# Ellipsometry

***(by Klaus-Jochen Eichhorn and Boris Mahltig)***

Ellipsometry measures variations of the polarization state of light reflected from a surface /1/ **(FIG.1)**. The experimental data are expressed as $\tan\Psi$ (relative amplitude ratio) and $\Delta$ (relative phase shift), related to the Fresnel-reflection-coefficients $R_p$ and $R_s$ for p- and s- polarized light, which are complex functions of the angle of incidence $\Phi_0$, the wavelength $\lambda$, the optical constants of the substrate ($N_S$) , the ambient medium ($n_0$) and the layers ($n_j$, $k_j$), and of the layer thicknesses ($d_j$), respectively:

$$\tan(\Psi)\exp(i\Delta) = \frac{R_p}{R_s} = F(\Phi_0, \lambda, N_S, n_0, n_j, k_j, d_j)$$

j = 0,1, 2... (number of layers)

N = n + ik (N: complex refractive index,n: refractive index, i: complex number, k: extinction index)

The optical constants can also expressed as complex dielectric function $\boldsymbol{\varepsilon}$ with

$\boldsymbol{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ and $N = \boldsymbol{\varepsilon}^{1/2}$ .

The fit of the parameters of an optical model to the determined values of $\tan\Psi$ and $\Delta$ provides layer thicknesses and optical constants of layered substrates. Strictly speaking the fundamental equations of ellipsometry are valid for systems consisting of homogeneous isotropic phases with smooth and parallel interfaces. Nevertheless surface roughness, graded or heterogenous composition and anisotropy can be modeled in some cases.

Using the **null ellipsometry** /1/ **(FIG.2)** the ellipsometric data $\Delta$ and $\Psi$ can be detected very sensitive ($\delta\Delta<0.02$, $\delta\Psi<0.01$), that means submonolayer precision. The vast majority of the ellipsometric data published so far was taken with null ellipsometry at a single wavelength (e.g. HeNe laser) and at one angle of incidence.

Thus, only one single $\Delta,\Psi$–pair is obtained to describe the surface. If the sample deviates from the idealized “substrate/layer/ambient“ structure it is hardly possible to determine d and n precisely from this single $\Delta,\Psi$–pair. In order to overcome this difficulty ellipsometric measurements at multiple wavelengths from the UV-Vis to IR region and/or variable angles of incidence have been proposed. By means of that large data sets of $\Delta,\Psi$–pairs can be aquired to characterize any interfacial state providing the capability of crosschecking the assumed optical model /2/. **Spectroscopic** or the fast **multiwavelength in-situ ellipsometry** are usually done using the photometric principle /1/ **(FIG.3)**.

Bare polymer surfaces, single polymer films on reflecting solid substrates, interphases in bilayers, adsorbed mono- and multilayers can be analyzed by ellipsometry in vacuum, in different atmospheres or under liquids as well. Layers were formed using spin- and dipcoating, grafting to- or from procedures, self assembly and Langmuir-Blodgett techniques. Recent results were reported for polyelectrolytes/3,4/, blockcopolymers /5-8/ and biomolecules /9/. The kinetics of the layer formation, adsorption and desorption processes can be studied in-situ respectively. So the adsorption of blood plasma proteins on fluorohydrocarbon surfaces were investigated /10/ **(FIG.4)** and the adsorption and displacement of beta-2-microglobulin on hydrophobic or hydrophilic substrates were analyzed quantitatively /11/ **(FIG.5).**

More and more complex optical models were applied to describe the real surface state and nature of the organic layers. Effective medium approaches /10,12/, Cauchy relations for nonabsorbing /13/ and Lorentz-oscillator parametrizations for absorbing /14/ as well as anisotropic models for oriented layers /15-17/ were useful for optimum fitting the data from the Variable Angle Spectroscopic Ellipsometry (VASE).

To investigate microstructured surfaces with a lateral resolution of some microns micro-ellipsometric methods namely spatially resolved and imaging ellipsometry /18,19/ were developed recently. So microdroplets /20/ or protein pattern /21/ could be analyzed.

## References


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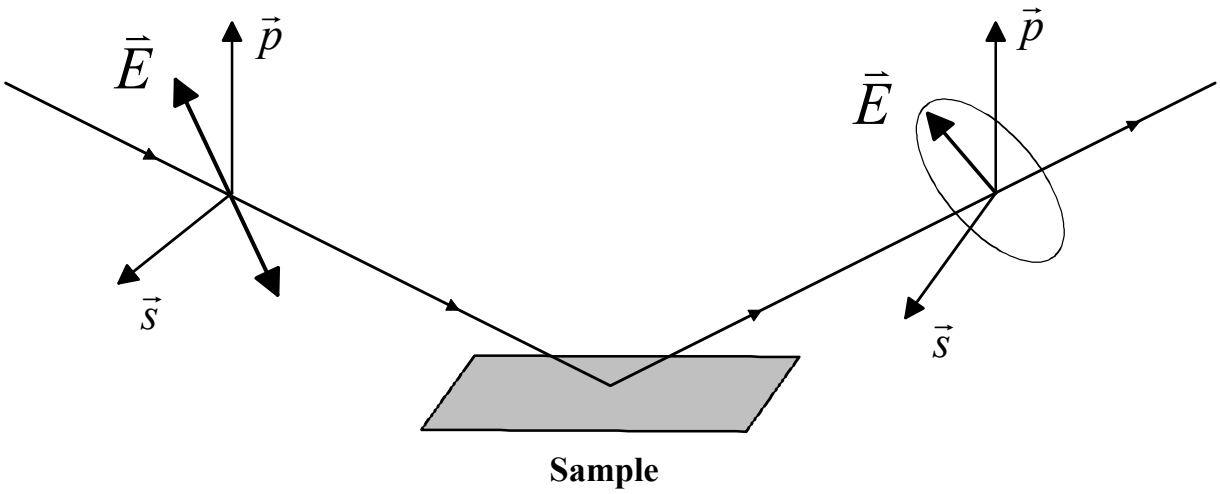


**Fig.1** Basic principle of ellipsometry: Lineary polarized light is incident at oblique incidence, the reflected elliptically polarized light is analyzed

(E: electric field with components parallel (p) and perpendicular (s) to the plane of incidence)

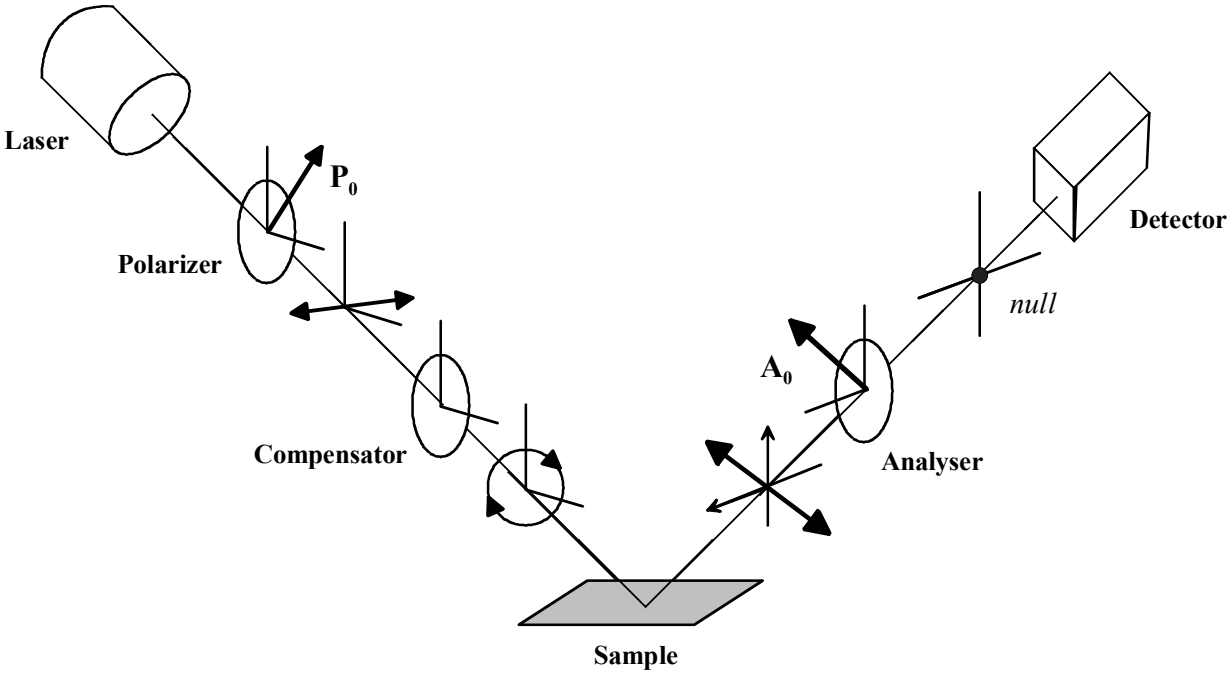


**Fig.2** Principle of a null ellipsometer

(with analyzer azimuth $A_0$ and polarizer azimuth $P_0$)

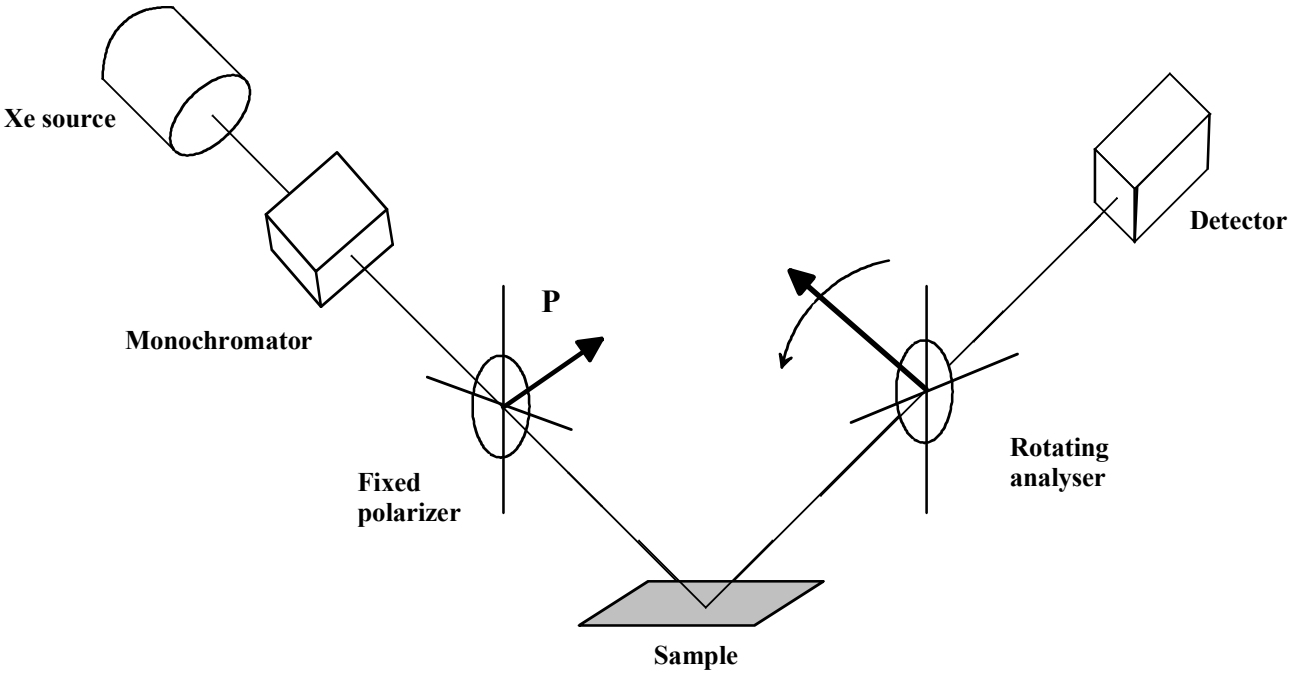


**Fig.3** Principle of a spectroscopic ellipsometer with rotating analyzer

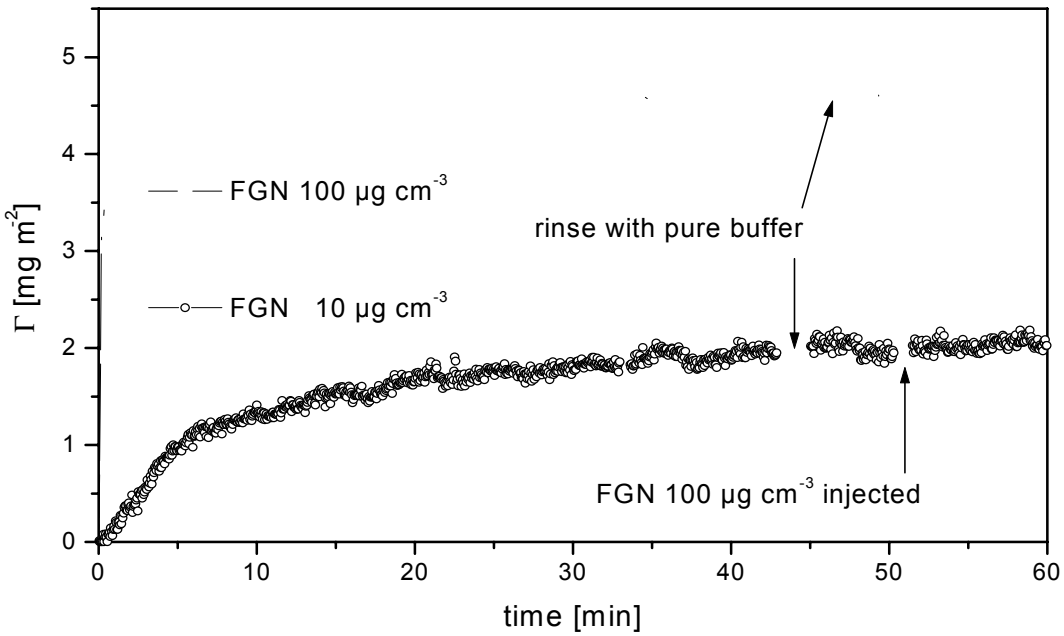


**Fig.4** Kinetics of adsorption of fibrinogen on a hydrophobic fluorohydrocarbon polymer from 10 and 100 µgcm$^{-3}$ buffer solution, measured by in-situ multiwavelength ellipsometry, from /9/

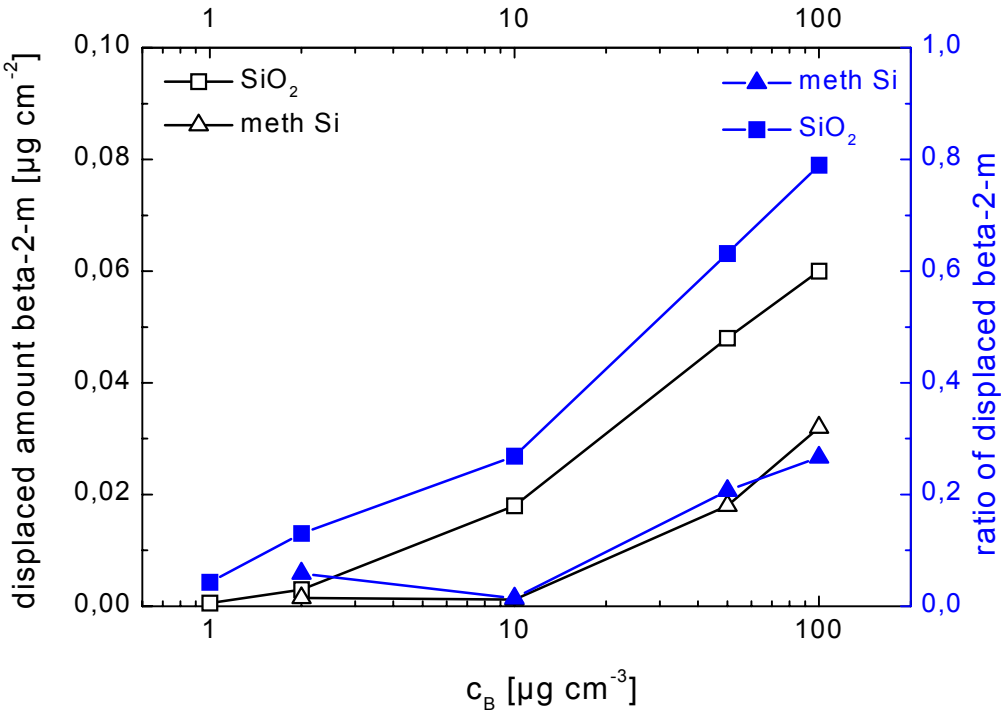


**Fig.5** Displaced amounts (left axis) and displaced fractions (right axis) of beta-2-microglobulin from unmodified and methylated Si-wafers after adsorption at different solution protein concentrations and subsequent contact of the samples with fibrinogen solution, from /10/