thick free-standing film with index of 1.40 and 1.50 shows high sensitivity to variation in Ψ for only the reflected SE data.

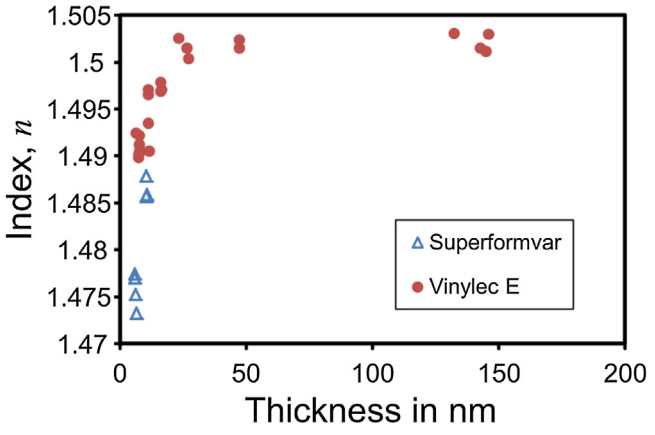

Fig. 10. Index of refraction at 633 nm wavelength for free-standing polymer films versus thickness.

We speculate the index decrease for thinnest films is related to a density decrease. Other film properties, such as modulus, glass transition temperature, yield stress, and failure strain also change at similar thicknesses for these films (publication in preparation). Changes in these properties have been observed at similar thicknesses for supported and unsupported ultra-thin films by other groups [15–20].

5. Conclusions

Ultra-thin free-standing polymer films with thickness down to 5 nm have been characterized with SE. Unlike characterization of films on Si substrate, which show primary sensitivity to optical thickness due to correlation between thickness and index, the characterization of free-standing films is sensitive to both thickness and refractive index, independently. Simulations show an orthogonal separation to the data changes from thickness and index. For free-standing ultra-thin films, it was shown that the index can be uniquely determined from measurement of Ψ, while thickness changes predominately affect the Δ parameter. This allows both thickness and index to be uniquely determined. Additional simulations show that improved measurements of free-standing films may require short wavelengths and very oblique angles exceeding 80°. Each can increase the reflected light intensity and oblique angles also increase sensitivity to thickness. SE characterization of free-standing films shows great potential to help characterize the optical properties of ultra-thin polymer films for comparison to their bulk, thick-film properties.

Acknowledgement

Work done at the Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy by under Contract DE-AC52-07NA27344 and funded by LDRD project 14-ERD-025.

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