# Chemical Imaging of Photoresists with Scanning Transmission X-Ray Microscopy

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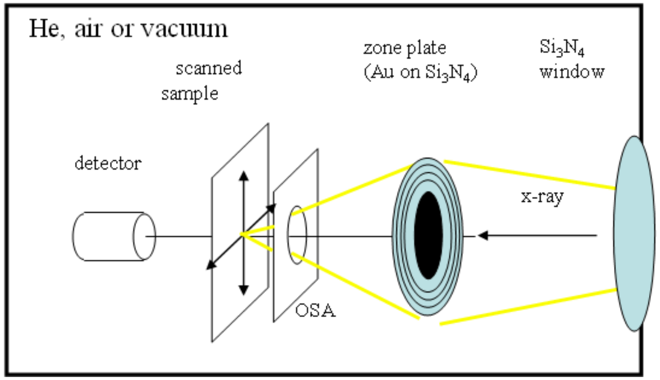
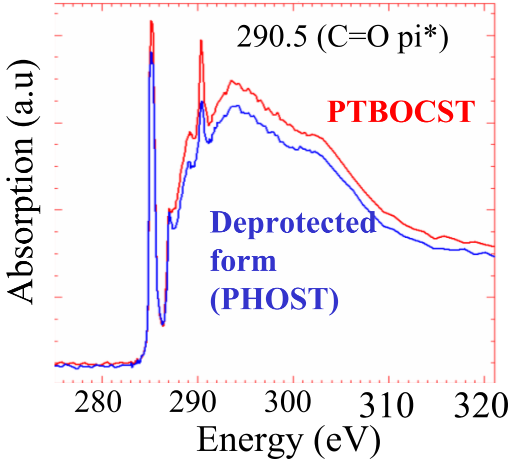
The demand by the semiconductor industry to fabricate smaller structures using lithography requires dimensional control at length scales below tens of nanometers. Chemically amplified photoresist lithography uses spatially selective radiation exposure followed by a complex reaction-diffusion process to delineate patterned areas with high spatial resolution. There are no convenient ways to monitor the line patterns prior to development.

We demonstrate the use of scanning transmission X-ray microscopy (STXM) as a powerful imaging technique with chemical specificity for studying chemically amplified polymer photoresists.

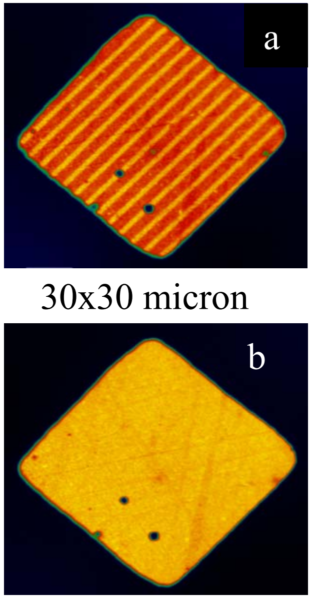
Concept of scanning transmission X-ray microscope.




Monochromated synchrotron X-rays (from the Advanced Light Source) are focused to a small spot (<50 nm, which gives the high spatial resolution) by a Fresnel zone plate. Images are obtained by measuring the intensity of the transmitted X-rays as the sample is raster scanned through the focused beam.




Spectra of UV exposed and unexposed poly(tertbutyloxy-carbonyloxystyrene) (PTBOCST) show that **good chemical contrast** can be obtained at the carbonyl core transition C 1s to pi* C=O (290.5eV).




Chemical images of PTBOCST patterned with 1μm/1μm lines/spaces, taken at a) 290.5 eV (good chemical contrast) and b) 287 eV (no chemical contrast).

The demand by the semiconductor industry to fabricate smaller structures using lithography requires dimensional control of length scales below tens of nanometers. Chemically amplified photoresist lithography uses spatially selective radiation exposure that produces an acid species in the photoresist only in the irradiated regions. This exposure is followed by a complex acid catalyzed reaction-diffusion process that takes place at elevated temperatures and changes the chemical and physical properties of the polymer. A limiting resolution factor in the lithographic process of writing sub-100 nm features is the spatial evolution of the reaction front. In order to visualize the latent image produced upon the deprotection reaction and to characterize the spatial evolution of the reaction front, imaging techniques with both good chemical selectivity and high spatial resolution are needed.

We demonstrate the use of scanning transmission X-ray microscopy (STXM) as a powerful imaging technique with chemical specificity for studying chemical amplified photoresists.

In scanning transmission X-ray microscopy a micro focused soft X-ray beam is generated by a zone plate, illuminates the sample, and the transmitted X-rays are detected. Transmission images are obtained by a raster scan of the sample.

Samples of poly(tert-butyloxycarbonyloxystyrene) (PTBOCST) resist imprinted by contact lithography with a pattern of lines/spaces of 1μm/1μm were used to test STXM imaging capabilities. Very good chemical contrast can be obtained at the carbonyl pi* transition of the carbon K shell electron at an energy of 290.5 eV. A high spatial resolution, better than 50 nm, which is given by the dimension of the X-ray focal spot, has been measured on test samples (data not shown). Besides the high spatial resolution and chemical selectivity, STXM has the advantage of providing short image acquisition times (a few minutes). This implies that samples can be rapidly inspected, which is attractive for high throughput screening. Furthermore, the possibility of writing lines by exposure to soft X-rays and of using heated cells to encapsulate the samples, makes possible experiments of studying the reaction-diffusion process at different stages in time.

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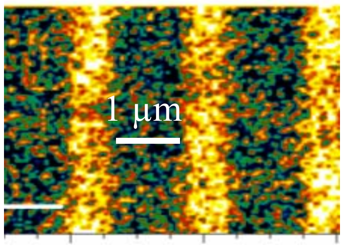


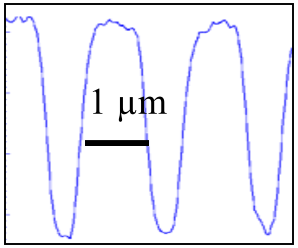


Line profile of patterned PTBOCST at 290.5 eV.

The chemical specificity and high spatial resolution (20-50 nm) of STXM suggests that this method will be a powerful technique for the direct measurement of the spatial evolution of the reaction-diffusion process in polymer photoresists.

## Examples of broader aspects of the research program

**Collaboration:** This research is being pursued in collaboration with Dr. Mary Gilles at the Advanced Light Source, Lawrence Berkeley National Laboratory.

**Industrial connections:** This work has been part of a continuing collaboration with William Hinsberg and Frances Houle of IBM Almaden Research Center. Parts of this collaboration have involved Near Field Scanning Optical Microscopy (NSOM) studies of polymer photoresists.

**Education and outreach** : Among the contributors to this work are one undergraduate student (Romain Planques) and a postdoctoral associate (Ligia Muntean). Romain Planques is an undergraduate having a major in physics at Laboratoire de Physique Statistique, Ecole Normale Superieure (ENS) and University of Paris VI, France. He has been granted a Fellowship from ENS and joined our group to work on this project. During his time on this project Romain Planques assisted a visiting high school teacher Bryan Marten on the data analysis for STXM, on a different project. Previous project members contributing to this on-going research program include Laurie McDonough (grad.) who works on water vapor uptake studies of polymer photoresists, Jan Preusser (grad), Bogdan Dragnea (postdoc). Bogdan Dragnea started a tenure track faculty position at the University of Indiana in 2001, Jan Preusser has been an exchange student from Technical University Clausthal, Germany, who received his Ph.D. in 2003, and Laurie McDonough will graduate in 2005.