Journal of Physics: Conference Series

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To cite this article: P Petrik *et al* 2017 *J. Phys.: Conf. Ser.* **794** 012004

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Nanophotonics of biomaterials and inorganic nanostructures

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Abstract.
Optical methods have been used for the sensitive characterization of surfaces and thin films for more than a century. The first ellipsometric measurement was conducted on metal surfaces by Paul Drude in 1889. The word 'ellipsometer' was first used by Rothen in a study of antigen-antibody interactions on polished metal surfaces in 1945. The 'bible' of ellipsometry has been published in the second half of the '70s. The publications in the topic of ellipsometry started to increase rapidly by the end of the '80s, together with concepts like surface plasmon resonance, later new topics like photonic crystals emerged. These techniques find applications in many fields, including sensorics or photovoltaics. In optical sensorics, the highest sensitivities were achieved by waveguide interferometry and plasmon resonance configurations. The instrumentation of ellipsometry is also being developed intensively towards higher sensitivity and performance by combinations with plasmonics, scatterometry, imaging or waveguide methods, utilizing the high sensitivity, high speed, non-destructive nature and mapping capabilities. Not only the instrumentation but also the methods of evaluation show a significant development, which leads to the characterization of structures with increasing complexity, including photonic, porous or metal surfaces. This article discusses a selection of interesting applications of photonics in the Centre for Energy Research of the Hungarian Academy of Sciences.

1. Introduction

Both destructive (e.g. Secondary Ion Mass Spectrometry [SIMS], Sputtered Neutrals Mass Spectrometry, X-Ray Photoelectron Spectrometry, Auger Electron Spectrometry, Glow-Discharge Mass Spectrometry, Raman Depth Profiling) and non-destructive (e.g. Rutherford Backscattering Spectrometry, Elastic Recoil Detection, Angle-Dependent Soft X-Ray Emission Spectroscopy, Grazing Incidence X-Ray Diffraction) depth profiling techniques for thin films are typically limited in measurement speed (minutes to hours) and lateral resolution (millimeters), and favorable in terms of depth resolution (nanometers or tens of nanometers) and sensitivity (detection limits from 1 at% down to 10^{-7} at%) [1]. A third group of techniques based on cross-sectioning (e.g. Transmission Electron Microscopy [TEM], Scanning Electron Microscopy

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[SEM], Scanning Auger Electron Microscopy, Raman Mapping, etc.) provide high resolution in both lateral and vertical directions, but require extensive sample preparations. Spectroscopic ellipsometry belongs to the group with limited lateral resolution and high sensitivity (for layer thickness, composition and vertical resolution), but its most important feature to our topic is the high speed combined with the non-destructive nature. This allows either the mapping of surfaces (instrumentation for imaging and mapping have long been existing [2, 3]) and the real time monitoring of solid state [4] or bio processes [5]. This article provides a short review of both bio and inorganic applications of ellipsometry. Because the field is large, we mainly focus on the results of our group from the recent years.

2. Characterization of biomaterials

2.1. Past developments

Already in the first significant book on ellipsometry published in 1977 by R. M. A. Azzam and N. M. Bashara, a 10-pages chapter titled 'Applications of ellipsometry in biology and medicine' was devoted to bioellipsometry [6]. This book was followed by other excellent ones on ellipsomery [7–10], many of them dealing with biological applications of ellipsometry as well (e.g. Chapter 12 of Ref. [8] or Chapter 7.4.2 of Ref. [9]). The first applications mentioned in Ref. [6] are by Poste et al. [11], Vroman et al. [12] and Rothen [13]. The word 'ellipsometer' was first used by Rothen in an article from the year 1945 [14], already motivated by the measurement of film thicknesses with 1 Å accuracy on polished metallic surfaces for antigen antibody investigations. These studies were based on single-wavelength ellipsometry, taking advantage of the high sensitivity and the *in situ* capability of monitoring the interface during immunological reactions and protein adsorption processes. The first spectroscopic ellipsometer was constructed in the middle of the '70s [15], and spectroscopic ellipsometry has been applied to biological materials already in the '80s [16]. There have been many direction of the development, including imaging [17, 18] or plasmonic [19] ellipsometry.

2.2. Recent developments

Depending on the optical properties of the surrounding media, ellipsometry has a typical sensitivity of $\approx 10^{-4}$ in refractive index units (which corresponds to $\approx$1 ng/mm^2 for surface mass density changes in a silicon substrate), when using a standard flow cell configuration, in which the sample surface is measured through the liquid [20]. A significant increase of the sensitivity can be reached by surface plasmon enhancement [19, 21]. In this configuration the interface is reached from the substrate, and measured by the evanescent field at the proximity of the interface. Using this concept, illuminating the interface through a semi-cylinder (figure 1), a wide range of incident angles can be used with a standard spectroscopic ellipsometer [22].

The performance of this setup has been demonstrated for different plasmonic gold layer thicknesses [23]. It can also be shown that using the ellipsometric approach with phase measurement capability, a sensitive region other than that for the optimum plasmonic configuration can also be found on the thickness-incident angle plane close to small (less than 10 nm) gold layer thicknesses (see figure 2). The best sensitivity values are $\approx 10^{-6}$ in refractive index units that have a potential to get close to advanced waveguide biosensors [24, 25] after further development and optimization.

Also, designing special lenses, the light can be focused on the plasmon layer through the semi-cylinder (figure 1) reaching a spot diameter below 0.5 mm. The focusing allows the use of a small volume (10 μL) flow cell with a channel length of 8 mm. When scanning the spot along the long axis of the channel that coincides with the axis of the cylinder, multi-surface (multi-channel) measurements are possible within one experiment [22]. The internal reflection, plasmon-enhanced measurement can also be combined with imaging ellipsometry [26]. A different method

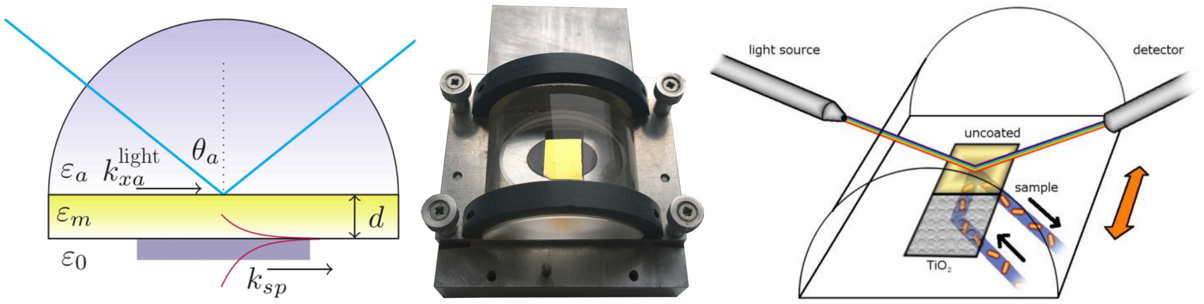

Figure 1. Schematic drawing of a 10-μL Kretschmann-Raether flow cell (left, ϵ_a, ϵ_m and ϵ_0 denote the dielectric fucntions of the BK7 glass semi-cylinder, the gold layer and the water in the flow cell, respectively; θ_a is the angle of incidence, d stands for the thickness of the gold layer), as well as the realized construction that can readily be put on the mapping stage of the ellipsometer (middle, see also Ref. [22]). To the right, the schematic view of the dual-channel configuration is shown. By preparing a sample surface divided into a processed (in this case covered by nanoparticles) and an unprocessed reference area, both of them can be measured in the same process by stepping the measurement spot along the axis of the cylinder that coincides with the long axis of the flow cell.

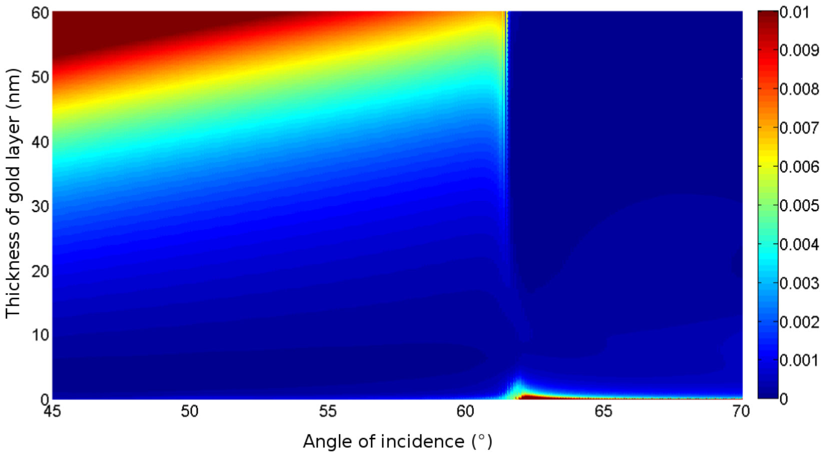

Figure 2. Calculated map of the absolute value of the complex reflection coefficient, $|\rho| = |r_p/r_s|$, as a function of the angle of incidence and layer thickness. r_p and r_s denote the reflection coefficients of light polarized parallel and perpendicular to the plane of incidence, respectively. The deep blue areas with the smallest values represent the most sentivite regions. Besides the usual plasmon resonance area in the top right part of the graph, there is another sensitive region for smaller angles of incidence (below 60°) and small (below 10 nm) thicknesses (bottom left part of the image).

of the surface field enhancement is the design of suitable multi-layer structures to generate Bloch surface waves (figure 3 from Ref. [27]).

2.3. Combination of techniques

The combination of characterization methods offers a range of benefits, such as the simultaneous measurement of the same process in space and time, as well as the complementary nature of sensitivities in terms of material properties or distance from the surface. The combined

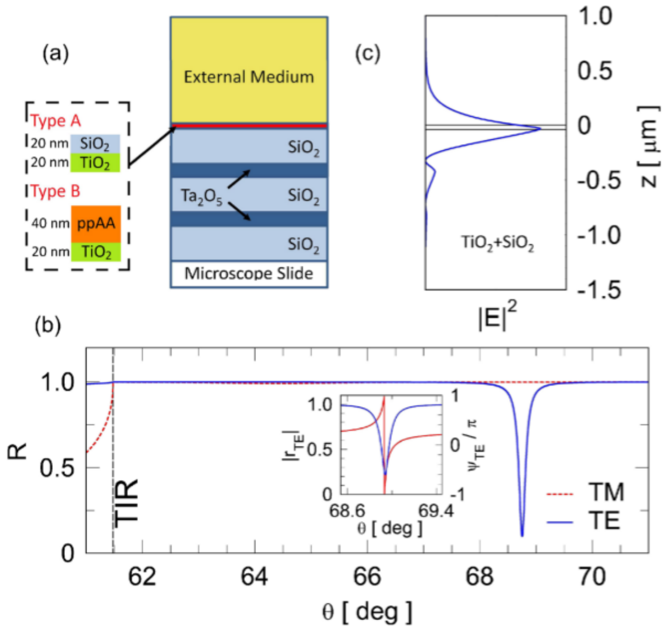

Figure 3. Schematic drawing of a one-dimensional photonic crystal to generate Bloch surface waves (reprinted from Ref. [27]).

application of quartz crystal microbalance (QCM) and spectroscopic ellipsometry unifies the mass sensitivity of QCM and the thickness sensitivity of spectroscopic ellipsometry [28–30]. The optical density can also be related to the mass. However, as usual, it is an important and complex task to turn the high sensitivity into a high accuracy, i.e. into a validated quantity verified by reference methods and calibration samples.

Using internal reflection ellipsometry [31], the increased sensitivity can only be exploited close to the interface, and the sensitivity exponentially decreases with increasing distance from the surface as the evanescent field vanishes. To overcome this issue, surface sensitive waveguide interferometry has been combined with standard flow cell ellipsometry to measure from both sides of the interface *in situ* and simultaneously (figure 4). In this combination, the high surface sensitivity of waveguide interferometry (typically better than 1 pg/mm^2) is extended with a spectroscopic and complex modeling capability of ellipsometry (although at a one or two orders of magnitude lower sensitivity), also at larger distances from the surface – because this measurement is performed from the other side, through the liquid. This technique has been demonstrated for the deposition of basic protein molecules, such as fibrinogen [32].

Further possibilities for the development of the internal reflection plasmonic design is the extension of the wavelengths towards the ultra-violet spectral region to utilize the absorption of protein molecules, using special optical components, as well as the application of structured substrates, for example to create Bloch surface waves for an increased sensitivity (≈2 pg/mm^2 was demonstrated in Ref. [27], however, only for single-wavelength ellipsometry, see figure 3). The enhanced electric field at the sensor surface increases the sensitivity of detecting the adsorption at the interface of the external medium and the Bragg structure. A key target of future developments is the increase of sensitivity combined with spectroscopic and complex modeling capabilities.

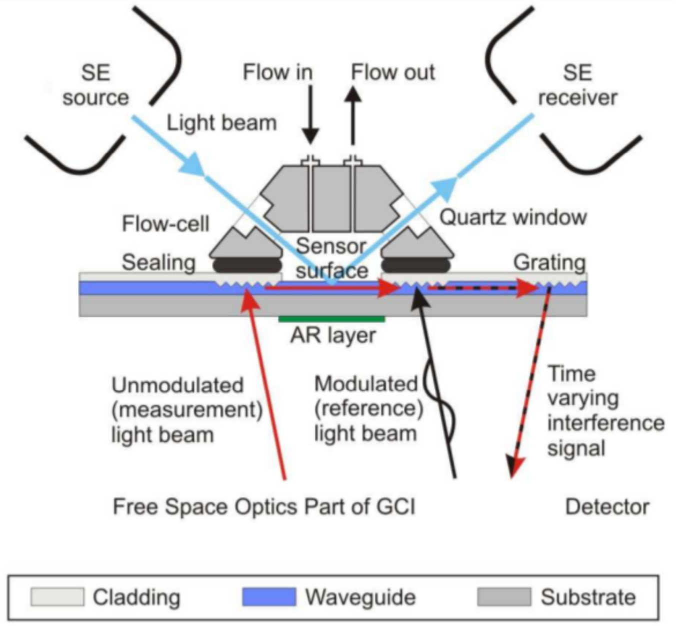

Figure 4. Schematic drawing on the combination of spectroscopic ellipsometry and waveguide interferometry [32].

3. Characterization of inorganic structures

Although the ellipsometric method is more than hundred years old [33], and it has been demonstrated already in 1945 for biological applications [14] as shown above, the technique has become widely used only from the second half of the ’80s (see figure 1 in Ref. [34]), because computers were needed for both the control of the instrument and for the evaluation of the measured data. Also, the first major application of ellipsometry was the measurement of the surface oxide on single-crystalline silicon wafers and other thin films in the microelectronics [35]. The reason is that being an extremely sensitive method, the samples had to be perfect on the nanometer scale, so that simple optical models can be used. The trend is today to measure less perfect samples like e.g. biological layers, however, the evaluation of these structures requires complex models with numerous parameters. To fit these models we need strong computers, sophisticated software, and a lot of measurement data, typically taken in a broad wavelength range and at many angles of incidence.

A recent example is shown in figure 5 demonstrating a multiple-angle of incidence ellipsometry measurement on a multi-layer structure with thicknesses in the nanometer range. It has been revealed that the minute changes in the amorphization of the substrate during RF-plasma deposition of Nb_2O_5 layers can sensitively be followed by ellipsometry. It has also been shown that a possible correlation between the thickness and the refractive index of these very thin layers can be circumvented by calculating the product of these two quantities defined as the amount of damage [36], similar to de Feijter’s method for calculating the adsorbed amount of proteins from the product of the refractive index and the layer thickness [37].

The development of ellipsometric modeling is not only directed toward complex multi-layer structures, but also nanostructures such as plasmonic, dielectric and other nanoparticles, solid state or biological nanostructures or periodic photonic structures. Figure 6 shows the ellipsometric modeling of Si nanowires with different lengths. It is shown that the wavelength range used for the fit is not only required to be adapted to the length of the nanowires, but the characteristic feature sizes can also be determined based on the used wavelength range [38, 39].

Surface roughness 2.25 ± 0.04 nm
Nb-oxide (TL model) 359.2 ± 0.2 nm
SiO_2 2.7 ± 0.1 nm
EMA, 87% c-Si + 14% ia-Si 6.8 ± 0.3 nm
c-Si substrate

Wall potential [kV]	Duration of rf sputtering deposition [sec]	Thickness of ion-implantation amorphized Si layer [nm]
2.0	100	1.35
1.5	150	1.02
1.0	300	0.84

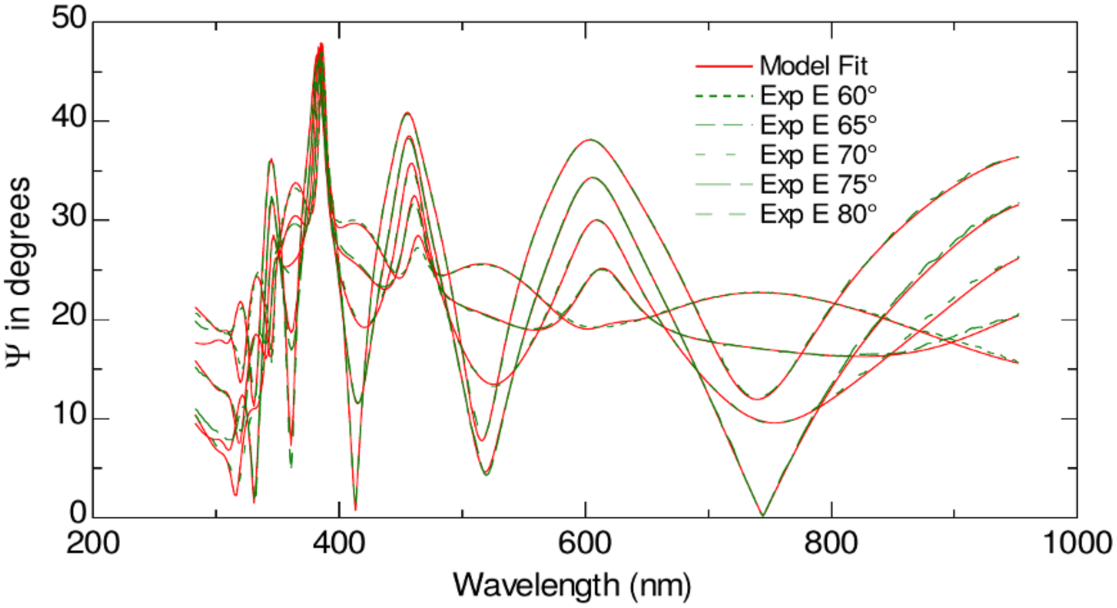

Figure 5. Measured and fitted ellipsometric angles of Ψ at different angles of incidence (shown in the legend) as a function of wavelength for Nb_2O_5 layers created by 120 minutes of RF-sputtering at a wall potential of 2.0 kV. The top left table shows the optical model (the abbreviations of TL and EMA stand for Tauc-Lorentz and Effective Medium Approximation, respectively). The thickness of the ion-implantation amorphized Si layer determined from ellipsometry is shown in the top right table for different wall potentials and sputter durations.

This work also shows how different kinds of anisotropies can be distinguised based on the fit results using different models and assumptions.

Another example of the rapid increase of the research on nanostructures is plasmonics as shown in figure 7, and its application in photovoltaics, typically following by a delay of 10-15 years (see also Ref. [40]).

As pointed out in the introduction, besides the high sensitivity, the major advantage of optical techniques is the high speed and the non-destructive nature. For example, even if it would be technically possible to measure on a large surface point-by-point using SIMS or SEM, it would take so much time, and it would require so much effort, that it's use wouldn't be a benefit. The most perspective capability of the optical techniques like ellipsometry is not the characterization of a completely unknown sample or structure, but the high throughput and high sensitivity testing and monitoring of processes, as in the above examples for bio processes, and also for solid state processes e.g. in photovoltaics. Figure 8 shows a prototype of a divergent

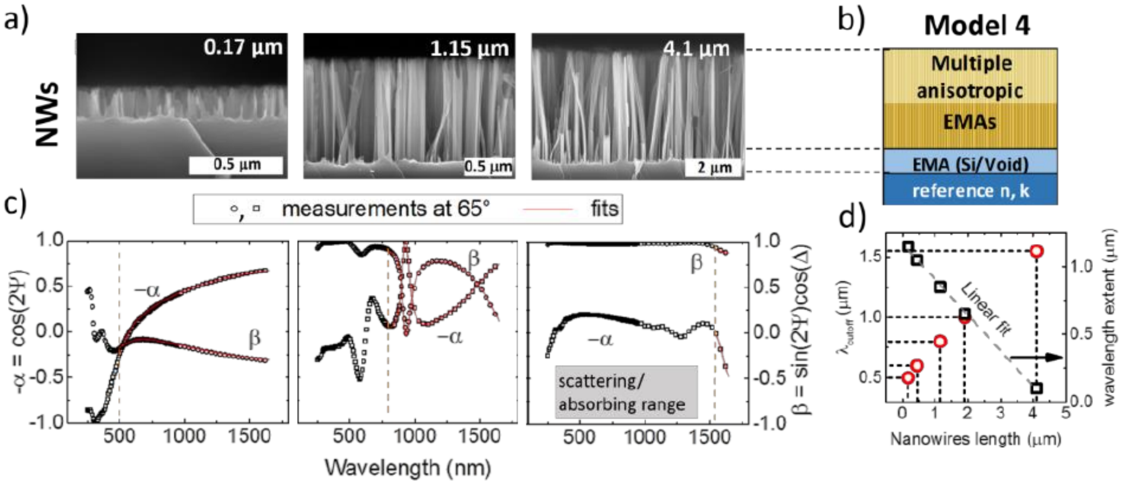

Figure 6. (a) Cross-sectional electron microscopy images of Si nanowires of different lengths; (b) effective medium approximation-based optical model used for the ellipsometric evaluations; (c) measured and fitted ellipsometric values (α and β) at an angle of incidence of 65°; (d) cut-off wavelengths and the width of the wavelength range (denoted as 'wavelength extent') as a function of the length of the nanowires.

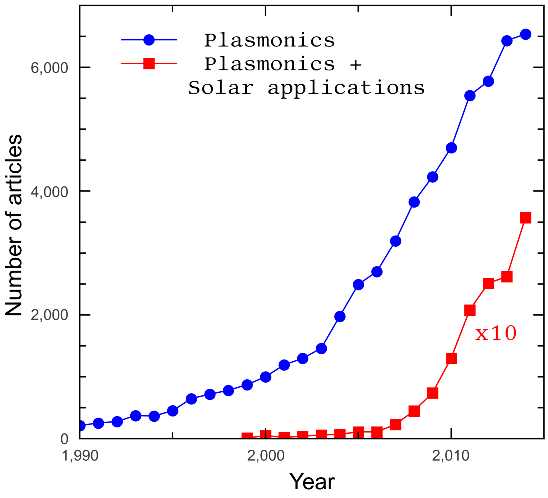

Figure 7. Number of publications over the years having the keyword 'Plasmon*' (denoted as 'Plasmonics') or 'Plasmon AND (Solar OR Photovoltaic)' (denoted as Plasmonics + Solar applications, with the number multipled by 10) in the title, keywords or abstracts.

light source ellipsometer that has been developed in our group for more than a decade [3]. The latest versions are capable of mapping a 30-by-30 point area within 2 minutes, even on surfaces as large as 90-by-90 cm [41]. The most important feature is that these maps can be recorded spectroscopically, which means that each point of the 30-by-30 area includes a whole spectrum in a range depending on the given configuration, which can always be adapted to the layer structures and materials to be measured. Using this approach, maps can not only be taken on the layer thicknesses even in multi-layer structures, but also on certain material properties like crystallinity, resistivity, band gap, and a lot more, depending on the possibilities to relate the dispersion of the material to its physical properties. These properties can be tested real time, during processing on solar panels, displays, sensors, etc., on large areas, non-destructively.

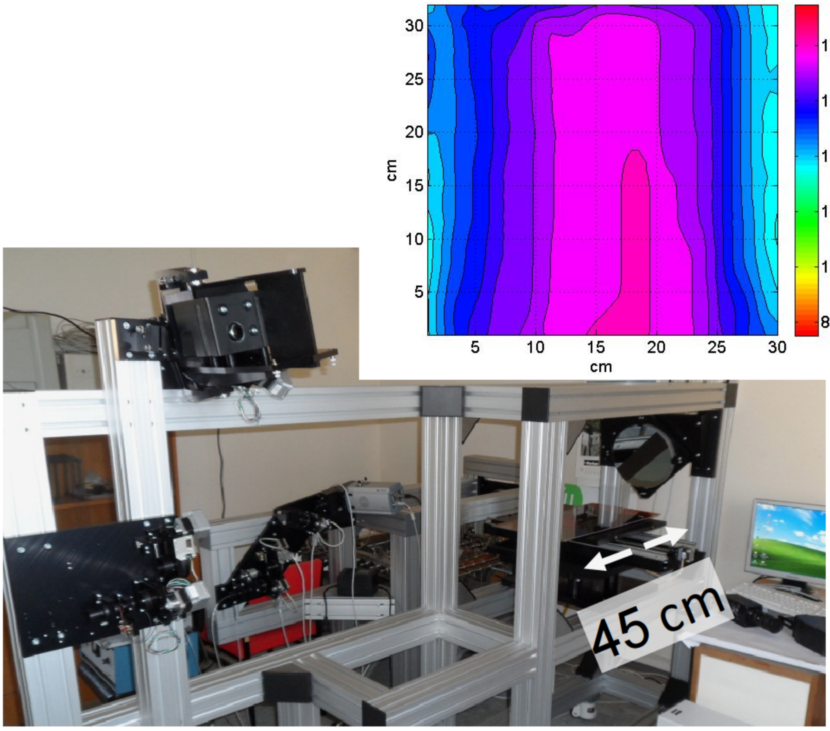

Figure 8. Prototype of a divergent light source mapping ellipsometer for sample sizes of 300-450-600-900 mm. The graph shows the thickness map of a ZnO layer deposited on a Mo-covered glass sheet on a 30 cm by 30 cm area that can be measured within 2 minutes using our mapping device. Using a commercial tool with point-by-point measurement, a map with the same resolution requires approximately 20 minutes.

Another example of the development in non-conventional directions toward new configurations and new materials is the investigation of Zr alloy tubes used for nuclear fuel cladding [42]. It was shown that the surface properties of such tubes can be measured by proper focusing directly on the tubes with diameters as small as 9.1 mm. Figure 9 shows the measurement setup, in which the light of the ellipsometer is focused on the outer surface of the Zr tube, allowing the determination of the thickness and the optical properties of the surface oxide. From a detailed investigation it is revealed that the oxide properties gradually change in depth. Consequently, improved optical models involving grading, multi-sample analysis and B-spline parameterization of the dielectric function are required [43]. As mentioned above, the power of the optical characterization is not to discover an unknown sample and structure. Those properties that can be measured by electron microscopy should not be measured by ellipsometry. However, ellipsometry can be measured on a large series of samples for qualifying, checking and testing the properties, it can measure samples in line, non-destructively, and a further possibility is to perform investigations during processing, like oxidation, which can lead to the understanding of the dynamics and kinetics of those processes. Finally, there are a range of material properties (refractive index, band gap, critical points, joint density of states and band structure related properties) that can most sensitively be determined by optical techniques.

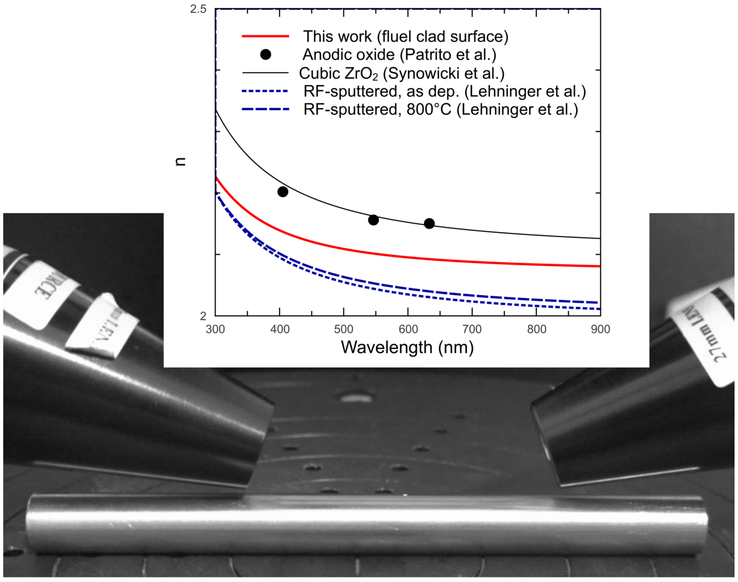

Figure 9. Setup for the measurement of a Zr tube for nuclear fuel cladding. The inset shows the refractive index of the ZrO_2 layer determined using the multi-sample method, together with other references from the literature.

4. Conclusions

In this summary it has been demonstrated that there are large opportunities in the development of optical characterizations for both biological and inorganic nanostructures and thin films. There is a significant progress in the instrumentation (plasmonics, combined methods) as well as in the evaluations (grading, anisotropy, scatterometry, multi-sample method and special parameterizations). The two straightforward major motivations are the improvement of the sensitivity and the extension of the method towards new materials and structures. Being an indirect method, the verification is also of primary importance using complementary techniques. Once verified, the optical techniques provide a way for the quick, high-sensitivity and non-destructive testing of the sample properties.

Acknowledgments

Support from OTKA K115852, M-ERA-NET 117847, ENIAC E450EDL, SEA4KET, TÉT-12-DE-1-2013-0002, TÉT-14-FR-1-2015-0041, Momentum, ERC_HU and EK (T123) internal research projects are gratefully acknowledged.

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