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Fast X-Ray Reflectivity Measurements Using a X-Ray Pixel Area Detector at DiffAbs Beamline, Synchrotron SOLEIL

Cristian Mocuta, Stefan Stanescu, Manon Gallard, Antoine Barbier, Arkadiusz Dawiec, Bouzid Kedjar, Nicolas Leclercq and Dominique Thiaudiere

We will give hereafter a brief reminder of the X-ray reflectivity (XRR) principle and classical (point detector) measurement setups (using monochromatic X-ray beams), but as well a short list of other possible XRR acquisition schemes.

S1. Classical X-ray reflectivity measuring scheme

We will briefly recall the measurement strategy used in a 'classical' XRR approach using a point detector. A more thorough and complete description can be found in dedicated textbooks and reviews devoted to X-ray interaction (reflection, refraction and scattering) with matter [Als Nielsen and McMorrow 2010, Yasaka 2010, Daillant and Alba 2000, Daillant and Gibaud 2009, Tolan 1999, Seeck 2014, Stoev and Sakurai 1999, Sakuray 2004, Holy *et al.* 1999].

In addition to the major points mentioned in the introduction section, one may also point out the following advantages of the method:

i) there is no need for the thin film to be crystalline; the method works for single- and poly-crystalline as well as amorphous or liquid samples, as long as there is an electron density contrast between the layers or between the thin film and the substrate;

ii) the film to be measured can be opaque to visible light, thus reflectivity / ellipsometry methods with visible light would not work. The relatively large penetration depth of several microns of hard X-rays (energy of about 10 keV) combined with high resolutions usually available on X-ray reflectometers allow measuring film thickness from nanometers up to microns. Moreover, this large penetration depth allows the use of a wide range of sample environments for in-situ studies (*e.g.* ultra-high vacuum, molecular beam epitaxy growth of thin films, thermal annealing in controlled atmosphere, film oxidation or reduction, catalysis, etc.);

iii) single- or multi-layer structures can be investigated;

iv) surface and interface roughness, as well as thickness of diffuse interface can be accessed;

v) there is a wide variety of materials which can be studied, from thin films and multilayers of metals, semiconductors or polymers to soft- and bio-materials (*e.g.* membranes). Liquid interfaces are also measurable with dedicated specific XRR setups: X-ray liquid reflectometers, see for example [Murphy *et al.* 2014, Seeck 2014, Metzger *et al.* 1994] and references therein;

vi) the method is non-destructive but organic or soft condensed matter films may evolve under X-ray beam irradiation;

vii) the information obtained is not local, like it would be in a microscopy like approach, but corresponds to average values from the area of the sample which is illuminated by the X-ray

beam. This area is of one to several mm^2, due to the very glancing angles of incidence, typically up to several degrees only, during XRR measurements.

In a classical acquisition scheme of XRR data, a monochromatic and low divergence (*i.e.* well collimated) X-ray beam illuminates the sample under a glancing angle (Fig. S1). The elastically scattered beam (*i.e.* incident $|\mathbf{k_i}|$ and emergent $|\mathbf{k_f}|$ wavenumbers are equal to $2\theta/\lambda$, λ being the X-ray wavelength) is detected using a point detector (scintillator, avalanche diode, etc.). Several pairs of slits placed in front of the detector define the angular position, the angular acceptance and the sample area viewed by the detector when measuring the XRR signal. The scattered intensity is recorded step by step while keeping the incident (sample) and emergent (detector) angles equal, $\alpha_i = \alpha_f$ (Fig. S1), so that the momentum transfer vector $\mathbf{q} = \mathbf{k_f} - \mathbf{k_i}$ amplitude will vary (as $q = |\mathbf{q}| = (4\pi/\lambda) \cdot \sin\alpha_i$), but will always stay perpendicular to the sample surface (*i.e.* will have only a q_z non-zero component, since $q_x = q_y = 0$, see Fig. S1). From a practical point of view, the XRR signal decays rapidly over an extended dynamical range while the detector offers only a limited dynamical linear response range. Overcoming this issue requires the use of calibrated beam attenuators.

Because the phase information is lost during the X-ray intensity measurement, a simple transformation of the data does not allow to retrieve the sample characteristics. The XRR data analysis is usually done by comparing the experimental data with model structures evaluated within the Parratt algorithm [Parratt 1954]. The model contains important sample characteristic parameters such as the electron density of the different layers (contrast), the roughness at the surface and interfaces, as well as the thickness of the constitutive layer(s). This qualitative 'line measurement' performed as described above allows, in many cases, to extract information like layer thickness rather accurately and rapidly (for example by a simple Fourier transform) [Brower *et al.* 1996]. Indeed, the measured signal is a combination of the Fresnel reflectivity (q_z^{-4} decay) and an interference pattern (Kiessig fringes) from the scattering originating from the different layers. Supplementary information like roughness cannot be extracted with reasonable accuracy (Fig. S1, right panel) without a reliable measurement of the total scattered signal. This implies integrating the scattered intensity in q-space, as well as a robust and reliable correction of the experimental data; two important corrections are the background subtraction and the illuminated area correction. A rapid but approximated way to do some background correction is to perform a similar XRR line scan while keeping a constant offset value between the incidence and exit angle (i.e. $\alpha_f = \alpha_i$ + offset). This offset XRR scan corresponds, in the reciprocal space, to a scan along the qz direction at $q_x \neq 0$. This background measurement can then be subtracted from the XRR line scan [Brower *et al.* 1996]. A more accurate way to measure the XRR signal is to perform an 'integrated intensity' (rocking scan) measurement: for each detector angle α_f, the sample angular position is scanned (rocked) around the value $\alpha_i = \alpha_f$ while recording the scattered intensity in each point. This scan corresponds to a circular line cut in the $q_y = 0$ plane, cut realized across the q_z line. Due to the relatively small angles involved (several degrees at most), this cut is almost performed at constant

q_z value (in fact, the trajectory is slightly curved since $|q| = (q_x^2+q_z^2)^{1/2}$ = constant during the scan, but q_x is close to 0). This cut across the qz direction translates into a peak of scattered intensity around $q_x \sim 0$. It allows extracting the integrated intensity (total scattering) together with a proper background correction. Thus, each rocking scan is used to generate one single point (referred to as background corrected integrated intensity) on the XRR curve. The different trajectories in reciprocal space are shown in Fig. S2.

The obtained dataset still needs to be corrected by the active area of the sample which is illuminated by the beam and seen by the detector (active area correction, which is a purely geometrical effect) [Yasaka 2010, Vlieg 1997, Schlepütz *et al.* 2005]. The area of the sample that is illuminated by the X-ray beam changes with the incident angle α_i and only a part of it is 'seen' by the point detector through the slits system, as α_f angle is changing. The measured scattered signal depends on this active area of the sample and consequently needs to be corrected for this geometrical effect. The knowledge of the sample shape is a mandatory prerequisite to make this correction.

A measurement as described above is rather time consuming. To give a rough estimate, let us consider a measurement spanning, in detector angle (2θ), over ~10° with a 0.01° resolution (*i.e.* 1000 points on the XRR curve). Each rocking curve will require a minimum of 20-30 points. With an exposure time per point of, let's say, 100 ms, a full measurement will still take more than 30 min. (in terms of exposure time only). Even reducing the exposure time to 10 ms per point (which can be done in some cases if a synchrotron source is used), a measurement will still take several minutes, especially when including the dead-times related to data reading and motor movements. Even a continuous acquisition mode (with a point detector) will require movement time between the scans (*e.g.* detector repositioning in α_f steps, acceleration and deceleration phases of the motor while perform α_i scan, etc.)

We also point out here that this classical approach (of using rocking scans and point detector) will generate a raster mapping image of the $q_y = 0$ reciprocal space plane in a region limited to the very near-by of the specular region ($q_x = q_y = 0$, *i.e.* $\alpha_i = \alpha_f$).

S2. Other proposed XRR data acquisition schemes

From the different attempts recently proposed towards this direction [Sakurai *et al.* 2007a], one can mention (Fig. S3):

i) the use of monochromatic X-rays combined with the use of an area detector [Fenter *et al.* 2006a]. This approach has the advantage of recording on the same image the background to be used for correcting the XRR data. With the experimental procedure depicted in [Schlepütz *et al.* 2005, AlsNielsen and McMorrow 2010, Vlieg 1997], this approach can be seen like a particular measurement of the specular reflectivity rod (*i.e.* 00ℓ direction in the reciprocal lattice units described by hkℓ indexes);

ii) the use of a monochromatic X-ray beam, an area detector (PILATUS 100k [Dectris]) combined with a 2 slits system; the proper movement of the slits positions ensures the detection of the specularly reflected X-ray beam on the area detector, at each θ-2θ pair. The XRR curve (line scan) is recorded on a single image taken by the detector, in slightly less than 1 minute [Wirkert *et al.* 2013];

iii) the use of a monochromatic highly divergent X-ray beam (angular dispersive setups). Various detection systems were proposed: point detectors and slits moving across the fan of the scattered X-ray beam [Niggemeier *et al.* 1997]; position sensitive detectors to record in one shot the XRR signal in a certain angular range [Naudon *et al.* 1989, Chihab and Naudon 1992, Albouy and Valerio 1997]; or the use of a Charge-Coupled Device (CCD) detector [Omote *et al.* 2000, 2001, Stoev and Sakuray 2013, Mizusawa and Sakurai 2011, Jibaoui and Erre 2012]. The XRR can be extracted from a single detector image, the exposure time being limited by the available photon flux only. Some maximal q-range (maximal 2θ) limitations might subsist, inherent to the particular setup;

iv) using a monochromatic well collimated and low divergent (0.01°) X-ray beam and an area detector: the sample is mounted on a wedge and rotated around the vertical axis direction (*i.e.* the rotation axis makes an angle with respect to the sample surface normal) [Buffet *et al.*, 2013]. During this rotation, the X-ray incident angle is changing from -α to + α, α being the wedge angle. Images are acquired rapidly and continuously during the rotation; the reflected beam is moving vertically and sideways on the area detector – its position gives directly the incident angle. This position is traced and recorded to generate XRR line scans. The acquisition time can be as low as sub-second;

v) using a polychromatic (white) X-ray beam coupled with an energy dispersive detector [Bhattacharya *et al.* 2003, Sakurai *et al.* 2007b, Nakano *et al.* 1978, Metzger *et al.* 1994, Sato *et al.* 2000] allows measuring in one shot (fixed angle) a certain momentum transfer range of the reflectivity curve;

vi) using a polychromatic (white) convergent X-ray beam with a one to one correspondence between X-rays energy and direction, coupled with an area detector [Voegeli *et al.* 2013, Matsushita *et al.* 2008, 2013, Abboud *et al.* 2011] (multiple wavelength angle-dispersive method). Again, the XRR curve is observed in (can be extracted from) a single detector image together with some background to be used for corrections. The exposure time can be as small as milliseconds;

vii) measuring the reflectivity signal at a fixed momentum transfer (q_z) value (*i.e.* fixed angular positions of the incidence and emergence angles) allows monitoring, with sub-second resolution, local changes in the reflectivity signal, at that particular position. This approach was

used as a diagnosis tool during in-situ thin film growth [Lueken *et al.* 1994, Peverini *et al.* 2007, Kozhevnikov *et al.* 2008];

viii) an approach on imaging sub-nm height steps on the surface of a sample was proposed by [Fenter *et al.* 2006b, Laanait *et al.* 2014]: it is based on reflectivity measurements with an area detector performed under fixed particular momentum transfer value, such that the contrast is obtained due to the phase shift and interference between X-ray beams scattered from terraces of the sample separated by these steps.

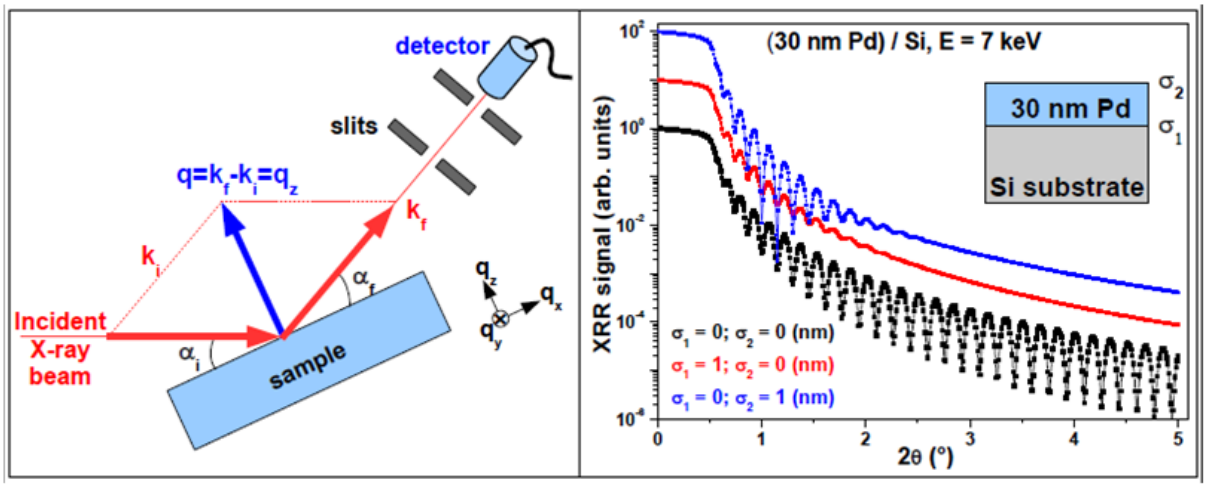

Figure S1 (left) Schematic principle of a X-ray Reflectivity (XRR) measurement using monochromatic X-ray beam and a point detector. The incident X-ray beam is impinging the sample under the incident angle α_i. The elastically scattered beam is detected by the point detector. The slits system defines the θ - 2θ geometry of the measurement, investigated area of the sample and the angular resolution. In the fast XRR approach depicted in the text, the slits and point detector are replaced by the area detector. (right) Simulated XRR curves (for a X-ray energy of 7.0 keV) using Ref. [Layered Mirror Reflectivity website] for a 30 nm Pd film on Si, with various roughness values at the film surface and interface with the substrate. The different datasets were shifted vertically for clarity. The inset shows schematically the sample; the indexes 1 and 2 refer to the roughness (σ) at the interface with the substrate and of the top layer respectively.

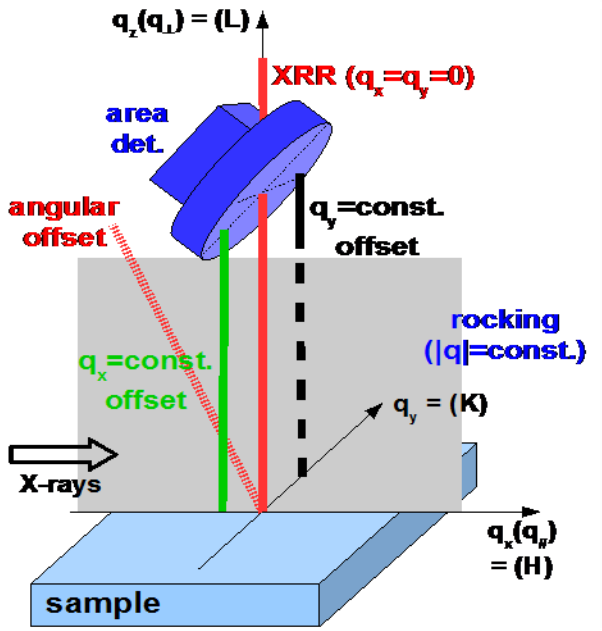

Figure S2 Scheme of the different trajectories of scans used to measure reflectivity signal in reciprocal space, using either a point detector or an area detector. The background measurement at q_x = constant or q_y = constant can be extracted, as line-cuts, from the dataset after the conversion into a 3D volume (in reciprocal space coordinates).

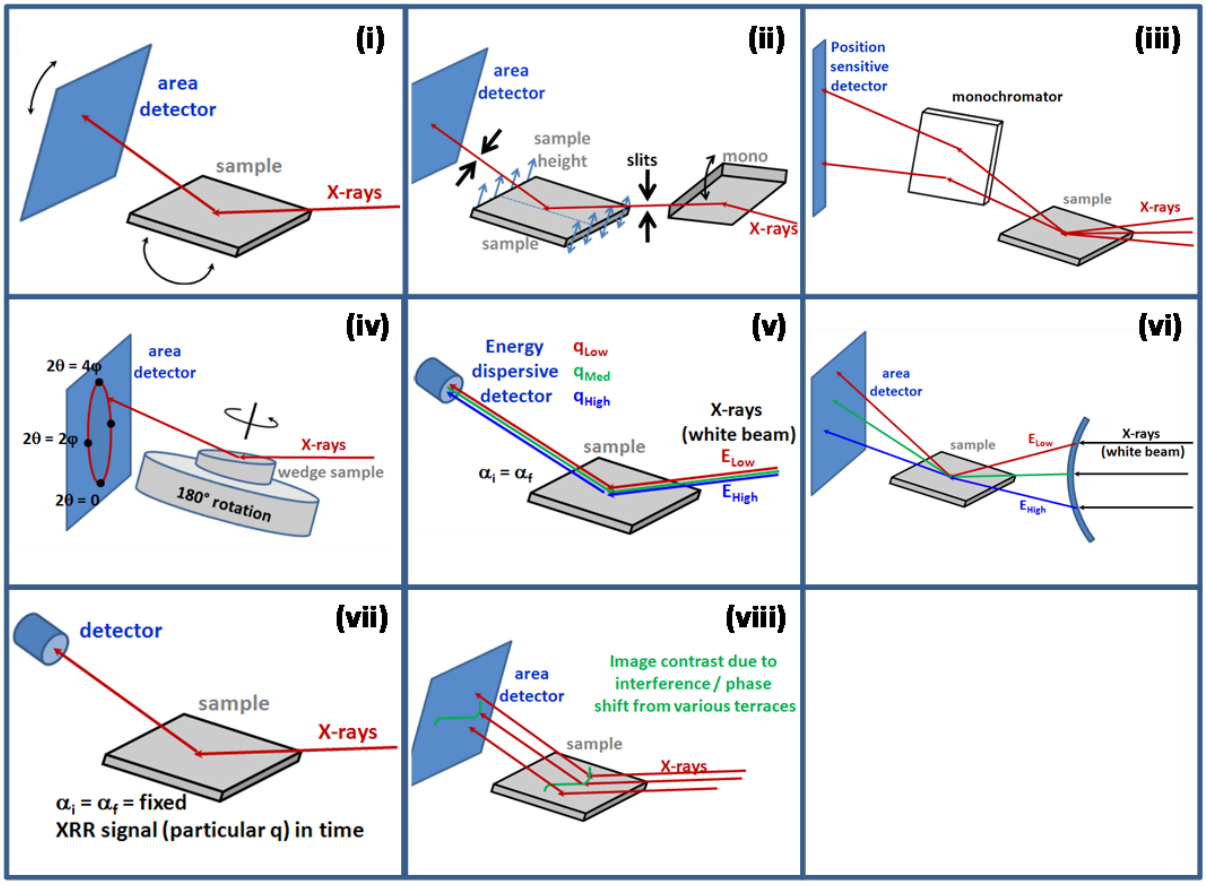

Figure S3 Schematics of various approaches to measure reflectivity signals using hard X-rays. See text for details and panels legend.

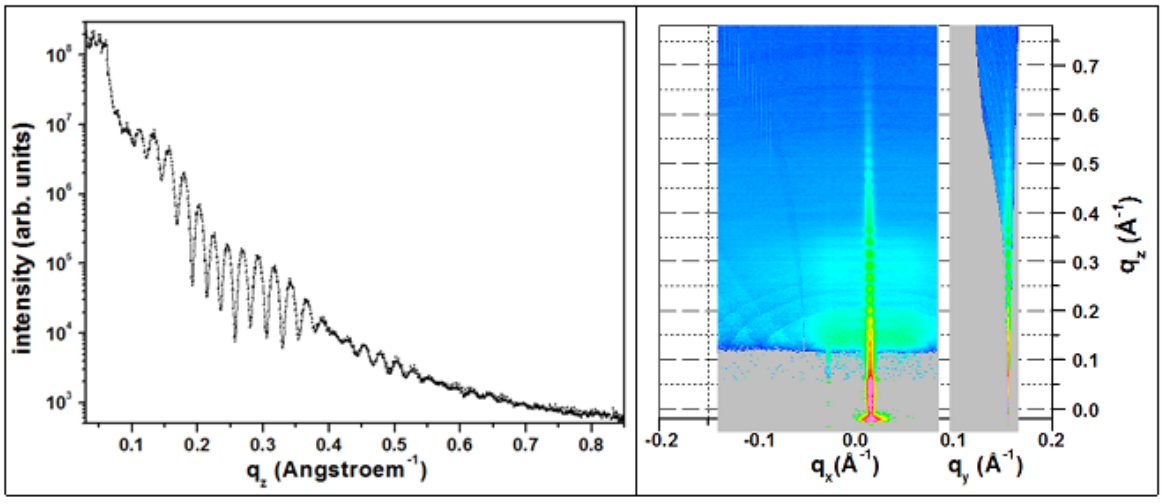

Figure S4 Soliton sample described in section 2.1. (left) XRR curve (10 ms exposure time per image) extracted from 3D data reconstructed using the area detector images; (right) 2D cuts in the reciprocal space along high symmetry directions, for the same dataset. The remarks noted in fig. 2 concerning horizontal axis apply here as well. The intensity color scale is logarithmic and spans over 5 orders of magnitude, from blue to red.

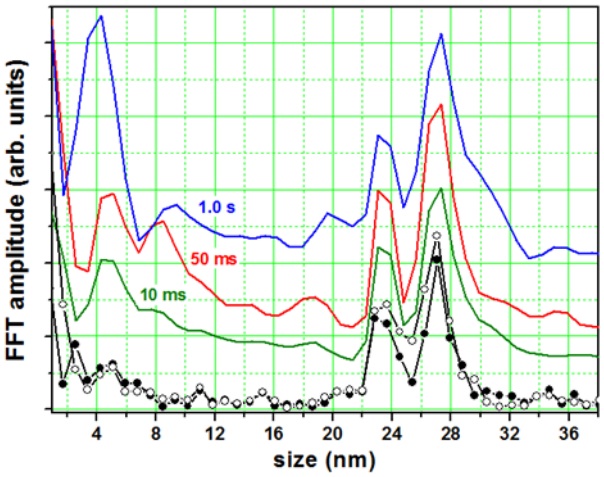

Figure S5 Fast Fourier Transform (FFT) performed (after re-binning on a regular q-space) on various XRR datasets recorded for the 'soliton' sample described in section 2.1. The black curves with open and filled symbols correspond to the data recorded using a point detector, with a correction corresponding respectively to background level subtraction or integrated intensity from each rocking scan. The colored curves correspond to datasets recorded using the XPAD detector – the corresponding exposure time per detector image is reported on each curve. Presence of periodic thickness oscillations translates into presence of sharp peaks (particular frequencies) on the FFT. The horizontal axis was converted from signal frequency into corresponding layer thickness.

References

References are given in the main paper.