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Stripe-Like Pattern Formation in Airbrush-Spray Deposition of Colloidal Polymer Film**

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We use the versatile technique of Grazing incidence small angle X-ray scattering (GISAXS) to investigate the ordering of colloidal polymer films deposited on Silicon substrate by airbrush-spray coating. A lateral ordering of the polymer colloids is highly desirable as it would open a promising route to generate laterally structured templates and scaffold for the fabrication of ultra-high density media. The study shows a strong dependency of the film homogeneity on the number of spray cycles and a strong influence of the solvent choice on the film lateral ordering.

Thin films and multilayer structures are used in a wide range of applications. To name just a few: sensor coating,^[1–3] microelectronics,^[4] solar cell technology,^[5,6] and magnetic recording.^[7] In the last few years, organic-based hybrid devices received strong attention from both academy and industry because of their potential for low-cost production and flexible device applications.^[5] In order to improve the device performances, new approaches are needed to install thin films showing lateral order and high uniformity over large areas. Many methods have already been developed: bottom-up approaches such as solution casting,^[8] spin-coating,^[5] inkjet printing,^[9,10] dip-coating,^[11] and also top-down approaches such as lithography^[12,13] or vacuum deposition.^[14] Recently, the novel technique of airbrush-spray deposition was used in the fabrication of organic-based multilayer devices such as diodes,^[15] transistors,^[16] semiconductors,^[17] electrolyte films,^[18,19] and solar cells.^[20–22] The airbrush-spray coating technique allows performing fast and economic deposition of organic-based layers showing high structural uniformity over large areas and is thus of great interest in industrial applications.

Experimental

For the polymer coating, we used a commercial airbrush-spray (Harder & Steenbeck, Evolution Silverline) with a needle diameter of 30 μm (see Fig. 1). Two different types of aqueous colloidal suspensions (provided by Kisker GbR, Steinfurt, Germany) were deposited: polystyrene (PS) colloids (initial concentration: 2.5 wt%) and carboxylated polystyrene (cPS) colloids (initial concentration: 5.0 wt%). Both types of colloids have a nominal diameter of 96 nm. Two different solvents were used for further dilution, namely deionized water and ethanol. Influence of the solvent on the film lateral ordering will be discussed later. Spray coatings were performed on flat Silicon (Si) substrates ($18 \times 30 \text{ mm}^2$) at an air pressure $P = 3 \text{ bar}$ in a horizontal configuration. Prior to use, the Si wafers were cleaned in a basic bath (35 mL of 25% ammoniac, 25 mL of 35% hydrogen peroxide, and 350 mL of deionized water) at a temperature of 75 °C. The cleaned substrates were further individually rinsed in deionized water and dried using nitrogen flow.

Two different spray-deposition modes were examined. In the first mode, the coating is performed in one single cycle at a short spray nozzle-to-substrate distance ($D_{\text{SS}} = 73 \text{ mm}$). In the second mode, the coating consists in three spray cycles at a larger spray nozzle-to-substrate distance ($D_{\text{SS}} = 142 \text{ mm}$). These two distances ensure a complete coating of the substrate. By enlarging the distance, one can reduce the amount of solvent (by evaporation) impinging on the substrate. A spray cycle is 1 s, the time between two successive spray cycles (second coating mode) 5 s. The total coating time is 1 s in the first mode and 3 s in the second mode. An overview of the parameter sets used in this study is given in Table 1.

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Fig. 1. Photograph of the airbrush-spray deposition setup. D_{SS} denotes the distance between the spray nozzle and the Si substrate.

The grazing incidence small angle X-ray scattering (GISAXS)^[23] experiments were performed at the beamline BW4^[24] of the DORIS III storage ring at HASYLAB (DESY, Hamburg). Sketch of the GISAXS geometry is shown in Figure 2. We used a wavelength $\lambda = 0.138$ nm. The sample-to-detector distances D_{SD} and incident angles α_i used for the different samples are given in Table A.1 (Appendix). The beam size was reduced to $20 \times 60 \mu\text{m}^2$ (vertical $\times$ horizontal) by using an assembly of parabolic beryllium compound refractive lenses. Samples were scanned to probe the uniformity of the coating over the whole substrates. For each specimen, GISAXS scans were performed over 20 mm in the deposited film with a scan step size of 1 mm.

Data Analysis

Figure 3 shows normalized average out-of-plane cuts extracted from the GISAXS 2D-data at the Yoneda maximum

Fig. 2. Sketch of the GISAXS geometry: a beamstop is used to protect the detector from the reflected beam which is much more intense than the diffuse scattering intensity. The white dashed line indicates the location of the out-of-plane cut selected for further analysis (see Figs. 3 and 4).

(see Table A.1 in the Appendix for the exact α_f -values), as indicated by the white dashed line in Figure 2. For each sample, one curve is obtained by averaging the out-of-plane cuts collected within a complete spatial scan. The error bars are used as a measure of the colloidal polymer coating uniformity.

The analysis of the data features a strong dependency of the film uniformity on the number of spray cycles. Out-of-plane cuts corresponding to the coatings performed according to the second coating mode (1b, 2b, 3b, 4b) show lower variance than the cuts corresponding to the coatings performed according to the first coating mode (1a, 2a, 3a, 4a). This result suggests that the lateral ordering can be improved by increasing the number of spray cycles. In other words, a better ordering is obtained when depositing PS (resp. cPS) layer onto an already deposited PS (resp. cPS) layer. The flow rate was measured as $10 \mu\text{L s}^{-1}$. The amount of deposited material depends on the solution concentration and the

Table 1. List of the samples and parameters used for the airbrush-spray deposition. C_0 : initial concentration in water (solvent 1). Solvent 2 was used for further dilution with the ratio (solvent 1:solvent 2). PS stands for polystyrene, cPS for carboxylated polystyrene. First coating mode (1N): the coating is performed in one single cycle at a spray nozzle-to-substrate distance $D_{SS} = 73$ mm. Second coating mode (3F): the coating is done in three subsequent spray cycles at a spray nozzle-to-substrate distance $D_{SS} = 142$ mm.

Sample	Colloids	C_0	Solvent 1	Solvent 2	Ratio	Coating mode
1a	PS	2.5 wt%	Water	–	1:0	1N
1b	PS	2.5 wt%	Water	–	1:0	3F
2a	PS	2.5 wt%	Water	Ethanol	1:1	1N
2b	PS	2.5 wt%	Water	Ethanol	1:1	3F
3a	cPS	5.0 wt%	Water	Water	1:1	1N
3b	cPS	5.0 wt%	Water	Water	1:1	3F
4a	cPS	5.0 wt%	Water	Ethanol	1:1	1N
4b	cPS	5.0 wt%	Water	Ethanol	1:1	3F

Fig. 3. GISAXS data – normalized average out-of-plane cuts in the case of PS (samples 1a, 1b, 2a, 2b) and cPS (samples 3a, 3b, 4a, 4b) colloids. The a-samples were prepared according to the first coating mode (one cycle, $D_{SS} = 73$ mm), the b-samples according to the second coating mode (three cycles, $D_{SS} = 142$ mm). For more details on the sample preparation, see Table 1. The black vertical bars highlight the positions of the maxima.

distance D_{SS} between the substrate and the spray nozzle. The waiting time between two successive cycles (in the second coating mode) allows for self-assembly of the colloids via evaporation of the solvent. Repetition of the spray cycles provides new material and solvent for self-assembly, allowing for further and improved ordering on the substrate surface. However, one can also observe that the intensity drops by about a factor of two for the samples prepared according to the second coating mode (2b, 3b, 4b). This result can be explained by the larger spray nozzle-to-substrate distance used in this mode leading to a decreased deposited amount of colloidal particles on the substrate per cycle and in total.

So, by repeating the number of cycles one brings new material and solvent on an already deposited layer, but also improves the self-assembly by enlarging the time window for the structure formation although the total amount of deposited material is reduced because of the larger D_{SS} distance in this case.

The study also reveals the strong influence of the solvent on the film lateral ordering. In the case of PS colloids (Fig. 3: 1a, 1b, 2a, 2b), out-of-plane cuts show a strong lateral ordering (up to 5th order peak) regardless of the solvent used: deionized water or ethanol. In the case of cPS colloids (Fig. 3: 3a, 3b, 4a, 4b), out-of-plane cuts show a strong lateral ordering (up to 4th order peak) when using deionized water. Lateral ordering vanishes when using ethanol. This result shows the importance of the nanoparticle surface chemistry. Because of the presence of additional polar carboxyl groups on the particle surface, cPS colloids are more hydrophilic than PS colloids and are thus more sensitive to the solvent used.

To quantitatively evaluate the length scales of the system, the out-of-plane cuts were further analyzed using the effective interface approximation (EIA^[23]). This study reveals the important lateral length scales of our system by bringing out the positions of the out-of-plane cut maxima (see Fig. 4). The 1st order peak observed at $q_y = (0.07 \pm 0.01) \text{ nm}^{-1}$ corresponds to a length in the direct space of $d = (90 \pm 13) \text{ nm}$ and is identified as the diameter of closely packed colloidal particles. The presence of higher order peaks stemming from the structure factor of closely packed colloids points out the strong lateral ordering of the colloidal polymer film.

The samples were also investigated by atomic force microscopy (AFM). The AFM measurements were carried out in the semi-contact mode (NTEGRA probe Nano-Laboratory). For each sample, surface topography images were taken at several sample positions and using different scan sizes. The AFM data are shown in Figure 5(b) and (c).

They show strongly oriented elongated domains or stripe-like structures. The typical domain dimensions are $(10 \pm 2) \text{ mm}$ in length, $(2 \pm 1) \text{ mm}$ in width, and $(130 \pm 30) \text{ nm}$ in height. The stripe-like structures are radially distributed around the center of the spray imprint, as can be seen in the microscope image in Figure 5(a). The structures are well-marked in the imprint center and become less marked when looking at larger distances from the spray imprint center. Formation of the stripe-like structures might result from an interplay between the movement of the individual particles induced by the kinetic energy of the incoming droplets and the following rapid solvent evaporation. In addition, strong capillary forces are present, which enforce the stripe-like structure formation. In Figure 5(c) one can see that the stripe-like structures actually consist in the stacking of hexagonally closed-packed

Fig. 4. Fitting of the out-of-plane cuts using the EIA^[23]: the length scales in the direct space corresponding to the out-of-plane cut maxima positions were calculated using the relation: $d = 2\pi/q_y$.

Fig. 5. (a) Microscope image (Keyence) and zoom-in of the sample 3a (see Table 1). (b, c) AFM topographic images (semi-contact mode, $f=150$ Hz) of the sample 2a (see Table 1). (d) Pictorial sketch of the trapezoidal domains: $w = (2 \pm 1)$ nm, $l = (10 \pm 2)$ nm, $h = (130 \pm 30)$ nm. (e) Sketch of the stripe-like structures. (f) Height profile obtained from the AFM data.

Fig. 6. (a) Experimental GISAXS 2D-data (a) and simulated (IsGISAXS^[25]) scattering 2D-data (b). Out-of-plane cuts (c) – $\alpha_i = 0.187^\circ$, as indicated by the white arrows in (a) – extracted from the experimental (data) and simulated (simu) GISAXS 2D-data and approximation (EIA^[23]) of the experimental curve. Positions of the maxima are highlighted by the black vertical bars. The curves were shifted for better visibility. Pictorial sketch of the model (d) used for the simulation of the GISAXS 2D-data shown in (b).

colloids over up to three layers. Lateral dimension ($2R$) of the colloids, as deduced from the AFM data (Fig. 5(f)) is (100 ± 10) nm.

Simulation

Scattering from hexagonal close-packed PS particles on a Si substrate was simulated using the software IsGISAXS^[25]. Computation of the scattered intensity was based on the distorted wave born approximation (DWBA^[26]). Here, we used the local monodisperse approximation (LMA) and a hexagonal-paracrystal model (2DDLh).

Gaussian distributions were assumed for the variance of the particle radius R as well as for the height over radius

ratio H/R (See Table A.2 in Appendix). Figure 6 shows for comparison the experimental GISAXS data (a) and the simulated 2D-data (b). We observe a very good agreement between the experimental and simulated data with the reproduction of the GISAXS data main features such as position and relative intensity of the maxima as shown in Figure 6(c).

For the simulation, hexagonal close packing of the colloids over the whole polymer film was assumed. This assumption is based on the AFM images, where hexagonal packing of the colloids can be locally observed. The good matching between the experimental and simulated GISAXS data confirm the hexagonal close packing of the colloids (as already locally observed by AFM) and indicates that it actually extends to the whole polymer coating.

Conclusions

Colloidal polymer thin films were deposited by using the novel technique of airbrush-spray deposition. Analysis of the GISAXS data reveals a strong dependency of the lateral ordering on the solvent used and the importance of the colloid surface chemistry. AFM images show that the colloids are hexagonally packed and that stripe-like structures can be installed. The observed structures form during rapid evaporation of the solvent. This novel deposition technique opens a promising route to generate laterally structured templates and scaffolds for the fabrication of ultra-high density media.

Appendix A

Table A.1. Sample-to-detector distance D_{SD} , incident angle α_i and exit angle α_f used for the GISAXS measurements carried out at the beamline BW4.^[24]

Sample	D_{SD} [mm]	α_i [deg]	α_f [deg]
1a	1.995	0.386	0.192
1b	1.995	0.386	0.192
2a	1.995	0.386	0.192
2b	1.995	0.386	0.192
3a	2.021	0.411	0.186
3b	2.021	0.411	0.186
4a	1.995	0.386	0.192
4b	1.995	0.386	0.192

Table A.2. Parameters used for the simulation (IsGISAXS^[25]) of the scattered intensity (Fig. 6(b)). The model is sketched in Figure 6(d).

Parameter X	Mean value	Distribution	σ_X/X	min	max
R [nm]	50	Gaussian	0.2	40	60
H/R	1.75	Gaussian	0.1	1.5	2.0

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