

Surface Characterization with Vacuum UV Radiation

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Introduction

In numerous areas, new materials are the key to technological developments. Hereby, the quantification of relevant material parameters – such as the electronic, chemical and morphologic structure and elementary composition – plays a central role. In this context, the lack of suitable reference samples for quantitative analytical procedures often makes metrological traceability indispensable. Therefore, with the commissioning of PTB's laboratory at BESSY II in 1999 and of the MLS in 2008, various areas of materials metrology with synchrotron radiation were taken up apart from radiometry but based on radiometry [1–5]; these topics have allowed PTB to contribute considerably to activities within the scope of the European Metrology Research Programme (EMRP). This applies to X-ray spectrometry and reference-free X-ray fluorescence analysis [6], nanometrology (i.e. the traceable determination of particle sizes [7]), surface texture [8] and layer thickness [5] in the nanometer range by means of small-angle X-ray scattering and X-ray reflectometry, micro- and nanospectroscopy in the infrared and the THz range [9] as well as surface investigations with synchrotron radiation in the spectral range of vacuum UV (VUV). To this end, the first results obtained with ellipsometry in this spectral range will be presented in the following; these were obtained within the scope of a contractual cooperation project with the *Leibniz Institute for Analytical Sciences* (ISAS, Group of Prof. N. Esser). Furthermore, results in photoelectron spectroscopy will be presented.

Ellipsometry

Spectroscopic ellipsometry is an extension of reflectometry [5] and represents a widespread optical method to analyze surfaces. It is based on the change in the polarization state of the radiation in the case of reflection on surfaces and enables the traceable determination of optical constants and of the linear dielectric response function of the material investigated as well as of further parameters such as, e.g., the layer thickness or the elemental composition of structured samples [10, 11]. Ellipsometry is a non-destructive method and is suitable both for fundamental and for application-oriented issues. Combined with conventional laboratory light sources in commercial devices, spectroscopic ellipsometry is used over a broad spectral range – from the far infrared up to ultraviolet radiation – for example in process monitoring and process control. In the VUV spectral range, ellipsometry can be used for more advanced issues, since materials can, in principle, also be excited in the energy range of the band gap and above. This, however, requires more effort. Firstly, sufficiently intense and polarized VUV radiation is necessary. Secondly, all components must be placed in an ultra-high vacuum (UHV) environment, both to prevent undesired absorption of the VUV radiation under ambient conditions and to keep the sample surfaces, which are in some cases specially prepared, free of contamination as ellipsometry is a surface-sensitive method.

The first ellipsometer for synchrotron radiation was developed in the late 1980s [12]. It could be used in the photon energy range above 6 eV, which is not covered by laboratory devices. Based on this, the ISAS developed a new ellipsometer in the past few years, which has been operated within the scope of a research cooperation with PTB at the insertion device beamline (IDB) of the MLS

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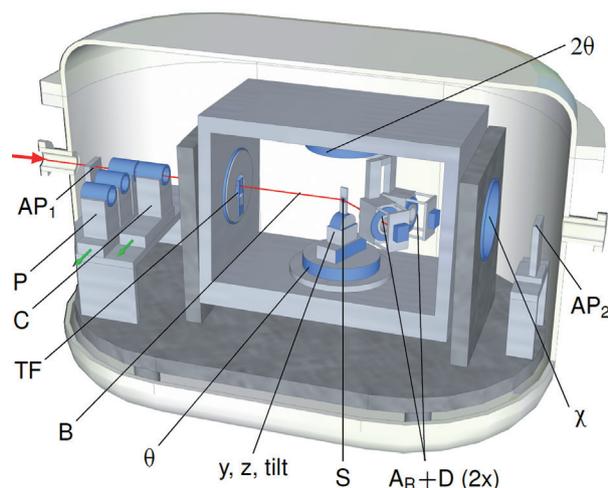


Figure 1: Scheme of the UHV-compatible ellipsometer at the undulator beamline (IDB) of the MLS [1, 13] (AP_{1,2}: aperture at radiation entry/exit; P: polarizer; C: compensator; TF: chopper; B: beam path; Φ : angle of incidence onto the sample surface; y, z, tilt: goniometer axes for sample adjustment; S: sample; A_R+D: rotating analyzer and detector; χ : rotation axis around the incident beam).

since 2012 [1, 13]. This unique device allows the change in the polarization degree at the reflection on a sample to be determined not only in a fixed geometry, but also at variable incidence and detection angles. Figure 1 shows a scheme of ISAS' new ellipsometer.

At the IDB of the MLS, in the storage ring's plane, highly linear polarized undulator radiation is available for VUV ellipsometry; due to scattering, its polarization degree is, however, attenuated at the optical components. In a first investigation, the polarization degree was therefore determined

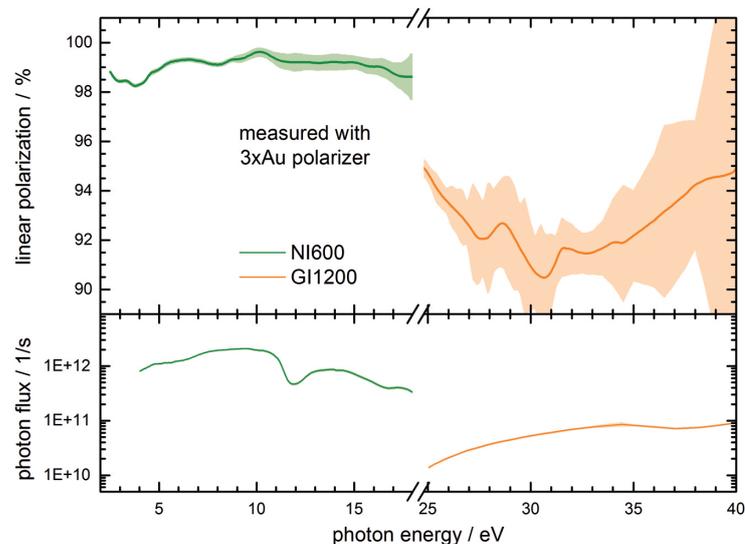


Figure 2: Linear polarization degree and photon flux at the undulator beamline (IDB) of the MLS for typical measurement conditions and two monochromator grating configurations (NI600 and GI1200).

by means of the VUV ellipsometer [13]. Figure 2 shows the result obtained for the photon energy range between 3 eV and 40 eV. Between 18 eV and 20 eV, the optical configuration of the monochromator is changed from a grating with 600 lines per millimeter working in normal incidence (NI) configuration to a grating with 1200 lines per millimeter in grazing incidence (GI) configuration. Whereas in the NI range, the linear polarization degree is higher than 98 %, it decreases by a few percent in the GI range, e.g. due to depolarized scattering at the grating's surface. All in all, the linear polarization degree of the beamline is, however, very high and ideal for ellipsometry.

First examples for the utilization of the ellipsometer refer to the characterization of epitaxially grown ZnO [13] and of thin-film energy materials within the scope of a European Metrology Research Project carried out together with the BAM Federal Institute for Materials Research and Testing [14]. Hereby, transparent and electrically conductive oxides (TCOs) as well as organic thin-film samples are investigated. The spectral range available at the IDB ranges from the VUV up to visible light and even to the near infrared; it therefore allows spectral overlap to results from measurements performed with commercially available devices under atmospheric pressure. Traceable measurements of dielectric functions and optical constants are envisaged for a series of technologically relevant optical standard materials and layer systems such as, e.g., SiC or SiO₂/Si for which experiments have shown that the corresponding values provided by literature [15] are inconsistent.

Photoelectron spectroscopy

Photoelectron spectroscopy (PES) is a widespread method in the field of materials research with synchrotron radiation, especially to characterize the surface of solids. It allows both the electronic structure of a sample to be investigated and analytical issues to be solved. PES is based on the photoelectric effect where the absorption of a photon with an energy $h\nu$ leads to the emission of an electron whose kinetic energy KE is yielded from the Einstein relation [16]:

$$KE = h\nu - (BE + \Phi).$$

If the work function Φ is known, then the binding energy BE of the electron can be determined.

Depending on the energy of the exciting photons, two main branches of PES can be distinguished which supply diversified information: in the case of ultraviolet photoelectron spectroscopy (UPS), photons in the spectral range from approx. 5 eV up to approx. 70 eV are used for excitation to eject electrons from the outer, energetically lowest (valence) states. This method therefore provides

information on the distribution of the binding energy of the valence electrons. When additionally measuring the angular distribution of the photoelectrons emitted, the valence states as well as the band structure can be determined [17].

Contrary to that, in the case of X-ray photoelectron spectroscopy (XPS), electrons are ejected from the inner shells of the atoms by means of higher-energy photons. The energy of these core levels is characteristic of each type of atom, so that it is possible to determine the elemental composition of a sample. Since core levels slightly shift due to the chemical structure of the sample, XPS additionally provides information about chemical properties of probed atoms.

The apparatus used at the IDB is a SCIENTA electron analyzer R4000 with complex electron pre-optics and a spatially resolving detector. In various operating modes, this spectrometer allows the simultaneous acceptance of both a large solid angle at a fixed electron energy and of an energy band at a fixed emission angle.

Figure 3 shows XPS spectra of an oxidized silicon surface in the spectral range of the Si-2*p* shell level which were recorded at the MLS, exciting with two different photon energies (280 eV, 130 eV). By setting the photon energy appropriately, the escape depth of the photoelectrons can be modified and, thus, a variation of the information depth of an XPS measurement is possible. The structures at a binding energy in the range of 100 eV result from the silicon substrate in the bulk of the sample and can, at approx. 104 eV, be easily distinguished from those of the outer SiO₂ layer. In the intermediate spectral range, Si-2*p* photoemissions of further suboxides at the interface layer can be seen. Traceable quantification of these different fractions plays a role, for example, in the characterization of the surface of silicon spheres which are to serve to redefine the unit *kilogram* by determining the Avogadro constant [5, 18, 19].

Figure 4 shows the result of UPS measurements on three organic thin films consisting of different transition metal/phthalocyanine complexes which were deposited under vacuum onto a titanium substrate. Such material systems are relevant for applications in organic solar cells (OSCs) and in organic light-emitting diodes (OLEDs). The spectra allow the determination of the energetic position of occupied valence states as well as conclusions about light-converting and light-emitting processes in OSCs and OLEDs, respectively, to be drawn [20]. On similar systems, already the influence of C₆₀ doping on the electronic structure and on the electro-optical properties has been investigated [21] as well as ageing effects due to quantitative UV irradiations [22].

By continuing these activities which have begun only recently, the objective is to establish photo-

electron spectroscopy as a complementary method to ellipsometry and X-ray spectrometry with synchrotron radiation [6] as a traceable method for the investigation of technologically relevant surface and layer systems and to implement it in cooperation with external partners within the scope of third-party-funded projects such as the EMRP project *ThinErgy* [14].

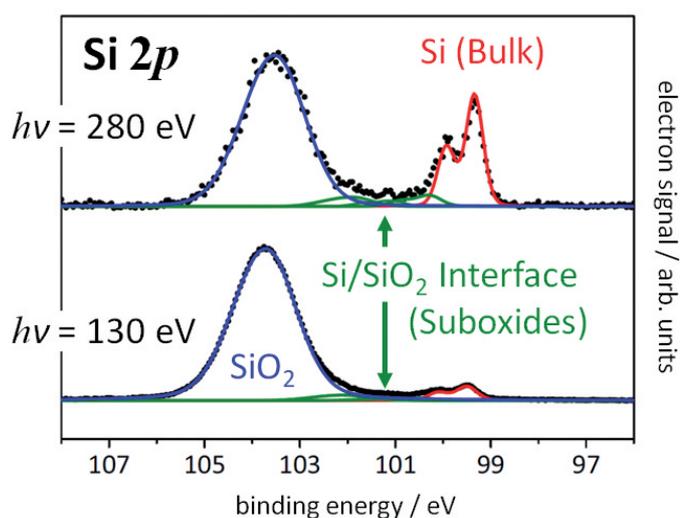


Figure 3: XPS spectra of a silicon oxide layer on silicon, recorded at different photon energies of the exciting radiation (280 eV, 130 eV) [18].

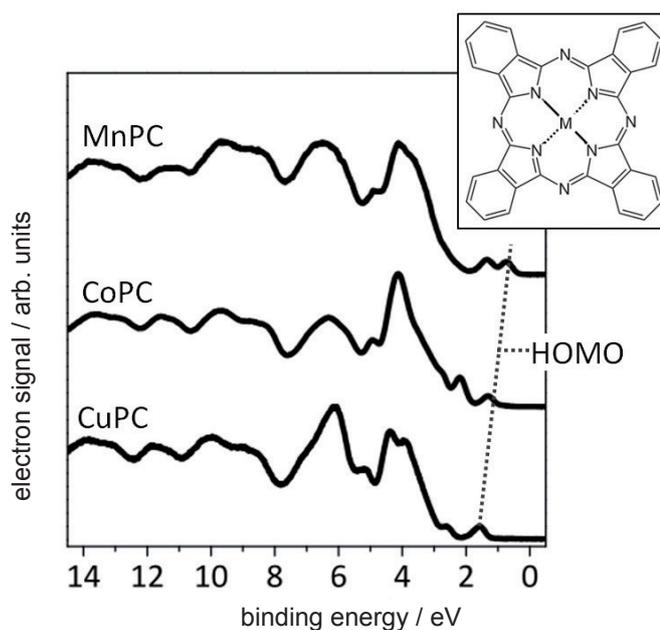


Figure 4: UPS spectra of 7 nm thick Mn(II), Co(II) and Cu(II) phthalocyanine thin films on Ti ($h\nu = 60$ eV).

References

- [1] *M. Richter, G. Ulm*: in this publication on p. 3
- [2] *R. Klein, R. Thornagel, G. Ulm*: in this publication on p. 7
- [3] *R. Klein, R. Fliegau, S. Kroth, W. Paustian, M. Richter, R. Thornagel*: in this publication on p. 16
- [4] *A. Gottwald, U. Kroth, M. Krumrey, P. Müller, F. Scholze*: in this publication on p. 21
- [5] *M. Krumrey, L. Cibik, A. Fischer, A. Gottwald, U. Kroth, F. Scholze*: in this publication on p. 35
- [6] *M. Müller et al.*: in this publication on p. 57
- [7] *M. Krumrey, R. Garcia-Diez, C. Gollwitzer, S. Langner*: in this publication on p. 53
- [8] *F. Scholze, A. Haase, M. Krumrey, V. Soltwisch, J. Wernecke*: in this publication on p. 48
- [9] *P. Hermann, A. Hoehl, A. Hornemann, B. Kästner, R. Müller, B. Beckhoff, G. Ulm*: in this publication on p. 64
- [10] *D. E. Aspnes*: Spectroscopic ellipsometry, in: *Optical Properties of Solids: New Developments*, B. O. Seraphin, (Eds.), North-Holland Publishing, Amsterdam (1976), pp. 799–846
- [11] *M. Schubert*: *Annalen der Physik* **518**, 480 (2006)
- [12] *R. L. Johnson, J. Barth, M. Cardona, D. Fuchs, A. M. Bradshaw*: *Rev. Sci. Instrum.* **60**, 2209 (1989)
- [13] *M. D. Neumann, C. Cobet, H. Kaser, M. Kolbe, A. Gottwald, M. Richter, N. Esser*: *Rev. Sci. Instrum.* **85**, 055117 (2014)
- [14] <http://www.ptb.de/emrp/thinergy.html> (retrieved: 2016-06-30)
- [15] *E. D. Palik* (Eds.): *Handbook of Optical Constants of Solids*, Academic Press, Orlando (1985)
- [16] *A. Einstein*: *Annalen der Physik* **322**, 132 (1905)
- [17] *S. Weiß et al.*: *Nat. Commun.* **6**, 8287 (2015)
- [18] *E. Darlatt, M. Kolbe, R. Fliegau, P. Hönicke, I. Holfelder*: EMRS-Spring Meeting, Lille (France), May 26 to 30 (2014)
- [19] *B. Andreas et al.*: *Phys. Rev. Lett.* **106**, 030801 (2011)
- [20] *N. R. Armstrong, W. Wang, D. M. Alloway, D. Placencia, E. Ratcliff, M. Brumbach*: *Macromol. Rapid Commun.* **30**, 717 (2009)
- [21] *F. Roth, C. Lupulescu, T. Arion, E. Darlatt, A. Gottwald, W. Eberhardt*: *J. Appl. Phys.* **115**, 033705 (2014)
- [22] *E. Darlatt et al.*: *Nanotechnology* **27**, 324005 (2016)