HARRICK SCIENTIFIC PRODUCTS

No. 21154

THE ADVANTAGES OF USING A POLARIZER FOR GRAZING ANGLE GE-ATR INFRARED SPECTROSCOPY

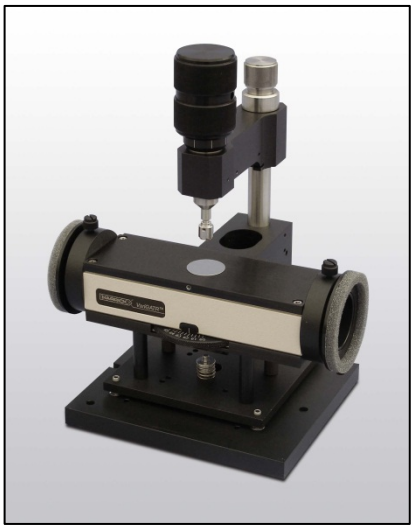

Figure 1. The VariGATR grazing angle ATR accessory.

INTRODUCTION

The spectra of very thin films on silicon substrates can be analyzed by so-called grazing angle ATR spectroscopy. The technique requires a Ge ATR element and an angle of incidence above 60°. This method exhibits a 20-100 times amplification of the absorption bands for p- polarized incident radiation. S-polarized incident radiation is also amplified, 2-3 times. But because of the extraordinary amplification for p- polarized light, it dominates the nature of the resulting spectra. [1, 2, 3]

This note presents the pros and cons of using a polarizer for grazing angle Ge-ATR measurements.

THEORETICAL BACKGROUND

The incident beam is composed of s- and p- polarized components $I_s(k)$ and $I_p(k)$ respectively:

$$I_0(k) = I_s(k) + I_p(k) \quad (1)$$

After the reflection on the sample the reflected light is:

$$I_R(k) = R_s(k)I_s(k) + R_p(k)I_p(k) \quad (2)$$

Therefore the ratio of the reflected and incident beams is:

$$R(k) = \frac{R_s(k)I_s(k)+R_p(k)I_p(k)}{I_s(k)+I_p(k)} \quad (3)$$

If we introduce the beam polarization ratio:

$$Z(k) = \frac{I_p(k)}{I_s(k)} \quad (4)$$

which, as indicated in (4), changes with wavelength, and is generally not too far from unity for a standard spectrometer.

The Eq. 3 can be rewritten as:

$$R(k) = \frac{R_s(k)+R_p(k)Z(k)}{1+Z(k)} \quad (5)$$

The absorbance transform of $R(k)$ yields absorbance:

$$A(k) = -\log_{10}\big(R(k)\big) \quad (6)$$

In the weak absorption approximation the absorbance is:

$$A(k) \approx 0.434(1 - R(k)) \quad (7)$$

and analogously for the s- and p-polarizations:

$$A_{s,p}(k) \approx 0.434(1 - R_{s,p}(k)) \quad (8)$$

By combining expressions 5 through 8, we find:

applications note

$$A(k) \approx \frac{A_s(k)+Z(k)A_p(k)}{1+Z(k)} \qquad (9)$$

For high angle Ge-ATR spectroscopy, $A_s(k) \ll Z(k)A_p(k)$. Since $Z(k) \approx 1$, the above result (9) indicates that the spectra collected without a polarizer in high angle Ge-ATR spectroscopy are roughly half the strength of the absorbance for the p-polarized light.

Any semi-quantitative work should take this factor of two into account and for a fully quantitative measurements it is obviously preferable to use a polarizer to avoid uncertainties due to the polarization ratio *Z(k)*. Use of a polarizer makes it possible to measure A_s and A_p independently and extract from such measurements a possible orientation of the absorbing bonds.

EXPERIMENTAL

Two sets of experiments were carried out to demonstrate the influence of a polarizer on the grazing angle Ge-ATR spectra. In keeping with the theoretical discussion above, the SOS software package[4] was used to model a thin polyethylene-like film on a silicon substrate. The parameters used to model the polyethylene film are shown in Table 1 and the silicon substrate was modeled as an infinity thick piece of Si, with an electronic polarizability of 2.342893023. ATR spectra were then simulated for a 0.010 um thick polyethylene-like film on Si at an incident angle of 65° on a Ge (n=4) ATR crystal.

In addition to the simulation, two samples, a thin coating on a Si wafer and an aged 1500Å SiO coating on Al, were measured using what is commonly considered s-, p- and unpolarized incident radiation. Data was collected using the Harrick VariGATR (see Figure 1) installed in an FTIR spectrometer. The VariGATR was set for a 65° incident angle and spectra were collected at 8 cm^{-1} resolution with a gain of 8, averaged over 32 scans. Background spectra were collected at the three polarizations, then the sample was compressed against the ATR crystal and the sample spectra collected at the three polarizations. These sample single beam spectra were then ratioed to the appropriate background. The unpolarized measurements were recorded without a polarizer. The s- and p- polarization results were obtained using a wire grid polarizer on a KRS-5 substrate. Note that none of these cases perfectly match the pure polarization used in the simulations. Wire grid polarizers allow some of the unwanted component to pass

Table 1: Polyethylene Parameters

Electronic Polarizability		0.867349115
Polarizability Parameters		
Wavenumber	Half-Width	Strength
1458.000	15.000	0.00500
1474.000	5.000	0.00250
2850.000	10.000	0.04500
2900.000	30.000	0.007000
2919.800	11.500	0.098000
2930.500	19.000	0.048000

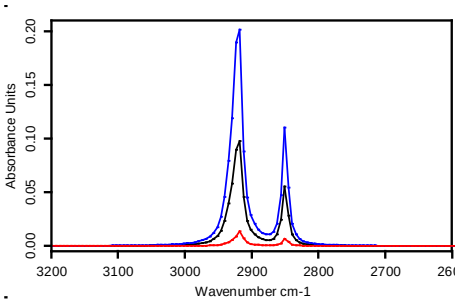

Figure 2. Simulated ATR spectra for a 0.010 um thick polyethylene-like film on Si using s- (red), p- (blue) and un-polarized (black) incident radiation.

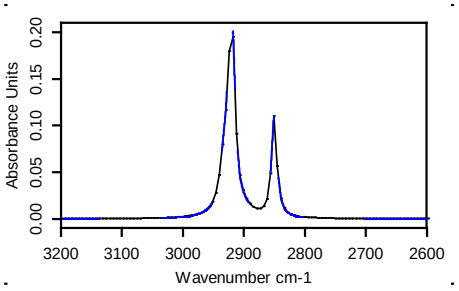

Figure 3. Comparison between the simulated ATR spectra for a 0.010 um thick polyethylene-like film on Si using p-polarization (blue) and two times simulated spectrum with unpolarized (black) incident radiation.

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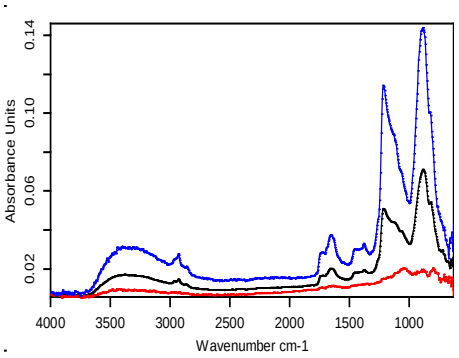

Figure 4. The ATR Spectra of a SAM on Si, measured with s- (red), p- (blue) and un-polarized (black) incident radiation.

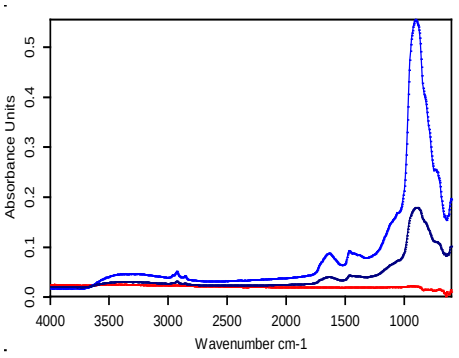

Figure 5. The ATR Spectra of a 1500Å SiO film on Al, recorded using s- (red), p- (blue) and unpolarizer (black) incident radiation.

through along with the wanted polarization. The degree to which this happens is generally known and characterized by the polarizer manufacturer. In addition, the spectrometer has some polarization bias in the beam due to its optical design which is usually less well characterized.

RESULTS AND DISCUSSION

The results of the simulation are presented in Figure 2 for p-polarization, s-polarization and a 50/50 mix (unpolarized). As expected from the theoretical discussion above, the spectrum calculated with unpolarized incident radiation is about half the strength of that with p-polarized radiation (see Figure 3). And the band intensities for s-polarization are significantly lower than for either p-polarization or unpolarized incident radiation.

Figures 4 and 5 show the spectra of two samples, a SAM on a Si wafer and an SiO coating on Al, measured with the three different polarization states. As expected, the s-polarized incident beam results in the lowest intensity bands and p-polarization generates the strongest bands.

Figures 6 and 7 compare the p-polarized measured spectra to the doubled unpolarized collected data. The p-polarized data matches the doubled

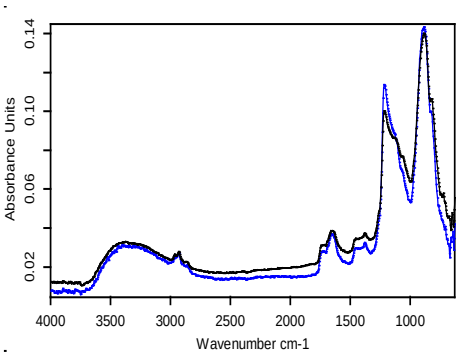

Figure 6. Comparison of the ATR spectrum of a SAM on Si measured with p-polarization (blue) to two times the spectrum recorded with unpolarized incident radiation (black).

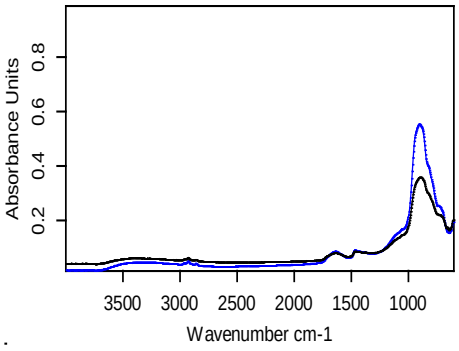

Figure 7. Comparison of the ATR spectrum of a 1500Å SiO film on Al, measured with p-polarization (blue) to two times the spectrum recorded with unpolarized incident radiation (black).

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unpolarized spectra reasonably well considering the assumptions of the theoretical model. The model assumes perfect polarization whereas, in practice, there is some seepage of the unwanted component through the polarizer. This reduces the difference in magnitude of the relative band intensities for s- and p-polarization. The model also assumes no noise. In reality, the band intensity levels observed for s-polarization are small and may become lost in the noise. A sensitive MCT detector and a large number of scans may be required to reduce the signal-to-noise sufficiently to observe those bands. And finally, the theory discussed here does not consider species oriented on the surface of the sample. In Figure 7, it is clear that the Si-O stretching band is much stronger in the spectrum collected with p-polarization than twice that of the unpolarized measurement. This might be an indication that the Si-O bend is oriented with its dipole perpendicular to the surface.

CONCLUSION

For any quantitative or semi-quantitative measurements by grazing angle Ge-ATR, it is preferable to use a polarizer to avoid uncertainties due to the unknown polarization ratio. Use of a polarizer also makes it possible to extract from such measurements a possible orientation of the absorbing bonds.

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[1]M. Milosevic, S. L. Berets and A. Y. Fadeev, *Appl. Spectrosc.* **57**, 724 (2003).

[2]M. E. Mulcahy, S. L. Berets, M. Milosevic and J. Michl, *J. Phys. Chem. B*, **108**, 1519 (2004).

[3]M. Milosevic, V. Milosevic, and S. L. Berets, *Appl. Spectros.*, **61(5)**, 530 (2007).

[4]M. Milosevic and S. L. Berets, Appl. Spectrosc. **47**, 5666 (1993).