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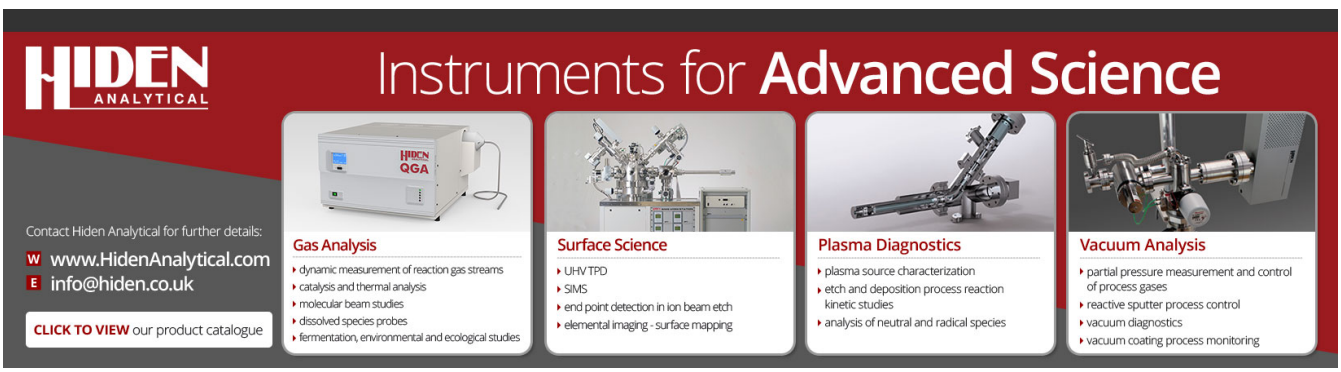

Brilliant mid-infrared ellipsometry and polarimetry of thin films: Toward laboratory applications with laser based techniques

Karsten Hinrichs,[a] Timur Shaykhutdinov, Christoph Kratz, and Andreas Furchner
Leibniz-Institut für Analytische Wissenschaften—ISAS—e.V., Schwarzschildstr. 8, 12489 Berlin, Germany

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Tunable quantum cascade lasers (QCLs) have recently been introduced as mid-infrared (mid-IR) sources for spectroscopic ellipsometric and polarimetric setups. QCLs, with their unique properties with respect to coherence and brilliance in either pulsed or continuous-wave operation, are opening up numerous new possibilities for laboratory and industrial applications. In this review, the authors will focus on thin-film characterization techniques like ellipsometric and nanopolarimetric methods and summarize related state-of-the-art techniques in this rapidly developing field. These methods are highly relevant for optical, electronical, and biomedical applications and allow detailed structural analyses regarding band properties, spectra–structure correlations, and material anisotropy. Compared to classical Fourier-transform-IR spectroscopy, thin-film sensitivity can be achieved at high spectral and spatial resolution (<0.5 cm^{-1}, <150 μm). Measurement times are reducible by several orders of magnitude into the millisecond and microsecond range with laser-based polarimetric setups involving modulation or single-shot concepts. Thus, mid-IR ellipsometric and polarimetric hyperspectral imaging can be performed on the time scale of minutes. For mid-IR ellipsometric imaging, thickness and structure information become simultaneously accessible at spatial resolutions of a few 100 μm and possibly even at the micrometer scale by the integration of microscopic concepts. With the atomic force microscopy-infrared spectroscopy based nanopolarimetric approach, anisotropy in the absorption properties can be investigated with lateral resolutions beyond the diffraction limit, reaching a few 10 nm. © *2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1116/1.5122869

I. INTRODUCTION

This article reviews polarization dependent mid-infrared (mid-IR) spectroscopic methods and several basic characteristics of the measurement concepts using brilliant light sources. Examples of recent results in this field related to the IR ellipsometric,[1–5] near-field microscopic,[6] and nanopolarimetric atomic force microscopy-infrared spectroscopy (AFM-IR)[7–14] analysis of organic thin films and anisotropic molecular aggregates are discussed.

Brilliant laboratory sources, such as optical parametric oscillators and laser sources, as well as tunable free-electron lasers (FELs) and synchrotron radiation sources, have been very important in pushing the development of modern mid-IR spectroscopy.[15–21] The availability of tunable quantum cascade lasers (QCLs)[22–25] significantly broadened the number of IR spectroscopic applications and motivated novel concepts in the research of solid, liquid, or gaseous materials.[1–14,26–39] However, elaborated polarization dependent IR spectroscopic methods, such as IR ellipsometric[1–5,40–55] and IR nanoscopic[6–14,33–38] techniques, are necessary for a reliable determination of band properties, spectra–structure correlations, and macromolecular orientations in thin films, thereby being essential for comprehensive studies of structured or anisotropic surfaces. The latter point is of particular importance in technological applications because anisotropy and structure are essential for physical, chemical, and functional properties of materials in optoelectronic, polymer, plasmonic, and biorelated research (see Refs. 1–34 in Ref. 11).

To understand the structural correlations over different length scales, our specific aim is to determine spectra–structure interrelationships from macroscopic to nanoscopic dimensions. In some cases, when having sufficient preknowledge of reference data or the specific optical and material properties, ellipsometric and polarimetric IR spectra might be interpreted with respect to the anisotropic structure, ordering and interactions by direct inspection. In the general case, calculations or simulations based on analytical and/or numerical methods are required in order to achieve a comprehensive in-depth interpretation.[40–45] For instance, measured IR spectra of inorganic and organic thin films can be interpreted within optical simulations involving oscillator models to describe vibrational or electronic absorptions.[11,43,45]

II. METHODIC ASPECTS

In this section, historical and technical aspects regarding brilliant light sources and their combination with polarimetric and ellipsometric methods are reviewed. The interplay between light source and method facilitates temporally and laterally resolved measurement conditions that are not achievable with classical Fourier-transform-IR (FT-IR) techniques. Single-shot optics can be introduced for simultaneous measurements of different polarization states, even for individual laser pulses.[2]

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[a]Electronic mail: karsten.hinrichs@isas.de

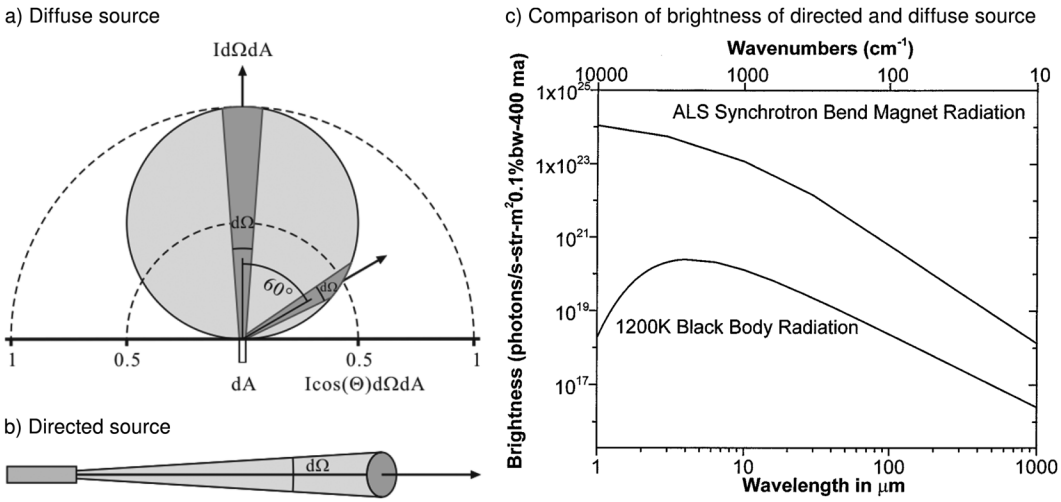

FIG. 1. (a) Schematic sketch of a diffuse (globar) and (b) directed radiation source (laser, synchrotron). (c) Brightness of the Advanced Light Source (ALS) synchrotron compared to 1200 K black body radiation. Reprinted with permission from Raab and Martin, Planta **213**, 881 (2001). Copyright 2001, Springer Nature.

A. Brilliant radiation sources for mid-infrared spectroscopy

For optical analytical methods in the mid-IR spectral range, many different brilliant radiation sources have been used in the last few decades. Beside FELs[21] and synchrotron radiation sources,[20,56] many different types of lasers, such as semiconductor lasers,[22–25,57] doped solid state lasers,[16,17] and gas lasers,[15] were utilized. Promising new tunable IR sources are based upon optical parametric oscillators,[18,19] external cavity quantum cascade lasers, and, since recently, frequency comb techniques.[19] Early semiconductor lasers in the mid-IR spectral range, e.g., lead salt laser,[58] suffered from several limitations like restricted temperature ranges for operation, limited power, and small tuning ranges.[25] Such lasers employ interband transitions of the material for their emission. In contrast, QCLs employ intersubband transitions in specifically designed and sophisticated multilayer quantum-well structures. The energy of intersubband transitions, and hence the emission of the QCL, can be finely tuned, e.g., during growth (stack-structure, QW thickness, QW composition)[22–24] and also during operation (e.g., operation current, external cavity), yielding tailored emission profiles of the laser in a broad range. For example, an external cavity configuration allows for a precise selection of the emission wavelength, offering a broad tuning range with distinctively improved operation characteristics.[24] Such QCLs have developed rapidly, as stated almost a decade ago in Ref. 25: "In the short span of fifteen years QCLs have gone from a lab curiosity to the role of major players in the high-power and chemical sensing sector."

Compared to classical thermal sources (e.g., globars), the brilliant radiation of synchrotron, FEL, and lab-based lasers offers, in addition to enhanced coherence properties, a much higher brightness in the IR spectral range. The photometric brightness (or luminance) of a flat diffuse emitter like a globar is defined as the luminous flux per unit solid angle (dΩ) and unit projected source area [cos(θ)dA].[15] For directed synchrotron sources, the corresponding term *brilliance*[59] is often used. It is typically defined per 0.1% bandwidth.[59] Schematically shown in Fig. 1 are the different emission characteristics of a diffuse source [see Fig. 1(a)] and a directed source [see Fig. 1(b)], responsible for the order-of-magnitude higher brightness of, e.g., a synchrotron source [see Fig. 1(c)].

B. Development of polarimeters and ellipsometers with brilliant radiation sources

In the last few decades, several IR ellipsometers were installed at synchrotron beamlines and FELs.[47–53,61,62] To our knowledge, the first far-IR synchrotron ellipsometer was installed at the National Synchrotron Light Source (NSLS) in Brookhaven in 1997,[47] followed in 1998 by one at MAX-lab in Lund, Sweden.[48] Mid-IR/far-IR ellipsometers came into operation in 2003 at BESSY (Refs. 49 and 62) in Berlin and at ANKA in Karlsruhe.[50] The ellipsometer at NSLS was updated in 2013 by a combined rotating-analyzer and Mueller-matrix ellipsometer.[51] In 2018, a Mueller-matrix ellipsometer for the mid-IR spectral range[52] was installed at SOLEIL in Paris.

However, in the recent years, brilliant IR sources have been adapted to polarimetric and ellipsometric laboratory setups. In 2011, a photoelastic-modulator-based setup equipped with a tunable QCL was applied for measuring vibrational circular dichroism of chiral solutions.[39] In contrast to these chirality studies, many other new applications in the field of polarization dependent infrared spectroscopy are aiming toward interface and thin-film characterizations. The first mid-IR laser mapping ellipsometric investigation for this purpose was reported in 2015 using multiple-angle rotating-analyzer ellipsometer equipped with a 3.39 μm HeNe laser.[4] It was applied for the mapping of inhomogeneous films of poly(3-hexylthiophene) and poly(*N*-isopropylacrylamide) (PNIPAAm).[4] Compared to classical IR ellipsometers[43–46] using the FT-IR technique, the laser ellipsometer enabled significantly shorter measurement times (80 ms) per measured spot, as well as about a tenfold increase in lateral resolution (120 μm) while retaining thin-film

sensitivity.[4] In 2017, two research groups have established IR spectroscopic ellipsometers equipped with tunable QCL sources. One device was an IR Mueller-matrix scatterometer with six tunable EC-QCLs from 4.35 to 9.71 μm and two gas lasers (3.39 μm—HeNe, 10.6 μm—CO_2) in a dual-rotating-retarder configuration[1] at single-wavelength operation. The other was a spectroscopic IR ellipsometer with a tunable QCL (5.56–6.49 μm) incorporating a single-shot concept for simultaneous measurements of different polarization states.[3] Both ellipsometers were intended for measurements of structured surfaces, the latter also for studies of thin films of organic materials. Following the photoelastic-modulator-based tunable QCL setup in Ref. 39, a spectroscopic ellipsometer with subsecond temporal resolution for transmission measurements was presented in 2019.[5] The latest development is a subdecisecond spectroscopic ellipsometer based on a tunable QCL with a single-shot design in reflection geometry.[2]

In Fig. 2, optical constants of a typical amide-polymer thin film are shown together with spectral ranges so far accessible by IR laser ellipsometers. It is apparent that a broad part of the so-called fingerprint range can be measured with the usage of QCL sources. For example, the spectral range of the amide I and amide II bands, which are highly relevant marker bands in the analysis of biorelated polymers, peptides, and proteins,[63] can now be sensitively studied.

For completeness, we would like to mention that laser-based time-domain ellipsometry typically used in the terahertz range can reach the lower part of the mid-IR spectral range.[64]

C. Single-shot concepts

In contrast to mid-IR ellipsometer designs based on rotating retarders, rotating polarizers, or polarization modulators as well as FT-IR devices, single-shot concepts[54,65] can be used for simultaneous measurements of different polarization states. Well-known approaches are division-of-amplitude (DoA), division-of-wavefront (DoW), and division-of-focal-plane (DoFP) optics. In DoA concepts, prisms or beamsplitters can be used to split the beam into multiple paths, which in turn are equipped with separate polarizers.[54,65] Single-path geometries that employ a sequence of detectors and polarizers are also possible.[54] In DoW optics, the wavefront of a light beam is split into segments upon separate polarization measurements.[54] In a DoFP optics, the polarizers are placed onto the pixels of an image detector.[65]

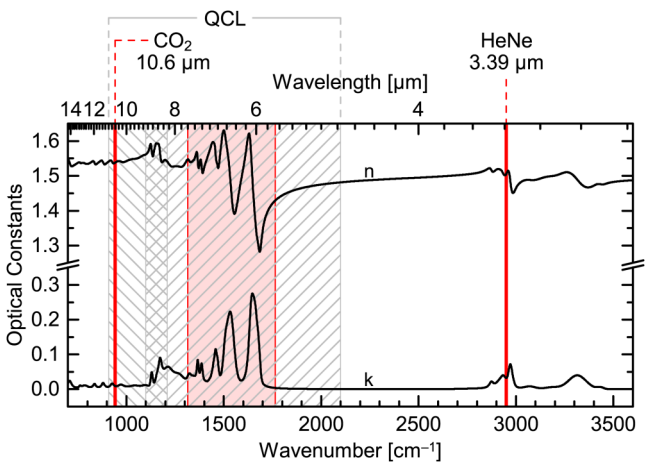

FIG. 2. PNIPAAm optical constants (data from Ref. 3) together with the spectral ranges so far accessed by mid-IR ellipsometers using IR laser sources in Refs. 1–5. The hatched areas indicate the different used QCL ranges.

Unlike in sequential measurements, the time-dependent variation of pulse energy or source intensity can be corrected for by the simultaneous measurement of different polarization states for single pulses or distinct time windows, enabling measurements even with noisy radiation sources. Regarding time-resolved measurements, such single-shot concepts can be combined with ellipsometers and polarimeters using pulsed sources, allowing one to perform ellipsometric measurements at the single-pulse level.[2]

III. SINGLE-SHOT MID-IR LASER ELLIPSOMETRY

Synchrotron IR ellipsometers have been in operation since decades, but for a long time there has been a lack of standard brilliant broadband sources for the laboratory. This might be the reason why the first spectroscopic IR ellipsometer in a DoA single-shot concept using a brilliant light source was realized in 2005 at the FEL at the electron linear accelerator in Rossendorf, Germany.[53] The ellipsometer measured sets of 0°/90° and 45°/135° polarizer settings simultaneously [see Fig. 3(a)]. Here, the usage of the single-shot concept made it possible to overcome problems with the noisy FEL radiation source. However, for quantitative ellipsometric single-shot measurements, the optical properties of the used mid-IR KRS5 polarizers turned out to be the most limiting part. Therefore, further work in our group was directed toward the development of a single-shot concept using a DoW approach by introducing a mirror beamsplitter that was moved half-way into the laser beam.[3] This measurement scheme enabled sequential quantitative measurements of sets of 0°/90° or 45°/135° polarization states [see Fig. 3(b)].[3] With this configuration, the first spectroscopic IR ellipsometric measurements utilizing a tunable QCL were performed in 2017.[3] Following this promising approach, a design based on a four-faceted gold-coated pyramid [see Fig. 3(c)] was introduced in 2019 for simultaneous measurements in four detection channels (e.g., 0°, 90°, 45°, and 135°).[2]

With this realized concept involving simultaneous measurements of multiple different polarization states, the following novel ellipsometric applications become available: (i) time-resolved IR measurements at the microsecond to millisecond scale, (ii) laterally resolved measurements in the 100 μm range, and (iii) simultaneous IR ellipsometric amplitude–phase measurements. The latter is potentially highly relevant for applications in the field of process monitoring as it allows sensitive in-line monitoring in ambient industrial environments. As an IR spectroscopic method, the concept is particularly interesting for chemical and structural analyses through inspection and modeling of specific absorption bands, offering new possibilities for the optical analysis of organic and hybrid surfaces, interfaces, and thin films. As such materials can be designed with specific sensing, protection, interaction, and

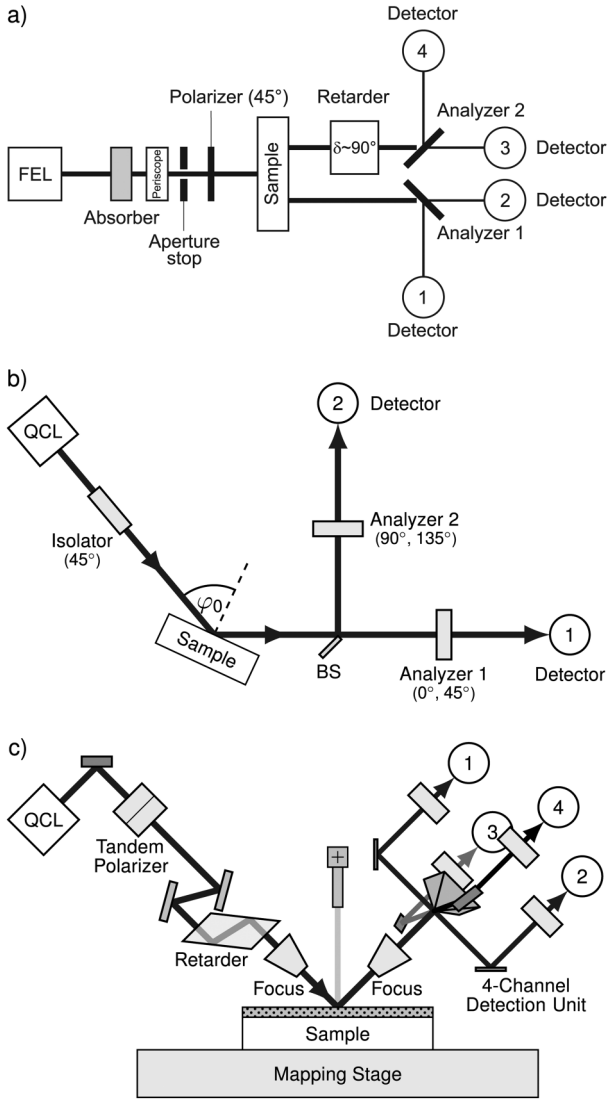

FIG. 3. Configurations of so far realized IR single-shot ellipsometers. (a) Two-channel DoA concept (Ref. 53), (b) two-channel DoW concept using a half-inserted gold mirror (Ref. 3), and (c) four-channel DoA concept using a four-faceted gold pyramid (Ref. 2).

optical properties, they are highly relevant for a plethora of technical applications in interdisciplinary fields ranging from optoelectronics to biomedicine.

Figure 4 highlights three examples of ellipsometric data obtained with such a multi-channel single-shot instrument. Figure 4(a) depicts time-resolved (385 ms) spectral phase–amplitude measurements during the thermoinduced phase transition of a 150 nm thin film of myristic acid (MyA), a fatty acid with potential applications in biomedicine[66,67] and phase-change materials for energy storage.[68,69] Different intermolecular interactions of MyA's carboxyl groups give rise to two ν(C═O) vibrational modes at 1705 and 1716 cm^{-1} with characteristic temperature responses. Figure 4(b) shows maps with $300 \times 130\,\mu m^2$ spatial resolution of the same carboxyl vibrational band extracted from a hyperspectral image of a circular-shaped MyA film. Figure 4(c) demonstrates the stability of the single-shot approach toward environmental changes like humidity. Here, the amide I band of a 14 nm thin PNIPAAm film was measured within 18 s using a conventional IR ellipsometer and compared with single-shot data. Clearly, minute changes in humidity as small as ±0.1% during the measurement cause the amide I band to be masked by water-vapor absorption bands, rendering conventional IR ellipsometry impracticable under such conditions. In contrast, the single-shot IR ellipsometer can handle even substantially higher ambient variations.

IV. MID-IR LASER NANOPOLARIMETRY

Lateral resolutions of a few micrometers, restricted by the diffraction limit, are typically seen as the limit of classical mid-IR techniques. For polarization dependent IR characterizations, microscopic studies of surfaces and thin films with lateral resolutions from about 10 μm are possible depending on the used radiation source.[55,70] Dichroitic measurements using a microscope and a brilliant synchrotron source have enabled lateral resolutions of $10 \times 10\,\mu m^2$.[70] For an ellipsometric IR microscopic study of oxide and polymer films,

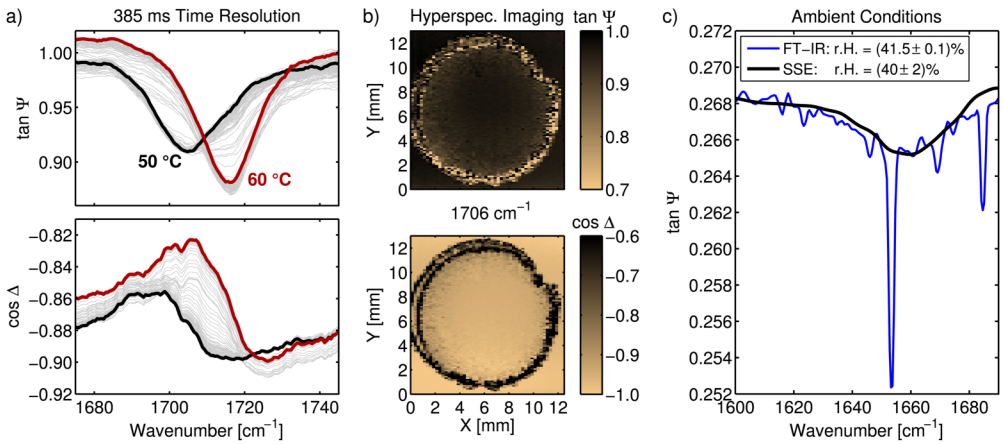

FIG. 4. Results for simultaneous four-channel single-shot IR ellipsometry: (a) time-resolved measurements of the solid-to-liquid phase transition of an MyA film, adapted from Furchner *et al.*, Opt. Lett. **44**, 4387 (2019) and Furchner *et al.*, Opt. Lett. **44**, 4893 (2019). Copyright 2019, Optical Society of America, (b) hyperspectral mapping of tanΨ and cosΔ at 1706 cm^{-1} of a circular-shaped, drop-cast MyA film taken with $300 \times 130\,\mu m^2$ spatial resolution, and (c) environmental measurements of IR single-shot ellipsometry compared with FT-IR data.

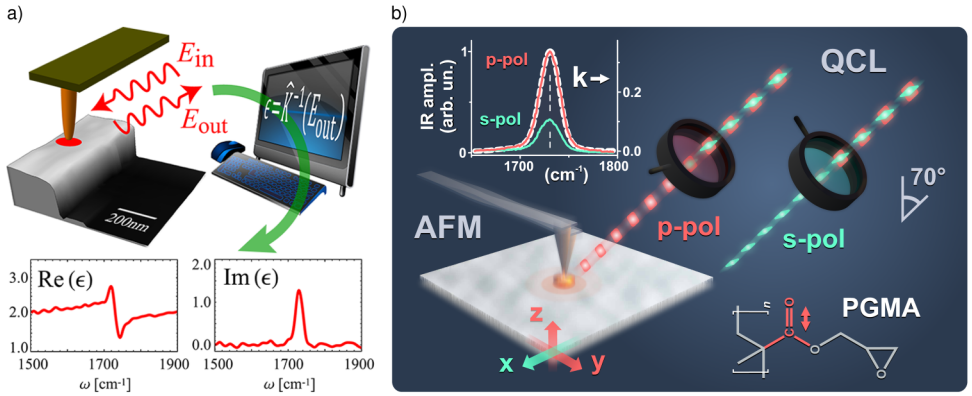

FIG. 5. (a) Schematic of measuring dielectric functions with tip-enhanced near-field microscopy (s-SNOM). Reprinted with permission from Govyadinov *et al.*, J. Phys. Chem. Lett. **4**, 1526 (2013). Copyright 2013, American Chemical Society. (b) Schematic setup of polarization dependent AFM-IR. The inset shows s- (solid line) and p- (solid line, stronger absorption) polarized measurements of a PGMA film together with the absorption index k (white dashed line) as determined from an evaluation of FT-IR ellipsometric data.

lateral resolution of a few 10 μm was realized using a conventional FT-IR globar source.[55]

Beyond the mid-IR diffraction limit, photothermal expansion measurements (AFM-IR) and scattering type near-field microscopic measurements (s-SNOM) can be used to achieve spatial resolutions down to the 10 nm range by combining brilliant light sources with atomic force microscopy.[6–14,33–35] The s-SNOM measurements can determine material related amplitude and phase information, rendering the method suitable for determination of dielectric properties at the nanoscale. This is demonstrated in Ref. 6 showing that dielectric functions can be deduced from an analytical model of sample specific scattering from the AFM tip [see Fig. 5(a)].

For high-sensitivity polarization dependent measurements required for studies of anisotropic organic samples, a restricting issue of s-SNOM is the weaker in-plane polarizability of the AFM tip.[36] This limits analyses of molecular orientation to the out-of-plane projection.[37] However, the in-plane near field of the tip can be enhanced by tilting it toward the sample plane, which is expected to expand the applicability of the method in the future.[38]

The complementary AFM-IR method can deliver both in- and out-of-plane polarization dependent, thin-film sensitive measurements at the nanoscale in the range of the tip radius (several 10 nm). Being a photothermal technique, AFM-IR probes absorption properties via sample expansion under the

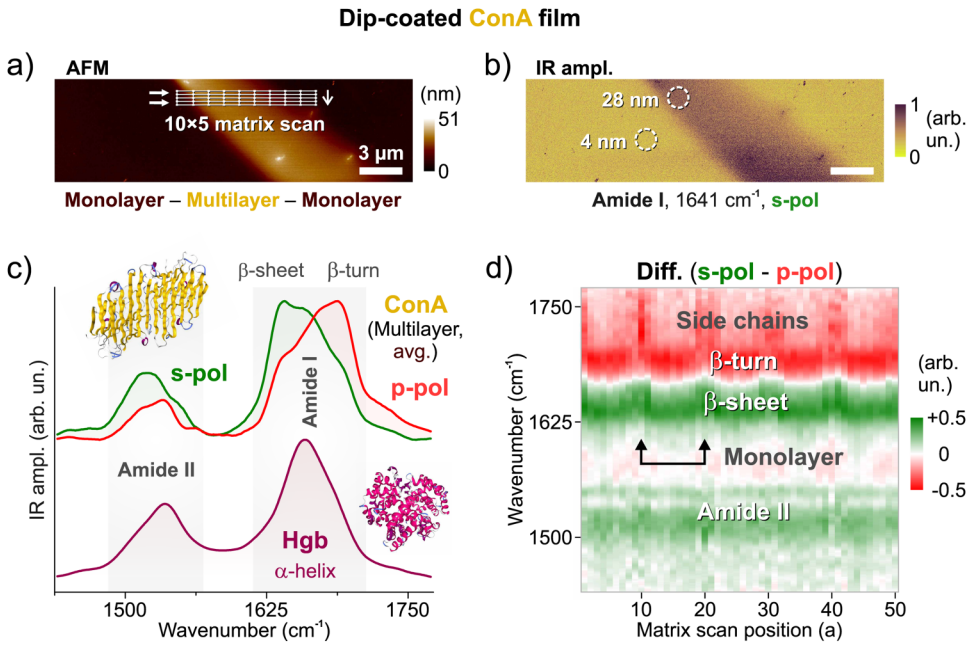

FIG. 6. Orientation of ConA in multi- and monolayers revealed by polarization dependent AFM-IR. (a) AFM image with indicated positions of the performed matrix scan. (b) Corresponding s-polarized IR image of the amide I band maximum with topological information. (c) Normalized spectra of ConA averaged over the entire multilayer region (top) marked in (a) and the isotropic Hgb reference (bottom). (d) IR nanopolarimetric matrix scan shown as (s – p) difference of normalized data. (b)–(d) are adapted with permission from Hinrichs and Shaykhutdinov, Appl. Spectrosc. **72**, 817 (2018). Copyright 2018, SAGE Publications, Ltd.

tip. AFM-IR was established in 2005.[33] By inserting a polarizing element in the incidence light path, defined IR nanopolarimetric absorption measurements can be performed.

First demonstrated using a polymer fiber in 2012,[7] polarization dependent measurements have enabled a wide range of biomedical[8,14] and plasmonic applications.[9,12,13] In Ref. 11, several absorption anisotropy characterizations at the nanoscale by the AFM-IR based IR nanopolarimetric setup used in our group [Fig. 5(b)] are reviewed focusing on various types of thin-film materials, e.g., polymer, protein, graphene, and polaritonic films as well as molecular aggregates. The inset of Fig. 5(b) shows polarization dependent spectra of the C═O stretching vibration of a 101 nm isotropic poly(glycidyl methacrylate) (PGMA) film on Si. The measurements coincide with the ellipsometrically derived absorption index k as demonstrated by the p-polarized spectrum.

Figure 6 summarizes the IR nanopolarimetric investigation of an anisotropic dip-coated Concanavalin A (ConA) film on Au in the range of amide I and amide II bands from Ref. 11. In this study, the correlation between spectra and secondary structure elements[63] revealed the molecular orientation of the β-sheet rich ConA in the monolayer (4 nm) as well as in the multilayer (up to seven molecular layers, 28 nm) regions depicted in Figs. 6(a) and 6(b). Averaged polarization dependent measurements of the anisotropic ConA multilayer together with a spectrum of the isotropic hemoglobin (Hgb) reference with mainly α-helix structure are shown in Fig. 6(c). The dominating β-sheet contribution and the strong β-turn signal in s- and p-polarized spectra of ConA, respectively, can be interpreted by the predominant orientation of β-sheets parallel to the surface confirmed by β-turns normal to it. The monolayer sensitivity of the method is demonstrated in Fig. 6(d).

Another photothermal technique that achieves high lateral resolutions by probing the IR laser induced thermal lensing effect at the VIS diffraction limit is *Mirage* IR microscopy.[71]

V. SUMMARY AND CONCLUSIONS

In the recent years, the development of mid-IR instrumentation for polarimetry and ellipsometry using brilliant light sources has made significant advances. The field is still developing rapidly for standard laboratory applications using commercially available QCL sources.

The combination of QCLs with single-shot concepts allows for simultaneous far-field mid-IR measurements of multiple polarization states, thus providing exceptional measurement parameters including high time (millisecond, microsecond), high spectral (<0.5 cm^{-1}), and high lateral (120 μm) resolutions. Classical FT-IR techniques can be outperformed by several orders of magnitude with respect to hyperspectral imaging, measurement times, and vulnerability to variations of ambient atmosphere. This enables new measurement possibilities for kinetic *in situ* research and the imaging of heterogeneities and anisotropic surfaces and thin films. We believe that such concepts have a high application potential for industrial process control, such as in-line quality control, because multipath optics can be realized with a directed source, and disturbances by absorption bands in the ambient atmosphere can be minimized via simultaneous detection of multiple polarization states. Combining QCLs with AFM allows for IR nanopolarimetric measurements with a lateral resolution down to a few 10 nm, opening up the door to multiscale anisotropic materials characterization.

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