Etching Applications and Discoveries Made Possible by Advanced Ion Energy Control

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Outline

- Parallel nano-patterning with a monoenergetic, low-energy ion beam.
- Using the monoenergetic, low-energy ion beam to do etching in the plasma.
- Details on generation the monoenergetic, low-energy ion flux with pulsed plasmas and synchronous bias.
- Discovery of an important new cause of anisotropic etching: indigenous photo-assisted etching (PAE).
Pantograph

Mechanical device used to copy drawings. Can be on a different scale
Nanopantography

**Side View:**

- Broad area ion beam

**Top View:**

- Metal, $V_m$
- Dielectric
- Conducting film or substrate, $V_s$

Essential components:

- **Parallel, monoenergetic ion beam** and **electrostatic lenses built on the wafer**

- **Sub-10nm** patterning **simultaneously**;
- **Self-alignment**, immune to vibration and thermal expansion;
- **Etching** (Ar+), **deposition** (M+).
Nanopantography: write **any** desired nanopatterns **simultaneously**

Whatever is “written” **once** on the imaginary plane here is reproduced at the bottoms of **all** the lenses here.
Setup of Nanopantography for Si etching

Ion source

Ar pulsed plasma

Collimated, monoenergetic Ar$^+$ beam

Etching Chamber

Lens array voltage

Cl$_2$ effusive beam

Sample with lens array
Details of Sample Tilting Stage

- In-vacuum gear
- Sample
- External gear
- Grounded mesh
- Lens sample
- Loadlock
- Motorized stage
- External motor
- In-vacuum motor
- To pump
Extract Ion Beams with Desired Narrow Energy Spread

- Extract ions at low $T_e$ and $T_i$ in afterglow decreases energy spread and increases the *directionality* of ions.
- Ring acceleration voltage (high-voltage pulse): *Set the desired ion beam energy.*
Nearly Monoenergetic Ar Ion Beam

- The energy spread was 3.4 eV (FWHM) for a peak ion beam energy of 102.0 eV.

Etching results with Cl₂ and monoenergetic Ar⁺ beams (ion incidence angle: normal and 5 degree)


SEM

Top view of lens array

Cr layer (top electrode)

Lens bottom surface

TEM

- Size reduction factor of ~95X
- Focused point can be displaced along the substrate surface
Setup of nanopantography for Ni deposition

**Plasma source**
- Ar pulsed plasma
- Ni target
- Ni coil
- Optical diagnostics (OAS and OES)

**Drift tube**
- Collimated Ni\(^+\) and Ar\(^+\) ions with energy spread 1.2 eV for 100 eV beam

**Deposition chamber**
- Sample with lens (ion landing energy: 20eV)
SEM images (top view) of sample after Ni deposition

Normal Incidence Ni⁺

Dark: bottom surface of lens

Bright: Metal top electrode

The focusing ratio is 70X for the Ni nanodots. Height = 5-10 nm by AFM.
Etching of Si with Cl₂ and Ar⁺ beams: X-tilting

Etching of Si with Cl₂ and Ar⁺ beams: X, Y-tilting
Another Motivation for Precise Control of IED

(I) Low energy ions: No reaction occurs except for pure chemical etching, if any.

(II) High energy ions: chemical sputtering, sub-surface ion penetration, physical sputtering → not well-controlled etching, substrate damage.

(III) Medium energy ions: Only chemical sputtering. More confined to surface. Etching slows or stops when adsorbed etchant reacts away. → minimum damage, layer-by-layer etching.

• Layer-by-layer etching, high selectivity, and no substrate damage are/will be critical requirements. To achieve these, one needs to control the IED.
  • Accurate control of peak ion energy.
  • Narrow width of IED.
  • Work with medium energy ions (region III).
Apparatus for Controlled Ion Energy

- Faraday-shielded ICP.
- Plasma power as well as voltage on **Boundary Electrode** can be pulsed.
- Diagnostics: Langmuir Probe, Ion Energy Analyzer, OES.

Normalized IEDs in cw Ar ICP with different continuous DC bias voltages applied to the boundary electrode

300 W, 14 mTorr Ar
Electron Temperatures and Number Densities in Different Rare Gas Pulsed ICPs

- $T_e$ decays more slowly in heavier gas – due to slower e-diffusion rate.
- $n_e$ larger in heavier gas – due to faster ionization and slower ion diffusion rates.
- $n_e$ (measured at the edge of the plasma) hardly decays in 80 $\mu$s.
Comparison of Measured and Modeled Decay of Electron Density in Afterglow of Pulsed Ar ICP

- Model in good agreement with experiment.

- The near-constant plasma density ~80 μs into the afterglow is due to diffusion of positive ions form the high density region near the center of the ICP to the edge.
Ion Energy Distributions (IED) in Different Rare Gas Pulsed ICPs

- Flux order Xe > Kr > Ar because of higher $n_e$ and afterglow $T_e$ in heavier gas.
- IED width Xe > Kr > Ar because of higher afterglow $T_e$ and $\Delta V_p$ in heavier gas.

\[ \Delta V_p = V_{p_f} - V_{p_i} = 2.6, 2.2, 1.8 \text{ V for Xe, Kr, Ar} \]
Normalized IEDs in pulsed Ar ICP with different continuous DC bias voltages applied to the boundary electrode.

112 W average power, 13.56 MHz, 10 kHz, 20% duty cycle, 14 mTorr Ar
Normalized IEDs in **pulsed Ar ICP** with different **synchronized DC bias** voltages applied to the boundary electrode.
Pulsed Plasma, Monoenergetic IEDs for Si Etching

- Faraday-shielded ICP.
- Plasma power as well as voltage on **Boundary Electrode** can be pulsed.
- Diagnostics: Langmuir Probe, Ion Energy Analyzer, OES.

Ion Energy Dependence of Si Etching in Chlorine-Containing Plasmas


Characteristics of polycrystalline Si etching with Cl and Ar⁺ beams in high vacuum:

- Etching exhibits a threshold ion energy of 16 eV.
- Above this threshold, etching rate increases with the square root of ion energy.

\[
\text{Yield (Si atoms etched per ion)} = \beta \sqrt{\text{ion energy (eV)}}
\]

\(E_{th} \approx 16 \text{ eV}\)
What We Expect in a Pulsed Plasma for Si Etching

- Ar/Cl₂ (few %) pulsed plasma.
- 20 µs ON 80 µs OFF.
- Synchronous DC bias in the afterglow at 70-97 µs.
- 10¹⁵ /cm³ p-type Si

- Above threshold etching looks like what we expect.

- Big question (and big problem): What causes sub-threshold etching?
What Causes Sub-threshold Etching?

- Spontaneous chemical etching by Cl atoms?
  - It has been reported that this does not happen for p-type or i-Si (only heavily doped n-type).
  - This is confirmed in our cross section SEMs: no undercutting of the mask.

• Therefore spontaneous chemical etching by Cl atoms is **not** the reason.
What Causes Sub-threshold Etching?

• Ar metastable-assisted etching?
  
  - Ar metastables energies (11.55, 11.72 eV for $^3P_2$ and $^3P_0$) sufficient to cause desorption of SiCl$_x$.
  
  - Never been reported. Unlikely, given the nearly unit efficient quenching of rare gas metastables on surfaces. Also, Cl$_2$(g) quenches Ar metastables.
  
  - We find pure Cl$_2$ plasmas have a constant, non-zero etching rate below ~12 eV, suggesting similar sub-threshold etching in Cl$_2$ and Cl$_2$/Ar plasmas.

• Therefore Ar metastables-induced etching is not the cause of sub-threshold etching.
What Causes Sub-threshold Etching?

• Neutralization of low energy ions?
  - Ar\(^+\) releases up to the ionization energy (15.76 eV) minus the work function when neutralized at a surface, sufficient to cause desorption of SiCl\(_x\).
  - Could an Auger electron (or hole created in the valence band), cause a reaction in the chlorinated layer that leads to etching.
  - If we positively bias the sample to reject low-energy Ar\(^+\), sub-threshold etching should stop.

• Photoassisted etching (PAE) induced by light produced in the plasma? PAE of Si with lamps and lasers in the presence of a high pressure of Cl\(_2\) has been reported.
  - If we positively bias the sample to reject low-energy Ar\(^+\), sub-threshold etching should not stop.

• Electron-assisted etching? Reported to be very weak effect. Should be much less important in Cl\(_2\) vs dilute Cl\(_2\)/Ar plasmas.
  - If we negatively bias the sample to reject electrons, sub-threshold etching should stop.
**Grids / Substrate Bias Experiments**

Energetic positive ions:
- Cl, Cl₂, photons

Positive ions:
- Cl, Cl₂, photons

**Conclusion:** Sub-threshold etching is due to photo-assisted etching induced by plasma light.
Wavelength Dependence for Photo-Assisted Etching

- Si mask blocks most light from reaching the sample.
- Quartz transmits $\lambda > 170$ nm.
- Seems $\sim 90\%$ of PAE due to $\lambda < 170$ nm.
- Both Cl and Ar known to have intense VUV lines between 100 and 140 nm.
Photochemical Etching with Tunable VUV Radiation

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Figure 4. Dependence of etching rate (left scale) and quantum efficiency $q$ (right scale) of the light induced reaction for the GaAs/Cl$_2$ system.
PHOTO-ASSISTED Si ETCHING: HALOGEN DEPENDENCE

- Photo-assisted etching:
  - fastest in Cl₂/HBr
  - slowest in Br₂

- Isotropic etching:
  - HBr-containing plasmas - probably H atoms

Photo-assisted etching rates = arrow lengths

Isotropic etching

Etching rate (nm/min) vs. E¹/² (eV¹/²)
PHOTO-ASSISTED Si ETCHING: HALOGEN DEPENDENCE

- Measure halogen by XPS
- Measure Ar 7504 A emission intensity. (Proportional to VUV intensity?)
- Photo-assisted etching rate scales as the product of light intensity times halogen coverage.
Summary

- Mono-energetic ion fluxes with selectable energy can be formed in the afterglow of a pulsed plasma with synchronous bias of a boundary electrode.

- This can be used to extract an ion beam through a grid for remote processing such as nano-pantography.

- The same approach could be used to improve etching processes (near-threshold energies, better selectivities and less physical damage), but...

- At low ion energies, photo-assisted etching, mainly from VUV light generated by the plasma, becomes dominant.

- This seems to be a serious problem for future etching processes.
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