

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

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Received: May 12, 1997; In Final Form: June 17, 1997

We would like to point out that error "estimate" of ± 1 Å in the plasmon determined thicknesses of a series of alkanethiols self-assembled on Ag and Au surfaces at the HeNe wavelength of 6328 Å was based on several factors.¹ It was not based on a single SPS measurement of a particular alkanethiol SAM. We obtained four ATR curves on four separate and distinct spots on each of four substrate slides, a total 16 measurements for a given alkanethiol SAM/metal system. One of the ATR curves on each slide was thorough analyzed, although all 16 "looked" identical. The agreement in thickness for a measurement set was ± 1 Å as determined by a three-parameter (n , k , and d) Gauss-Newton fitting algorithm found in the programming language ASYST (Keithley Instruments, Inc.). We set the fit tolerance for the *overall* plasmon curve fit at 1 Å for d and 0.001 for n and k . Typical k 's were found to be ~ 0.01 for the Ag thiolate films and ~ 0.05 for the Au films, low enough for minimal absorbance and scattering, but important in plasmon curve shape variations found in close fits. Residuals were not greater than $\pm 1\%$, the main variations coming in the wings of the plasmon curves and caused, we believe, by a slight experimental base line drift. Noise in our germanium diode op-amp circuit showed up in typical residuals plots² at $\pm 0.25\%$, so in effect conclusions drawn from our residuals plots are limited by this noise.

As detailed in our report,¹ we also used ellipsometric measurements as an independent method to corroborate the plasmon results by collecting substrate slide data on four distinct spots. We used the plasmon determined indices, n , to obtain ellipsometric thicknesses that agreed with the plasmon determined thicknesses within ± 1 Å for Ag and ± 2 Å for Au. We do not believe that this agreement is fortuitous; rather, we believe it supports the accuracy of our reported plasmon results.

In previous work^{1,2} we do point out the utility of two-color experiments to determine n , k , and d simultaneously, taking advantage of dispersion. This is particularly applicable for the SPS study of thin metals. When the metal film is overcoated with a SAM or other dielectric bed, a complete and unique simultaneous analysis for the both the metal and dielectric overcoat thicknesses and indices (n , k , and d) at two wavelengths does not appear to be possible. In the present study under question, we first determine the metal parameters and assume they do not change after coating the same slide with the SAM. This is a practical way of determining the optical constants of the SAM with minimal absorption using SPS, although a two-color experiment would clearly be beneficial in attempting to unambiguously pin down these parameters.

Considering the agreement in our SPS analysis of redundant spots on different substrate slides and the favorable agreement with the ellipsometric results, we believe our reported film thicknesses and indices for C₁₂₋₂₀ alkanethiol SAMs and the conclusions drawn regarding tilt angles are reasonable.

References and Notes

- (1) Ehler, T. T.; Malmberg, N.; Noe, L. J. *J. Phys. Chem. B* **1997**, *101*, 1268-72.
- (2) Ehler, T. T.; Noe, L. J. *Langmuir* **1995**, *11*, 4177-79.