Field Manipulation of Infrared Absorption Properties in Thin Films

Karsten Hinrichs,* Jörg Rappich, and Timur Shaykhutdinov

Infrared (IR) spectroscopy is a sensitive technique for fast and comprehensive analyses of organic and hybrid organic–inorganic materials, surfaces, and thin films. For interpretation of reflection and absorption IR spectra of thin films, vibrational bands in unpolarized IR spectra are often directly inspected. This approach can lead to misinterpretations. Herein, the influence of anisotropy and oscillator strength on the frequency and shape of observed vibrational bands in IR spectra of thin films is investigated. IR ellipsometric, polarization-dependent reflectance spectra and polarization-dependent atomic force microscope–IR spectroscopy (AFM–IR) nanopolarimetric absorption measurements of an about 84 nm thick anisotropic polyimide film (PI-2611) are compared. The s- and p-polarized spectra are used for separation of in-plane and out-of-plane absorption components. The far-field spectra are interpreted by analytical modeling. In detail, the frequency range of bands related to antiphase and in-phase C=O stretching vibrations of the imide rings is investigated. For the antiphase C=O vibration as a relatively strong oscillator, the manipulation of absorption by the incident radiation-induced electric fields in direction normal to the surface can be revealed in p-polarized reflectance spectra and is identifiable in the p-polarized IR nanopolarimetric absorption spectra.

1. Introduction

Because of its high sensitivity and the access to chemical and structural analyses, infrared (IR) spectroscopy is used for sensing and analytical purposes as state-of-the-art spectroscopy for noncontact and nondestructive characterizations. In particular, IR characterizations of thin films and surfaces of organic and hybrid materials are of high relevance for research and technological applications in many fields of optics, electronics, and biomedicine. IR ellipsometric and related polarimetric methods (“Ellipsometry and reflection polarimetry are almost synonymous”) offer the possibility to investigate thickness as well as anisotropic and structural properties of the specimen in detail. With respect to the lateral resolution, classical far-field IR spectroscopies can probe samples down to the mid-IR diffraction limit of a few micrometers. For the IR spectroscopic analyses beyond the mid-IR diffraction limit, photothermal techniques can achieve high chemical and structural contrast at high sensitivity.

Combining the photothermal atomic force microscope–IR spectroscopy (AFM–IR) technique with a polarizing unit (also called IR nanopolarimetry) enables studies of local anisotropic film material properties with lateral resolutions around 30 nm.

A textbook example for a film with isotropic morphology exhibiting anisotropic absorption is a thin silicon oxide film. Here, both the far-field spectroscopic and the AFM-related photothermal expansion measurements can identify vibrations and field-related absorptions. Figure 1 shows the measured p-polarized reflection spectrum of an 11 nm thick amorphous oxide film and an AFM–IR spectrum of a 100 nm thick silicon oxide at 70° incidence angle.

Apart from the band around 1060 cm⁻¹ corresponding to the SiO₂ stretching vibration, also another band shifted by about 185 cm⁻¹ to higher wavenumbers is seen in the p-polarized spectra. Note that the observed band positions may vary in dependence of preparation conditions of the oxides and their thicknesses as well. This band is present at the frequency of the Berreman mode (BE) in both the electrochemically prepared or native amorphous oxide film and the thermally grown SiO₂ layer, and is well known for thin films of SiO₂ [15,16] and other materials with strong oscillators (e.g., Si₃N₄[16]). The band is caused by the enhanced out-of-plane (z) electric fields in the film leading to absorption manipulation. This example shows that even for a thin film with isotropic material properties (absorption indices: kₓ = kᵧ = kₚ) without scattering centers or a structured surface, the absorption properties of the film in the x,y (in-plane) and z-direction can be manipulated to be anisotropic. This holds in a classical reflection measurement as well as in a photothermal absorption experiment (see also Figure S1 and S2, Supporting Information).
However, organic films with weaker oscillators might show complex band shapes in ellipsometric\cite{18,19} or polarization-dependent IR reflection spectra.\cite{20,21} Figure 2 shows measured and calculated ellipsometric tanΨ spectra of a self-assembled monolayer (SAM) on GaAs displaying orientation-dependent band shapes in the CH$_x$ absorption range. Data were taken from ref. [18]. The ellipsometric parameter is defined by tan Ψ = $\sqrt{R_p/R_s}$, where $R_p$ and $R_s$ are p- and s-polarized reflectances, respectively. Apart from the differences of the vibrational band shapes mainly originating from the anisotropic absorption indices of the SAM, also slight frequency shifts of the observed bands relative to the frequencies of the related vibrational oscillators (thin vertical lines in Figure 2c) can be observed.

Summarizing here both the anisotropic absorption indices as well as strong oscillators may be responsible for the fact that IR spectra of thin films are not directly interpretable. Ellipsometric tanΨ spectra may show complex vibrational band shapes because of the dependence on both the in-plane and the out-plane absorption properties. As shown in ref. [21] for a thick polymer film, similar complex band shapes can be observed in p-polarized reflection spectra. In this article, we will study such effects in detail by a thorough discussion of s- and p-polarized reflection and photothermal absorption spectra for a thin film of an organic material.

The optical properties of a thin anisotropic PI-2611 film and bandshape manipulation observable for polarization perpendicular to the surface will be discussed in the frequency range of the anti- and in-phase C=O vibrations of the imide rings of PI-2611.

Anisotropic polyimide films and materials have various applications, for example, in display technology,\cite{22,23} and encapsulation and protection of electronic devices,\cite{24} or as colloidal materials or emulsions at interfaces which are stabilized by particles,\cite{25} gels for Li-ion batteries,\cite{26} and membranes for pervaporation and biofuels separation.\cite{27}

The effect of manipulation of absorption by the incident radiation-induced electric fields in direction normal to the surface discussed in this article is also relevant for interpretation of typical (unpolarized) reflection and transmission measurements of materials exhibiting strong oscillators. This manipulation of absorption also affects unpolarized reflection spectra of PI-2611 (see Figure S1, Supporting Information). In addition, an example for an isotropic thin organic film is provided in the Supporting Information. Figure S2, Supporting Information, shows polarization-dependent AFM–IR spectra of a 4.5 nm thick maleimidophenyl film where manipulation of absorption can be observed as well. Such effects may also occur in IR spectra of thin films of biomedical compounds and proteins.

![Figure 1](https://example.com/figure1.jpg)

**Figure 1.** a) The p-polarized reflectance spectrum of an 11 nm thick electrochemically prepared silicon oxide film at 70° incidence angle. b) AFM–IR spectrum of a thermally grown SiO$_2$ film. Adapted with permission.\cite{14} Copyright 2017, Optical Society of America.

![Figure 2](https://example.com/figure2.jpg)

**Figure 2.** a) Measured tanΨ spectra of an octanedithiol (C8DT) and a hexadecanethiol (HDT) SAM on GaAs. b) Sketch of the respective layers on GaAs. c) Calculated spectra for tilt angles of 12°, 18°, 24°, 30°, 36°, and 42°, respectively. Details on measurement and optical layer calculation can be found in the study by Rosu et al.\cite{18} In ref. [18], the determined tilt angles for HDT and C8DT were 19° and larger than 30°, respectively. Adapted with permission.\cite{18} Copyright 2009, American Chemical Society.
and could in particular be relevant when IR spectra in the amide-I range are interpreted with respect to structural properties.

2. Results and Discussion

In the following part, first in-plane properties in the s-polarized reflection spectra \( R_s(y) \) are discussed followed by the discussion of the in-plane and out-of-plane properties in the p-polarized spectra \( R_p(x,z) \). As the polymer film has uniaxial symmetry, the same absorption index for the in-plane directions \((x,y)\) can be assumed. The observed optical anisotropy of the film is a result that is typically found for such polyimide films (see ref. [21] and references therein). The difference in anisotropy of the bands related to the antiphase and in-phase vibrations is a result of the twisted imide rings of the polymer chains, which can be proven by density functional theory (DFT) calculations.[10]

The in-plane absorption index of the 84 nm thick polyimide film is shown in Figure 3a together with the respective oscillator parameters applied for the simulation (see the Experimental Section). Two characteristic bands can be identified in the in-plane absorption index \( k_x = k_y \). The weak band at 1775 cm\(^{-1}\) is related to the in-phase C=O vibrations of the imide ring and the stronger one at 1715 cm\(^{-1}\) to the antiphase C=O vibrations.[10,21] The latter band shows a slightly asymmetric shape pointing to an additional oscillator contribution on the higher frequency side at 1725.7 cm\(^{-1}\) as it also was required for the best-fit simulation of the spectra. In Figure 3b, the measured and simulated s-polarized reflectance spectra are shown. The measured s-polarized reflectance spectrum is almost identical to the calculated spectrum and the related \( k_x = k_y \) spectrum. A minor deviation can be explained by the overlapping second component at 1725.7 cm\(^{-1}\).

Figure 3c shows the out-of-plane absorption index \( k_z \) of the 84 nm thick polyimide film together with the respective oscillator parameters.
parameters applied for the simulation. Comparing in-plane \((x,y)\) and out-of-plane \((z)\) parameters, a similar set of oscillators, but with slightly shifted frequencies, can be found. While inspecting the values for oscillator strengths \(F_i\) in Figure 3c for the in-plane \((x,y)\) and the out-of-plane \((z)\) directions, it can be seen that the antiphase vibration is almost isotropically distributed in contrast to the weaker in-plane vibration that shows a strong anisotropy with preferential in-plane orientation.

Inspecting now the \(p\)-polarized reflectance spectrum in Figure 3d in detail, it can be decomposed into contributions related to the in-plane and out-of-plane components. Here, the spectra were calculated considering the complete oscillator set and either the in-plane or out-of-plane absorption only by setting the respective projected oscillator components of the other direction to zero. The calculated in-plane spectrum almost reproduces the shape of the in-plane \(k_x = k_y\) (shift \(<1\ cm^{-1}\) ), whereas the spectrum calculated for the out-of-plane components shows significant differences with the out-of-plane absorption index \(k_z\). For the \(\nu_{\text{C}=\text{O}}\) anti-phase vibration, the band frequency is considerably shifted by about \(17\ cm^{-1}\) with respect to the frequency of the maximum of the same band in the out-of-plane absorption index \(k_z\). In this case, the manipulation of the out-of-plane absorption by the electric fields perpendicular to the surface leads to a downward-pointing part of the band in the \(p\)-polarized reflection spectrum.

Compared with the silicon oxide films (Figure 1), the observed shift is smaller because of the weaker oscillator strengths in the polyimide. However, for silicon oxides, smaller shifts can be found during initial oxidation of the silicon surface where the density of oscillators (corresponding to the oscillator strengths per volume) is lower than in a thicker film.\(^{15}\)

The discussed behavior of the measured and calculated \(p\)-polarized reflection spectra as shown in Figure 3d can also be verified at the nanoscale by means of polarization-dependent AFM–IR absorption measurements (Figure 4a). Here, the data interpretation is consistent with the reflection results. The anisotropy in \(k_x = k_y\) and \(k_z\) (Figure 3a,c respectively) manifests itself in a corresponding \(3\ cm^{-1}\) shift of the antiphase \(\nu_{\text{C}=\text{O}}\) stretching vibration where the \(p\)- and \(s\)-polarized maxima in the IR nanopolarimetric spectra in Figure 4a are around \(1718\) and \(1715\ cm^{-1}\), respectively. The higher amplitude of the in-plane \(\nu_{\text{C}=\text{O}}\) vibration around \(1775\ cm^{-1}\) in the \(s\)-polarized IR nanopolarimetric spectrum is due to the predominant in-plane orientation of the PI-2611 polymer chains in accordance with \(k_x = k_y\) and \(k_z\). However, the manipulation of the out-of-plane absorption is a stronger effect. It can be identified as a shoulder of the anti-phase \(\nu_{\text{C}=\text{O}}\) band in the \(p\)-polarized measurement toward higher wavenumbers and is better represented by calculating the difference between the \(s\)- and \(p\)-polarized spectra as shown in Figure 4c. Here, the minimum at \(1735\ cm^{-1}\) cannot be explained by considering the absorption indices only. This dominating effect coincides with the calculated \(R_p\) (\(z\)-component only) from Figure 3d proving its origin.

The manipulation of the out-of-plane absorption can also be mapped as demonstrated by the IR nanopolarimetric scan consisting of ten spectra for each polarization in Figure 4d. The data were collected according to the markings in the AFM image of the \(84\ nm\) thick PI-2611 film (Figure 4e, left to right starting with the top row). The spectra show the homogeneity of absorption properties at the nanoscale where the field-induced effect is seen in \(p\)-polarized measurements in consistency with Figure 4c.

---

**Figure 4.** a) Normalized polarization-dependent AFM–IR spectra with marked \(3\ cm^{-1}\) shift of the antiphase \(\nu_{\text{C}=\text{O}}\) maximum. b) Schematic of the experimental setup. c) Difference spectrum \((s - p)\) of the data shown in part (a) highlighting the field manipulation of the absorption properties. d) Film homogeneity via spectral mapping of the IR nanopolarimetric line scan with the normalization applied for each spectrum. e) Corresponding AFM image with the indicated positions of the line scan.
3. Conclusion

For a thin polymer film, both field and anisotropic absorption indices-related band manipulations were identified in the p-polarized reflection spectra. In contrast, the s-polarized reflection spectra resemble the in-plane absorption properties of the material. A corresponding result was also identified in absorption measurements at the nanoscale using the photothermal AFM–IR technique. The observed effect, the occurrence of a considerably frequency-shifted band (of about 17 cm\(^{-1}\)) for the organic film, is less strong compared with the silicon oxide film but arises in both cases because of the electric fields in direction normal to the surface. The smaller shift is a result of the much weaker oscillator strength of the polymer compared with the silicon oxide.

This study shows that for thin films of materials with weak oscillators a direct discussion of IR band properties in reflection and in nanoparticlespectra is possible. The situation is much more complex for materials with stronger oscillators because of the manipulation of the band shapes and frequencies by the electric fields within the thin films. For the interpretation of IR reflection measurements of thin films with strong oscillators, it is essential to consider (even for isotropic thin films) that band shapes and frequencies cannot be comprehensively understood without complementing analytical optical calculations.

4. Experimental Section

Materials and Chemical Reagents: Organic layers. Polyimide layers of PI-2611 (DuPont) on thin oxide-covered c-Si substrates were prepared by imidizing a precursor by thermal annealing of the spin-coated polymer layer. The thin oxide film below the polyimide film consisted of a native oxide film with amorphous SiO\(_2\) structure. Studies of comparable polyimide films showed a glassy polymer with a density of about 1.46 g cm\(^{-3}\).[10] Further details on the preparation and properties can be found in the study by Buchhold.[10] The molecules of such polyimide films showed a uniaxial geometry with preferential orientation parallel to the surface plane.[11] The different anisotropic behavior of in-phase and antiphase C=O stretching vibrations in such a film could be explained by the different directions of the transition dipole moments of the respective vibrations where the one of the in-phase vibration was predominantly parallel to PI-2611 backbone orientation.[10]

Silicon oxide (Figure 1a) formation. The p(B)-doped c-Si(111) sample with a specific resistance of 0.5–2 \(\Omega\) cm (Sierteg Wafer, Germany) was electrochemically oxidized in two steps. First, the sample was galvanostatically anodized in pure water at 10 \(\mu\)A cm\(^{-2}\) until a voltage of 3 V was reached. Then, the Si sample was polarized at \(+8\) V for 1 h so that the current decayed slowly.

Spectroscopic Methods: Visible (VIS) ellipsometric measurements were performed with an M-44 from J.A. Woollam, USA. The thickness of the PI-2611 polyimide layer was determined from VIS ellipsometric measurements at four incidence angles (60°, 65°, 70°, and 75°) in a three-layer model (silicon/1.9 nm SiO\(_2\)/uniaxial PI-2611) to be at 83.8 ± 0.3 nm.

For an optically homogenizable material, an analytical simulation in an optical layer model was used for the interpretation of the measured IR spectra. The calculations[16,18] were performed in a model for isotropic and uniaxial layers. The dielectric functions in the \(n=x=y\) (in-plane), \(z\) (perpendicular to the surface plane) directions are given by \(\varepsilon_n = \varepsilon_x = \varepsilon_y\) and the complex refractive index is defined as \(n = \sqrt{\varepsilon_n}\), where \(n = n + i k\) is the sum of the real part of the refractive index and the absorption index \(k\). The vibrational bands are represented by Lorentzian oscillators with wavenumber \(\nu_0\), parameter for the oscillator strength \((F)\) and full width at half maximum (FWHM) \((F')\) to yield the complex dielectric function \(\varepsilon = \varepsilon' + i \varepsilon''\) with

\[
\varepsilon' = \varepsilon_\infty + \sum_i \frac{F_i (\nu_0^2 - \nu^2)}{\nu_0^2 - \nu^2 + (\Gamma_i \varepsilon)^2}
\]

\[
\varepsilon'' = \frac{8 \pi F_i \varepsilon_n}{k_\text{B}T} \sum_i \frac{F_i}{\nu_0^2 - \nu^2 + (\Gamma_i \varepsilon)^2}
\]

The measured IR spectra of the polymer films were analyzed within a uniaxial three-layer model (Si/1.9 nm SiO\(_2\)/83.8 nm PI-2611). The high-frequency values were adapted from ref.[21] \(\varepsilon_\infty = \varepsilon_\infty = 3.0976\), \(\varepsilon_\varepsilon = 2.4336\). The thickness of 83.8 nm was taken from the VIS ellipsometric evaluation. As the ellipsometric spectra were calculated from a set of spectra taken at different polarizations, they represented absolute values and no further reference sample was required.

The reflectance spectra were measured against the empty channel as reference. The baselines showed a slight mismatch with the calculated spectra that was corrected by a scaling factor of about 0.9522. The IR optical constants \(n'\) and \(k\) were determined from a combined fit on \(R\) and \(tan\Psi\).

IR spectroscopic and ellipsometric tan\(\Psi\) spectra were taken with an ellipsometric setup externally attached to a FT-IR spectrometer (TENSOR 37 or IFS 55, Bruker, Germany) with a spectral resolution of 4 cm\(^{-1}\) at an incidence angle of 65° using a liquid nitrogen-cooled mercury cadmium telluride detector (for details, see refs. [8,16,18]). The evaluation of the IR spectroscopic spectra was performed with the SpectraRay3 software from SENTECH Instruments GmbH, Germany. A lateral variation of anisotropy was not observed for a thicker similarly prepared PI-2611 film where a slight variation of thickness of about 1% (17 nm) over the length scale of 13 mm was detected in the study by Hinrichs.[10] For the 84 nm sample, we found a maximum thickness variation of about 2 nm along a line of 13 mm. For all IR- or VIS ellipsometric measurements, the probed spot sizes were dependent on the incidence angle.

The polarization-dependent AFM–IR measurements were performed using a commercial NanoIR2-FS setup (Anasys Instruments Corporation) equipped with a pulsed mid-IR QCL (MIRCat, Daylight Solutions Inc.) in top-down configuration and a polarizing unit. All measurements were performed in contact mode using gold-coated silicon AFM tips with a nominal radius of curvature of the tip apex of 30 nm corresponding to the typical lateral resolution of the method. Spectra were collected at 70° angle of incidence to the surface normal and normalized to QCL light intensity. Spectral resolution of 1 cm\(^{-1}\) was accessible at 20 cm\(^{-1}\) s\(^{-1}\) sweep rate. Savitzky–Golay filtering was applied to spectral data. The AFM height image was collected using a scan rate of 0.2 Hz per line with a rectangular resolution of 500 × 200 pixels for faster data acquisition. For further details regarding the experimental setup, please see ref. [31].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Ilona Engler and Özgür Savaş at ISAS, Department Berlin, for their technical support. The authors are indebted to Margarita Günther from TU Dresden, Klaus-Jochen Eichhorn and Karin Sahre from IPP Dresden for preparation and VIS ellipsometric characterization of the polymer film. The authors thank Andreas Furchner from ISAS for fruitful discussions and valuable comments. The financial support by the Ministerium für Innovation, Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Regierende Bürgermeister von Berlin—Senatskanzlei Wissenschaft und Forschung, and the Bundesministerium für Bildung und Forschung are also gratefully acknowledged. K.H. acknowledges funding by the European Union through EFRE 1.8/13.

Phys. Status Solidi B 2020, 257, 1900490
1900490 (5 of 6) © 2019 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
Conflict of Interest
The authors declare no conflict of interest.

Keywords
absorption, anisotropy, chemical analyses, nanospectroscopy, polarimetry, polymer films, thin films