Applications of Chemical Force Microscopy in EUV Lithography

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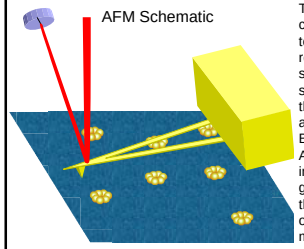
GOAL

To develop chemical force microscopy (CFM) into a metrological tool to quantify the surface chemistry and morphology with nanometer spatial resolution. This will allow direct imaging of latent chemical images in resist films as well as chemical heterogeneities in unexposed resist films.

MATERIALS

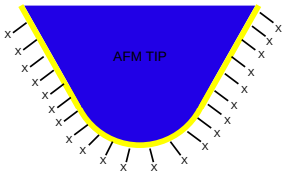
We are currently working with model resist systems to develop competence on simplified systems with a minimal set of chemical species. These include pure polymers of TBA, PAA, HOST and 50/50 TBA/HOST. TPS-PFBS was used as a photoacid generator. Polymers were provided by Jim Sounik and Michael Sheehan at DuPont Electronic Technologies

CHEMICAL FORCE MICROSCOPY



The atomic force microscope (AFM) can be used to image surface topography with sub-nanometer resolution. The AFM works by scanning a very sharp tip across the surface and sensing the forces on the tip by measuring the deflection of a laser beam in a split photodiode. By chemically functionalizing the AFM tip we can enhance the interaction with specific chemical groups on the surface. This forms the basis for making a chemical map of the surface or chemical force microscopy (CFM).

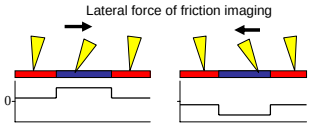
The surface chemistry of the AFM tip is controlled by incubating a gold-coated tip in a solution of alkanethiol. The alkanethiol forms a self-assembled monolayer (SAM) and the surface chemistry is dominated by the terminal group of the alkanethiol molecule. Unless otherwise noted all images were taken with an octadecanethiol coated tip, giving a CH_3 tip chemistry.

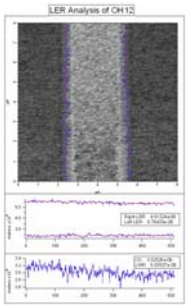


X = CH_3, OH, NH_2 ...

PROOF OF CONCEPT

Lateral force of friction imaging





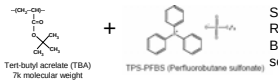
Several AFM imaging modes including lateral force, phase imaging, and direct force measurements have been shown to be sensitive to chemical interactions between the AFM tip and sample surface. All surface chemistry images shown here are lateral force images taken under a dry nitrogen environment. As the tip is scanned over the surface the differing interactions cause the cantilever to twist more in areas of higher friction. The trace and retrace scans have been aligned and subtracted to yield the images shown.

The figure on the right is a lateral force image taken with a hydroxy (OH) functionalized tip. The sample is a self-assembled monolayer of alternating hexadecanethiol and mercaptododecanol stripes. The different chemical interactions between the OH functionalized AFM tip and the CH_3 or OH terminated stripes are easily resolved. The blue line is the line edge and the red is a ten point box car average. The hydroxy terminated stripe is 3 microns wide and has a line width roughness (LWR) of 50 nm.

CHEMICAL HETEROGENEITY

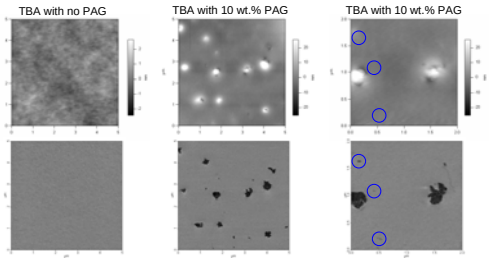
Chemical heterogeneity in the resist can occur at many length scales. It may occur due to large scale phase separation or immiscibility of resist components such as the PAG or from small scale self-organization of polymer blocks or additives. As resist formulations trend toward high PAG loading for EUV-sensitivity our initial work has focused on PAG segregation from the polymer matrix.

The System



Spun cast at 2000 RPM for 60 seconds. Baked at 130 C for 60 seconds.

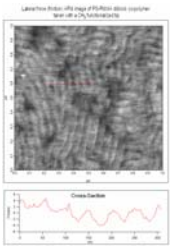
The images below show that the TBA film with no PAG (left) is smooth and has no chemical contrast. The film doped with 10 wt% PAG has a heterogeneous surface with regions of very low friction associated with the aggregate. We believe these are areas where the PAG has separated from the polymer matrix. The top row of images are surface topography and the bottom row is simultaneously collected lateral force.



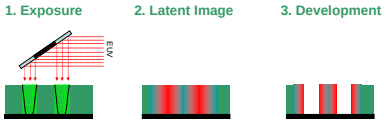
The image at right is a higher resolution scan of the 10% PAG sample. In addition to the large areas of low friction associated with the peaks in the topography image there are a number of smaller features that have no corresponding feature in the topography image (blue circles). Thus the chemical image can resolve heterogeneities that are not revealed in the topographic image.

RESOLUTION

The figure to the right is a lateral force image of a PS-PMMA diblock co-polymer with the lamellae oriented perpendicular to the surface. The repeat distance of the lamellae is 48 nm. By imaging a sample with a known pattern of chemical heterogeneity we are able to assess the spatial resolution capabilities of our instrument. We are exploring the use of these samples as resolution standards for the CFM. The diblock co-polymer sample was provided by Sang-Min Park and Paul Nealey in the Department of Chemical and Biological Engineering at the Univ. of Wisconsin.

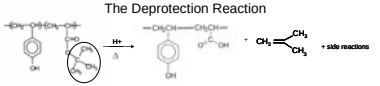


LATENT IMAGES



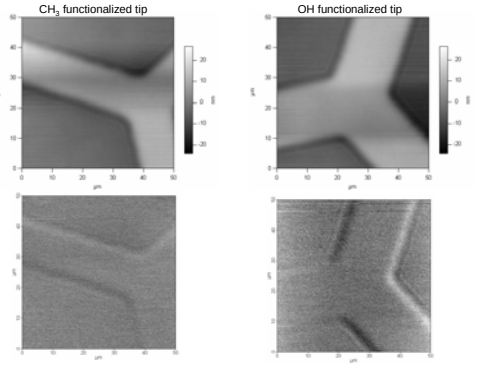
Current CD and LWR measurements are made after lithographic samples have been developed and little direct information is available about the evolution of the pattern during the earlier stages of the lithographic process.

The Deprotection Reaction



We have exposed samples of a 50/50 HOST/TBA copolymer with 10% PAG using an electron microscope grid as a contact mask. Total exposure was 7.8 mJ/cm^2 and the post exposure bake was for 30 seconds at 90 C.

In the AFM images below the pattern is clearly resolved in the topographic images (Top) with the exposed areas 20 nm lower than the unexposed areas. There is however very little contrast in the lateral force images (Bottom) when using either a CH3 or OH terminated tip. This may indicate that the tip chemistry does not have a sufficiently different interaction with the components to give good contrast or that one component is segregating to the surface and obscuring the chemical changes in the bulk of the film.



Future work will use tips of different functionality to look at TBA, HOST, PAA, and 50/50 TBA/HOST samples to find tip chemistries that optimize the contrast between the different possible components. This information will be used to determine which component is on the surface in which area of the sample.

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