Analysis of Silicon Surface by Single Reflection ATR

The attenuated total reflectance (ATR) method is widely used for FTIR analysis because the spectra obtained without performing sample pretreatment are comparable to those collected with traditional transmittance measurement of thin films (1μm), the spectral information from the sample surface is also obtained, and finally, the use of a single reflection ATR accessory allows easy analysis of minute objects (<1mm) and rough or curved surfaces which are difficult to perform using multi-reflection ATR accessories.

We introduce here the analysis of a silicon surface as examples of showing the advantage of "good contact" between the sample and the ATR crystal afforded by the single reflection method.

■ Advantage of Single Reflection ATR

There are two types for ATR methods. The multi-reflection type uses a prism which is several centimeters in size to obtain multiple reflections, and the single reflection type uses a smaller prism (1-2mm) so that only a single reflection occurs.

The multi-reflection type uses repeated reflections at the interface of the sample and prism to obtain a large peak, and for samples those contact the total surface of the prism, like liquid samples, multiple reflections type provides substantially larger peaks than the single reflection type does. However, almost all solid samples have a somewhat non-uniform surface, and unless the sample is a liquid or is extremely soft like raw rubber, it will not intimately contact the entire surface of the prism. In addition, even if the sample appears to have a mirror-like surface, as with silicon wafers and glass substrates, any scratches or cruds on the surface of the prism or sample will result in noticeably poor contact. Further, if strong pressure is applied to achieve better contact, the load may be applied unevenly on the prism, possible causing either the sample or the prism to break.

On the other hand, since the single reflection type uses a small prism, even if there are small amounts of crud on the surface of the sample, those areas can be avoided to achieve good contact. In addition, since it is unlikely that the load will be applied to only a portion of the prism, more pressure can be applied than in the multi-reflection type.

Fig.1 shows the contact images of the multi-reflection ATR and the single reflection ATR.

Fig.2 shows the results of measurement of a silicon wafer by multi-reflection ATR (ATR-8000) and single reflection ATR (MIRacle). The average incidence angle was 45° and Ge prism was used for each measurement. The MIRacle ATR, utilizing only a single reflection, achieved larger peaks.

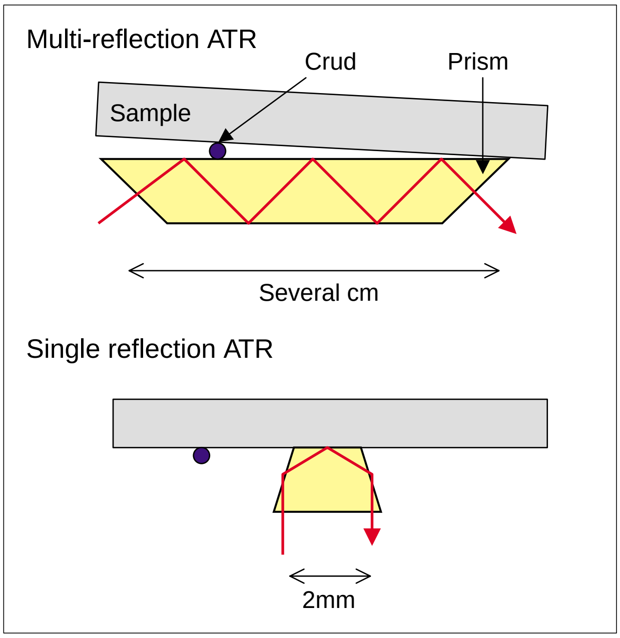

Fig.1 Contact Image of Multi-Reflection ATR & Single Reflection ATR

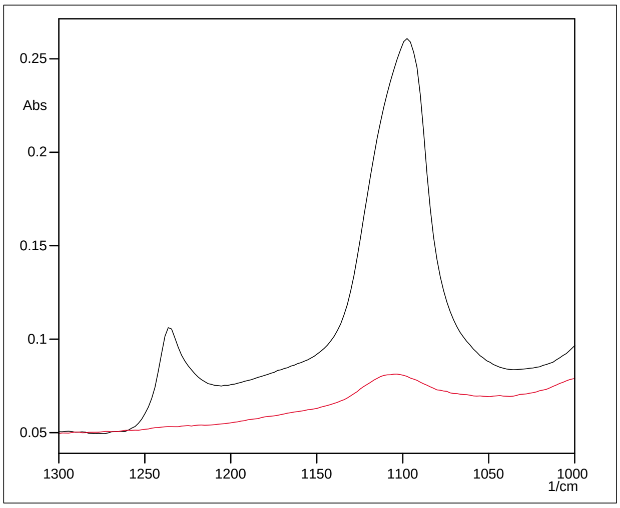

Fig.2 ATR Spectra of Silicon Wafer
Red: Multi-reflection ATR Method,
Black: Single Reflection ATR Method

Table 1 Analytical Conditions

Resolution	: $4cm^{-1}$
Accumulation	: 40
Detector	: DLATGS

■ SiO_2 Thin Film on a Si Wafer

Fig.3 presents the results of the single reflection ATR measurement (with Ge prism) of a silicon wafer and a SiO_2 coated (0.4nm) silicon wafer, and the difference spectrum of the two. It is evident that the peaks of the SiO_2 film at $1200cm^{-1}$ and $1100\text{-}1000cm^{-1}$ are distinguishable despite the extremely thin nature of the film.

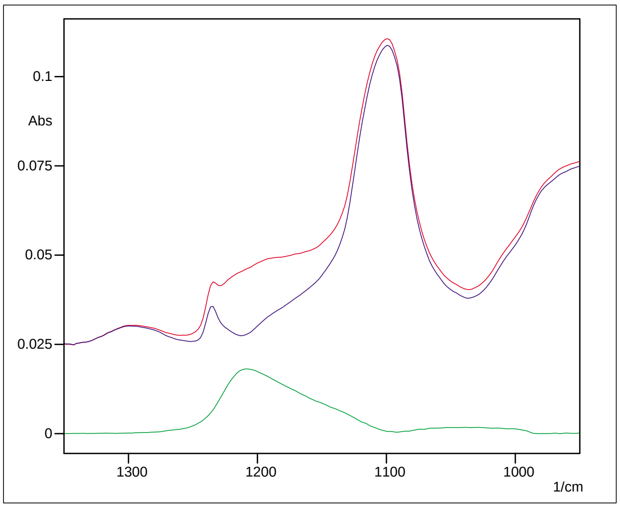

Fig.3 ATR Spectra of SiO_2 Thin Film (0.4 nm) on Si Wafer. Red: SiO_2 Film on Si Wafer, Blue: Si Wafer, Green: Difference Spectrum

■ Analysis of Hydrogen-Terminated Silicon Surface

A SiO_2 thin film on a Si wafer can be removed by etching the surface with hydrofluoric acid. Etching causes hydrogen-termination on the surface of the silicon, in which the surface groups Si-H, Si-H_2, and Si-H_3 are formed. In addition, the resultant ratios of the three functionalities is directly dependent on the smoothness of the silicon surface involved, with the Si-H termination becoming dominant as the smoothness increases.

Fig.4 shows the spectra obtained from the single reflection ATR measurement (with Ge prism) of two types of silicon wafers (Upper: Si(111), lower: Si(100)) following etching with a 1% solution of hydrofluoric acid (aq.). The difference in smoothness is clearly reflected in the band ratios of the spectra. It should be noted that the silicon surface smoothness also depends on a function of the etching conditions. The etching conditions used here to remove the SiO_2 film effect the Si wafer as evident by the strong Si-H_2 peak in the Si(111) spectrum. When the Si wafer surface is made smoother, the Si-H band is a stronger and sharper peak (Fig.5).

Fig.5 is the spectral data collected by Mr. Tokuda Norio using a FTIR-8400 and published here with the permission of the Yamabe Hasunuma Research Laboratory of the Tsukuba University Graduate School of Pure and Applied Sciences.

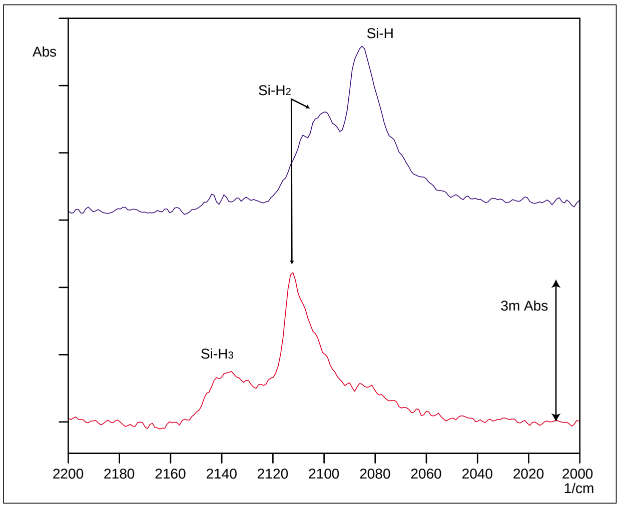

Fig.4 ATR Spectra of Hydrogen-Terminated Silicon Surface Blue:Si (111), Red:Si (100)

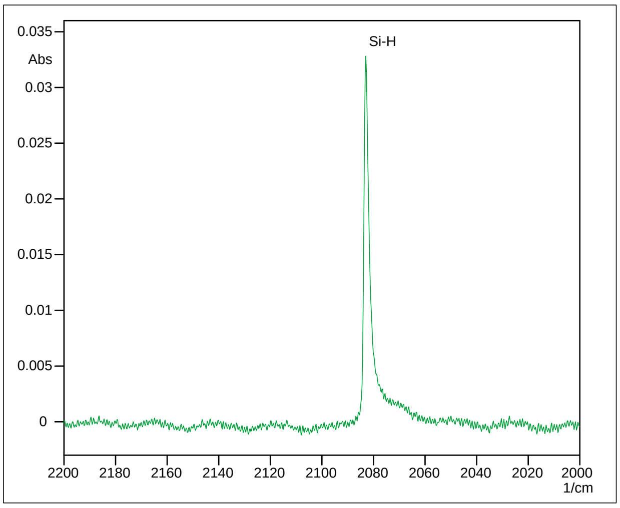

Fig.5 ATR Spectrum of Hydrogen-Terminated Silicon Surface

Table 2 Analytical Conditions

Resolution	: $2cm^{-1}$(Fig.4), 0.85 cm^{-1}(Fig.5)
Accumulation	: 100(Fig.4), 50(Fig.5)
Detector	: DLATGS

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