Comment on "Characterization of Self-Assembled Monolayers on Silver and Gold Using Surface Plasmon Resonance Spectroscopy"

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Recently, Ehler, Malmberg, and Noe[1] reported measurements of the thicknesses, refractive indices, and calculated tilt angles of *n*-alkanethiol films on gold and silver obtained from surface plasmon resonance (SPR) spectroscopy. Film thicknesses are to found to range from 19 to 27 Å and 14 to 21 Å for silver and gold, respectively, for *n*-alkanethiol films containing between 11 and 17 methylene carbons. The refractive index of the films increases on both substrates as the number of methylene carbons increases. This observation was interpreted to be suggestive of chain length dependent differences in packing on both silver and gold. In contrast, the alkanthiolate tilt angles, which are calculated from the same SPR data, follow distinctly different trends for silver compared with gold.

All SPR spectroscopic results in this study are based on very precise measurements of two[2] parameters: the alkanethiol film thickness, *d*, and the film refractive index, *n*. Unprecedented accuracy (±1 Å in the thickness of the film and in the third decimal place of the refractive index of the film) is reported to be obtained from nonlinear least-squares analyses of single-wavelength SPR reflectance curves. This accuracy is attributed to what the authors refer to as "exact fits" with extremely small residuals that were never greater than 1% in the worst case.

We wish to comment on the derivation of thickness and refractive index from single-wavelength SPR measurements.[3] Unfortunately, thickness resolution of ±1 Å can only be obtained if the experimental uncertainties are several orders of magnitude smaller than those of Ehler et al. When the reported experimental uncertainties are taken into account, interpretation of the SPR data of Ehler et al. results in large errors in the determination of the refractive index, *n*, and the thickness, *d*. The magnitude of the errors calls into question the conclusions of the paper regarding refractive index, film thickness, and the calculated tilt angles.

Optical measurements using both SPR and ellipsometry have been made on similar transparent films. In most of these studies, both the refractive index, *n*, and thickness, *d*, can be determined only for films with thickness greater than 50 Å; for thinner films, the film thickness, *d*, is calculated using an estimated value of *n* (typically 1.5 for alkanethiol films).[4] The choice of refractive index has to be made with caution[4] because indeed *n* and *d* are inherently coupled such that, for a given ellipsometric or SPR measurement, increasing the estimated value of *n* will decrease the calculated value of *d*.[4−7]

In contrast with many SPR measurements where the shift in the minimum reflectance intensity is used to determine *d* for an assumed value of *n*, Ehler et al. report that detailed fitting of an entire SPR spectrum can be used to extract both *n* and *d*, somehow decoupling *n* and *d*. Specifically, Ehler et al. state that, "At 6328 Å the SAM film presents no absorption or imaginary index component; therefore, a single-wavelength SPS curve can uniquely determine the thickness and refractive index of this monolayer from the reflectivity versus angular position of the SPS spectrum."

We have simulated the experimental uncertainties reported by Ehler et al. (0.3−1%), using SPR data sets constructed by adding 50 different 0.5% random noise distributions to a single simulated model SPR curve. The simulated SPR curve was calculated using reasonable parameters[1,5] for a four-layer model: (layer 1) glass substrate, $n = 1.5151$; (layer 2) gold film, $\epsilon = -12 + 1.6i$, $d = 500$ Å; (layer 3) organic film, $n = 1.45$ ($\epsilon = 2.10$), $d = 14$ Å; and (layer 4) air, $n = 1$. Each of 50 different "data" sets generated in this manner was fit using a nonlinear least-squares routine to obtain the best fit thickness, *d*, and refractive index, *n*, for layer 3. Figure 1 shows the range of values for the best fit thicknesses and refractive indices. Note that, although there is a definite relationship between calculated thickness and refractive index, the uncertainty in the film thickness is ±5 Å while the uncertainty in *n* is ±0.18

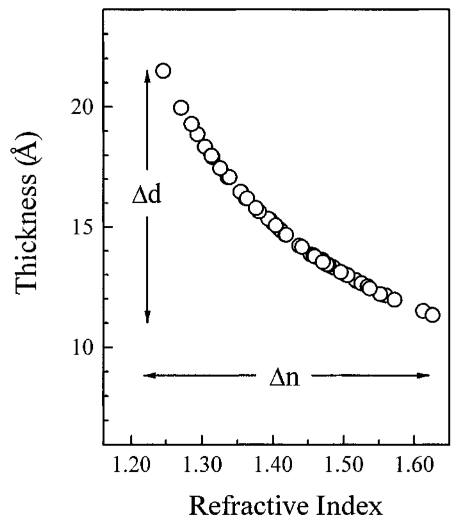

Figure 1. Determining thickness and refractive index from SPR data with 0.5% noise. Shown are the range of best fit parameters (refractive index, *n*, and thickness, *d*) for simulated SPR data consisting of a single SPR spectrum with 0.5% random noise distributions added. Fitting parameters range from about $n = 1.25$, $d = 22$ Å to about $n = 1.63$, $d = 11$ Å. The parameters used to construct the simulated SPR data are given in the text ($n = 1.45$, $d = 14.0$ Å). See text for details.

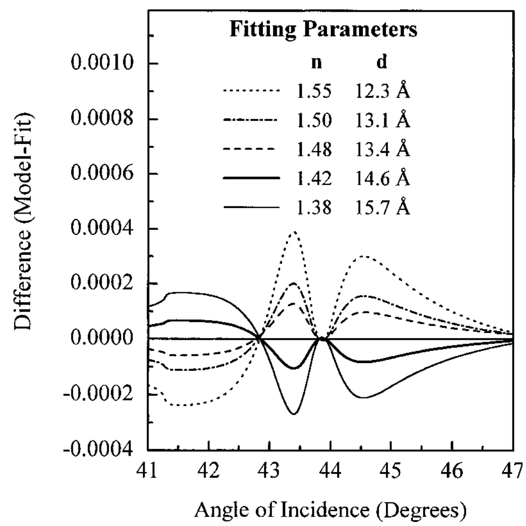

Figure 2. Sensitivity of SPR fits to changes in film parameters. Shown are the differences in reflectivity between a model, noise-free, SPR curve (parameters given in the text, $n = 1.45$, $d = 14.0$ Å) and five "best fit" curves. The "best fits" are obtained by holding the refractive index, *n*, fixed at each of the five given values and calculating the corresponding "best fit" thickness, *d*. These parameters are tabulated in the figure. The largest difference between the model curve and the calculated "best fit" curves corresponds to a residual of approximately 0.04%.

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Can the "exact" fits used by Ehler et al. determine these film parameters more precisely? Figure 2 shows the differences in reflectivity between a noise-free model SPR curve (parameters as above, $n = 1.45$, $d = 14$ Å) and five calculated "best fit" curves. The "best fits" are obtained by holding the refractive index, n, at five fixed values in the range of $n = 1.38-1.55$ and calculating the corresponding best fit value for the thickness, d. Note that, although the fitting parameters n and d vary over a wide range ($n = 1.38-1.55$ and $d = 12-16$ Å), the largest difference between the model curve and the calculated best fits corresponds to a residual of approximately 0.04%. Clearly, residuals of up to 1% reported Ehler et al. are not sufficient to unambiguously determine the values of n and d for the organic layer within the claimed precision. To unambiguously determine both thickness to within ±1 Å and refractive index to within ±0.05 from a single-wavelength SPR reflectance curve, the noise level in the experimental data would have to be less than 0.01%.

While most SPR experiments are conducted at a single excitation wavelength and representative "best fits" are sometimes reported, quantitative conclusions are not drawn from the values of the fitting parameters since there are many equally good fits to the data. When quantitative information is extracted from single-wavelength SPR experiments, it is done with the caveat that the film refractive index must be assumed in order to determine the film thickness, or vice versa. To overcome this known limitation, various approaches have been developed[5−7] for unambiguously determining both the thickness and refractive index of ultrathin organic films by comparing results from at least two different SPR reflectance curve.

References and Notes

(1) Ehler, T. T.; Malmberg, N.; Noe, L. J. Characterization of Self-Assembled Alkanethiol Monolayers on Silver and Gold Using Surface Plasmon Resonance Spectroscopy. *J. Phys. Chem. B* **1997**, *101*, 1268−72.

(2) The authors find the extinction coefficient, k, to be negligible as expected for these transparent films.

(3) The experimental approach for data collection and the optical model for data analysis used by Ehler et al. are the same as those used by many other laboratories, including ours. The optical constants of the metal film and any organic material (such as an alkanethiolate monolayer) deposited onto the metal surface can be determined by optimizing the fit for an optical model to the SPR spectra. The model used is an optical multilayer model adapted from a code supplied by J. D. Swalen (IBM Almaden).

(4) Ulman, A. *An Introduction to Ultrathin Organic Films: from Langmuir−Blodgett to Self-Assembly*; Academic Press: New York, 1991; Chapter 1.1.

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(6) de Bruijn, H. E.; Altenburg, B. S. F.; Kooyman, R. P. H.; Greve, J. Determination of Thickness and Dielectic Constant of Thin Transparent Dielectric Layers using Plasmon Resonance. *Opt. Commun.* **1991**, *82*, 425−32.

(7) Peterlinz, K. A.; Georgiadis, R. Two-color Approach for Determination of Thickness and Dielectric Constant of Thin Films using Surface Plasmon Resonance Spectroscopy. *Opt. Commun.* **1996**, *130*, 260−6.