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LETTERS

Enhanced Sensitivity in Single-Reflection Spectroscopy of Organic Monolayers on Metal Substrates (Pseudo-ATR)

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The present work demonstrates that the observed intensity of an infrared spectrum of a thin film or monolayer on a metal substrate can be increased an order of magnitude by using attenuated total reflection (ATR) instrumentation with a single reflection (pseudo-ATR). The intensities of signal peaks in the pseudo-ATR IR spectrum of a sample of *n*-octadecane-1-thiol-d_{37} on gold exceed by an order of magnitude those in a spectrum taken using traditional grazing angle specular reflectance. The reproducibility of the two spectra is comparable.

Introduction

Attenuated total reflectance (ATR) spectroscopy has been in use as a common method for investigating monolayers and thin films on nonmetallic substrates.[1] The method has also been used to examine very thin films on hard substrates.[2,3] In single reflection ATR spectroscopy, a sample is brought into intimate contact with a high refractive index optical element and light impinges at the interface through this element. If the angle of incidence is chosen to be above the critical angle, as determined by the refractive indices of the two materials in contact, internal reflection occurs and the absorption characteristics of the sample can be measured. The refractive index of a metal substrate is higher than that of any infrared transparent material, and therefore it is impossible to meet the criteria for ATR. Nevertheless, the use of single-reflection ATR instrumentation (pseudo-ATR spectroscopy) still yields sensitivity enhancements for a monolayer on a metal substrate that are comparable to those achievable with multiple-reflection ATR instrumentation.[2] This sensitivity follows from the exact description of the system given by the Airy formula, although it is anything but intuitive.

Experimental Part

Materials: *n*-Octadecane-1-thiol-d_{37}. A round-bottom flask was charged with *n*-octadecanol-d_{37} obtained from Cambridge Isotope Laboratories, Inc. (1 g, 3.7 mmol) and P_2S_5 (0.2 g, 0.46 mmol) under nitrogen, and the mixture was heated at 110 °C. To the hot mixture was added KSH (0.26 g, 3.7 mmol) in small portions. After the addition was complete, the reaction mixture was heated at 160 °C for 24 h. The mixture was allowed to cool to 100 °C, and water (5 mL) followed by HCl (2 mL, 35%) was added dropwise. The product was extracted into CH_2Cl_2 (3×30 mL) and washed with water and brine, and the solvent was evaporated under reduced pressure to yield 0.7 g of viscous yellow-brown oil. The crude product was purified by distillation (kugelrohr, 0.5 mmHg, 160−180 °C) to give 0.38 g of a soft white solid (mp 40 °C).

Sample Preparation. The gold substrates used (~3 cm × ~1.5 cm) were prepared by thermal evaporation of a titanium adhesion layer (200 Å) onto a microsope slide followed by 2000 Å of gold and were subsequently stored in ambient conditions for up to a month. The substrates were submerged overnight into a 7×10^{-4} M solution of the thiol in tetrahydrofuran (THF). The sample was rinsed with excess THF and dried under argon before the quality of the SAM formed was assessed through ellipsometry and FTIR measurements.

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Measurements. Ellipsometer measurements were made using a Rudolph Research/AutoEL instrument. Optical constants for the gold were measured immediately before putting the substrate into solution and the index of refraction for the monolayer was assumed to be $n = 1.462$. ATR measurements were carried out using Harrick's GATR, a 65° fixed grazing angle ATR accessory in a Nicolet Nexus 670 FTIR spectrometer (1000 scans, 2 cm^{-1} resolution). The background was the clean gold substrate in contact with the Ge crystal of the GATR attachment. The GATR accessory is equipped with a special pressure applicator to optimize contact between the sample and the crystal by using a torque screwdriver (0.35 Nm). The experimental apparatus focuses the beam onto the sample and hence employs a range of incident angles, as opposed to the single angle of incidence assumed by the theoretical model outlined below.

For comparison, grazing angle specular reflectance measurements were also made using Harrick's Refractor accessory.[4] A freshly prepared gold substrate was again used for the background spectrum. The same spectrometer settings were used in both measurements.

Numerical Analysis. Numerical simulation and measurements were carried out to examine the sensitivity that results in analyzing thin films on metal substrates using a relatively high angle of incidence and a Ge crystal. The reflectivity of a thin film sandwiched between two different materials can be expressed by the Airy formula:[5,6]

$$\rho^p = \{r^p_{12} + r^p_{23}\exp[4\pi ikd({n_2}^2 - {n_1}^2\sin^2\theta)]^{1/2}\}/\{1 + r^p_{12}r^p_{23}\exp[4\pi ikd({n_2}^2 - {n_1}^2\sin^2\theta)^{1/2}\}$$

where r^p_{12} and r^p_{23} are Fresnel amplitude coefficients for the interface between the two materials and the film:

$$r^p_{12} = \{{n_2}^2\cos\theta - n_1({n_2}^2 - {n_1}^2\sin^2\theta)^{1/2}\}/\{{n_2}^2\cos\theta + n_1({n_2}^2 - {n_1}^2\sin^2\theta)^{1/2}\}$$

$$r^p_{23} = -\{{n_3}^2({n_2}^2 - {n_1}^2\sin^2\theta)^{1/2} - {n_2}^2({n_3}^2 - {n_1}^2\sin^2\theta)^{1/2}\}/\{{n_3}^2({n_2}^2 - {n_1}^2\sin^2\theta)^{1/2} + {n_2}^2({n_3}^2 - {n_1}^2\sin^2\theta)^{1/2}\}$$

and p is the polarization direction of incident light, k is the wavenumber ($k = 1/\lambda$), and θ is the incident angle. The square of the absolute value of the amplitude coefficient ρ^p is the reflectance of the film.

Results

Numerical Simulations. For numerical analysis, the following parameters were selected as typical: $n_1 = 4.0$ (Ge crystal), $n_2 = 1.5 + 0.5i$ (organic thin film), $n_3 = 20 + 40i$ (metal substrate), $k = 1000\ \text{cm}^{-1}$ (wavenumber of incident light, $\lambda = 10\ \mu\text{m}$). A typical organic sample has the real part of the refractive index around 1.5. The value of the imaginary part of the refractive index (i.e., the absorption index) of the sample was chosen to correspond to a center of a fairly strong absorption band. The results for net absorbance as a function of incident angle are presented in Figure 1 for p-polarized light. The net absorbance is defined as the difference between the absorbance of sample with a monolayer and the clean metal. Absorbance is calculated from the reflectivity of the system using eq 1.

For Figure 1, film thickness was increased from 0 to 150 Å in 10 Å increments. The absorbance increases strongly and reasonably linearly with film thickness until approximately 80 Å. Then, the trend reverses sharply and the peak absorbance starts decreasing with increasing film thickness. Additionally, the angle of maximum sensitivity moves toward smaller angles in the thicker films. Even at angles of incidence well below the angle of maximum sensitivity the sensitivity is surprisingly high. The level of change in the shape of the curves occurring at film thicknesses up to 100 Å indicates that the quality of the sample−ATR crystal contact is critical. Thus the level of sensitivity achieved in practice may not reach that indicated theoretically. However, even a small fraction of theoretical sensitivity makes this technique superior to any other type of surface IR spectroscopy for species adsorbed on a metal surface.

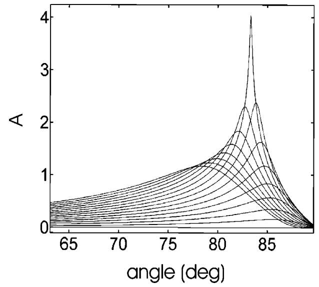

Figure 1. Net absorbance of a thin film on a metal substrate calculated from reflectance through a Ge crystal as a function of thickness from 0 Å (bottom curve) to 150 Å in 10 Å increments.

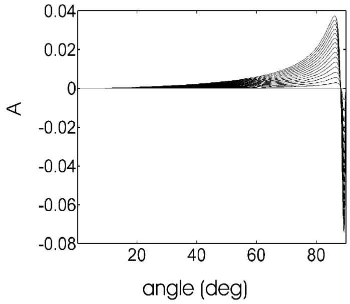

Figure 2. Net absorbance of a thin film on a metal substrate calculated from reflectance through air as a function of thickness from 0 to 150 Å (top curve) in 10 Å increments.

To appreciate the magnitude of this sensitivity enhancement with respect to ordinary grazing angle spectroscopy, the above results were recalculated using air instead of the germanium crystal (Figure 2). Note that a "negative" net absorbance occurs above 87°, because such a thin coating actually enhances the reflectivity of the metallic surface at these angles. In practice, such high incident angles cannot be easily attained and hence this curious behavior does not cause problems.

Measurements. From the simulations, it is clear that utilizing a Ge crystal to transfer the radiation to and from the sample should increase sensitivity by more than 10-fold. A sensitivity enhancement is indeed observed experimentally.

Figure 3 shows a part of the IR spectra of *n*-octadecane-1-thiol-d_{37} monolayer supported on a gold substrate. The bands in the pseudo-ATR spectrum are much more intense than those in the ordinary grazing angle incidence spectrum. The self-assembled monolayers are easily detected from the peaks around 2194 and 2221 cm^{-1}, attributed to the CD_2 groups in the alkyl chain. The CD_3 stretches are too weak to be resolved in this region. Figure 4 shows a different part of the spectral region, from 1000 to 1140 cm^{-1}. The KBr spectrum of the neat sample has been included for comparison. With the GATR attachment the CD_2 deformation vibrations are apparent at 1058 and 1089 cm^{-1}, but they are not detectable in the ordinary grazing incidence external reflection spectrum.

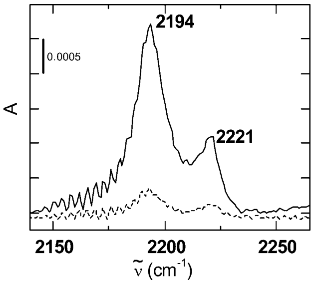

Figure 3. The 2140−2265 cm^{-1} region of the absorption spectrum of a monolayer of *n*-octadecane-1-thiol-d_{37} on gold: (top curve) pseudo-ATR spectrum; (bottom curve) ordinary grazing angle external reflectance spectrum.

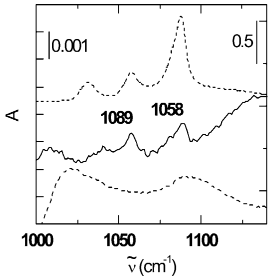

Figure 4. The 1040−1100 cm^{-1} region of the absorption spectrum of *n*-octadecane-1-thiol-d_{37}: (top curve) the spectrum in a KBr pellet (right scale). Spectra of a monolayer on gold: (center curve) pseudo-ATR; (bottom curve) ordinary grazing angle external reflectance spectrum (left scale).

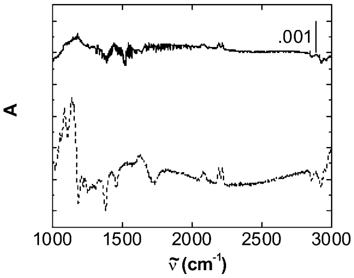

Figure 5. The 1000−3000 cm^{-1} region of the absorption spectrum of a freshly deposited gold substrate in air: (top curve) ordinary grazing angle external reflectance spectrum; (bottom curve) pseudo-ATR spectrum.

To test the reproducibility of the GATR instrumentation, another sample was prepared under identical conditions and was measured three times over a period of 2 days, removing the sample and then replacing it, with the same contact pressure applied, between each run. Measuring the peak height at 2194 cm^{-1} for each spectrum resulted in a mean peak height of 4.87×10^{-4} absorbance units and a standard deviation of 1.15×10^{-4}. For comparison, an octadecanethiol sample was prepared and observed under similar conditions and measured with the ordinary grazing angle specular reflectance attachment. The peak at 2916 cm^{-1} had a mean height of 6.87×10^{-4} absorbance units with a standard deviation of 1.15×10^{-4}. Figure 5 compares baselines measured on a freshly prepared gold substrate, once using an ordinary reflectance attachment and once using the GATR attachment. Like the pseudo-ATR spectrum, the pseudo-ATR baseline is more sensitive than that taken with a spectral reflectance attachment and more clearly shows the presence of impurities collected from the laboratory air.

Discussion

It is obvious from the above results that pseudo-ATR is a highly sensitive technique for analyzing monolayers and very thin films on metal substrates and yields higher signal-to-noise ratios for IR peaks than ordinary grazing angle specular reflectance. At the same time, it also amplifies the signals from all impurities present on the surface, and the baseline appears less constant. The reproducibility of the technique depends greatly on the quality of the contact between the substrate and the germanium window, which is why the torque screwdriver is necessary. With proper care, it is comparable to the reproducibility of ordinary grazing angle incidence spectroscopy. The difficulty of maintaining excellent contact over a large area has so far discouraged us from attempting to achieve additional enhancement by using multiple reflections.

The origin of the increased sensitivity can be understood intuitively if one considers what would happen if the gold substrate were not present and instead the molecules were adsorbed onto the Ge ATR crystal. If air were present above the adsorbed material, given the 65° angle of incidence in the GATR, the IR radiation would be totally internally reflected and an evanescent wave would be established in the rarer medium.[2] Its penetration depth in air (~450 nm for 10 μm radiation) would be much greater than the thickness of the monolayer (~2 nm). If the material on the other side of the monolayer had an index of refraction similar to that of germanium, the radiation would be mostly transmitted across such a thin barrier. When the material is gold, the attempted transmission is thwarted by its reflectivity, and total reflection is restored. Now, the evanescent wave is compressed into a much smaller volume and it is qualitatively sensible that its amplitude is increased. Because the absorption is proportional to the electric field amplitude squared, an enhancement in the electric field strength of 10 times results in a 100-fold enhancement in absorption.

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