

Highly spatial-resolved chemical metrology on latent resist images

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Abstract

Patterning photoresist with extreme control over dose and placement is the first crucial step in semiconductor manufacturing. But, how to accurately measure the activation of modern complex resists components at sufficient spatial resolution? No exposed nanometre-scale resist pattern is sufficiently sturdy to unaltered withstand inspection by intense photon or electron beams, not even after processing and development.

This paper presents experimental proof that Infra-Red Atomic Force Microscopy (IR-AFM) is sufficiently sensitive and gentle to chemically record the vulnerable-yet-valuable lithographic patterns in a chemically amplified resist *after exposure, prior* to development. Accordingly, IR-AFM metrology provides the long-sought-for insights in changes in the chemical and spatial distribution per component in a latent resist image, both directly after exposure as well as during processing. With these to-be-gained understandings, a disruptive acceleration of resist design and processing is expected.

Introduction

To support the global trend of further shrink of transistors, satisfactory pattern fidelity in the photoresist at the nanometre scale is needed (1) (2). After lithographic patterning, resist processing is the next crucial step in semiconductor manufacturing. By processing, the vulnerable latent pattern is translated, via a more sturdy form in developed resist, into the target wafer by e.g. etching or ion implantation (3). Resist processing requires extremely sophisticated know-how and control, to optimally and reproducibly transfer (feature size) or suppress (variation of feature size) especially the high-spatial frequencies from latent pattern via processed resist into the substrate. Since the economic value of lithography can only be harvested after defect-free pattern transfer into the silicon, tight control over resist processing is of key importance. Recently, metrology by AFM has been demonstrated for 16 nm half-pitch lines on processed and developed resist (4) and 26 nm posts (5). Ideally, similar metrology would be made available to quantify the pattern development per step, i.e. after post-expose bake, develop and rinse, thus providing insight in which step is the most critical bottleneck (6). However, currently no commercial method exists that can resolve control parameters like critical dimension (CD) or line edge roughness (LER) in latent or partially processed resist patterns. This paper introduces a metrology method that provides insight at changes in photoresist during processing, which hitherto were not observable at the nanometre scale, without inflicting damage to or shrink of the exposed resist.

The semiconductor industry has developed a very sophisticated infrastructure and way of working to establish high-volume manufacturing of semiconductor circuits with deep-submicron dimensions, as reported by e.g. (7), (8) (9) (10). These sources all emphasize that LER control is critical for manufacturing, as excessive LER correlates with yield loss (11). Such will amplify for sub-10 nm patterning, as the industry foresees the need for control over the stochastics of the lithographic (EUV) image as well as the granular components of photoresist (12). Modern photoresists are complex mixtures in which each component has a specific function to yield a sensitive resist that can capture high

resolution images with a low roughness of the patterns (13), (14) (15) (16) (17) (18) (10). Gallatin's landmark paper pointed out that a trade-off between resolution (R), uniformity (L) and sensitivity (S) exists (19). Wallow translated this insight into a first widely accepted metric for a CAR's performance; the Z-factor, which quantifies the area of RLS triangle (20). In response, industry standardised LER metrology to establish a globally uniform comparison between resists performance (21). However, unravelling the chemistry in resists during processing remains a big scientific challenge (22) (23) (24). In addition, industry kept on looking for additional metrology techniques to reduce the measurement error (25) (26) (27) (28) (29) (30) (4). Further work identified and quantified the impact of (blur by e.g. shot noise in) the expose tool image on the Z-factor (31) (32) (33) (34) (35) (36) (37), which lead to the introduction of k_4 as the latest resist metric (38). Following the proposed protocol, it is now possible to separate the contribution to the non-uniformity by shot noise in the exposed image on the one hand from the stochastic variations in the resist and processing on the other hand. Still, accurate metrology for resolution and uniformity is required for a reliable evaluation of both the Z and k_4 -factor.

As outlined in a recent LER metrology review paper by Cutler et al., there is additional unique information on a photoresist's qualities disclosed in the power spectral density (PSD) of all spatial frequencies that contribute to the total LER (39). Thus, if a line pattern is properly imaged, measured and analysed, the obtained metrics for the LER PSD can be used to accelerate the development of both high-performance photoresists as well as of resist processing and metrology equipment, recipes and protocols. However, at the moment, LER can only be measured *after* resist processing. This renders it impossible to identify the LER contribution by a specific resist component or per processing step. For the same reason, one cannot investigate the impact of exposure tool parameters on these individual contributions. Hence process development and control would benefit tremendously from a metrology tool that can resolve (some of) these blur factors during processing and *before* development. This paper shows the first experimental results for such a disruptive metrology method by deploying infrared atomic force microscopy (IR-AFM) (40). In IR-AFM, an IR beam is tuned to a resonance specific to an activated resist component, while a scanning probe records the locally induced force field in non-contact mode. This unlocks the practical evaluation of the two geometrical factors R and L in Gallatin's $R-L-S$ resist metric in latent images, thereby enabling the tracking of a resist's performance *between* exposure and development. We believe that in the near future IR-AFM will record chemical maps of the latent image per resist component after (during) each processing step that directly reflect or even resolve these stochastics, to resolve where patterning resolution and uniformity is lost most.

Results

Topographical versus chemical contrast using by AFM versus IR-AFM imaging

To perform metrology on latent patterns in cured photoresist, images have been recorded by regular AFM as well as with Infrared-Atomic Force Microscopy (IR-AFM) (41). To serve metrology, images shall have both a sufficient signal-to-noise (S/N) and spatial resolution (21). Figure 1 shows AFM and IR-AFM images of a pattern of 500 nm wide line at 2000 nm pitch as written by electron beam lithography. The

200 nm thick chemically amplified resist layer has been cured by a post-expose bake, but has not been developed, yielding a relatively flat sample that is easy to scan by AFM and IR-AFM. As is to be expected from un-developed resist, the S/N in the topography image by regular AFM is too low to extract a clear waveform, let alone to sustain metrology (see e.g. the left panel of Figure 1). In addition, the observed pattern is hard to interpret. Resist shrinkage is inherently non-local in effect and non-linear, and the resulting patterns are not straightforwardly linked to the actual lateral distribution of chemical changes in the resist. In IR-AFM, to enhance the chemical contrast in the sample, a narrow-band IR beam is tuned to an IR absorption resonance that is specific to *exposed* (and cured) resist only, while a nanometre-sized tip scans the sample with a spatial resolution of at least 10-20 nm, or better (41) (42) (43) (44) (45). The IR-AFM image (centre panel of Figure 1) shows a remarkable increase in S/N that has a direct link to the exposed pattern, when compared to regular AFM. As a result, edge detection in the IR-AFM image is straightforward (Right panel of Figure 1), while nearly impossible from the regular AFM image.

Table 1

Metrology data for the CD, pitch and roughness of the latent lines and spaces pattern, as retrieved from purified IR-AFM images. Roughness data are reported for direct analysis of the edge positions directly (left numbers) as well as by integration of the PSD (right numbers).

Dose	CD	Pitch	LER-L	LER-R	LWR	used edges
$\mu\text{C cm}^{-2}$	nm	nm	nm (1σ)	nm (1σ)	nm (1σ)	%
40	559.1	1969.3	54.1 / 54.1	63.6 / 63.7	93.4 / 93.5	94.6
80	587.3	1995.0	60.6 / 60.6	63.6 / 63.6	98.9 / 99.0	95.3

Thus, IR-AFM enables reliable LER metrology of latent patterns in resist, thereby serving the development of a CAR resist that complies with the strict semiconductor industry requirements for beyond sub-7 nm patterning (46).

Discussion

Our experimental IR-AFM data on post-bake pre-development exposed images has provided reliable chemical metrology numbers for the line width as well as for the roughness of the line edges and width. Currently, such a result is not achievable by conventional AFM or any other imaging technique. Future IR-AFM metrology work is needed to e.g. resolve finer lines and produce chemical maps of individual resist components. Albeit our proof of principle has been on relatively wide lines, IR-AFM chemical imaging of sub-10 nm structures on similar materials has been demonstrated (43) (47).

To better facilitate the identification of the spectral lines of interest for IR-AFM, as needed for chemical mapping at the nanometre scale, it will be beneficial to conduct more detailed IR spectroscopy on the bulk resist in both fresh and activated state. Having more detailed spectroscopic data per resist component will pave the way for visualisation of resist chemistry per processing step per component at the sub-10 nm scale. Such analysis might enable chemical metrology after/during each processing step, thereby

disclosing insights in resist component stochastics, which recently has been recognised for its pivotal role the resolution limit of lithographic patterning (48) (35).

It is worthwhile to consider to what degree IR-AFM is (not) altering the resist during the imaging. CD-SEM for instance, is known to cause shrink of the resist (21) and can also deposit a thin contamination layer on (un)inspected areas. So far, IR-AFM seems harmless. After repeatedly imaging of the same part of the exposed resist at up to five different IR wavelengths, no alterations to the topography image have been observed. This observation is sustained by our (unpublished) Finite Element Modelling of local sample heating by the tip-enhanced IR intensity during the 40 ns IR pulse for a wavelength tuned to an absorption peak of either SiO_x or a PMMA resist sample at room temperature. For the typical IR intensity, the simulated transient temperature raise during the IR pulse never exceeded 50 degree Celsius and lasted less than the IR pulse duration. A technical review on IR-AFM reports a typical transient temperature rise of a few degree Celsius on generic polymer samples, which is a material class that comprises chemically amplified resists (49). Such minor thermal loads are negligible when compared to either the heating during the exposure by the EUV scanner or an effective bake to induce any chemical change during resist processing. Furthermore, the IR photon energy is insufficient to directly alter or activate any resist component. Lastly, interaction of an AFM tip with soft-matter samples is known to be potentially harmful. A recent metrology benchmark study involving CD-SEM, HIM, AFM and optical metrology on developed chemically amplified EUV resist showed repeated damage-free imaging of sub-50 nm contact holes by AFM for a practical range of peak forces settings (28). In our application of IR-AFM, a non-contact mode has been selected that is known to be even more gentle on the sample surface than the peak-force tapping mode.

In summary, IR-AFM metrology on latent resist patterns has the potential to provide pivotal information to develop and optimise resist composition and processing, as it may resolve the development of resolution and roughness without altering the resist by e.g. charging, contamination, shrink or heat (40).

Methods

A chemically amplified resist has been activated by electron beam lithography and then cured by a post expose bake. To find Infrared fingerprints, two sets of experiments have been conducted. First, the presence of any IR fingerprint has been established by FTIR. Then, using the strongest line in the IR fingerprint, the pattern resist has been imaged by IR-AFM at sufficiently high spatial resolution for metrology of pitch, line width and edge roughness. The raw data have been purified by rejection of statistically significant outliers in edge positions. By the purification of the raw IR-AFM images, the artifacts in their Power Spectral Density (PSD) of both LER and LWR has disappeared and the corresponding LER/LWR metrology now complies with SEMI Standard P47-0307 (50).

Sample preparation by electron beam lithography and post expose bake

A 4" silicon XX-flat wafer has been precleaned in an acetone bath for 5 minutes and, after rinsing in isopropyl alcohol, was spun dry at 2000 rpm and dried further by a 10 minute bake on a hot plate at 150

degree Celsius. An HDMS primer was applied to the wafer shortly prior to spinning a layer of 200 nm thick NEB 22A (Sumitomo Chemical Co.) chemically amplified e-beam resist at 6000 rpm (51). To remove the solvent, the wafer was baked at 110 degree Celsius for 2 minutes. In a Raith EBPG 5200, 4 mm wide squares and 500 nm lines at 2 micron spacing have been exposed at areal doses of 40 and 80 $\mu\text{C}/\text{cm}^2$. The EBPG raster pixel size has been set to 120 nm, and a spot size of 160 nm has been selected, warranting for a continuous exposure of the patterns by the minor overflow of each pixel. To cure the resist, the wafer has been baked at 105 degree Celsius for 2 minutes. The wafers with the cured resist have been stored at room temperature in a closed box until either large-area analysis by FTIR or high-resolution imaging by IR-AFM. Figure 2 shows a cross sectional schematic of the line pattern in the resist.

Scout for chemical fingerprint of resist activation

No literature data on the IR spectra of (un)cured NEB e-beam resist could be found. Hence, in a first round of exposures, it has been determined by Fourier-transform infrared spectroscopy (FTIR) (52) at which IR wavelength(s) a significant detectable change was observable above what large area electron dose at the resist. A Bruker Invenio R (53) with wide band IR DLATGS-detector has been used with default settings for transmission measurements: 16 scans were made with a resolution of 2 cm^{-1} after zero padding. FTIR spectra have been measured for three cases: I. a bare silicon wafer, II. a silicon wafer after coating with 150 nm NEB-22 (photoresist, before exposure), III. Idem after a cured exposure. Figure 3 shows FTIR results as recorded in transmission mode for case II and III. The difference between the spectra before and after cured exposure is relatively small because the resist layer is rather thin (150 nm), yet significant. The most prominent differences occur at ~ 985 , 1030, 1175 and 1220 cm^{-1} , with a typical width of tens of cm^{-1} . The presence of the IR peaks at the large area exposed and cured areas provided experimental evidence that indeed chemical changes in thin layers of photoresist can be noticed in IR spectroscopy, albeit not yet at the high spatial resolution as is required for metrology on undeveloped resist images.

IR-AFM to resolve chemical contrast at the nanometre scale

The sample, as prepared by e-beam lithography, was examined by IR-AFM. A commercially available system, the Vista One by Molecular Vista with a Block Engineering QCL tuneable mid-IR laser, was used with an NCH-Au cantilever, having a tip radius of 20 nm. For topography imaging the second cantilever mode was selected with about 1 nm free air amplitude and a setpoint of 75%. The written pattern could be recognized from the topography images (figure 1), due to the well-known effect of resist shrinkage (54). This pattern allowed to locate positions to capture IR spectra from exposed and un-exposed areas of the same sample. For the IR-AFM operational conditions we applied standard settings as suggested by the manufacturer (41). For chemical contrast imaging by IR excitation used the difference frequency between first and second mode. Frequency mixing then generates a signal at the first cantilever mode. IR laser power was set to 20%, scan speed was 0.25 line s^{-1} and images were 512×512 pixels at a field of view of 10×10 micron. Figure 3 shows how large area FTIR spectra compare to single-pixel IR-AFM spectra. Generally, there is good agreement between the IR-AFM and FTIR spectra with reproduction of the same absorption peaks in both methods. At several frequencies there are clear IR absorption difference

between exposed and un-exposed resist. Although the IR-AFM is mainly surface sensitive, it appears that there is a contribution of the SiO₂ absorption peak present in the data. For imaging in IR-AFM we selected the wavelength of 984 cm⁻¹ (indicated by the black line in Fig. 3), as the corresponding signal enhancement is not influenced by the SiO₂ absorption peaks around 1100-1200 cm⁻¹ and therefore provides best contrast.

It is appropriate to have a short look at the comparison between topography and IR-AFM operation. Although topography imaging (left panel of Figure 1) reveals hints of the printed pattern it has poor contrast and the AFM image is not directly/easily related to the exposed pattern (54). The latter is attributed to non-local changes in topography by resist shrinkage and/or local resist stiffness changes, which fundamentally complicate accurate edge placement metrology from these data. Instead, the IR-AFM image is directly related to the written pattern through the induced chemical changes. Figure 4 shows the distribution of AFM and IR-AFM signal strength after classification of each pixel as from either “exposed” or “non-exposed” resist, based on the detected edges (right panel of Figure 1). Clearly, the topography contrast is just a minor a fraction of the distribution widths, while chemical contrast by the IR-AFM is a significant fraction of the distribution widths. This confirms that IR-AFM provides a reliable signal that, next to delivering straightforward-to-interpret images of latent resist patterns, supports quantitative analysis for e.g. LER metrology.

Waveform extraction, edge detection and data purification

To extract the line edge and line width roughness from the IR-AFM images, line edge positions need to be evaluated over a length of at least 2 micrometre (21). To this end, after some image processing to purify the IR-AFM images from instrument artefacts, the average waveform has been determined by fitting a raised-cosine function to each edge in the average line profile. Figure 5 shows a typical fitted waveform. The line width and centre have been determined from fitted edge positions at half height (indicated by green and red dashed lines).

Figure 6 shows the extracted edge positions for each image line before and after purification. The left-centre panel of Figure 6 shows all retrieved left and right edge positions relative to the line centre. The right-centre panels shows all retrieved line widths. The vertical black lines indicate a 2σ deviation from the average. A first Power Spectral Density analysis of all extracted edges (left panel of Figure 6) showed un-physical features, e.g. the LWR at lower spatial frequencies was less than the corresponding LER. Analysis of the extracted edge profiles yielded the insight that ~5% of isolated edge positions has been shifted by more than 2σ from neighbouring lines. Such shifts can be considered as un-physical, hence we purified the edge profiles by replacing these outliers by the average edge position of the neighbouring lines (right panel of Figure 6). The PSD of the purified edge positions (Figure 7) no longer shows unphysical features and can be used for chemical metrology.

Chemical metrology from line edge and width power spectral densities

Figure 7 shows a typical IR-AFM Power Spectral Density graph as calculated from the purified line profiles. The left panel also contains a $\{PSD(f), \xi, H\}$ fit to the LER PSD after (39), following her suggestion to fix $H = 0,5$ (i.e. the theoretical value for the exponent). The right panel shows the (artefact-free) integrated PSD for the LER and LWR from the purified data.

The purified edge positions as displayed in Figure 1 have been analysed for LER and LWR in three independent ways, yielding a highly similar outcome, as reported in Table 1 and Table 2. Firstly, the RMS value from the average edge position has been calculated. Secondly, the PSD of the edge positions has been integrated after (25). Thirdly, the PSDs of the LER and LWR from both areal doses have been fitted after (39), see Table 2. For the latter, the obtained IR-AFM LER as calculated by Eq. (1) in (39) differs by a factor of 2 from the values as reported in Table 1. This difference is attributed to the arbitrary choice of evaluating the $PSD(f)$ with or without negative lateral frequencies, which obviously changes the energy per frequency.

Table 2
Fit parameters $\{PSD(f), \xi\}$ as obtained from IR-AFM LER and LWR PSDs for $H = 0.5$, following (39). The average LER values calculated with these parameters differ by 1% from the values reported in Table 1.

	PSD(f)	PSD(f)	ξ	ξ
Dose	LER	LWR	LER	LWR
$\mu\text{C cm}^{-2}$	nm^3	nm^3	nm	nm
40	0,17e6	0,43e6	5,9	5,8
80	0,20e6	0,51e6	6,4	6,7

Albeit the values of the parameters reported in Table 1 and Table 2 in itself are not remarkable, the mere fact they could be extracted from an IR-AFM chemical image of a latent resist pattern is.

Declarations

Author contributions

D. Maas partly conceived the method, outlined the experimental program, wrote most of the manuscript and, with Laurent Fillinger, purified the IR-AFM images to extract metrology data. J. van der Donck partly conceived the method and assisted in setting up the experiments. E. van Zeijl selected the NEB resist and conducted the electron beam lithography exposures. R. Bloem set up, conducted and analysed the FTIR spectroscopy of the (cured) photoresist. S. Tamer performed the IR-AFM experiments and advised on data interpretation. M. van Es and K. Maturová partly conceived the method and advised on IR-AFM experiments and data interpretation. L. Fillinger purified the IR-AFM images and extracted reliable

metrology numbers. R. Willekers partly conceived the method and assisted in defining the scope of the experiments and contributed to the literature study.

Competing interests

None of the authors have competing interests.

Materials & Correspondence

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Figures

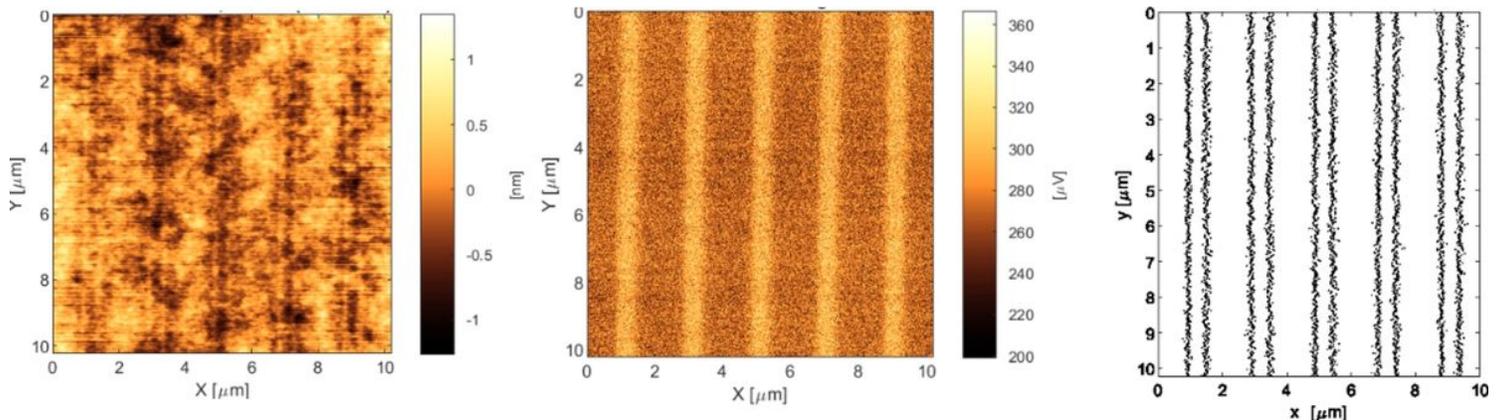


Figure 1

Images of 500nm wide lines at 2 um pitch in exposed and baked NEB22 chemically amplified resist. The pattern has been exposed by electron-beam lithography at a dose of $40 \mu\text{C cm}^{-2}$. The AFM image (left panel) hints at the presence of some topography, yet is incapable to support metrology data extraction. The IR-AFM image (centre panel), recorded at an infrared frequency of 984 cm^{-1} , yields a clear 'chemical map' of post-bake undeveloped resist. This first-of-a-kind IR-AFM image from a latent pattern in cured resist shows similar S/N as is currently used in state-of-the-art CD-SEM. The right panel shows line edges as extracted from tilt-angle-corrected IR-AFM data. The data set has been purified by discarding isolated edge positions that are displaced by more than 2σ from edges positions in both neighbouring lines (i.e. $\sim 5\%$ out of 5120 edges per image).

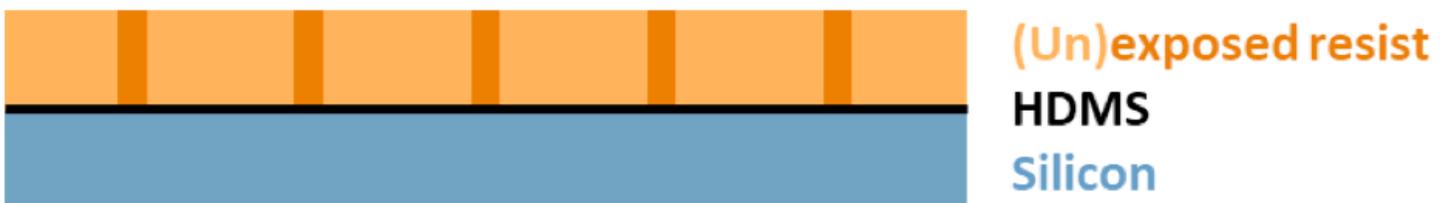


Figure 2

Schematical cross-section of the sample. A 200 nm thick NEB-22 CAR resist layer is spin coated on a silicon wafer with a monolayer HDMS. The resist is exposed to a 500 nm line and spacers pattern at 2 micron pitch using electron beam lithography with areal doses of 40 and 80 $\mu\text{C cm}^{-2}$.

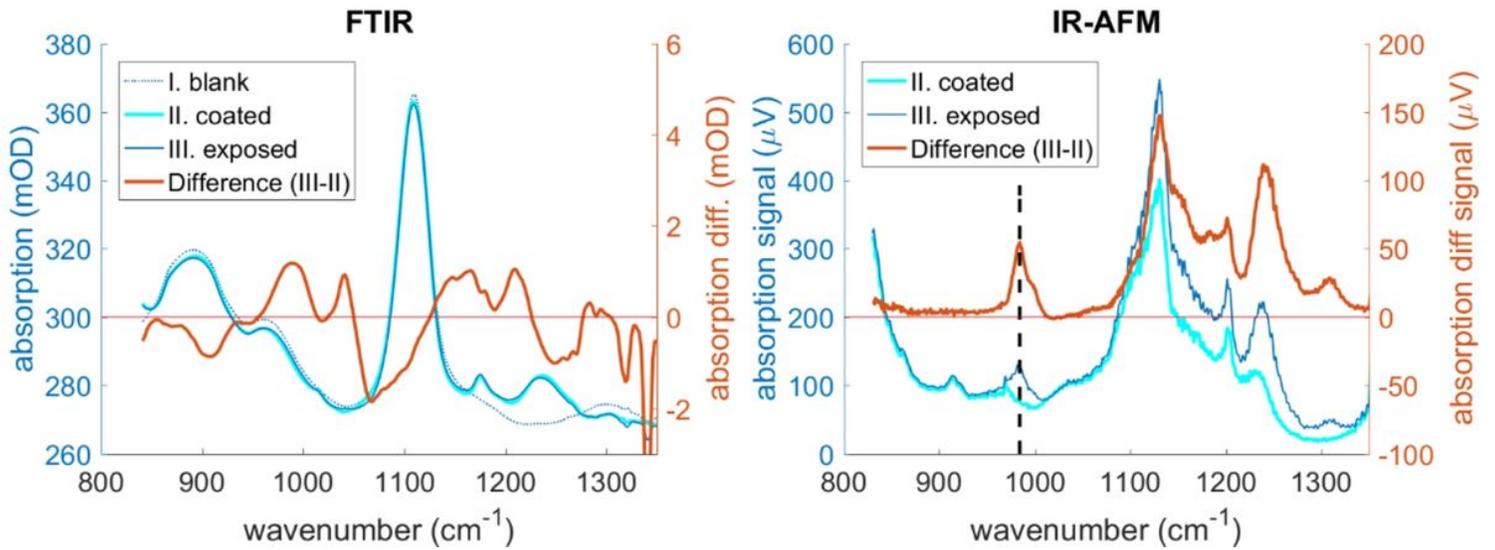


Figure 3

Measured infrared spectra of the (un)coated and exposed-and-cured NEB 22 resist on a Si wafer. Left: absolute (left axis) and difference (right axis) optical density as measured by FTIR. Right: comparable spectra as measured by IR-AFM. The IR wavelength used for imaging is depicted by the black dashed line.

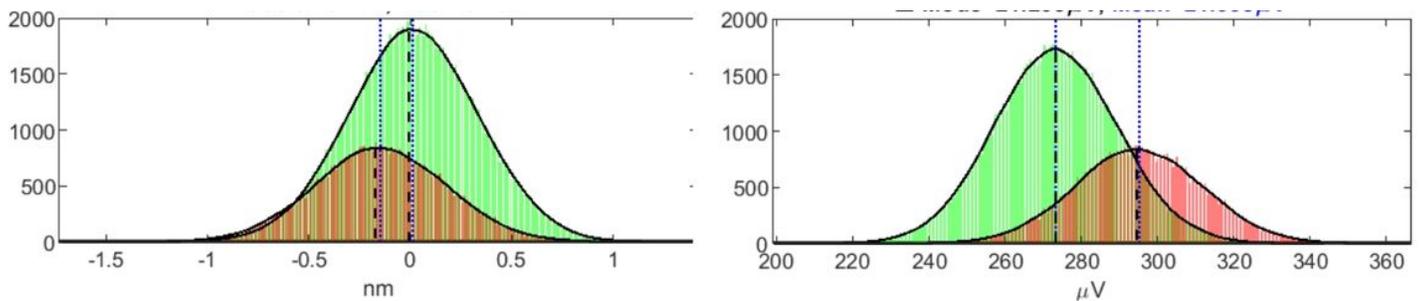


Figure 4

Bottom: histograms of pixel values for exposed (green) and unexposed (red) areas. The 0,16 nm average height difference is just a fraction of the distribution width ($\sigma_{AFM} = 0,23 \text{ nm}$). The 21,7 μV difference in IR-AFM signal strength between exposed and unexposed areas is about twice the distribution width ($\sigma_{IR-AFM} = 11,7 \mu\text{V}$).

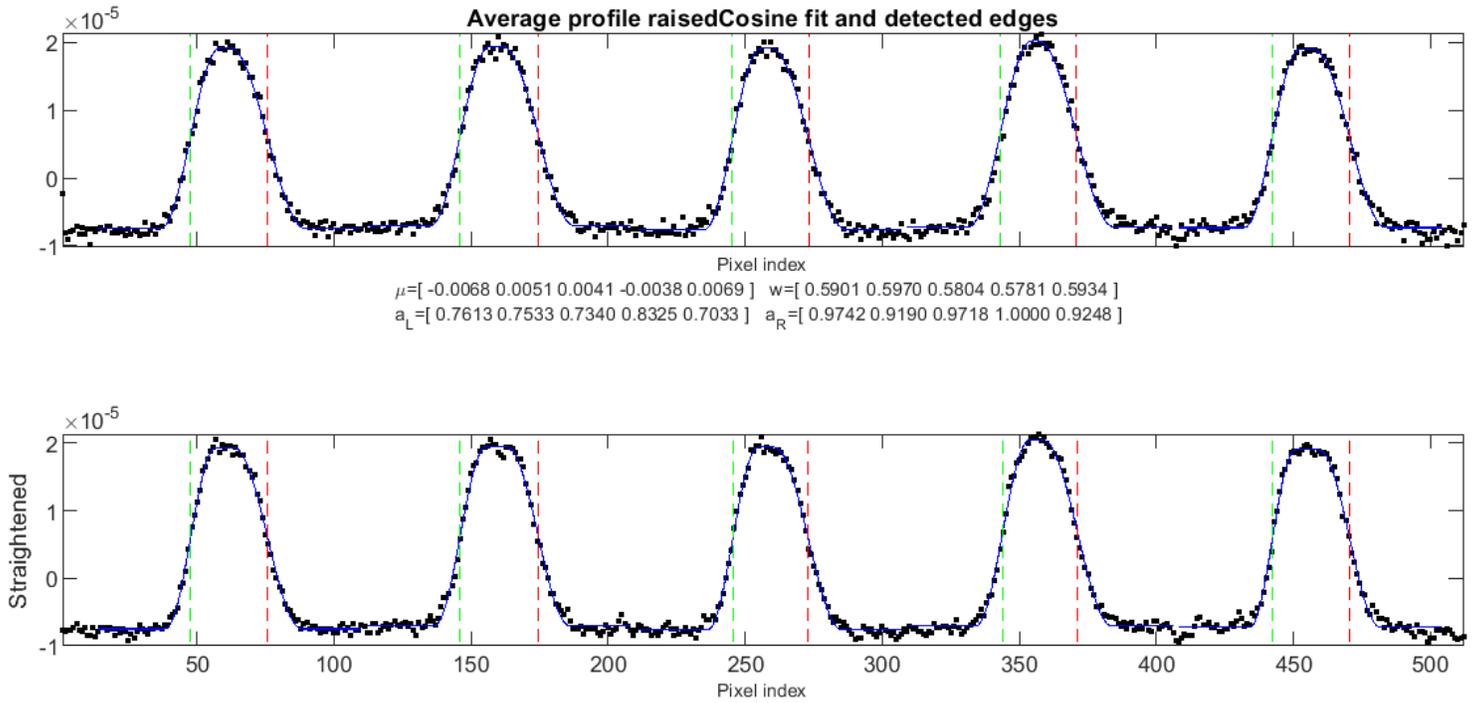


Figure 5

Average waveform (squares = data, blue line = raised cosine fit) from the IR-AFM image of Figure 1. Top: fitted waveform used to determine the line tilt of 0.88 degree. Bottom: final fitted waveform after correcting for line tilt. The edge positions are determined at half-height, indicated by green/red dashed lines for left/right edges.

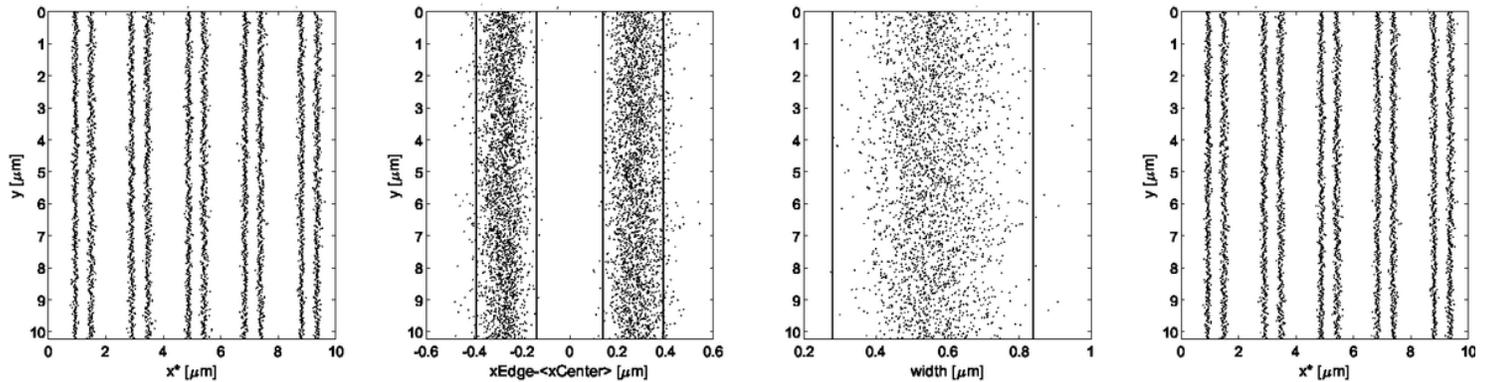


Figure 6

Detected edges before (left panel) and after purification (right). Purification involved minor tilt correction and identification of individual edge positions and/or line widths that differ by more than 2σ (indicated by the vertical straight lines in the centre panels) from both neighbouring lines. For the final LER and LWR analysis, each outlier was replaced by the average position of neighbouring edges.

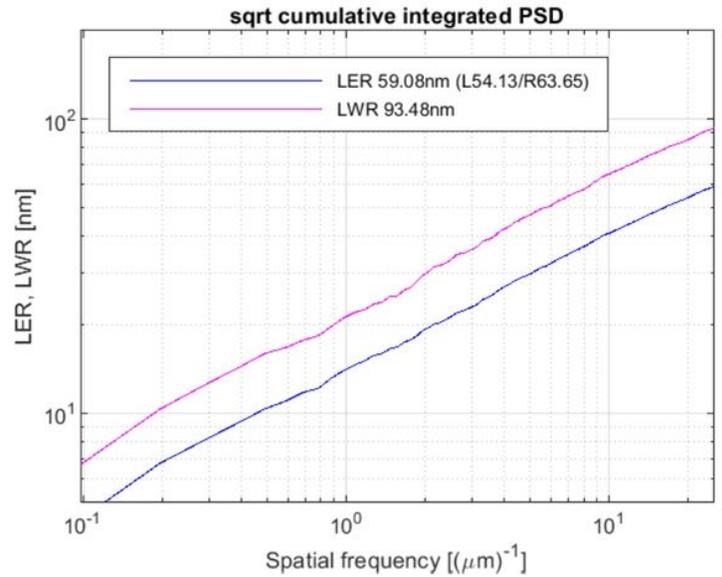
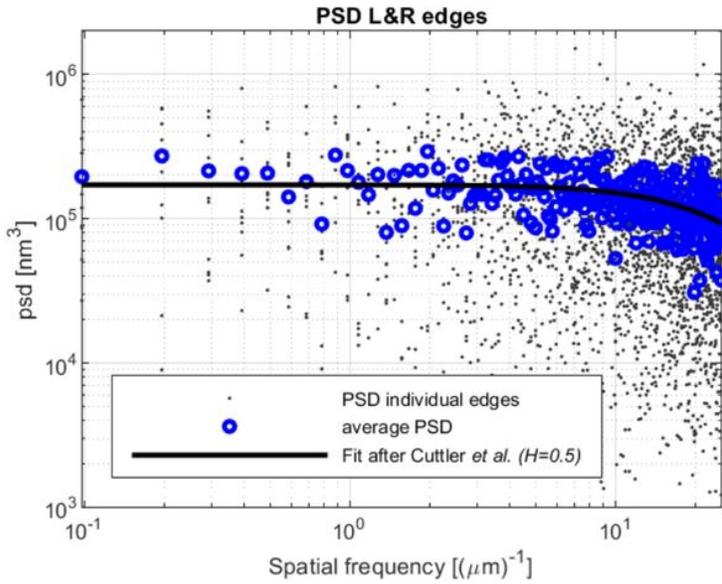


Figure 7

Power Spectral Density graph (right: integrated PSD) as calculated of the half-height edge positions after fitting a raised cosine waveform to each individual line of the IR-AFM image in Figure 1. Detected edges that were displaced over 2σ from direct neighbouring lines have been replaced by the average edge position of the neighbouring lines.