**Spectroscopic Analysis of Thin Films: A Comparison of FTIR Sampling Methods**

**Introduction**

Thin films are an important type of sample that can be analyzed using optical spectroscopy. While some thin films can be self-supporting, ultra thin films must be deposited onto a substrate. Such films can be as thin as a single monolayer. In some cases thin films grow naturally on a particular substrate, such as an aluminum oxide film on aluminum. Other films can be deposited on an arbitrary substrate. For these films, the choice of an appropriate substrate could be influenced by the ability to analyze the films spectroscopically. The films could be deposited on a transparent substrate, such as calcium fluoride, so that the analysis could be performed by transmission spectroscopy. Alternately, some films could be deposited on a metal, such as gold or platinum, for analysis by reflection spectroscopy. Other common substrates for thin film deposition include glass, silicon, germanium, gallium arsenide, titanium dioxide, and diamond.

Three spectroscopic techniques for analyzing ultra thin films on different substrates are examined and compared for sensitivity: transmission, grazing angle Ge-ATR, and grazing angle reflection. The transmission results are used as yardstick with which to measure the relative sensitivities of the other two techniques.

**Experimental/Theory**

The simulations were performed using the theoretical considerations described elsewhere\(^1\). The specific parameters used for the sample and substrates are shown in Table 1.

All simulations were performed with p-polarized light at 10\(\mu\)m. The refractive indices listed in Table 1 are indicated for that wavelength. The specific results may differ if a different set of indices for the sample and metal are used. However, the general behavior of the absorbance vs. film thickness curves is the same.

For the transmission simulation, the film was assumed to be free-standing and the incident radiation impinged upon the sample at normal incidence (0\(^\circ\)).

For grazing angle ATR, the film was supported on either a Si or metal substrate. The refractive index of Ge was assumed to be 4.0. Results are reported for two incident angles: 60\(^\circ\), which is slightly above the theoretical critical angle for the Si-Ge interface, and 65\(^\circ\), safely above the experimental critical angle given the typical beam spread of an FTIR spectrometer.

For the grazing angle specular simulation, the film was...

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<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive index at 10(\mu)m</th>
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<tbody>
<tr>
<td>Film</td>
<td>1.40 + 0.1i</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.42</td>
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<tr>
<td>Metal</td>
<td>10 + 20i</td>
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</tbody>
</table>
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Results are presented for two different incident angles: 75° and 80°, the two angles for which commercial grazing angle specular reflectance accessories are offered.

Results and Discussion

Figure 1 shows the absorbance versus film thickness for the three techniques.

As expected, transmission shows a linear relationship between film thickness and absorbance. After the thickness exceeds 0.5 μm, transmission yields the highest absorbance.

The two reflection techniques are both more sensitive than transmission for the ultra-thin films. Grazing angle specular reflection has been a time-honored technique for the analysis of ultra-thin films, and the general, but flawed assumption is that the higher the angle of incidence the higher the sensitivity. As seen in Figure 1, the absorbance for an 80° angle of incidence is indeed higher for ultra-thin films, but barely so. As soon as the film thickness exceeds about 1000 Å the curves reverse and the 75° angle of incidence yields higher absorbance. When this insight is combined with the practical difficulties brought about by a high beam spread over the sample for an 80° angle of incidence, it is much better to use a 75° angle of incidence for grazing angle specular reflection spectroscopy. Note also that the benefit of using the grazing angle specular reflection technique over transmission is not as large as generally assumed.

Grazing angle Ge-ATR, however, does offer a considerable advantage over transmission. The absorbance is stronger for the angles closer to the critical angle, so a 60° angle of incidence provides a 50% gain over the 65° angle of incidence. This gain, however,
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has to be weighed over the possible spectral artifacts induced by the beam spread of the spectrometer beam. As the incident angle approaches the critical angle, a higher fraction of rays from the incoming beam will be below the critical angle.

A common feature of both reflection techniques is that they do not follow a linear relationship between absorbance and thickness. A degree of caution in interpreting experimental results is required. For instance, a thinner film can exhibit a higher absorbance than a thick film. Actually, two films of different thicknesses can yield the same absorbance spectrum. However, for the really thin films, those under about 200 Å, the thickness vs. absorbance relationship is sufficiently linear so that the grazing angle ATR technique can be used with great advantage in sensitivity.

REFERENCES