Large-scale arrays of ordered nanoparticles are fascinating materials for science and technology, e.g., data storage, or DNA sensing, due to their distinct optical properties.

To deposit the nanoparticle layer on top of the substrate, various methods are available, e.g., vacuum deposition and solution casting. Solution casting allows nanostructuring of large-area two-dimensional thin films with specific morphology, offering the possibility to design 2D or three-dimensional photonic crystals. This method is especially important and applicable in the field of colloidal particles, as colloidal particles are often suspended in aqueous solutions.

Nanostructuring, however, is a very complex process involving several mechanisms. The solvent evaporates and increases the concentration of the colloidal particles. The increased evaporation near the contact line drives a convective flow within the drop that transports material toward the periphery. Additionally, an increased solute concentration and a decreased temperature near the three-phase contact line (TPCL) may trigger solutal and thermocapillary Marangoni flows. Furthermore, the interaction with the substrate and transversal contact line instabilities have to be taken into account. Finally, capillary forces come into play as soon as the solution film has a comparable thickness as the colloidal particles’ diameter.

Previous studies addressed the ordering of nanoparticles at the liquid-air interface. However, for technical applications it is of great importance to transfer this order to a solid substrate. The interaction with the substrate allows for tuning the arrangement of the nanoparticles and thus the layer’s optical properties. Hence, it is only natural to investigate in situ the evolution of ordering at the TPCL liquid-air substrate.

Grazing incidence small angle x-ray scattering (GISAXS) has proven to be a well suited technique for real-time studies. Here, the x-ray beam impinges under a small angle $\alpha$ on to the sample surface. We combined a nanobeam small angle x-ray scattering (nano-SAXS) geometry of ID13/ESRF with a grazing incidence setup, allowing for nanobeam-grazing incidence small angle x-ray scattering (nano-GISAXS) experiments. We used the extremely brilliant 300 nm size beam (full width at half maximum) produced by Fresnel zone plates at a wavelength of 0.0976 nm. The angle of incidence was $\alpha = 0.543^\circ$. The resulting footprint on the sample of $0.3 \times 32 \mu m^2$ reduced the beam size compared to previous microbeam and submicrobeam GISAXS experiments up to a factor of 10.

The samples consisted of commercial unconjugated colloidal gold solutions of 2 nm particle size (Kisker Biotech). Gold nanoparticles are inert and provide strong scattering contrast to the solvent (water). A droplet of 25 $\mu l$ volume was deposited on a blank, acid cleaned Si-wafer surface using a high-precision, remote controlled syringe pump. The resulting droplet diameter on the surface was 3 mm. Hence, the surface curvature of the droplet can be neglected and the droplet surface with respect to the beam can be considered as locally flat (see Fig. 1). The beam was positioned at the TPCL. As an example, we focused on a colloidal particle diameter of 2 nm. Figures 1(b)–1(d) shows the different

**FIG. 1.** (Color online) Geometry of the nanobeam-grazing incidence small angle x-ray scattering (nano-GISAXS) experiment: (a) Si denotes the silicon substrate and D the droplet. The beam position and direction (X) is shown as an arrow as well as a scale bar. X, Y denote a coordinate system parallel to the sample surface. Due to an angle of incidence of $\alpha = 0.543^\circ$, the beam footprint is $0.3 \times 32 \mu m^2$ (X×Y). (b)–(d) Sketch of the droplet evolution during solvent evaporation. The nanobeam is positioned within 50 $\mu m$ of the initial three-phase contact line (TPCL) after deposition of the droplet. (b) TPCL is far away. (c) TPCL reaches the beam. (d) TPCL has passed the beam. $R_i > R_j > R_k$ during solvent evaporation with $R_j$ (j=1, 2, 3) being the droplet radius.
stages of solvent evaporation. For the \textit{in situ} experiment, an acquisition time of 120 s and a time between frames of 130 s were chosen. The acquisition of the nano-GISAXS pattern started immediately after casting of the droplet. Figure 2 shows the corresponding results. The 2D nano-GISAXS signal at a sample-to-detector distance \( L_{SD}=0.809 \) m is decomposed in two components. The so-called detector cut\(^5,6\) shown in Fig. 2(a) probes the intensity distribution as a function of scattering vector component \( q_y \) (vertical to the sample surface). From bottom to top, the time after deposition increases. In Fig. 2(b), the so-called out-of-plane cut is presented. It shows the intensity distribution \( I(q_x) \) of the scattering vector component \( q_x \) (parallel to the sample surface) and hence probes lateral length scales, e.g., most-prominent radii of clusters.

For times \( < t_b = 3250 \) s, no change in the nano-GISAXS spectra is observed. At time \( t_b \), corresponding to Fig. 1(c), the TPCL reaches the beam position and clear changes in the nano-GISAXS pattern occur. From Fig. 2(b), we are able to extract a most-prominent length scale \( \xi \) using a Guinier approximation \( I(q_x) \propto \exp(-q_x^2 R_g^2/3) \) as a function of time within the region \( 0.037 \text{ nm}^{-1} \leq q_x \leq 0.08 \text{ nm}^{-1} \). Here, \( R_g \) is the Guinier radius\(^15\) and \( \xi = \sqrt{5/3} R_g \). The results are shown in Fig. 3(b), with the time \( t \) being calculated relative to \( t_b \), i.e., time after deposition is \( t+t_b \). At \( t=0 \) s, corresponding to Fig. 1(c), the droplet volume has considerably decreased, and we observe that the lateral growth sets in. \( \xi \) increases according to a power law as function of time, \( \xi(t) \propto t^{0.32\pm0.06} \), indicating that the structure formation is not governed by diffusive processes, which would lead to \( t^{1/2} \). Additionally, the detector scan in Fig. 2(a) shows the decreasing solution film thickness, as indicated by the arrows. We analyzed the detector cuts using the distorted wave born approximation which includes refraction and reflection effects.\(^16\) Following Ref. 17, we estimate the layer thickness by using the formula for the Bragg reflections,

\[
q_c = \frac{2 \pi}{\lambda} \left[ \sin(\alpha_i) + \sqrt{\sin^2(\alpha_{c,Au}) + \left[ BL(m, \alpha_i, t) \right]^2} \right],
\]

where \( \alpha_i \) denotes the incident angle, \( \alpha_{c,Au} \) the critical angle of gold, \( H \) the height of the resulting layer as a function of time \( t \), \( m \) the order of the Bragg reflection, and \( \lambda \) the wavelength. In our case, \( \alpha_i \) is fixed, and we observe Bragg reflections for different times at different \( q_y \). As can be seen in Fig. 2(a), higher orders \( (m > 1) \) can occur. From the fits of the positions of the Bragg peaks in Fig. 2(a) using Eq. (1), we can analyze the height of the resulting nanoparticle layer. The result is shown in Fig. 3(a). For times \( t < 2000 \) s, a constant height is found. This seems to correspond to a rapidly deposited, short-range order hexagonal close packing of an \( n=2 \) layer of colloidal spheres of 2 nm diameter, yielding a thickness of about 3 nm. For \( t > 2260 \) s, which is much larger than the time where lateral growth sets in, a linear growth following \( 0.0049 \text{ nm/s} \times t \) in height \( H \) of the layers is found. At \( t=3770 \) s the vertical growth is essentially finished and levels of into its final value \( H=9.2 \) nm due to compaction. From the linear time dependence of \( 2080 \) s \( < t < 3770 \) s, one can estimate the establishment of a full layer with height increase of \( 2 \text{ nm} \times \sin 60^\circ = 1.7 \text{ nm} \) every \( 340 \) s, assuming close packing of the colloidal particles. This would correspond to a layer-by-layer growth every \( 340 \) s assuming close packing. As one can see the final ordering in this aqueous colloidal solution takes place with time scales on the order of some \( 10 \) s. More remarkably, the lateral growth is finished \textit{before} vertical growth sets in. This time delay between vertical and lateral growth has not been reported yet.

We have for the first time employed nanobeam GISAXS to follow \textit{in situ} the nanostructuring during solution casting quantitatively. The lateral assembly manifesting itself in the length scale \( \xi \) precedes the vertical growth of the nanolayer.
This structure formation can be interpreted as clustering of nanoparticles and domain formation during evaporation of the solvent. We finally speculate that the nondiffusive character of lateral clustering as indicated by the power-law behavior might be caused by convective flows, reducing the exponent.

This work was financially supported by the DFG Schwärzpunktprogramm SPP 1164 “Nano- and Microfluidics” (Mu1487/2).