

MICROSCOPY AND SPECTROSCOPY OF  
WATER UPTAKE  
IN POLYMER PHOTORESISTS

by

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Microscopy and Spectroscopy of Water Uptake in Polymer Photoresists

Thesis Directed by Professor Stephen R. Leone

Water uptake in polymer photoresists is investigated with a combination of methods. An infrared near-field scanning optical microscope (IR-NSOM) is incorporated into an environmental chamber for the measurement of samples composed of alternating lines of poly(*t*-butylmethacrylate) (PTBMA) and the photochemically modified poly(methacrylic acid) (PMAA) in both low and high water vapor environments. The degree of water vapor sorption is measured using the infrared transmission of 2.85  $\mu\text{m}$  light on a small spatial scale ( $< 500 \text{ nm}$ ). The accompanying topographic swelling of the samples is measured using a shear-force feedback loop. Distortion of the topographic structure and variation in transmission contrast indicate that the PMAA zones absorb more water than the PTBMA regions in the water vapor environment.

Atomic Force Microscopy (AFM) is used to measure the same PTBMA/PMAA photoresist along with another sample consisting of poly(*t*-butylcarbonylstyrene) (tBOC) and its modified counterpart, polyhydroxystyrene (PHOST). Distance sweep measurements show that the tip indents further into PHOST than tBOC regions. The tip-sample interactions do not change when exposed to humidity, thus allowing the measurement of differential swelling. The PTBMA/PMAA photoresist is found to display more differential swelling than the tBOC/PHOST photoresist.

Fourier-Transform Infrared (FTIR) absorption spectroscopy is implemented to measure the infrared spectrum of water absorbed by the ketal-protected poly(hydroxystyrene) (KRS-XE) and tBOC photoresists. The shape and intensity of the OH stretching band of the water spectrum is monitored in a variety of humidity conditions in order to obtain information on the hydrogen-bonding interactions between the water and the polymer chains. The band is deconvoluted into four sub-bands, which represent four types of water molecule environment. A large portion of the sorbed water molecules is believed to be strongly bound to the polar sites of the polymer. The ratios of each type of water are found to be dependent on the humidity conditions to which the sample was exposed. These findings are used to explain the humidity dependence of the deprotection reaction rates, since certain types of water may slow transport of reactive species within the polymer network.

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