HARRICK SCIENTIFIC PRODUCTS

No. 10129

EXTERNAL REFLECTION SPECTROSCOPY: SELECTION OF THE OPTIMUM PARAMETERS FOR THIN FILMS ON SMOOTH METALS

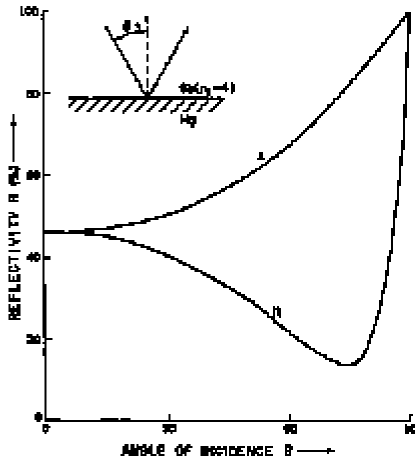

Figure 1a. The Reflectivity of a Ge-Hg Interface at λ=3µm for light approaching the interface through the Ge. An example of the reflectivity of a dielectric-metallic interface.

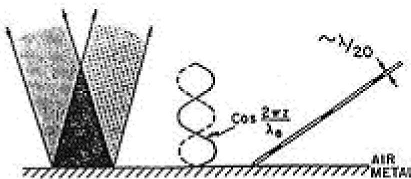

Figure 1b. Experiment of O. Wiener (1980). The superposition of the incoming waves with those reflected from the metal mirror establish the standing-wave pattern shown in the center. A thin photographic emulsion placed in this field will show the interaction (darkened areas) only near the maximum electric fields (loops) of the standing waves. Because of the high conductivity of the metal, there is a node near the surface. The angle of the emulsion relative to the surface is highly exaggerated.

This article summarizes requirements both on the choice of parameters for recording spectra of thin films on metal surfaces via external reflection spectroscopy and pitfalls of which the must be aware. Necessary information is found in Figures 2 and 3 which show that parallel polarized light must be used and that a practical working angle is 75º. These results apply to most situations.

External reflection spectroscopy is one of the six optical spectroscopy sampling techniques commonly used. It is a non-contact method and is particularly useful in recording interference fringes for film thickness measurements[1] and in the study of thin films on metal surfaces. Here the light impinges on the surface of the sample and the specular component is recorded (Figure 1a). The sensitivity of the method for thin films on metal surfaces is dependent on the polarization of the light and the angle of incidence. The discussion here will be limited to recording spectra of thin films.

Polarization

It is clear from Figures 2 and 3 that the spectra of thin films can only be recorded with parallel polarization, i.e. light whose electric field vector is in the plane of incidence. The reason for this is that for perpendicular polarization (and parallel polarization near normal incidence) there is an interaction between the incident and reflection light which sets up a standing light wave (Figure 1B) with a node (E=0) at the surface. At this node, there can be no interaction with an absorbing film and therefore a spectrum cannot be recorded.

Angle of Incidence

Figure 2 shows that to record spectra, not only must the light be polarized parallel but that large angles must be used. In actual practice, the angle should be about equal to the polarizing or Brewster's angle. For a dielectric, this is given by:

$$\theta_\beta = \tan^{-1} n$$

and is equal to 76º for Ge (n=4), 67º for ZnSe (n=2.4) and 54º for quartz (n=1.4). For a conductor, on the other hand, this angle is given by[2]

$$\sin\phi \tan\phi = \frac{\sqrt{2}}{1.05\text{x}10^{-6}(\nu\varepsilon\rho)^{1/2}}$$

Here, ν is the frequency of light, ε is the dielectric constant of the adjoining medium (for air, ε=1), and ρ is the resistivity (in ohm-cm) of the metal. For high conductivity materials, such as Al, Ag, Au, Cu and Pt, this angle is very large (greater than 89.5º) and is not readily attainable.

application note

External Reflection Spectroscopy: Selection of the Optimum Parameters for Thin Films on Smooth Metal

Figure 2 shows that the greater the angle, the higher the sensitivity. The highest practical angle to work at is 87 to 88°, but this generally required vignetting of the beam (with loss of energy) to reduce the angular beam spread.

Pitfalls

The light beam is partially polarized in FT spectrometers and the degree of polarization differs between spectrometers. For a flat baseline, the sample spectrum must be ratioed against a reference with the appropriate polarization. When employing unpolarized light, the state of polarization of the instrument must be known when recording external reflection spectra.

Beam Width

An oblique angle of incidence gives rise to smearing or spreading of the beam on the sample and follows a $1/\cos\theta$ law. Note in the table in Figure 2 that at 75°, the beam width has increased by about a factor of 4 over normal incidence, while at 88° it has increased by almost a factor of 30.

Non-Linearity of Absorption with Film Thickness

It is clear from Figure 1b that because we are dealing with standing waves[3] and non-propagating waves with absorption, $\Delta I/I$, will not increase linearly with increasing film thickness. A confirmation of this non-linearity was demonstrated by Allara and co-workers[4]. They also demonstrated that, for external reflection spectra, significant band distortions occur with broadening shifts to higher frequencies relative to transmission spectra. The phenomena contributing to these effects are also discussed by the author in "Characterization of Metal and Polymer Surfaces[5]."

Experimental

The spectra shown here were recorded with the aid of a Harrick Variable Angle Reflection Accessory (see Figure 4) and a single diamond Brewster's Angle Polarizer. Once this accessory is aligned, it can be used over a wide range of angles of incidence without need for realignment. Even though the Variable Angle Reflection Accessory provides 1:1 imaging, vignetting of the beam to reduce the angular beam spread is necessary at high angle (above 85°) of incidence.

The Ge Brewster's Angle Polarizer gives high transmission and a high degree of polarization. In addition, its polarization is independent of wavelength. Alternatively, a KRS-5 wire grid polarizer with a large, 25 mm clear aperture, compact design, and a 250 cm^{-1} long wavelength cut-off can be used in this application.

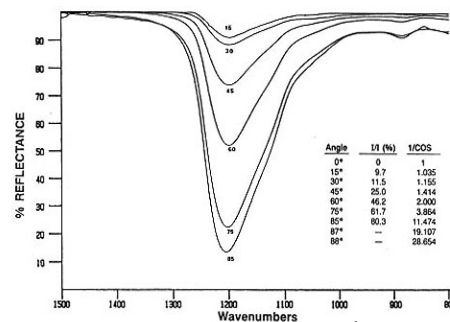

Figure 2. Spectra of 700Å of SiO on an Al substrate at various incident angles with parallel polarized light.

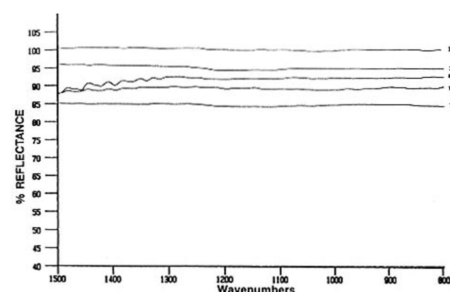

Figure 3. Spectra of 700Å of SiO on an Al substrate at various incident angles with perpendicular polarized light.

Figure 5 shows the Refractor2, an accessory for a popular application of high angle specular external reflection spectroscopy using polarized light. This accessory enables the user to measure and control film thickness on substrates.

Conclusion

Based on the above considerations, it can be concluded that a good choice for the optimum angle of incidence for an external reflection

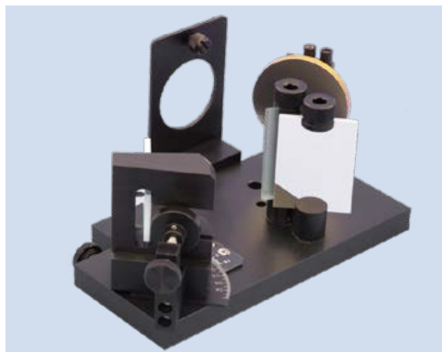

Figure 4. This variable angle specular reflection accessory, with the addition of a polarizer, is particularly useful for grazing incidence experiments to study thin films on metal surfaces.

Figure 5. The Refractor2 is a fixed 75º accessory with a built-in polarizer used to examine thin films on reflective substrates.

accessory is 75º using, of course, parallel polarization. At this angle, the absorption coefficient is more than one-half of the highest attainable and the beam width is one-fifth of that attainable at the highest angles. Furthermore, at 75º, it is possible to utilize the light beam at full aperture with a moderate beam demagnification. At 87º, on the other hand, no demagnification is possible. In fact, it is necessary to vignette the beam by a factor of 2-3 to reduce the beam spread to about ±2º.

---

[1]N.J. Harrick, *Appl. Opt.* **10**, 2344 (1971).
[2]N.J. Harrick, *J. Opt. Soc. Am.* **49**, 376 (1959).
[3]O. Wiener, *Ann. Physik* **40**, 203 (1890).
[4]D.L. Allara, A. Baca and C. A Pryde, *Macromolecules* **11**, 1215 (1978).
[5]Characterization of Metal and Polmer Surfaces, ed. by L.H. Less, Vol. 2, Academic Press, New York, 1977, p. 153.

HARRICK SCIENTIFIC PRODUCTS
141 Tompkins Ave., 2nd floor • PO Box 277 • Pleasantville, NY 10570
www.harricksci.com • E-mail: info@harricksci.com
Phone (international): 914-747-7202 • Phone (in USA): 800-248-3847 • Fax: 914-747-7209