Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Surface Roughening: The Dependence on Polymer Structure

Ting-Ying Chung and David B. Graves\textsuperscript{1,2}  
Department of Chemical Engineering, University of California, Berkeley, USA

Abstract  
Previous results have shown that simultaneous ion bombardment, VUV radiation, and moderate substrate heating result in similar levels of photoresist (PR) surface roughness as observed during typical plasma etching conditions\textsuperscript{3-5}. We further examined associated homopolymer to better understand the role of the side groups in roughening. It suggests that the leaving group in 193 nm PR, designed to cleave in the presence of photolysis during lithographic exposure and post-exposure bake, is the primary cause of 193 nm PR roughening, when combined with energetic ion bombardment, VUV irradiation and elevated heating.

Motivation/Goal  
- PR roughening during plasma processes is of critical importance as device dimensions are approaching nanometer scales. 
- Understand scientific principles of polymer texturing during plasma exposure.

Previous Results  
Synergistic ion/VUV and substrate heating\textsuperscript{3,4}

- Enhanced 193 nm PR surface roughening is observed only under simultaneous ion/VUV exposure at elevated substrate temperatures.

Chemical Modification  
VUV-only exposure: polymer structure-dependent bulk modification

- p-MAMA: VUV photons cleave the adamantane leaving group and also generate CO and CO\textsubscript{2}.
- An elevated substrate temperature promotes the loss of photolysis products.

Surface roughness: simultaneous ion/VUV exposure

- Under the same experimental condition, surface roughness: p-MAMA > 193 nm PR > p-RAMA 
- Enhanced surface roughness of p-MAMA at 65°C corresponds to the high extent of adamantane group loss.

Materials  
Model 193 nm Photoresist

- Polymers are supplied by the Dow Chemical Company with a film thickness ~250 nm.
- The PR polymer consists of methyl adamantryl methacrylate (MAMA), \(\alpha\)-gamma butylactone methacrylate (\(\alpha\)GBLM) and an R-functionalized adamantryl methacrylate (RAMA) group.
- Without photacid generator and base quencher.

Experimental Setup / Characterization  
Side-view of the ultra-high vacuum beam system

- Ion gun (Commonwealth Scientific) \(\times 1900\) VAr ion, normal incidence
- Xe VUV lamp (Resonance Ltd.) \(147\) nm photon, \(45^\circ\) with respect to surface normal
- An external water bath is connected to the sample dock. The substrate temperature is held at 25°C and 65°C.
- Sample characteristics:  
  - In situ photolysis products evolution: Residual Gas Analyzer  
  - Ex situ chemical modifications: Transmission FTIR  
  - Ex situ surface roughness: Atomic Force Microscope (AFM)

Concluding Remark  
- VUV sensitivity: p-MAMA > 193 nm PR > p-RAMA
- VUV photolysis products:  
  - p-MAMA: VUV photons cleave the adamantryl leaving group and also generate CO and CO\textsubscript{2}
  - 193 nm PR: the main photolysis products are CO and CO\textsubscript{2} while adamantryl leaving group and free lactone are also detected.
  - p-RAMA: except for CO and CO\textsubscript{2}, no other products can be distinguished.
- An increased substrate temperature promotes the loss of photolysis products.
- The extent of adamantryl leaving group loss corresponds to the degree of PR surface roughening.

1. Financial support from the National Science Foundation under Award number No. DMR-0406120, DMR-0705953.
2. Completed with F. Wielibork, G. S. Deehrin, University of Maryland, College Park, Maryland; M. Li, the Dow Chemical Company, Marlborough, Massachusetts, and E. A. Hudson, Lant Research Corp., Fremont, California