

# Optimizing Detection of Thin Films on High Refractive Index Substrates using FTIR-ATR Spectroscopy

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## INTRODUCTION

Extremely thin films and monolayers on silicon and metal substrates are challenging to measure by infrared spectroscopy. The most sensitive FTIR spectroscopic method for probing these coatings is ATR spectroscopy using a Ge ATR crystal at a relatively high incident angle. Typically these measurements are carried out at an incident angle of 65°. Under these conditions, the evanescent wave is 'trapped' within the coating between the two high refractive index materials, resulting in a signal enhancement.<sup>1</sup>

In principle, the sensitivity of this method depends on the properties of the sample, primarily coating thickness and the substrate refractive index. It also depends on the experimental conditions, specifically the effective incident angle, the incident polarization and the degree of contact between the ATR crystal and the sample.

This paper will explore the role of various experimental parameters to optimize the sensitivity of this method. In particular, the effect of incident angle, the degree of contact, and polarization will be investigated.

## THEORY

The theoretical foundations of ATR were developed by Harrick and duPre.<sup>2,3</sup> To summarize, radiation is directed through a prism, typically referred to as the ATR crystal, at an angle higher than the critical angle for internal reflection. The critical angle,  $\theta_c$ , is defined as:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

where  $n_1$  is the refractive index of the ATR crystal and  $n_2$  is the refractive index of the sample. Above the critical angle, an evanescent wave is created at the reflecting surface. When a sample comes in contact with the surface, this evanescent wave interacts with the sample and a spectrum can be recorded to measure this interaction. This interaction is theoretically described by the Fresnel equations, detailed elsewhere.<sup>1,2</sup>

For a silicon wafer, with a refractive index of 3.24 and a Ge ATR crystal, with its refractive index of 4, the critical angle is 58.8°. As the incident angle approaches the critical angle, the evanescent wave penetrates more deeply into the sample and the band intensities increase. In the case of a very thin film on a silicon substrate, this increase in penetration does not change the

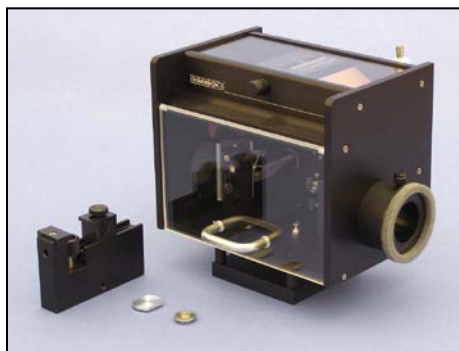


Figure 1. The [Seagull™](#) Variable Angle ATR



Figure 2. The [VariGATR™](#) Grazing Angle ATR Accessory.

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absorption by the sample. The change in the band absorption results from the change in coupling efficiency of the electric field of the incident light through the interface to the electric field of the evanescent wave.

## EXPERIMENTAL

Three sets of FTIR measurements were made: variable angle, variable contact pressure, and two-polarization. For the first two experiments, the composition of the coatings was unknown. For the polarization study, the sample was prepared by the attachment of nitro-benzene diazonium salts to H-terminated <100> Si in HF. All three ATR studies used a Thermo Nexus spectrometer and a torque wrench (Harrick Scientific) for repeatable compression of the sample against the ATR crystal.

For the variable angle studies, the Seagull™ (Figure 1) and the VariGATR™ (Figure 2) were used. The single beam background spectra were collected first and then sample was compressed against the ATR crystal. The single beam sample spectra were recorded at each angle and referenced to the appropriate background. The data were collected at 8cm<sup>-1</sup> resolution. The Seagull™ was used with a Ge ATR crystal with

a specially configured crystal holder and pressure plate, designed to optimize contact between the ATR crystal and the sample. The incident angle was varied from 54° to 68°, in 2° increments, and 128 scans were signal averaged. With the VariGATR™, the angle was varied in 1° increments from 60° to 65° and 32 scans were collected at each angle.

To study the effect of the degree of contact, the GATR™ (Figure 3) was used with its Ge ATR crystal. The degree of contact was varied by changing the torque wrench from its lowest setting, 20 in-oz, to the upper limit of the GATR™, 56 in-oz. These spectra were also recorded at 8cm<sup>-1</sup> resolution and 128 scans.

For the polarization study, the Harrick GATR™ was used along with a Wire Grid Polarizer on a KRS-5 substrate. The single beam background spectra were recorded at both s- and p-polarization. Then the sample was compressed against the crystal using its 56 in-oz Slip-Clutch. Single beam sample spectra were collected at both polarizations and ratioed to the corresponding background. All spectra were recorded at 2cm<sup>-1</sup> resolution and 32 scans. The baseline-corrected experimental data was further examined by spectral subtraction and fitting to theoretical simulations using the

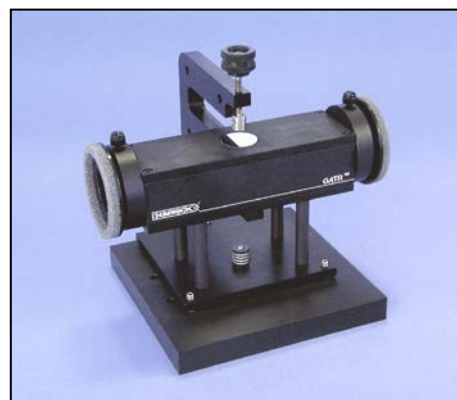


Figure 3. The GATR™ Grazing Angle ATR Accessory.

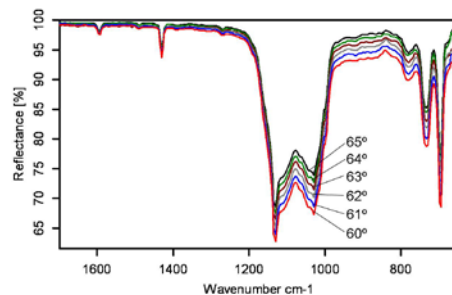


Figure 4. ATR Spectrum of a Thin Film on Si, measured with the VariGATR™ as a function of incident angle.

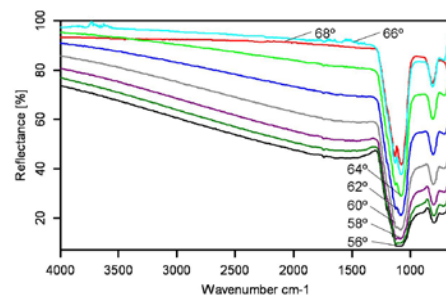


Figure 5. ATR spectrum of a coated Si wafer at various incident angles measured with the Seagull™.



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SOSTM software.<sup>4</sup>

## RESULTS AND DISCUSSION

Figures 4 and 5 show the spectra of two different thin films on silicon, measured as a function of the incident angle. Figure 4 shows increasing band intensities as the critical angle is approached. Note that the spectra near critical angle may show a small degree of dispersion, since the baseline appears to be sloping slightly. Figure 5 shows several spectra recorded below critical angle. These spectra show a strongly sloping baseline and an inverted band around  $1288\text{cm}^{-1}$ . As the incident angle increases, the baseline straightens out, the inverted band disappears, and two bands in the  $1130\text{-}1050\text{cm}^{-1}$  region become better resolved. At an incident angle of  $68^\circ$ , the anomalies are essentially gone and the spectrum looks similar to a transmission spectrum. Thus the ideal angle for measuring this particular sample is significantly higher than the critical angle.

There are several phenomena influencing the experimentally found ideal incident angle. The spectrometer has a focused beam, typically with a  $\pm 8^\circ$  beam spread where the incident angle is defined as that of the central ray. All of these rays interact with the

sample, not just the central ray. Both the VariGATR<sup>TM</sup> and the Seagull<sup>TM</sup> use a Ge hemisphere as the ATR crystal. The VariGATR uses the spectrometer's beam as is while the Seagull<sup>TM</sup> uses a 1:1 imaging. The spectrometer beam refracts at the air-Ge interface, enlarging the beam spread. Note that the hemisphere creates a small illuminated spot, as required for good contact between the ATR crystal and the sample. So there is a trade-off between a smaller beam spread and the degree of contact. The imaging optics of these accessories also differ slightly. The beam spread of the Seagull<sup>TM</sup> is probably somewhat larger than that of the VariGATR<sup>TM</sup>. If this difference was significant, experimental differences in the dispersion effects would be observed.

Since the sensitivity of an ATR measurement increases approaching the critical angle, it is important to work as close to the critical angle as possible while still collecting transmission-like spectra for ease of interpretation. A variable angle accessory allows optimization of the incident angle for a particular spectrometer and sample. Choice of accessory and possibly the installation of an aperture<sup>5</sup> can be used to reduce the angular spread and further

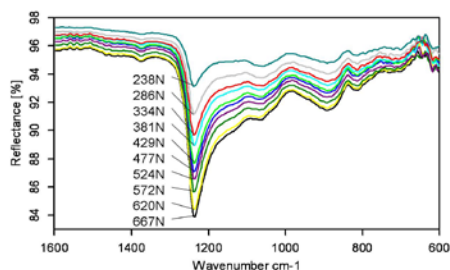


Figure 6. ATR spectra of a thin coating on Si as a function of the force applied to obtain contact.

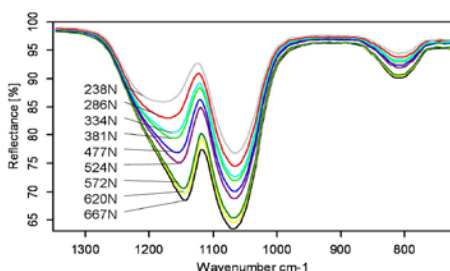


Figure 7. ATR spectra as a function of the force applied to obtain contact.



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optimize sensitivity.

Another experimental parameter that influences the quality of the spectra is the degree of contact between the ATR crystal and the sample. Figures 6 and 7 show the effect of changing the force applied to the sample on the spectra. Both figures show increasing band intensity with force indicating that better contact is obtained with greater force applied. For ATR measurements of flexible materials, the increase in band intensity eventually saturates as more force is applied. Here, the maximum possible force is applied before the band intensities saturate. Note that the degree of contact is also restricted by the flatness of the sample and ATR crystal. Figure 7 also shows band structure changes around  $1200\text{cm}^{-1}$  with increasing applied force. This may indicate a conformational change in the coating. If the coating incorporated an oriented polymer, for example, compressing the sample might alter its orientation.

According to theoretical considerations,<sup>1</sup> the ATR spectra measured at  $65^\circ$  of thin films on Si show sensitivity enhancement for s- and p- polarized light. The spectrum collected with p-polarization is generally enhanced to a greater degree than that collected with s-polarization. In principle, this

should provide a clearer distinction between the bonds that are perpendicular to the surface and those that are parallel than other ATR methods. Figure 8 shows the spectra of a thin coating on Si recorded with s- and p-polarization. Bands appear at  $1226\text{cm}^{-1}$  and  $1112\text{cm}^{-1}$  in the spectrum recorded with p-polarization that are not present in the s-polarized spectrum. The band at  $1226\text{cm}^{-1}$  is clearly comparable in strength to the bands at  $1526\text{cm}^{-1}$  and  $1350\text{cm}^{-1}$  and is likely to be from an oriented species on the surface.

Two other major bands, at  $1526\text{cm}^{-1}$  and  $1350\text{cm}^{-1}$ , are stronger in the p-polarized data than in the s-polarized data. To determine if this was just due to signal enhancement, the data was further examined by subtraction and simulation. The baseline-corrected s-polarized spectrum was multiplied by four and subtracted from the p-polarized spectrum. The resulting difference is shown in Figure 8. The bands at  $1526\text{cm}^{-1}$ ,  $1350\text{cm}^{-1}$ ,  $1600\text{cm}^{-1}$  and  $1112\text{cm}^{-1}$  all subtract reasonably well. The two stronger bands have a small residual feature from a slight band shift. The band at  $1226\text{cm}^{-1}$ , however, is just reduced slightly in intensity, indicating that this band is oriented perpendicular to the surface of the wafer.

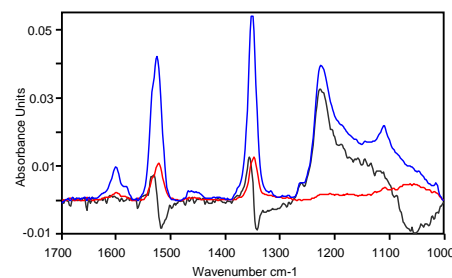


Figure 8. Baseline-corrected ATR spectra of a thin film on  $\langle 100 \rangle$  Si recorded with s polarization (black) and p polarization (red). The difference is shown in blue.

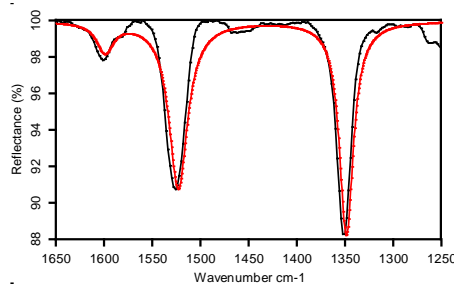


Figure 9. The ATR spectrum of a thin film on  $\langle 100 \rangle$  Si measured (black) and simulated (red) with p-polarized radiation.

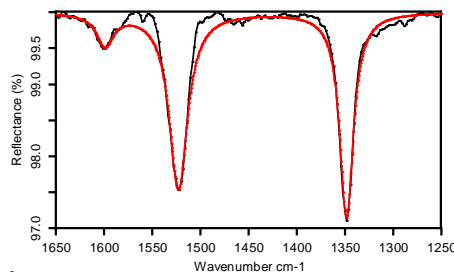


Figure 10. The ATR spectrum of thin film on  $\langle 100 \rangle$  Si measured (black) and simulated (red) using s-polarized radiation.



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To further explore whether or not those bands are oriented, the spectra were fitted using the SOS<sup>TM</sup> software, which calculates the reflectance of a multilayer sample from the Fresnel equations, assuming homogeneous layers. Since the thickness of the coating was unknown, both the peak parameters and the thickness were fit to the s- and p-polarized data. The substrate was assumed to be optically thick with a refractive index of 3.42, and the radiation was perfectly polarized. The resulting coating parameters are shown in Table 1. The simulated spectra are shown in Figures 9 and 10 with the corresponding experimental data. The simulated spectra closely resemble the experimental, supporting the lack of orientation effects in those bands. Note that the coating thickness does influence the appearance of the spectrum and should be measured by independent methods to verify the simulations.

Table 1: Simulation Coating Parameters.

Electronic Polarizability	0.88235	
Sample thickness	108nm	
Wavenumber	Half-Width	Strength
1349.00	17.00	0.02200
1523.50	23.00	0.02800
1599.00	21.00	0.00480

The band at  $1226\text{cm}^{-1}$  is clearly from an oriented species because it only shows spectral features in the p-polarized spectrum. The expected species in the coating, however, do not have characteristic bands at that wavenumber or at  $1110\text{cm}^{-1}$ . This, combined with the band location, suggests that it is due to a species that bound to the surface after its preparation, such as  $\text{SiO}_2$ .  $\text{SiO}_2$  naturally forms on Si upon exposure to air, with its dipole moment perpendicular to the surface.<sup>6</sup>

## CONCLUSION

The most sensitive FTIR spectroscopic method for probing extremely thin films and monolayers on Si is ATR spectroscopy using a Ge ATR crystal at an incident angle above  $58.8^\circ$ . The readily controllable experimental parameters that control sensitivity include:

- The incident angle. For best sensitivity, collect the data at an incident angle as close to the experimental critical angle as possible.
- The degree of contact. For optimal results, use as much contact force as the ATR accessory can deliver without deforming the film.
- Polarization. P-polarization exhibits enhanced sensitivity

relative to s-polarization. The polarization dependence of the method makes it possible to extract information on the orientation of species on the surface using spectral subtraction or spectral simulation methods.

Additional work is in progress to better understand the effect of film thickness in regard to the critical angle and polarization measurements.

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