

Surface characterization by spectroscopic infrared ellipsometry

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Summary. For ellipsometry in the infrared range the advantages of Fourier-transform spectroscopy can be exploited when the experimental procedure is based on photometry. The measured intensities are interpretable in terms of the so-called ellipsometric parameters which describe the polarization state of the radiation after having been reflected from the sample. These parameters in turn are correlated with the optical constants of the sample such as the dielectric function or the complex refractive index as well as with its geometrical structure. The potential of spectroscopic infrared ellipsometry for the characterization of surfaces and surface films is demonstrated by examples including compounds with spectral intervals of strong absorption and assemblies of semiconductor films.

Introduction

The reflection of linearly polarized radiation at a surface or interface generally results in elliptical polarization. If an experimental procedure is suited to reveal the parameters of the elliptical helix on which the tip of the electric vector travels, the procedure is called ellipsometry. The state of polarization – in comparison to that prior to the reflection – characterizes the interaction of the radiation with the reflecting sample. Ultimately the interaction depends on the optical properties of the sample and thus the optical properties can be evaluated from ellipsometric results. Several remarkable features of this method [1, 2] will be outlined here.

Different from the well established measurements of reflectance, in ellipsometry two quantities are determined for each spectral point. The optical behaviour of a bulk material is completely defined by one complex figure such as the refractive index \hat{n} or the dielectric function $\hat{\epsilon}$ and thus, by two (real) figures. These can both be evaluated from ellipsometric measurements so that the entire information is obtained without referring to other spectral ranges or other sources. Furthermore the measurements are independent of standards of any kind [3]. Thus the derived optical constants do not depend on any reference experiment.

The method enables the reliable measurement of the absorption, when it is too strong for accurate transmittance measurements, and the refraction even in spectral intervals with anomalous dispersion (i.e. within absorption bands).

The evaluation of ellipsometric measurements to give optical properties is straightforward as long as the reflection occurs at a sufficiently plane surface (this requirement is met in the vast majority of cases) of a thick sample. From the theoretical point of view this should be infinitely thick; from the practical point it should be thick enough to prevent radiation reflected at the back surface or interface from contributing to the detected radiation. However films on surfaces of any material and even multi-layer systems are addressable as outlined by the examples given in this contribution.

Some versions of ellipsometry have been employed routinely for years in research and even in industrial production. In most cases only one wavelength is used, normally, in the visible range of the spectrum. Ellipsometry in the infrared range was impeded by severe intensity shortcomings which limited precision. These problems can be overcome by use of a Fourier-transform spectrometer [3] and in this way the so informative spectral range of molecular and lattice vibrations has been opened for ellipsometry.

1 Ellipsometric parameters and optical constants

The change in the state of polarization occurring with reflection is primarily due to different phase shifts for the components of the electric vector oscillating either in the plane of reflection (azimuth $\alpha_1 = 0$) or perpendicular to it. The effect of the reflection on each of these components is described by a complex amplitude factor of the form $|r_i| \exp(i\delta_i)$ where $i = x$ refers to the parallel and $i = y$ to the perpendicular [1]. By ellipsometry the state of polarization is experimentally determined and – in its photometric version – characterized by the ratio $|r_x| / |r_y|$ and the phase difference $\delta_x - \delta_y$. Both quantities show up in the quotient of the complex amplitude factors

$$\frac{r_x}{r_y} = \tan \psi \exp(i\Delta) \quad \text{where} \quad (1)$$

$$\tan \psi = \frac{|r_x|}{|r_y|}; \quad \Delta = \delta_x - \delta_y$$

ψ , Δ are called ellipsometric parameters [2]; if they are interpreted on the basis of physical effects, the optical properties of the sample can be derived. However, except for the favourable case of a semi-infinite medium, the evaluation

requires an optical and geometrical model of the sample. The reliability of the results depends strongly on how far the model corresponds to reality.

The optical properties of a medium can be characterized by the (real) refractive index n and the absorption index k , which are usually combined to form the complex refractive index [1, 3]

$$\hat{n} = n + ik$$

Equivalent to this description is the one for the complex dielectric function $\hat{\epsilon}$

$$\hat{\epsilon} = \epsilon' + i\epsilon'' = (n^2 - k^2) + i2nk$$

At any given wavenumber, $\tilde{\nu}$, the absorption index k is directly related to the absorption coefficient, a , by

$$a = 4\pi \tilde{\nu} k$$

This absorption coefficient, a , is used in Lambert-Beer's law

$$I/I_0 = \exp(-ad)$$

where I and I_0 denote the actual and the initial intensities, respectively, and d the thickness of the absorbing layer. Furthermore, a is related to the decadic molar absorptivity ϵ by

$$a = \epsilon \times c \times \ln 10$$

where c is the concentration. In order to convey an impression of the magnitude of k , an absorption band around 1000 cm^{-1} is assumed so that a sample of $10 \mu\text{m}$ thickness transmits 1% of the incident intensity: this corresponds to $k \approx 0.4$ and – at least in the context of organic compounds – might be called a very strong band. Both \hat{n} and $\hat{\epsilon}$ are called optical constants since they are not subject to any method, experimental parameter, or reference.

The interaction of radiation with a sample at its surface is described by the well-known Fresnel equations in combination with Snell's law: the amplitude factors mentioned above are interpreted in terms of e.g. the optical constants. In order to derive these from the ellipsometric parameters measured, the inverse functions of Fresnel's equations need to be solved. The solution is well known from metal optics as far as semi-infinite samples are concerned. In all the cases of other sample geometry (such as absorbing thin films, surface coatings, stratified media) one must employ iterative approaches unless additional information is available and can be included.

In the most simple case of one interface separating a non-absorbing ambient medium such as air (refractive index n_0) from a semi-infinite, or at least sufficiently thick homogeneous sample, the components of the dielectric function $\hat{\epsilon}$ of the latter are related to the measured ellipsometric parameters by [1]

$$\begin{aligned} \epsilon' = n^2 - k^2 &= (n_0 \sin \varphi_0)^2 \left[1 + \frac{\tan^2 \varphi_0 (\cos^2 2\psi - (\sin 2\psi \sin \Delta)^2)}{(1 + \sin 2\psi \cos \Delta)^2} \right] \\ \epsilon'' = 2nk &= \frac{-(n_0 \sin \varphi_0 \tan \varphi_0)^2 \sin 4\psi \sin \Delta}{(1 + \sin 2\psi \cos \Delta)^2} \end{aligned} \quad (2a)$$

from which in turn the components of the (complex) refractive index are obtained as

$$\begin{aligned} n &= \{0.5[(\epsilon')^2 + (\epsilon'')^2]^{1/2} + \epsilon'\}^{1/2} \\ k &= \{0.5[(\epsilon')^2 + (\epsilon'')^2]^{1/2} - \epsilon'\}^{1/2} \end{aligned} \quad (2b)$$

The phase shifts introduced by reflection at an interface between two non-absorbing media would be either 0° or 180° , but no intermediate values are possible. This is different from the considered case here of one absorbing medium where phase shifts of $0^\circ \leq \delta_{x,y} \leq 180^\circ$ can occur. The same holds for an interface separating two absorbing materials, e.g. stratified media. As pointed out before, these (differences in) phase shifts constitute the source of additional information.

Equations 2a and b are generally valid for isotropic media. It must be emphasized that the experimental conditions known as attenuated total reflection (ATR) are included. In such a case φ_0 and n_0 are determined by the shape and the material of the ATR prism, respectively. No further modification of the experimental procedure or the evaluation algorithm is necessary, and there is no marked difference in the ellipsometric behaviour when changing from a spectral range of refraction to one where total reflection takes place [3].

2 The photometric ellipsometer

The principle of photometric ellipsometry suitable for Fourier-transform-spectroscopic investigations in the infrared range is schematically shown in Fig. 1. The (first) polarizer is

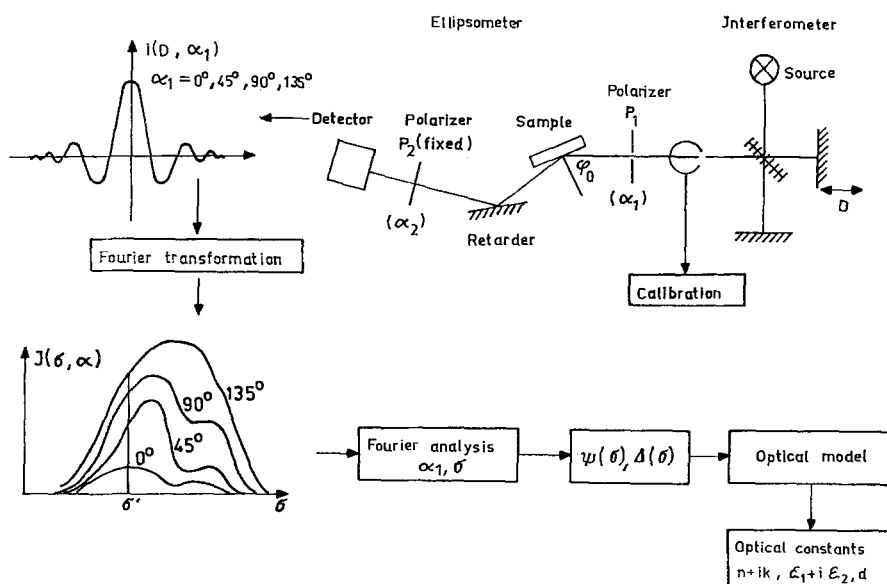


Fig. 1. Principle of photometric ellipsometry in the infrared range

used to provide radiation being polarized linearly with an azimuth of α_1 . The state of polarization resulting from the reflection process is indicated by the intensities measured after the second polarizer ("analyzer", azimuth α_2). For practical reasons, e.g. to account for a polarization-sensitive detector, the azimuth of the analyzer is kept fixed, while the polarizer is rotated stepwise. This leads to a modulation of the intensity reaching the detector [3] as given by

$$I(\alpha_1) = \frac{I_0}{2} [1 - \cos 2\psi \cos 2\alpha_1 + \sin 2\psi \cos \Delta \sin 2\alpha_1] \quad (3)$$

The limited precision with respect to Δ in some ranges can be improved considerably by introducing an additional phase shift, preferably of 90° , by means of a retarder. Among the different types those based on internal reflection offer the essential advantage of being (sufficiently) achromatic over wide spectral ranges [4]. Furthermore this allows the degree of polarization to be stated as well as the precision of the actual phase shift; however, the implications of this quantity [5] are beyond the scope of this paper. In any case the polarizing properties of the attached Fourier interferometer, and in particular of its beam splitter have to be considered carefully and to be balanced by the calibration procedure.

The results presented in this contribution were obtained using the infrared ellipsometers and the dedicated software developed in the Central Institute for Optics and Spectroscopy of the Academy of Sciences of the former GDR, the interferometer is a model IRF 180 (Centre of Scientific Instruments). Details can be found elsewhere [3].

3 Results from spectroscopic infrared ellipsometry

A pre-requisite for reflection is the existence of a surface or, strictly speaking, of an interface between two media of different optical constants. Sufficient transmittance provided, radiation reflected at a deeper interface can contribute (directly and by multiple-beam interference) to the overall reflectance observed.

As an example for the simple two-media situation, the optical constants of SiC were evaluated from ellipsometric measurements performed with an angle of incidence of 70° ; the results are shown in Fig. 2. The main feature is considerably broadened in comparison to single-crystal spectra; this can be traced back to the ceramic structure of the actual sample. The obvious deviations of the main feature from (possibly expected) symmetry are due to the strength of the absorption band. It should be noted that around 900 cm^{-1} for the same reason the (real) refractive index decreases to values below unity. The features close to 1000 cm^{-1} must be attributed to a weak absorption band. Interesting enough, this appears much more pronounced in the spectrum of the (real) refractive index than in that one of the absorption index.

Since the ellipsometric results are determined by just an interface, differences with respect to the bulk material cannot be excluded a priori. Furthermore extra features can occur for thin layers of a given material. Such a case of three or even more media is discussed here with examples from coated silicon wafers. In Fig. 3 the results are presented which were obtained with a silicon sample covered with a 75-nm-thick layer of SiO_2 . At 1264 cm^{-1} a minimum in the spectrum of $\tan \psi$ indicates the position of the so-called LO mode (i.e. longitudinal optical mode), while the maximum at

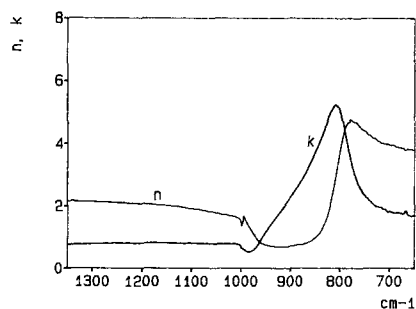


Fig. 2. Spectra of the refractive index n and the absorption index k of ceramic SiC

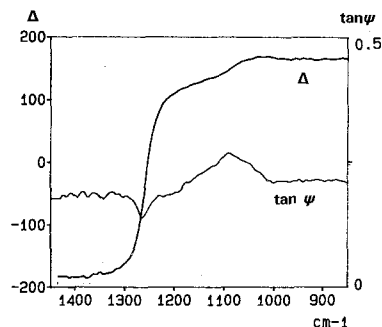


Fig. 3. Spectra of the ellipsometric parameters of a 75-nm thick SiO_2 film on silicon ($\varphi_0 = 68^\circ$) with Berreman effect and TO mode

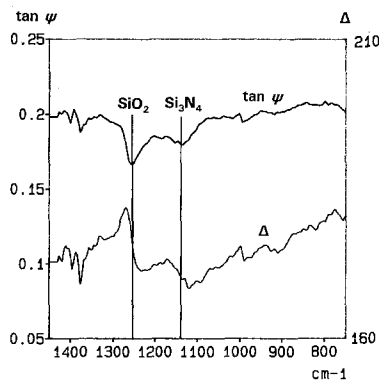


Fig. 4. Wavenumber-separated responses of the individual films in a stack of SiO_2 and Si_3N_4 (6 nm each) on silicon ($\varphi_0 = 68^\circ$)

1091 cm^{-1} indicates the TO (i.e. transversal optical) mode of SiO_2 [3]. Additionally in the spectrum of the phase difference Δ a striking slope is found in the spectral range of the LO mode. This finding is typical for strongly absorbing layers of similar thickness; being known as the Berreman effect [6], it is a consequence of exciting a leaky guided wave between the two surfaces of the layer [3].

Analogous results for a double layer of SiO_2 and Si_3N_4 on silicon are presented in Fig. 4. Each of the two layers is just about 6 nm thick, which causes the response to be observable only for the LO mode. However, the LO modes of the two layers are excited at different wavenumbers, namely around 1264 cm^{-1} for SiO_2 and around 1137 cm^{-1} for Si_3N_4 so that the two layers can be studied independently. Among the accessible information are deviations from the stoichiometry which would be indicated by wavenumber shifts in comparison to the spectrum of the bulk material.

Up to about 20-nm-thick films, the amplitudes of $\tan \psi$ and Δ related to the LO modes are approximately proportional to the thickness [7]. Therefore this information can

easily be extracted from the spectrum. For thicker samples and for a more detailed analysis, the parameters under consideration have to be calculated iteratively on the basis of an appropriate model.

4 Conclusions

It has been shown that spectroscopic infrared ellipsometry owns a high potential for the characterization of surfaces and surface films. The theoretical background, the experimental details and the evaluation algorithms have been developed so far that they now are readily usable. It is worth mentioning that with infrared radiation the wavelength of which is about $10\ \mu\text{m}$, structures of a few nanometers can be revealed, which means a scaling factor in the order of one thousand. As to the depth from which the reflected radiation brings information, one usually refers to the contribution from radiation having been reflected at a deeper interface. However the interfacial thickness which actually causes

reflection seems to be extremely thin, most probably in the order of a few nanometers.

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