Ion Beam Interactions with Advanced Photoresist Polymers

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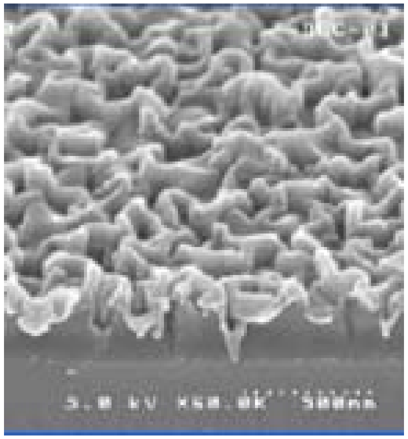
Introduction

- Motivation:
  - There is little understanding of fundamental etching and roughening mechanisms of polymer masking materials.
  - Increased etch resistance is required as thinner masking films are needed.
  - Photoresist roughening, resulting in poor pattern transfer, becomes increasingly important as device dimensions shrink.



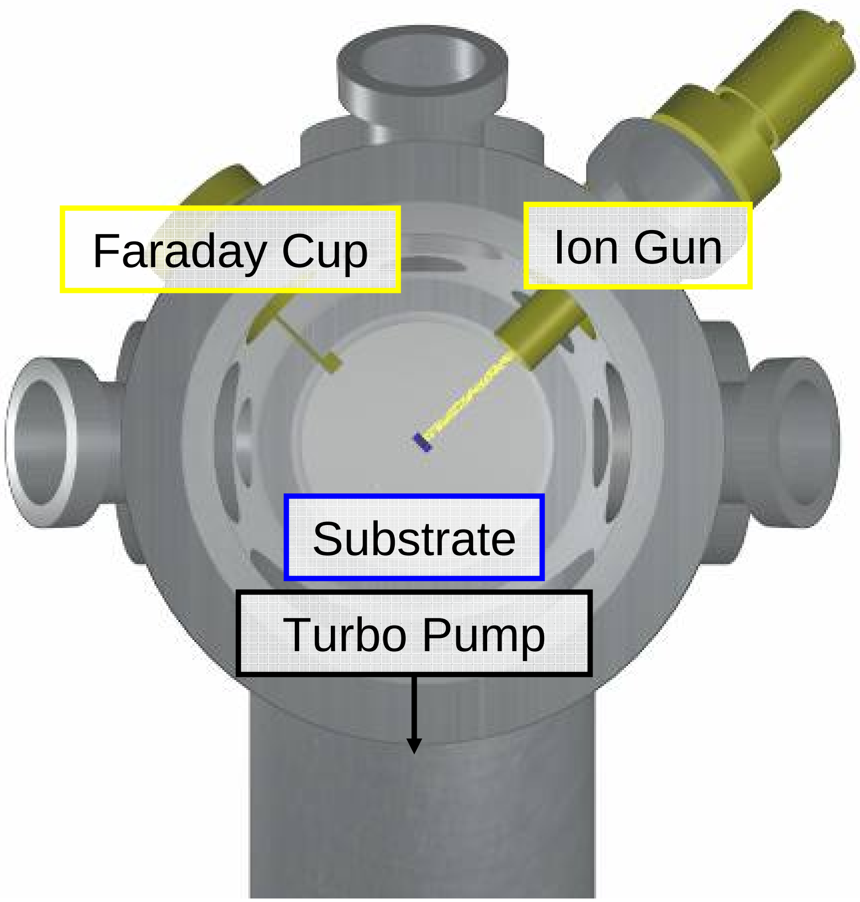
- Goals
  - Determine important variables when considering roughness and etching mechanisms of polymer masking materials.
- Outline: Beam system studies
  - Sputtering of photoresist under ion bombardment.
  - Roughening of photoresist under ion bombardment.

E. Hudson, Z. Dai, et al. "Control of Line Edge Roughness for Etching with 193nm Photoresist." *Proc. Dry Process Int. Symp.* 253 (2003).

Experimental Technique

- UHV Chamber:
  - Base Pressure: ~$5x10^{-8}$ Torr pumped with a 2000 L•s^{-1} turbo pump

- PHI Model 04-191 Ion Gun:
  - Chamber pressure rises to ~$1x10^{-6}$ Torr
  - Ions: He^+, Ar^+ and Xe^+
  - Energies: 0.5 keV and 1 keV
  - Beam Size: ~0.5 cm
  - Substrate temperature control
  - Neutralizing filament to prevent surface charging



Samples and Analytical Tools

- Samples:
  - Rohm and Haas methacrylate-based 193 nm photoresist
    - Coated on Quartz Crystal Microbalances (QCM) for sputter yield studies
    - Samples cleaved from coated 8" wafers for roughness studies

- Analytical Tools:
  - Sputter yield studies: QCM monitored for mass change during ion impact
  - Roughness studies: ex situ Atomic Force Microscopy (AFM) surface roughness analysis

Definitions

- Ion Flux Φ (ions·cm^{-2}·s^{-1}) on the sample:
  - I = current measured by Faraday cup (~nA)
  - A = Faraday cup area (A = 4.55x10^{-4} cm^{-2})
  - q = elemental charge

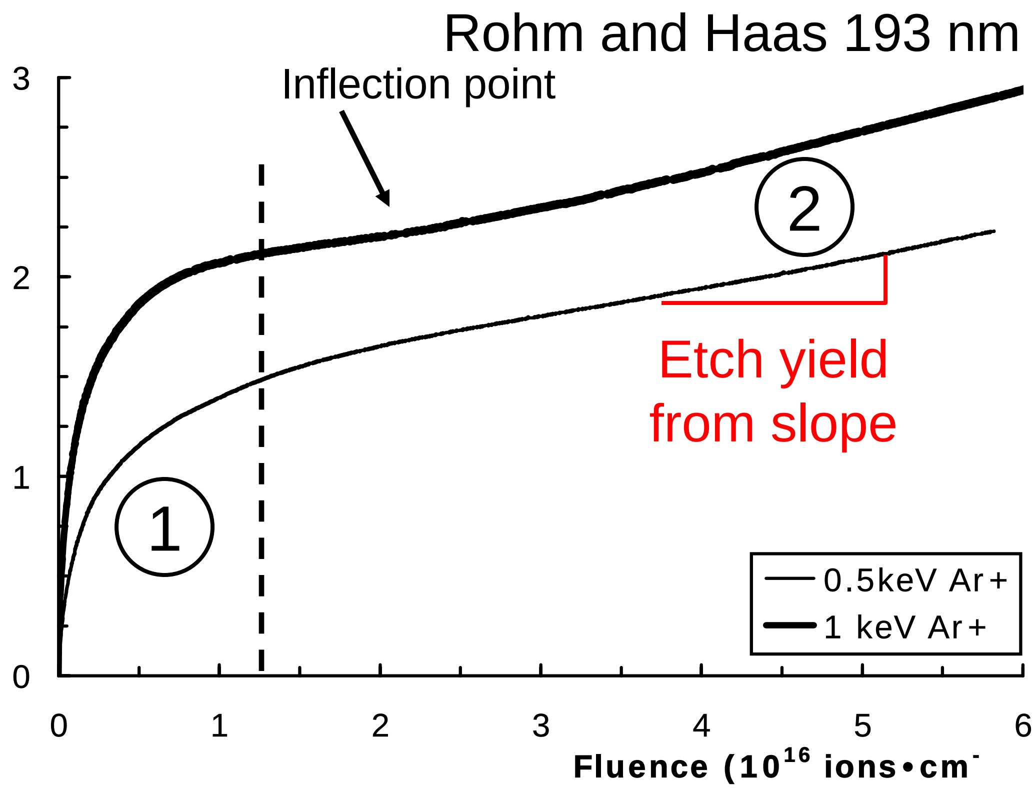
$$\boxed{\Phi = \frac{I}{A \cdot q}}$$

- Ion Fluence Γ (ions·cm^{-2}):
  - Φ = ion flux (ions·cm^{-2}·s^{-1})
  - t = exposure time (s)

$$\boxed{\Gamma = \Phi \cdot t}$$

- Equivalent carbon etch yield (EY) (eq C·ion^{-1}):
  - Number of equivalent carbons removed per incoming ion
  - Obtained from slope of mass removed vs. fluence plot from QCM measurements.

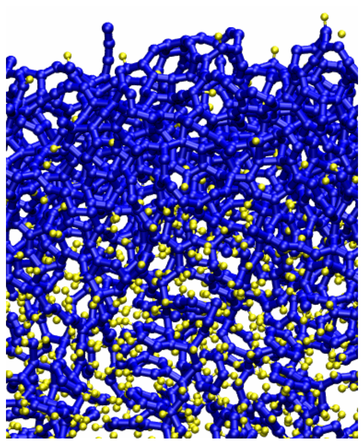
Evolution of Etch Yield with fluence: Ar^+



1 Formation of carbon-rich surface layer

2 Steady-state sputtering / sputtering of already implanted material

ion penetration depth (~nm)



dehydrogenated surface layer

} transition region: large changes in materials properties over a very small thickness

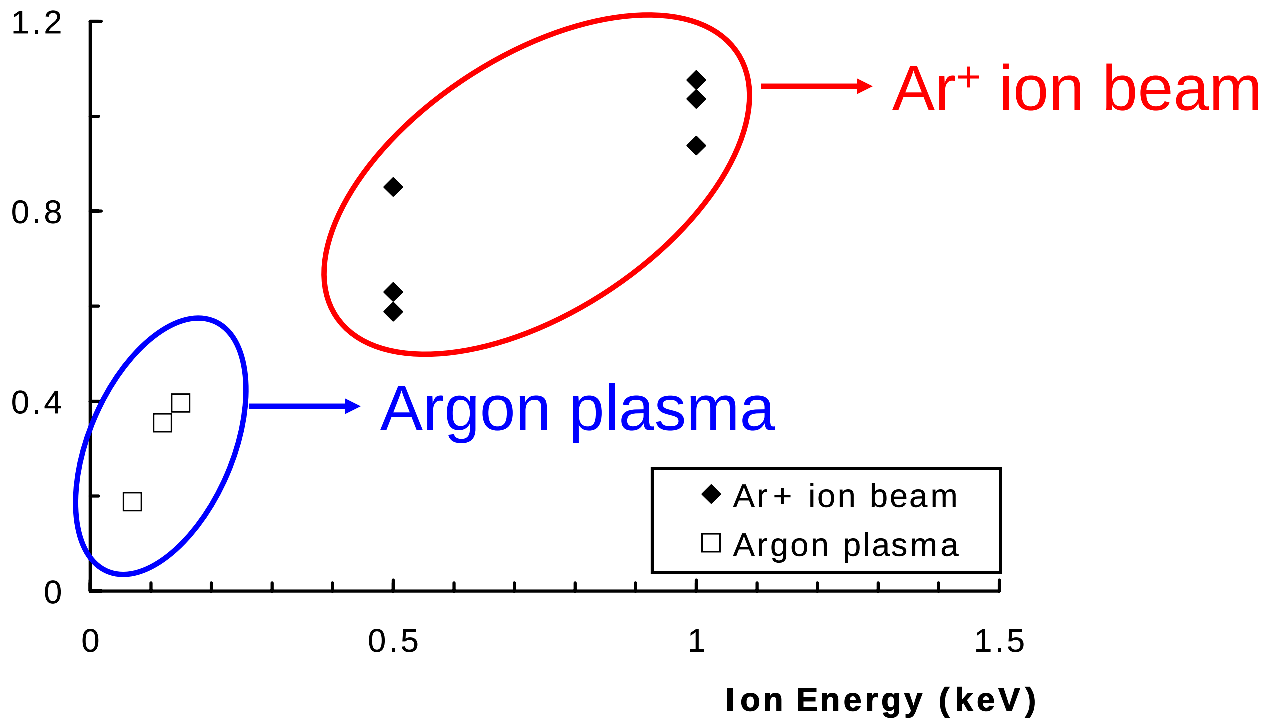
undisturbed polymer

Molecular Dynamics Simulations,
J.J. Vegh, UCB

Steady-state etch yield: comparison to plasma experiments

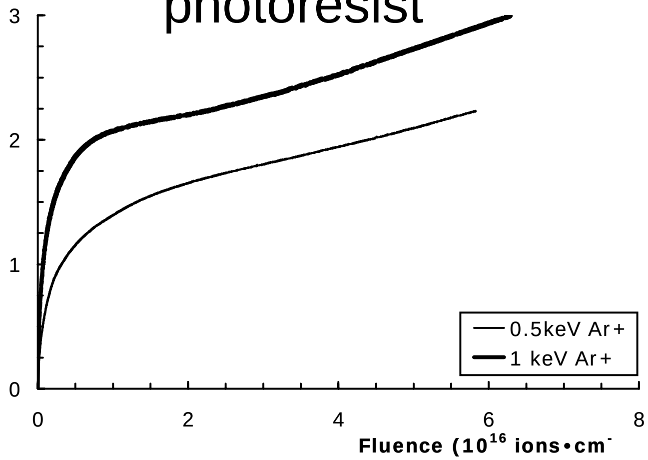
Rohm and Haas 193 nm photoresist

- Ion beam etch yields:
  - 0.5 and 1 keV ion beam steady-state etch yields from QCM experiments for fluences > 5×10^{16} ions•cm^{-2}.
- Plasma etch yields:
  - Argon plasma experiment etch yields

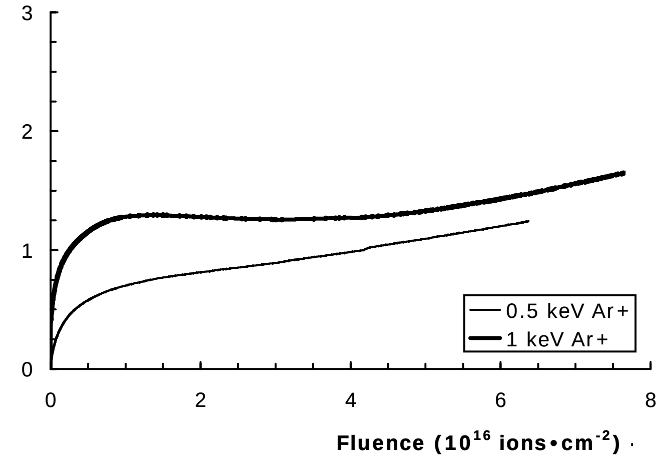


Evolution of etch yield with fluence: comparison of 193 nm and 248 nm photoresist

Rohm and Haas 193 nm photoresist



248 nm photoresist



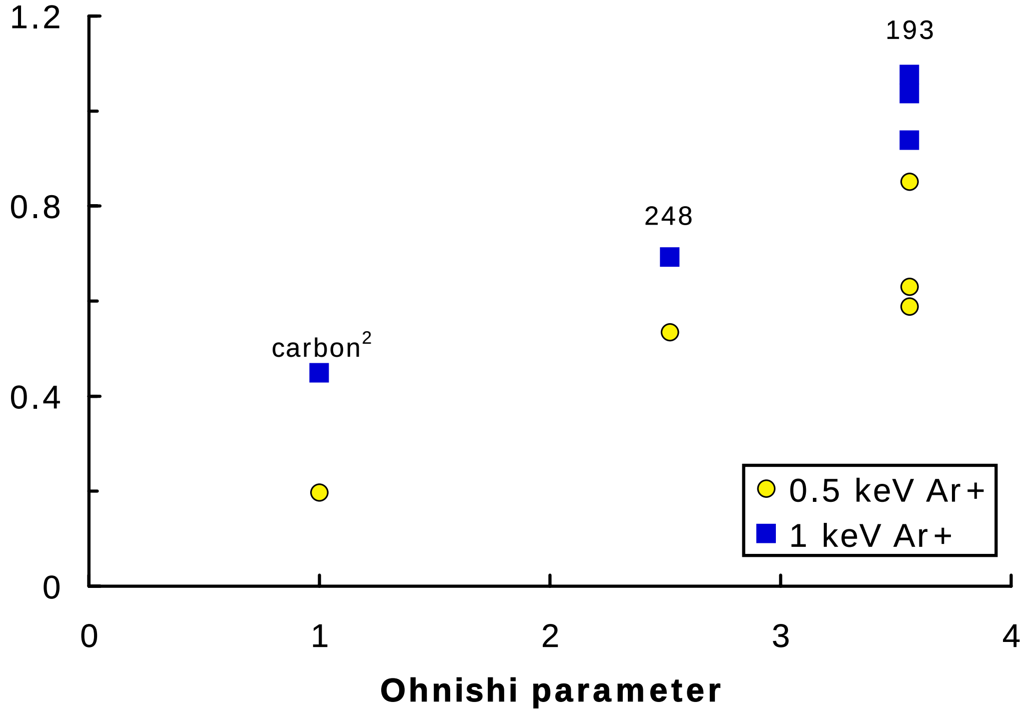
- More mass removed prior to reaching steady-state for 193 nm photoresist.
- Comparison of steady-state etch yields:
  - Higher ion energy results in higher etch yields (for a given material).
  - Etch yield of 193 nm is higher than 248 nm (at a given energy).

Comparison of steady-state etch yields

- Empirical formula: etch yield is proportional to Ohnishi parameter[1]

$$EY \propto \frac{N}{N_C - N_O}$$

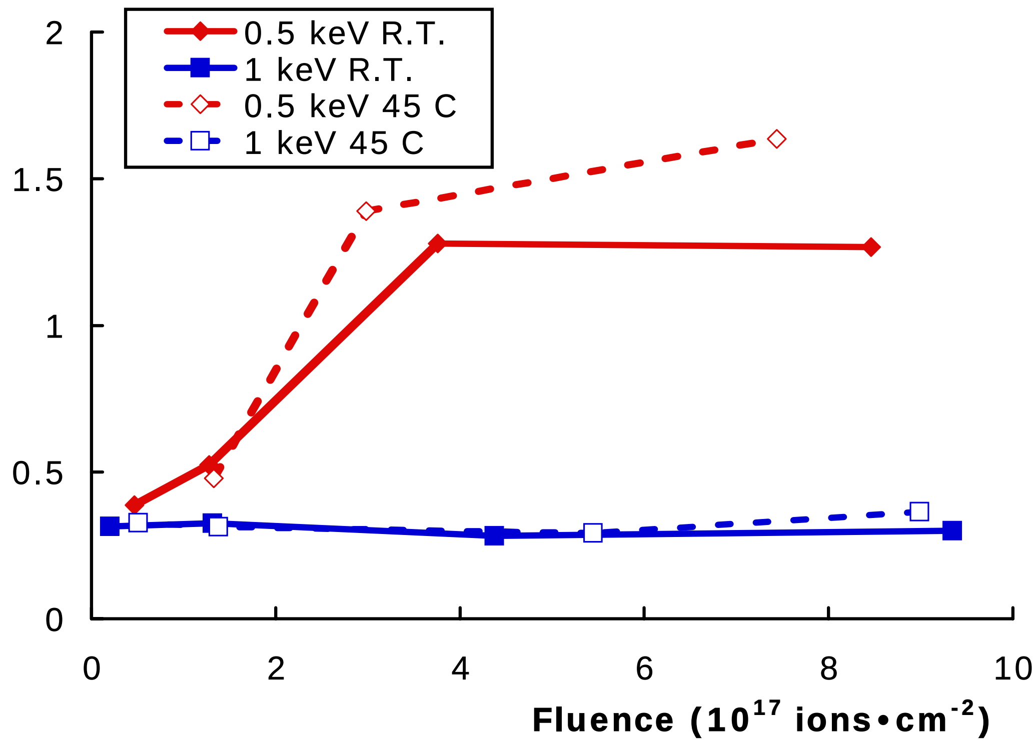
N: total number of atoms in monomer
N_C: number of carbon atoms in monomer
N_O: number of oxygen atoms in monomer



[1]Gokan, H., S. Echo, and Y. Ohnishi, Journal of the Electrochemical Society, 1983. **130**(1): p. 143-146.
[2]National Physics Laboratory, UK

Surface roughening of 193 nm photoresist: Argon ion bombardment

- Surface roughness obtained from 1x1 μm^2 AFM images.
- Ar^+ bombardment: ion energy and substrate temperature
- Surface roughness of unprocessed sample: ~0.3 nm

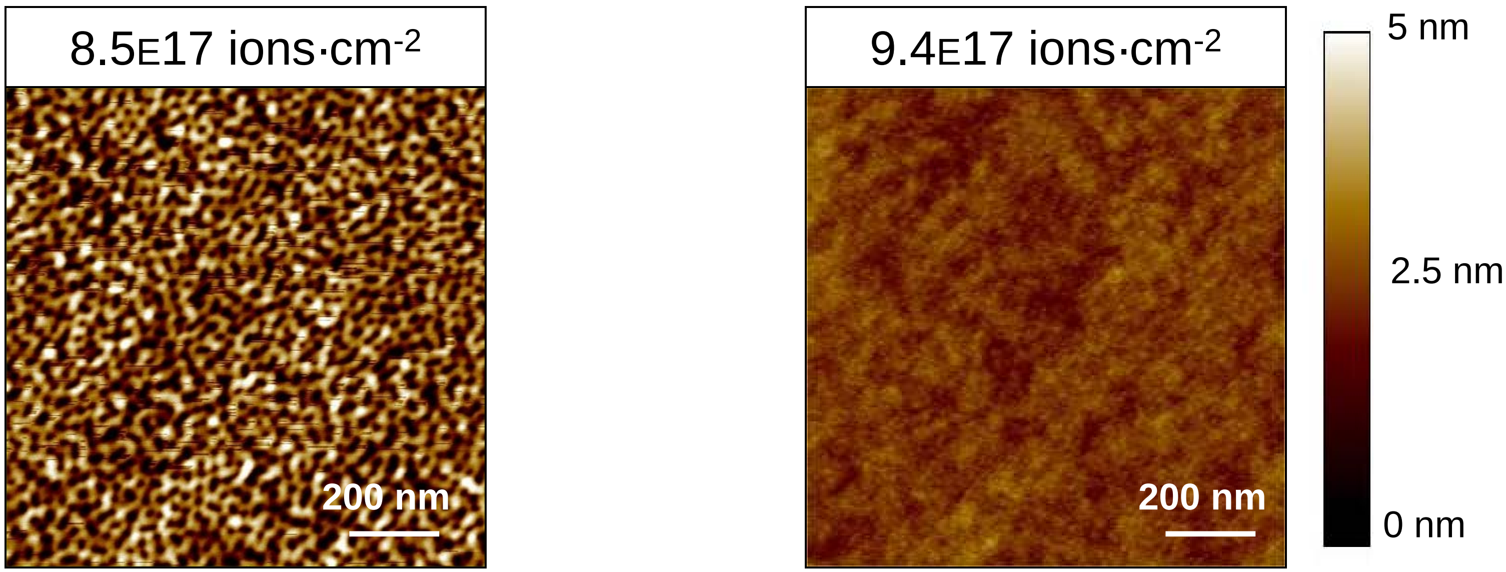


- Decreasing ion energy increases roughness.
- Increasing substrate temperature increases roughness.
- Heating alone does not roughen the surface.

Surface roughening of 193 nm photoresist: effect of Ar^+ ion energy

- Ion energy effect (20°C):

0.5 keV | **1 keV**



1.27 nm | **0.30 nm**

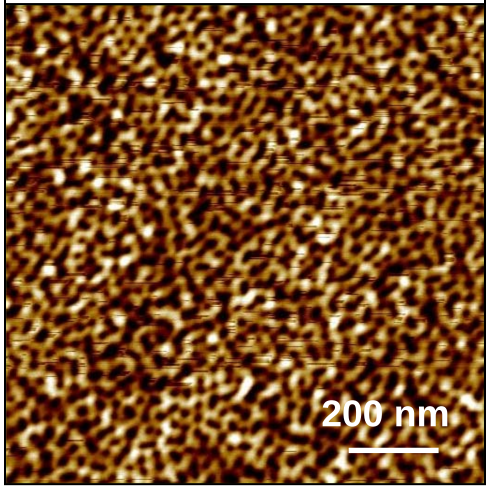
- Ion beam studies: increased roughness at lower ion energies
- Also seen on polystyrene derived materials.
- Argon plasma exposures at lower ion energy resulted in greater roughness.

Surface roughening of 193 nm photoresist: effect of substrate temperature

- Substrate temperature effect (0.5 keV Ar^+):

20°C

8.5E17 ions·cm^{-2}

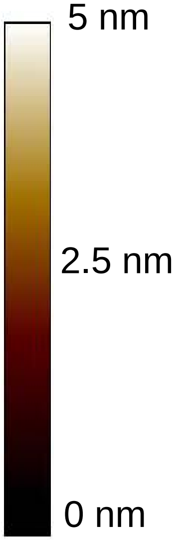


1.27 nm

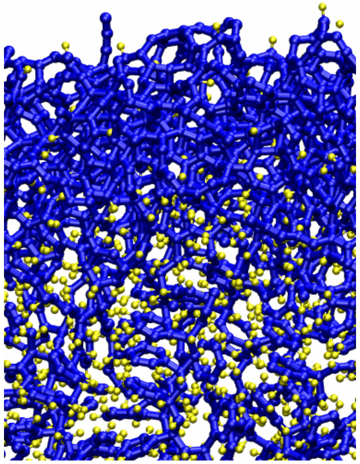
45°C

7.4E17 ions·cm^{-2}

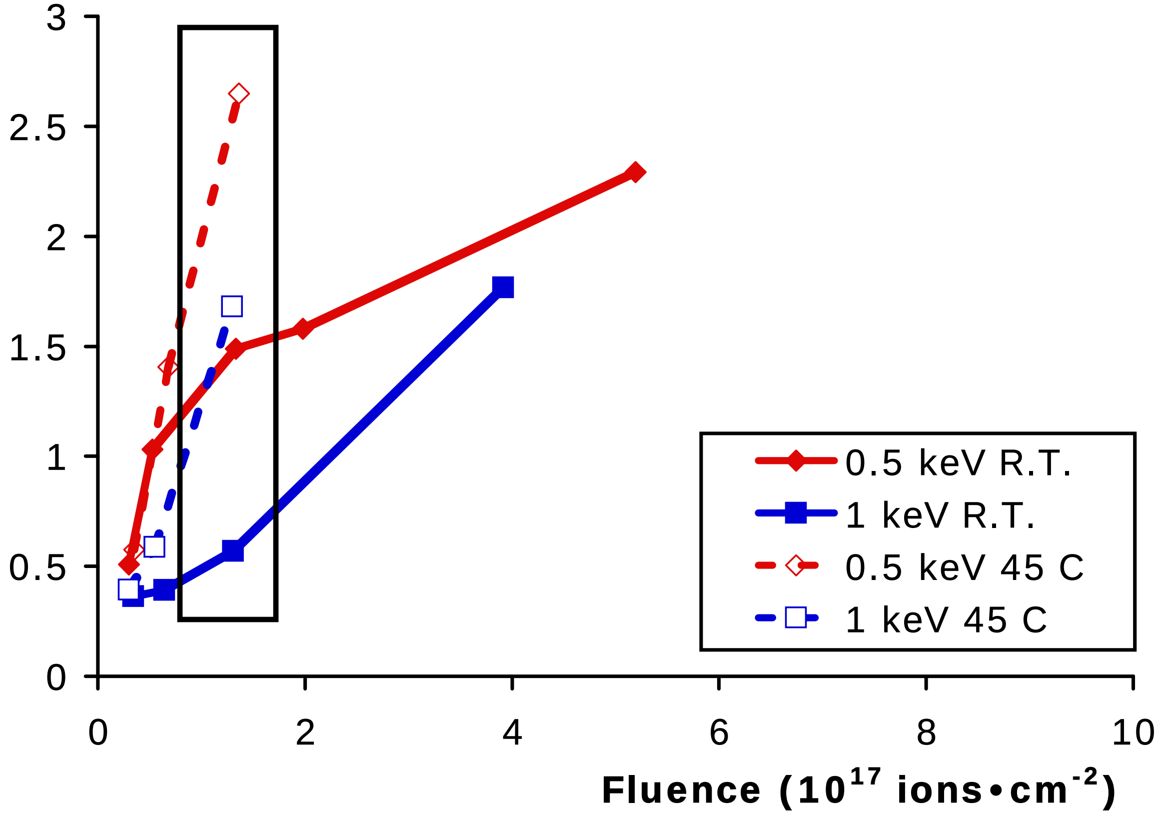
1.64 nm



- Literature: increasing substrate temperature on amorphous materials should promote diffusion, decreasing surface roughness.
- Uniqueness of polymers:
  - highly modified surface layer
  - large gradient in composition and structure over a few nanometers



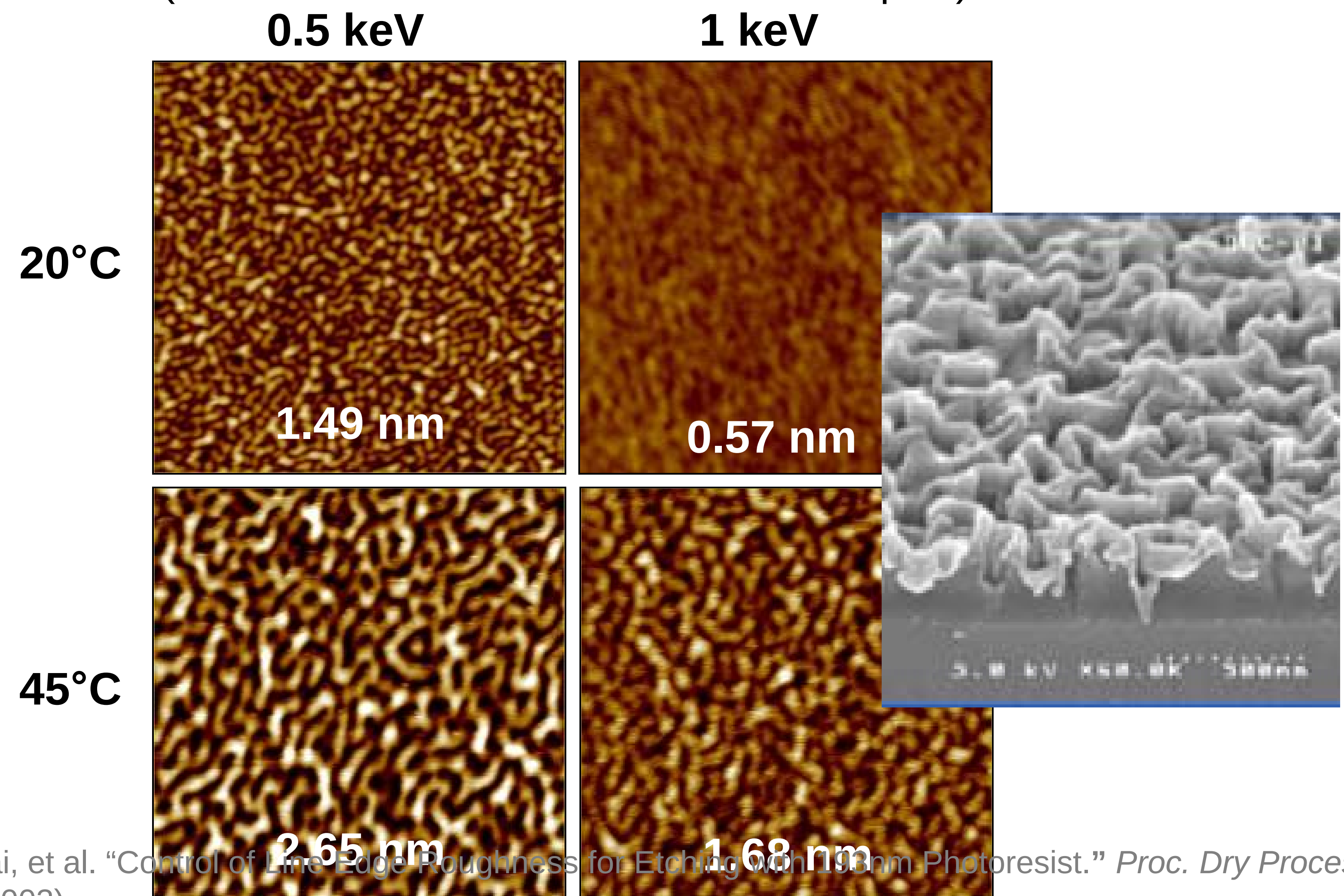
Surface roughening of 193 nm photoresist: Xenon ion bombardment



- Similar trends to argon bombardment:
  - Lower ion energy produces increased surface roughness
  - Increased substrate temperature produces increased surface roughness
- Roughness is greater than Ar^+ bombardment.
- Roughness develops with 1 keV Xe^+ bombardment.

Surface roughening of 193 nm photoresist: ion energy and substrate temperature

- Xe^+ bombardment: ion energy and substrate temperature effect
  (fluence ~1.3×10^{17} ions•cm^{-2} for all samples)



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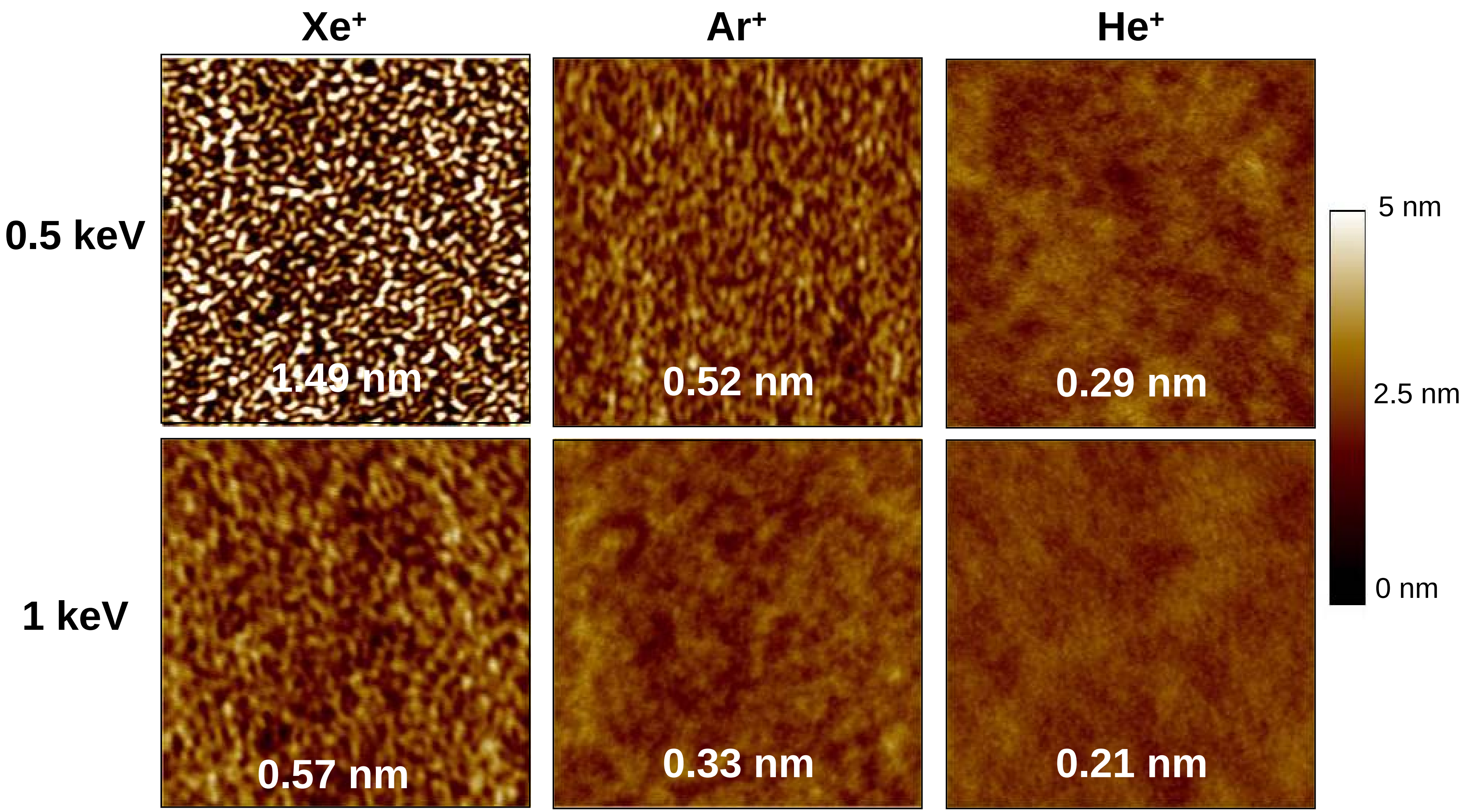
Surface roughening of 193 nm photoresist: comparison of Xe^+, Ar^+, and He^+ bombardment

(fluence ~1.3×10^{17} ions•cm^{-2} for all samples)



Conclusions: sputtering of polymers

- Polymer sputtering characterized by an initial high etch rate. A lower steady-state etch yield similar to that of carbon is reached after fluences of ~5×10^{16} ions•cm^{-2}.
- Steady-state etch yields of Ar^+ bombardment follow the empirical Ohnishi parameter taking into account inherent chemical effects of the polymer. Ohnishi parameter does not necessarily hold true in the presence of chemistry.
- The amount of material removed prior to reaching steady-state is polymer dependent.
  - more mass removed prior to reaching steady-state for 193 nm photoresist compared to 248 nm photoresist
- Ion beam etch yields consistent with argon plasma experiments.

Conclusions: roughening of polymers

- **Ion energy effect**
  - Increased roughness at lower ion energies (0.5 keV > 1 keV)
- **Ion mass effect**
  - Increased roughness with increased ion mass ($Xe^+ > Ar^+ > He^+$)
- **Substrate temperature effect**
  - Increased roughness with increased substrate temperature (45°C > 20°C)
- Experiments completed on polystyrene derived materials are consistent with these conclusions.
- Any roughness theory developed that also includes chemical effects must agree with these observations.

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