Supporting Information for

Parameterization of the Optical Constants of Polydopamine Films for Spectroscopic Ellipsometry Studies

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S1. XPS data of PDA films: **Figure S1** demonstrates the high resolution XPS spectra and peak deconvolution of C 1s, N 1s and O 1s of the PDA films (6 and 12 h). The estimated percentages of the functional groups of the PDA films (2, 6, and 12 h) are summarized in Table S1.

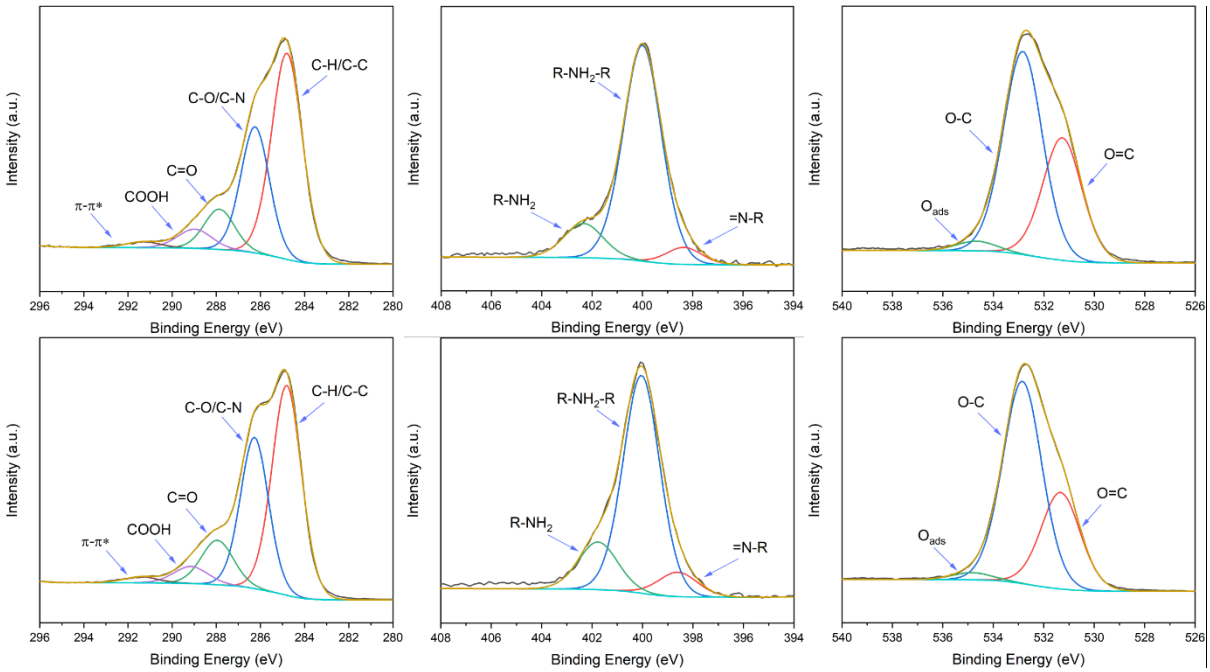

Figure S1 High-resolution XPS spectra of C 1s, N 1s and O 1s of PDA films; (top row) 6 h deposition, (bottom row) 12 h deposition

Table S1 XPS functional group percentages for PDA films of different deposition times

	C 1s				O 1s			N 1s		
Deposition time	CHx, C-NH_2	C-O, C-N	C=O	COOH	O=C	O-C	Oads	=N-R	R-NH-R	R-NH_2
2 h	50.6	31.8	9.2	8.4	25.8	70.5	3.7	7.1	74.6	18.3
6 h	53.6	30.9	9.3	6.2	36.5	60.6	2.9	6.3	80.5	13.2
12 h	51.0	32.1	11.7	5.2	31.5	66.2	2.3	8.4	74.6	17.0

S2. Water contact angle of PDA films: The water contact angles of bare and PDA-coated silicon wafers were measured using Theta Lite optical tensiometer (Biolin Scientific, Sweden). Measurements were conducted using a 1.5 µl water droplet at ambient temperature. **Figure S2** shows the representative contact angle (15 measurements: 5 randomly chosen areas on 3 specimens) of PDA samples of different deposition times.

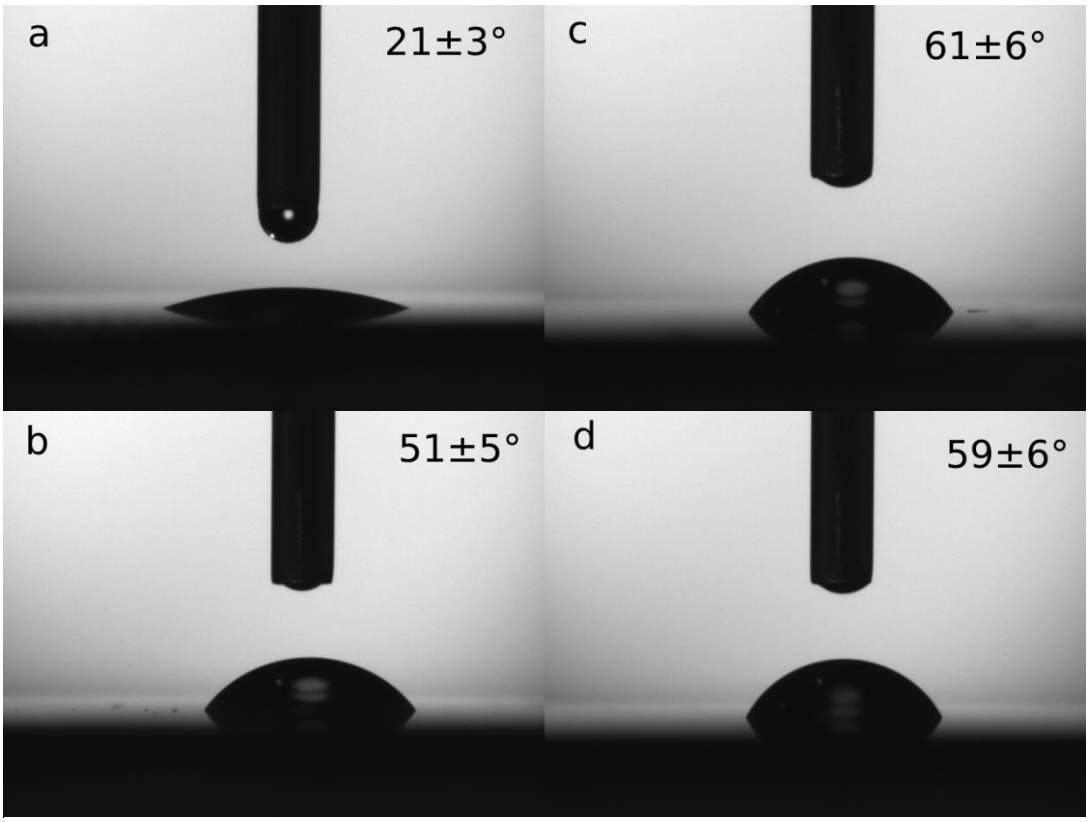

Figure S2 Water contact angle of bare and PDA-coated silicon wafers; (a) bare wafer, (b) PDA 2 h, (c) PDA 6 h, and (d) PDA 12 h deposition. The reported value represents the average of 15 data points.

S3 Step-by-step modeling of the ellipsometry data: as discussed in the main manuscript, a step-by-step construction of an appropriate optical model is required for the ellipsometry analysis of PDA films, depending on various aspects of the film such as thickness, roughness, and light absorption. When constructing the optical model, one should always consider that the minimum number of "free" parameters in the model is desired, and that adding further free parameters to the model should significantly improve the quality of the fitting (as a rule of thumb: at least 20% reduction in MSE when a free parameter is added to the model). In the following, the step-by-step construction of the appropriate optical models for the PDA films of this study (in each case, the representative median sample from 15 data measurements) is provided in **Figure S3-S11**.

We begin with the simplest optical model, i.e., Cauchy relation (2 free parameters: PDA film thickness (layer # 3) and A of Cauchy), then advance the optical model to Cauchy with an Urbach absorption term (4 free parameters: PDA film thickness (layer # 3), A of Cauchy, amplitude and exponent of the Urbach relation), KK-consistent B-spline (9 free parameters: PDA film thickness (layer # 3), 6 nodes, 2 KK-relation parameters), and ultimately KK-consistent B-spline with an EMA roughness layer (10 free parameters: PDA film thickness (layer # 3), 6 nodes, 2 KK-relation parameters, thickness of the roughness layer).

Fit Results	Optical Model
MSE = 37.783 Thickness # 3 = 5.88 ± 0.107 nm A = 1.714 ± 0.0117 Total Thickness = 107.80 ± 0.107 nm	- Layer # 3 = Cauchy Thickness # 3 = **5.88 nm** (fit) A = **1.714** (fit) B = 0.01000 C = 0.0000 + **Urbach Absorption Parameters** Layer # 2 = SIO2_JAW Thickness # 2 = 100.93 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

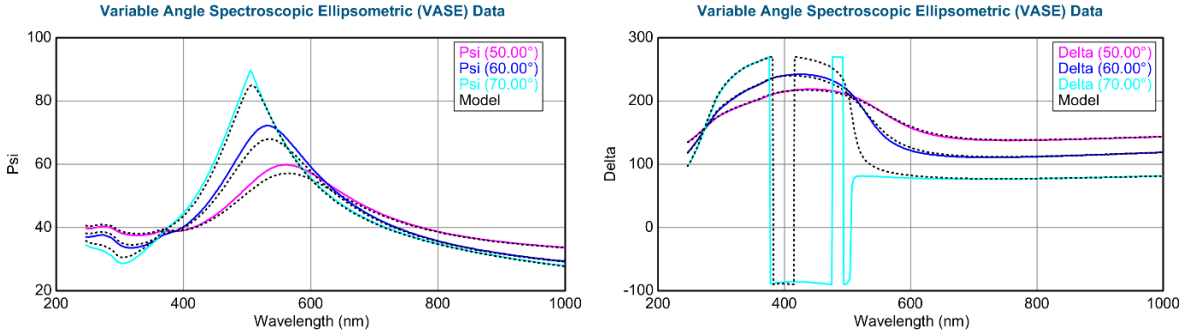

Figure S3 PDA 2 h deposition, Cauchy model

Fit Results	Optical Model
MSE = 7.041 Thickness # 3 = 6.50 ± 0.021 nm A = 1.655 ± 0.001984 k Amplitude = 0.15071 ± 0.001020 Exponent = 0.319 ± 0.007785 Total Thickness = 108.43 ± 0.021 nm	- Layer # 3 = Cauchy Thickness # 3 = **6.50 nm** (fit) A = **1.655** (fit) B = 0.01000 C = 0.0000 - **Urbach Absorption Parameters** k Amplitude = **0.15071** (fit) Exponent = **0.319** (fit) Band Edge = 400.0 nm Layer # 2 = SIO2_JAW Thickness # 2 = 100.93 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

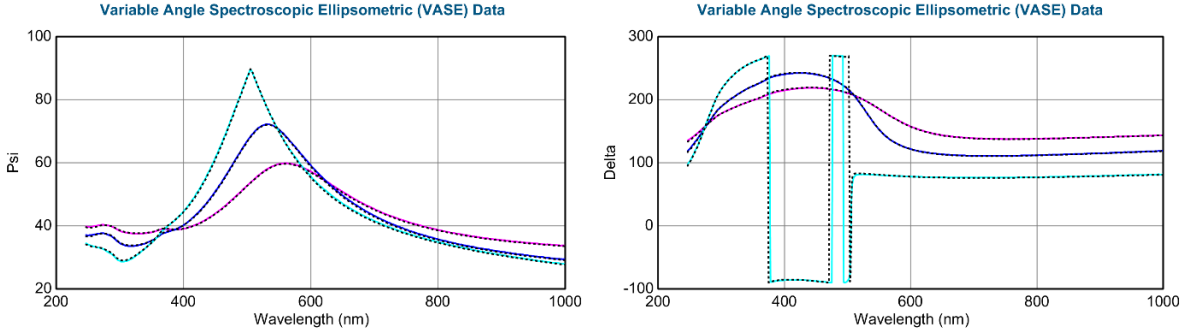

Figure S4 PDA 2 h deposition, Cauchy with Urbach absorption model

Fit Results	Optical Model
MSE = 101.135 (Out-Of-Spec) Thickness # 3 = 15.70 ± 0.227 nm A = 1.927 ± 0.0114 Total Thickness = 119.08 ± 0.227 nm	- Layer # 3 = Cauchy Thickness # 3 = **15.70 nm** (fit) A = **1.927** (fit) B = 0.01000 C = 0.0000 + **Urbach Absorption Parameters** Layer # 2 = SIO2_JAW Thickness # 2 = 102.38 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

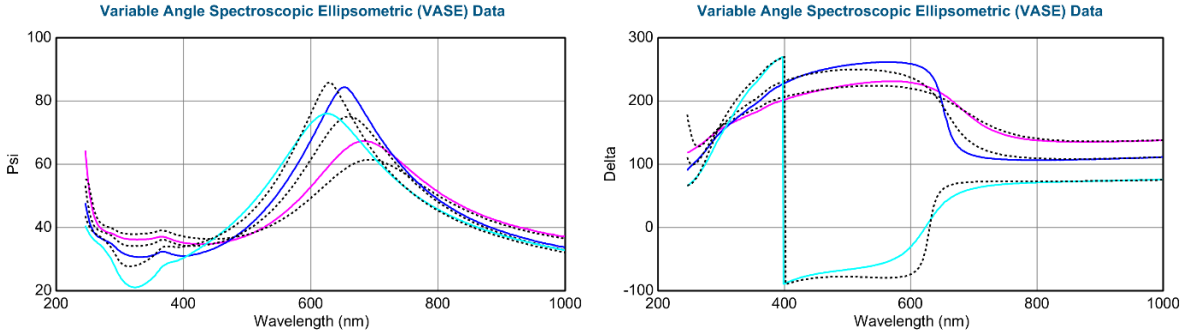

Figure S5 PDA 6 h deposition, Cauchy model

Fit Results	Optical Model
MSE = 39.641 Thickness # 3 = 18.75 ± 0.121 nm A = 1.791 ± 0.004675 k Amplitude = 0.14243 ± 0.001384 Exponent = 0.273 ± 0.007101 Total Thickness = 122.13 ± 0.121 nm	- Layer # 3 = Cauchy Thickness # 3 = **18.75 nm** (fit) A = **1.791** (fit) B = 0.01000 C = 0.0000 - **Urbach Absorption Parameters** k Amplitude = **0.14243** (fit) Exponent = **0.273** (fit) Band Edge = 400.0 nm Layer # 2 = SIO2_JAW Thickness # 2 = 102.38 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

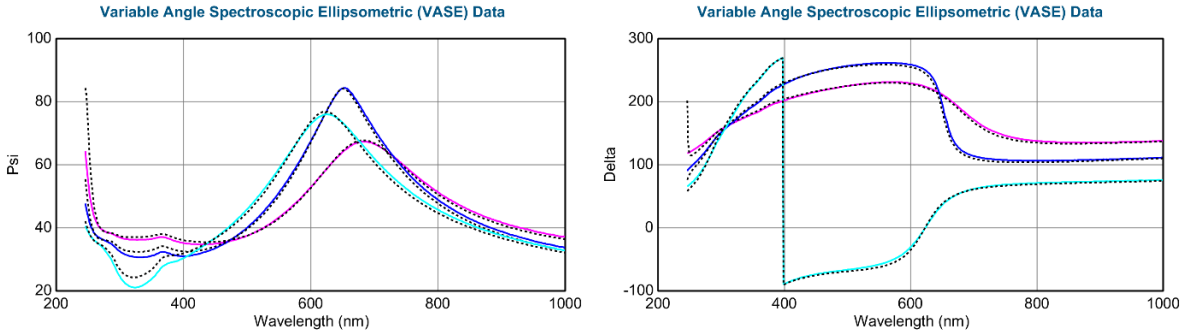

Figure S6 PDA 6 h deposition, Cauchy with Urbach absorption model

Fit Results

MSE = 5.550
Thickness # 3 = 22.37 ± 0.038 nm
E Inf = 1.330 ± 0.0109
IR Amp = 0.557 ± 0.0115
Total Thickness = 125.74 ± 0.038 nm

Optical Model

- Layer # 3 = B-Spline Thickness # 3 = **22.37 nm** (fit)
  - Resolution (eV) = 0.700 6 Pts. (1.241-5.039 eV) Draw Node Graph
  - Fit Optical Constants = ON
  - Use KK Mode = ON (In Use)
  - + **Kramers-Kronig**
  - - **Nodes**
    - Init. values: n = 1.500 k = 0.00 Starting Mat. = Cauchy
    - Force E2 Positive = ON
    - Assume Transparent Region = OFF
    - Show Nodes = OFF
    - Node Spacing Spectral Ranges: Add Delete Delete All
  - + **Advanced**
- Layer # 2 = SIO2_JAW Thickness # 2 = 102.38 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

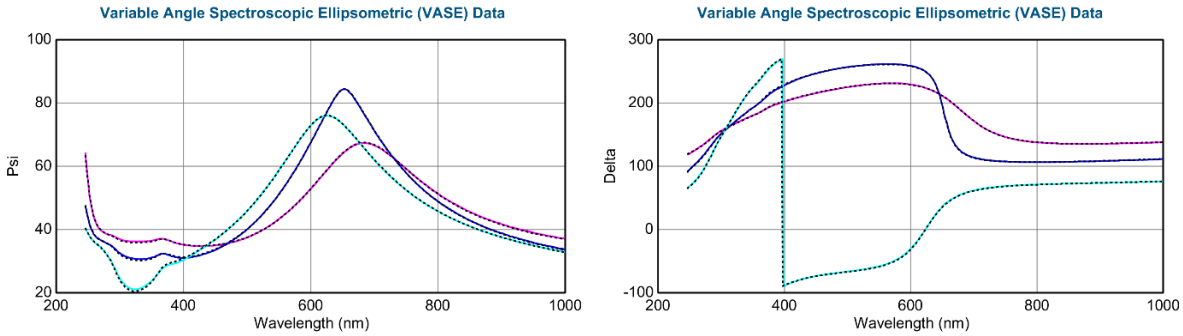

Figure S7 PDA 6 h deposition, KK-consistent B-spline model

Fit Results

MSE = 149.089 (Out-Of-Spec)
Thickness # 3 = 34.28 ± 0.220 nm
A = 1.970 ± 0.005785
Total Thickness = 136.71 ± 0.220 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **34.28 nm** (fit)
  - A = **1.970** (fit) B = 0.01000 C = 0.0000
  - + **Urbach Absorption Parameters**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.43 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

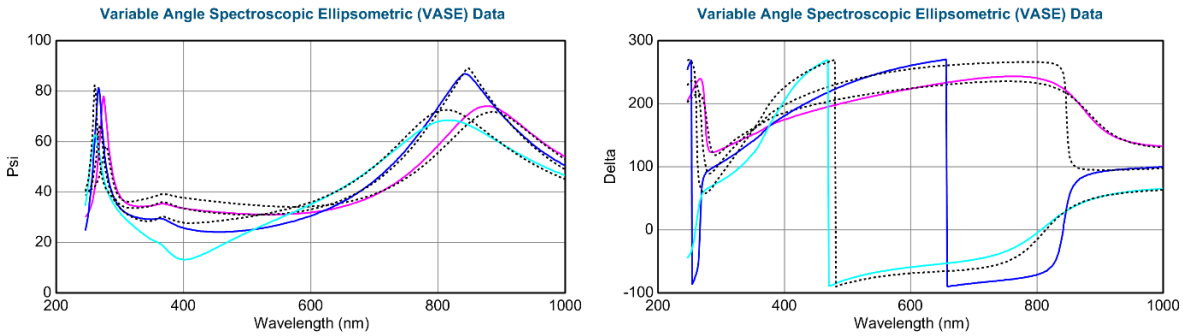

Figure S8 PDA 12 h deposition, Cauchy model

Fit Results

MSE = 98.520
Thickness # 3 = 37.55 ± 0.158 nm
A = 1.888 ± 0.003644
k Amplitude = 0.09725 ± 0.001561
Exponent = 0.457 ± 0.0100
Total Thickness = 139.98 ± 0.158 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **37.55 nm** (fit)
  A = **1.888** (fit) B = 0.01000 C = 0.0000
  - **Urbach Absorption Parameters**
    k Amplitude = **0.09725** (fit) Exponent = **0.457** (fit)
    Band Edge = 400.0 nm
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.43 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

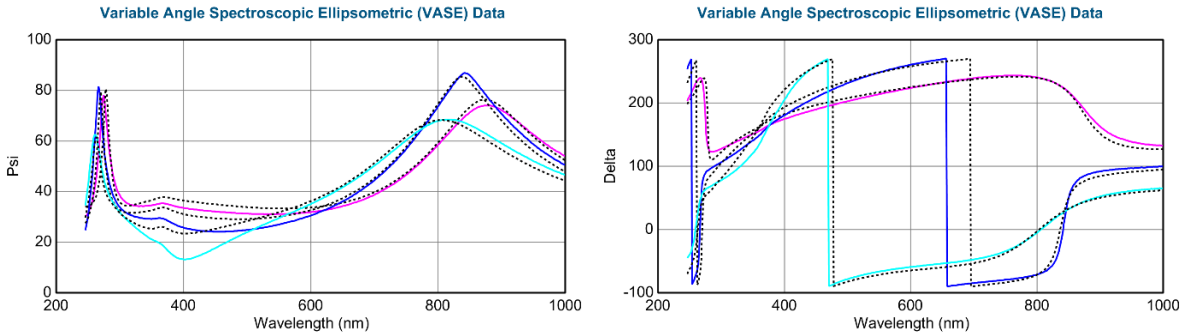

Figure S9 PDA 12 h deposition, Cauchy with Urbach absorption model

Fit Results

MSE = 12.619
Thickness # 3 = 48.70 ± 0.060 nm
E Inf = 1.289 ± 0.008047
IR Amp = 0.350 ± 0.008563
Total Thickness = 151.14 ± 0.060 nm

Optical Model

- Layer # 3 = B-Spline Thickness # 3 = **48.70 nm** (fit)
  Resolution (eV) = 0.700 6 Pts. (1.241-5.039 eV) Draw Node Graph
  Fit Optical Constants = ON
  Use KK Mode = ON (In Use)
  + **Kramers-Kronig**
  - **Nodes**
    Init. values: n = 1.500 k = 0.00 Starting Mat. = Cauchy
    Force E2 Positive = ON
    Assume Transparent Region = OFF
    Show Nodes = OFF
    Node Spacing Spectral Ranges: Add Delete Delete All
  + **Advanced**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.43 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

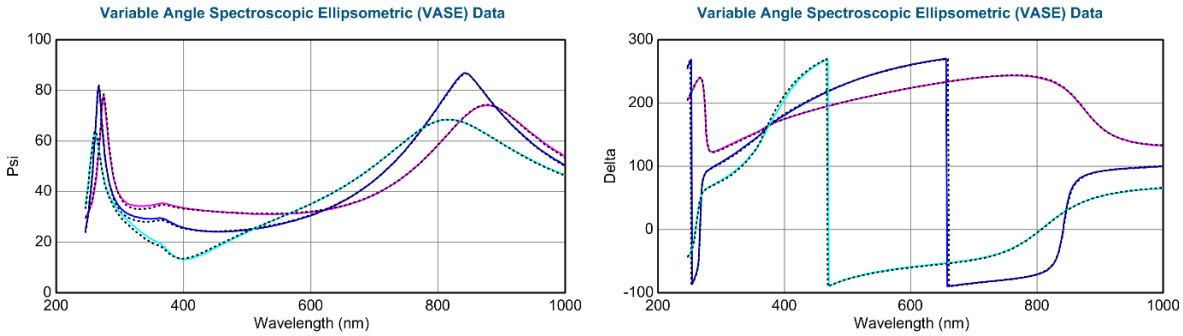

Figure S10 PDA 12 h deposition, KK-consistent B-spline model

Fit Results

MSE = 6.874
Roughness = 10.42 ± 0.125 nm
Thickness # 3 = 45.30 ± 0.052 nm
E Inf = 1.184 ± 0.005049
IR Amp = 0.163 ± 0.005700
Total Thickness = 147.74 ± 0.052 nm

Optical Model

Roughness = **10.42 nm** (fit)
- Layer # 3 = B-Spline Thickness # 3 = **45.30 nm** (fit)
  - Resolution (eV) = 0.700 6 Pts. (1.241-5.039 eV) Draw Node Graph
  - Fit Optical Constants = ON
  - Use KK Mode = ON (In Use)
  - + **Kramers-Kronig**
  - - **Nodes**
    - Init. values: n = 1.500 k = 0.00 Starting Mat. = Cauchy
    - Force E2 Positive = ON
    - Assume Transparent Region = OFF
    - Show Nodes = OFF
    - Node Spacing Spectral Ranges: Add Delete Delete All
  - + **Advanced**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.43 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

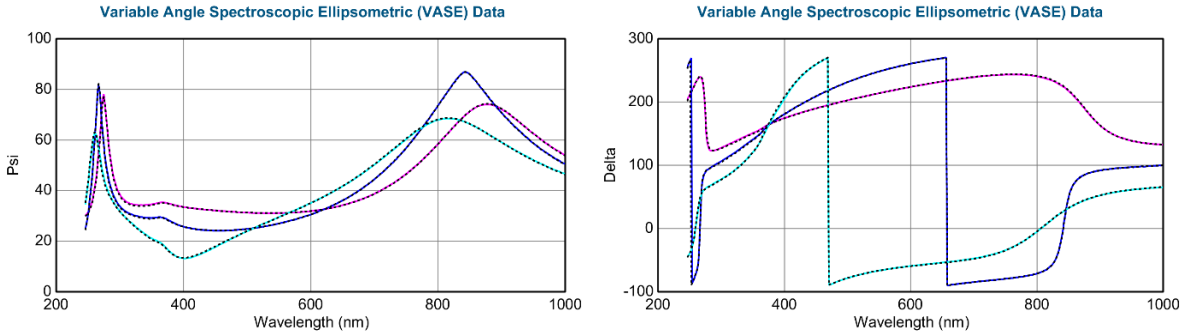

Figure S11 PDA 12 h deposition, KK-consistent B-spline with roughness model

In addition, we tested an alternative approach to estimate the thickness of the films. Herein, the optical constants (from B-spline parametrization) of PDA 6 h sample were used to analyse the data for PDA 2 h and 12 h samples. In this approach, the optical constants of the material are obtained from a "reference" sample that not only is relatively thick (i.e., not 2 h sample) but also is not too rough (i.e., not 12 h sample). Thus, one can argue that the modelled optical constants for the reference sample are the most trustable. Assuming that the optical constants of the material are the same for all the samples, one can use the "reference" optical constants to estimate the thickness of the other samples. **Figure S12** summarizes the modeling data for PDA 2 h sample using this approach. An acceptable MSE value is found, also the estimated thickness agrees with **Figure S4** (when using Cauchy with Urbach absorption, i.e., modeling both thickness and optical constants). **Figure S13** shows the modeling data for PDA 12 h sample using the fixed optical constants. Herein, the modelled data doesn't match the experimental data completely, i.e., MSE is notably large, compared with **Figure S11** (when modeling both thickness and optical constants). Overall, while this approach is commonly used in the literature, the variable chemistry and microstructure of PDA films (depending on the deposition conditions) could contradict the assumption of having fixed optical constants for samples of varying thicknesses.

Fit Results	Optical Model
MSE = 7.379 Thickness # 3 = 6.41 ± 0.005 nm Total Thickness = 108.34 ± 0.005 nm	Layer # 3 = 6h PDA (Tabulated B-spline) Thickness # 3 = **6.41 nm** (fit) Layer # 2 = SIO2_JAW Thickness # 2 = 100.93 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

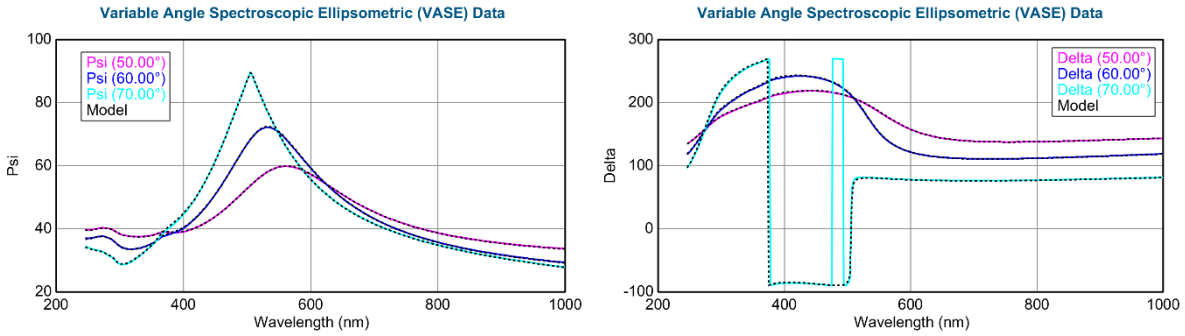

Figure S12 PDA 2 h deposition, fixed (tabulated) optical constants of PDA 6 h used in the model, leaving thickness as the only free parameter

Fit Results	Optical Model
MSE = 45.250 Roughness = -0.47 ± 0.411 nm Thickness # 3 = 50.62 ± 0.038 nm Total Thickness = 153.05 ± 0.038 nm	Roughness = **-0.47 nm** (fit) Layer # 3 = 6h PDA (Tabulated B-spline) Thickness # 3 = **50.62 nm** (fit) Layer # 2 = SIO2_JAW Thickness # 2 = 101.43 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

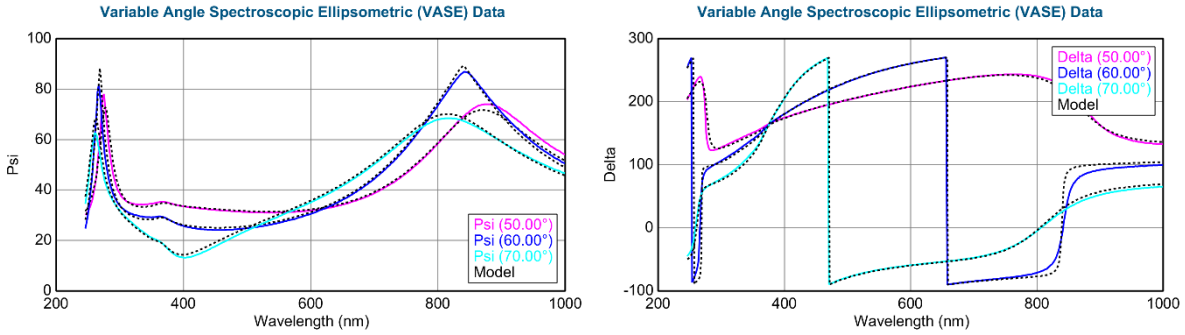

Figure S13 PDA 12 h deposition, fixed (tabulated) optical constants of PDA 6 h used in the model, leaving thickness as the only free parameter

S4. Sensitivity analysis for the B-spline function (PDA 6 h and 12 h): as discussed in the main article, optimizing the number of nodes of the B-spline function is crucial to avoid over-parametrization and correlation between the free parameters. Herein, we provide a detailed sensitivity analysis for the PDA films modelled with the B-spline function. **Figure S14** demonstrates the MSE as a function of number of nodes (left panel) as well the film thickness (right panel) for PDA 6 h sample. Herein, increasing the number of nodes has a minor effect on both MSE value and the film thickness. The former suggests that MSE value is not an appropriate parameter to decide on the minimum number of nodes. The later however suggests that thickness of the film is roughly around 22 nm regardless of the number of nodes (i.e., thickness is not sensitive to the number of nodes). **Figure S15**

shows the diagram of nodes (for the dielectric functions) for various numbers of nodes (4 to 19). Herein, one requires a minimum number of nodes so that the spline e2 (imaginary part of the dielectric function) curve goes through the free nodes (in the range of 1.2 – 5.3 eV), without showing small features in the dispersion (forcefitting, risk of overparameterization). Thus, **Figure S15** suggests that a total number of 6-7 nodes can provide a smooth spline e2 curve without overparameterization (see the plot for 10 nodes as an example of overparameterization). A similar deduction can be made from **Figure S16**, in which the n and k dispersions are plotted for different numbers of nodes. Accordingly, the overall shapes of n and k dispersions are independent of the number of nodes. Besides, the range of n and k are roughly 1.6-1.7 and 0-0.25 regardless of the number of nodes. Nevertheless, when the number of nodes is roughly larger than 6, extra features, i.e., wiggles in n and peaks in k, appear in the optical dispersions, which are unknown to be a physical feature of the sample or simply just due to overfitting. Hence, based on **Figure S14-S16**, we conclude that merely 6 nodes are enough in this case to obtain a reliable thickness value using the least number of free parameters in the model.

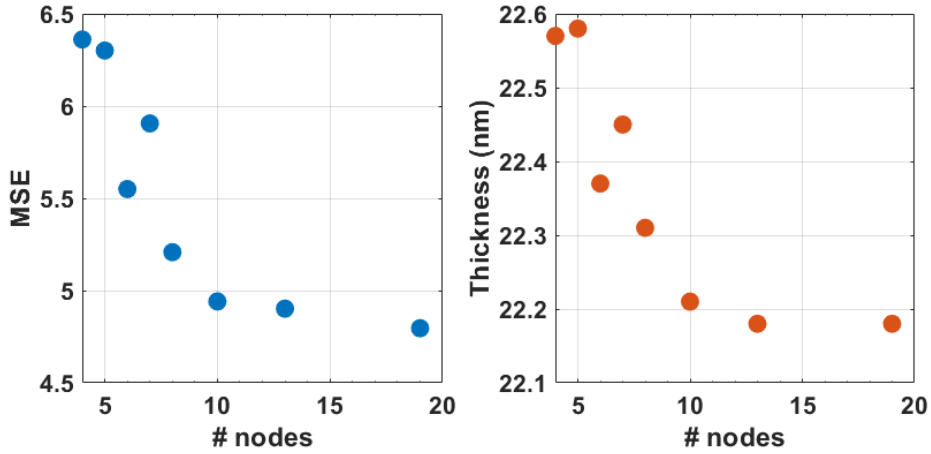

Figure S14 PDA 6 h deposition: sensitivity analysis for the number of nodes of the B-spline function (left) MSE vs. # nodes and (right) thickness vs. # nodes

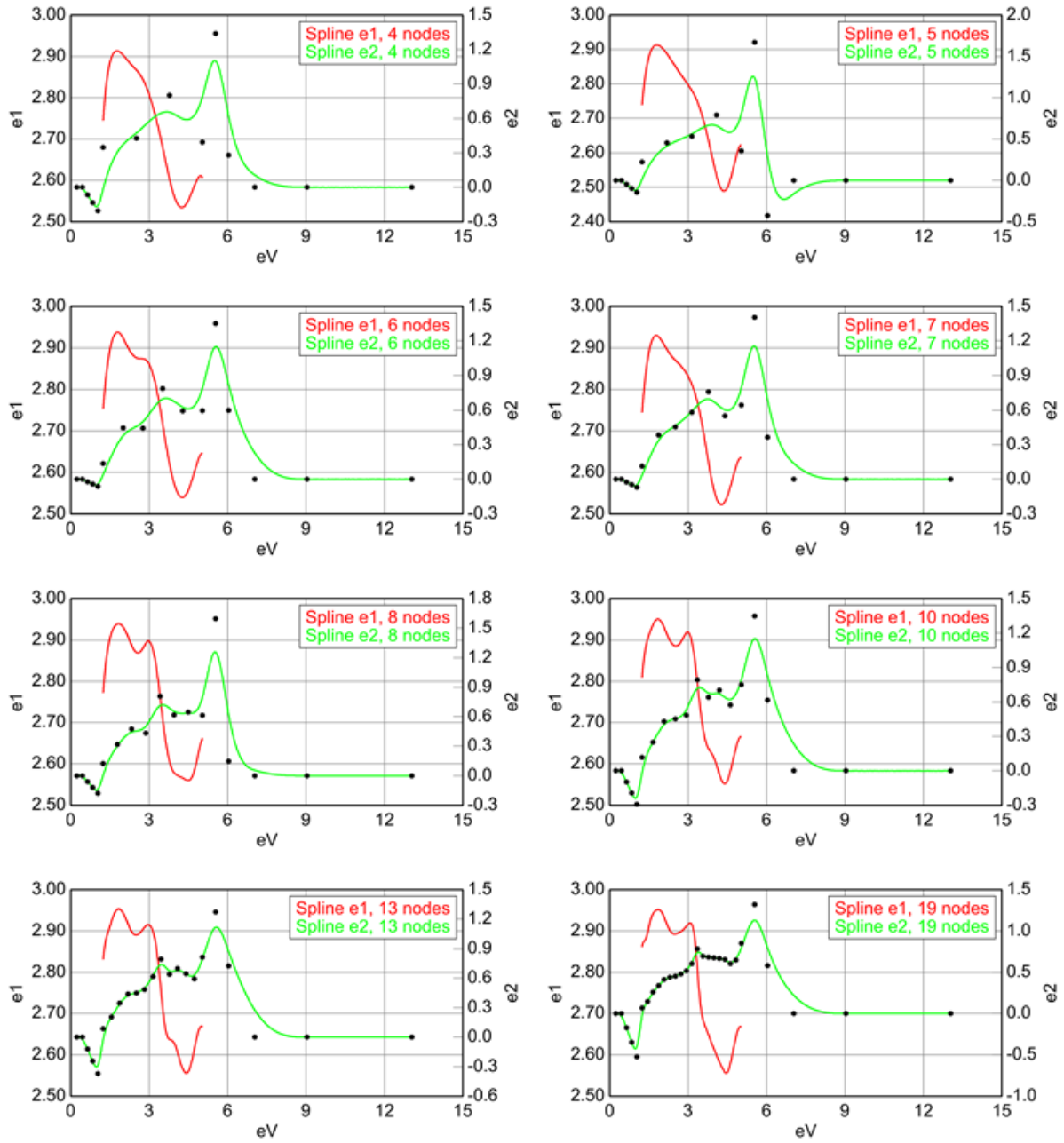

Figure S15 PDA 6 h deposition: sensitivity analysis for the number of nodes of the B-spline function; diagram of the nodes as a function of the number of nodes (4 to 19 nodes)

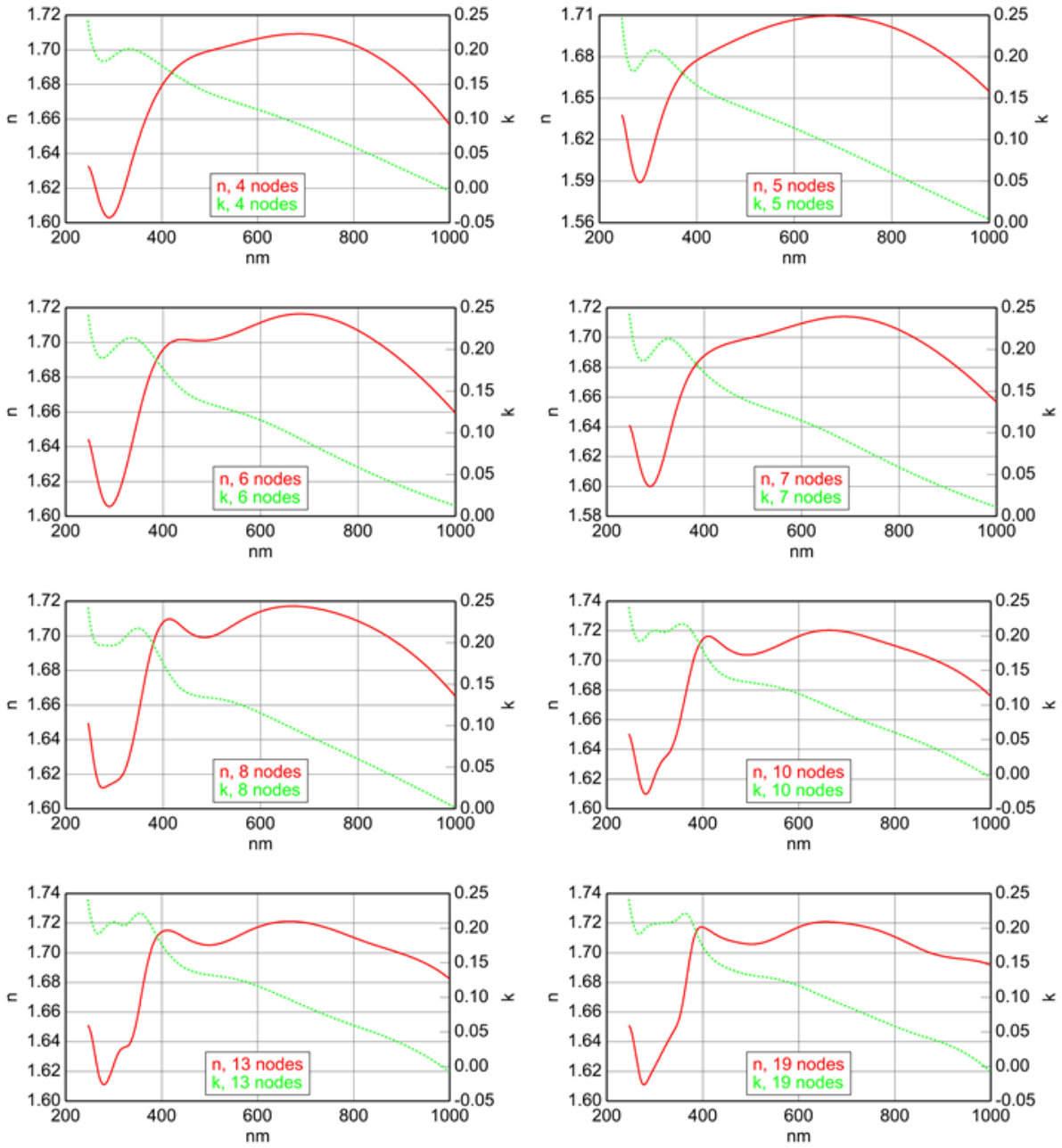

Figure S16 PDA 6 h deposition: sensitivity analysis for the number of nodes of the B-spline function; n and k dispersions as a function of the number of nodes (4 to 19 nodes)

Table S2 demonstrates the correlation matrix for the representative PDA 6 h sample. Herein, the larger the values (closer to 1) the more correlated the model parameters are. As a rule of thumb, a correlation value > 0.9 suggests that the two corresponding parameters are strongly correlated. Herein, none of the free parameters show strong correlation with each other. Noteworthy, the three outlier nodes of the KK-consistent B-spline, i.e., spline_e2(1.041), spline_e2(5.539), and spline_e2(6.039), do not show correlation with other parameters unlike what is typically observed. **Figure S17**, in which MSE is plotted against thickness, also suggests uniqueness of the estimated film thickness in the range of 15-30 nm. Finally, **Table S3** summarizes the modeling outcome for all studied PDA 6 h samples (15 measurement data) using 6 nodes. Herein, the thickness value shows a narrow standard deviation that suggests not only the uniformity of the film structure, but also that the modeling outcome is not model-dependent and is reliable.

Table S2 PDA 6 h deposition: correlation matrix for KK-consistent B-spline mode (6 nodes)

	Thickness # 3	***E Inf***	***IR Amp***	***spline_e2(1.041)***	***spline_e2(5.539)***	***spline_e2(6.039)***	***spline_e2(1.241)***	***spline_e2(2.000)***	***spline_e2(2.760)***	***spline_e2(3.520)***	***spline_e2(4.280)***	***spline_e2(5.039)***
Thickness # 3	1.000	0.596	0.268	0.132	0.469	-0.718	0.203	-0.479	0.148	-0.611	-0.491	-0.430
E Inf	0.596	1.000	0.716	-0.196	0.811	-0.957	0.352	-0.340	0.012	-0.648	-0.212	-0.728
IR Amp	0.268	0.716	1.000	-0.712	0.436	-0.566	0.467	-0.255	0.077	-0.362	-0.095	-0.408
spline_e2(1.041)	0.132	-0.196	-0.712	1.000	-0.090	0.081	-0.587	0.322	-0.285	0.087	-0.140	0.101
spline_e2(5.539)	0.469	0.811	0.436	-0.090	1.000	-0.895	0.274	-0.340	0.136	-0.592	0.151	-0.897
spline_e2(6.039)	-0.718	-0.957	-0.566	0.081	-0.895	1.000	-0.318	0.413	-0.091	0.687	0.192	0.792
spline_e2(1.241)	0.203	0.352	0.467	-0.587	0.274	-0.318	1.000	-0.794	0.564	-0.408	0.044	-0.282
spline_e2(2.000)	-0.479	-0.340	-0.255	0.322	-0.340	0.413	-0.794	1.000	-0.763	0.611	0.046	0.351
spline_e2(2.760)	0.148	0.012	0.077	-0.285	0.136	-0.091	0.564	-0.763	1.000	-0.479	0.193	-0.180
spline_e2(3.520)	-0.611	-0.648	-0.362	0.087	-0.592	0.687	-0.408	0.611	-0.479	1.000	-0.090	0.632
spline_e2(4.280)	-0.491	-0.212	-0.095	-0.140	0.151	0.192	0.044	0.046	0.193	-0.090	1.000	-0.299
spline_e2(5.039)	-0.430	-0.728	-0.408	0.101	-0.897	0.792	-0.282	0.351	-0.180	0.632	-0.299	1.000

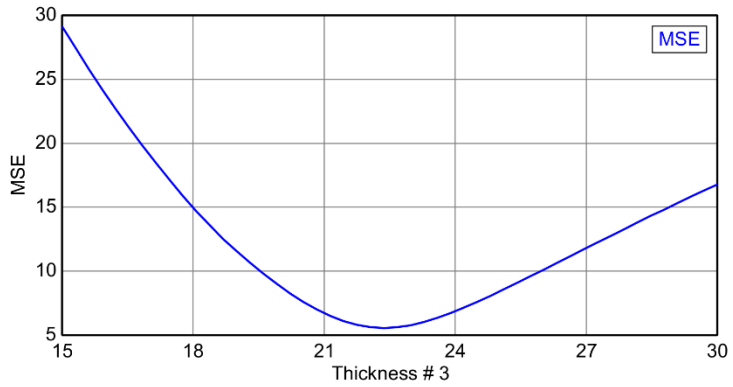

Figure S17 PDA 6 h deposition: thickness uniqueness analysis for 6 nodes

Table S3 PDA 6 h deposition: summary of the modeling results

Sample no.	MSE	Thickness # 3 (nm)	E Inf	IR Amp
1	7.668	23.52	1.280	0.535
2	6.133	21.61	1.254	0.513
3	4.859	21.71	1.291	0.514
4	5.550	22.37	1.330	0.557
5	5.462	20.91	1.311	0.582
6	8.163	22.99	1.243	0.507
7	4.429	21.95	1.261	0.463
8	4.493	22.15	1.270	0.465
9	4.278	19.51	1.296	0.533
10	4.557	21.03	1.302	0.520
11	7.161	23.08	1.241	0.473
12	4.511	22.82	1.259	0.443
13	4.708	23.78	1.261	0.430
14	4.843	24.19	1.263	0.435
15	4.659	21.99	1.295	0.497
Average	5.43151	22.241	1.27713	0.49784
Std. Dev.	1.27015	1.224	0.02627	0.04545

The sensitivity analysis was also performed for the PDA 12 h sample. Similarly, it was found the number of nodes has little effect on MSE and estimated thickness, and 6 nodes were enough to obtain a smooth e2 spline function, as well as n and k dispersions. However, we herein have an additional free parameter, i.e., thickness of the roughness layer. Thus, we performed sensitivity analysis in terms of the correlation between the film thickness and the film roughness. **Figure S18** depicts the 2-parameter uniqueness chart where MSE is calculated for various combinations of thickness and roughness values. The areas indicated in red represent the smallest MSE values

(best match between the modelled and the experimental data). The left panel shows a larger range of values for thickness and roughness. Accordingly, a combination of thickness (~ 40-50 nm) and roughness (~ 0-20 nm) is the only combination that provides small MSE values. The right panel shows a higher resolution (smaller range of MSE values) chart for this combination. Accordingly, the modeling outcome (thickness ~ 45 nm and roughness ~ 10 nm) is unique and other thickness/roughness combinations yield excessively larger MSE values. Finally, **Table S4** summarizes the modeling outcome for all the studied PDA 12 h samples. Again, the thickness value shows a relatively narrow standard deviation that affirms reliable modeling outcome.

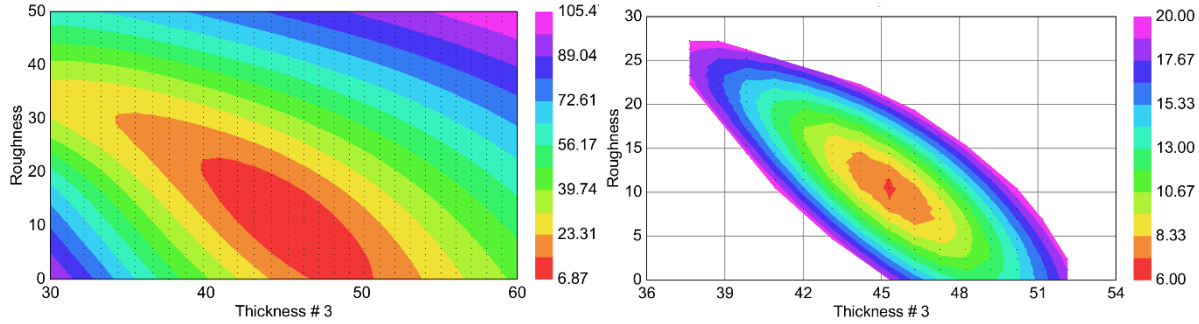

Figure S18 PDA 12 h deposition: thickness-roughness uniqueness analysis for 6 nodes (the panel on the right shows the chart with MSE values of 6-24)

Table S4 PDA 12 h deposition: summary of the modeling results

	MSE	Roughness (nm)	Thickness # 3 (nm)	E Inf	IR Amp
1	11.450	9.54	46.62	1.213	0.208
2	6.874	10.42	45.30	1.184	0.163
3	6.314	9.86	44.31	1.186	0.166
4	5.342	8.61	43.08	1.189	0.166
5	5.779	8.38	38.98	1.216	0.193
6	10.088	8.37	48.26	1.191	0.180
7	6.634	9.28	46.39	1.177	0.160
8	7.865	12.27	46.38	1.177	0.156
9	7.494	12.41	45.44	1.184	0.159
10	5.777	8.87	44.39	1.186	0.162
11	12.009	8.22	44.27	1.206	0.221
12	6.850	8.64	42.83	1.182	0.177
13	6.330	10.16	42.31	1.184	0.164
14	9.325	14.65	41.73	1.190	0.159
15	10.418	15.55	41.32	1.203	0.180
Average	7.90334	10.347	44.108	1.19104	0.17423
Std. Dev.	2.18922	2.331	2.433	0.01245	0.01938

S5. Roughness from Ellipsometry: we have here used the simplest approach (50:50 model) to implement a roughness layer into the optical model. As shown in **Figure S19**, a rough film is considered as a bilayer, i.e., a homogenous layer at the bottom and a layer comprising 50:50 mixture of material/void on top. The optical dispersions of the roughness layer are then described using an effective medium approximation (EMA) equation. The thickness of the EMA layer is then a "free" parameter in the model and is considered as the ellipsometry roughness. Thus, the optical constants of the material (when unknown, free parameters) vary in two layers, which may cause correlation between the parameters of the two layers as well as the modelled optical constants. In this study, we assessed merely if having a "roughness" layer can improve the quality of the modeling. Accordingly, it was found that for PDA films obtained by relatively long deposition times, having an EMA roughness layer improves the quality of the model. Nevertheless, a more accurate description of the PDA films roughness for ellipsometry modeling requires careful analysis of the roughness profiles of PDA films in different length scales and then obtaining the corresponding void profile in the vertical direction (Z axis). Such realistic profiles may then be used for the EMA model (instead of 50:50 assumption). Such analysis would be

more trustable if the optical constants of the material are known or at least a simple dispersion equation (e.g., transparent Cauchy equation) is required to model the optical behaviour. Considering the unknown and complex optical dispersion of PDA and its variable roughness in different length scales, determination of the correlation between the ellipsometry-AFM roughness values remains a challenge and needs further investigation.

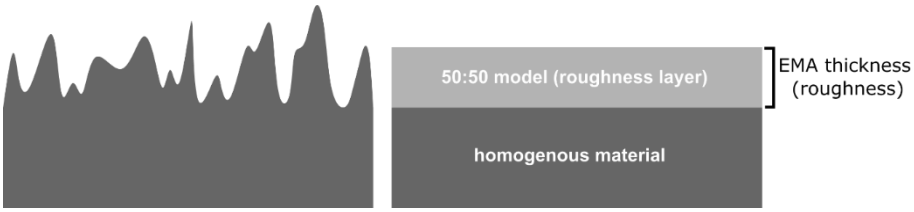

Figure S19 Ellipsometry roughness using 50:50 effective medium approximation (EMA)

S6. Optical dispersions of PDA films (2, 6, and 12 h): while spectroscopic ellipsometry cannot always be an accurate way of measuring the optical dispersions (when both thickness and optical dispersions of the material are unknown), it may provide an overall picture of the optical behaviour if the model is not overparameterized and the modeling outcome is unique (**Figure S20**). Regarding the PDA 2 h sample (left panel), the choice of model obviously affects the dispersion shape, but also the ranges of values (in particular n) are affected. In this case, since the film thickness is ≤ 10 nm, using a B-spline model is not favourable to estimate the film thickness due to the higher number of free parameters. Nevertheless, the B-spline model provides n and k dispersion shapes that are like those of 6 h and 12 h samples. Comparing the optical dispersions of all the samples (right panel), we can suggest that the overall shape of the dispersions (n relatively featureless at large wavelengths, decreasing in the UV range) is similar for all samples and could be the physical behaviour of PDA. However, the absolute values of the optical constants seem to depend on the deposition time (in particular n dispersion is shifted upwards with deposition time), which could be due to both the time-dependent physicochemical properties of the material and some degree of correlation between the model parameters.

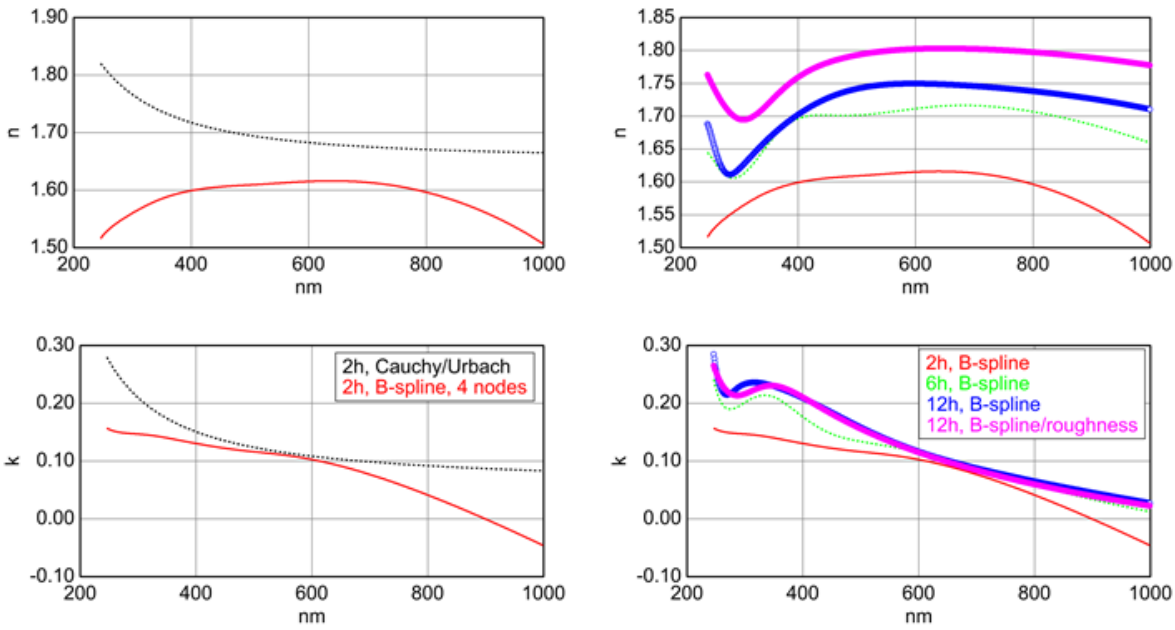

Figure S20 n (top row) and k (bottom row) dispersions obtained from the modeling of the ellipsometry data: (left) 2 h PDA sample modelled by Cauchy with the Urbach absorption term and KK-consistent B-spline with 4 nodes, (right) all samples modelled with KK-consistent B-spline without (2 h, 6 h, and 12 h PDA) or with roughness (12 h PDA) .

To see if we could more accurately estimate the optical dispersions of PDA using ellipsometry, we tried fixing the film thickness in the model, thus only having the B-spline parameters as the free model parameters. Herein, the average thickness values estimated from AFM were used. **Figure S21** displays the optical dispersions obtained from this modeling approach. The overall shape of the dispersions is similar to those in **Figure S20**, suggesting that the overall shape of the dispersions represent PDA optical behavior. Similarly, it is also found that n dispersion shows a shift to higher values with the deposition time, which can be an indication of the variable physicochemical/optical properties of PDA (considering that the thickness is fixed in the model). Unlike **Figure S20**, it is herein found that k values seem to be slightly dependent on the deposition time.

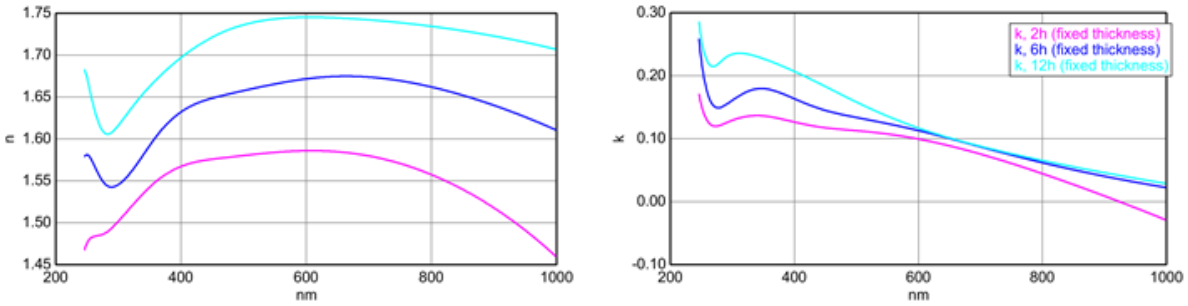

Figure S21 optical dispersions of PDA films obtained by B-spline model using fixed thickness values (from AFM)

S7. Step-by-step modeling approach for a PDA film obtained using the standard one-step deposition procedure: As discussed in the main article, the PDA films studied herein were all obtained using a multi-step deposition method to minimize the surface roughness/thickness ratio of the films and thus improve the quality of the ellipsometry data. To test if the step-by-step modeling approach is valid for PDA films obtained through the standard one-step deposition, we herein prepared a PDA film by 24 h one-step deposition as a model sample for thick and rough PDA films.

Figure S22-S25 summarize the modeling outcome for the following step-by-step model construction: Cauchy relation (2 free parameters: PDA film thickness (layer # 3) and A of Cauchy), Cauchy with an Urbach absorption term (4 free parameters: PDA film thickness (layer # 3), A of Cauchy, amplitude and exponent of the Urbach relation), KK-consistent B-spline (9 free parameters: PDA film thickness (layer # 3), 6 nodes, 2 KK-relation parameters), and ultimately KK-consistent B-spline with a EMA roughness layer (10 free parameters: PDA film thickness (layer # 3), 6 nodes, 2 KK-relation parameters, thickness of the roughness layer). The KK-consistent B-spline function with a roughness layer can provide a satisfactory match with the experimental data suggesting applicability of the modeling approach for studying thick/rough PDA films. However, it should be noted that the excessive surface roughness/heterogeneity herein seem to promote some degree of correlation between the estimated thickness and roughness values.

Figure S26 depicts the 2-parameter thickness-roughness uniqueness chart. Herein, it can be seen that the mathematical model can yield two solutions that both satisfactorily match the experimental data (MSE ~ 25 nm): (i) a film with a thickness ~ 50-55 nm and roughness ~ 20-25 nm and (ii) a film with a thickness ~ 30-35 nm and roughness ~ 45-50 nm. While both solutions match the experimental data, in this case, one can safely choose the former modeling outcome as the second solution represents a layer with a roughness much larger than the film thickness. Regardless, this observation suggests that excessively rough and heterogeneous PDA films require more in-depth modeling and more importantly verification with another thickness/roughness analysis method, e.g., AFM imaging (**Figure S27**: representative AFM height image/height profile of a scratched 24 h one-step deposited PDA). The model parameters do not show any significant degree of correlation as shown in **Table S5**.

Fit Results
MSE = 176.220 (Out-Of-Spec)
Thickness # 3 = 45.95 ± 0.246 nm
A = 1.931 ± 0.004978
Total Thickness = 148.92 ± 0.246 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **45.95 nm** (fit)
  A = **1.931** (fit) B = 0.01000 C = 0.0000
  + **Urbach Absorption Parameters**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.97 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

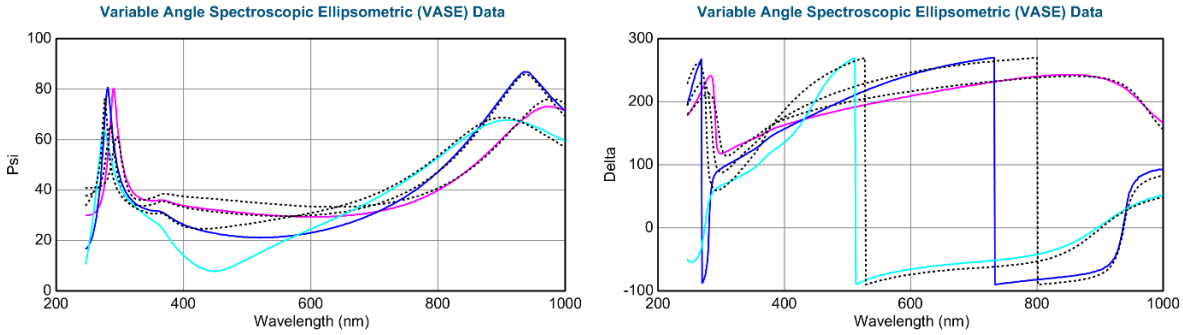

Figure S22 PDA 24 h one-step deposition, Cauchy model

Fit Results
MSE = 135.572 (Out-Of-Spec)
Thickness # 3 = 47.50 ± 0.191 nm
A = 1.897 ± 0.003765
k Amplitude = 0.07846 ± 0.002397
Exponent = 0.688 ± 0.0215
Total Thickness = 150.47 ± 0.191 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **47.50 nm** (fit)
  A = **1.897** (fit) B = 0.01000 C = 0.0000
  - **Urbach Absorption Parameters**
    k Amplitude = **0.07846** (fit) Exponent = **0.688** (fit)
    Band Edge = 400.0 nm
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.97 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

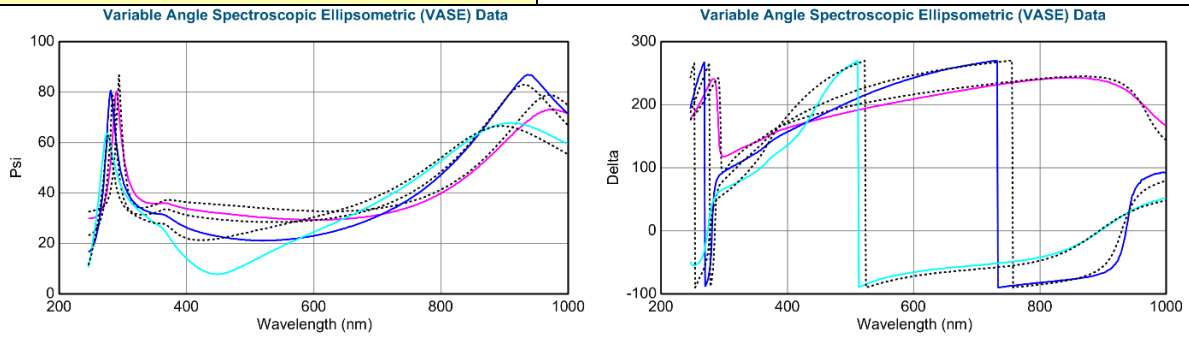

Figure S23 PDA 24 h one-step deposition, Cauchy with Urbach absorption model

Fit Results
MSE = 41.522
Thickness # 3 = 61.70 ± 0.193 nm
E Inf = 1.670 ± 0.0271
IR Amp = 0.541 ± 0.0244
Total Thickness = 164.67 ± 0.193 nm

Optical Model

- Layer # 3 = B-Spline Thickness # 3 = **61.70 nm** (fit)
  Resolution (eV) = 0.700 6 Pts. (1.241-5.039 eV) Draw Node Graph
  Fit Optical Constants = ON
  Use KK Mode = ON (In Use)
  + **Kramers-Kronig**
  - **Nodes**
    Init. values: n = 1.500 k = 0.00 Starting Mat. = Cauchy
    Force E2 Positive = ON
    Assume Transparent Region = OFF
    Show Nodes = OFF
    Node Spacing Spectral Ranges: Add Delete Delete All
  + **Advanced**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.97 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

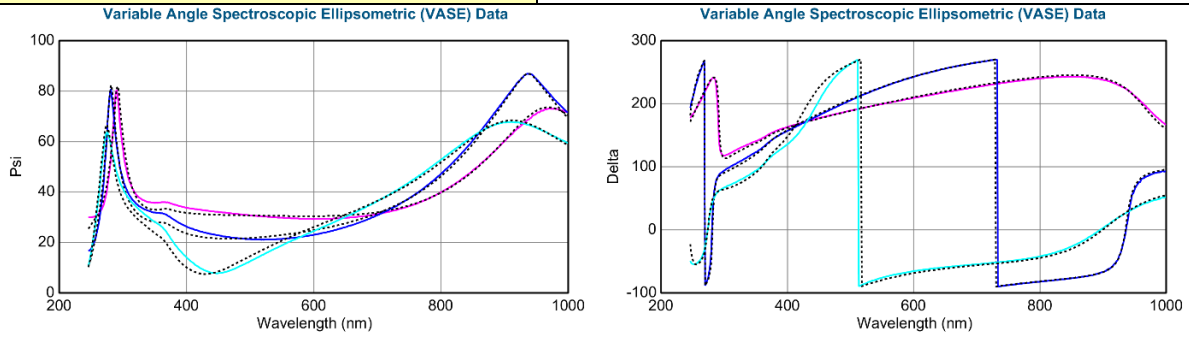

Figure S24 PDA 24 h one-step deposition, KK-consistent B-spline model

Fit Results
MSE = 25.022
Roughness = 27.17 ± 0.357 nm
Thickness # 3 = 52.63 ± 0.201 nm
E Inf = 1.158 ± 0.0228
IR Amp = 0.111 ± 0.0191
Total Thickness = 155.60 ± 0.201 nm

Optical Model

Roughness = **27.17 nm** (fit)
- Layer # 3 = B-Spline Thickness # 3 = **52.63 nm** (fit)
  Resolution (eV) = 0.700 6 Pts. (1.241-5.039 eV) Draw Node Graph
  Fit Optical Constants = ON
  Use KK Mode = ON (In Use)
  + **Kramers-Kronig**
  - **Nodes**
    Init. values: n = 1.500 k = 0.00 Starting Mat. = Cauchy
    Force E2 Positive = ON
    Assume Transparent Region = OFF
    Show Nodes = OFF
    Node Spacing Spectral Ranges: Add Delete Delete All
  + **Advanced**
- Layer # 2 = SIO2_JAW Thickness # 2 = 101.97 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

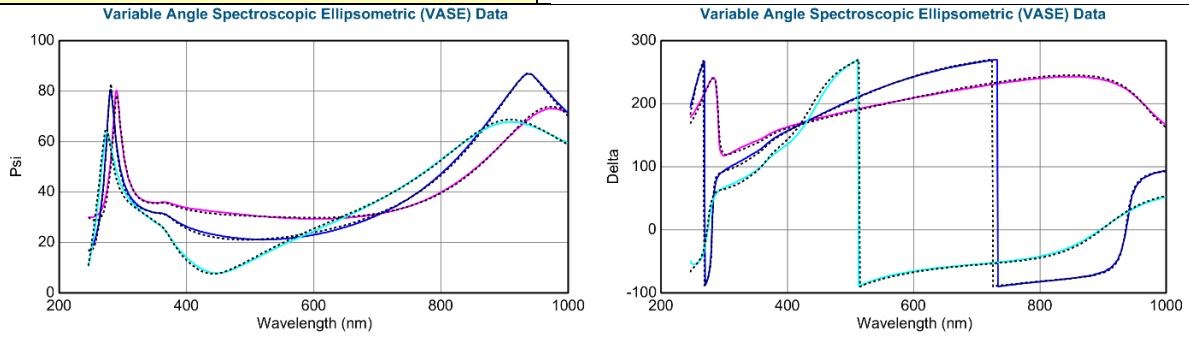

Figure S25 PDA 24 h one-step deposition, KK-consistent B-spline with roughness layer model

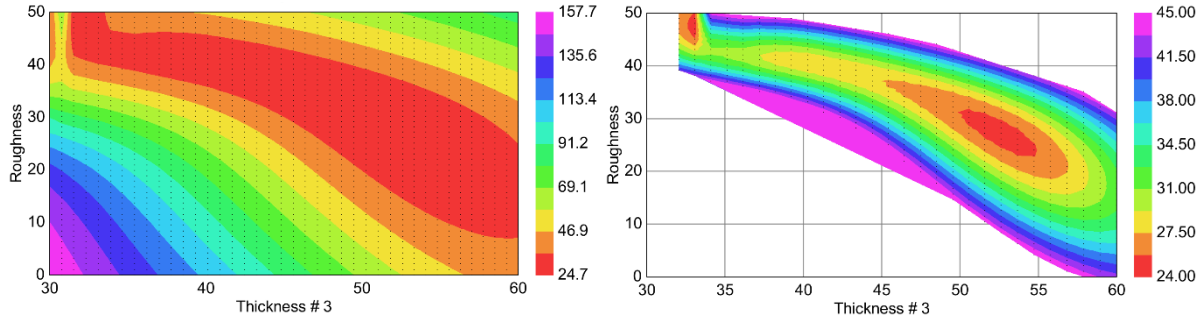

Figure S26 PDA 24 h one-pot deposition: thickness-roughness uniqueness analysis for 6 nodes, (the panel on the right shows the chart with MSE values of 24-45)

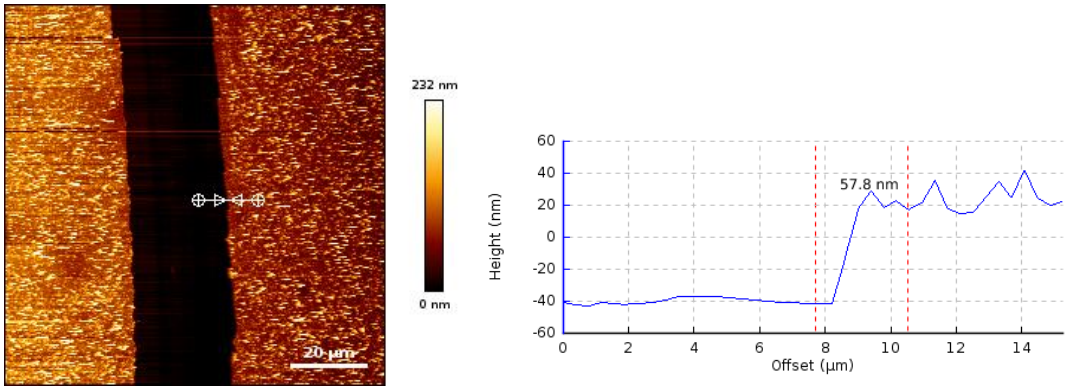

Figure S27 Representative AFM height image/profile of the scratched area of PDA 24 h one-step deposition, estimated thickness = 57.8 ± 4.3 nm estimated roughness (Rq) = 40.0 ± 8.5 nm.

Table S5 PDA 24 h one-step deposition: correlation matrix for KK-consistent B-spline with roughness model

	Roughness	***Thickness # 3***	***E Inf***	***IR Amp***	***spline_e2(1.041)***	***spline_e2(5.539)***	***spline_e2(6.039)***	***spline_e2(1.241)***	***spline_e2(2.000)***	***spline_e2(2.760)***	***spline_e2(3.520)***	***spline_e2(4.280)***	***spline_e2(5.039)***
Roughness	1.000	-0.812	-0.571	-0.444	-0.085	-0.515	0.723	-0.148	0.143	0.324	-0.032	0.728	0.611
Thickness # 3	-0.812	1.000	0.477	0.237	0.302	0.630	-0.780	0.011	0.048	-0.540	0.085	-0.588	-0.754
E Inf	-0.571	0.477	1.000	0.784	-0.206	0.769	-0.893	0.411	-0.338	-0.119	-0.433	-0.227	-0.634
IR Amp	-0.444	0.237	0.784	1.000	-0.627	0.423	-0.567	0.699	-0.381	0.136	-0.279	-0.173	-0.381
spline_e2(1.041)	-0.085	0.302	-0.206	-0.627	1.000	0.051	-0.041	-0.856	0.555	-0.489	0.251	-0.170	-0.107
spline_e2(5.539)	-0.515	0.630	0.769	0.423	0.051	1.000	-0.911	0.193	-0.164	-0.235	-0.357	-0.083	-0.835
spline_e2(6.039)	0.723	-0.780	-0.893	-0.567	-0.041	-0.911	1.000	-0.243	0.192	0.329	0.288	0.366	0.810
spline_e2(1.241)	-0.148	0.011	0.411	0.699	-0.856	0.193	-0.243	1.000	-0.725	0.424	-0.317	0.045	-0.172
spline_e2(2.000)	0.143	0.048	-0.338	-0.381	0.555	-0.164	0.192	-0.725	1.000	-0.592	0.434	-0.080	0.143
spline_e2(2.760)	0.324	-0.540	-0.119	0.136	-0.489	-0.235	0.329	0.424	-0.592	1.000	-0.494	0.421	0.269
spline_e2(3.520)	-0.032	0.085	-0.433	-0.279	0.251	-0.357	0.288	-0.317	0.434	-0.494	1.000	-0.504	0.369
spline_e2(4.280)	0.728	-0.588	-0.227	-0.173	-0.170	-0.083	0.366	0.045	-0.080	0.421	-0.504	1.000	0.058
spline_e2(5.039)	0.611	-0.754	-0.634	-0.381	-0.107	-0.835	0.810	-0.172	0.143	0.269	0.369	0.058	1.000

Table S6 summarizes the modeling outcome for all the studied 24 h one-pot PDA samples. Herein, the estimated film thickness shows relatively narrow standard deviation, suggesting reliability of the modeling procedure and output. However, the estimated roughness value (27.8 ± 8.9 nm) demonstrates a relatively larger standard deviation, which could be either due to heterogeneity of the PDA film surface or some degree of correlation between the roughness and other model parameters. According to AFM images, the film has a Rq roughness of 40.0 ± 8.5 nm. Thus, while the large standard deviation can be attributed to the heterogeneous surface structure, it appears that the estimated roughness from ellipsometry is relatively smaller than what is estimated by AFM. Interestingly, plotting the obtained n and k dispersions (**Figure S28**) for all 15 measurement data renders two types of dispersions: (i) a smaller population with relatively smaller roughness/MSE and (ii) a larger population with relatively larger roughness/MSE. The former group are characterized by optical dispersions that are more consistent, are closer to the range of values of optical constants of organic materials and show smoother dispersions. The optical dispersions of the latter group, however, demonstrate excessive sample-dependence, are relatively larger than the expected values for organic materials, and finally show various features in the dispersion (could suggest parameter correlation). This observation again suggests that PDA films, in particular those with excessive surface heterogeneity and roughness, need a careful optical modeling.

Table S6 PDA 24 h one-pot deposition: summary of the modeling results

	MSE	Roughness (nm)	Thickness # 3 (nm)	E Inf	IR Amp
1	34.092	33.74	54.88	1.236	0.212
2	31.116	32.55	52.95	1.107	0.117
3	26.670	26.33	55.95	1.066	0.0721
4	28.776	29.24	58.12	1.003	0.0408
5	42.483	37.71	53.29	1.006	0.193
6	25.022	27.17	52.63	1.158	0.111
7	17.452	18.53	54.69	1.145	0.119
8	15.778	15.52	55.52	1.144	0.123
9	14.703	13.22	57.10	1.144	0.125
10	20.716	17.55	57.87	1.110	0.100
11	37.197	35.70	51.95	1.104	0.166
12	31.736	32.89	53.91	1.068	0.0918
13	32.271	31.75	54.34	1.080	0.0993
14	38.549	35.68	54.45	0.904	0.0411
15	30.935	29.49	55.38	1.085	0.0873
Average	28.49971	27.805	54.869	1.09063	0.11325
Std. Dev.	8.41440	7.945	1.843	0.07841	0.04847

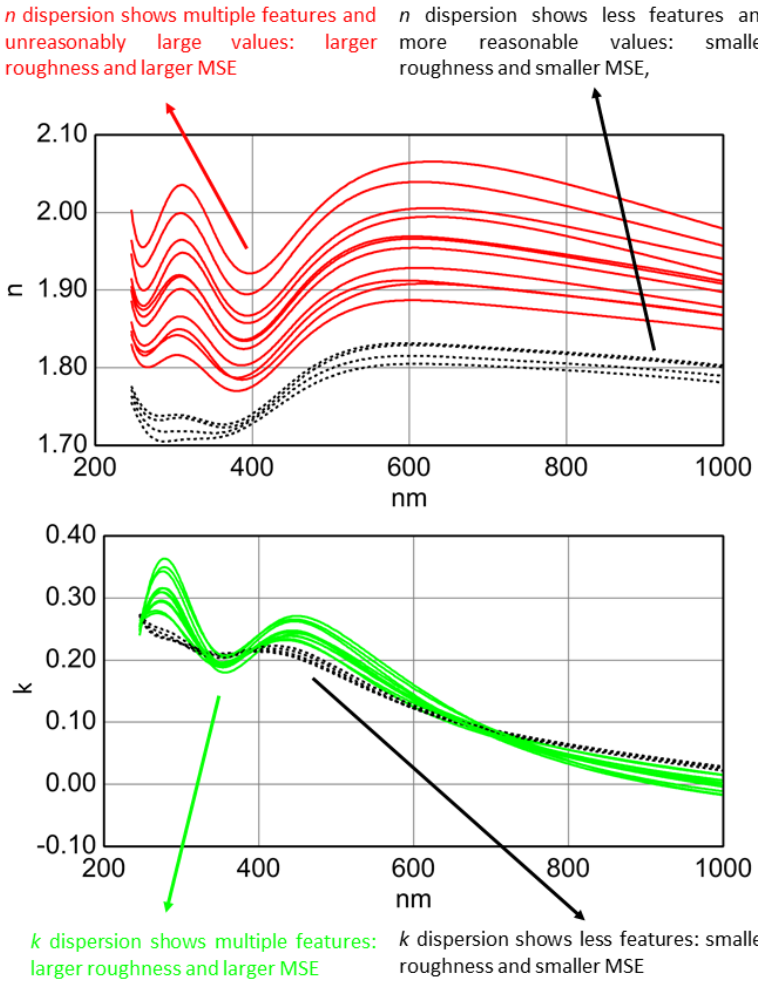

Figure S28 PDA 24 h one-step deposition: n and k dispersions obtained from the KK-consistent B-spline model with a roughness layer (15 samples)