Analysis of Monolayers on Si and of Neat Powders by Single Reflection ATR

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ATR, being a surface technique, is frequently used for examining very thin films on hard substrates. However, when it comes to examining thin films on Silicon substrates, the inherently high refractive index of the substrate seems to preclude ATR analysis. This paper demonstrates that an extraordinary sensitivity can be achieved by using the ATR technique to analyze monolayers on silicon.

ATR is also frequently used to analyze powders. The advantage of ATR with respect to the more traditional Diffuse Reflectance Spectroscopy is the ability to analyze samples neat. The problem with using standard ATR accessories to analyze powders is that it is somewhat awkward to apply pressure to the sample and to clean up the sample after the analysis. The unusual downward sampling orientation of the Seagull accessory enables a novel sample cup design that makes handling of powdered samples easy.

Discussion of the GA ATR experiment for Si wafers

The theoretical foundations for this technique have been established by Harrick [1] very early on in the development of the ATR as a spectroscopic technique. Harrick developed formulae for ATR analysis of very thin films (film thickness much smaller than the wavelength) where in addition to the ATR element and the thin film there was also a substrate onto which the thin film was deposited. When the formulae are applied specifically to the case of a thin film on silicon wafer with Ge ATR element and the angle of incidence above the critical, the result exhibits extraordinary sensitivity to thin films. The sensitivity arises from sandwiching of the lower refractive index film between the two very high refractive index materials (Ge and Si). Since the normal component of electric field displacement must be continuous through the interface, the electric field inside the film is greatly magnified. This sensitivity enhancement was sized upon by Olsen and Shimura [2,3] who found that for the case of SiO_2 film on Si wafer and 60° angle of incidence the enhancement was over 100 times per reflection over what would be measured in transmission. Olsen and Shimura used multiple reflection ATR in attempt to even further enhance sensitivity. The results, although impressive, fall short of exhibiting enhancement of over 1500 that was predicted by the authors. Olsen and Shimura didn't dwell over the amount of enhancement itself; they were quite content with getting good experimental results. It was thus left to us to guess that the reason why they didn't reach the theoretical enhancement was due to the lack of a high quality contact between the sample and the ATR element. Fig.1 shows the absorbance of a 10 Angstroms thick film on Si substrate taken with p-polarized light on Ge ATR element at 60° angle of incidence. The real part of the refractive index of the film was chosen to be

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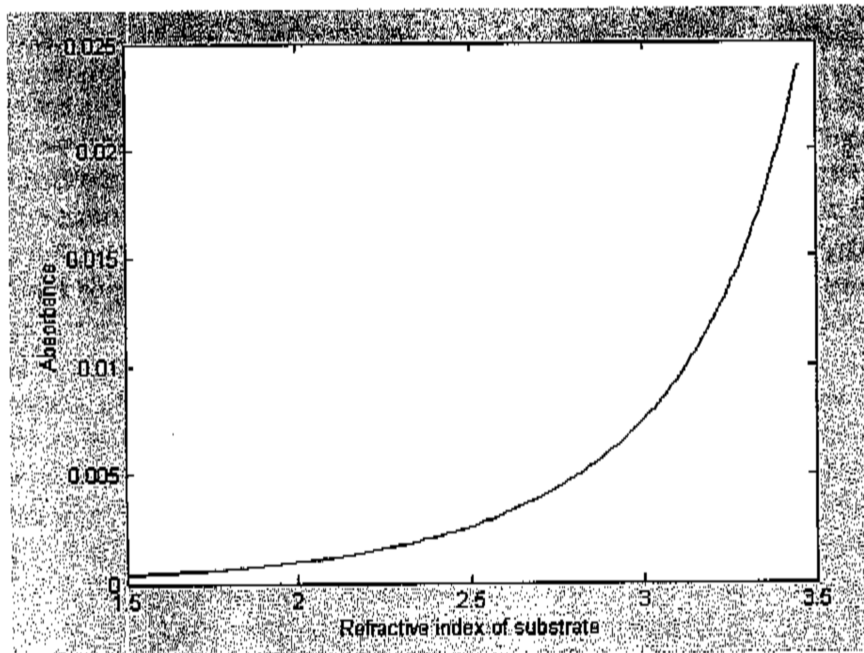

Figure 3. Absorbance of a thin film shown as a function of refractive index of the substrate.

Fig. 3 shows an intriguing dependence of the measured absorbance of the thin film on the refractive index of substrate. Angle of incidence was kept constant at 60° and absorption index of the film at 0.5 . The change in the refractive index of the substrate is between that of the thin film (1.5) and the silicon wafer (3.45). The increase in sensitivity is remarkable. It clearly shows that high refractive index of the substrate is the crucial ingredient leading to the high sensitivity.

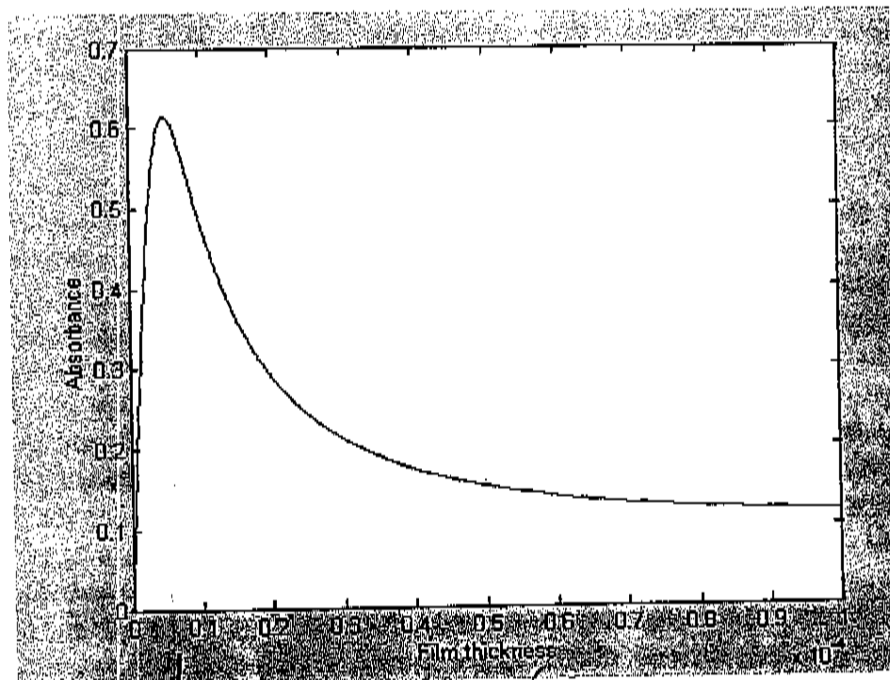

Figure 4. Absorbance Vs film thickness

400 Å

in Cm

1 Å = 10^{-8} cm

400 Å = 400×10^{-8} cm

= .0400 × 10^{-4}

Fig. 4 shows the most interesting feature of the system. The film thickness was let to increase from 10 Angstroms to 1 μm. The measured absorbance of the film first dramatically increases reaching a maximum for film thickness of around 400 Angstroms. After that the absorbance dramatically decreases although more film is being added into the evanescent wave and hence more light could be absorbed. The fact that the absorbance decreases is indicative of the decrease in the strength of the electric field of the evanescent wave, and that decrease in the strength of electric field dominates over the increase in film thickness. If there were no substrate in this case, the increase in film thickness would lead to increase in absorbance. For very thin films (compared to the wavelength of light) the absorbance and film thickness are proportional. As film thickness reaches the penetration depth, the linear relationship turns into saturation, where further increase in film thickness brings no increase in measured absorbance. The absorbance never decreases with increase in film thickness. This is what makes this case very interesting both from the theoretical point of view as well as from the practical point of view. Next we calculated the level of enhancement as a function of film thickness for the case where film is placed onto a silicon substrate Vs the case where no substrate is present. The result is shown in Fig.5.

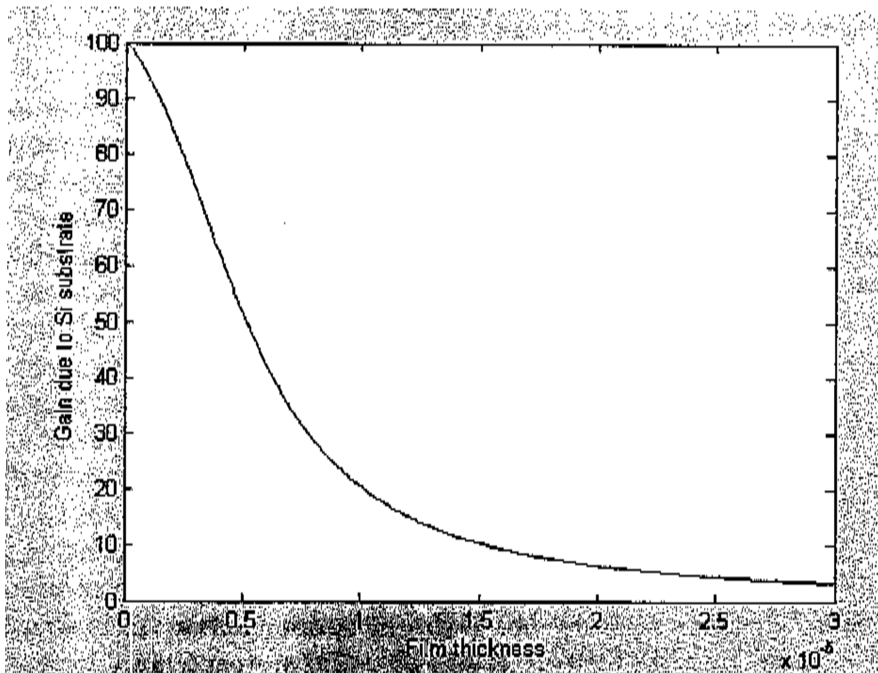

Figure 5. The enhancement of absorbance due to silicon substrate Vs film thickness

Although the absorbance as a function of film thickness exhibited a sharp maximum (Fig. 4), the enhancement in sensitivity is a monotonically decreasing function of film thickness. The enhancement for very thin films is roughly a factor of one hundred. Thus the method is the most sensitive for the thinnest films, just where the sensitivity is most needed.

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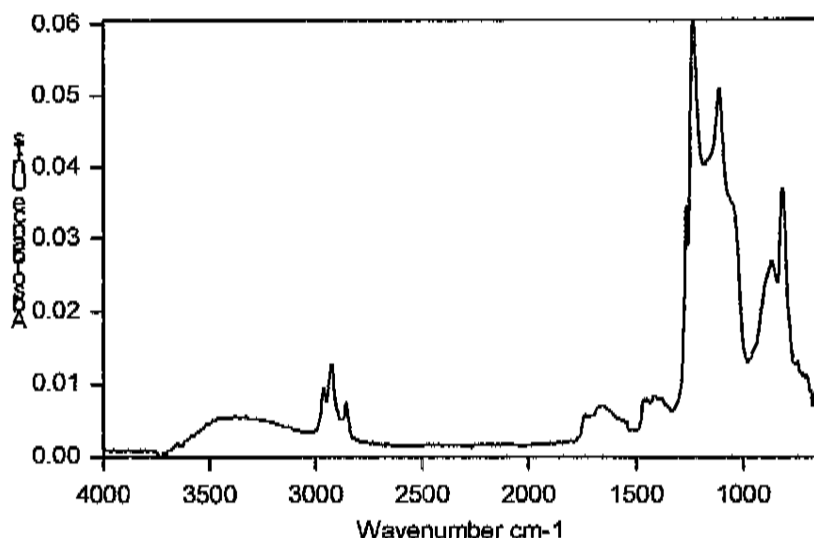

Figure 6. ATR spectrum of an organic monolayer on silicon wafer

Note that experimentally acquired spectrum of monolayer on silicon wafer exhibits extremely strong absorbance levels. The spectrum was recorded at 65° angle of incidence.

It is obvious from the above considerations that 'Grazing Angle ATR' is a highly sensitive technique for analyzing monolayers and very thin films. What remains to be better understood is the physical picture underlying this extraordinary sensitivity. First, the sensitivity is obviously contained in the exact description of the system given by Airy formula and Fresnel Equations [4]. Above graphs were calculated using this exact description. However, the mathematical formalism is not very transparent in elucidating the underlying mechanism. The general statements made in [2] and [3] are not satisfactory. The main argument given for enhanced electric field strength inside the thin film is the continuity of the perpendicular component of the electric field displacement vector. However, the same argument holds for the thin film backed by air instead of silicon. Thus, the explanation does not work. So let us look closely into the mechanism behind the enhancement. Below the critical angle the electromagnetic wave refracts into the film, propagates to film-silicon interface, partially reflects of that interface (some light being refracted into silicon), propagates back to germanium ATR element, partially reflects of the germanium-film interface and so on. Within the film, electric field vectors of all of the partially reflected waves add. Thus the resulting wave is an infinite sum of the contributions from reflected waves. As the reflected portion of the wave is generally only a small fraction of the wave, the total field is usually dominated by the initial refracted wave. In the case of total internal reflection (above the critical angle for germanium-silicon system), the electromagnetic wave beyond the totally internally reflecting interface is evanescent. This means that the wave is propagating parallel to the interface and hence the concept of reflection of the evanescent wave from the film-silicon interface becomes unintuitive. However, each term in the infinite sum still remains meaningful although the interpretation of it as a contribution from a reflected wave becomes dubious. The contributions for the electric field component perpendicular to the interface of all terms are now constructive, hence enormous enhancement.

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Monolayers On Metal Substrates

Next we examine monolayers on metal substrate. Again, we consider reflectance for p-polarized light. Film is assumed to have refractive index 1.50, absorption index 0.5 and thickness 10 Angstroms. Fig. 6 shows comparison between the standard specular reflectance and ATR for angles of incidence between normal and grazing.

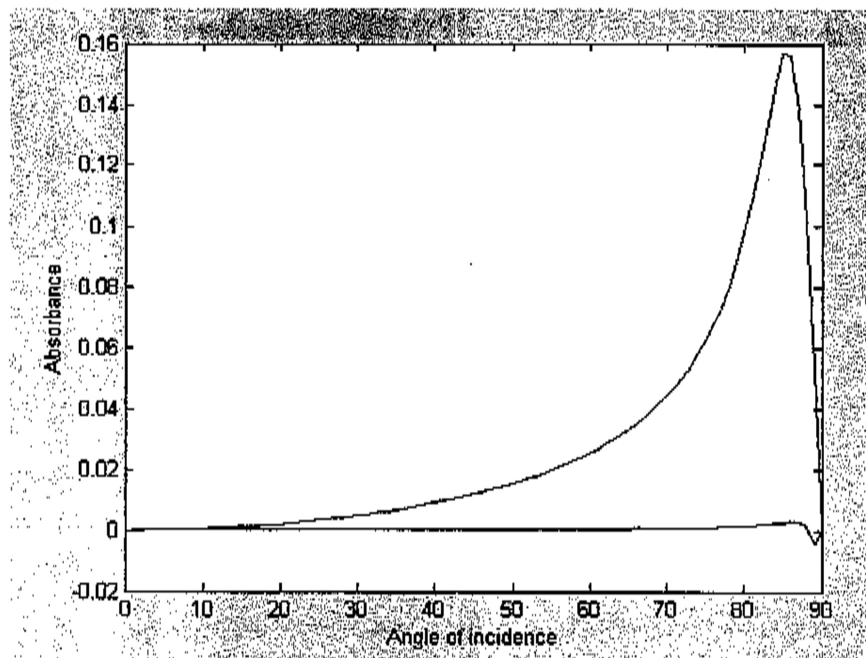

Figure 7. Comparison between the classical grazing angle specular reflectance (lower curve) and grazing angle ATR (upper curve).

As Fig. 7 clearly shows, the sensitivity exhibited by grazing angle ATR is extraordinary. The negative peak in absorbance measured by specular reflection above 85° angle of incidence is due to increase in reflectivity of the metal surface coated with the thin film over that of the bare metal surface. The curves shown in Fig. 7 represent reflectance of the thin film covered surface divided by the reflectance of bare metal under the same conditions.

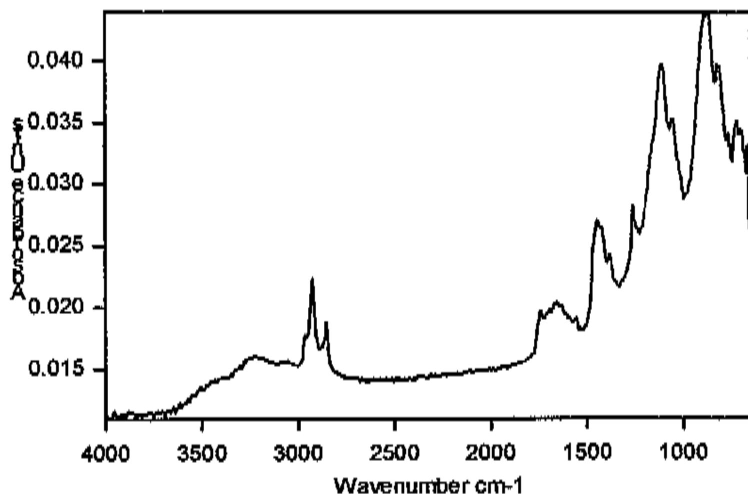

Figure 8. ATR spectrum of an organic monolayer on gold substrate

Fig. 8 shows ATR spectrum of an organic monolayer on gold coated microscope slide. The spectrum was recorded at 65° angle of incidence.

Analyzing Powders by ATR

The next section deals with taking spectra of powders. Spectra of powders are traditionally taken by mixing the sample with KBr or other nonabsorbing powder, and acquiring a diffuse reflection spectrum of the mixture. The spectra thus acquired are usually analyzed after being transformed by Kubelka-Munk function. If the sample is not sufficiently diluted, uniformly mixed or if the specularly reflected component is collected alongside with the diffuse component, the spectra may exhibit spurious bands, band inversions and other artifacts. All the complications of sample preparation, spectral interpretation etc. can be avoided by replacing the diffuse reflection technique with ATR technique. The only problem with that is one of applying the necessary pressure to the sample for the required good contact with ATR element. We describe here a specially constructed sample cup.

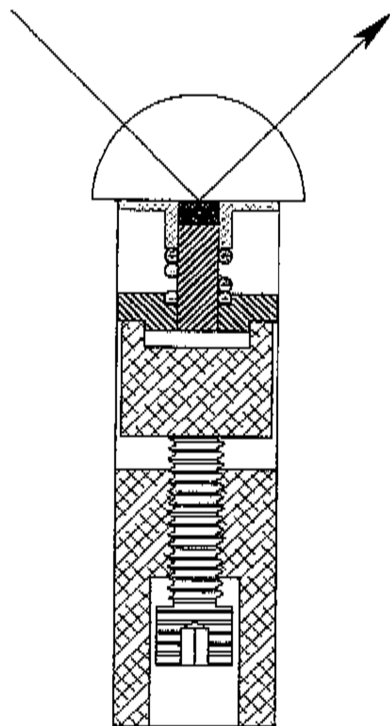

Figure 9 Construction of Powder Sample Cup

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The construction is of the piston and cylinder type. That allows the pressure to be applied through the piston directly to the sample while cylinder part serves to retain the sample. The sampling surface of the ATR element that is oriented in such a way to require sample to be pressed upward against the sampling surface. This orientation is uniquely suited to analysis of powdered sample. Some representative spectra obtained with this sample cup are shown below.

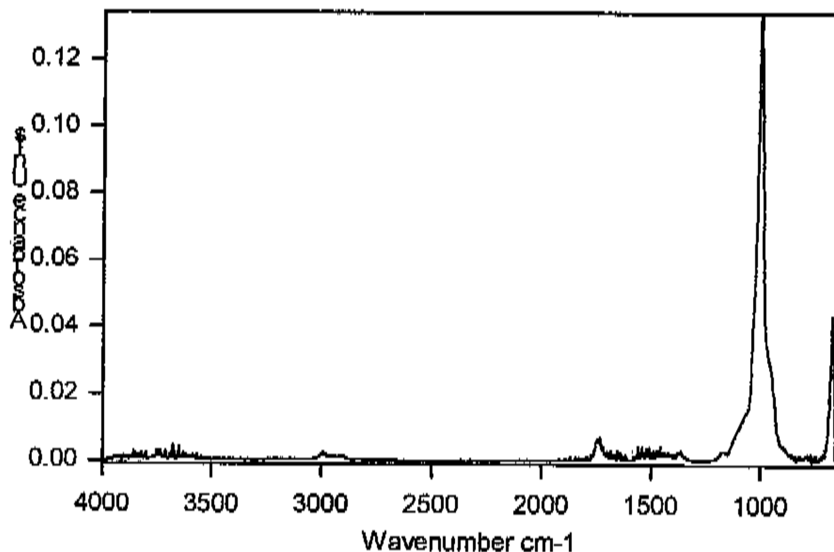

Figure 10. ATR Spectrum of Talcum Powder.

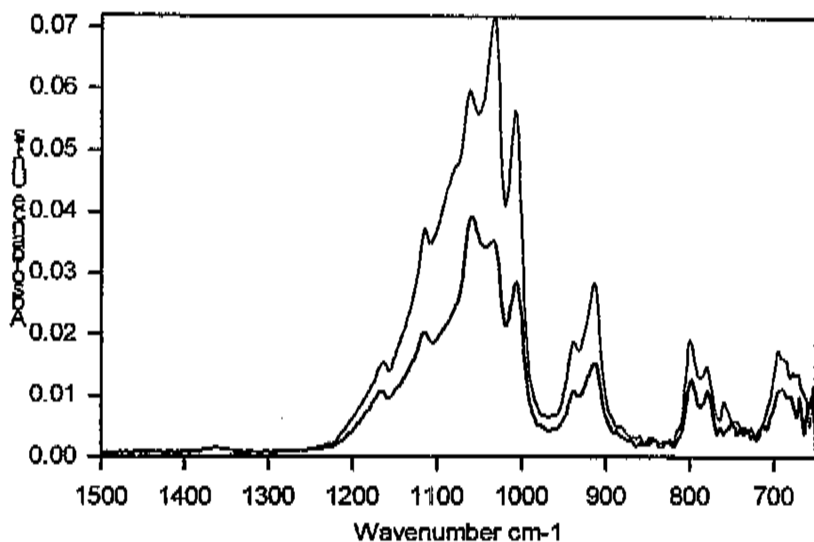

Figure 11. ATR Spectra of Silica Powders. Red: 0-5 um; Blue: 10 um.

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