Views

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Mid-infrared laser ellipsometry: a new era beyond FTIR

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Abstract: This view highlights a revolutionary change in IR ellipsometry, namely, the incorporation and application of tunable lasers. The presented instrumental developments beyond classical FTIR-based approaches are coming precisely at the right time for today's demands for *in situ, operando* and hyperspectral characterization methods required in bioanalytics, catalysis and surface science.

Keywords: hyperspectral imaging; infrared polarimetry; metrology of thin films and surfaces; quantum cascade lasers; single-shot infrared ellipsometry; time-resolved in situ spectroscopy.

Pioneered by Arnulf Röseler in the 1980s and 1990s, FTIR-based infrared spectroscopic ellipsometry (IR-SE) [1] became an established and routine non-destructive optical method in research, metrology and process control of thin films and functional surfaces. Coupling the IR ellipsometric technique to a Fourier-transform infrared (FTIR) spectrometer was a groundbreaking milestone that for the first time made possible sensitive IR-SE measurements within minutes.

Combined with modern ultra-sensitive detectors, laboratory FTIR-based IR-SE typically achieves thin-film sensitive measurements of mm^2 spot sizes and at 4 cm^{-1} spectral resolution within a few 10 s. However, driven by today's demand for *in situ* and *operando* characterization methods in important technological and research fields such as bioanalytics, catalysis and surface science, there is an ever-growing need for contactless, sensitive and much faster next-generation IR ellipsometers that overcome the limitations of FTIR-based instruments.

In FTIR, the achievable optical throughput, spot size on the sample, spectral resolution and signal-to-noise ratio are dictated predominantly by the brilliance of the radiation source, thus far typically a globar for lab devices. Not considering detection and electronics read-out times, the temporal resolution of single-detector IR ellipsometers that deploy sequential measurement routines in non-cyclic experiments is limited by the interferometric measurement principle but also by the time to move and/or rotate optical elements like polarizers and phase manipulators. Beam-division or fast polarization-modulation concepts can in principle circumvent these constraints when using brilliant light sources.

The opportunity to overcome these limitations of FTIR-based IR-SE came within reach for laboratory applications with the advent of tunable IR lasers—in particular, quantum cascade lasers (QCLs)—as brilliant, portable infrared light sources beyond free electron lasers and synchrotron sources (see Refs. [2–5] and references therein). Such QCLs provide coherent radiation at high spectral resolution (<0.2 cm^{-1}) for applications with high throughput, sub-mm spot sizes, and excellent temporal resolution.

Although QCLs have been available for decades, single-wavelength lasers and tunable QCLs have only first been incorporated into mid-IR ellipsometers in the late 2010s, demonstrating the prospects for laser-based IR mapping and spectroscopic ellipsometry of thin films. Frequency-domain transmission and reflection measurement concepts based, respectively, on photoelastic modulators (PEMs) and beam-division single-shot schemes finally fully exploited the so far untapped potential of the rapidly developing QCL technology. Upcoming time-domain approaches such as dual-comb techniques could also prove to be powerful applications of QCLs in IR ellipsometry.

In fact, the successful implementation of QCLs in novel ellipsometer designs in our opinion constitutes a revolution in IR ellipsometry, ushering in a new era of thin-film and surface metrology for *in situ* investigations and hyperspectral measurements far beyond the capabilities of the FTIR technique.

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QCL-based IR ellipsometry combines a multitude of new advantages—such as sub-second and sub-ms time resolution, multi-timescale access, and the ability of spatial focusing without sacrificing throughput—resulting in fundamental methodological advances of the IR-ellipsometric technique.

The currently realized time resolution of up to 10 μs at a single wavelength, and 100 ms or less for acquiring full ellipsometric amplitude and phase spectra sets a new milestone for *in situ* and *operando* measurements. QCL-based IR ellipsometry therefore for the first time enables the monitoring of non-cyclic and irreversible processes and reactions on the sub-s or even sub-ms timescale. IR-ellipsometric access to these timescales has been much sought-after for applications in catalysis, process control, microfluidics and thin-film research, and has now finally become available in the lab.

Furthermore, IR laser ellipsometry offers multi-timescale capabilities, covering several magnitudes of order in time, from hours down to the microsecond range. Facilitated by single-shot concepts, environmental-robust measurements over such vast timescales enable new technological applications of laser-based IR-SE. In thin-film reactions, binding events and growth processes at solid–liquid interfaces, for instance, anisotropic effects, structural modifications and changes in molecular interactions often occur over different timescales and can now be probed IR-ellipsometrically.

The sub-mm^2 lateral resolution of IR laser ellipsometry in combination with fast spectra acquisition also makes possible detailed spatially resolved hyperspectral amplitude and phase measurements of large sample areas within a few min to 10 min. Thus, rapid imaging applications as known from VIS ellipsometry are now accessible in the mid-IR spectral range. Moreover, QCL ellipsometry in the IR fingerprint region provides superior material specificity while at the same time delivering comprehensive information on sample properties such as thickness, ordering, anisotropy, depolarization and molecular interactions.

Such extensive sample characterization prospects present previously inaccessible opportunities in research and thin-film metrology. For example, QCL-based IR-SE allows the sub-second and sub-ms real-time monitoring and ellipsometric analysis of dynamic processes and reactions, which find application in studies of thin-film phase-change materials [4] and in polymer processing [5].

Incorporating brilliant laser sources into IR-SE makes available formerly unfeasible characterization set-ups, new detection schemes and more convenient realizations of optical paths for sensitive high-throughput measurements at increased lateral and temporal resolution. For instance, the implementation of fast PEM approaches facilitates IR laser ellipsometry measurements independent of ambient variations. Single-shot beam-division and dual-comb concepts can even provide simultaneous amplitude and phase information via the synchronized detection of different polarization states and channels. Laser-based IR-SE could thus prove highly advantageous for field and process applications under varying environmental conditions.

In addition, the compactness and brilliance of QCL radiation sources will bring forth new technological and practical features of following IR laser ellipsometer generations. As the most important ones, we see instrument portability, mobility and miniaturization but also the coupling of laser-based IR-SE with other characterization techniques such as optical microscopies, Raman spectroscopy, XPS, photothermal methods and UV/Vis or X-ray imaging. In our view, these applications are likely to cement the role of lasers in IR ellipsometry and lift the technique to a new level of importance and usability in a wide array of metrology and research fields.

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