

THE RELATIONSHIP BETWEEN POLARIZATION AND SENSITIVITY FOR GRAZING ANGLE ATR STUDIES OF THIN COATINGS ON SILICON

INTRODUCTION

There is much interest in examining thin films or monolayers deposited on silicon substrates, particularly in the electronics and semiconductor industries. Since these coatings are so tricky to detect by infrared spectroscopy, most of the work in this area has to do with identification or confirmation of the species deposited on the surface. The development of more sensitive detection methods, like 65° single-reflection Ge-ATR, has spurred investigations into the orientation of these monolayer coatings on Si by using polarized incident radiation. The interaction between polarized light and oriented surface species in ATR is commonly used, so applying this well-known method to 65° Ge-ATR is an obvious extension.

However, little is known in practice about the effect of polarization on the sensitivity enhancement. A better understanding of this phenomenon is vital to optimizing the experimental conditions and interpreting the results obtained. With this in mind, this application note explores the effect of polarization on the sensitivity enhancement for 65° single-reflection Ge-ATR. Both

theoretical and experimental considerations are discussed.

THEORY

The theoretical foundation of ATR was developed by Harrick and duPre^{1, 2}. They provided formulae for ATR analysis of very thin, weakly absorbing films deposited on a substrate, where the film thickness is much smaller than the wavelength. When these formulae are applied to a thin film on a silicon substrate, using a Ge ATR crystal and an angle of incidence above critical, the result exhibits extraordinary sensitivity to thin films^{3, 4, 5}.

The expression for the reflectivity of a thin film between two media^{6,7} is:

$$\rho^\mu = \frac{r_{12}^\mu + r_{23}^\mu e^{4\pi i k d \sqrt{n_2^2 - n_1^2 \sin^2 \theta}}}{1 + r_{12}^\mu r_{23}^\mu e^{4\pi i k d \sqrt{n_2^2 - n_1^2 \sin^2 \theta}}}$$

where the index μ indicates polarization of incident light, r_{12}^μ

and r_{23}^μ are Fresnel amplitude coefficients⁶ for the interface between media (1 and 3) and the film (layer 2), k is the wavenumber ($k = 1/\lambda$) and θ is the incident angle. The refractive indices of the media are complex, permitting this to be applied to both absorbing and non-absorbing media. The above

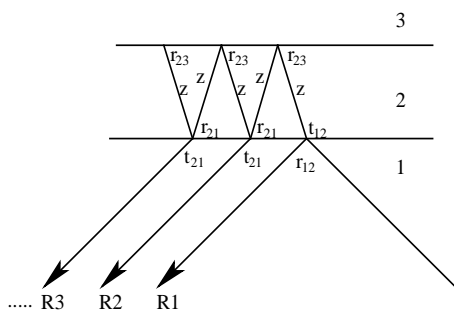


Figure 1. Multiple reflections in the sample layer.



Figure 2. The GATR [Ge-ATR Accessory](#).

application note

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expression is the ratio of reflected and incident electric field amplitudes and it describes the magnitude of the reflected electric field in addition to the phase shift of the reflected field with respect to the incident field. The square of the absolute value of the result of this is the theoretical quantity comparable to the measured reflectance.

When a thin film is sandwiched between a germanium ATR crystal (n_1) and a silicon wafer (n_3), below the critical angle, the electromagnetic wave refracts into the film, propagates to film-silicon interface, partially reflects from that interface (some light is refracted into the silicon), propagates back to germanium ATR element, partially reflects from the germanium-film interface and so on (see Figure 1). Within the film, electric field vectors of all of the partially reflected waves add. The resulting electric field is an infinite sum of the contributions from all of the reflected waves.

The above equation can be expanded using a Taylor series, taking advantage of the identities: $r_{n,n+1} + t_{n,n+1} = 1$ and $r_{n,n+1} = -r_{n+1,n}$. Omitting the polarization index μ and introducing the shorthand

$$z = e^{2\pi i k d \sqrt{n_2^2 - n_1^2 \sin^2 \theta}}$$

gives:

$$\rho = \frac{r_{12} + r_{23}z^2}{1 + r_{12}r_{23}z^2} = r_{12} + t_{12}t_{21}z(zr_{23}) + t_{12}t_{21}z(zr_{23})^2(zr_{21}) + t_{12}t_{21}z(zr_{23})^3(zr_{21})^2 + \dots$$

The terms in the above sum can be related to the components of reflected wave in a direct one-to-one fashion. The first term is just the reflection coefficient of the interface between materials 1 and 2, corresponding to R1 in Figure 1. The second term corresponds to the ray R2 in Figure 1 and all the following terms correspond to the subsequent reflections. Thus there is a strict geometric representation of the Taylor series terms. Since this is just a re-expression of reflectivity, the geometrical representation is applicable for both the subcritical and supercritical incident angle regimes.

Above the critical angle for this system, the electromagnetic wave beyond the totally internally reflecting interface is evanescent. So the wave propagates parallel to the interface and cannot reflect from the film-silicon interface. However, each term in the infinite sum remains meaningful. Since the reflectance amplitude coefficients become of unit amplitude above critical angle, the higher terms in Taylor series expansion become more significant. For very thin films, the phase shifts between the

components are negligible and the contributions to the electric field component perpendicular to the interface from all terms become constructive. Similarly, the subsequent contributions to the electric field component parallel to the interface become alternately destructive and constructive. Thus the electric field strength is greatly enhanced within the film for p-polarized radiation and only slightly enhanced for s-polarized radiation. Since absorption is proportional to the square of the electric field amplitude, an enhancement in the electric field strength of ten times results in a hundredfold enhancement in absorption.

EXPERIMENTAL

Two coated Si wafers were examined. One was a 16Å thick photoresist film on a silicon wafer and the other was an optically thick (2-3 μm) coating of the same photoresist. The samples were examined using the GATR single reflection Ge-ATR accessory with a 65° incident angle (Figure 2), in an FT-IR spectrometer. The spectra were collected with 32 scans at 8 cm⁻¹ resolution using a DTGS detector.

The samples were placed on the ATR crystal and intimate contact obtained using the GATR slip-clutch driven pressure applicator, which



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delivers 56 in-oz of pressure, and referenced against the clean ATR crystal. Spectra were collected using unpolarized and polarized radiation. The polarization experiments utilized the optional GATR KRS-5 wire grid polarizer.

RESULTS AND DISCUSSION

Figure 3 shows the ATR spectra of an optically thick film of the photoresist measured with two different polarizations of incident radiation as well as with unpolarized incident radiation. As expected, the band intensities are strongest for the p-polarization. The intensities for s-polarization are the weakest and roughly half that of p-polarized light. The peak intensities in the spectrum recorded with unpolarized light falls somewhere between.

The ATR spectra of the 16Å film on Si, shown in Figure 4, has the same general trend, with the p-polarized incident radiation resulting in a spectrum with the most intense bands. Furthermore, the bands at 1500 cm^{-1} and 1250 cm^{-1} , which are clearly visible in the p-polarized spectrum, fall below the detection limit for s-polarization. This indicates a much stronger sensitivity to the p-polarization relative to the s-polarization for thin films on Si substrates than for bulk materials.

Since p-polarized light

probes only the component of the bonds perpendicular to the interface, the difference between the spectra shown in Figures 3 and 4 shows the preferential orientation of certain bonds in a very thin film of photoresist.

SUMMARY

As seen above, the high sensitivity of 65° Ge-ATR to thin films on Si substrates is highly dependent on the incident polarization. The p-polarized component is enhanced, while the s-polarized component is not. Thus this method has higher sensitivity to the only the component of the bonds perpendicular to the interface. It would be interesting to see how the bonds orientation evolves with increase in film thickness by recording spectra of films with increasing thickness.

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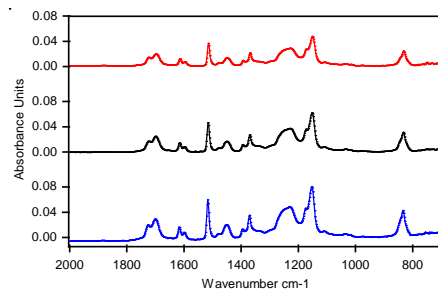


Figure 3. ATR spectra of a 2-3 μm thick photoresist on Si recorded with unpolarized (black), s-polarized (red) and p-polarized (blue) incident radiation.

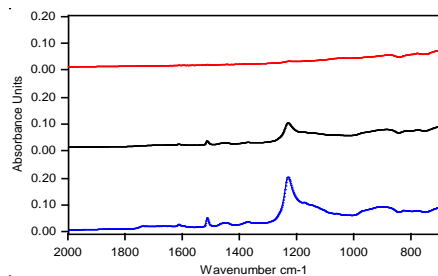


Figure 4. ATR spectra of a 16Å thick photoresist on Si recorded with unpolarized (black), s-polarized (red) and p-polarized (blue) incident radiation.



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