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No. 21157

An FTIR Comparison of Grazing Angle Ge ATR, Transmission and Coupled Multiple Reflection ATR for Studying Coated Si Wafers

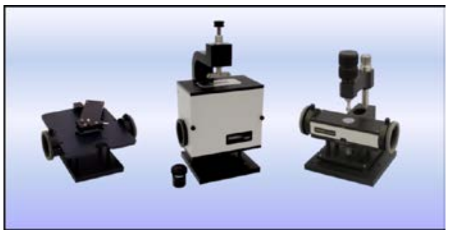

Figure 1. Accessories for each technique: Four-Pass Transmission (left), WalfIR™ (middle), VariGATR™ (right).

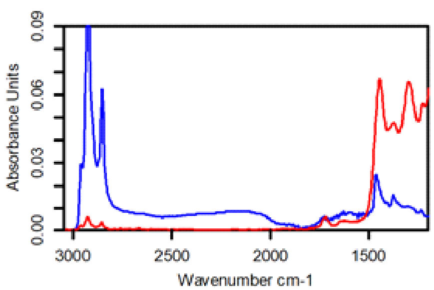

Figure 2. Transmission spectra for each sample, where Sample 1 (red) is a DSP single-side coated wafer with an unknown SAM coatings, and sample 2 (blue) is a DSP single side coated wafer with a toluene residue atop a 1000 Å thick Al coating.

Introduction

ATR spectroscopy is a surface-sensitive infrared sampling method and is frequently used for analyzing thin films and monolayers on surfaces. This is particularly important in the semiconductor, electronic and optical industries.

A number of approaches have been used to examine coatings on semiconductor substrates like Ge and Si, and on metallic substrates, like gold and aluminum. For reflective substrates, these methods include grazing angle specular reflectance and grazing angle Ge-ATR, where the former is a non-contact method and the latter requires contact between the coated surface and the ATR crystal. For transmissive substrates, the methods commonly used include making ATR crystals from coated wafers, pressing a coated wafer against an ATR crystal under above-critical angle conditions and transmission.

This work compares three methods used to examine double-side polished coated wafers: grazing angle Ge-ATR spectroscopy, transmission and an ATR technique where the infrared is coupled into the wafer. In addition to this comparison, an overview of the advantages and disadvantages of the various methods used for infrared analysis of thin coatings on single side polished wafers and coatings on metals will be given.

Experimental

All spectra were collected in a commercial FT-IR spectrometer at 8 cm^{-1} resolution and 64 scans using a DTGS detector. To investigate each technique, three Si wafers were examined. The three samples are as follows: one double-side polished (DSP), 0.770-mm thick single-side coated wafer with an unknown SAM; one DSP, 0.50-mm thick single side coated wafer with a toluene residue atop 1000 Å thick Al coating (EMF); and one single-side polished (SSP) 0.770-mm thick wafer with an unknown SAM. Toluene residue was attained by using a pipette to disperse toluene (Alfa Aesar, CAS# 108-88-3) on one side of the wafer and then letting it evaporate before collecting data. Data was then baseline corrected for the toluene coated sample.

For the transmission method, a four-pass transmission accessory was used to collect spectra of the samples. It has a

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75° incident angle and a built-in polarizer which minimizes interference fringes. Data was adjusted from four pass to single pass transmission by dividing the absorbance by a factor of 4.

For the grazing angle ATR measurements the VariGATR™, a variable grazing-angle accessory with a mounted germanium crystal, was used at a 65° incident angle. This technique requires contact between the Ge crystal and the coated surface of the Si wafer. This contact was attained by compressing each sample against the crystal using the built-in slip-clutch.

For the ATR technique where the infrared radiation is coupled into the wafer, the WafIR™ was used. The WafIR is a multiple reflection accessory which uses the Si wafer as the ATR crystal, coupling the light into and out of the wafer using two 45° prisms. It gives 33 reflections from the coated surface for a 0.770-mm thick silicon wafer and 51 reflections of the coated surface of a 0.50-mm thick Si wafer. The WafIR is designed to limit the contact area on the sample and to apply contact to the coating outside the sampled area. Force is applied using the 112 in-oz (0.79 N-m) slip-clutch.

Results and Discussion

Figure 2 displays the spectra of all the DSP single side coated wafer samples measured withthe four-pass transmission accessory. All of the samples have peaks at 2922 cm^{-1} and 2852 cm^{-1} as a result of the C-H stretches. The DSP single-side coated (non-metallic coating) wafer sample for transmission show weak band intensities.

Figure 3 compares the spectra of sample 1 measured with Ge-ATR and internal-wafer ATR. There are peaks at 2922 and 2852 cm^{-1} for both methods from the C-H stretches. Note the relatively strong intensity of the C-H stretches with the internal-wafer ATR technique. The internal-wafer ATR spectrum shows these band intensities to be about 10 times greater than Ge-ATR. This sensitivity is due to the infrared energy coupled into the wafer, resulting in multiple bounces within the wafer and greater interaction of the evanescent wave with the sample.

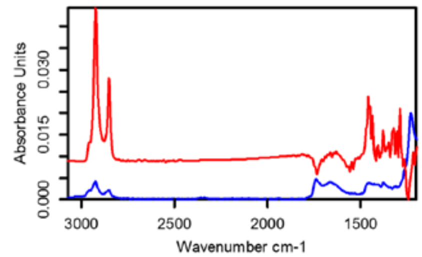

Figure 3. Internal-wafer ATR (red) vs Ge-ATR (blue) spectra of a DSP single-side coated wafer with an unknown SAM coating.

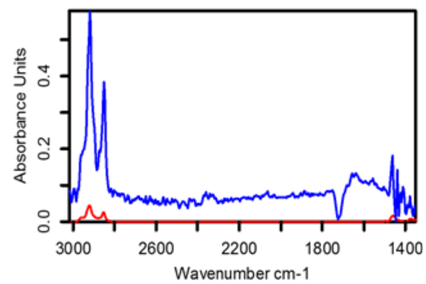

Figure 4: Internal-wafer ATR (red) vs Ge-ATR (blue) spectra of a DSP single side coated wafer with a toluene residue atop a 1000 Å thick Al coating.

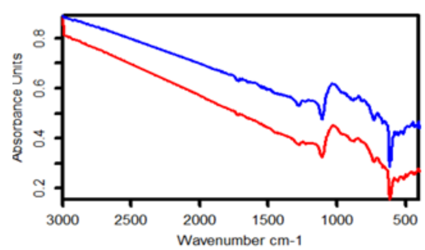

Figure 5. Transmission spectra for a SSP single-side coated wafer (non-metallic coating), where polished side up is red and polished side down is blue.

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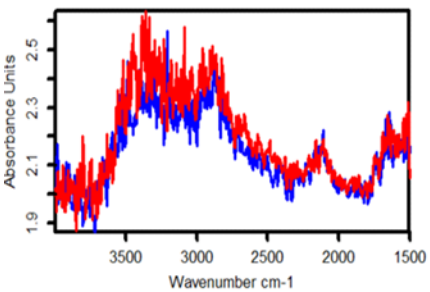

Figure 6. Internal-wafer ATR spectra of a SSP single-side coated wafer (non-metallic coating), where polished side up is red and polished side down is blue.

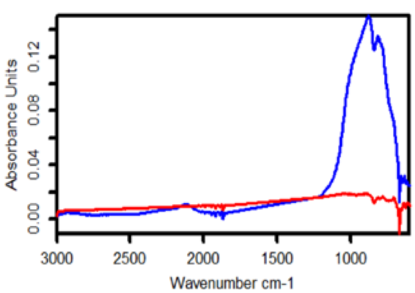

Figure 7. Ge-ATR spectra of a SSP single-side coated wafer (non-metallic coating), where polished side up is red and polished side down is blue.

Figure 4 displays the spectra of toluene residue on a single side 1000 Å thick aluminum coated DSP Si wafer measured using Ge-ATR and internal-wafer ATR. The transmission spectrum for this sample is shown in Figure 2 for comparison. For the toluene residue, transmission is more sensitive than internal-wafer ATR with peak intensities that are approximately double that of the internal-wafer ATR.

Yet, Ge-ATR is clearly more sensitive with peak intensities about twenty times greater than internal-wafer ATR. When comparing all three methods, Ge-ATR has a greater sensitivity overall, which demonstrates that the best method depends on the type of sample. For DSP single-side coated wafers with a metallic coating, grazing angle Ge-ATR is advantageous.

For further investigation, unlike the other samples, which are all DSP single-side coated wafers, a SSP single-side coated wafer with a non-metallic coating was examined. A spectrum was measured of the wafer placed polished side up and polished side down for each method for comparison. For transmission, (Figure 5) it was difficult to examine the sample spectra because it produced a sloping baseline, likely attributed to scattering. Scattering causes even greater difficulties in analyzing this sample using internal-wafer ATR (Figure 6), resulting in spectra with a lot of noise regardless of wafer orientation.

However, (Figure 7) for the Ge-ATR method, the polished side down spectrum shows absorption in the 800-900 cm^{-1} spectral region. No absorption is observed for the polished side up measurement due to the poor contact between the unpolished surface of the wafer and the ATR crystal.

Conclusion

In conclusion, the effectiveness of the internal wafer ATR and the Ge-ATR method depends on the wafer, its size and its surface finish. The internal wafer ATR method produced stronger band intensities in comparison to the grazing angle Ge-ATR technique and the transmission measurements for the DSP single-side coated wafer with non-metallic coating. However, Ge-ATR was the most sensitive in examining the DSP single-side coated Si wafer with an optically thick 1000 Å metallic coating as well as the SSP single-side coated Si wafer. Transmission was the weakest method overall for coated Si wafers.

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Additional work is in progress to see if the internal-ATR method retains polarization sufficiently to study the orientation of species on the surface of the wafers and to compare the sensitivity to that of grazing angle Ge-ATR. Further work will also be done on a metallic coated SSP single side coated wafer, which would be theoretically expected to have similar results as a SSP non-metallic single side coated wafer.

Method	**Accessory (sample size, mm)**	**Wavelength Range (cm^{-1})**	**DSP wafers with single side non-metal coatings**	**DSP wafers with single-side metal coatings**	**SSP wafers with single-side metal or non-metal coatings**
Transmission	Four-Pass Transmission Accessory (50 x 13 to 152 dia.)	9500-400	Weak absorbance	Weak absorbance	Negligible
Grazing angle Ge-ATR	VariGATR (203.2 dia.)	5000-650	Weak absorbance	Strong absorbance	Strong absorbance
Internal-wafer ATR	WafIR (52 x 10 to 203.2 dia.)	9500-1500	Strong absorbance	Weak absorbance	Negligible

Table 1. Comparison of the techniques.

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