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Thickness Dependence of Reflection−Absorption Infrared Spectra of Supported Thin Polymer Films

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S *Supporting Information*

■ INTRODUCTION

At present, supported thin and ultrathin films of various synthetic and native polymers are used for multiple purposes, including sensors,[1] transistors,[2] and model systems[3] among many others. In addition, the fundamental properties of ultrathin polymer films can be intriguing as witnessed by, for example, deviations observed in crystallization[4,5] or glass transition temperature.[6−8] Chemical characterization of such films is important when one wants to know about, e.g., film composition, its purity, chemical modifications performed after the initial preparation of the film, aging effects, or film's performance as a model substrate. Reflection−absorption infrared spectroscopy (RAIRS) is an indispensable tool for analysis of polymer thin films because of its surface sensitivity coupled with the analytical fingerprint detail on organic compounds in contrast to many other popular techniques like X-ray photoelectron spectroscopy which yields data mainly on the elemental composition of the film surface. As RAIRS on metallic substrates is based on the excitation caused by the p-component (perpendicular to the surface) of the infrared radiation reflecting at a grazing angle on the sample, a number of film properties, such as roughness and thickness, affect the spectrum.[9,10] The effect of film thickness on the spectrum is usually omitted, but it is potentially important when characterizing films over a wide thickness range. In the current study, we have performed RAIRS analysis of polymer films with thickness values ranging from 1 to >500 nm, and we go on to show that film thickness has a systematic influence on the spectral band intensities, a factor that must be considered when quantifying chemical changes in films characterized by RAIRS. The chosen film material was amorphous cellulose on a silicon substrate due to its well-characterized properties and reliable preparation in various thickness regimes by consecutive spin-coating steps.[11,12] To corroborate the interpretation arising from the influence of thickness on the spectra, we have also performed spectral simulations.

■ EXPERIMENTAL SECTION

Amorphous cellulose films were prepared by regenerating spin-coated films of trimethylsilyl cellulose (TMSC) on silicon wafers into cellulose by exposing the films to the vapor of aqueous 2 M HCl solution for 2 min as described in ref 11. The IRRAS spectra were measured under vacuum by using a reflection unit with variable angle and a polarizer from Bruker Optics with an incidence angle of 74°. The spectral simulations were carried out with the simulation tool SCOUT 3.1701. Film thickness was experimentally determined by spectroscopic ellipsometry (picometer ellipsometer, Beaglehole Instruments, Wellington, New Zealand) that was performed within 380−725 nm wavelength range at 75° measurement angle. Full experimental details are available in the Supporting Information.

■ RESULTS AND DISCUSSION

Cellulose films with thicknesses between 1 and 539 nm have been prepared on single side polished silicon wafers. The p-polarized IRRAS spectra of the clean substrate as a reference and four cellulose films with different thickness in the fingerprint region (1500−500 cm^{-1}) and in the OH region (4000−2500 cm^{-1}) are shown in Figure 1 together with the structure of cellulose. The reference spectrum from a plain silicon wafer shows that there are seven bands that stem from the substrate in the fingerprint region (Figure 1). With increasing film thickness, seven new bands arise at 670 cm^{-1} (OH out-of-plane bending), 1024 cm^{-1} (CO stretching), 1064 cm^{-1} (CO stretching), 1153 cm^{-1} (antisymmetric bridge COC stretching), 1199 cm^{-1} (OH in-plane bending), 1257 cm^{-1} (OH in-plane bending), and 1369 cm^{-1} (CH bending), all corresponding to the reported IR spectra of cellulose,[13] including amorphous cellulose.[14] Similarly, the bands in 3600−3000 cm^{-1} (OH stretching) and 2900 cm^{-1} region (CH and CH_2 stretching) in Figure 1 are characteristic of cellulose.[13,14] All of these bands increase in intensity, but there is no shift and no change in the band shape as a function of cellulose film thickness. These films have been shown to be amorphous in the ultrathin regime (few tens of nanometers).[12] Since crystallinity induces distinct patterns to the IR spectra of cellulose,[15] the lack of band shift in Figure 1 is a clear indication that the films stay amorphous to as thick as 539 nm.

Figure 2 shows the integrated bands from Figure 1 as a function of film thickness. It is apparent that the IR intensities are not a function of film thickness up to 50 nm, which can be ascribed simply to the IR signal noise being too large to see clear distinctions due to thickness. As the film thickness increases further, the intensities of the bands increase with different slopes depending on the vibration. However, the intensity of the

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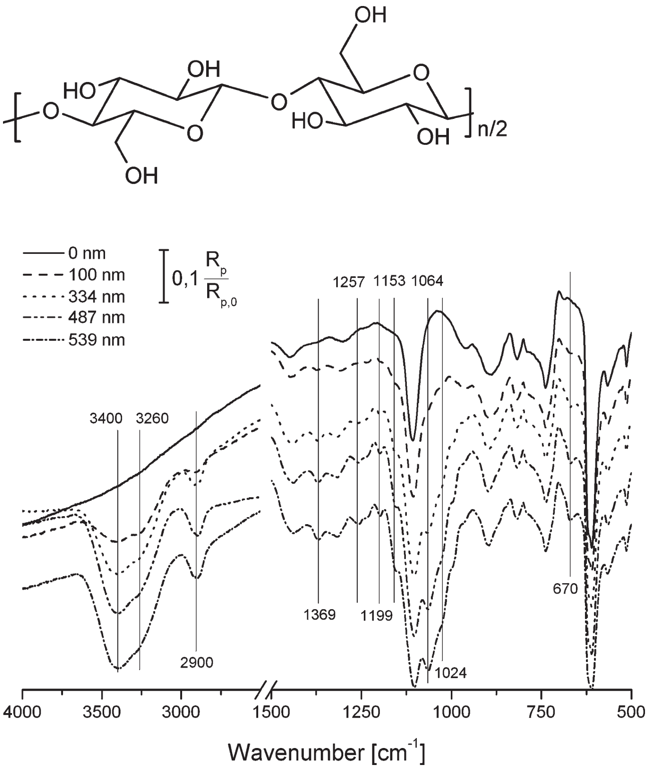

Figure 1. Top: structure of the repeating unit of cellulose. Bottom: p-polarized IR reflectance spectra of silicon-supported cellulose films of different thickness values. 0 nm thickness denotes the reference spectrum for a plain, uncoated silicon wafer.

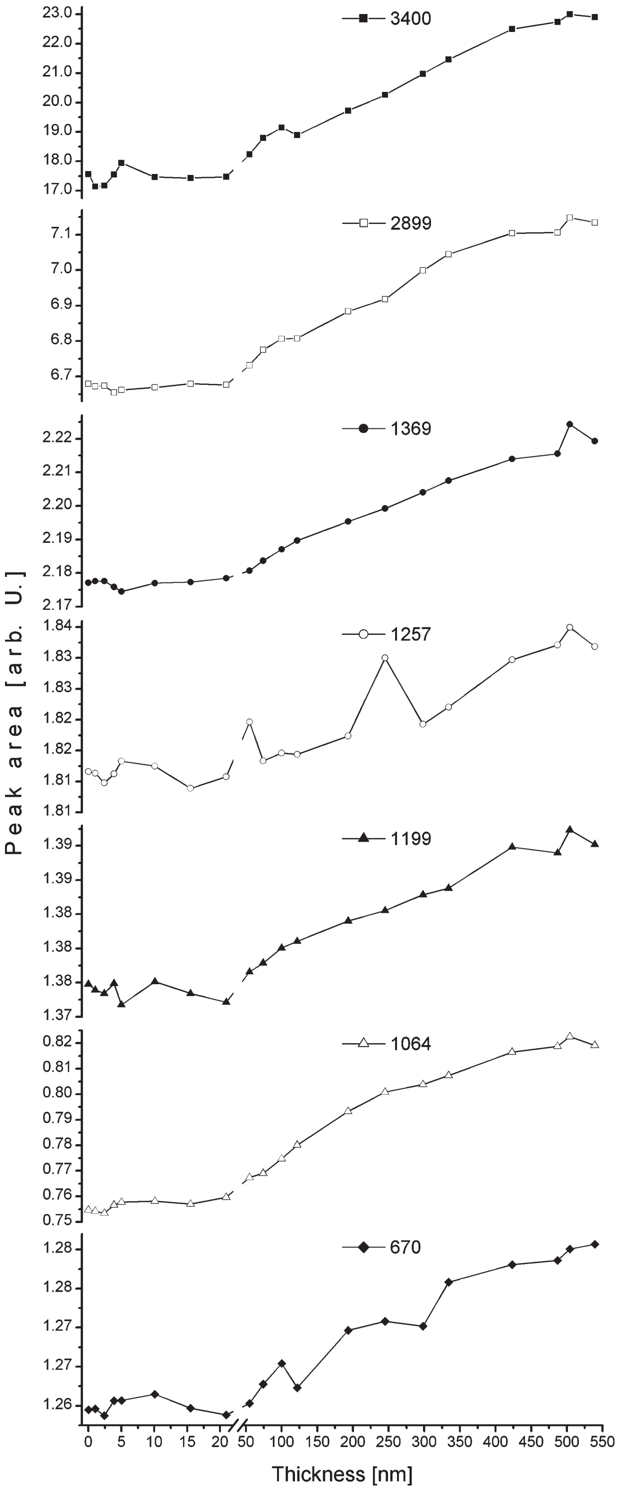

Figure 2. Integrated areas from the bands from Figure 1 as a function of cellulose film thickness obtained from ellipsometry. Note that all the curves have a different scale in the intensity. Upon integration, a common baseline for all spectra was used, which was made by normalizing the spectra to the lowest value of the peak (see Supporting Information for details).

infrared spectra measured in reflection depends not only on the amount of absorbing material but also on the reflectivity of the surface.[16] The latter is not the same for s- and p-polarized light, and it changes with surface roughness. Because of these facts, a steady increase of the intensity of any given vibration is not necessarily related to an increase in film thickness. Therefore, simulations of the spectra have been made to clarify if the increase found in Figure 2 is due to film thickness or reflectivity changes.

Measured s-polarized spectra have been juxtaposed with their simulated counterparts in Figure 3. The increase in the band intensities as a function of growing cellulose film thickness is clearly a trend which is reproduced both in measured and in simulated spectra in all regions. The biggest difference between experiment and simulation can be found in the OH region. This is due to the slow accumulation of water on the liquid nitrogen cooled detector during the experiments (see below).

It is immediately visible from Figure 3 that the simulation is capable of reproducing the dramatic baseline drop of the measured data, which is not featured in, for example, conventional transmission IR spectra of cellulose.[13,14] The strong drop of the baseline for thick cellulose films at high wavenumbers is caused by Fabry—Pérot resonances between the cellulose surface and the cellulose silicon interface.[17] Thicker films yield a lower central wavenumber (corresponding to a greater wavelength) of this absorption resonance. Therefore, this drop of the baseline arises at the high wavenumber limit for thin films, moving more toward the center of the spectral range for thick films, leading to the observed drop in the baseline (Figure 3). The systematic baseline drop, however, is not the reason for increased band intensities upon growing film thickness (Figure 2) because of the normalization procedure (see Supporting Information).

The only adjustable parameter used to simulate the spectra is the film thickness which can therefore be evaluated and then

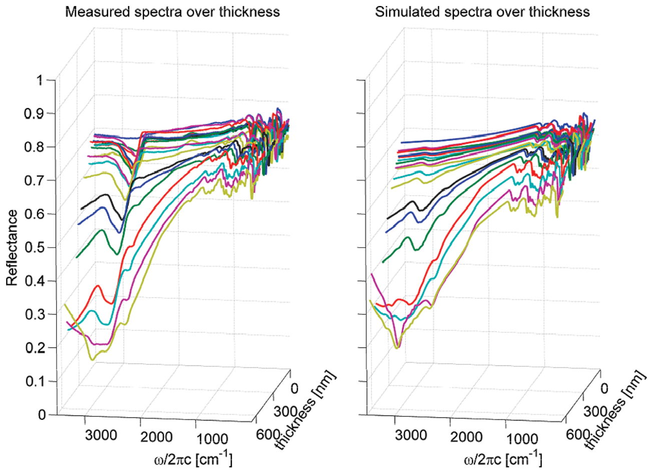

Figure 3. The s-polarized IR spectra as a function of cellulose film thickness: (left) measured spectra, (right) spectral simulations.

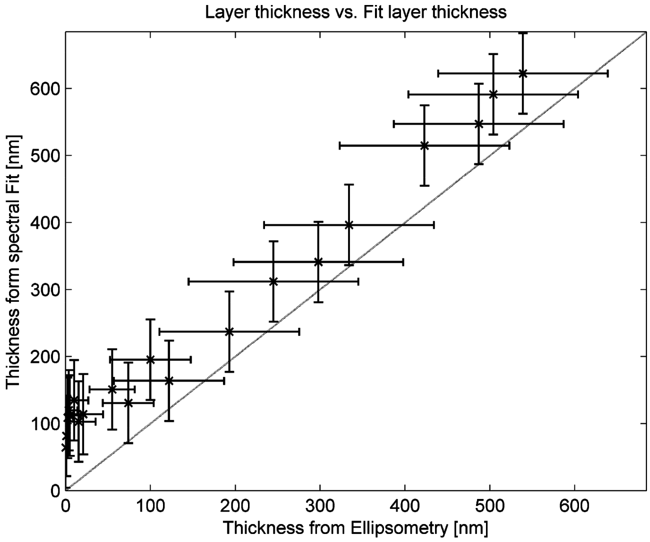

Figure 4. Thickness obtained from the simulated spectra versus the film thickness measured via spectroscopic ellipsometry in the visible range.

plotted against the film thickness (Figure 4), as measured by spectroscopic ellipsometry. This is a more direct approach to illuminating the systematic influence of cellulose film thickness on the RAIRS data than merely calibrating the measured band intensities (compare to Figure 2).

In fact, RAIRS data can be applied to estimate the thickness of the measured films. Figure 4 reveals that the thickness values are in good agreement within their confidence intervals for values over 100 nm. Below 100 nm the spectroscopic approach does not seem to be sufficiently sensitive for thickness determination. This is due partly to the aforementioned noise and partly to unknown optical constants of the cellulose film in the infrared region, which are approximated from a Kramers—Kroning transformation[18] of a cellulose sample. There is a constant overestimation of the film thickness by the spectral fit. However, the correlation is linear with the correct slope, and the deviation is within the confidence intervals (see line in Figure 4).

Here, one has to note two factors that influence the data. First, the liquid nitrogen cooled detector has a tendency to adsorb water on its window, which cannot be avoided completely, leading to an increase in the OH intensity over time, which cannot be distinguished from the increase due to cellulose. Second, there is an influence on the signal due to the surface roughness which increases with increasing cellulose film thickness.[11] This also leads to a change in the background of the IR signals, which cannot be accounted for in the simulation.

A way to get rid of the water signal on the MCT detector is to look at the ratio of p-polarized to s-polarized spectra. Here the signal of the ultrathin water layer on the detector will cancel itself out because the layer is isotropic in the lateral directions and measured under vertical illumination.[10] This leads to the same signal for s- and for p-polarization. However, the problem with the different roughness of the films still plays a role, and in the simulation of the ratio of p- to s-polarization one would have to take into account the effect of depolarization on the rough surface.

In our simulation approach, the roughness can only be simulated by an energy loss function, which is sufficient for normalized single spectra but does not account for depolarization. This causes a large difference in the baselines between simulation and experiment for the ratio of p- to s-polarized light, and fitting the ratio of p- and s-polarized spectra becomes impossible. Therefore, only the s-polarized spectra were used for fitting within the scope of this paper.

The experimental results (Figures 1 and 2) together with spectral simulations (Figures 3 and 4) demonstrate that the band intensities in a RAIR spectrum are quantitatively influenced by the thickness of a supported polymer film. Because RAIRS is one of the few ways to gain information about organic functional groups in supported films, this finding has implications in characterization of thin polymer films. For example, if aging has resulted in chemical alterations and thickness loss in a thin polymer film, the thickness change must be taken into account when quantifying the extent of chemical changes by RAIRS.

CONCLUSIONS

With thin supported polymer films, the spectral data from RAIRS were systematically influenced by the film thickness. This effect must be considered when RAIRS is applied to characterize the impact of treatments that may affect the film thickness, such as solvent-induced swelling, aging effects, or chemical reactions within the film. In addition, when an optical simulation of the obtained spectra was carried out, it was actually possible to quantify the film thickness from the RAIRS spectra if the thickness values were above 100 nm.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, specific information on the simulation of the IR spectra, and detailed description on the integration of the IR bands. This material is available free of charge via the Internet at http://pubs.acs.org.

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