Electron, Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Roughening

Department of Chemical Engineering, University of California, Berkeley, California 94720

F. Weilnboeck, R.L. Bruce, G.S. Oehrlein  
Department of Material Science and Engineering, Department of Physics, and Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland 20742

E.A. Hudson  
Lam Research Corp., 4650 Cushing Parkway, Fremont, California 94538

M. Li, D. Wang  
Dow Electronic Materials, The Dow Chemical Company, 455 Forest Street, Marlborough, Massachusetts 01752

56th AVS – San Jose – November 2009
Introduction

- **Motivation**
  - While plasma can play a role in both “roughening” and “smoothing” of the photoresist, the fundamental understanding of “texturing” mechanisms is under-developed.

- **Goals**
  - Provide scientific principles of polymer texturing during plasma exposure.

- **Outline**
  - Previous conclusion: Synergistic effect of ion/VUV and substrate heating
  - Materials and the beam system
  - 1keV electron effect
  - Simultaneous ion/VUV/electron effect on surface roughening

800 W / 20 sec Ar plasma (193 PR)

250 nm
Previous results from our group:
Synergistic ion/vacuum ultraviolet (VUV) and heating effect

Poly (methyl methacrylate)
Carbon Oxygen Hydrogen

AFM
2.25

65°C

Pristine photoresist

G. Choudhary, J. J. Vegh, and D. Graves, (submitted)
Previous results from our group:
Synergistic ion/vacuum ultraviolet (VUV) and heating effect

<table>
<thead>
<tr>
<th>AFM</th>
<th>2.25</th>
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<td>[Image: 250nm x 65°C]</td>
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**Pristine photoresist**

- **Ar⁺**
- **VUV**
- **2nm**
- **VUV-modified layer**
- **~100nm**

- **Ar⁺**
- **VUV**
- **65°C**
- **Pristine photoresist**
Previous results from our group:
Synergistic ion/vacuum ultraviolet (VUV) and heating effect

Ion flux: 2.9×10^{14} \text{ ion/sec} \cdot \text{cm}^2
Photo flux: 1.3×10^{14} \text{ photons/sec} \cdot \text{cm}^2

AFM 4.00

150eV ion/VUV

Surface roughness (nm)

Exposure time (min)

0 10 20 30 40 50 60

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0

VUV-modified layer

Pristine photoresist

VUV
Overview: 1keV electron study

Exposure protocols:
1. Ion/VUV/Electron
2. Ion/Electron
3. VUV/Electron

Electron-modified layer
Pristine photoresist

Simultaneous exposure
VUV or low fluence electron

Pristine photoresist
Scissioned layer
**Materials**

- **Model 193 nm photoresist**
  - Random terpolymer, supplied by Dow Electronic Materials with a film thickness ~250 nm. Tg ~ 180°C, Mw = 10,000 g/mol
  - Without photoacid generator and base quencher

Methyl adamantyl methacrylate (MAMA)
α- gamma butyrolactone methacrylate (α-GBLMA)
R-functionalized adamantyl methacrylate (RAMA)
**Experimental setup**

- **Ion gun** (Commonwealth Scientific)
  - 150eV Ar ion
  - Normal incidence

- **Xe VUV lamp** (Resonance Ltd.)
  - 147 nm photon (8.4eV)
  - 45° respect to surface normal

- **Electron gun** (Kimball Physics)
  - 1keV electron
  - 57° respect to surface normal

- **In situ** etch rates: Quartz Crystal Microbalance (QCM)
- **Ex situ** chemical modifications: Transmission FTIR
- **Ex situ** surface roughness: Atomic Force Microscope (AFM)
Transmission FTIR spectra of pristine 193 PR

C=O bonds

Ester  Lactone

Absorbance (abs)

Wavenumber (cm⁻¹)

CH₂/CH₃ bonds

Absorbance (abs)

Wavenumber (cm⁻¹)

MAMA  α-GBLMA  RAMA
1keV electron effect – bulk modification (FTIR)

C=O bonds

Increasing exposure time

$\text{CH}_2/\text{CH}_3$ bonds

Increasing exposure time

Electron flux: $9.8 \times 10^{12}$ electrons/sec·cm$^2$

Fluence (electrons/cm$^2$) = Flux (electrons/sec·cm$^2$) $\times$ exposure time (sec)

- MAMA
- $\alpha$-GBLMA
- RAMA

Unprocessed
1000eV 5min
1000eV 10min
1000eV 15min
1000eV 30min
1000eV 60min
1keV electron effect – *in situ* etch yield (QCM)

- Etch yield = slope of mass removal vs. fluence

- A high initial etch yield is followed by a decreased steady-state etch yield.
1keV electron effect – *scissioning vs cross-linking*

![Graph showing the relationship between fluence (charge density) and mass removed.](image)

- At lower fluences, electron-induced scissioning dominates.
- At higher fluences, electron-induced cross-linking dominates.
- RMS surface roughness: 0.3~0.4 nm

The cross-linked region is not soluble in tetrahydrofuran (THF).
Texturing of individual species

2.25

0.28

0.34

250nm 65°C 250nm 65°C 250nm 65°C

VUV

Ar+

Ar+

Ar+

Ar+

Ar+

Electron

~2nm

~100nm

~55nm

Pristine photoresist

VUV-modified layer

Pristine photoresist

Electron-modified layer

Pristine photoresist
Surface roughness – Ion/VUV/Electron

- Ion fluence: $1 \times 10^{18}$ ions/cm$^2$, VUV photon fluence: $4.8 \times 10^{17}$ photons/cm$^2$
- Substrate temperature: 65°C
- The surface morphology and roughness change dramatically with the electron dosage

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Electron-induced scission
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Electron-induced scission

Electron-induced cross-linking
Ion/VUV/Electron and Ion/Electron

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**Electron-induced scission**

**Electron-induced cross-linking**
Surface roughness vs. electron fluence: temperature effect

Electron Fluence (mC/cm²) vs. RMS Roughness (nm)

- Ion+VUV 65°C
- Ion 65°C
Surface roughness vs. electron fluence: temperature effect

- Elevated substrate temperature increases surface roughness.
- Low fluence electrons (1 mC/cm²) enhance surface roughness.
- Electron-induced cross-linking changes surface morphology.
- High fluence electrons (8 mC/cm²) reduce surface roughness.
Surface roughness vs. electron fluence: temperature effect

- Elevated substrate temperature increases surface roughness.
- Low fluence electrons (1mC/cm²) enhance surface roughness.
- Electron-induced cross-linking changes surface morphology.
- High fluence electrons (8mC/cm²) reduce surface roughness.
- Intermediate fluence electrons (4mC/cm²) result in temperature-dependent surface roughness.
Surface roughness vs. electron fluence: importance of ion bombardment

- Elevated substrate temperature increases surface roughness.
- Low fluence electrons (1mC/cm²) enhance surface roughness.
- Electron-induced cross-linking changes surface morphology.
- High fluence electrons (8mC/cm²) reduce surface roughness.
- Intermediate fluence electrons (4mC/cm²) result in temperature-dependent surface roughness.
- No surface roughening is observed on VUV/electron exposed samples: ion bombardment resulting ion-modified surface layer is necessary for surface roughening.
Conclusions (1/2)

- Effects of ion, VUV, electron exposure:
Conclusions (2/2)

- **Enhanced surface roughness:**
  - Simultaneous exposures, providing a combination of a surface carbon-rich layer (~2 nm) by argon ion bombardment and a bulk-scissioned layer.
  - Bulk-scissioned layer can be formed by VUV or low fluence electron exposures.

- **High fluence electrons** (8mC/cm²) suppress roughening by generating bulk cross-linking.

- **Temperature effect:**
  - An increased substrate temperature amplifies surface roughness.
Acknowledgements

• Professor Rachel Segalman, UC Berkeley
• Dr. John Coburn

• Financial support from the National Science Foundation under Award number No. DMR-0406120, DMR-0705953.