Supporting Information

Going beyond the Surface: Revealing Complex Block Copolymer Morphologies with 3D SFM

Alexandra Sperschneider,[†] Markus Hund,[*,‡] Heiko G. Schoberth,[§] Felix Schacher,[†] Larisa Tsarkova,[‡] Axel H.E. Müller,[†] and Alexander Böker[*,§]

Lehrstuhl für Makromolekulare Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany, Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany, and DWI an der RWTH Aachen e.V. and Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen University, D-52056 Aachen, Germany

E-mail: markus.hund@uni-bayreuth.de; boeker@dwi.rwth-aachen.de

Quasi *in–situ* SFM Nanotomography

The quasi *in-situ* SFM (QIS-SFM) utilizes a modified commercial SFM (Dimension™ 3100 equipped with a NanoScope® IV SPM controller, both from Vecco Instruments Inc., USA). The SFM provides a hybrid XY closed-loop scanner and software which allows to control the instrument for custom experiments (NanoScript™ software option). A detailed description of the QIS-SFM is given elsewhere.[1,2] In this work, the used setup additionally features an automatic tip/sample separation and approach (subsequent relative movements of the z-stage of ±4.8 mm

† Universität Bayreuth
‡ Universität Bayreuth
§ RWTH Aachen

with help of self-developed NanoScript^{TM} C++ applications using the NanoScript^{TM} function *StageMoveAxis*). Moreover an automatic and triggered grounding of the sample during scanning is implemented. The plasma etching is performed with a RF power of about 3 W at a process pressure of 5 mbar (atmospheric air). Each of the SFM data sets is acquired with a specific SFM tip operating in TappingMode^{TM}. S_3N_4 cantilevers from Olympus are used which have a typical spring constant of 42 N/m and a typical resonance frequency of 300 kHz (OMCL-AC160TS). All measurements are performed at free amplitudes of about $30-50$ nm and a relative set point of about 0.7. The drive amplitudes and the corresponding drive frequencies are 123.2 mV at 334.4 kHz (Figure 1) and 81 mV at 320.4 kHz (Figure 3). We check the tapping conditions by using the commands *Sweep on surface* provided by NanoScope® software (Version 6.14R1) with a tip offset of 100 nm (z-direction). The drive frequency and the drive phase is slightly adjusted in some images by using the commands *Center Peak* and *Zero Phase*. All measurements are performed without Q control (typical Q values of the used cantilevers are about 500). The total acquisition time to acquire the raw data sets (Figure 1, Figure 3) is dominated by the total time to scan the SFM images and the time for processing (see below).

The acquisition time for a SFM scan is $\approx$17.07 min (scan rate 1 Hz, 1024×1024 pixels) whereby 3 channels (Height/Amplitude/Phase) are simultaneously acquired. The channel holding the amplitude data is not used in this paper. The acquisition times for 9 images (Figure 1) amounts to $\approx$153.6 min and for 14 images (Figure 3) $\approx$238.9 min. The total cumulative etch time for the data sets amounts to 51 s (Figure 1) and 98 s (Figure 3). Additional time is needed to perform the automated treatment steps (evacuation, LP-plasma treatment and ventilation). Moreover time is needed to perform Engage, Withdraw, tip/sample separation, and the manually operation of the closing system. The total time for these tasks is $\approx$53 min (Figure 1) and $\approx$85 min (Figure 3). The total time to acquire the raw data sets is therefore $\approx$207 min (3.45 h, Figure 1) and $\approx$325 min (5.4 h, Figure 3). We note that the developed LabVIEW^{TM} application enables reproducible LP-treatments with a smooth evacuation process followed by a closed-loop control of the pressure, plasma treatment, and ventilation in order to establish a high position stability.[1,2] The time needed for a developed LabVIEW^{TM} application to perform a single process step is ≈3 min plus the time for the LP-plasma treatment.

The obtained data sets are post-processed using a bunch of self-developed stand alone command-line programs (written in C++) and suitable bash scripts in order to perform image registration. The calculated 3D raw data file (see below) is further processed and visualized with commercial 3D-software AMIRA® (Visage Imaging Inc., USA). The developed software package consists of small, specialized command-line applications which can be combined to rather complex functionalities by launching them from suitable bash scripts. The software serves also as a code basis that can be extended and modified in order to control a fully automated QIS-SFM equipped with an automatic operated reaction chamber.[3] The phase contrast in Figures 1 and 3 is enhanced by using an adaptive mapping algorithm (Gwyddion SPM software, http://gwyddion.net).

Pre-processing. For a successful reconstruction procedure, the SFM data set passed through standard 2D-image processing tasks like file format conversion, flattening, normalization and contrast-enhancement. Thereby the developed applications are called customarily from suitable bash scripts.

Image registration. For reliable nanotomography, it is indispensable to consider exactly the same area on the sample. This alignment process was performed using rigid image registration based on cross-correlation in spatial domain.[4,5] In order to facilitate this process, we implemented the histogram matching technique, whereby a processed image series is produced with each image having approximately the same specified reference histogram.[6] The histogram matched image series is then further processed in a bash script. A first crop command generates a small target image from the very first image of the series. Afterwards, the following command performs cross-correlation by moving the target image to every possible position in the second image of the series. At each location, the cross-correlation value is computed. From this data, the best matching position could be easily extracted and a new current target image is generated. In the subsequent processing steps, this chain-like computation is repeated resulting in a file holding the best matching coordinates of the target images. An additional application use this file and automatically produces a bash script containing commands to cancel displacements. For every image in the series a command produces a image having a black margin of suitable size around the image. The following command cancels the displacement by performing a crop with appropriate computed offsets. For these tasks the application *convert* is used (ImageMagick, http://www.imagemagick.org). The target position of the first image serves as a reference coordinate. Non-linear registration methods as described by Scherdel *et al.*[7] are capable to correct local deformations. We note that the used SFM is equipped with a state-of-the-art closed-loop scanner, which drastically reduces image distortions. Moreover, due to the exceptional high position stability of the QIS-SFM, the scan size can be kept constant during the acquisition of the image series and only small changes of scanner offsets are applied (if necessary at all). The computing time of the cross-correlation could be reduced by taking only image cut-outs (reduced number of pixels) or by performing the cross-correlation in frequency domain.[5]

Tomography computation. The 3D reconstruction algorithm suggested by Magerle[8] combines topography images $z_n(x,y)$ and phase images $\varphi_n(x,y)$ of a series of TappingMode$^{\mathrm{TM}}$ SFM images to phase maps $\Phi = [x, y, z_n(x,y) - n < d >]$ whereby d denotes the constant thickness of the removed layers and n is the number of layers.

For the sake of clarity we describe the reconstruction procedure used in this paper in case of a constant etch rate (Figure 2). A 3D image can be considered as a 3D matrix. The 3D discrete space is a set of integral grid points in 3D Euclidean space defined by their Cartesian coordinates (x,y,z). A voxel is the unit cubic volume centered at the integral grid point[9,10]. In order to generate a 3D volume graphics representation of the sampled data set, a developed C++ program decodes in the simplest case the following command-line arguments: A constant etching rate, a parameter file holding a list of file names (registered topography and phase images), corresponding cumulative etching times, and the file name of a output file (see also Table 1). Special care was taken to realize a computation with correctly scaled topographic data. For this reason, the topographic data was converted into a normalized portable gray map images (PGM) without loss of information (16 bit per pixel) compared to the raw data (NanoScope® files). These images can be easily registered by using the previously computed result (specific bash script). Scaling factors and other meta data like scan size are available for every image file in the PGM-header and are used by the application for re-transformation into scaled height values and for other calculations. The digital images representing the topographic (height) and material properties (phase) can be represented by $m \times n$ matrices ($h_0 \dots h_k$ and $p_0 \dots p_k$) of the form:

$$h_i = \begin{pmatrix} h_i(0,0) & \cdots & h_i(0,n-1) \\ \vdots & \ddots & \vdots \\ h_i(m-1,0) & \cdots & h_i(m-1,n-1) \end{pmatrix} p_i = \begin{pmatrix} pi(0,0) & \cdots & p_i(0,n-1) \\ \vdots & \ddots & \vdots \\ p_i(m-1,0) & \cdots & p_i(m-1,n-1) \end{pmatrix}$$

The number of pixels in y-direction (number of lines) is denoted to m (rows) and the number of pixels in x-direction (samples per line) denotes n (columns). The matrix elements of the matrices $h_0 \dots h_k$ (image pixels) are integers in the range $[0,...,65535]$ and the corresponding matrix elements of the phase matrices $p_0 \dots p_k$ ranges from $[0,...,255]$.

Table 1: Topography and phase matrices with corresponding cumulative etching times for process step $0 \dots k$.

Topography	Phase	Cumulative etching time
h_0	p_0	t_0
h_1	p_1	t_1
$\vdots$	$\vdots$	$\vdots$
h_k	p_k	t_k

Basically, the program use the following three 3D matrices: H for topographic data, P for phase data and R for the reconstructed 3D volume graphic. First of all, the matrix elements of h_i are re-transformed back into physical values (unit nanometer) and assigned to a 3D floating-point matrix H with the dimensions $m \times n \times (k+1)$ whereby $(k+1)$ denotes the total number of processing steps. The thickness d_i of the removed material can be calculated by $d_i = E \cdot t_i$ whereby E (< 0) denotes the etch rate (see Table 1, Figure 2b). From the matrix elements of matrix H the corresponding d_i is added according ($H[row][col][i] = H[row][col][i] + d_i$. The data range (*D_Range*) of H is the difference of the maximum and minimum value of H. It is shifted by subtraction of the minimum value of H so that the elements ranges from $[0,\dots,D\_Range]$ (floats). The matrices p_i (material property) are assigned to a 3D unsigned char matrix P (range: $[0,...,255]$). The dimension of the result matrix R is $m \times n \times r$ whereby r denotes the total number of voxels in z-direction and can be calculated by $r = (int)round(D\_Range/D_z)$. D_x (and analogous D_y) can be calculated by the scan size width (3 μm) divided by the number of samples per line (3000 nm$/1024 \approx 2.93$ nm). In this study we use the same physical size of the voxels in z-direction D_z as for D_x and D_y. The matrix elements of the R matrix ranges from $[0, ..., 255]$. The property of the material P (phase) is re-distributed by using the height information H to calculate a new z-index z_{new} for the matrix element R by linear transformation of the H data into the z-index range of R (integers). Before this operation takes place all matrix elements of R are filled with zeros.

```
for(int z=0;z<r;z++)
{
 for(int row=0;row<m;row++)
 {
  for(int col=0;col<n;col++)
  {
   z_new = round((H[row][col][z]/D_Range) * (r-1));
   R[row][col][z_new] = P[row][col][z];
  }
 }
}
```

Finally, the number of $m \times n \times r$ matrix elements (bytes) are written to a binary 3D raw data file which can be read by 3D software AMIRA® for further processing and visualization. We note that the contrast of the phase images is enhanced followed by a 3 *x* 3 median filtering prior to the application of the above described reconstruction algorithm. In particular the typical thickness of the removed layer (here ≈5.4 nm, Figure 2b) limits the z-resolution. We note that usually voxel values are represented with 8-bit accuracy.[10] Alternatively, a 16-bit workflow for the property data can be implemented easily.

Further 3D image processing. The produced 3D image data is further processed and visualized with commercial 3D software. In order to gain closed isosurfaces a noise reduction/interpolation is performed by a Gaussian filter in the XZ- and YZ-planes with a convolution kernel of the size 9×9 with a relative width of the Gauss function of 0.4, Figure 2a).

Resolution issues. The gained vertical resolution of a 3D volume graphic can be high compared to the lateral resolution, because of the high vertical resolution of the SFM (typically tens of nanometers) compared to the lateral resolution (typically in the order of few nanometers) and the possibility to remove thin layers step by step with LP-plasma technique (short treatment times, many process steps). In this paper we measured the etch rate with a similar prepared calibration sample, whereby the polymer film was partly removed by a canula syringe in order to establish a reference area which is not affected by the plasma treatment for further evaluation of the film thickness. Alternatively, an internal reference area can be used (for example by including a part of a scratched sample area into the scan area). In both cases the above described procedure can be extended, even if the etch behavior is non-linear, by replacing d_i by $d_i(t)$. The theoretical reachable resolution is a convolution of the lateral and vertical resolution whereby the typically lateral resolution of a SFM is limited by the tip radius. Because of the high vertical resolution of the SFM and the possibility to remove layers down to 1 nm we estimate a high z-resolution. The curved height maps are separated by ≈5.4 nm in z-direction which is a hindrance to visualize closed isosurfaces. Therefore we apply the Gaussian filter in the XZ- and YZ-plane (see above) to interpolate in z-direction in order to visualize closed isosurfaces.

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