Real-Time Monitoring of Growing Nanoparticles

Gilles Renaud, Rémi Lazzari, Christine Revenant, Antoine Barbier, Marion Noblet, Olivier Ulrich, Frédéric Leroy, Jacques Jupille, Yves Borensztein, Claude R. Henry, Jean-Paul Deville, Fabrice Scheurer, Jeannot Mane-Mane, Olivier Fruchart

Supporting Online Material

Materials and methods:

Experimental set-up

A major constraint in GISAXS is to decrease as much as possible the small angle background arising from beam divergence, from the beamline optical elements, and from windows placed in the beam path. This requires a bright beam with a very low divergence, high quality optical elements and several pairs of slits to define the beam and remove unwanted low-angle scattering. More important, when performing surface x-ray scattering in UHV, beryllium windows are usually present on the sample chamber and at the end of the beamline, as well as some air-path of the x-ray beam between the beamline and the chamber, which all generate large background scattering at small angles. To avoid it, the chamber was directly hooked to the beamline, without any window between the sample and the X-ray source. Fig. 1 shows a schematic drawing of the experimental set-up, whose different parts are described below. Fig. 2 and 3 show photographs of the main parts of the set-up.

The ID32 undulator beamline of the European Synchrotron Radiation facility (ESRF, Grenoble, France) (1) is windowless, and delivers a doubly focused monochromatic X-ray beam. The full width at half maximum (FWHM) beam size and divergence at the sample location are 0.5 × 0.2 mm² (HxV) and 2×10⁻⁵ (H) and 4×10⁻⁶ rad (V), respectively, with a flux ~10¹³ ph s⁻¹.

Two pairs of motorized slits (the first defining the beam size, 0.05 mm H × 0.2 mm V, and the second removing the scattering by the primary slits) working in high vacuum were installed respectively 1 meter and 5 meters upstream of the sample. A fast beam shutter was installed in a dedicated UHV cross, and a hollow diode was mounted in vacuum just
before the secondary slits. This latter was used to monitor the primary beam intensity by measuring the beam scattered by the primary slits. This beam-defining assembly was pumped down to \(5 \times 10^{-8}\) Torr. A differential pumping pipe allowing a differential pressure of more than 4 orders of magnitude was installed between this beam-defining line and the UHV chamber (base pressure \(10^{-10}\) mbar). The UHV chamber was mounted on a diffractometer, which is described elsewhere (2). The chamber could be equipped with up to 5 evaporation sources: two MECA-2000 evaporation Knudsen cells and 3 Omicron EFM4 electron-beam evaporators. Evaporation of Ag, Pd, Pt, Au, Co, Ge and Si have been performed, with deposition rates between 0.01 and 1 Å/min as calibrated in situ by a quartz microbalance and ex situ by Rutherford Back Scattering and X-ray microprobe. Remote controlled shutters were installed on the different evaporators, as well a general one in front of the sample. A load-lock system was used to insert the sample into the chamber, in which it was held by a custom horizontal axis manipulator holding a high temperature (up to 1400°C) furnace. \(\text{Ar}^+\) ion bombardment and heating under \(\text{O}_2\) partial pressure (up to \(5 \times 10^{-4}\) mbar) were available, as well as a quadrupole mass analyzer. The sample manipulator was directly connected to and held by an additional goniometric \(\omega\) 360° rotation with horizontal axis. The manipulator had three precise in-vacuum motorized motions, to allow the sample surface to be located at the goniometer center, and to precisely align the surface normal with the \(\omega\) axis. Two view ports were located on opposite sides of the chamber, to allow alignment of the surface using a laser beam, and pyrometric measurement of the sample's temperature.

The beam entered the UHV chamber by a CF38 bellows hooked to the entrance line, allowing for a small rotation of the chamber around the vertical axis, thus defining the angle of incidence of the x-ray beam with respect to the (vertical) sample surface. At the opposite side, a 0.8 meter-long cone was connected to an exit pipe through a CF38 bellows, and terminated by a 100 mm diameter beryllium window placed in front of the two-dimensional detector, thus avoiding small angle scattering background. The cone and detector were hooked to the goniometer detector arm, allowing precise vertical and horizontal alignment.
A motorized tungsten beam-stop with a T-shape was introduced between the exit Be window and the 2D detector to hide the direct and reflected beams. The X-ray detector was a 1242×1153 pixels 16 bits high grade CCD from Princeton coupled via fiber optics to a scintillator with a square acceptance of 65 × 65 mm. It could be placed at a variable distance (between 900 and 1500 mm) from the sample. The data have been corrected for the flat field and the dark counts, and the reference signal from the bare substrate prior to deposition has been subtracted.

**Experimental details**

The (15 ×15 × 0.5 mm³) MgO(001) substrates provided oriented and polished by Earth Chemical (Japan) were first annealed in air at 1500°C for 24 hours, which yields crystals of very high quality with micron-size large (001) terraces. The contaminants segregated at the surface were next removed in a remote UHV chamber by Ar+ ion bombardment (IB, 10µA current and 0.6 keV energy) at 1500°C, thus yielding clean flat terraces while keeping the high crystallinity, and finally annealed at 900°C for 20 min. and cooled down under 10^{-4} Torr of O₂ in order to restore a perfect surface stoichiometry. The resulting stoichiometric MgO surfaces of very low roughness, with large terraces, i.e. a very small defect density, and high crystalline quality have been characterized elsewhere {\cite{3}}. These surfaces were protected by a ~1000 Å-thick Ag film before being transferred in the x-ray chamber, where the Ag film was desorbed by annealing at ~700 °C. The deposition procedures for Pd, Ag and Pt were very close to those described in {\cite{4, 5}}. Pd and Pt were evaporated thanks to Omicron EFM4 e-beam bombardment deposition cells, using 2 mm diameter, high purity (99.99%) rods, while Ag (99.9999% purity) was deposited using a MECA-2000 Knudsen cell heated up to 900°C. The deposition rate for Pd and Ag was ~1 Å/min. (except when real-time GISAXS measurements were performed without interrupting the growth, for which the deposition rate was decreased down to ~0.1 Å/min), and that for Pt was 0.2 Å/min.

The MgO(001) substrates were stuck on 1 mm thick Ta plate thanks to a thin indium film. Heating was performed by a filament placed behind the Ta plate. The temperature of the MgO substrate was measured thanks to an infrared pyrometer looking at the Ta plate, and
previously calibrated using the thermal expansion of the MgO lattice parameter as deduced from grazing incidence x-ray diffraction measurements.

The 10 mm diameter and 3 mm thick Au(111) substrate provided (to within 0.1°) and polished by the Surface Preparation Laboratory (6) was mounted on a Ta plate using spot-welded Ta sheets. Repeated cycles of annealing up to 700°C and Ar+ IB (15 µA, 1 keV) were performed in a remote chamber until a clean surface (as checked by Auger Electron Spectroscopy) displaying a nice long-range ordered $22\times\sqrt{3}$ reconstruction (as checked by low-energy electron diffraction) was obtained. The substrate was next transferred into the x-ray chamber in which a few cycles of IB and annealing were done to restore a fresh $22\times\sqrt{3}$ reconstruction before starting the measurements. Co was deposited at 1 Å/min. using an EFM4 Omicron e-beam bombardment cell with a high purity 2 mm diameter Co rod.
Supporting figures and captions:

**Fig. 1.** Schematic drawing of the experimental setup located in the experimental x-ray hutch. The entire beam path between the x-ray source and the sample is in high or ultra-high vacuum, with no scattering element such as Be window in between, thus suppressing the usual small angle scattering background due to windows.
**Fig. 2.** Photograph of the experimental setup viewed from the end of the experimental hutch. The X-ray beam enters from the right; the sample is vertical, in the center of the UVH chamber.
Fig. 3. Photograph of the experimental setup viewed from the sample transfer line. The X-ray beam enters from the right.

Supporting references and notes:

1. A description of the ESRF and of the ID32 beamline can be found at http://www.esrf.fr.