Determination of refractive index of ultrathin dielectric films prepared via layer-by-layer polyelectrolyte deposition

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Introduction

Layer-by-layer deposition of oppositely charged polyelectrolytes originated in the 1990s following seminal work by Decher et al. [1-3] and has since attracted considerable interest owing to its versatility and the ability to modulate polyelectrolyte multilayer film properties at the nanoscale [4]. Furthermore, it has been shown that for certain layer-by-layer polyelectrolyte systems, such as multilayers composed of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS), the growth scales linearly with the number of assembled layers [5].

In this work, layer-by-layer polyelectrolyte deposition has been studied by alternately immersing the Si/SiO_2(300 nm) substrates into successive aqueous solutions of cationic PAH and anionic PSS polyelectrolytes with intermediate rinsing steps [6]. Base piranha surface functionalization (SF) approach has been adopted by dipping the substrates into the NH_4OH/H_2O_2 mix for 2 h at 50°C in order to create an OH^- terminated surface prior to exposing the samples to the positively charged PAH. Due to their thickness at the nanometer scale, the characterization of polyelectrolyte multilayer films requires highly sensitive techniques such as spectroscopic ellipsometry (SE) and atomic force microscopy (AFM) which were employed in order to verify the presence of polyelectrolyte multilayer films. Finally, parametric fitting based on the Cauchy model and direct inversion have been utilized in order to determine the real and imaginary parts of the refractive index of ultrathin polyelectrolyte multilayer films in the wavelength range of 200-800 nm.

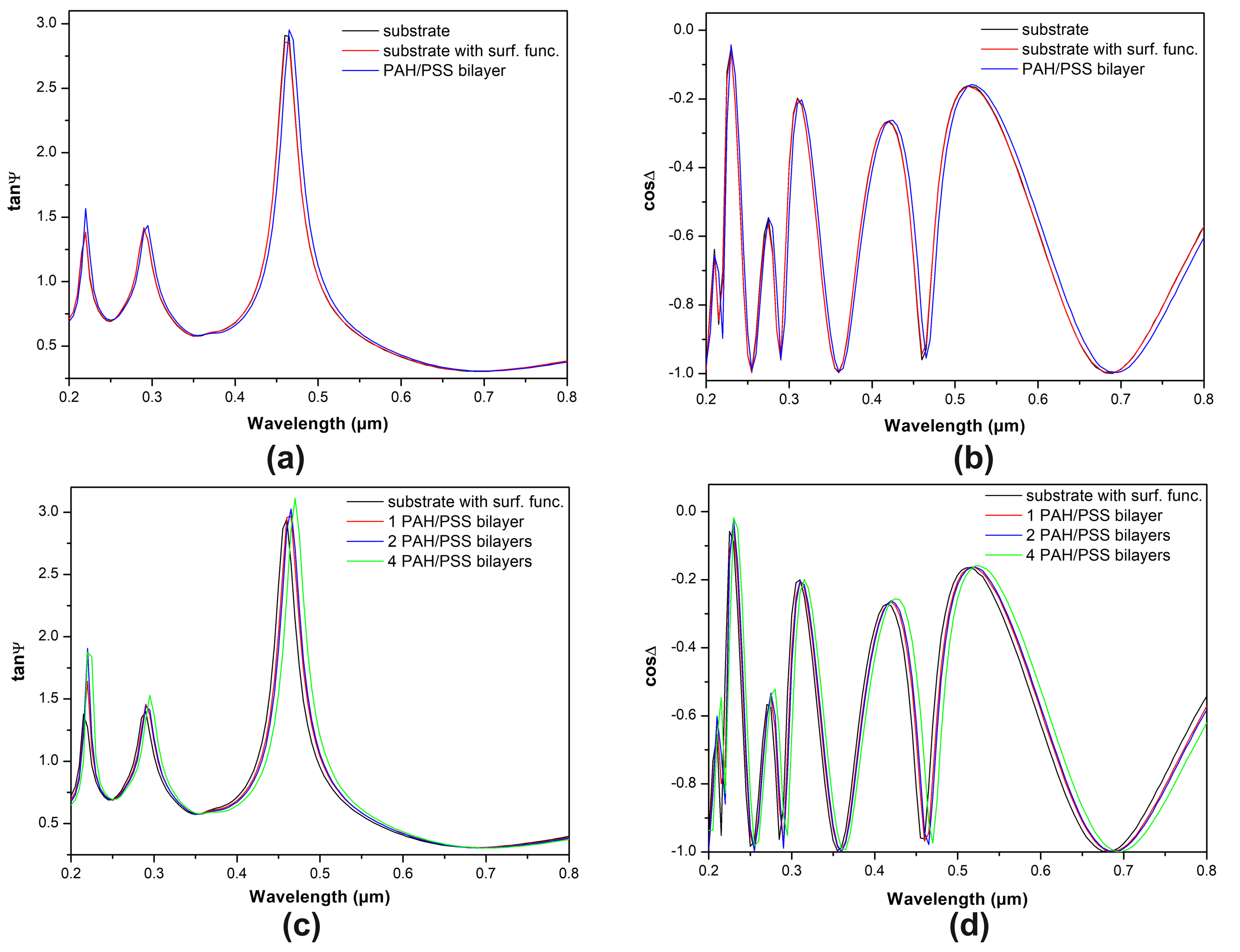
Spectroscopic ellipsometry

Spectroscopic ellipsometry measures the change in the state of polarization of the incident light upon reflection from the sample [7].

It gives the ratio of the two complex Fresnel reflection coefficients, for light polarized parallel and perpendicular to the plane of incidence, respectively:

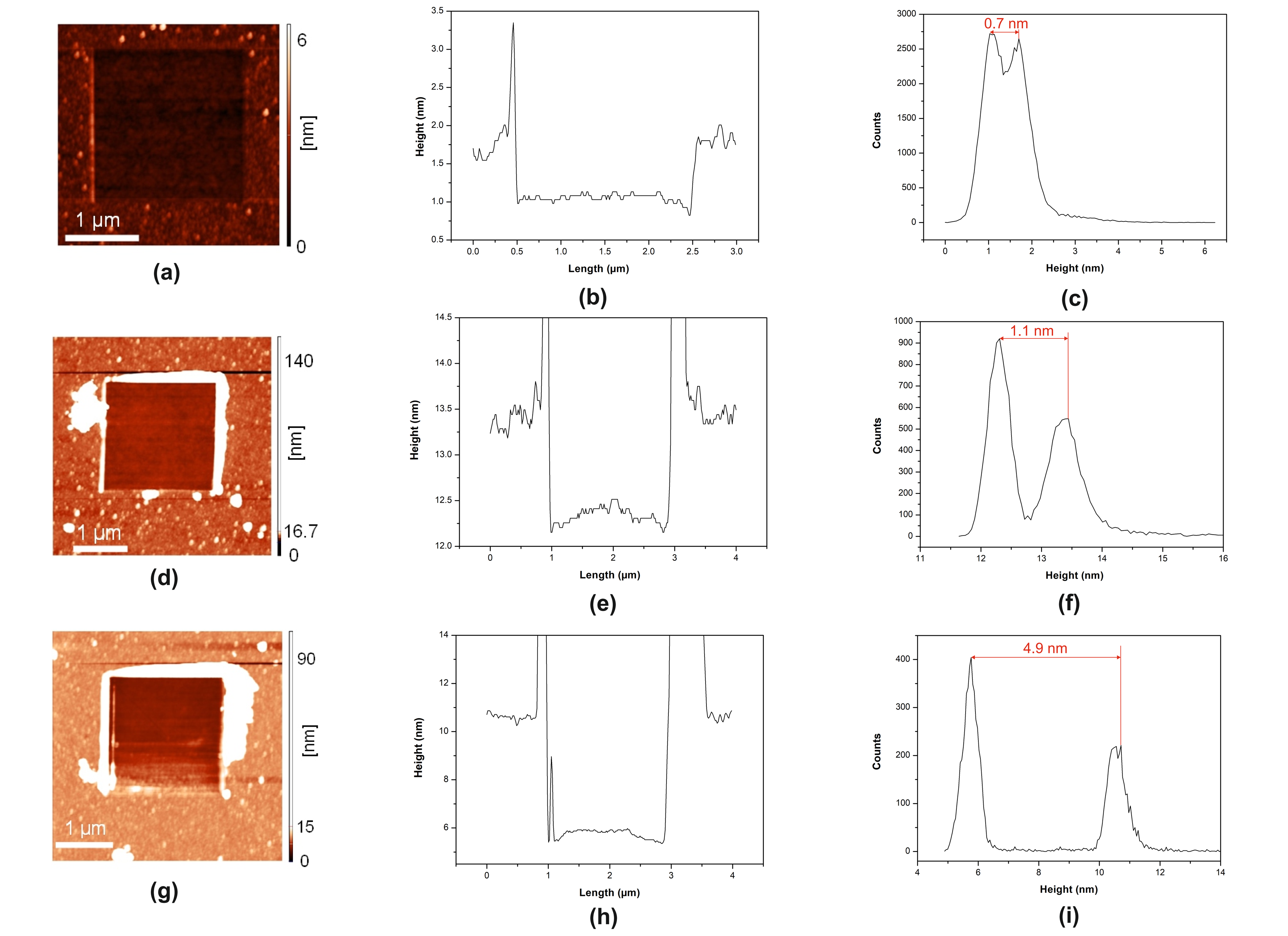
$$\rho = \frac{r_p}{r_s} = \tan\Psi \cdot e^{i\Delta}$$

The output parameters of ellipsometric measurements are quantities *tanΨ* and *cos*Δ, as indicated in the Figure, with an observable wavelength shift of the prominent *tanΨ* peak in the positive direction with additional PAH/PSS bilayers.



Experimentally measured ellipsometric spectra at *Θ* = 65° of (a)-(b) Si/SiO_2 substrate, substrate after SF, and an additional PAH/PSS bilayer on top, and (c)-(d) substrate after SF, and one, two and four additional PAH/PSS bilayers on top.

Atomic force microscopy



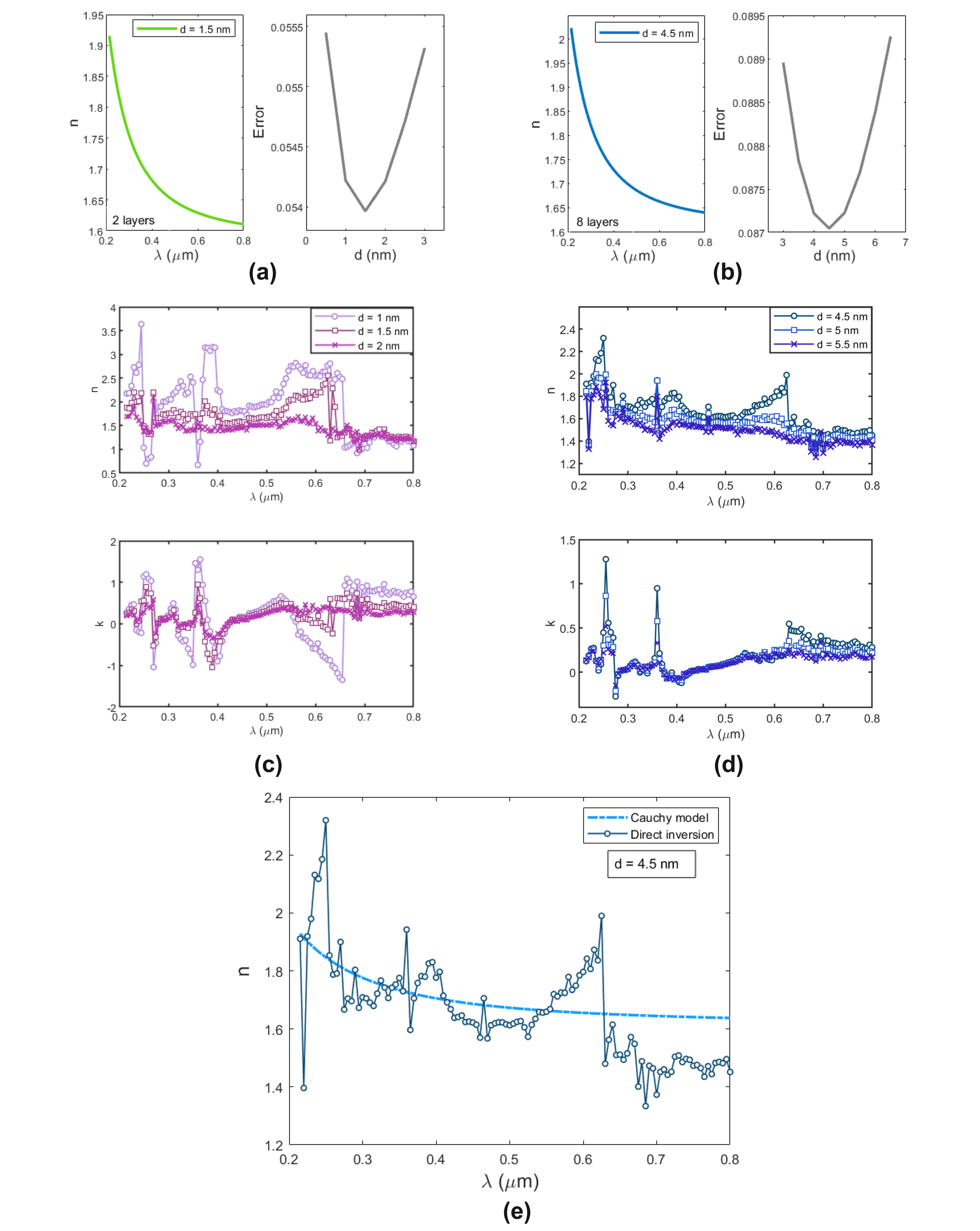
AFM imaging and cross section measurements after AFM tip scratching; (a)-(c) SF layer, (d)-(f) SF layer and a single PAH/PSS bilayer, (g)-(i) SF layer and four PAH/PSS bilayers. (a), (d), (g) 2D topography images, (b), (e), (h) average cross section scan profiles across the homogeneous part of each square-shaped feature, and (c), (f), (i) histograms associated with the 2D topography images.

Cauchy model and direct inversion

The empirical Cauchy model can be used for approximation of the real part of the refractive index within spectral regions for which the material has very low or non-existing absorption [7].

$$n = A + \frac{B}{\lambda^2} \qquad \sigma = \sqrt{\frac{1}{2NN_\theta - 1}\sum_{i=1}^{N}\sum_{\theta=\theta_1}^{\theta_m}\sigma^2(\lambda,\theta)} \qquad \sigma(\lambda,\theta) = \sqrt{(\tan\psi_{ex} - \tan\psi_{mod})^2 + (\cos\Delta_{ex} - \cos\Delta_{mod})^2}$$

Furthermore, complex refractive index of a layer in a multilayer structure can be extracted by direct inversion when the thickness of the layer is known (e.g. established by AFM).



(a)-(b) The real part of the refractive index against wavelength as obtained via the parametric Cauchy model and the calculation error dependence on the film thickness for (a) a single PAH/PSS bilayer, and (b) four PAH/PSS bilayers. (c)-(d) Both real and complex parts of the refractive index obtained by direct inversion (for several fixed thicknesses) for (c) a single PAH/PSS bilayer, and (d) four PAH/PSS bilayers. (e) Cauchy model versus direct inversion for a 4.5 nm thick polyelectrolyte film with four PAH/PSS bilayers.

Conclusion

Spectroscopic ellipsometry measurements demonstrated an observable wavelength shift of the prominent *tanΨ* peak with the deposition of additional PAH/PSS bilayers.

Cross section scan profiles following AFM tip scratching indicated that the thicknesses of the SF layer and the PAH/PSS bilayer are approximately ~0.7 nm and ~1.1 nm, respectively.

Finally, the Cauchy model and direct inversion methodologies were utilized to determine the real and the imaginary parts of the refractive index of the prepared ultrathin dielectric films in the wavelength range of 200-800 nm. It has been found that, disregarding the sharp discontinuities obtained via direct inversion, the values of *n* vary in the range of ~1.2 – 2 for all films, whereas *k* oscillates around zero.

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