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Bipin K. Singh
Iowa State University

Andrew C. Hillier
Iowa State University, hillier@iastate.edu

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Abstract
We demonstrate how grating-coupler assisted infrared reflection absorption spectroscopy can be used to simultaneously determine the chemical identity and relative thickness of organic thin films. With a grating substrate, a threshold anomaly associated with passing off of the −1 diffracted order occurs at grazing angles of incidence, resulting in a sharp absorbance in the infrared. The position of this peak is sensitive to the grating geometry as well as the dielectric environment near its surface. Thus, shifts in the peak position can be used to determine the relative thickness of adsorbed films or quantify molecular adsorption events. To illustrate the characteristics and sensitivity of this phenomenon, several samples were prepared and tested, including self-assembled alkanethiolate monolayers with 11-mercaptoundecanoic acid, 11-mercapto-1-undecanol, decanethiol, and a covalently linked layer of bovine serum albumin on a commercial, gold-coated grating. For these samples, the position of the threshold absorbance peak shifted to lower wavenumbers as film thickness increased, which is consistent with calculated shifts based upon an increasing refractive index at the interface. The sensitivity of this shift was measured to be 3.7 cm⁻¹ nm⁻¹. These results illustrate how a grating substrate can be exploited in a standard infrared reflectance measurement to provide additional information about the relative thickness of adsorbed surface films.

Disciplines
Chemical Engineering | Chemistry

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Grating-Coupler Assisted Infrared Reflection Absorption Spectroscopy for the Characterization of Organic Thin Films

Bipin K. Singh and Andrew C. Hillier*

Department of Chemical and Biological Engineering and Department of Chemistry, Iowa State University, Ames, Iowa 50011

We demonstrate how grating-coupler assisted infrared reflection absorption spectroscopy can be used to simultaneously determine the chemical identity and relative thickness of organic thin films. With a grating substrate, a threshold anomaly associated with passing off of the −1 diffracted order occurs at grazing angles of incidence, resulting in a sharp absorbance in the infrared. The position of this peak is sensitive to the grating geometry as well as the dielectric environment near its surface. Thus, shifts in the peak position can be used to determine the relative thickness of adsorbed films or quantify molecular adsorption events. To illustrate the characteristics and sensitivity of this phenomenon, several samples were prepared and tested, including self-assembled alkanethiolate monolayers with 11-mercaptoundecanoic acid, 11-mercapto-1-undecanol, decanethiol, and a covalently linked layer of bovine serum albumin on a commercial, gold-coated grating. For these samples, the position of the threshold absorbance peak shifted to lower wavenumbers as film thickness increased, which is consistent with calculated shifts based upon an increasing refractive index at the interface. The sensitivity of this shift was measured to be 3.7 cm⁻¹ nm⁻¹. These results illustrate how a grating substrate can be exploited in a standard infrared reflectance measurement to provide additional information about the relative thickness of adsorbed surface films.

Infrared reflection absorption spectroscopy (IRRAS) is a popular surface-sensitive technique that can be used to provide both chemical and structural information about thin organic films and adsorbates on surfaces. Typically, metal substrates are used for these measurements due to their large infrared extinction coefficients. High extinction coefficients are necessary to detect the intrinsically low absorbances of thin films. The ability of IRRAS to interrogate molecular structure and composition has been routinely used in the characterization of various films, including self-assembled alkanethiolate monolayers, polymers, and glasses.

IRRAS has also been applied to biological systems, such as protein adsorption, avidin–biotin binding, and the assembly of peptide nucleic acids. Most of these studies have exploited the fact that IRRAS provides information about film properties, such as chemical composition, bond orientation, conformation, and details of the local interfacial environment. However, quantitative determination of film thicknesses in these systems requires an additional measurement, such as ellipsometry, surface plasmon resonance, or atomic force microscopy. Although there are examples combining infrared spectroscopy with ellipsometry, the ability to quantitatively measure film thickness directly with the infrared signal has not been reported.

Diffraction methods are widely used to interrogate structure and ordering in materials at various length scales. Grating-based diffraction sensor strategies have generated renewed interest due to their surface-sensitive optical properties. Examples include two-photon fluorescence enhancement and light reflection spectroscopy, which have been used for the characterization of colloids and nanoparticles as well as the determination of bulk refractive indices. The detection of volatile organic compounds by chemoselective polymeric gratings has recently been demonstrated as well as “tunable” diffraction gratings constructed from electroactive materials. The ability of metal gratings to excite surface plasmons has also been used in surface-enhanced Raman spec-

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troscopy, in traditional grating-based surface plasmon resonance sensors, and for developing new geometries for biosensing such as surface plasmon-enhanced diffraction.

In this work, we demonstrate how coupling thin-film samples to a diffraction grating substrate can be used to yield information about film thickness simultaneously during IRRAS measurements. Although grating-coupler assisted infrared spectroscopy has been reported for investigation of the excitation spectrum of inorganic multilayers, it has not previously been combined with IRRAS for film thickness measurements. In this work, film thickness information is obtained through an anomalous absorbance in the infrared spectrum that appears at grazing angles of incidence. This absorbance occurs as the −1 diffracted order becomes parallel to the grating surface and disappears, as shown in Scheme 1. This disappearance, which is referred to as passing off of the diffracted order, is a threshold anomaly that significantly impacts the diffraction efficiency of the other propagating orders. The threshold conditions are sensitive to the refractive index at the grating interface, which is modified by the adsorption of ultrathin molecular films. We provide both experimental and theoretical evidence of the properties of this threshold absorbance, including tests with several thin molecular films. This work demonstrates a new capability for IRRAS measurements, which can be simply employed in a standard instrument to provide additional characterization for thin films.

**EXPERIMENTAL SECTION**

**Materials and Reagents.** Absolute ethanol, decanethiol (DT), 11-mercapto undecan-1-ol (MUA), 11-mercapto-1-undecan-1-ol (MUL), HEPES, N-hydroxy succinimide (NHS), N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC), and bovine serum albumin (BSA) were purchased from Sigma-Aldrich (St. Louis, MO). Nitric acid was from J. T. Baker (Phillipsburg, NJ). All chemicals and reagents were used as received. Recordable compact disks (MAM-A Gold CD-R) were purchased from Inkjet Art Solutions (Salt Lake City, UT). Gold (99.999%) was purchased commercially available, gold-coated recordable compact disks (CD-R) as described in a previous publication. Following removal of the protective polymer and lacquer layers by wet chemical treatment, the underlying gold grating was cleaned in an oxygen plasma for 1 min to remove any residual organic impurities (plasma cleaner PDC-32G, Harrick Scientific, Ossining, NY). It was subsequently washed several times with water and ethanol followed by drying with a nitrogen stream. The grating was then placed in a vacuum chamber for deposition of additional gold (Denton Vacuum Turbo III, Morrestown, NJ). Approximately 50 nm of gold was deposited onto the existing ~50 nm at a rate of 1–2 Å/s and a pressure of 7 × 10⁻⁵ Torr under nitrogen atmosphere.

**Formation of Thin Organic Films.** Gold gratings were kept under a UV lamp (Spectroline model SB-100P, Spectronics Corp., Westbury, NY) for 30 min and then cleaned in an oxygen plasma for 1 min before soaking in 10 mM ethanolic solutions of DT, MUL, or MUA for 4 h. After incubation, the gratings were rinsed vigorously with ethanol and dried in a nitrogen stream immediately prior to characterization. Activation of carboxylic acid terminated surfaces of MUA was achieved by exposing the sample to an aqueous solution containing 150 mM EDC and 30 mM NHS for 30 min. This reaction resulted in the formation of reactive succinimide esters on the surface. Subsequent attachment of BSA to the array surface was achieved by exposing the sample for 90 min to a 0.5 mg mL⁻¹ solution of BSA in HBS. The sample was then rinsed with HBS and dried under nitrogen.

**Infrared Reflection Absorption Spectroscopy.** A Nicolet MAGNA 750 Fourier transform infrared spectrometer using a liquid nitrogen-cooled MCT detector was used to obtain infrared spectra. Reflection spectra were collected with p-polarized light incident at 80° with respect to the surface normal. These spectra are presented as −log(R/R₀), where R is the sample reflectance and R₀ is that from a reference sample. Each spectrum represents an average of 512 individual sample and reference scans acquired at 2 cm⁻¹ resolution. An octadecaethiolate-dsg monolayer on a gold-coated glass slide served as the reference sample. IRRAS spectra were collected for each sample with a grating orientation both parallel and perpendicular to the incident light.

**Ellipsometry.** Film thickness measurements were performed using ellipsometry. A motorized, variable-angle null ellipsometer (Multiskop, Optrel GbR), operating in the PCSA configuration at a single wavelength (632.8 nm) at 70° angle of incidence, was used to measure ellipsometric parameters Δ and Ψ. The values from Ernest Fullam (Latham, NY). All experiments used 18 MΩ deionized water (NANOPure, Barnstead, Dubuque, IA). The 10 mM solutions of DT, MUA, and MUL were made in ethanol. HEPES-buffered saline (HBS, 10 mM HEPES, 150 mM sodium chloride) was prepared with the pH adjusted to 7.4 using 10 mM NaOH and stored at 4 °C.
of \( \Delta \) and \( \Psi \) were translated into equivalent optical thicknesses using a three-medium model. The optical constants of the gold substrate (refractive index \( n \) and absorption coefficient \( k \)) were first determined using a two-phase model (air/substrate). The thickness of the adsorbed film was then found using a three-phase model (air/film/substrate) with a value of 1.45 for the refractive index of the film.\(^{31}\)

**RESULTS AND DISCUSSION**

The gratings used in this study were prepared from gold CD-Rs as previously reported.\(^{25}\) Briefly, square pieces were cut from a CD-R such that one side was parallel to the grating direction. The size of the pieces was kept small (25 \( \times \) 25 mm) to minimize the influence of grating curvature. Cut pieces were exposed to concentrated nitric acid solution for 5 min to remove the protective layers. The gold gratings prepared in this manner were visibly translucent with a \( \sim \)50-nm layer of as-received gold. To minimize artifacts due to underlying dye and polycarbonate layers, 50 nm of additional gold was deposited on top of these gratings to render them opaque. The topography of the grating samples was visualized by atomic force microscopy operating in tapping mode. Figure 1A shows the topography of a typical grating surface. Roughness analysis revealed a root-mean-squared roughness of 1.2 nm \( \mu \)m\(^{-1}\). A cross-sectional profile perpendicular to the grating direction (Figure 1B) depicts a pitch of \( \sim \)1500 nm and an amplitude of \( \sim \)80 nm. Although it is possible that AFM tip convolution could impact the measured cross section, the shallowness of the grating and the sharpness of the AFM tips used for measurement suggest that these data provide an accurate representation of the sample profile. The shape of this surface profile approximates that of a trapezium with rounded corners.

The gold gratings were subsequently used as substrates to prepare alkanethiolate self-assembled monolayers. A variety of surface functionalities can be readily fabricated on gold surfaces by tailoring the headgroup, \( X \), of an \( \omega \)-functionalized \( n \)-alkanethiol, \( \text{HS}-(\text{CH}_2)_n-X \), and allowing it to self-assemble on gold.\(^{30,33}\) Spontaneous chemisorption of alkanethiol molecules occurs from ethanol solutions.\(^{25,30}\) The 10 mM solutions of DT, MUL, and MUA were prepared in ethanol, and the gold gratings were immersed for 4 h. The samples were rinsed with ethanol to remove unbound and weakly attached molecules from the surface. The films thus formed showed a wetting behavior that was consistent with the literature.\(^{34}\) DT film showed strong hydrophobic behavior due to exposed methyl and methylene groups as indicated by the beading of water droplets. MUL and MUA films were hydrophilic and completely wetted by water. These preliminary results indicated well-formed surface films.

The formation of well-defined alkanethiolate monolayers was confirmed by IRRAS measurements. Figure 2 shows absorbance spectra for the various alkanethiolate films with the grating oriented such that the groove direction was parallel to the incident light beam (vide infra). Spectra for the C–H stretching region (2800–3000 cm\(^{-1}\)) are shown in Figure 2A while the positions of the absorbance peaks are provided in Table 1. The various peaks are consistent with previous reports.\(^{35,36}\) The peak at 2965 cm\(^{-1}\) in DT spectra corresponds to asymmetric in-plane C–H stretching \( \nu_s \) of the terminal methyl groups. The absence of this peak in spectra of MUL and MUA films clearly distinguishes them from DT. The two peaks at 2935 and 2879 cm\(^{-1}\) in DT are due to Fermi splitting of symmetric methyl C–H stretching mode \( \nu_a \). The peaks at 2921 and 2851 cm\(^{-1}\), which are present for all three films, are due to symmetric \( \nu_s \) and asymmetric \( \nu_a \) C–H stretching modes in the substituent methylene groups. In MUL, the hydroxyl-terminated surface is reflected by a broad absorbance in the OH stretching region (Figure 2B).\(^{36}\) MUA shows peaks at 1740 and 1721 cm\(^{-1}\) due to non-hydrogen-bonded and hydrogen-bonded C=O stretching modes associated with the terminal carboxylic acid group (Figure 2C).

MUA surfaces can be readily activated with NHS/EDC to create reactive succinimide esters that can combine with primary amine groups on BSA.\(^{25,37}\) A sample was made using this method in which BSA protein was covalently attached to the chemisorbed MUA on gold. Infrared absorption spectra of this sample (Figure 2C) show a strong absorption centered at 1662 cm\(^{-1}\), which can be attributed to hydrogen-bonded C=O mode in bundled internal \( \alpha \)-helices.\(^{36,38}\) Loss of the majority of the signal from the C=O peaks at 1740 and 1721 cm\(^{-1}\) indicates formation of a dense layer of protein on MUA. These results illustrate that gold gratings provide suitable substrates for construction of molecular alkanethiolate films that are consistent with films formed on typical gold-coated glass.\(^{34}\)

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In addition to the expected vibrational spectra for these adsorbed films, a strong absorbance was also observed at 3400 cm$^{-1}$ when the grating direction was oriented perpendicular to the plane of incidence of the light beam (Figure 3A). No such absorbance was observed when the sample was rotated with the grooves parallel to the plane of incidence. This suggests that this "anomalous" absorbance was related to diffraction from the grating. To investigate the origin and characteristics of this absorbance, the optical response of the grating was simulated using a commercial solver (PCGrate, International Intellectual Group, Inc., Penfield, NY) that employs an integral method to numerically solve the electromagnetism equations. The profile of the gold grating was modeled as that obtained from the AFM scan of the surface (Figure 1B). The grating solver used a frequency-dependent refractive index for gold. Details of the input parameters for the calculations are provided in the Supporting Information. This calculation revealed that, under these experimental conditions, only the 0 and $-1$ orders appear for the wavenumbers between 3213 and 4000 cm$^{-1}$ while no propagating diffracted orders appear at 700–3213 cm$^{-1}$. As the wavelength is increased (wavenumber is decreased), the propagating $-1$ diffraction order becomes parallel to the grating surface. Once parallel, this order passes off and becomes evanescent (Scheme 3).

Table 1. C-H Stretching Mode Peak Positions (cm$^{-1}$) for Functionalized Alkanethiolate Monolayers Chemisorbed on Gold Gratings

<table>
<thead>
<tr>
<th></th>
<th>DT</th>
<th>MUL</th>
<th>MUA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$-s</td>
<td>2851</td>
<td>2850</td>
<td>2854</td>
</tr>
<tr>
<td>CH$_2$-a</td>
<td>2921</td>
<td>2918</td>
<td>2923</td>
</tr>
<tr>
<td>CH$_3$-s</td>
<td>2879, 2935*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$-a</td>
<td>2965</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Band split by Fermi resonance.

In addition, a strong absorbance was also observed at ~3400 cm$^{-1}$ when the grating direction was oriented perpendicular to the plane of incidence of the light beam (Figure 3A). No such absorbance was observed when the sample was rotated with the grooves parallel to the plane of incidence. This suggests that this "anomalous" absorbance was related to diffraction from the grating. To investigate the origin and characteristics of this absorbance, the optical response of the grating was simulated using a commercial solver (PCGrate, International Intellectual Group, Inc., Penfield, NY) that employs an integral method to numerically solve the electromagnetism equations. The profile of the gold grating was modeled as that obtained from the AFM scan of the surface (Figure 1B). The grating solver used a frequency-dependent refractive index for gold. Details of the input parameters for the calculations are provided in the Supporting Information. This calculation revealed that, under these experimental conditions, only the 0 and $-1$ orders appear for the wavenumbers between 3213 and 4000 cm$^{-1}$ while no propagating diffracted orders appear at 700–3213 cm$^{-1}$. As the wavelength is increased (wavenumber is decreased), the propagating $-1$ diffraction order becomes parallel to the grating surface. Once parallel, this order passes off and becomes evanescent (Scheme 3).

1). This threshold phenomenon can occur on metallic as well as dielectric gratings. Indeed, one can estimate the conditions at which this threshold occurs with the grating equation

$$\sin (\theta_i) + m\lambda/d = \sin (\theta_r) \tag{1}$$

where $\theta_i$ and $\theta_r$ are the angles of incident and reflected light, $m$ is the diffracted order, $\lambda$ is the light wavelength, and $d$ is the grating pitch. Using an incident angle of $\sim 80^\circ$ and a pitch of $\sim 1500$ nm, eq 1 predicts that the $-1$ order passes off at $\sim 3350$ cm$^{-1}$, which is similar to the position of the anomalously absorbance observed in Figure 3A. This loss of the $-1$ order results in a redistribution of energy into the 0th order and, consequently, a strong absorbance at the associated wavelength (or wavenumber).

Although eq 1 can be used to estimate the conditions of this threshold, it does not take into account several important details. For instance, threshold phenomena are especially sensitive to the refractive index of the medium next to the grating surface. Any changes in the dielectric environment at the grating surface are capable of changing the properties of evanescent waves generated and, thus, the threshold characteristics. Indeed, sensing methods based on threshold phenomena have been reported for determination of bulk refractive indices and size characterization of colloidal suspensions. It has been established that strong changes in reflectivity of highly conducting gratings can occur in the vicinity of threshold phenomena when $p$-polarized light is used, which explains the sharp absorption seen in the measured infrared spectrum.

Since a threshold phenomenon such as this is sensitive to changes in the refractive index near the grating surface, we chose to test the sensitivity of the measured peak position to the thickness of the alkanethiolate molecular films. The position of the threshold absorbance peak was measured for the DT, MUL, MUA, and BSA on MUA films. For all the samples, the spectra obtained with the grating oriented parallel to the incident light were featureless except for the molecular absorption regions as shown in Figure 2. However, a strong absorbance was observed near $\sim 3300$ cm$^{-1}$ for all films with the grating oriented perpendicular to the incident light. Figure 4A depicts the absorbance peaks for each of the samples under perpendicular illumination. A spectrum from a bare gold grating is also shown for comparison. The peak appears at the highest wavenumber for bare gold and shifts to lower wavenumbers in the presence of the absorbed films. The shift in wavenumber was compared to the absolute film thickness as determined by ellipsometry (Figure 4B and Table 2). The DT, MUL, and MUA films showed film thicknesses that are consistent with those reported in the literature at 1.62, 1.58, and 1.55 nm. The thickness of the film containing BSA covalently attached to MUA was 5.17 nm, which is in agreement with earlier reports. A comparison of the film thickness and infrared absorbance provides a near-linear relationship (Figure 4B). With increasing film thickness, the absorbance peak shifts to lower wavenumbers. A linear fit of this trend gives a sensitivity of 3.7 cm$^{-1}$ nm$^{-1}$.

The response of the grating was simulated to theoretically evaluate the sensitivity of peak position toward changes in the

Figure 4. (A) Absorbance spectra in threshold region for DT, MUL, MUA, and BSA on MUA films. (B) Ellipsometrically measured film thickness versus shift in threshold absorbance.
index of refraction at the grating surface. Figure 5 shows that the position of the absorbance peak shifts to lower wavenumbers in a linear fashion as the refractive index is increased, which is in agreement with the trend observed in the experimental results. The slope of the line gives a sensitivity of $3100 \text{ cm}^{-1} \text{ RIU}^{-1}$. In terms of wavelength, this translates to $\sim 3000 \text{ nm RIU}^{-1}$, which is comparable to the sensitivity of surface plasmon resonance-based sensors ($3100–8000 \text{ nm RIU}^{-1}$).\(^\text{42}\) We also investigated the impact of changing the angle of incidence and grating pitch on the position of this peak. It was found that an increase of 1° in angle of incidence shifted the peak position by 6 cm\(^{-1}\) while a 10-nm increase in pitch shifted the peak position by 20 cm\(^{-1}\). Although this sensitivity of peak position to system geometry limits the ability to quantitatively predict the exact position of this absorbance, relative changes due to absorbed films or refractive index changes were not very sensitive to these differences. Indeed, calculations using three different grating geometries with sinusoidal, triangular, and trapezoidal profiles exhibited the exact same shift in wavenumber with increasing refractive index. Thus, with proper calibration, relative film thicknesses can be quantitatively determined by shifts in this threshold absorbance peak. In addition, the ability to shift the peak position by tuning the pitch of the grating or the angle of incidence can be used to provide flexibility to the platform. For example, pitch modulation could be used to shift the absorption peak outside the spectral region where molecular absorbance peaks appear.

**CONCLUSIONS**

We have described a grating-coupler platform as a simple and sensitive method for determination of film thicknesses using a conventional IRRAS instrument. With a grating substrate, a sharp absorbance is observed at grazing angles of incidence associated with passing off of the $-1$ diffracted order. Both experimental measurements and theoretical calculations demonstrated that the position of this peak was a strong function of the dielectric properties of the grating interface. Although the exact position of this peak was found to be highly dependent upon the details of the grating geometry, the shift in wavenumber due to a change in the refractive index near the grating interface could be used to quantitatively determine relative film thicknesses. This behavior provides a simple sensing platform for thin films or molecular adsorption events. The sensitivity of this absorbance shift was found to be 3.7 cm\(^{-1}\) nm\(^{-1}\), which is sufficient to detect the formation of monomolecular films. These results illustrate how a grating substrate can be exploited in a standard infrared reflectance measurement to independently determine the chemical identify and relative thickness of adsorbed surface films.

**ACKNOWLEDGMENT**

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**SUPPORTING INFORMATION AVAILABLE**

Input parameters for grating calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Table 2. Position of Threshold Absorbance Peak of Various Samples**

<table>
<thead>
<tr>
<th>surface</th>
<th>peak position (cm(^{-1}))</th>
<th>ellipsometric film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>3430</td>
<td>0</td>
</tr>
<tr>
<td>Au/HS(CH(_2)(_9)CH(_3)</td>
<td>3419</td>
<td>1.62</td>
</tr>
<tr>
<td>Au/HS(CH(_2)(_10)OH</td>
<td>3421</td>
<td>1.58</td>
</tr>
<tr>
<td>Au/HS(CH(_2)(_9)COOH</td>
<td>3421</td>
<td>1.55</td>
</tr>
<tr>
<td>Au/HS(CH(_2)(_9)COOH + NHS + BSA</td>
<td>3411</td>
<td>5.17</td>
</tr>
</tbody>
</table>

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