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In-situ Non-Invasive Imaging of Liquid-Immersed Thin Film Composite Membranes

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ABSTRACT

We present a non-invasive method to directly image liquid-immersed thin film composite membranes. The approach allows accessing information not only on the lateral distribution of the coating thickness, including variations in its swelling and density, but also on the distribution of substrate porosity, roughness, accessibility of pores to liquid, and even the degree of pore intrusion related to the thin layer deposition process. The method can be particularly helpful in the fields of functional coatings or membranes to allow laterally-resolved studies under realistic application conditions thereby opening completely new research avenues. The approach is demonstrated in a study of two polymers of intrinsic microporosity, PIM-1 and PIM-6FDA-OH, coated on polyacrylonitrile support and immersed in water. Variations of the skin morphology using different coating methods (floating, spin-coating and dip-coating) are evaluated with the help of the presented method. Surfaces of at least tens of cm^2 can be potentially analyzed.

Introduction

Direct imaging of lateral surfaces is pertinent to many fundamental- and application-oriented studies. The control of thickness and density distributions on planar substrates is crucial, for instance, in the fields of coatings, catalysis, biosensors, micro-nano fabrication, microfluidics or membrane technology. Among numerous available imaging methods the light-based techniques, such as Brewster angle microscopy (BAM)¹, microinterferometry², total internal reflection ellipsometry³, imaging spectropolarimetry⁴, or (spectroscopic) ellipsometry imaging^{5,6} have the advantage of being relatively easily implementable, inexpensive, fast, non-contact and non-destructive. These characteristics are key when considering possibilities of in-situ analysis of coatings or membranes immersed in a fluid.

The possibility to image thin films on porous substrates in the presence of a liquid medium would be of large benefit for membrane applications. Industrial membranes are used to efficiently separate mixtures on size-scales ranging from several mm down to single molecules. For the separations on a molecular level often layered composite configurations are used, where a thin, dense layer is deposited on a porous, highly mechanically stable and permeable substrate. During membrane operation various factors play important roles, including the behavior of both the support and the skin layer in terms of swelling, stability or stimuli responsiveness, as well as a possible deposition of other components on the membrane surface (e.g. fouling). When a membrane is removed from its operating environment, for instance to perform surface analysis, its structure may change irreversibly thus complicating drawing meaningful conclusions about the in-situ state. Moreover, in reverse osmosis (RO), organic solvent nanofiltration (OSN) or gas separation (GS) only the very interaction of the membrane with the separated mixture gives rise to its proper operation as membrane transport properties adapt to the liquid feed and permeate compositions. Until now a suitable non-invasive method for investigations of operating membranes was lacking.

One of the most powerful of the optical techniques is spectroscopic ellipsometry⁷, where a change in the light polarization state reflected from a thin film is used to gain information on the sample structure, including the thicknesses and refractive indices of multilayers. Because ellipsometry is non-destructive, as opposed to e.g. scanning electron microscopy, the technique can be used to study thin films on dense or porous substrates in-situ in a presence of the separating medium. In-situ ellipsometry requires the use of a dedicated measurement chamber with optical windows to feed the probing light in and out while maintaining the desired measurement environment (high pressure, liquid, desired pH etc.)⁸. Ellipsometry has been used to study swelling and aging phenomena in thin films of glassy polymers designed for gas separation applications^{9,10}, study diffusion kinetics of organic solvents in thin polymer layers¹¹, investigate the response of swollen layers under

hydrostatic pressures in the context of the solution-diffusion or pore flow models⁸, or pH-responsiveness of ultra-thin RO skins¹².

While ellipsometry imaging on dense substrates, e.g. silicon wafers, glass slides or metals, has been under accelerating development roughly since the mid 1990-s, it remained challenging to apply the technique on porous substrates in-situ. The main difficulties are the reduced reflected light intensity, surface scattering and light depolarization originating from the roughness of porous materials, as well as typically rather poor optical contrast between the thin film and the porous substrate. Overcoming these challenges at least in some cases would open a range of entirely new possibilities in studying the processes of swelling⁸, fouling¹³, surface modification^{14,15}, stimuli-responsiveness¹⁶ or stability of various membrane systems.

In this work we present a novel method based on spectroscopic ellipsometry to directly image interface structure of composite membranes in-situ in a liquid environment. The sample membrane consists of a dense polymeric glassy film made of either one of two polymers of intrinsic microporosity (PIMs), PIM-1 or PIM-6FDA-OH, deposited on a well defined, relatively smooth porous polymer support (polyacrylonitrile, PAN). The used PIMs belong to a promising class of new membrane materials with permeabilities and selectivities much above those of the state of the art polymers. The presented approach is, however, not limited to PIMs and will be largely analogous in case of other composite membranes.

Results and discussion

Polyacrylonitrile (PAN)-based polymeric supports are frequently used in membrane technology because they show very limited swelling and high stability in most common solvents. PAN can also be easily prepared as a relatively smooth and highly porous substrate, which aids subsequent deposition of separating dense layers. PIM-1 and PIM-6FDA-OH belong to a very promising class of polymers of intrinsic microporosity (PIMs) where an exceptionally rigid polymer backbone hinders chain packing and creates excess free volume fractions often above 25 %. As a result very high permeabilities and good selectivities are observed when PIMs are used as a membrane to separate mixtures. PIM-1 has been under intense research in such applications as gas separations^{17,18}, solvent filtration¹⁹ and even battery technology^{20,21}. PIM-6FDA-OH²² combines features of PIMs (microporosity) with those of functional polyimides (higher polarity and affinity to water), and has been developed for natural gas processing. The approach presented in this paper is valid for other types of substrates and coatings as well, for instance, for membranes used in RO or NF, bio-sensors, barrier layers, as well as ceramics²³. The necessary conditions include limited surface roughness, with size-scale much below light wavelength to limit scattering and depolarization effects, and sufficient optical contrast at the fluid/thin film and thin film/substrate interfaces.

In spectroscopic ellipsometry the reflection coefficients (r_p for in-plane, r_s for out-of-plane of incidence, respectively) are measured and converted to two characteristic angles, psi and delta by:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \cdot e^{i\Delta} \quad (1)$$

To extract useful sample properties, such as film thickness or refractive index, optical modeling is necessary. For thin films deposited on substrates the optical models usually consist of a layer(s) representing the film(s) and a bulk layer representing the support. Each of these layers is assigned a set of fit parameters related with, e.g. refractive index, extinction coefficient or thickness (for films). In this process psi and delta generated for a particular optical model are fitted to the measured data. Fit quality is often evaluated based on the value of (root) mean square error parameter (MSE) or χ^2 parameter. More details on the technique and its application to study films on substrates in-situ can be found in the literature^{7,24,25}. Optical models used to image the sample membranes in this study are shown in Figure 1a. Two types of models were used. For the bare PAN support a substrate-type optical model was used where optical dispersion was fitted to a simplified Cauchy type of equation with only two dispersion fit parameters, A and B:

$$n(\lambda) = A + \frac{B}{\lambda^2} \quad (2)$$

Membrane total porosity, ϕ , was calculated from the Bruggeman effective medium approximation (EMA²⁶), where the refractive index of two materials (1 and 2) is self-consistently mixed to obtain their respective volume fractions:

$$\phi_1 \cdot \frac{n_1^2 - n_{mix}^2}{n_1^2 + 2n_{mix}^2} + \phi_2 \cdot \frac{n_2^2 - n_{mix}^2}{n_2^2 + 2n_{mix}^2} = 0 \quad (3)$$

Figure 1. Scheme of the optical models used to image membranes together with model fit parameters (a) Psi and delta spectra (red and green lines) together with model fits (black lines) for bare dry and water-immersed porous PAN support (b) Psi and delta spectra (red and green lines) together with model fits (black lines) for a dry and water-immersed 200 nm PIM-1 coated on top of the porous PAN support (c). The data in (c) shows oscillations in the Psi and Delta spectra as a result of polarized light interference caused by a film presence on top of PAN support.

When equation 3 is applied to the porous support to extract the porosity, ϕ_2 , index 1 refers to the dense polymer and index 2 to the pores, while "mix" to the experimentally determined properties of the whole layer.

The substrate was assumed to consist of a dense PAN polymer (with $n_{PAN} = 1.514$ at 589 nm, supplier data sheet) and void (with $n_{void} = 1.000$). When immersed in water the optical dispersion of the liquid was taken into account ($n_{water} = 1.332$). For the polymer coated PAN substrate, the previous optical model was expanded by adding a thin layer representing the polymer with its thickness ($h_{polym.}$) and refractive index ($n_{polym.}$). To account for the intrusion of the skin polymer into the pores of PAN one could attempt to introduce an extra optical layer representing the intermix between the skin and the substrate. However, we have found that such procedure only increased the number of fit parameters without improving the fit and introduced unwanted fit parameter correlations. Therefore, the single layer/substrate optical model was considered sufficiently accurate. The physical reason is most probably preservation of the sharp optical PAN/PIM-1 interface after deposition of the PIM-1 layer which also leads to simplification of the optical modeling.

Figures 1b and c show the psi and delta data of dry and water-immersed samples for both bare (b) and PIM-1 coated (c) samples together with model fits. The data in 1 shows oscillations in the Psi and Delta spectra as a result of polarized light interference caused by a film presence on top of PAN support. In all cases the fit quality is good, with MSE values on the order of 10 or less, despite the fact, that the noise levels increase upon immersion in liquid due to partial loss of light intensity. The spectra of bare PAN supports are, as expected, relatively simple (so called envelopes), which is typical for bulk-like interfaces in the absence of a thin film. In contrast, the PIM-1 coated PAN shows a very pronounced spectral oscillation both in psi and delta being a signature of the deposited 200 nm film. The amplitude of oscillation reduces upon immersion in liquid water which is a known

Figure 2. AFM topography maps (a and b) together with cumulative height distributions (c) indicate that PIM-1 coated on PAN has significantly smaller roughness as compared with bare PAN. An example of a cross-sectional FeSEM micrograph of a 400 nm PIM-1 layer coated on top of a PAN support (d). Membranes with selective layers below about 400 nm, although easily characterizable with ellipsometry (200 nm in Figure 1), were found not clearly visible in FeSEM. Therefore, for the purpose of FeSEM analysis samples of about 400 nm were fabricated with the same preparative method. Additional SEM images of membrane cross-section are included in the supplementary information.

effect of reduced optical contrast at the air-sample interface in comparison to the water-sample interface¹¹. The depolarization for water-immersed samples increases and shows unphysical, negative values which is a result of reduced reflected light intensity. For this reason the depolarization, usually carrying additional information about sample morphology (e.g. non-uniformity) could not be interpreted and was not included in the optical modeling. Nevertheless, even after immersion in a liquid the refractive indices of bare PAN and PIM-1 remain sufficiently different ($\Delta n \sim 0.2$) and the contrast is high enough for optical modeling.

The AFM-determined microscopic surface roughness (on the lateral size-scale of tens of nm) of both bare PAN and PIM-1 was found to be relatively small 24.1 and 9.6 nm, respectively (Figure 2). As a consequence, roughness need not to be included in the ellipsometry analysis, which simplified the optical parametrization. However, if of particular interest, roughness within the measuring light spot can also be accounted for by including an additional layer comprising 50 % material and 50 % void per volume. As the addition of roughness leads to an introduction of additional fit parameters, it has to be done carefully to avoid high numerical correlations between the added and already present fit parameters. The scanning electron microscopy (SEM) images of membrane cross-section clearly indicated the presence of a dense PIM-1 skin on top of the porous PAN with a sharp PAN/PIM-1 interface, Figure 2d. The (partial) intrusion of PIM-1 polymer during formation, inferred from ellipsometry and discussed later, could not be detected due to insufficient resolving power of SEM. Attempts to image the cross-section with transmission electron microscopy were not successful due to lack of contrast related with the similar elemental composition

Figure 3. In-situ ellipsometry maps of surface topologies for dry and water-immersed PAN support, refractive index (a and c) and void fraction (porosity) (b and d); sample area 10 by 10 mm with a step of 0.3 mm. Not all substrate pores are evidently accessible to water, since the remaining porosity in the immersed substrate does not equal 0, but about 6.4 %. This effect is captured by the EMA optical model for a substrate (Figure 1a) and calculated using equation 4. Errors next to the mean values represent standard deviation from all points comprising a map.

and mass density of the two polymers.

Ellipsometry imaging-derived surface topology (refractive index and porosity) maps for dry and water-immersed PAN support are shown in Figure 3. The refractive index map of the dry support shows a relatively low average value of 1.320 (for comparison $n = 1.514$ for dense PAN) which is a consequence of large pore volume fraction (n_{void}). Upon immersion in water the pores become filled with the liquid, with $n_{water} \gg n_{void}$, thus the support index increases to 1.482. The standard deviation of all 1225 x-y points is low, 0.018, indicating high support uniformity and lack of significant morphological changes upon immersion in water. From the Bruggeman EMA, equation 3, it is possible to calculate and laterally image substrate void fraction representing porosity (Figure 3b and d). The resulting value of $\phi_{void} = 37.0 \%$ for the dry PAN substrate agrees with the manufacturer's specifications (approx. 25 - 35 %). To calculate the remaining, unfilled pore volume fraction in the water-immersed PAN support, $\phi_{rem,void}$, one can assume lack of swelling of PAN (*i.e.* n_{PAN} does not deviate from its dry value upon immersion in water, therefore is denoted as $n_{PAN,intrinsic}$) and that the total porosity stays the same upon immersion in water ($\phi_{void} = \phi_{water} + \phi_{rem,void}$). With these assumptions a three component EMA (equation 4) and volume additivity (equation 5) can be used:

$$\phi_{PAN} \cdot \frac{n_{PAN,intrinsic}^2 - n_{mix}^2}{n_{PAN,intrinsic}^2 + 2n_{mix}^2} + \phi_{water} \cdot \frac{n_{water}^2 - n_{mix}^2}{n_{water}^2 + 2n_{mix}^2} + \phi_{rem.void} \cdot \frac{n_{rem.void}^2 - n_{mix}^2}{n_{rem.void}^2 + 2n_{mix}^2} = 0 \quad (4)$$

$$\phi_{PAN} + \phi_{water} + \phi_{rem.void} = 1 \quad (5)$$

As seen in Figure 3d, a small, but quantifiable amount of pores remains unfilled ($\phi_{rem.void} > 0$) when PAN support is immersed in water. Thus the presented method can also be used to learn not only about the total porosity and its lateral distribution in membrane supports, but also about pore accessibility to penetrating liquids. For analysis in solvents, which swell the support material, its refractive index has to be appropriately adjusted. Such data can be obtained by measuring the properties of a dense film comprising the substrate polymer in a solvent of interest^{8,11} and then recalculating the swelling degree and the corresponding refractive index of a 2D-constrained film to swelling of 3D, bulk sample⁸ which better represents the behavior of an actual membrane substrate. With this information at hand, a possible change in the porosity in a given solvent can be quantified. Being difficult to obtain with other methods, such information can be crucial, for instance, to explain variations in solvent convective flux through porous substrates in e.g. solvent filtration.

To determine the fraction of pores that have been intruded by the top layer material during the process of deposition the remaining void fraction in the supporting PAN can be fitted. This can be done even in the presence of the deposited PIM-1. As an illustration Figure 4 shows PIM-1 thicknesses (a and c) and PAN-porosity (b and d) maps for PIM-1 films deposited either by spin coating from THF or floating following dewetting of a fully solidified film from a non-porous substrate (Si wafer). The floated sample is significantly smoother which is a direct result of the difference in the deposition method. The floated film is formed on a dense, nm-scale flat Si wafer and is thus very smooth. The spin coated PIM-1 layer needs to follow the morphology dictated by a slightly rough PAN support and as a result becomes more rough itself. As expected, the spin coated sample shows significantly lower substrate porosity, on average 12.9 %, as compared with the spin coated sample, 39.7 %, due to a major pore intrusion of the polymer solution during the layer preparation. The substrate porosity of the floated samples is virtually equal to the uncoated PAN support itself. Thus the method presented here can also be reliably used to assess the degree of pore intrusion, which is a crucial parameter often limiting the composite membrane permeance²⁷.

Figure 5 shows the impact of the spin coating solution concentration on the PIM-6FDA-OH layer thickness and the remaining porosity within the PAN substrate. Clearly, the layer thickness increases while the remaining porosity decreases with increasing solution concentration. The thickness increase with solution concentration is very typical for spin coating as the amount of deposited material per area is larger for more concentrated solutions. The effect is non-linear, because the larger concentrations also increase solution viscosity which promotes faster than linear thickness increase²⁸. In addition, the variations of the coating thickness, in particular an increase in the layer inhomogeneity, are well-resolved on the size-scale of several mm. Particularly striking is the quick reduction in the substrate sub-surface porosity with increasing concentration of the coating solution. Apparently, the effect of the larger net mass transfer into the PAN pores related with the larger concentrations is dominating over the increased viscosity which would have lead potentially to less intrusion.

Figure 6 shows maps of the PAN support with a 350 nm PIM-1 thin film formed by dip-coating the support in THF solution of PIM-1. The map shows an area of 9 by 9 mm imaged with a lateral resolution of 600 microns. The refractive index of PIM-1 increases by about 3 % upon immersion in water as a result of the liquid penetrating into the polymer's microporosity. The thickness of PIM-1 is shown in Figures 6b and d and does not significantly change upon immersion in water. For both refractive index and thickness the behavior upon immersion in water is consistent with the typical behavior of this polymer²¹ and proves the possibility to correctly extract the thickness and refractive index from the immersed membrane sample. Overall, the dip-coated PIM-1 film is found to be relatively non-uniform, with a standard deviation of about 35-40 nm from 256 collected points, which may stem from the unoptimized coating procedure.

A clear trend of increasing sub-mm-scale roughness going from floating, spin-coating to dip-coating has been found, as confirmed by the increase in the point-by-point calculated relative standard deviation of the layer thickness, which were 3.1 %, 8.9 %, and 11.4 %, respectively. For comparison, the standard deviation of 20 consecutive measurements from the same spot equals only 0.2 nm or below 0.1 % for thickness. This very low value includes both data acquisition and modeling uncertainties,

Figure 4. PIM-1 film thickness and remaining porosity in the substrate for spincoating (a and b) and floating (c and d) methods; all images taken from the same area size of 9 x 9 mm with resolution of 0.2 mm. The floated membrane is much smoother and shows virtually no pore intrusion as compared with the spin coated membrane. The partial intrusion of the PAN support porosity for the spin coated sample is captured with the optical model. The pore intrusion is virtually absent, as expected, for the sample with floated PIM-1 film onto porous PAN. Errors next to the mean values represent standard deviation from all points comprising a map.

and therefore signifies the very high precision of the measurement itself. Ellipsometry is known to be extremely sensitive and sub-nm precisions are routine for well defined systems.

Although in this work only a relatively small fragment of the membrane was imaged, the method can be scaled up to larger areas, potentially in the tens of cm^2 range. The current system allows for up to 50 x 50 mm area imaging, which is sufficient for most lab-scale investigations. The disadvantage is the relatively long acquisition time per spot necessary to off-set low light intensity. The loss of intensity is related to a focus - defocus misalignment due to light transmission through the medium with a refractive index larger than that of the air for which the focal point of the focusing optics is not optimized. While the polarization information is preserved, only a fraction of light is refocused back to the collecting probe and can be used for analysis. This drawback is not severe though because ellipsometry is an intensity-independent optical technique which does not require referencing in contrast to, for instance, reflectometry. Potential improvements may include an additional refocusing lense installed on the outside of the in-situ optical measurement chamber. The time necessary to collect an entire image scales quadratically with surface area (A) and resolution (R): $t \propto A^2 \cdot R^2$. If low spacial resolutions are acceptable, time-resolved in-situ imaging of surface processes occurring on timescales of tens of minutes is possible. Another significant advantage of the presented method in comparison to other imaging techniques is that it can be applied in conjunction with, adequately designed, permeation in-situ chambers, e.g. presented earlier⁸. Such combination could open up the possibility not only to study membrane surfaces in a static state (as presented here), but also under realistic transverse and/or perpendicular flow conditions. As a result entirely new possibilities could be accessed for investigations of swelling changes, surface modification,

Figure 5. Thickness of the spin-coated PIM-6FDA-OH film and the remaining porosity within the PAN support as a function of the coating solution concentration. Clear variations in the layer homogeneity on a size-scale of several mm are seen. Remaining porosity upon deposition of top skins is captured by the optical model and drops rapidly with increasing solution concentration as a result of intrusion into the pores. Errors next to the mean values represent standard deviation from all points comprising a map.

stimuli responsiveness, or stability under flow conditions. Imaging of multilayer membrane systems may also be feasible, provided sufficient optical contrast exists between the respective layers.

Conclusions

In conclusion, we have presented a non-destructive, non-invasive optical method to directly image surfaces of thin film composite membranes immersed in liquids. This versatile approach can be used to investigate skin morphology or observe surface phenomena occurring in membranes under realistic in-situ operation and is anticipated to open up entirely new venues in multilayer, composite surface characterization in both fundamental- and application-driven studies.

Figure 6. In-situ ellipsometry imaging surface topology maps of dry and water-immersed PIM-1 coated PAN support, refractive index (a and c) and PIM-1 film thickness (b and d); sample area 9 by 9 mm with a step of 600 micron. Upon immersion PIM-1 refractive index increases as a result of water penetration into its microporosity while the thickness remains almost the same. This behavior is typical for this polymer²¹. Errors next to the mean values represent standard deviation from all points comprising a map.

Materials and methods

Polyacrylonitrile (PAN) support was obtained from SolSep BV (The Netherlands) in a form of A4-sized sheets which were subsequently cut into 1 x 1 cm pieces for the analysis. PIM-1 was synthesized as described previously²⁹. After synthesis PIM-1 was dissolved in tetrahydrofurane (THF) at about 5 wt.% to prepare a coating on top of PAN support by slow withdrawal from the solution. The procedure was designed to limit the intrusion of the PAN with polymer solution, which could hinder the subsequent ellipsometry analysis by making the optical interface less defined. The prepared membrane was dried in air for several hours. The usual procedure of high temperature annealing of PIM-1 to remove residual solvent was omitted due to risk of pore collapse of the support. Traces of the residual solvent were considered irrelevant for this study. PIM-6FDA-OH was synthesized as described in²², precipitated in methanol/water (1/1 by volume) mixture and dried under vacuum to form a light yellow powder to be later dissolved in THF for preparation of coatings. For the ellipsometry imaging the RC2 multi-angle spectroscopic ellipsometer (J.A. Woollam Co., Inc.) was used. It was equipped with focusing optics with 40 mm focal length, lense diameter of about 5 mm and 300 micron spot (short axis). Because of an elliptical shape of the beam footprint on the sample the lateral resolution along the short axis is inherently larger than along the long axis. The use of smaller spots to increase topology resolution is possible, however, the impact of inherent roughness of the support (in this case on the scale of hundreds of microns, which is typical for most polymer-based membrane supports) may hinder such analysis by a loss of defined reflection angle. We found, that the deviation of both spot size and its position, including the height position of the optics over the sample were only affected to a minor extent by the presence of liquid. The reason was the relatively large ratio between the focal length (40 mm) and lense diameter (5 mm) which limited deviations in beam focus by the presence of water. Nevertheless, the slight, unavoidable

beam defocus lowered reflected light intensity which increased the noise levels. A use of a smaller in-situ cell, installation of an additional refocusing lense, or placing the optics underneath the liquid surface could potentially help to overcome this limitation.

The used ellipsometer measured psi and delta angles over a wavelength range from 193 - 1000 nm. Fitting for dry samples was done in a range 450 – 1000 nm. For the water-immersed samples the range was reduced to 450 – 940 nm to exclude a region of slight water light absorption. The lower wavelength limit was chosen to avoid modeling of UV absorption of both PAN and PIM-1. The Urbach tail of the UV absorption band was included in the models by using an extinction coefficient k as an additional fitting parameter, where $k = k_{amp} \cdot e^{(E-Bandedge)}$. This was found necessary and gave reliable and robust fitting results. Fit parameter correlations were always carefully investigated to avoid overparametrization and thus loss of their physical meaningfulness. Correlations not larger than about 0.5 were found. Throughout this work, unless otherwise stated, refractive index values are given at 632.8 nm. Sample translation was performed by a precise, motorized and computer-controlled translation stage (OWIS, Germany) with position reproducibility < 10 microns. Optical modeling was done with CompleteEASE 5.07 software package.

In the in-situ measurements a trapezoidal liquid chamber was used. The chamber was custom made from quartz glass small enough to fit in-between the focusing optics of the ellipsometer (base ca. 45 x 45 mm, height ca. 30 mm). It possessed windows perpendicular to probing beam at 70° angle of incidence (AOI). The chosen angle of incidence was a compromise between small enough beam footprint giving higher lateral resolution (for lower AOI) and large enough reflected light intensity (for higher AOI). For all measurements the samples were immobilized inside of the chamber by thin, double-sided duct tape. Window birefringence-induced effects and angle offset were carefully corrected for by using a 25 nm calibration wafer (SiO_2 on Si). It is stressed here, that to obtain high enough intensity of reflected light the in-situ chamber geometry needs to be near perfect to limit beam deviation by refraction in the liquid. To reduce the noise level all ellipsometry measurements were performed at rather long acquisition times of at least 20 s per point. Impact of the acquisition time on the obtained data is shown in Supplementary Information. Still, a certain increase in the noise levels, impacting data accuracy, was found. This can potentially be improved by periodically repeated sample alignment during scanning, however, at a risk of lower x-y position precision. For the sample alignment a four-screw alignment platform was 3D-printed (Ultimaker) and mounted directly beneath the measurement chamber. AFM analysis was performed with Veeco Nanoscope device in a tapping mode over an area of 3 x 3 micrometers and the data was processed with Gwyddion 2.45 package. FeSEM images were acquired at 5 kV and 5 μ A after sputtering the sample with $\sim$ 6 nm of Tungsten.

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W.O. conceived and performed the experiments. W.O., I.P. and M.W. analyzed the results. All authors reviewed the manuscript.

Additional information

Authors declare no competing financial interests.

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