Use of Molecular Vibrations to Analyze Very Thin Films with Infrared Ellipsometry

Harland G. Tompkins,[†] Tom Tiwald, and Corey Bungay

J. A. Woollam Co., Inc., 645 M Street, Suite 102, Lincoln, Nebraska 68508

Andrew E. Hooper*

Motorola Labs, 2100 East Elliot Road, Tempe, Arizona 85284

Using nylon-6 and polystyrene as prototypical materials with organic functional groups, we have demonstrated that for silicon or gold substrates, features due to the molecular vibrations can be seen in the ellipsometric spectra for films as thin as 50 Å with signal-to-noise ratios ranging from 2 to 10. It is expected that with some additional optimization, this could be improved by a factor of 2 to 4. For films on a gold substrate, due to the high reflectivity, one would expect to be able to see these features for 10 Å or thinner. For films on the glass substrate (or any other substrate that has an index of refraction near that of the film in the nonabsorbing region), IR ellipsometry provides thickness information that cannot readily be obtained from traditional ellipsometry. For all of the substrates, IR ellipsometry provides molecular structure information.

1. Introduction

Thin layers containing organic functional groups (i.e., polymer films, organic films, and biological films) are used in a variety of scientific, engineering, and manufacturing disciplines. Examples of this are HMDS as an adhesion layer for photoresist in the microelectronics industry, passivation layers for bioimplants, adhesion layers on metals, etc. We shall refer to these films containing organic functional groups generically as "organic films", although this will include polymer films and biological films.

The analytical method of choice for these materials has traditionally been Fourier transform infrared spectroscopy (FTIR), usually done in the transmission mode. This method is very appropriate when the material is in the liquid form, a self-supporting layer, or a thick layer on a transparent substrate. Infrared reflection absorption spectroscopy (IRAS)[1–3] is often used to analyze organic functional group films on an opaque substrate (usually metals) and this method works well for films with thicknesses ranging from several micrometers down to several hundred angstroms. For films thinner than 100 Å, IRAS is a demonstrated technique[4,5] that has been extensively used for the characterization and molecular structure determination of self-assembled monolayers.[6a–i]

Spectroscopic ellipsometry[7] is often used to determine the thickness and optical functions of thin layers. Traditionally, this method has been used in the visible wavelength range and has been paramount in the development of the microelectronics industry. In the past decade, the wavelength range has been extended into both the ultraviolet[8] and the infrared wavelength range.[9,10] For example, in situ infrared spectroscopic ellipsometry has been used to characterize the adhesion and growth of plasma deposited a-SiO_2 on stainless steel.[11, 12]

The purpose of this work is to determine the thickness ranges and possible substrates where infrared spectroscopic ellipsometry

* To whom correspondence should be addressed. E-mail: andy.hooper@motorola.com.
† Consultant.
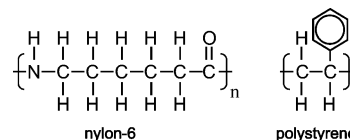
Figure 1. The repeat units for nylon-6 and polystyrene.

(IR-SE) can be readily used to determine the thickness and molecular structure of thin organic/polymer/biological layers and to explore the parameter space to optimize the analysis to obtain maximum signal-to-noise for reasonable analysis times.

An additional problem addressed in this work is the analysis of organic films on a glass substrate. This film–substrate combination occurs regularly for biological films. It is very difficult to determine the thickness of these films with traditional ellipsometry (wavelengths in the visible range) since the optical constants of the film and those of the substrate are almost identical. We will investigate using the molecular vibrations in the infrared region to overcome this difficulty.

2. Experimental Section

2.1. The Samples. For this study, we use the nylon polymer and the polystyrene polymer as a prototypical material containing organic functional groups. The repeat unit for each of these two polymers is shown schematically in Figure 1. The nylon repeat unit has five CH_2 groups that are present in many polymers, self-assembled monolayers, etc., a carbonyl group, and an N–H bond. The peaks for these units are distinctive and do not overlap. The polystyrene repeat unit has a benzene ring, the H bonded to the same carbon, and another CH_2 group.

The substrates used were bare silicon wafers (with a thin native oxide), an opaque gold layer deposited on a silicon wafer, and a glass wafer. The glass was borosilicate glass. A solution of nylon in *o*-chlorophenol was used to deposit the nylon films on substrates of each of the three materials, sequentially, using a spin-on technique similar to that used for putting photoresist onto silicon wafers. Another solution with a different concentration of the solute in solution was then made and the process

repeated with new substrates. Four films of each polymer were deposited on substrates of each of the three materials. The thicknesses of the films ranged from about 1000 Å down to about 50 Å. Samples prepared in a similar way have been analyzed with transmission FTIR previously.[13] Polystyrene films were deposited in a similar manner with xylene as a solvent.

2.2. The Analysis. The samples were analyzed on a J. A. Woollam Co. IR-VASE, which consisted of a Bomem FTIR along with the necessary polarizers, compensators, goniometers, etc. needed to do ellipsometry as a rotating compensator instrument. The light source was a glo-bar typical of most FTIR instruments. The detector was a DTGS detector. Although the instrument automatically collects data over a wavenumber range from about 200 to 8000 cm^{-1}, we concentrated on the wavenumber range of 500−4000 cm^{-1} (wavelength range of 2.5−20 μm), as this is the range where the characteristic molecular vibrations absorb radiation. We concentrate on the peaks that represent strong absorptions only, since the weakly absorbing peaks will be in the noise level for the thinner films.

After determining the optimum angle of incidence, typically near the Brewster angle for the substrate, analysis was done at a single angle of incidence (73° for Silicon substrates, 83° for gold substrates, and 52° for glass substrates). It should be noted that for this instrument the ellipsometer angle of incidence is defined as 0° for normal and 90° for grazing. Spectra were taken with a 4-cm^{-1} resolution. The data collection time was about 3 h for a single angle of incidence. For the thicker films, the data could have been collected in a shorter period of time with some increase in the noise level. Prior to analysis, the samples on Si substrates and glass substrates were roughened by a bead-blasting technique to eliminate backside reflections.

The film material was analyzed with use of Gaussian oscillators to represent the molecular vibrations (the absorbing regions). By using the thickness determined in the transparent region, the parameters for the oscillators were determined to best fit the spectra. Simulations were done by simply assigning different thicknesses and using the "generate" function of the Woollam WVASE (registered trademark) software to generate the simulations. By using this process, relative peak heights of the various species could then be generated as a function of thickness.

In addition, to provide additional backup information, spectroscopic ellipsometry analysis was done in the visible range, using a rotating compensator multiwavelength instrument (J. A. Woollam Co., M2000) for the films on silicon and on gold and for the glass substrate. Data were taken with this instrument at 668 different wavelengths ranging from 200 to 1600 nm.

3. Results

3.1. Nylon on Silicon. The Δ and Ψ spectra for the four nylon films on silicon are shown in Figure 2 and the resulting optical constants are shown in Figure 3. The feature with the peak in the k spectrum at about 1645 cm^{-1} is due to the carbonyl (C=O) stretch. The features at 2860 and 2932 cm^{-1} are due to the symmetric and asymmetric CH$_2$ stretch. The feature at 3285 cm^{-1} is due to the N−H stretch.
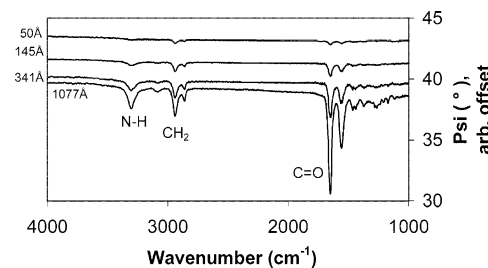
The nonabsorbing regions (e.g. 2000−2800 cm^{-1}) provide information about thickness in the same manner as traditional visible ellipsometry, and the thickness values agree with those obtained in the visible region. In addition, the size of the "peaks" in the Δ spectrum is related (although not necessarily linearly) to the thickness (actually to the number of bonds/cm^2). From the spectra in Figure 2, we estimate that the signal-to-noise ratio for the carbonyl band near 1645 cm^{-1} is about 5 for the 47-Å film.
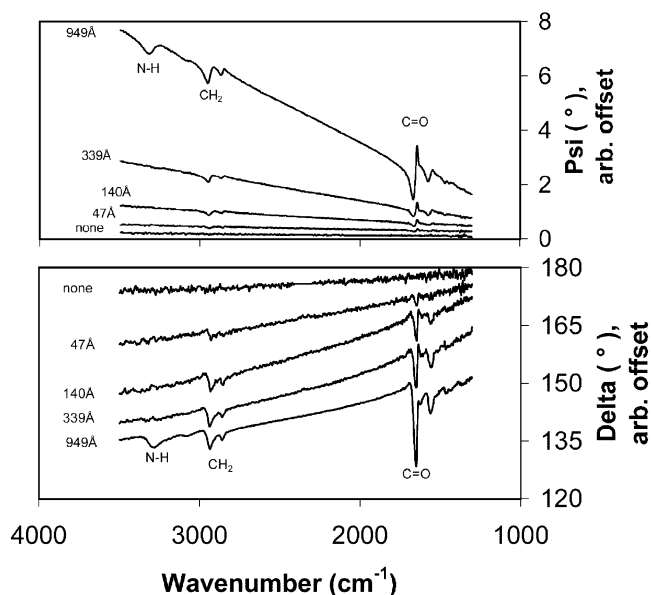
Figure 2. Ψ and Δ as a function of wavenumber for four different thicknesses of nylon films on silicon wafers and for a reference bare silicon wafer (with about 20 Å native oxide). The scale is the same for all five plots although each plot is offset slightly for clarity. The signal-to-noise ratio for the carbonyl peak for the 47-Å film is estimated to be about 5.
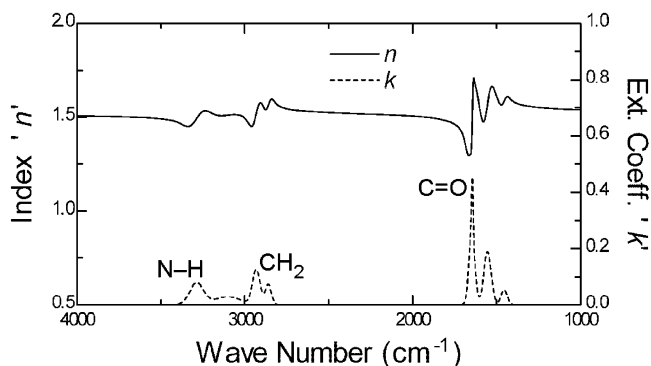

Figure 3. The optical functions for nylon-6 as determined from the spectra shown in Figure 2.


Figure 4. The Ψ spectra for four nylon-6 films on an opaque gold substrate. The scale is the same for all four films, but they are offset slightly for clarity.

3.2. Nylon on Gold. As with nylon on Si, the nonabsorbing regions provide information about thickness in the same manner as traditional visible ellipsometry. The Ψ spectra are shown in Figure 4. The flat parts of the spectra for all thicknesses lie essentially on top of each other, hence we offset these spectra for clarity. The scale is maintained, however. Figure 5 shows an expanded version of the spectra for the thinnest film (about 50 Å). From this figure, we estimate the signal-to-noise ratio to be about 10. It is not surprising that the signal-to-noise ratio is greater on Au than on Si since the amount of light reflected

Analysis of Very Thin Films with IR Ellipsometry

J. Phys. Chem. B, Vol. 108, No. 12, 2004 **3779**
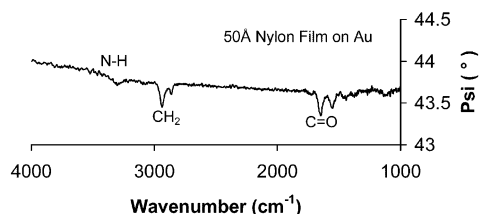
Figure 5. The Ψ spectrum shown in Figure 4, with expanded scale. The signal-to-noise ratio for the carbonyl peak is estimated to be about 10.
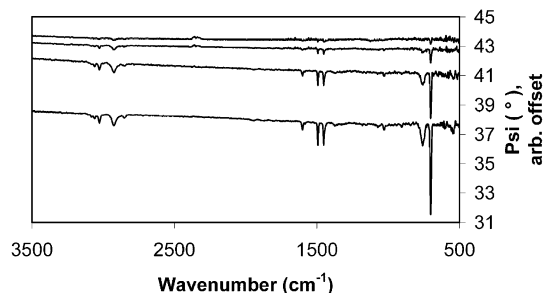
Figure 6. The Ψ spectra for four polystyrene films on an opaque gold substrate. The thicknesses are comparable to those on silicon.

Figure 7. The Ψ spectrum for four nylon films on glass. Since the deposition conditions were the same as for the silicon and gold substrates, the thicknesses are expected to be comparable.

Figure 8. The index of refraction of the glass substrate and of the nylon film that includes the visible region.

Figure 9. The optical functions of the glass substrate and the nylon film. The index of refraction of the glass substrate was measured directly and the index and extinction coefficient are those determined for the nylon film on silicon.
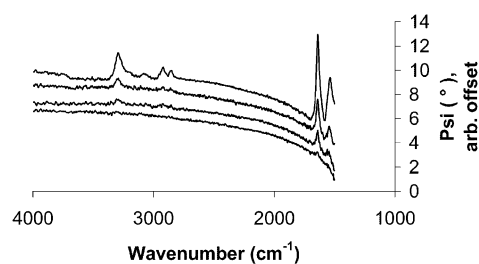
from Au is significantly greater than that reflected from Si. Note that for reflections on metal surfaces, only the vibrations that are perpendicular to the surface are excited. As we expect this material to be randomly oriented, no one vibrational mode is enhanced or eliminated from the spectrum. In Figure 4, note that as we go from thicker films to thinner films, the ratio of the peak height of the CH_2 peaks to that of the carbonyl peaks does not remain constant. Simulations suggest that this is to be expected.

3.3. Polystyrene on Gold. As with nylon on Au, the thickness could be determined from the Δ spectra by using traditional ellipsometric techniques. Figure 6 shows the Ψ spectra for the four films, which ranged from about 1000 Å down to about 50 Å. The CH_2 peaks can be observed at 2851 and 2925 cm^{-1}, in roughly the same location as for the nylon films. The peaks above 3000 cm^{-1} are due to the C−H stretching of the hydrogen atoms that are attached to the benzene ring and to the single hydrogen attached to the carbon in the backbone chain to which the benzene ring is attached. The peaks at 1453 and 1494 cm^{-1} are due to C−C stretching vibrations in the benzene ring and the peak at 702 cm^{-1} is due to a ring deformation vibration. Although the peak at 702 cm^{-1} is the largest peak in the polystyrene spectrum, it is located in a region where the noise is larger than (for comparison) the largest peak in the nylon spectrum (the carbonyl peak at 1645 cm^{-1}). This results in the nylon-on-Au sample having the lowest detection limit of all the samples analyzed. In contrast, for polystyrene on either Si or glass, the molecular vibrational peaks for the benzene ring were difficult to observe for the thinner samples (a few hundred angstroms).

3.4. Nylon on Glass. The Ψ spectra of nylon on glass are shown in Figure 7 for the four films.
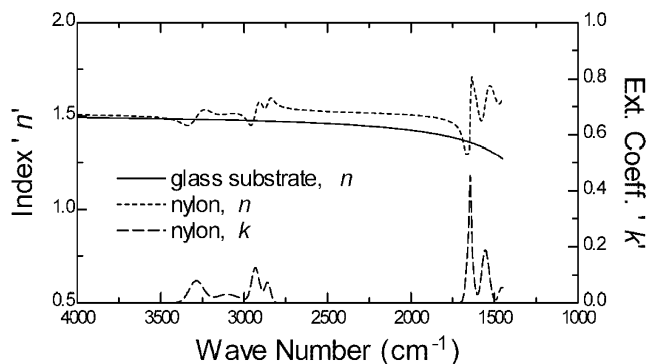
4. Discussion

Because the optical constants of the film were very different from those of the substrates, the thickness of the nylon films on Si and Au and of the polystyrene films on Au could be readily determined from the nonabsorbing spectral regions in either the visible or infrared regions. This is not the case,
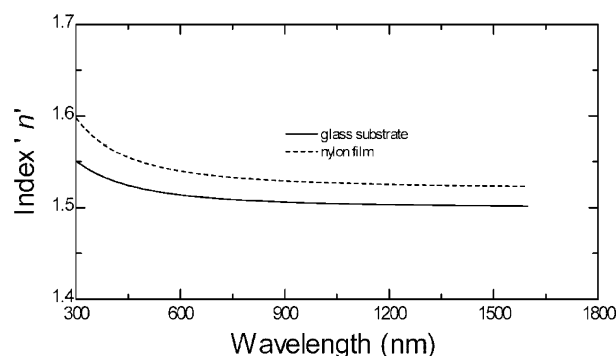
however, for the glass substrate. Figure 8 shows the index of refraction of the glass and nylon that includes the visible region. As can be seen in the figure, the index of the substrate differs by only 0.03−0.05. In the nonabsorbing regions of the IR, the situation is not much better, as shown in Figure 9. In this figure, we plot the index of the substrate as determined from a bare glass substrate and the index and extinction coefficient for the film, as determined on the nylon-on-Si films. Whereas in the nonabsorbing regions the index for nylon is almost identical with that of glass, in the absorbing regions, the index and extinction coefficient of the film are significantly different from those of the substrate.

For determining thickness, then, the nonabsorbing regions are useless. This is shown in Figure 10 where we simulate the Ψ spectra for both a bare glass substrate and a glass substrate with 400-Å nylon film. As can be seen in the figure, in the nonabsorbing regions (e.g., 1750−2600 cm^{-1} and above 3400 cm^{-1}), the Ψ curves virtually overlap. The peaks in the absorbing regions, however, are a function of the nylon film
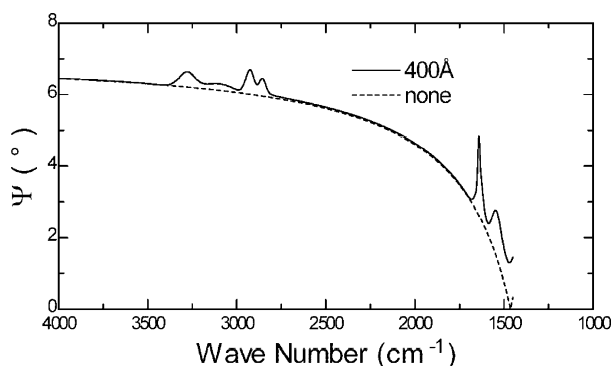
Figure 10. Simulated Ψ spectra for a 400 Å nylon film on a glass substrate and a film-free glass substrate, using the optical constants determined from the bare glass substrate and the optical functions for the nylon film on silicon.

thickness. Using the peak heights of the carbonyl alone, we estimate the thickness of the four films on glass to be 1100, 365, 165, and 50 Å, with an uncertainty of about 20%. To do this rigorously, a calibration is needed where the height (or peak area) is related to a known bond area density. This work is in progress.

5. Summary and Perspective

5.1. On Metal or Silicon Substrates. We have demonstrated that for silicon or gold substrates, features due to the molecular vibrations can be seen in the ellipsometric spectra for films as thin as 50 Å with signal-to-noise ratios ranging from 2 to 10. For films on a gold substrate, due to the high reflectivity, one would expect to be able to see these features for 10 Å or thinner films. The signal-to-noise ratios could be improved either by using a mercury cadmium telluride (MCT) detector or by simply scanning for a longer time (e.g. overnight). There is no significant advantage for thickness determination with IR ellipsometry compared to the classical visible ellipsometry. The main advantage for films on these types of substrates is the determination of molecular structure and/or orientation relative to the substrate. Infrared reflection absorption spectroscopy (IRAS) can also provide this information. IRAS is a two-beam technique in that one must obtain the intensity both with and without the film. IR ellipsometry compares the light polarized in the plane of incidence to that polarized perpendicular to the plane of incidence. Since this is normally done with a rotating element (either a rotating polarizer or a rotating compensator), ellipsometry can be thought of as a single beam technique that carries its reference beam along with it. It is possible that thinner films can be observed with ellipsometry although this is, to some extent, a function of how long a time one chooses to signal average the beam and the stability of the instrument.

On a metal substrate, functional group vibrations will not absorb radiation if the dipole is oscillating parallel to the surface. Orientation information can therefore be obtained in both IRAS and IR ellipsometry. The phenomena are the same for both techniques and hence neither has an advantage.

Most IRAS is done with an attachment inserted into the beam of a transmission FTIR. By the nature of the size of the sample compartment, focusing the beam is necessary. Because of this, multiple angles of incidence are used (and are not detected separately). The angular spread of the light in ellipsometry, by the nature of the goniometers, polarizers, and compensators, is normally significantly less than that of an FTIR machine used for IRAS. IR ellipsometry is therefore more amenable to quantitative calculations.

5.2. On Glass Substrates. For films on the glass substrate (or any other substrate that has an index of refraction near that of the film in the nonabsorbing region), IR ellipsometry provides thickness information that cannot readily be obtained from traditional ellipsometry. In addition, it also provides molecular structure information.

References and Notes

(1) (a) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310. (b) Greenler, R. G. *J. Chem. Phys.* **1969**, *50*, 1963.

(2) Tompkins, H. G. In *Methods of Surface Analysis*; Czanderna, A. W., Ed.; Elsevier: Amsterdam, The Netherlands, 1975; Chapter 10.

(3) Allara, D. L. In *Characterization of Metal and Polymer Surfaces*; Lee, L. H., Ed.; Academic Press: New York, 1977; Vol. 2, pp 193–206.

(4) Tompkins, H. G.; Greenler, R. G. *Surf. Sci.*, **1971**, *28*, 194.

(5) Porter, M. D. *Anal.Chem.*, **1988**, *60*, 1143A.

(6) (a) Allara, D. L. In *ACS Symposium Series*; Bell, A. T., Hair, M. L., Eds.; Vol. 137; American Chemical Society: Washington, DC, 1980; pp 37–49. (b) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45. (c) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559. (d) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558. (e) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152. (f) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96* (2), 927. (g) Mielczarski, J. A.; Mielczarski, E. *J. Phys. Chem.* **1995**, *99*, 3206. (h) Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663–7676. (i) Arnold, R.; Terfort, A.; Wöll, C. *Langmuir* **2001**, *17*, 4980.

(7) Tompkins, H. G.; MaGahan, W. A. *Spectroscopic Ellipsometry and Reflectometry: A User's Guide*; John Wiley & Sons: New York, 1999.

(8) Hilfiker, J. In *Handbook of Ellipsometry*; Tompkins, H. G., Irene, E. A., Eds.; Noyes Press: Park Ridge, NJ, Chapter 10; in press:

(9) Röseler, A.; Korte, E.-H. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; John Wiley & Sons Ltd: Chichester, West Sussex, UK, 2002; Vol. 2, p 1065

(10) Röseler, A. In *Handbook of Ellipsometry*; Tompkins, H. G., Irene, E. A., Eds.; Noyes Press: Park Ridge, NJ, Chapter 11; in press:

(11) Bertrand, N.; Drévillion, B.; Klemberg-Sapieha, J. E.; Martinu, L. *Thin Solid Films* **1996**, *290–291*, 264.

(12) Bertrand, N.; Drévillion, B.; Bulkin, P. *J. Vac. Sci. Technol. A* **1998**, *16* (1), 63.

(13) Hooper, A. E.; Tompkins, H. G. *Surf. Interface Anal.* **2001**, *31*, 805.