Surface Texturing of 193 nm Photoresist under Ar^+ Bombardment: Effect of Ion Energy, Angle of Incidence and Substrate Temperature

D. Nest, E. Pargon and D. Graves
Department of Chemical Engineering, ***University of California****, Berkeley, CA 94720*

S. Engelmann and G. S. Oehrlein
Department of Material Science and Engineering and
Institute for Research in Electronics and Applied Physics
University of Maryland*, College Park, Maryland, 20742*

C. Andes
Rohm and Haas Electronic Materials*, 455 Forest Street, Marlborough, MA 01752*

E. A. Hudson
Lam Research Corp*., 4650 Cushing Pkwy., Fremont CA 94538*

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Introduction

➢Context

The integration of 193 nm photoresists remain today an issue because of:

- their lack of etch resistance
- their surface roughness after exposure to a plasma process

➢Aim of this work

Bring some answers on the roughness formation of a 193 nm photoresist

➢Outline

I. Argon ion beam experiments on R&H 193 nm photoresist
   - Impact of the ion beam energy on the etch yield and roughness
   - Impact of the ion beam incidence on the etch yield and roughness
   - Impact of the ion fluence on the etch yield and roughness

II. Latest Argon ion results
   - Impact of lower energy ions (300 eV) on roughness
   - Impact of elevated substrate temperature on roughness

Experimental set-up

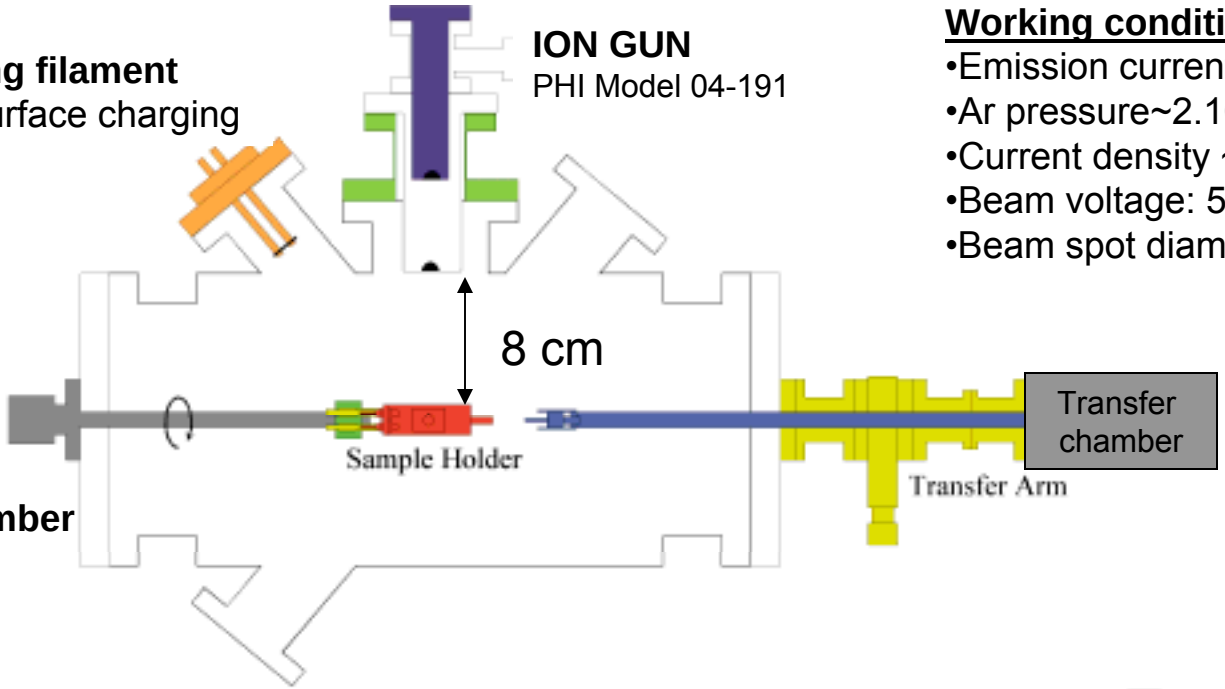
➢Top view

Neutralizing filament
To avoid surface charging

ION GUN
PHI Model 04-191

Working conditions:
- Emission current=25mA
- Ar pressure~2.10^{-4} Torr
- Current density ~ 10 µa.cm^{-2}
- Beam voltage: 500eV, 1keV, and 2keV
- Beam spot diameter: 2-5 mm

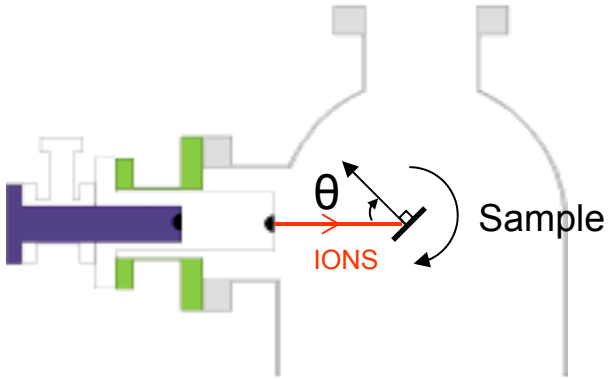
Rotating arm



Vacuum chamber
P=5.10^{-8} Torr

➢Side view

⇒Sample can be rotated from 0° (normal incidence) to 80° (grazing incidence) with respect to the ion beam direction

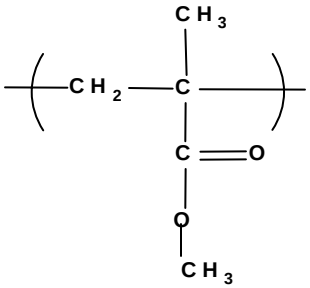


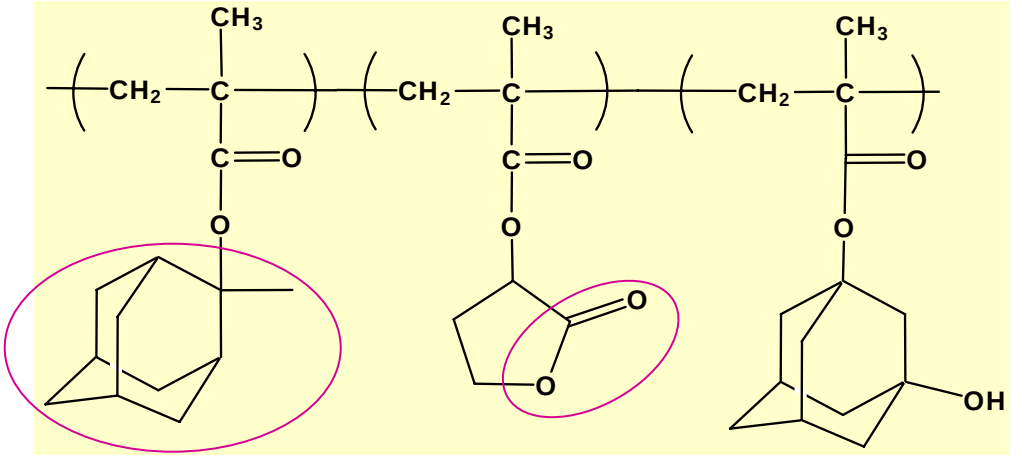
Samples and diagnostic tools

➢Samples:

- ✓**Rohm and Haas** 193 nm photoresist coated on silicon wafers
- ✓Thickness ~250 nm
- ✓Sample size ~1 cm^2
- ✓Chemical formula:

PMMA derived polymer





Adamantyl (MAMA) | Lactone | HAMA

➢Diagnostic tools:

- ✓Reflectometer: thickness measurements for etch yields
- ✓AFM: roughness
- ✓SEM at LAM RESEARCH CORPORATION : surface observation

Some definitions

➢Flux Φ (ions.cm^{-2}.s^{-1}) on the sample: $$\Phi = \frac{I}{A.q}\cos(\theta)$$

With Φ = flux (ions.cm^{-2}.s^{-1})
I= current measured by a Faraday cup (~nA)
A= Faraday cup area (A= 4.55.10^{-4} cm^{-2})
q= elementary charge (1.6.10^{-19} C)
θ= angle between the ion beam direction and the normal at the sample surface (from 0° to 80°)

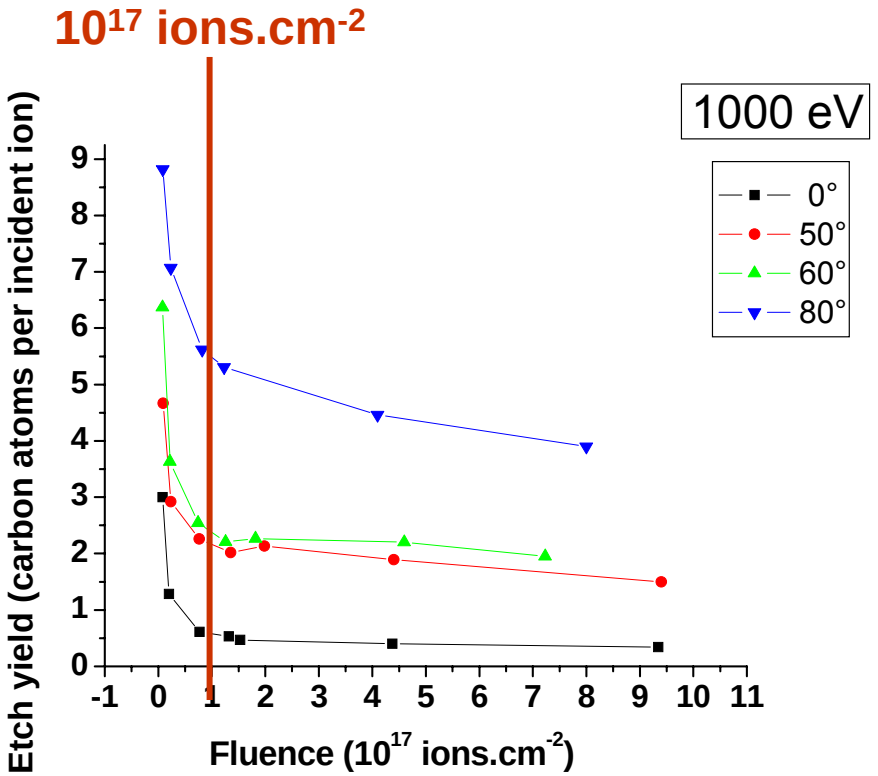
➢Fluence Γ (ions.cm^{-2}): $$\Gamma = \Phi \times t$$

With Φ = flux (ions.cm^{-2}.s^{-1})
t = exposure time (s)

➢Etch yield (EY) (carbon atoms ejected per incident ion): $$EY = \frac{N_C \rho N_a d}{M\Gamma}$$

With N_c= Average number of carbon atoms in the molecule
d = Etched thickness (cm)
ρ = Density of the polymer (density of PMMA taken~1.19 g.cm^{-3})
N_a= Avogadro number (6.02. 10^{23} at.mol^{-1})
M = Molecular weight
Γ = Fluence (ions.cm^{-2})

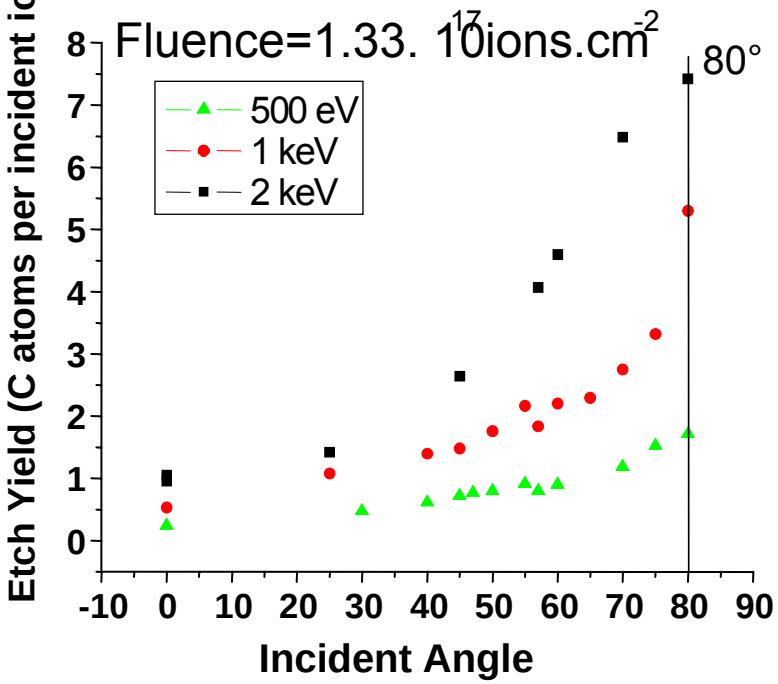
Evolution of Etch Yield with fluence at different angles



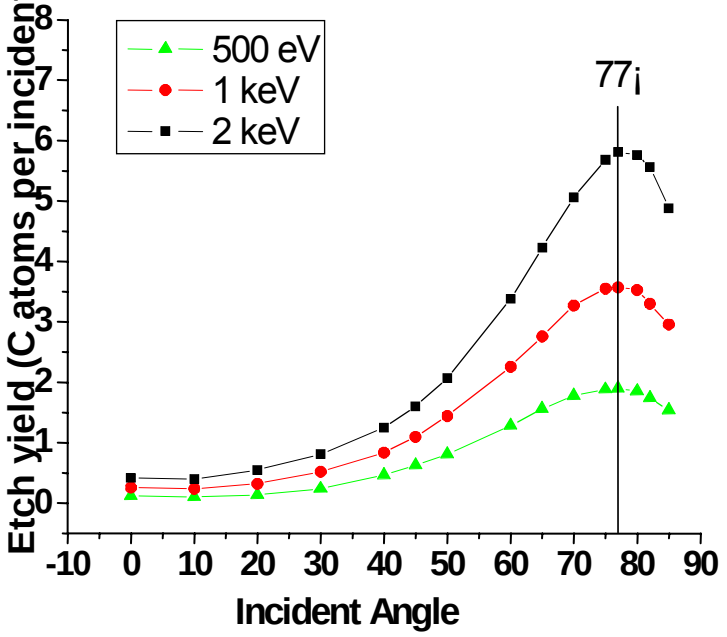
- Whatever the fluence, the etch yield increases with the beam angle of incidence
- Etch yield higher at low fluence (<10^{17} ions.cm^{-2}) and then reaches a steady value

Angular and energy dependence of the etch yield

R&H 193 nm photoresist
(Experimental data)



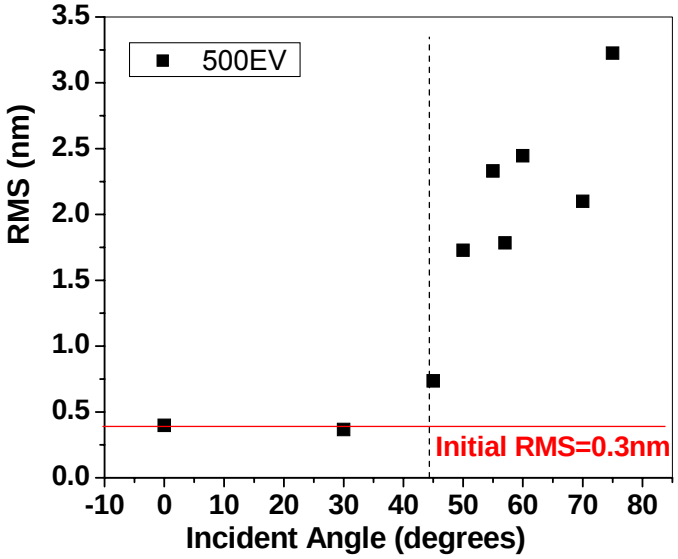
Graphite
(Simulated data SRIM software)
www.srim.org

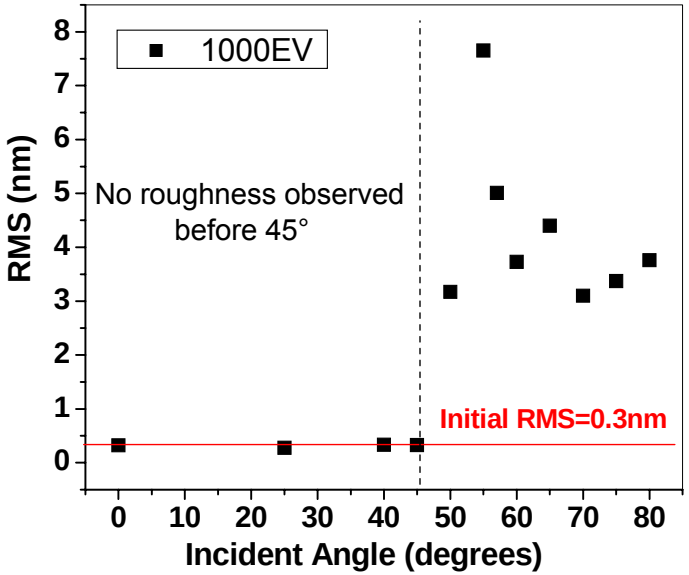


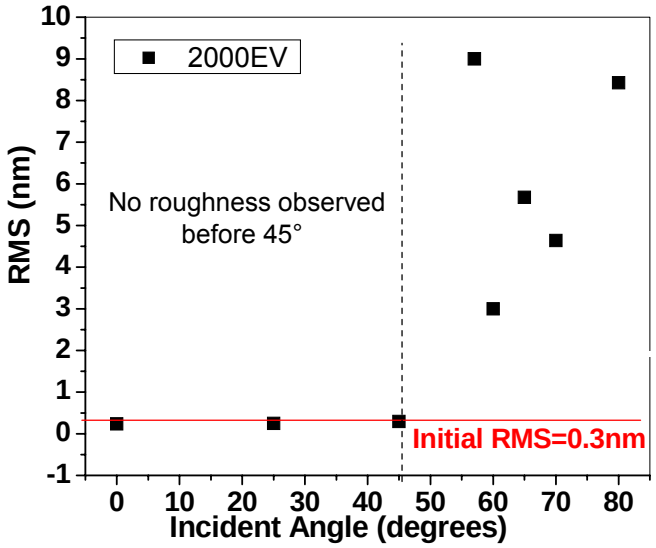
- Etch yield higher for photoresist but same etch yield profile
- The etch yield increases with the ion energy
- The etch yield keeps increasing with angle and reaches a maximum near 80°, whatever the energy.

Impact of the ion beam incidence angle and energy on roughness

Same Fluence = $1.33.10^{17}$ ions.cm^{-2} for all samples, 300K







✓No roughness observed before 45°

✓Maximum RMS observed :

- At 500 eV ~ 3.5 nm
- At 1000 eV ~ 7.5 nm
- At 2000 eV ~ 9 nm

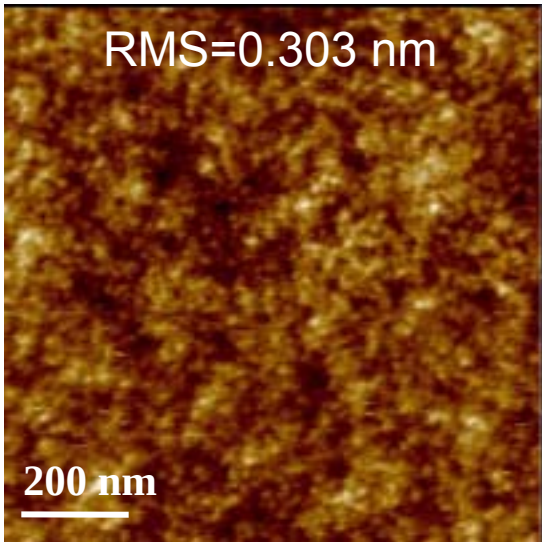
⇒The roughness increases with the ion energy

Impact of the ion beam incidence on roughness at 1000 eV

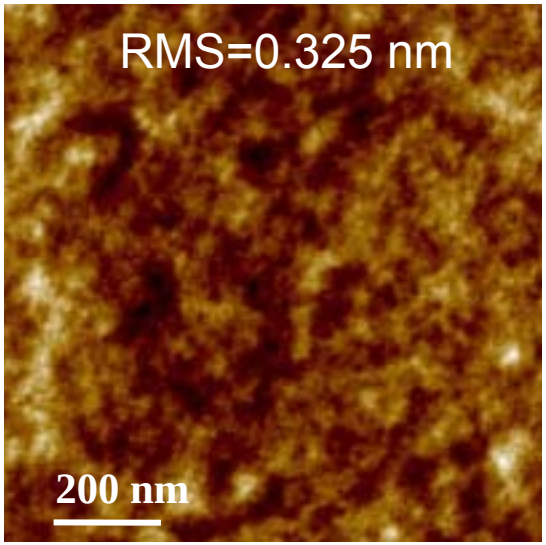
➢ Below 45°:

Same fluence=$1.33.10^{17}$ ions.cm^{-2} for all samples, 300K

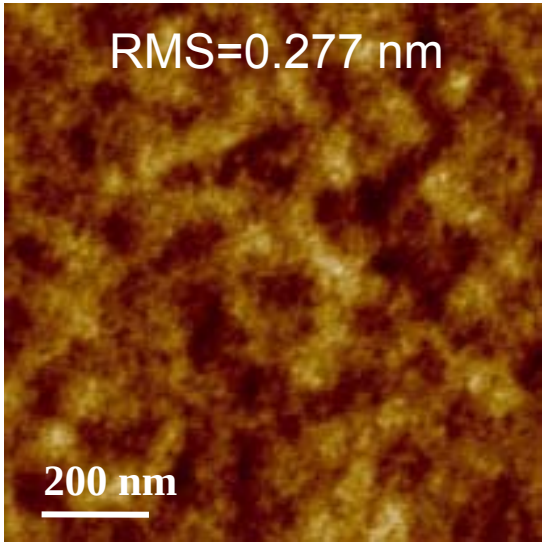
Initial roughness

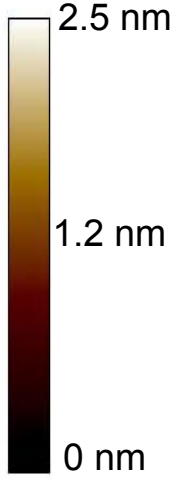


Angle 0°



Angle 25°





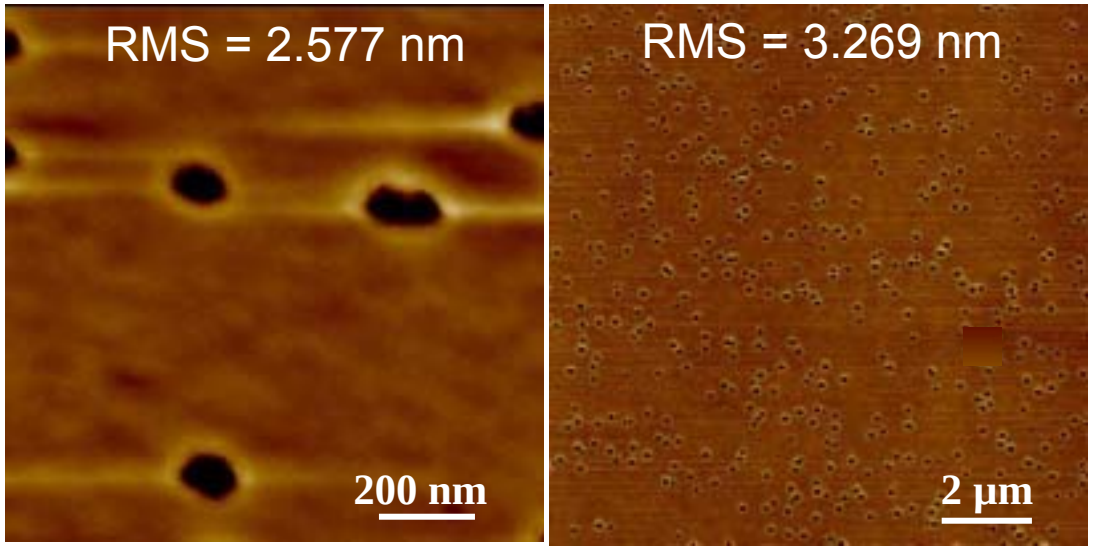
No roughness observed below 45°

Impact of the ion beam incidence on roughness at 1000 eV

➢Between 45°-55°: Formation of **holes**

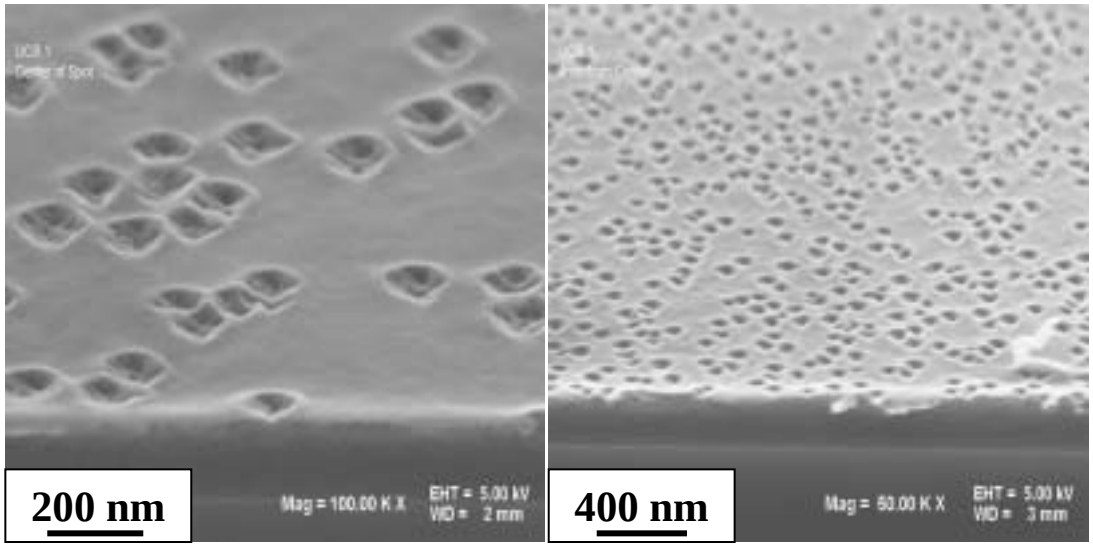
Same fluence=$1.33.10^{17}$ ions.cm^{-2}, 300K

AFM



Estimated hole diameter ~ 100 nm

SEM



Estimated
- Hole diameter ~ 120 nm
- Hole Depth ~ 30 nm

SEM @ LAM RESEARCH CORP.

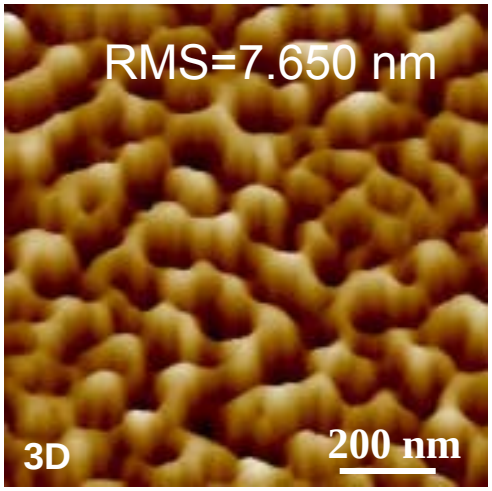
Impact of the ion beam incidence on roughness at 1000 eV

➢ Between 50°-70°:

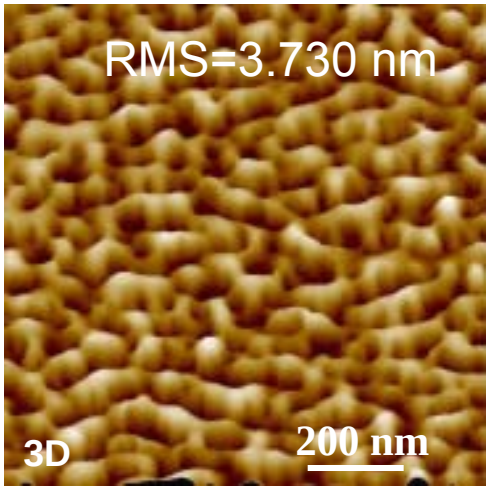
Same fluence=$1.33.10^{17}$ ions.cm^{-2}, 300K

AFM

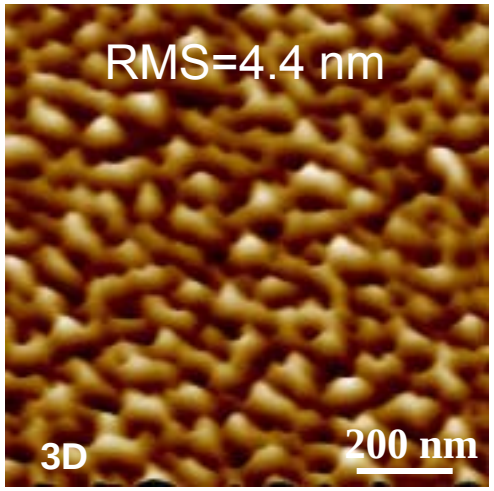
Angle 55°

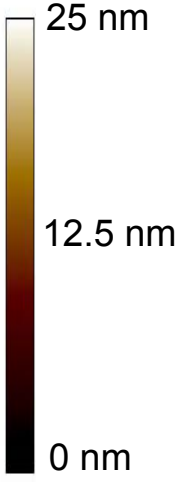


Angle 60°

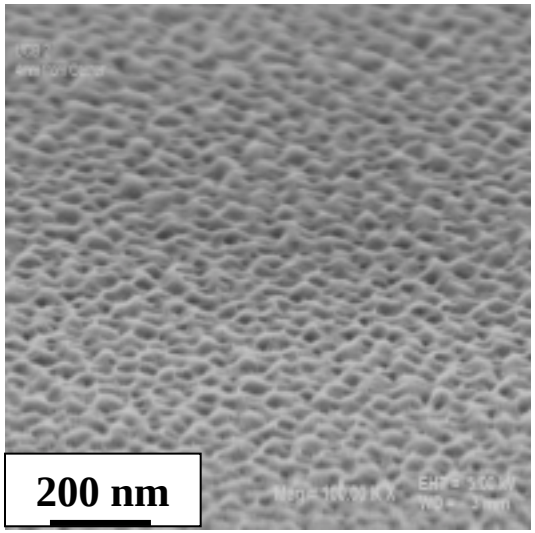


Angle 65°





SEM
Angle 60°



Roughness is characterized by **“ripples”**

Impact of the ion beam incidence on roughness at 1000 eV

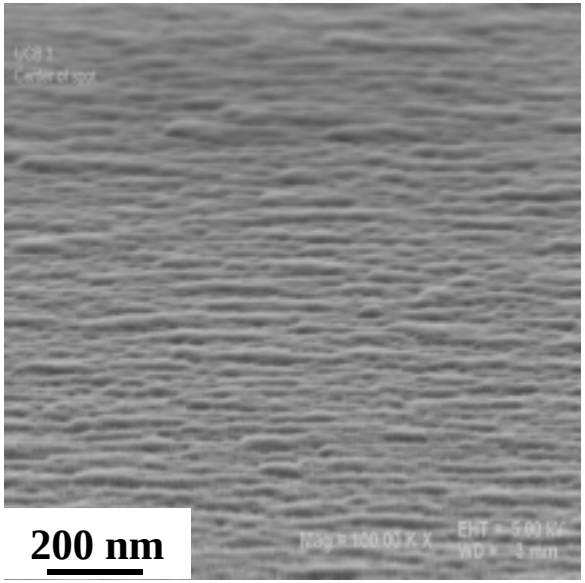
➢ Above 70°:

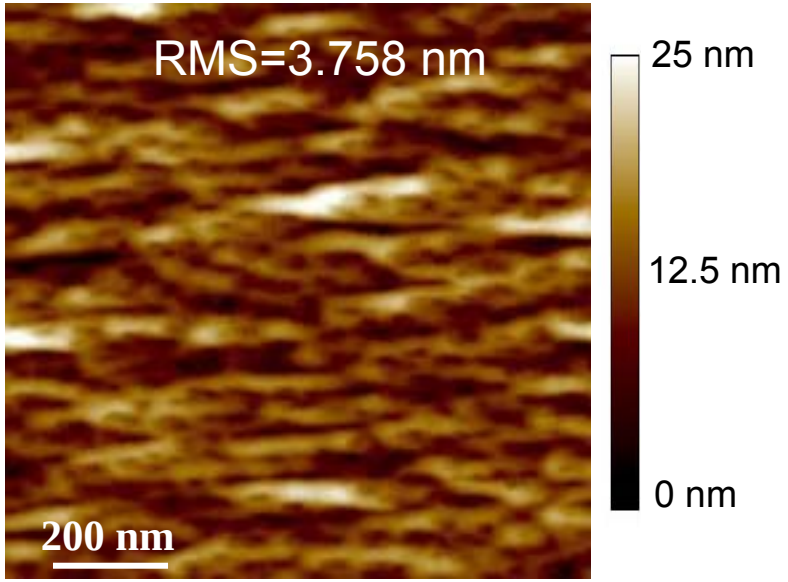
Angle 80°, Fluence=$1.33.10^{17}$ ions.cm^{-2}, 300K

SEM

AFM

IONS



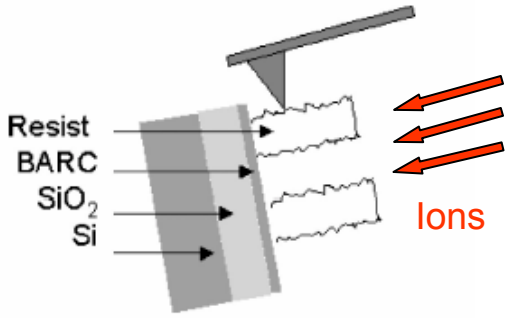


Roughness is characterized by **striations** parallel to the ion beam direction

Comparison ion sputtering at glancing incidence/plasma etching processes

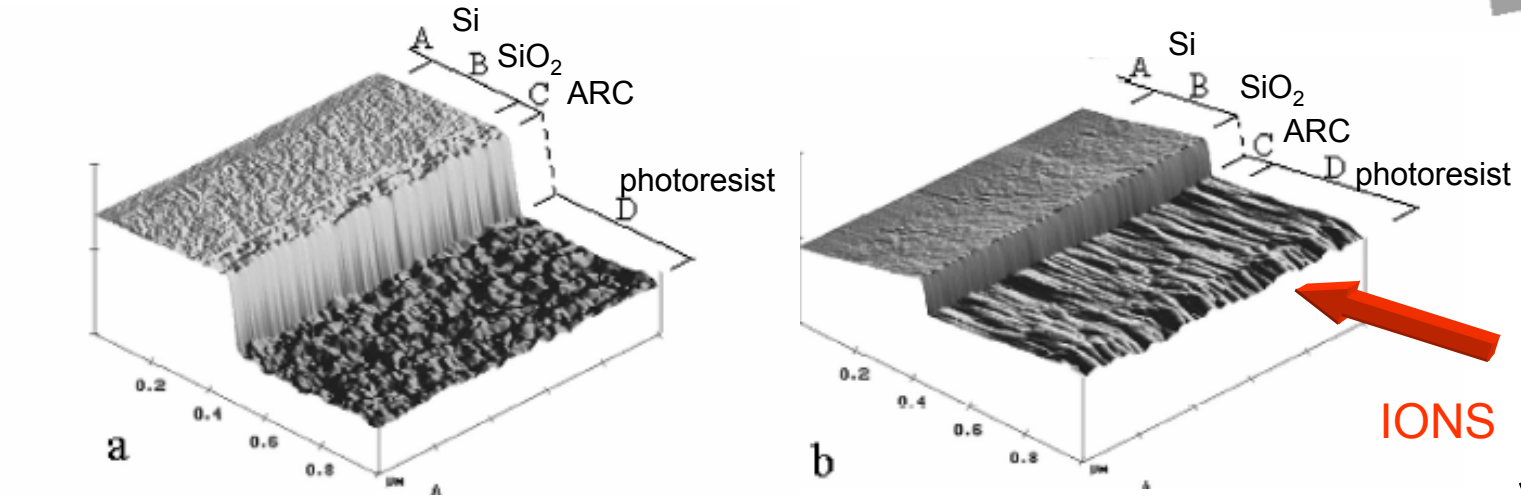
Goldfarb *et al*, JVSTB 22, 647, (2004)

AFM imaged sidewalls of patterned photoresist

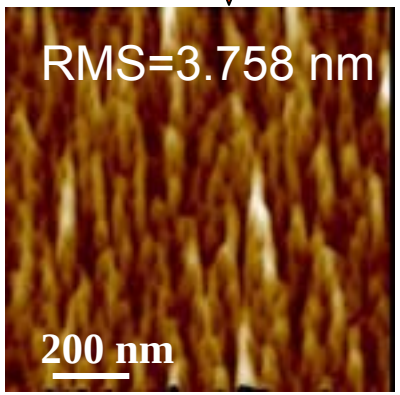


Before etching process

After ARC opening process in N_2-H_2



Angle 80°



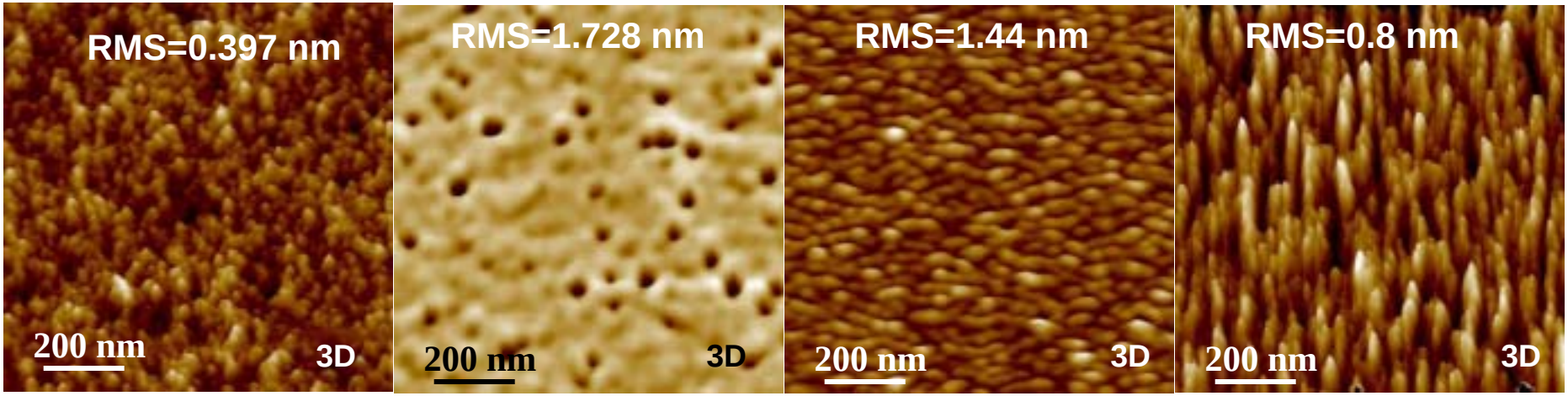
Striation formation on photoresist sidewalls after etching process very similar to what has been observed in Ar ion sputtering at glancing incidence

Impact of the ion beam incidence on roughness at 500 eV

➢Summary:

Energy: 500 eV
Fluence=$1.33.10^{17}$ ions.cm^{-2}
Temp=300K

Below 45°	Between 45°-55°	Between 55°-70°	Above 70°
Angle 0°	Angle 50°	Angle 60°	Angle 80°



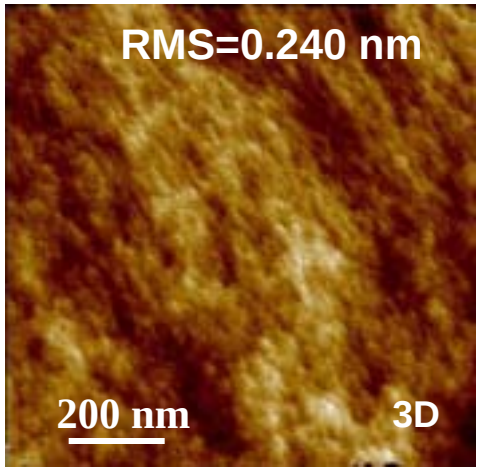
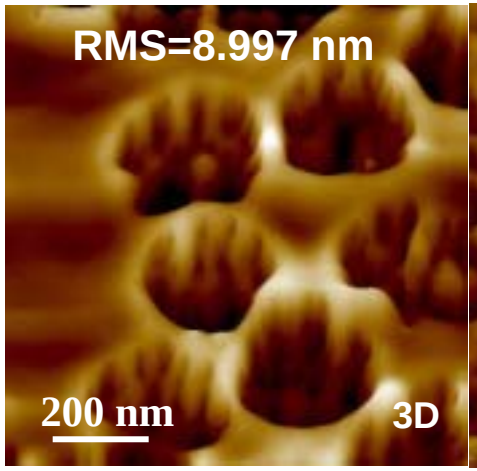
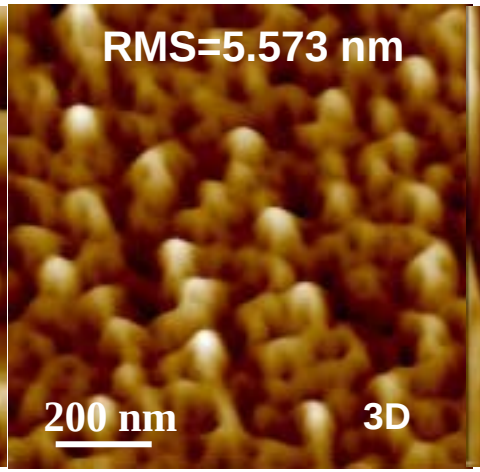
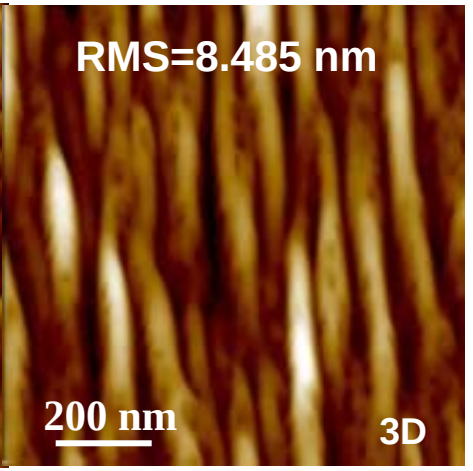
Color scale: **2.5** nm	Color scale: **25** nm	Color scale: **25** nm	Color scale: **2.5** nm
	Formation of holes Diameter ~ **50** nm	"Ripples"	Striations parallel to the ion beam direction

IONS

Impact of the ion beam incidence on roughness at 2000 eV

➢Summary:

Energy: 2000 eV
Fluence=$1.33.10^{17}$ ions.cm^{-2}
Temp=300K

Below 45°	Between 45°-55°	Between 55°-70°	Above 70°
Angle 0°	Angle 50°	Angle 65°	Angle 80°
			
Color scale: **2.5** nm	Color scale: **25** nm	Color scale: **25** nm	Color scale: **2.5** nm
No roughness	Formation of holes Diameter ~ **250** nm	“Ripples”	Striations parallel to the ion beam direction

IONS

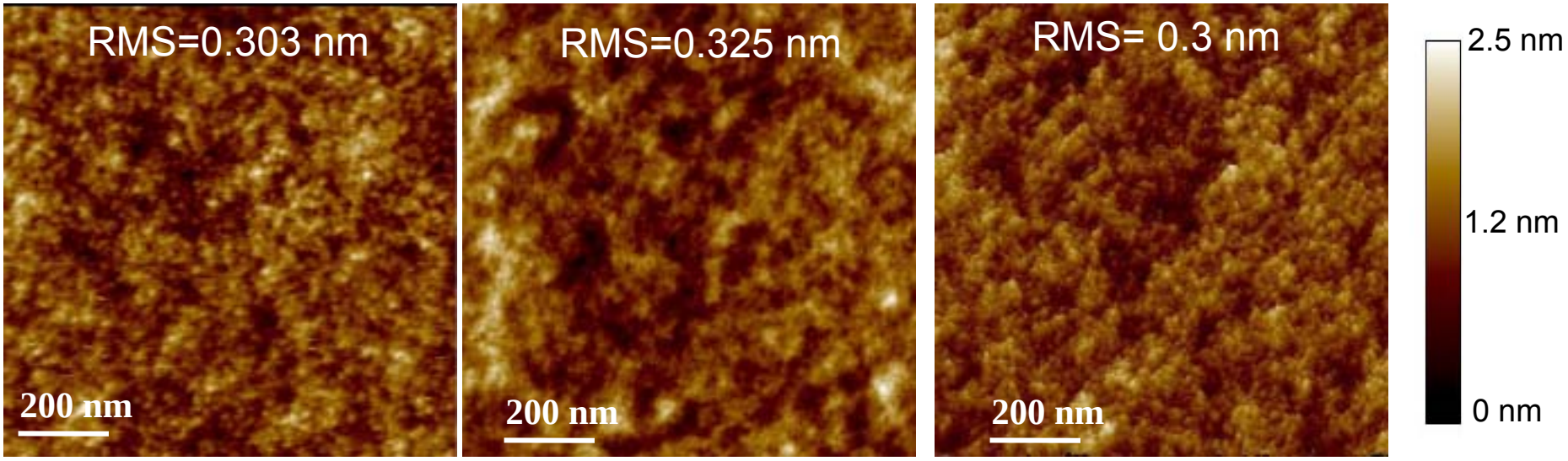
Evolution of roughness with fluence at 1000eV and 0°

Temp=300K

Initial roughness

Medium Fluence:
$1.3.10^{17}$ ions.cm^{-2}

High Fluence:
$9.3.10^{17}$ ions.cm^{-2}



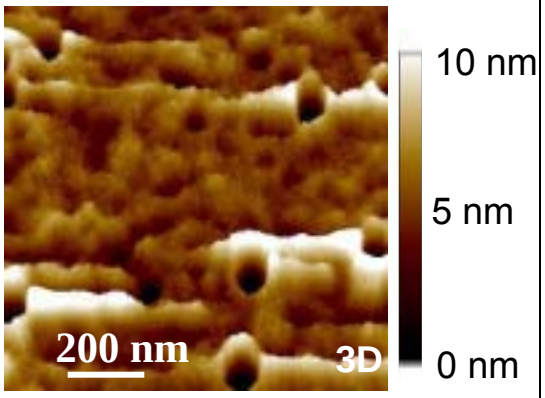
Etched thickness: 17 nm

Etched thickness: 77 nm

No roughness observed at 0° whatever the exposure time

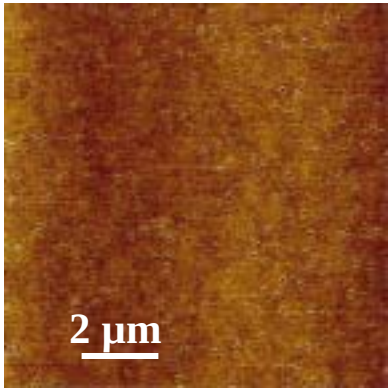
Evolution of roughness with fluence at 1000eV and 50°

Low Fluence:
7.10^{16} ions.cm^{-2}



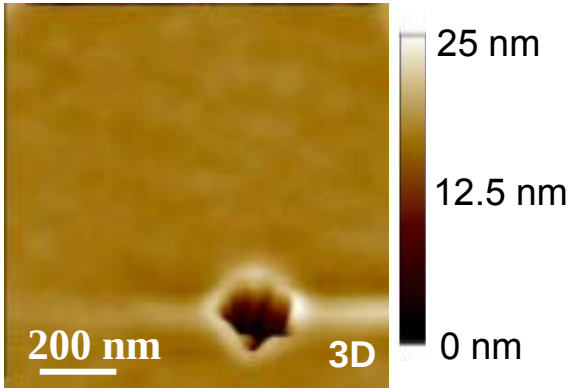
RMS = 1.863 nm

Hole diameter ~ 80 nm



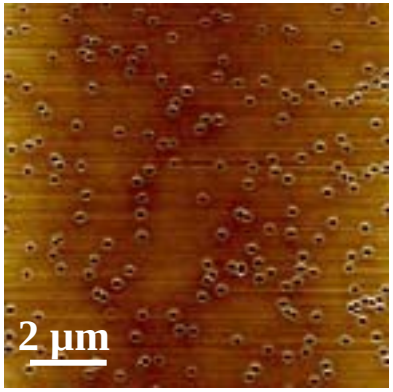
RMS = 1.660 nm

Medium Fluence:
2.10^{17} ions.cm^{-2}



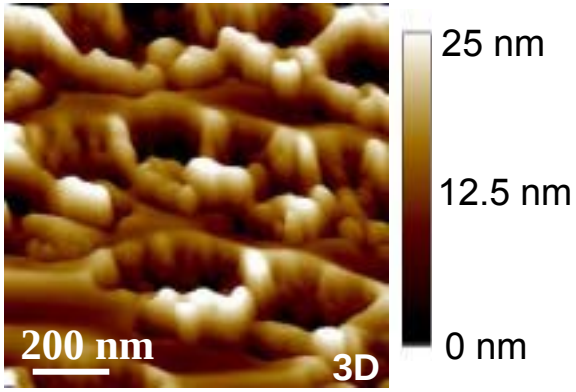
RMS = 2.52 nm

Hole diameter ~ 175 nm



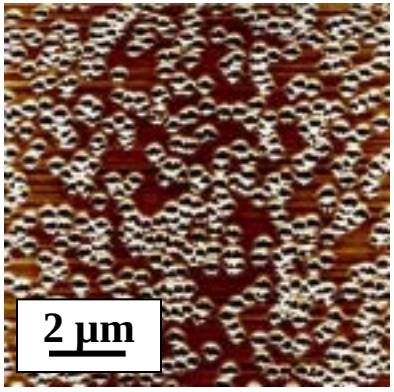
RMS = 4.069 nm

High Fluence:
4.10^{17} ions.cm^{-2}



RMS = 11.84 nm

Hole diameter ~ 370 nm



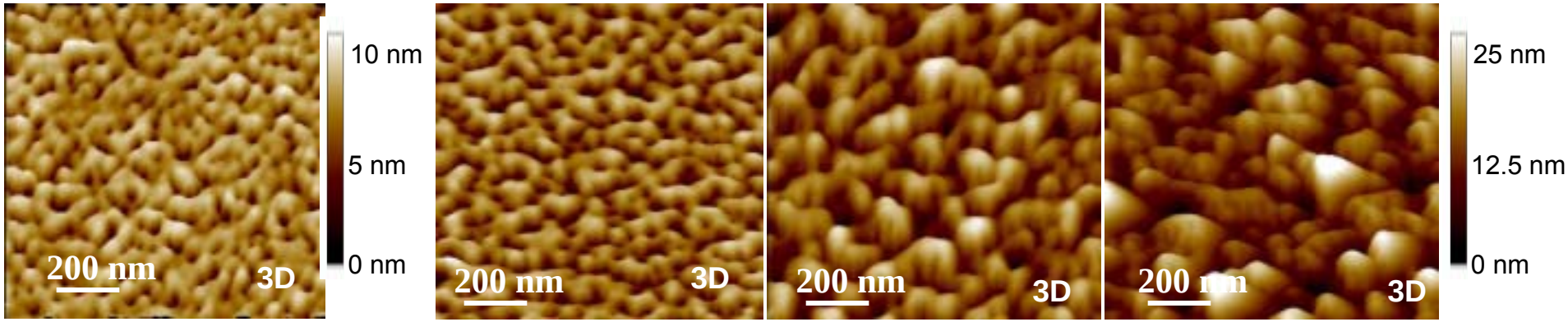
RMS = 12.41 nm

⇒Hole diameter increase with exposure time

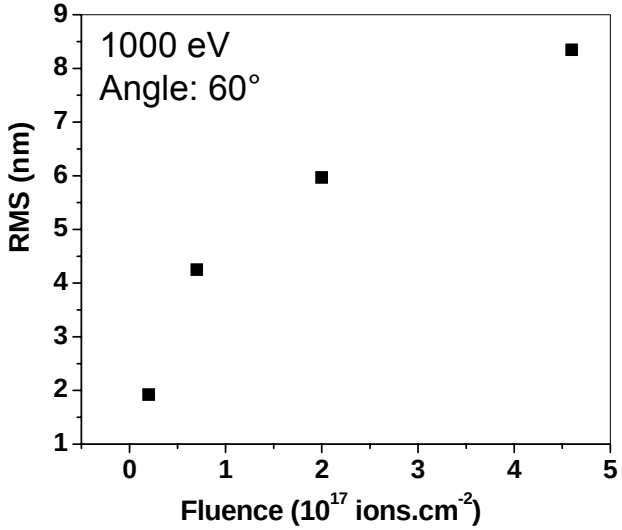
⇒RMS increases with exposure time

Evolution of roughness with fluence at 1000eV and 60°

Low Fluence 2.10^{16} ions.cm^{-2}	**Medium low Fluence**: 7.10^{16} ions.cm^{-2}	**Medium Fluence:** 2.10^{17} ions.cm^{-2}	**High Fluence:** 4.10^{17} ions.cm^{-2}



RMS = 1.921 nm RMS = 4.248 nm RMS = 5.967 nm RMS = 8.344 nm



⇒ At 60°, it seems that roughness starts with the formation of holes. The holes gather to form ripples

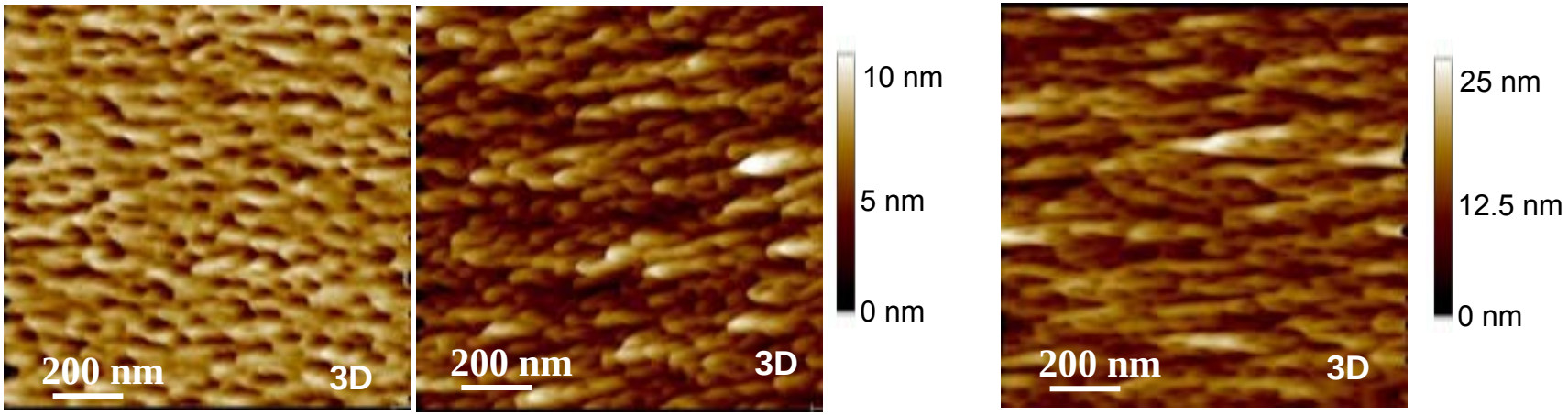
⇒ RMS increases with exposure time

Evolution of roughness with fluence at 1000eV and 80°

Low Fluence:
2.10^{16} ions.cm^{-2}

Medium Fluence:
7.10^{16} ions.cm^{-2}

High Fluence:
2.10^{17} ions.cm^{-2}

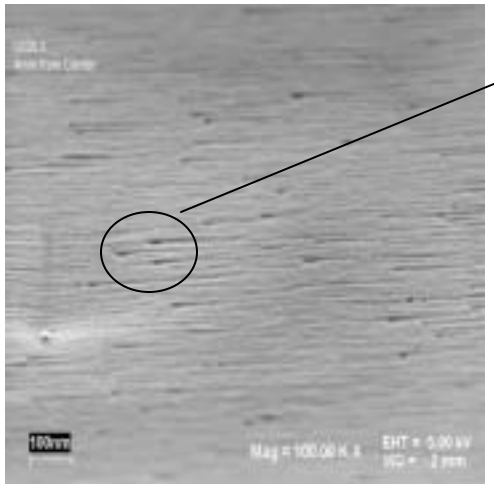


RMS = 1.568 nm

RMS = 2.844 nm

RMS = 3.758 nm

IONS



SEM observations of these holes at low fluence

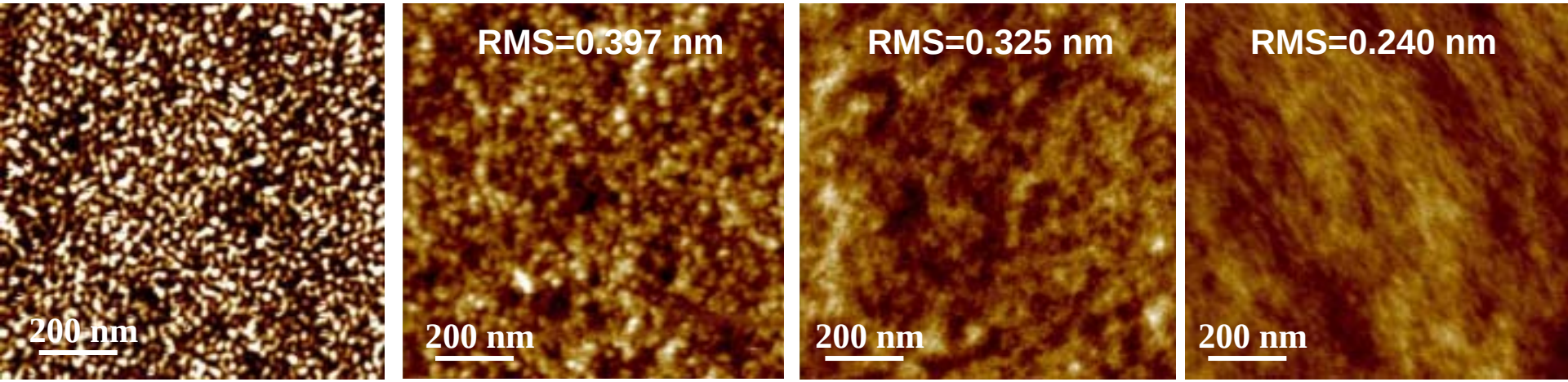
⇒ At 80°, it seems that roughness starts with the formation of holes and turns into striations

⇒ RMS increases with exposure time

Roughness at normal incidence

Same fluence=$1.33.10^{17}$ ions.cm^{-2} for all samples, 300K

300 eV | 500 eV | 1 keV | 2 keV



⇒Low energy ions have large effect on surface roughness

⇒High energy ions may possibly be activating smoothing mechanisms not active at 300 eV

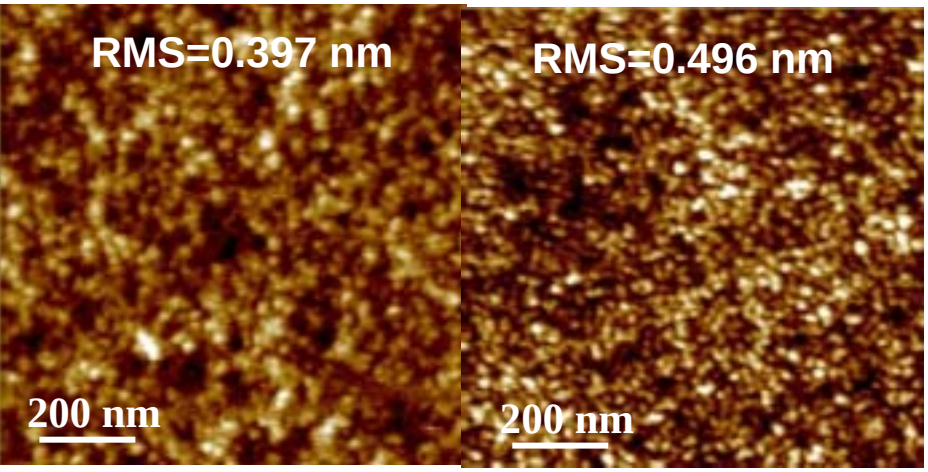
Roughness at elevated substrate temperatures

Same fluence=$1.33.10^{17}$ ions.cm^{-2} for all samples

500 eV

300K

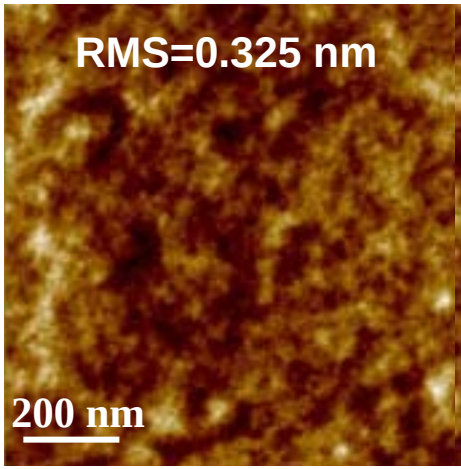
335K

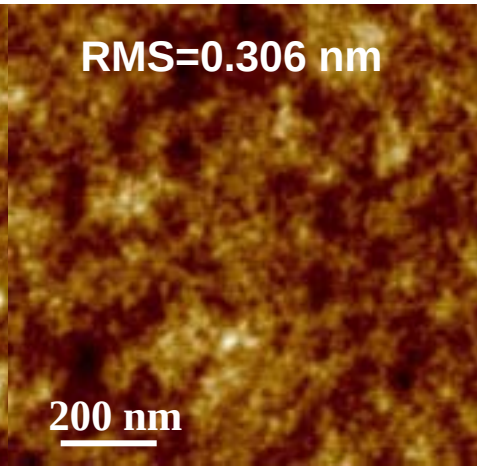


1 keV

300K

335K





⇒Elevated substrate temperatures do not spontaneously roughen the surface.

⇒Elevated substrate temperatures increase roughening effect of ions at lower energies. Further evidence of an activated smoothing mechanism at higher ion energies.

Conclusions (1/2)

- Effect of Ar^+ beam exposure:
  - ✓ High fluence photoresist EY (both energy and angle dependence) similar to graphite
  - ⇒ It may suggest that photoresist surface (depth ~ 2-10 nm) is graphitic after Ar^+ exposure
  - ✓ No roughness observed for ion angle of incidence from normal to about 45° at higher ion energies
  - ✓ The formation of holes may be roughness precursor:
    - At 50°, their diameter grows with fluence
    - At 60°, they appear at low fluence, transforming into ripples at higher fluence
    - At 80°, their presence can also be guessed but they are rapidly replaced by striations.
  - ✓ Striations at grazing incidence may be related to sidewall roughness

Conclusions (2/2)

- Effect of Ar^+ beam exposure:
  - ✓ Lower ion energies produce rough surfaces at normal incidence. Possible evidence for an activated smoothing mechanism at higher ion energies.
  - ✓ Elevated substrate temperatures increase roughening effect of 500 eV Argon ions while 1 keV Argon ions maintain a smooth surface. Reason unknown, but further evidence that 1 keV ions may be smoothing the surface.
- Chemistry is known to affect roughening in etch plasmas and we plan to investigate this in the future.
- Future work will also include direct comparison to plasma studies at the University of Maryland. (Professor Gottlieb Oehrlein)

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