Electronic Supplementary Information

Pre-treatment of silicon substrates

Vacuum sputter deposition was performed onto inert polished boron-doped silicon (Si) substrates (Si-Mat) diced to an area of 20 x 20 mm² with a precision diamond saw. In order to remove organic residuals, the Si-wafer pieces were first cleaned for 15 minutes in acetone using an ultrasonic bath and further rinsed with acetone, isopropanol and ultra clean water. The silicon substrates were subsequently oxidized in an acid bath (200 mL of 96 % sulfuric acid, 88 mL of 35 % hydrogen peroxide (Carl Roth GmbH) and 37.5 mL of deionized water) at a temperature of 80°C for 15 min. Finally, the cleaned substrates were rinsed with ultra clean water (18.2 MΩ cm^{-1}) several times and dried in a nitrogen flow.

X-Ray reflectivity

The X-ray reflectivity data was taken after gold sputter deposition on a D5000 (Siemens) diffractometer at a wavelength of 0.154 nm (CuKα radiation) in an angular range from 0° to 6°. A knife edge was used to reduce the beam size and the background noise. The obtained reflectivity curve was fitted using the transfer-matrix method implemented in PyXRR software.[79]

Field emission scanning electron microscopy

The SEM images were taken with an NVision 40 Gemini (Zeiss) field emission SEM operating at an accelerating voltage of 5 kV and at a low working distance of 3.0 mm. The cross-sectional image (Figure 4) was taken at a tilt angle of 54° relatively to the surface normal.

IsGISAXS simulation

Simulations were performed with IsGISAXS software V2.6 for comparison of the µGISAXS data with the model parameter.[78] Full 2D scattering patterns were calculated based on an input file containing all relevant information about geometry and arrangement of nanoparticles. The calculation of the interference function is based on a regular 1D lattice with a loss of long-range order. The cluster distances were varied by the fitted exponential decay of the measured peak position. The Gaussian disorder parameter ω of the distance D was calculated to $\omega = 0.25\ D$. The distorted-wave Born approximation was used to calculate the form factor. The radii at different film thicknesses were calculated by use of the model-based combined exponential equation (Equation 2). A log-normal distribution function with a relatively width of $\sigma = 1.2$ was assumed for the particle sizes.

Sampling statistics

The beam sizes on the microscale allow for a statistically significant evaluation of the data, as we have also mentioned in previous publications [see manuscript references 23, 58, 67]. The beam size is chosen in such a way to reduce the beam footprint in grazing incidence to approx. 25% of sample size to avoid any noise from the sample edges, which might disturb the 2D scattering pattern. The cluster density is on the order of $>10^{12}$/cm², see Figure 5f. This means, the number of clusters in the footprint is 10^{8}, which is sufficient for statistical significance. The photon flux in the footprint is on the order of 10^{11}ph/s. This allows for a reasonable time resolution and a still large enough photon density, because the amount of scattered photons scales proportional to scattering cross section [see manuscript reference 77].

Comparison µGIWAXS/µGISAXS

The presented results were obtained within our technical feasible deposition rates in a range from approximately 1 to 2 Å/s. They show a negligible effect of deposition rates in the given deposition regime, which ensured a very good comparison between wide-angle and small angle scattering data considering the error environment (Figure S1).

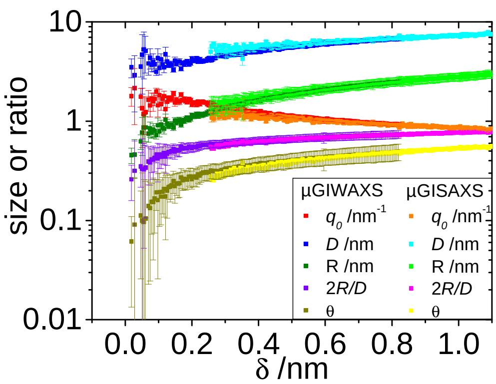

Fig. S1 Comparison µGIWAXS/µGISAXS-data obtained at different deposition rates: the evolution of out-of-plane peak position q_0 and the model-based morphological parameters (distance D, radius R, coverage θ) as a function of film thickness is in very good agreement.