Reflectometry with Synchrotron Radiation

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Introduction

High-quality reflection measurements for the characterization of optical components, for layer thickness determination, or for the determination of optical constants of solids and thin layers, are performed for a variety of applications. The objects to be measured may be mirrors or other reflecting objects such as diffraction gratings or crystals, but also (foil) filters whose transmittance often varies with the wavelength by many orders of magnitude. At PTB, reflectometry with synchrotron radiation has a long tradition: the first measurements were already carried out in 1986 at BESSY I [1]. Currently, four reflectometers are operated at the beamlines at PTB's laboratory at BESSY II and at the MLS. This article provides a survey of these devices and of their properties, of the measurement procedures and the achievable measurement uncertainties, and of the different applications of reflectometry in the X-ray, EUV and VUV ranges.

Measuring stations for reflectometry

Reflectometry can be performed on all beamlines for detector calibration [2, 3]. These measuring set-ups provide radiation of high spectral purity which is spatially well defined, without a stray light halo, and with a high temporal stability. In addition, the monochromators have a very good reproducibility of the energy or wavelength setting. As the characterization of optical components often also requires the measurement of position- and angle-dependent properties, the beam size and the beam divergence may become vitally important. For applications in the X-ray region under grazing incidence, a good angular resolution is, therefore, often more important than a particularly good spatial resolution on the samples. This has been especially taken into account for the optical design of the beamlines.

For the characterization of optical components, four reflectometers are available by which the sample to be investigated can be positioned in all degrees of freedom. The essential properties are compiled in Table 1.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Beamline</th>
<th>Polarization</th>
<th>Max. sample size and mass</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>VUV reflectometer [6]</td>
<td>NIM MLS</td>
<td>optional</td>
<td>(155 mm)$^2$ 5 kg</td>
<td>Load lock</td>
</tr>
<tr>
<td>EUV reflectometer [4]</td>
<td>EUVR MLS</td>
<td>S</td>
<td>550 mm 50 kg</td>
<td>Firmly installed at the EUVR beamline</td>
</tr>
<tr>
<td>EUV ellipso-scatterometer</td>
<td>SX700 BESSY II</td>
<td>optional</td>
<td>(190 mm)$^2$ 5 kg</td>
<td>Load lock, polarization analyzer</td>
</tr>
<tr>
<td>X-ray reflectometer [5]</td>
<td>FCM (PGM) BESSY II</td>
<td>S</td>
<td>(150 mm)$^2$ 5 kg</td>
<td>Load lock, X-ray detector for single-photon counting</td>
</tr>
</tbody>
</table>

Table 1:
Summary of some of the essential properties of PTB’s reflectometers.
Due to its size, the EUV reflectometer [4] is firmly installed on the EUVR beamline at the MLS. The X-ray reflectometer [5] is used on the FCM beamline and at the PGM monochromator of PTB’s undulator at BESSY II. The VUV reflectometer [6] can be rotated around the optical axis and allows measurements to be performed with any polarization orientation. It is used at the NIM beamline of the MLS. The new EUV ellipsometer, which is used on the SX700 beamline, also allows any linear direction of polarization to be selected.

Measurement procedures and uncertainties

In contrast to source calibration or detector calibration, no standards are required for reflectometry, as these measurements are relative measurements of the intensity of the reflected (or, in the case of filters or partially reflecting samples: of the transmitted) beam compared to the intensity of the incident beam, measured with the same photodetector, respectively. But also here, diverse influence quantities must be taken into account in order to achieve lower measurement uncertainties. These are, in the case of incident radiation, the beam divergence and the spectral bandwidth – in addition to the stability and spectral purity, which are also important for detector calibration. For reflectometers, the homogeneity and linearity of the detectors used (mostly semiconductor photodiodes) and the linearity of the associated amperemeters are essential in addition to the accuracy of the angle adjustment. Table 2 provides an overview of the measurement uncertainties which can be achieved at the different beamlines.

Applications

X-ray range

In the X-ray range, the reflectance of mirrors is investigated for applications in astrophysics [7] or plasma diagnosis [8]. In addition, optical components are examined with regard to their use at other synchrotron radiation sources [9]. Currently, reflectometry in the X-ray region is, however, mainly used to determine the thickness of nanolayers which play an important role, e.g., in nanotechnology, in the semiconductor industry, and in the optical industry for the manufacture of mirrors and optical coatings. Thereby, the function of the layer often decisively depends on its thickness. X-ray reflectometry (XRR) is an established non-destructive procedure for layer thickness determination [10]. In a layer-substrate system, reflection occurs both at the surface of the layer and at the layer-substrate interface (as shown in Figure 1). According to Bragg’s equation, constructive interference occurs for X-rays – which, in most cases, hit the surface under a grazing angle of incidence – if the path of the radiation in the layer with the thickness \( d \) is an integer multiple of the wavelength \( \lambda \) of \( m \cdot \lambda = 2 \cdot n \cdot d \cdot \sin \Theta \). Here, \( n \) is the refractive index of the layer, and \( \Theta \) is the angle in the layer which differs from the external angle of incidence \( \Theta_1 \) by the refraction. The influence is, however, insignificant because – although \( n \) is smaller than 1 in the X-ray region – it mostly differs from 1 only by values \(< 10^{-4} \). For certain optical constants, a phase shift may also occur at the interface by which the conditions for minima and maxima are reversed.

| Table 2: Summary of typical measurement uncertainties for the determination of the reflectance. |
|---|---|---|---|
| Beamline | NIM | EUVR | SX700 | FCM |
| Storage ring | MLS | MLS | BESSY II | BESSY II |
| Typical wavelength/ nm | 300 | 13.5 | 13.5 | 0.2 |
| Contribution to relative standard uncertainty \( u / \% \) | 0.14 | 0.01 | 0.03 | 0.20 |

Stability of the radiant power

Angle adjustment and beam divergence

Homogeneity of the detector

False light (higher harmonic of the monochromator and stray light)

Relative measurement uncertainty for the reflectance
In each case, the reflectance shows – at a fixed wavelength as a function of the angle of incidence – characteristic oscillations whose period is used to determine the layer thickness. The traceability of the layer thickness determination – i.e. of a length measurement – is obtained from the wavelength calibration of the monochromator, which can, in turn, be traced back via Bragg’s back reflection on a silicon single crystal to the lattice constant of this crystal [11], and from the calibration of the goniometer in the reflectometer by a calibrated optical polygon, using an electronic autocollimator.

Figure 2 shows the experimental realization in the X-ray reflectometer with a very specific sample: a sphere of isotopically pure silicon, 95 mm in diameter, which – via the determination of the Avogadro constant – is intended to serve to redefine the unit “kilogram” [12]. XRR is used to determine the thickness of the unavoidable silicon oxide layer on the sphere surface. On the oxide there is, in addition, also an unavoidable, carbon-containing contamination layer. To separate the two layer thicknesses from each other, the measurements are carried out with focused undulator radiation on the PGM beamline at BESSY II at different energies around the oxygen absorption edge in the range from 480 eV to 560 eV [13]. In this range, the optical properties of the oxide change very strongly, whereas they are largely constant for silicon and for the contamination layer. For these energies, angles of incidence up to 40° can be used. This makes it possible to carry out the measurements on the strongly curved surface. The measured reflectance is shown in Figure 3. The oscillations are very pronounced, in particular close to the absorption edge (529 eV). Although the photon energy changes by only approx. 20°, the curves are quite varied. From the simultaneous fit, which is also shown [11], a thickness of 7.1 nm is obtained for the oxide, and a thickness of 0.3 nm for the contamination layer. The layers can be distinguished only if measurements are performed at several photon energies (at one single energy, only the total layer thickness can be determined).

The selection of the photon energy offers similar advantages, for example, for Cu- and Ni-double layers on a Si-substrate. Whereas Cu-Kα radiation, which is usually used for laboratory X-ray sources, only allows the total thickness to be determined from the angular dependence of the reflectance (Figure 4, top), a measurement at 8400 eV, i.e. at a photon energy between the K absorption edges of Ni (8333 eV) and Cu (8980 eV), exhibits the double structure which is characteristic of double layers (Figure 4, bottom) and from which the single layer thicknesses can be obtained [14].
For the layer thickness determination of organic layers on oxidized silicon wafers – as well as for SiO$_2$ layers on plane surfaces – a photon energy of 1841 eV (i.e. directly above the Si-K absorption edge) is suitable, as the contrast of the optical constants of Si and SiO$_2$ is particularly high here due to the shift of the edge in the oxide [15, 16]. For complex systems, the evaluation can also be performed via a Fourier transformation of the oscillatory fraction of the measured reflectance clearly above the critical angle for the total reflection (Figure 5, top). The visible peaks in Figure 5 (bottom) correspond to the thickness of single layers or layer groups. The peak at the largest correlation length corresponds to the total layer thickness. The combination of the maxima allows the individual layer thicknesses to be determined [17].

All in all, X-ray reflectometry offers the possibility to determine layer thicknesses in the nanometer range with relative uncertainties down to approx. 1 %. By the use of monochromatized synchrotron radiation, this is also possible for layer combinations for which a sufficient contrast cannot be observed with conventional X-ray sources.

**EUV range**

For many years, the main field of work in the EUV range at PTB has been the characterization of optical components and detectors for EUV lithography. These activities are shown in a separate article in this publication [18]. Quite generally, short-wave radiation, however, also offers manifold application possibilities for the characterization of micro- and nanostructures. This application, too, will be presented in more detail in another article of this publication [19]. In principle, the measurements which can be performed in the EUV spectral range are the same as those which can be performed with hard X-rays. The critical angles for the reflection are, however, larger and it is, thus, possible to carry out measurements at steeper angles of incidence. This is, for example, of advantage for curved surfaces – as in the case of the above-mentioned silicon sphere – or smaller samples. A further particularity of the spectral range of EUV and soft X-ray is that – although the reflectance is practically negligibly small for all materials under normal incidence – the reflectance in the maximum of the resonance can, due to the structure of multi-layer Bragg reflectors, amount to clearly more than 50 %. This allows mirror-optical systems with a large numerical aperture and a large field of view to be established, similar to the UV or VUV range. The most important application is EUV lithography for the semiconductor industry at a wavelength of 13.5 nm [18]. There are, however, also multi-layer systems which have
been optimized for reflection at shorter wavelengths, for example at 3 nm in the so-called “water window” between the absorption edges of carbon and oxygen. In this spectral range, organic substances can very well be investigated in an aqueous environment and can, for example, be imaged microscopically with high resolution. For optimization of the respective optics based on layer systems, their optical material properties must be investigated. This can be done by measuring the angle-dependent reflectance, making use of the Fresnel equations. The refractive index in its complex form $n = 1 - \delta + i \beta$ allows the formulas to be uniformly represented also for absorbing media – by recursive application also for multi-layers. For S- or P-polarized radiation, which occurs from the vacuum under the angle $\Theta_1$ to the surface (for angles which are defined in a complex manner), the reflectance $R$ of a thick layer can be calculated according to:

$$R_s = \frac{\sin \Theta_1 - (1 - \delta + i \beta) \sin \Theta_2}{\sin \Theta_1 + (1 - \delta + i \beta) \sin \Theta_2},$$  \hspace{1cm} (1)$$

$$R_p = \frac{(1 - \delta + i \beta) \sin \Theta_1 - \sin \Theta_2}{\sin \Theta_1 + (1 - \delta + i \beta) \sin \Theta_2},$$  \hspace{1cm} (2)$$

with $\Theta_2$ being the angle of the layer which can be calculated in its complex form using the law of refraction according to [20]:

$$\cos \Theta_2 = \frac{\cos \Theta_1}{1 - \delta + i \beta}. \hspace{1cm} (3)$$

Figure 6 shows an example of the determination of the optical constants from angle-dependent reflection measurements for a thick SiO$_2$ layer (see the clear deviations of the measured optical constants in the spectral range from 7 nm to 16 nm from the generally used tabulated values [21]).

Another application of reflectometry in the EUV range is shown in Figure 7. Here, the specular reflection was measured on a grating structure with a rectangular line profile [22]. The interference of the partial waves reflected on the surfaces of the lines and on the bases of the grooves leads, as described above for the reflection of a homogeneous layer, to an interference effect which, in this case, allows the line height to be determined.

Figure 6:
The optical constants $\delta$ and $\beta$ of SiO$_2$ (refractive index $n = 1 - \delta + i \beta$) in the spectral range from 7 nm to 16 nm determined from the reflectance $R_\delta$ as a function of the angle of incidence $\Theta_1$ to the surface. On the left, some measurement curves are shown which have been obtained at different wavelengths and from which the values shown on the right for $\delta$ (blue circles) and $\beta$ (red points) have been determined for each single wavelength. For comparison, tabulated data from literature [19] are shown. The dashed and the solid lines in the left figure represent adaptations of the measurement points with the old and new optical constants.

Figure 7:
Reflectance of an etched silicon grating as a function of the angle of incidence at 13.5 nm. From the oscillations, a line height of 114 nm can be determined.
UV/VUV range

In the range of UV and vacuum-UV (VUV) radiation, i.e. in the wavelength interval between 40 nm and 400 nm, optical components (e.g. mirrors, filters, dispersion lattices) are also investigated routinely with reflection and transmission measurements at the normal incidence monochromator (NIM) set-up for detector calibration [2, 3]. The reflecting layer is, in most cases, metallic. Metal carbides or dielectric layers for wavelength-selective reflection or anti-reflection coatings (AR coatings) are, however, also used.

In particular in the VUV spectral range, i.e. for wavelengths below 200 nm, the depth of penetration of the radiation is very small (only a few 10 nanometers or less, depending on the wavelength and on the material) so that the optical properties are predominantly determined by the quality of the immediate surface. Depth profiles and multi-layer systems are, however, of subordinate importance (unlike in the regions of shorter wavelengths). In addition to the direct determination of the reflectance for applications or for reference mirrors, the curve of the spectral reflectance or transmittance also provides data for the determination of the optical constants of solids or thin layers [23]. Fundamental investigations of the electronic states (band gaps) of a solid can also be performed, whereby the variation of the temperature during the measurement provides, for example, information about the origin of the different absorption and reflection processes [24, 25].

The possibility of measuring the polarization-dependent reflectance as a function of the angle of incidence allows polarizing optical elements to be investigated and developed in a dedicated way. An example are polarization mirrors for the hydrogen-Lyman-α-wavelength at 121.6 nm, which are of outstanding importance in stellar astrophysics (Figure 8) [26].

The polarization $P$ is calculated as follows:

$$ P = \frac{R_s - R_p}{R_s + R_p} $$

The measurement requires a previous determination of the polarization degree of the monochromatized synchrotron radiation. These techniques also provide the basis for VUV ellipsometry [27, 28], in which case the change in the polarization during reflection is measured in order to determine layer thicknesses and material properties.

Figure 8:
Measured properties of an MgF$_2$ reflection polarizer.
(a) Polarization for the hydrogen-Lyman-alpha-wavelength of 121.6 nm as a function of the angle of incidence.
(b) Reflectance and polarization in the wavelength range between 80 nm and 140 nm. The lines indicate the range of the standard uncertainty.
References