Optimization of Grazing Angle Attenuated Total Reflection for the Analysis of Monomolecular Layers on Silicon

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Introduction

Interest in the analysis of monomolecular layers on silicon has grown significantly with the development efforts for molecular electronic devices.[1,2] The need now exists to probe layers a few nanometers in thickness reliably and reproducibly. Traditional FT-IR sampling techniques such as transmission or ATR typically measure samples or coatings on samples where the thickness is 3 orders of magnitude greater. Grazing angle reflection techniques have been used successfully to measure monomolecular layers on reflective substrates.[3] However, in the case where silicon is the substrate, the reflection spectrum contains the signature of the base material in addition to the monolayer and resolving the distinctive features of the surface film becomes difficult. As early as 1966, Harrick saw the need for the analysis of thin films on another substrate by ATR and provided detailed theoretical description of the phenomena.[4,5] Harrick's publications further described equations for calculation of effective thickness of very thin films on a base layer measured at parallel and perpendicular polarization. Later Olsen and Shimura proposed an ATR method for the analysis of thin layers on silicon at 60 degrees using a germanium (Ge) crystal and proposed a theoretical absorbance amplification of 3 orders of magnitude relative to traditional measurements[6]. Recently Milosevic, et al. further described a method of grazing angle single reflection ATR analysis using 60 and 65 degree Ge crystals for organic monolayers on silicon[7]. Lummerstorfer and Hoffmann have published a detailed comparison of experimental and calculated absorbance for octadecylsiloxane (ODS) on Si by ATR and by grazing angle specular reflectance[8,9]. This publication describes theoretical detail for the enhancement in sensitivity relative to traditional ATR sampling of bulk materials and provided examples of spectral data for the analysis of organic monolayers on silicon using this optical configuration.

Efforts by the authors to reproduce these measurements has been successful and this has led to the current effort to detail an optimization of the configuration of a grazing angle ATR accessory for the FT-IR analysis of monomolecular layers on silicon.

Experimental

All spectral measurements were done using the VeeMAX II specular reflectance accessory equipped with a single reflection ATR crystal and a high pressure clamp.[10,11] Pressure studies were performed using the digital high pressure clamp enabling a characterization of force applied to the sample. The pressure clamp was fitted with a 7.8 mm diameter swivel pressure tip. ATR crystals used were germanium (Ge) with 45, 60 and 65 degrees face angles and the VeeMAX II angle of incidence was selected by adjustment of the dial to the desired value. Effective angle of incidence for ATR measurements was calculated using PIKECalc software from crystal face angle and accessory set angle.[12] The sample interface of the ATR crystals used in these measurements is 20 mm in diameter and the sample is placed face-down upon the crystal and force is applied via the pressure clamp. Measurements were made using a zinc selenide (ZnSe) polarizer (PIKE Technologies) installed within the VeeMAX II accessory.

FT-IR data collection was done at 4 cm-1 spectral resolution using a deuterated, L-alanine doped triglycine sulfate (DLaTGS) detector, KBr beamsplitter, J-stop of 6 mm and globar mid-IR source. Background and sample spectra were measured using 4 minute data collection time. The FT-IR spectrometer was sealed and desiccated using KBr windows within its sample compartment. Purge tubes of the VeeMAX II with ATR were friction fit to the side walls of the FT-IR sample compartment.

Monolayer on silicon samples were of 2 types. The first was a functional organic monolayer on silicon, approximately 2 cm x 2 cm and 0.4 mm thick. The second sample type is a thin layer (50 nanometers) of hafnium oxide (HfO2) on silicon, of about the same size.

Results and Discussion

It is well known in ATR analysis that intimate contact is required between the sample and ATR crystal. In the case of a solid sample such as silicon, where sample deformation is not possible due to hardness, any surface contamination on the ATR crystal or sample will likely prevent the collection or minimize reproducibility of the spectrum. This problem is overcome by first swabbing the ATR crystal with 70% isopropanol in water using a cotton tipped swab and then placing a piece of lens tissue over the ATR crystal (Universal Photonics, Inc., Type 1, Class 1, 3 cm x 10 cm in size). Now we place the monolayer on silicon sample face down over the lens tissue. We apply light pressure onto the back side of the silicon and pull the lens tissue from its placement, while the sample remains in place and then comes into contact with the ATR crystal when the lens tissue is fully extracted. Now the silicon sample and ATR crystal are free of any lint or debris and then maximum pressure is applied to the sample.

We studied the effect of pressure upon the absorbance achieved in this analysis. Figure 1 shows the spectrum of the functional organic monolayer on silicon. We mea-

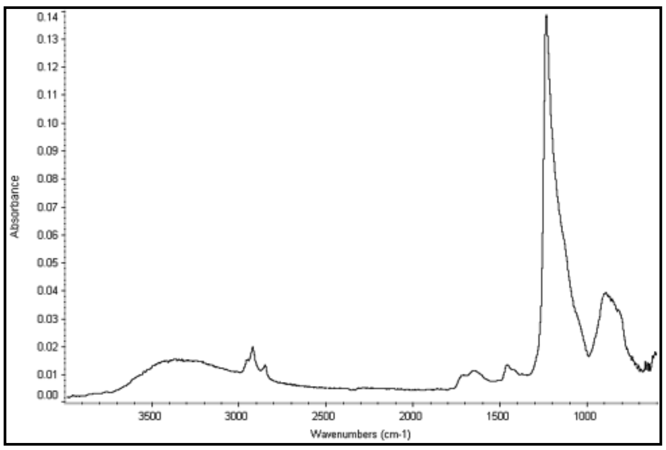

Figure 1. Grazing angle ATR spectrum of functional organic monolayer on silicon

sured the corrected absorbance of the IR band at 1209 cm-1 relative to force applied and found an increase in absorbance with force to about 35 pounds as shown in Figure 2. Increased force to 40 pounds provided no significant increase in absorbance. From these results it is clear that an excess of 35 pounds force is required upon the 7.8 mm pressure tip to achieve a reproducible sample absorbance. For the remainder of the analysis we used maximum set force of the pressure clamp – 40 pounds which is 540 pounds per square inch (psi).

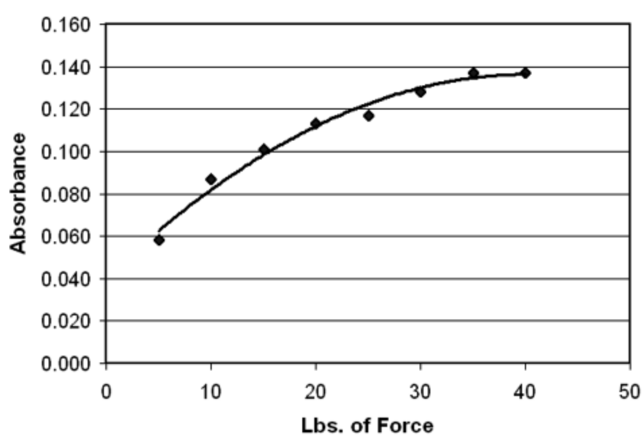

Figure 2. Sample absorbance vs. pounds of force for functional organic monolayer on silicon

For the case of very thin film samples on a substrate where the film thickness is much less than the ATR depth of penetration, Harrick proposes that the critical angle (θ_c) is defined by the inverse sine of the ratio of refractive index of the ATR crystal (n_1) and the substrate (n_3) shown in Eg. 1.[5] Therefore in the case of silicon as our substrate, we are practically limited to Ge as an ATR crystal and the critical angle calcuated by Eq. 1 is 58.5 degrees.

$$\theta_c = \sin^{-1}\left(n_{31}\right) \quad (1)$$

Published use of grazing angle ATR for the analysis of monomolecular layers on silicon have reported using incident angles of 60 and 65 degrees; however we have not found references to the experimental optimization of the ATR angle of incidence for this measurement.

For this study we measured ATR / FT-IR spectra of the functional organic monolayer on silicon at 55, 58.5, 60, 62, 63.5 and 65 degrees angle of incidence using parallel (p) polarization and calculated the corrected intensity of the 1209 cm-1 absorbance band. The results of these measurements are shown in Fig. 3.

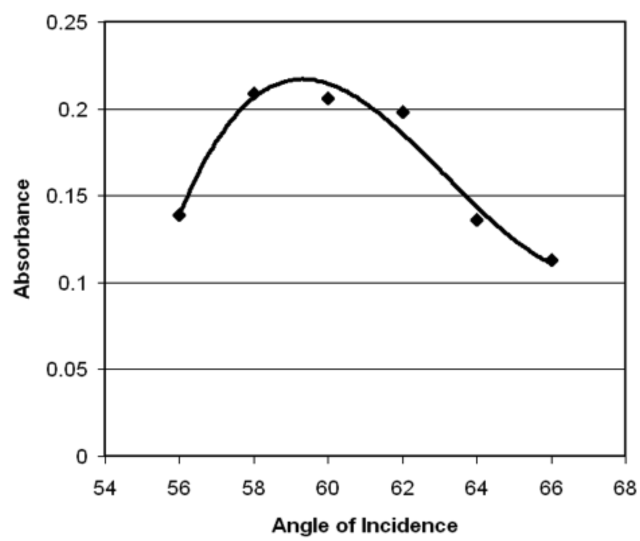

Figure 3. Absorbance of functional organic monolayer on Si vs. ATR incident angle

The same experiment was done using the HfO2 thin layer on silicon sample and the result was similar to that shown in Fig. 3. For the HfO2 thin layer on silicon sample the band at 619 cm-1 was used for the absorbance measurement and the spectrum is shown in Fig 4. The maximum ATR / FT-IR absorbance for both samples occurs at about 59.5 degrees angle of incidence. Harrick's equation (Eq. 2) for p-polarized effective thickness of a very thin film using refractive indices of 4.0 for Ge as the ATR crystal and 3.41 for Si as the substrate predicts an increase as the angle of incidence decreases. Therefore we would like to choose the lowest ATR angle of incidence without exceeding the critical angle.

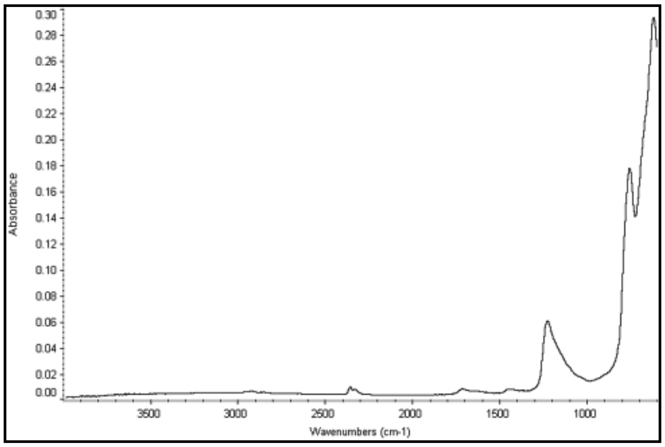

Figure 4. *HfO_2 thin layer on Si by ATR / FT-IR*

$$d_{e\parallel} = \frac{4n_{21} d \cos\theta \left[\left(1 + n_{32}{}^{4}\right) \sin^2\theta - n_{31}{}^{2} \right]}{\left(1 - n_{31}{}^{2}\right) \left[\left(1 + n_{31}{}^{2}\right) \sin^2\theta - n_{31}{}^{2} \right]} \quad (2)$$

It is interesting to note that the measured optimum angle of incidence observed for these samples is just above the critical angle we calculate in Eq. 1. Measured absorbance values at 60 degrees are found to be about 80% greater than data collected at 65 degrees angle of incidence.

Harrick's equations for effective thickness near the critical angle predicts that when the result of $n_{32}{}^{4} / n_{31}{}^{2}$ is greater than unity that parallel polarization will provide increased thin film absorbance vs. that for perpendicular polarization. In the case of the functional organic monolayer (refractive index of 1.5) on silicon with Ge as the ATR crystal this result is 36.7 so we would expect parallel polarization to be the favorable sampling condition.

The functional organic monolayer on silicon sample was measured using the VeeMAX II with Ge ATR crystal at 60 degrees angle of incidence using parallel, perpendicular, and no polarization. The corrected band absorbencies at 1209 cm-1 were found to be 0.063, 0.0, and 0.009 respectively. Parallel polarization is clearly advantageous vs. no polarization with its 7x factor of absorbance improvement even with the expected 50% attenuation of throughput due to the polarizer.

Conclusions

In this application note we have found optimized sampling conditions for the grazing angle ATR / FT-IR analysis of monomolecular layers on silicon. When the ATR crystal surface is cleaned with solvent and the interface between the ATR crystal and monolayer are cleaned using a lens tissue wiping technique an intimate contact is achieved for ATR analysis. Application of 540 pounds per square inch of pressure to the sample generates consistent absorbance results. An optimum angle of incidence for the analysis of monomolecular layers on silicon by grazing angle ATR using a Ge crystal was found to be 60 degrees. And finally it was found that the use of parallel polarization is essential for optimized absorbance of the monomolecular layer on silicon.

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References

1. Brillouet, M., CLEFS CEA, Vol. 52, Summer, 31, (2005).
2. M. Modreanu, J. Sancho-Parramon, D. O'Connell, J. Justice, O. Durrand, B. Servet, Mat. Sci. and Eng. B 118 (2005).
3. R. J. Greenler, J. Chem. Phys., 44, 10 (1966).
4. N. J. Harrick and F. K. duPre, Appl. Opt. 5, 1739 (1966).
5. N. J. Harrick, Internal Reflection Spectroscopy (John Wiley and Sons, New York, 1967).
6. J. E. Olsen and F. Shimura, Appl. Phys. Lett. 53, 1934 (1988).
7. M. Milosevic, S. L. Berets, and A. Y. Fadeev, Appl. Spectrosc. 57, 724 (2003).
8. T. Lummerstorfer and H. Hoffmann, Langmuir, 20, 6542-6545 (2004).
9. T. Lummerstorfer, J. Kattner, H. Hoffmann, Anal. Bioanal. Chem. 388 (1), 55 (2007).
10. Philip R. Brierley, U.S. Patent 5,106,196.
11. PIKE Technologies, VeeMAX with ATR, Product Data Sheet, www.piketech.com.
12. PIKE Technologies, PIKECalc Software, Product Data Sheet, www.piketech.com.