Micropatterned Polymer Films

Characterization of micropatterned polymer films by imaging ellipsometry

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Introduction

Sometimes lateral structures of polymer films on solid surfaces prevent a correct estimation of interesting film properties (thickness d, refractive index n).
Common ellipsometric techniques give only average values of the thickness and optical constants of the entired illuminated surface region (light spot in mm^2 range). However, imaging ellipsometry is able to detect the lateral inhomogenities and microstructures in detail, and furthermore, to analyze them by fitting the ellipsometric data using an appropriate optical model.

Samples

- Surface-grafted Polypeptides
- Thin films of hydrogels

Instrumentation

Imaging Ellipsometer I-Elli 2000, λ= 633 nm, 10x objective; Imaging Ellipsometer EP³, λ= 532 nm, 10x objective, Solid-Liquid cell

Task

We applied this method

1. to verify the formation of patterned arrays of surface-polymerized polypeptides [1] and
2. to study the thermo-responsive behavior of micropatterned hydrogel films in water by temperature-dependent in-situ measurements in a solid-liquid cell [2].

Steps of evaluation

1. **Surface-grafted *Polypeptides***, e.g. Poly-g-benzyl-glutamate (PBLG) can be prepared by surface initiated ring-opening polymerisation of N-Carboxyanhydrides of the corresponding amino acids. The initiator molecules ($HS-(CH_2)_n-NH_2$) have been attached to gold using their self-assembly properties.
We obtained *micropatterned samples of surface-polymerized PBLG* by micro-contact printing of the initiator molecules onto the gold substrate using PDMS stamps [3]. After that the polymerization was carried out on this initiator array. Thus, polypeptides should be formed only in these pre-defined domains, which is checked by imaging ellipsometry and other surface sensitive methods.
The ellipsometric experiments were done on dry samples at 22°C and 40-50% r.h at λ= 633 nm and an angle of incidence of 50°.
Fig. 1 displays the ellipsometric contrast image of our sample to visualize the thickness distribution of the microstructured polypeptides. It shows clearly the expected polypeptide pattern as black areas. The image width is 0.4 mm.
If we define the “Region-Of-Interest” (ROI) only in black areas (a), a thickness of 44 ± +/-2 nm is determined for the surface-polymerizsed polypeptide. A restriction ristriction to gray areas (b) does not deliver a “free” gold surface but 4 ± +/-1 nm thick layers.
For the calculation of the layer thickness a refractive index of n = 1.56 (with k = 0) was used which could be obtained by independent variable angle spectroscopic ellipsometry measurements on unstructured homogeneous polypeptide layers. It can be concluded that the grafting polymerization procedure on the microprinted initiator pattern has been successful. Surprisingly the rest of the surface is covered with a thin adsorbed layer of polypeptide, which has been formed in solution as a by-product.

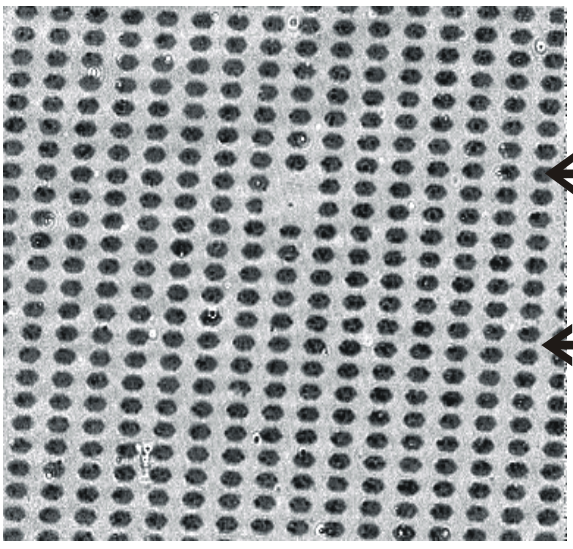

Fig.1: Ellipsometric contrast image (0.4 x 0.4 mm^2) of patterned polypeptide on gold. Arrows indicate two interesting „regions of interest“ (ROI) : a) the pattern with the grafted polypeptide (44 nm thick) and b) the space between them with loosely adsorbed polypeptides (4 nm thick). [1]

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2. Thin films of **hydrogels with stimuli-responsive behavior** receive growing attention in the development of advanced *in-vitro* cell carriers for regenerative medicine. Such hydrogels, exposing or hiding surface functionalities and changing integral characteristics (hydrophilicity, charge) related to varied degrees of swelling in the aqueous medium, were prepared using poly(N-isopropylacrylamide)/poly(ethylene glycol) PNiPAAm/PEG copolymers. Thin patterned hydrogel films were produced on fluoropolymer/silicon substrates by simultaneous crosslinking and immobilization using low pressure argon plasma treatment. The films show a thermoreversible behaviour and transitions between 30 and 40°C in water, which have been characterized with imaging ellipsometry at λ = 532 nm in the dry and in the wet state.

Fig. 2 gives an ellipsometric contrast image of our dry sample. The two boxes indicate the ROI, which were analyzed with the EP³. For each region of interest, four-zone-averaging has been performed. Within the pattern, the hydrogel sections (d = 18nm, n = 1.503) are separated by grooves of 60 mm width where the fluoropolymer layer of the substrate is the top layer (d = 78 nm, n = 1.375).During the *in-situ* experiments the samples were heated and cooled in a water ambient inside the solid-liquid cell (angle of incidence 60°). Fig. 3 gives the results (second heating scan) for Δ, Ψ, n and d, after waiting for about 15 – 30 min at each point for thermal equilibrium.

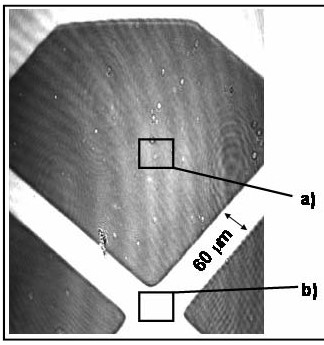

Fig.2: Ellipsometric contrast image of the patterned gel in the dry state; the boxes a) "hydrogel" and b) "substrate" indicate the ROI with a size of about 50 x 50 mm^2. [2]

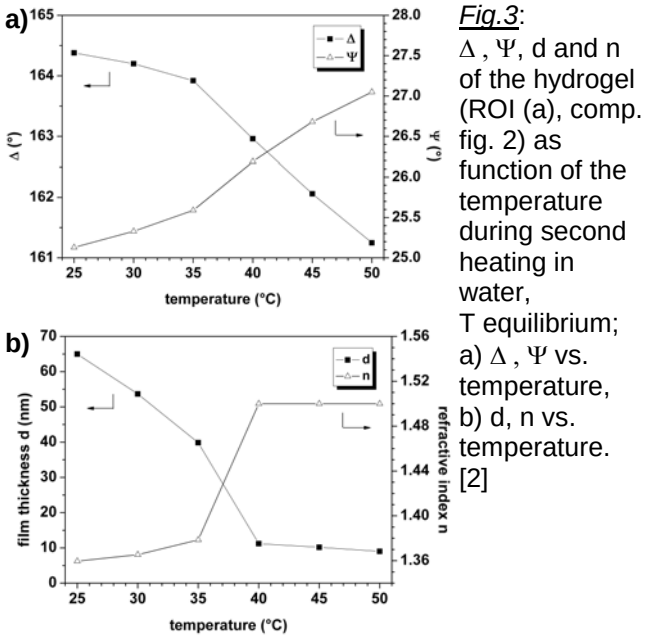

Fig.3: Δ, Ψ, d and n of the hydrogel (ROI (a), comp. fig. 2) as function of the temperature during second heating in water, T equilibrium; a) Δ, Ψ vs. temperature, b) d, n vs. temperature. [2]

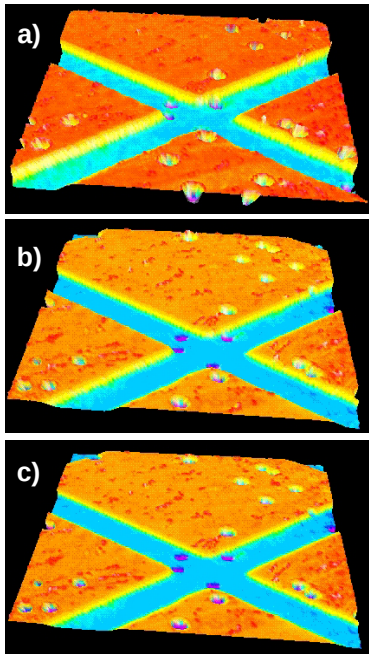

Fig.4: 3D-profile of Δ during collapsing of the hydrogel upon heating; a) T = 25 °C, b) T = 30 °C, c) T = 35 °C. [2]

Conclusion

An important advantage of imaging ellipsometry, compared to conventional ellipsometry techniques, is the potential to generate a two-dimensional map of an ellipsometric parameter resulting in a 3D-profile as shown in fig. 4 for Δ at three selected temperatures. Now also some small heterogeneities at the surface are visible as a result of the prolonged exposure of the samples to the aqueous ambient.

References

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