



Figure 1. The [DiaMaxATR™](#) diamond ATR accessory.

Investigating Thin Coatings on Glass Using Diamond ATR

INTRODUCTION

Thin coatings on glass are particularly challenging to study using mid-infrared spectroscopy. Generally the samples are deposited or grown on glass slides. Because glass absorbs in the mid-infrared, transmittance and reflectance methods are not effective. ATR can also be problematic, as many of the coatings are too close in refractive index to either the glass substrate or the ATR crystals. Simulations¹ show that the most sensitive ATR experiment for thin films on glass uses a relatively low refractive index ATR crystal as close to critical angle as is reasonable.

Here, we investigate the potential of using a 45° single-reflection diamond ATR to detect coatings and changes on the surface of glass.

EXPERIMENTAL

Harrick's DiaMaxATR™ single-reflection diamond ATR accessory (Figure 1) was used for this study. This accessory was installed in an FTIR spectrometer and purged to minimize water vapor and CO₂. Spectra were collected with 32 scans at 8 cm⁻¹. The background was collected from the clean ATR crystal under ambient conditions. The glass samples were pressed against the ATR crystal with the maximum force allowed by the integral slip-clutch.

Five soda-lime glass samples were examined: fresh glass, corroded glass and three with a ~225 nm layer of silicon oxynitride, each with differing compositions.

¹ Using the SOS™ software.

RESULTS AND DISCUSSION

The resulting spectra from the measurements are shown in Figure 2. The fresh soda-lime glass has a small peak at 3586 cm^{-1} which is likely due to the Si-O-H stretch. It also has a small peak at 1625 cm^{-1} which is likely due to water which also contributes to the broad weak band in the OH stretching region. The bands at 914 and 768 cm^{-1} are due to the Si-O bends and stretches.

All of the other samples have weak bands around 2970 and 2850 cm^{-1} , indicating the presence of hydrocarbons. So they were likely not prepared in clean conditions. These hydrocarbons likely contribute to the non-water bands in the 1776 - 1320 cm^{-1} region due to siloxanes or Si bounded alkenes. These spectra also show a broad band in the 3700 - 2600 cm^{-1} region. While there is a contribution to this band from the O-H stretch, the various shoulders are probably due to Si-O-H at 3586 cm^{-1} in addition to NH and NH_2 at 3500 - 3390 cm^{-1} .

In the fingerprint region, the fresh soda-lime glass has the highest intensity at 914 cm^{-1} , as expected because it has the most Si-O on the surface. The corroded sample has the weakest band here, perhaps indicating a thicker coating on the surface and masking of the underlying glass substrate. The underlying bands here are the 770 cm^{-1} Si-N stretch and the N-H bend at 1033 cm^{-1} . Based on the relative band intensities at 770 cm^{-1} , it is clear that the Si-N concentration is higher for the samples shown by the spectra in green and brown.

The other interesting feature to note is the band shift for the peak at 914 cm^{-1} . All the samples have this band shifted to lower wavenumbers than the fresh glass (blue). For the samples represented by the brown and green spectra, this is likely partly due to broad underlying portion of the Si-H stretch at 770 cm^{-1} . For the other samples, it may be a shift induced by the broad N-H bend at 1033 cm^{-1} . There is, of course, also the possibility that the Si-O is bound to slightly different species inducing the shift.

SUMMARY

As shown here, single reflection diamond ATR spectroscopy can be used for analysis of the oxidation of glass. This points to the possibility of using this method to investigate other coatings on low refractive index substrates.