Diffraction gratings as small-angle X-ray scattering calibration standards

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It is shown that diffraction gratings can be used as accurate momentum-transfer calibration standards in small-angle X-ray scattering experiments. For demonstration purposes, a silicon diffraction grating with a period of 400 nm is used. The data exhibit 50 diffraction peaks evenly distributed in the momentum-transfer range $q = 0.0\text{--}0.8\text{ nm}^{-1}$, a regime that is not accessible using the traditional silver behenate standard.

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1. Introduction

Small-angle X-ray scattering (SAXS) is a versatile tool for structural studies of mesoscopic materials, providing information on the spatial electron density variations in the range from one to a few hundred nanometres (Glatter & Kratky, 1982). Presently the technique is routinely used, for example, to determine the structure of biomolecules in solution, for studying the interactions and kinetics in soft condensed matter, and as a contrast mechanism in X-ray imaging. Moreover, experimental work can be carried out using both synchrotron radiation and laboratory-based sources, thus further enhancing the impact of the technique.

In a SAXS experiment one determines the scattered intensity as a function of the momentum transfer $q = (4\pi/\lambda) \sin(\theta/2)$, with λ and θ denoting the X-ray wavelength and the scattering angle, respectively. In practice, the momentum transfer is determined either from an accurate knowledge of the scattering geometry and the X-ray wavelength or using a well known calibration standard. For the latter purpose silver behenate, $[\text{CH}_3(\text{CH}_2)_{20}\text{COOAg}]$, has proved useful (Huang *et al.*, 1993). It exhibits regularly spaced (001) Bragg diffraction peaks at momentum-transfer values $q_l = 2\pi l/d$, with l denoting the Miller index and $d = 5.8380$ (3) nm. However, its use as a calibration standard is limited to SAXS setups covering the momentum-transfer value of $q_1 = 2\pi/d \simeq 1.08\text{ nm}^{-1}$. An alternative is provided by (wet) rat-tail collagen, which exhibits equidistant Bragg diffraction peaks at smaller q_l values than silver behenate, because of a larger periodic repeat distance of approximately 67 nm (see, *e.g.*, Fratzl *et al.*, 1997). However, owing to a relatively large scatter in the experimentally determined unit-cell size, the inaccuracy in the momentum transfer q as calibrated using rat-tail collagen is several percent. Hence, an accurate calibration standard for SAXS setups working in the range of tens to some hundreds of nanometres is called for.

Polymer-based diffraction gratings were proposed as possible future calibration standards for diffraction experiments 20 years ago (Rupp *et al.*, 1990). In the meantime, there have been great advances in SAXS instrumentation, as exemplified, for example, by SAXS becoming a standard technique for accurate characterization of topologically nanopatterned polymer films (Jones *et al.*, 2003). In this short communication we demonstrate that diffraction gratings can indeed be used as accurate momentum-transfer calibration standards in SAXS experiments. We make use of high-quality and high-aspect-ratio linear silicon diffraction gratings, which have previously been

utilized, for example, for differential phase contrast imaging (David *et al.*, 2002), for quantifying the coherence of hard X-ray beams (Pfeiffer *et al.*, 2005) and in structural studies of complex fluids in confinement (Satapathy *et al.*, 2008). Analogous to silver behenate, the grating diffracts into orders m at the positions $q_m = 2\pi m/p$ in reciprocal space, with p denoting the period of the grating. Consequently, by choosing a period $p \gg d$, the grating diffracts in a momentum-transfer regime not accessible using silver behenate (down to the ultra-small-angle X-ray scattering regime).

2. Experimental details

For demonstration purposes we used a diffraction grating with the following parameters: a period of $p \simeq 400\text{ nm}$, a depth of $h \simeq 3.5\text{ }\mu\text{m}$, a channel width $w \simeq 250\text{ nm}$ and a total area of $1 \times 1\text{ mm}$. The grating was fabricated into a $300\text{ }\mu\text{m}$ -thick (110)-oriented silicon wafer by means of electron-beam lithography and anisotropic KOH etching, leading to a high aspect ratio, $h/w \simeq 14$, and nearly vertical channels. We note that the grating is fabricated with a sub-nanometre accuracy of the period, when averaged over the transverse coherence lengths of the incident X-ray beam. Moreover, the diffraction grating neither is prone to radiation damage nor suffers from long-term storage effects. Details on the grating fabrication can be found elsewhere (Nygård *et al.*, 2009).

The experiment was carried out at the cSAXS beamline (X12SA) of the Swiss Light Source, Paul Scherrer Institut. The X-rays impinged on the grating at normal incidence and the diffracted X-rays were detected 7.124 m behind the sample using a two-dimensional pixel detector (Pilatus 2M, 1461×1560 pixels with a size of $172 \times 172\text{ }\mu\text{m}$ each). The incident X-ray beam had a wavelength of $\lambda = 0.11070\text{ nm}$ (energy $\hbar\omega = 11.200\text{ keV}$) and a size of $0.1 \times 0.1\text{ mm}$ at the sample position. Despite a moderate momentum-transfer resolution of $\Delta q \simeq 5.5 \times 10^{-3}\text{ nm}^{-1}$ in the present study, the diffraction peaks were easily distinguished.

We determined the complete diffraction pattern by combining two separate exposures: the low- q data were obtained without a central beam stop and using attenuators, while the high- q data were collected using a central beam stop and without attenuators. The exposure time in both cases was 10 s. Owing to the large dynamic range of the detector, two exposures were sufficient to clearly observe 50 diffraction orders in the range $q = 0.0\text{--}0.8\text{ nm}^{-1}$. However, the quality

Figure 1
Diffraction pattern acquired from the SAXS calibration standard. Top: Two-dimensional image of the diffraction pattern (logarithmic scale). Bottom: One-dimensional diffraction pattern, as obtained by integrating the data of the top panel perpendicular to the grating direction. Because of the intrinsic symmetry of the diffraction pattern, only positive diffraction orders are shown. The inset shows a magnification in the momentum-transfer range $q = 0.45\text{--}0.75\text{ nm}^{-1}$, comprising diffraction orders $m = 29\text{--}47$.

of the data could be further improved, for example, by using longer exposure times.

3. Results and discussion

The diffraction pattern obtained from the grating is shown in Fig. 1. We can clearly distinguish 50 diffraction peaks evenly distributed in the momentum-transfer range $q = 0.0\text{--}0.8\text{ nm}^{-1}$. Within the kinematic approximation, the relative intensities of the different diffraction orders m vary according to the square modulus of the grating form factor as $I_m/I_0 \propto \text{sinc}^2(\pi m w/p)$ (Nygård *et al.*, 2009). Since the grating profile is known, the diffraction pattern could in principle be used for calibration of SAXS intensities on an absolute scale. We also note that the diffraction peaks sit on top of a slowly varying background, which we attribute to defects in the diffraction grating resulting from the fabrication process.

From the diffraction pattern we can, using the known sample-to-detector distance and X-ray wavelength λ , determine the grating period $p_{\text{XRD}} = 399.8(5)\text{ nm}$. This value is in excellent agreement with the nominal period of $p = 400\text{ nm}$. The small relative inaccuracy in the period, $\Delta p_{\text{XRD}}/p_{\text{XRD}} \simeq 1.3 \times 10^{-3}$, demonstrates that diffrac-

tion gratings can indeed be used as accurate momentum-transfer calibration standards in SAXS experiments.

It should be noted that, for linear diffraction gratings as used here, the diffraction condition will be fulfilled even if the grating is misaligned with respect to the propagation direction of the incident X-ray beam. In this case the intersection with the Ewald sphere is shifted, leading to a different momentum-transfer value along the nominal grating direction. However, the grating is easily aligned with an inaccuracy below 0.1° , rendering this effect negligible.

Finally, we comment on the use of such diffraction gratings in different SAXS setups. The possibility of selecting the grating period p in the fabrication process provides access to different parts of reciprocal space, allowing the calibration standard to be optimized for a specific SAXS setup. This property makes the use of diffraction gratings as momentum-transfer calibration standards particularly appealing. As a drawback, we note that the present wafer thickness of $300\text{ }\mu\text{m}$ is problematic because of absorption for longer X-ray wavelengths. However, this problem is readily overcome by etching the diffraction gratings into thinner silicon wafers (David *et al.*, 2002).

4. Conclusions

We have demonstrated that diffraction gratings can be used as accurate momentum-transfer calibration standards in SAXS experiments. Since the accessible momentum-transfer range is easily tuned by using a different grating period, the standard can be optimized for a specific SAXS setup. In particular, the diffraction gratings allow calibration in momentum-transfer regimes not accessible by the traditional silver behenate standard.

The experiment was carried out at the cSAXS beamline of the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland.

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