HARRICK SCIENTIFIC PRODUCTS

No. 70523

application note

ATR Spectroscopy of Thin Films on Silicon and Metallic Substrates

Figure 1. GATR Ge-ATR Accessory.

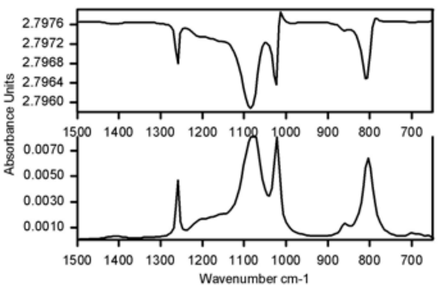

Figure 2. Simulated Spectra of a Monolayer on Si Recorded with P-Polarized Light. Upper Curve: Grazing Angle Specular Reflectance at 75º. Lower Curve: ATR Spectrum at 65º.

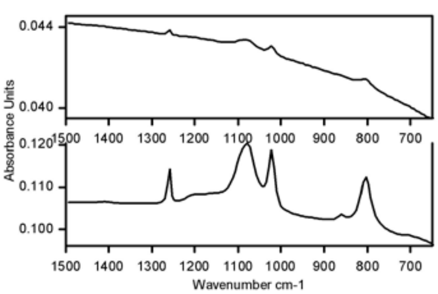

Figure 3. Simulated Spectra of a Monolayer on Au Recorded with P-Polarized Light. Upper Curve: Grazing Angle Specular Reflectance at 75º. Lower Curve: ATR Spectrum at 65º.

Introduction

In recent years, there has been a renewed interest in studying monolayers on silicon and gold substrates by infrared spectroscopy. These materials are ideal substrates. They are chemically inert and optically inactive in the infrared spectral region.

Various approaches have been taken in attempts to examine these types of samples. The thin silicon wafers used as substrates are essentially transparent in the infrared and hence could be examined by transmission. However, the absorbance bands from the monolayer are weak, on the order of the noise of the typical FTIR spectrometer.

Traditionally, grazing angle reflection is the technique of choice for thin films on metal substrates.

Grazing angle reflectance may also seem to be applicable to monolayers on silicon, due to its high refractive index. However, the Brewster's angle for silicon (74°) is close to the grazing angle. So, at grazing angles with p-polarized light, the reflectively is very low and the absorption bands due to sample can be either positive or negative peaks, making interpretation and quantification ambiguous.

Another potential alternative is ATR. To meet the conditions for ATR, a high refractive index crystal and a high angle of incidence must be used. Germanium is the only commonly used ATR material with a sufficiently high refractive index.

Previous ATR analyses of monolayers on silicon with a germanium crystal used A multiple reflection ATR approach[1]. Since the substrate is hard and inflexible, it can be difficult to obtain the intimate contact required between the crystal and sample. In some cases the contact problem has been avoided by depositing the thin films directly onto the ATR element[2,3,4], eliminating the need for a substrate. This, however, is much more costly and time consuming than examining the coated substrates directly.

This paper demonstrates that extraordinary sensitivity can be achieved by using single reflection ATR to analyze monolayers on silicon and metal substrates. A theoretical model is used to explore the advantages of the proposed method. Experimental data illustrate the high sensitivity achieved.

Experimental

To investigate this technique, we examined a silicon wafer and a gold substrate that were coated with organic monolayers. Two types of investigations were carried out: numerical simulations and spectroscopic measurements.

The simulations were done using Harrick Scientific's SOS™ software, which employs the theoretical model described previously[5]. To obtain a set of parameters for the simulation of silicone, a spectrum of silicone was recorded using a 45° single reflection ZnSe ATR accessory, the FastIR™. The data were transferred via JCAMP-DX to the SOS™ software and a set of parameters was chosen to more or less fit the measured spectrum. For the silicon substrate, the electronic contribution to the refractive index was set to 3.45. No additional polarizability parameters were used, since silicon is essentially non-absorbing for the short pathlengths involved. For the gold substrate, the reflectivity was calculated by fitting the plasma wavenumber and damping coefficient to the refractive index at several wavelengths[6-10].

To model a silicone monolayer on silicon, the thickness of silicone was chosen to be 5.0Å and the substrate was selected to be optically thick.

The ATR measurements were carried out using Harrick's GATR™ (see Figure 1). The GATR™ is a grazing angle ATR accessory with a fixed 65° incident angle and a hemispherical Ge crystal. The pressure applicator on the GATR™ features a flexible rubber pad to optimize contact between the sample and the ATR crystal. All spectra were recorded with 32 scans at 8 cm^{-1} resolution.

Two samples were examined. One was an organic monolayer deposited on a silicon wafer, which had been polished on one side. The other was an organic monolayer on a gold-coated glass micro-slide. The samples were analyzed as is, with pressure applied to make contact between the sample and the crystal.

RESULTS AND DISCUSSION

The difficulties in examining monolayers on silicon and metal substrates using conventional methods are clearly illustrated by the simulated spectra.

For both samples, the grazing angle reflectance and ATR spectra with p-polarization were calculated. The grazing angle simulation assumed an incident angle of 75° and the ATR simulation used a 65° incident angle with a germanium ATR element. The resulting spectra are shown in Figures 2 and 3.

In both cases, the band intensities are extremely weak for grazing angle specular reflectance and hence it would

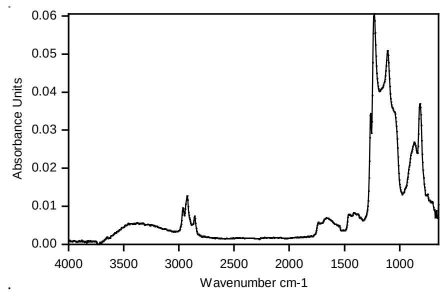

Figure 4. ATR Spectrum of an Organic Monolayer on a Silicon Substrate.

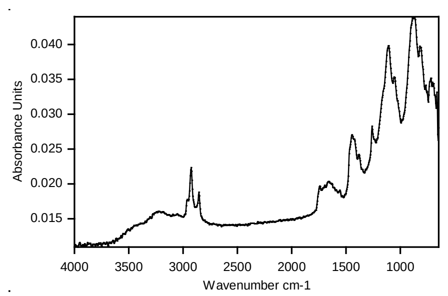

Figure 5. ATR Spectrum of an Organic Monolayer on Gold.

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difficult to resolve the bands from the noise in experimental data. In addition, the bands for the monolayer on silicon are inverted, complicating interpretation.

Figures 4 and 5 show the experimental spectra for a monolayer on silicon and a different monolayer on gold respectively. In both cases, the bands are clearly resolved.

SUMMARY

ATR is an excellent method of obtaining high quality spectra of monolayers on silicon substrate. Using a single reflection Ge ATR crystal at a 65° incident angle with a rubber padded pressure applicator optimizes the spectral sensitivity. The GATR™ makes this a practical method for routine analysis.

ATR also makes the analysis of monolayers on metal substrate routine. The sensitivity achieved by far exceeds the sensitivity obtained by the more commonly used grazing angle specular reflection spectroscopy.

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