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Full Length Article

# Visualization of low-contrast surface modifications: Thin films, printed pattern, laser-induced changes, imperfections, impurities, and degradation

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ABSTRACT

Visualization of surface modifications may be very challenging for coating/substrate systems of either almost identical optical constants, e.g. transparent films on substrates of the same material, or minor film thickness, substance quantity and affected area, e.g. ultra-thin or island films. Methods for visualization are optical microscopy (OM), imaging ellipsometry (IE), and referenced spectroscopic ellipsometry (RSE). Imaging ellipsometry operates at oblique incidence near Brewster angle of the bare, clean or unmodified substrate. In this configuration, reflected intensities are rather weak. However, the contrast to add-on and sub-off features may be superior. Referenced spectroscopic ellipsometry operates in a two-sample configuration but with much higher intensities. In many cases, both ellipsometric techniques reveal and visualize thin films, printed-pattern, laser-induced changes, and impurities better than optical microscopy. In particular for stratified homogeneous modifications, ellipsometric techniques give access to modelling and hence thickness determination. Modifications under investigation are polymer foil residue on silicon, laser-induced changes of ta-C:H coatings on 100Cr6 steel, imperfections of ta-C:H on thermal silicon oxide, degradation of glass, thin film tin oxide pattern on silicon, printed and dried pattern of liquids such as deionized water, cleaning agents, and dissolved silicone.



## 1. Introduction

For the evaluation of functionality and reliability, quality control (QC) requires the visualization of surface features from the macroscopic down to the microscopic or even nanoscopic scale. The diversity of applications ranges from low-E glazings and solar panels, micro- and optoelectronics, micro- and smart devices to sensor-on-chip and lab-on-chip systems [1]. These functional features are based on tailored materials, in particular modified surfaces, thin films, and micro- and nano-scaled pattern [2–6]. The fabrication of pattern requires lithographic techniques or the direct material treatment by laser (micrometer range) or e-beams and ions (nanometer range). For example, laser-induced modifications in the micrometer range such as cavities are usually accompanied by micro- to nanometer-scaled changes in the adjacent material within the heat affected zone (HAZ).

For nondestructive far-field inspection, optical microscopy, interferometry, and scatterometry [5,7–9] are established QC tools. In addition to dimensional information, ellipsometry provides material information even from the technical far-field in terms of optical and dielectric functions. The vertical resolution is in the sub-nanometer range for interferometry, scatterometry, and ellipsometry whereas lateral resolution is mainly given by the diffraction limit for optical microscopy, interferometry, and ellipsometry. Vacuum-based imaging techniques such as scanning electron microscopy (SEM) [5] and optical near-field techniques such as atomic-force microscopy (AFM) with nanometer-scaled vertical and lateral resolution are not discussed here despite the fact that they are also applied to the investigations of low-contrast glass surfaces with artifacts, defects, chemical changes, and corrosion phenomena [10–12].

Optical microscopy (light, confocal laser scanning, white light interference) is operated at normal incidence, i.e. p- and s-polarization are undistinguishable. In case of ellipsometry, operated at oblique incidence, p- and s-polarization matter, and amplitude ratios and phase shifts upon reflection are directly measured. Hence, information content must be higher.

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As macro-functionalities are nowadays based on micro- and nano-features, well-defined and clean surfaces are a prerequisite for reliable processing.

Ellipsometry allows e.g. thin film characterization under ambient conditions [2,13], studies of surface cleanness and in-situ film growth under vacuum conditions for sputtering [14], and investigations of chemisorption of monolayers of oxygen on metals under ultra-high vacuum conditions [15]. Two-dimensional materials and thin films are getting more and more important [1,4,16] with physical quantities (e.g. band gaps) different from bulk, shown for graphene vs. carbon [16] and monolayer $MoS_2$ vs. bulk $MoS_2$ [4]. From the near-field, $MoS_2$ monolayers have been visualized by means of scanning tunneling microscopy (STM) [17]. Recently, a transistor with 1 nm gate lengths made of $MoS_2$ with a single-walled carbon nanotube as gate electrode was introduced [18]. Even under liquid ambient conditions, liquid-solid interfaces can be visualized by imaging ellipsometry [19]. Moreover, the shape of deformable droplets [20] and the proof of fingermarks [21] were studied by imaging ellipsometry.

The diversity of applications is on an individual sample demonstrated in [22] by means of IE with regard to the visualization of protein pattern, thickness gradients, thickness steps in $SiO_2$, and grooves in $SiO_2$ on silicon.

By means of Mueller matrix ellipsometry, the full optical response is described by a $4 \times 4$ matrix. The characterization of nanostructures, e.g. substrates with nano-textured pattern produced by nanoimprint lithography (NIL) is described in [23]. For improved analysis efficiency and lateral resolution, advantages of scatterometry and Mueller matrix ellipsometry are combined in a Mueller matrix imaging ellipsometer for nanostructure metrology. It acquires a $4 \times 4$ Mueller matrix in a single measurement with pixel-sized illumination spots for NIL and etched trench nanostructures [24].

Process chains consist of several process steps, e.g. delivery, cleaning, deposition, etching, and flushing. The process cycle is repeated until the functionalized surface is completed. The aim of visualization is the verification of cleanness as well as the absence of imperfections on larger and samples in a short period of time prior to the subsequent process.

## 2. Experimental

### 2.1. Measurement techniques

For the visualization of low-contrast surface modifications three optical far-field techniques are applied: optical microscopy (OM), imaging ellipsometry (IE), and referenced spectroscopic ellipsometry (RSE).

OM (Reichert-Jung Polyvar-Met, Cambridge Instruments) is operated at normal incidence and intensity-based contrast in the visible wavelength range (360 nm–780 nm) in three modes: bright field (BF), dark field (DF), and differential interference contrast (DIC). In dependence on the size of add-on- or sub-off-features, magnifications (mag.) from 5× to 500× and digitally image enhancements are applied.

IE (EP3, Accurion GmbH) is applied at oblique incidence with angles of incidence (AOI) from 45° to 80° in the visible/near infrared wavelength range (44 discrete wavelengths between 351 nm and 1000 nm from a Xe discharge lamp with unsteady wavelength steps). Measured ellipsometric quantities are amplitude ratio ($\Psi$) and phase shift ($\Delta$), see Eq. (4). In a simple air (0), thin film (1), substrate (2) system, the incident beam is refracted and reflected at the air/thin film interface (01). The refracted part of the light undergoes an internal reflection in the thin film. In relation with the reflected part of the light a phase change $\beta$ occurs. This phase change is correlated to the thickness $d_1$ of the thin film and the refractive index $n_1$ [25].

$$\beta = 2 \cdot \pi \cdot \frac{d_1}{\lambda} \sqrt{n_0 - n_1 \cdot sin^2(\gamma_0)} \tag{1}$$

in which λ represents the wavelength of incident light. The Fresnel equations of reflected p- and s-polarized light are

$$r_p = \frac{r_{p,01} + r_{p,12} \cdot \exp(-i \cdot 2 \cdot \beta)}{1 + r_{p,01} \cdot r_{p,12} \cdot \exp(-i \cdot 2 \cdot \beta)} \tag{2}$$

$$r_s = \frac{r_{s,01} + r_{s,12} \cdot \exp(-i \cdot 2 \cdot \beta)}{1 + r_{s,01} \cdot r_{s,12} \cdot \exp(-i \cdot 2 \cdot \beta)} \tag{3}$$

The parameters $r_{01}$ and $r_{12}$ are the reflection coefficients at the corresponding interface. The quotient of Eqs. (2) and (3) describes the fundamental equation of ellipsometry (Eq. (4)) with the ellipsometric quantities $\Psi$ and $\Delta$ [25].

$$\tan(\Psi) = \frac{r_p}{r_s} \cdot \exp(i \cdot \Delta) \tag{4}$$

IE provides intensity- ($I_{ISC}$), amplitude- ($\Psi$), and phase- ($\Delta$) information, usually with vertically nanometer- and laterally micrometer-scaled resolution. Near Brewster angle of the substrate, one is able to identify tiny changes with regard to the unmodified surface. Moreover, it is possible to determine layer thickness $d$ and optical constants, i.e. refractive index $n$ and extinction coefficient $k$.

The EP3 set-up is shown in Fig. 1, left. After the light (1) passes the polarizer (2) and the compensator (3), it is generally elliptically polarized. The reflected light from the surface is collected by a system of lenses (5), directed trough the analyzer (6), and recorded with a CCD detector (7). The objectives (5×, 10×, 20×, or 50×) are selected in dependence on the investigated field of view. Regions of interest (ROIs) can be defined and are used to adjust the nulling conditions for the spectroscopic measurements or for $\Psi$- and $\Delta$-maps. To achieve good signal-to-noise-ratios, most of the measurements are carried out in the four-zone-mode, for details see [25]. Simulations are made using the EP4 software, version 1.2. For transparent substrates, the backside reflection from the substrate has to be considered. To minimize this effect, the knife edge illumination was applied.

RSE (Accurion GmbH) measures referenced intensities in the technical far-field in the visible wavelength range. A super continuum laser was applied (1), see Fig. 1 right. The reflected intensities (at the same AOI away from Brewster angle) of the sample $R_{sample}$ (4) and a 90° turned reference $R_{reference}$ (3) are folded, see Eq. (6). The layout with two reflections (reference in the beam pass) allows AOIs away Brewster angle and hence increases measurement speed at high sensitivity. Small deviations do not take weight as a summand (Eq. (5)) but as a quotient (Eq. (7)) [26].

$$R_{sample} = \begin{pmatrix} r_s + \delta r_s & 0 \\ 0 & r_p + \delta r_p \end{pmatrix} \tag{5}$$

$$R_{reference} = \begin{pmatrix} r_s & 0 \\ 0 & r_p \end{pmatrix}, R^{turned}_{reference} = \begin{pmatrix} r_p & 0 \\ 0 & r_s \end{pmatrix} \tag{6}$$

$$R^{turned}_{reference} * R_{sample} = r_p \cdot r_s \cdot \left[ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \frac{\delta r_p}{r_p} & 0 \\ 0 & \frac{\delta r_s}{r_s} \end{pmatrix} \right] \tag{7}$$

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