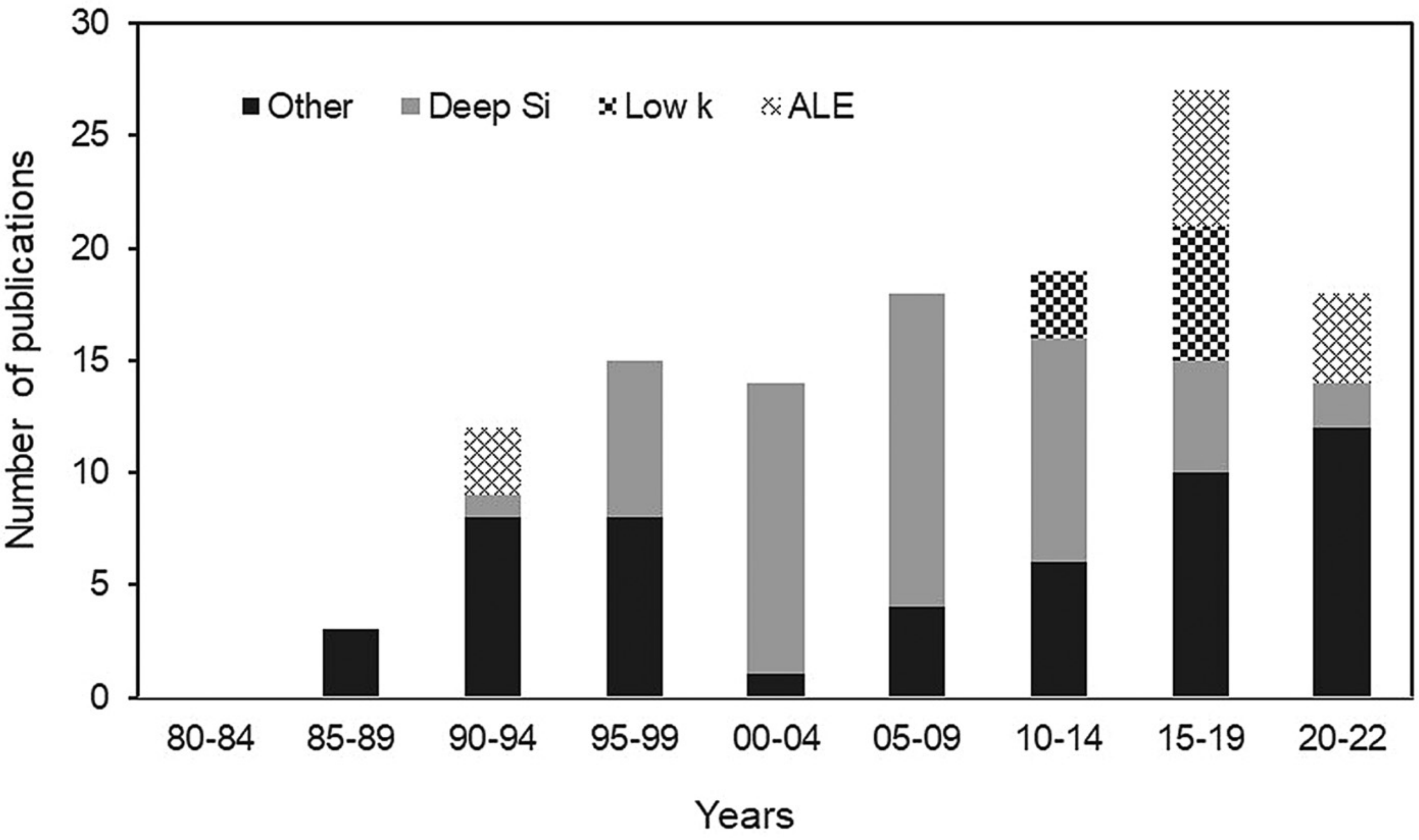
HAR Dielectric Cryo Etch: Mechanisms, Hypotheses, Gaps

Prepared for PPPL

Thorsten Lill, Mingmei Wang

Lam RESEARCH

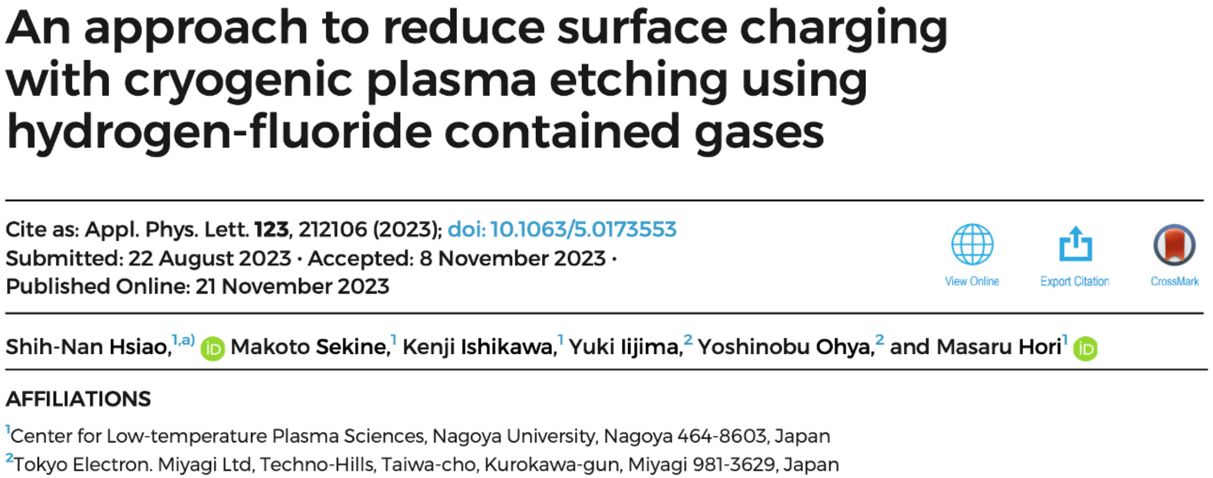
History of Cryogenic Etching



Cryo etching has historically been used for deep silicon etching (profile control). Recently, it finds application in deep dielectric etching.

Lill et al., J. Vac. Sci. Technol. A 41, 023005 (2023)

Recent progress in etching of dielectric structures with high aspect ratios (HAR)



An approach to reduce surface charging with cryogenic plasma etching using hydrogen-fluoride contained gases

Cite as: Appl. Phys. Lett. **123**, 212106 (2023); doi: 10.1063/5.0173553
Submitted: 22 August 2023 · Accepted: 8 November 2023 ·
Published Online: 21 November 2023

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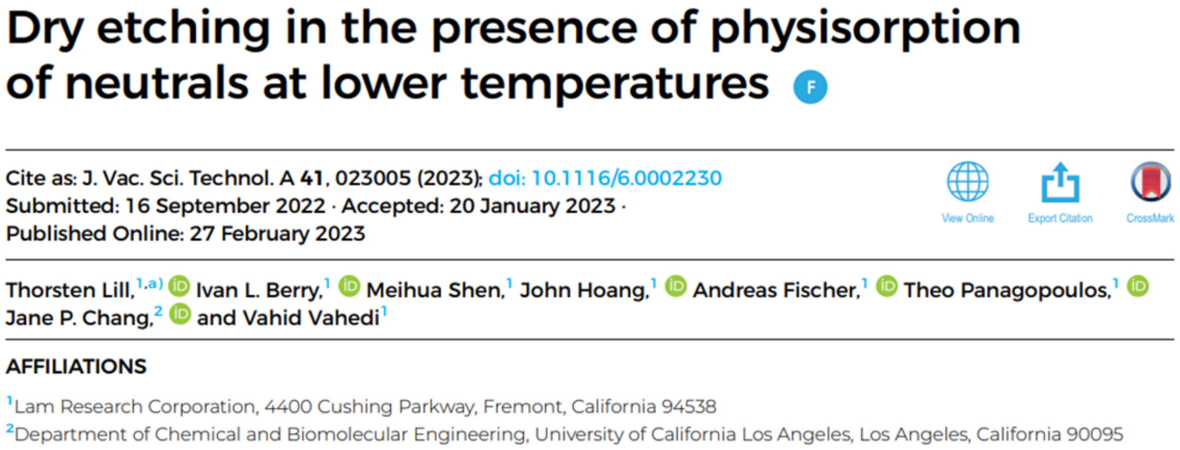

Dry etching in the presence of physisorption of neutrals at lower temperatures

Cite as: J. Vac. Sci. Technol. A **41**, 023005 (2023); doi: 10.1116/6.0002230
Submitted: 16 September 2022 · Accepted: 20 January 2023 ·
Published Online: 27 February 2023

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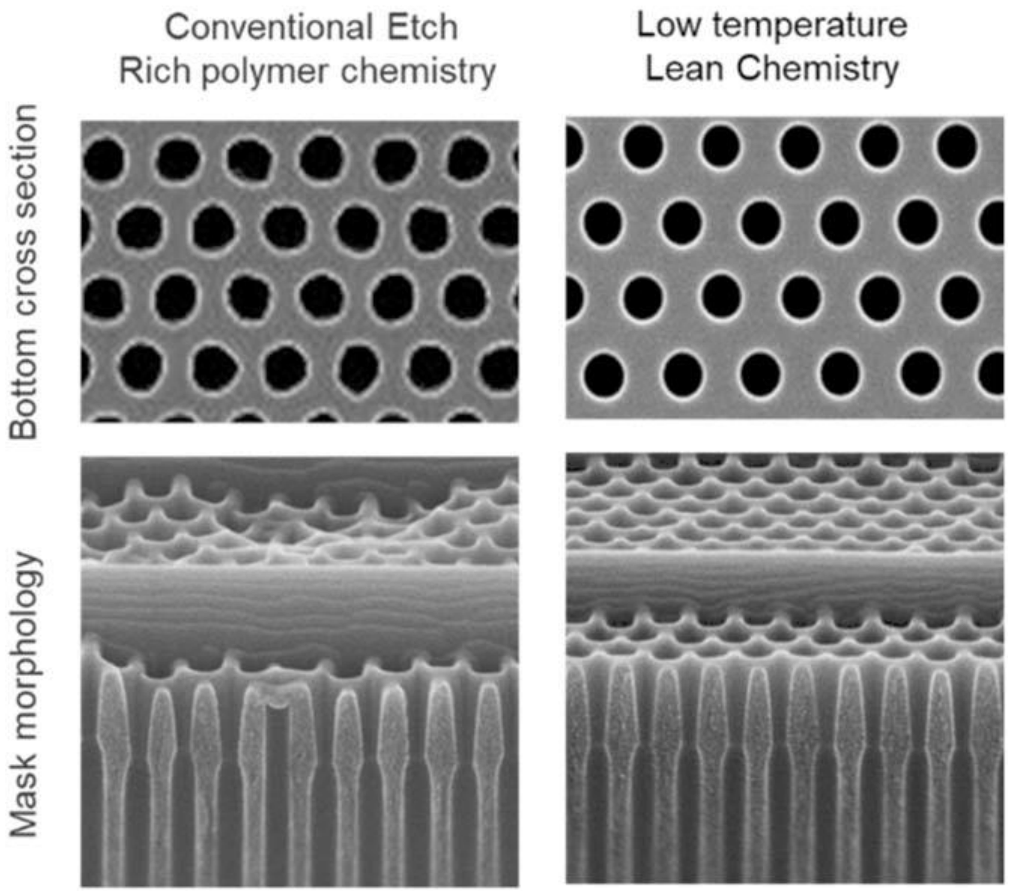
What are the advantages of low temperature etching?
What are the underlying mechanisms?

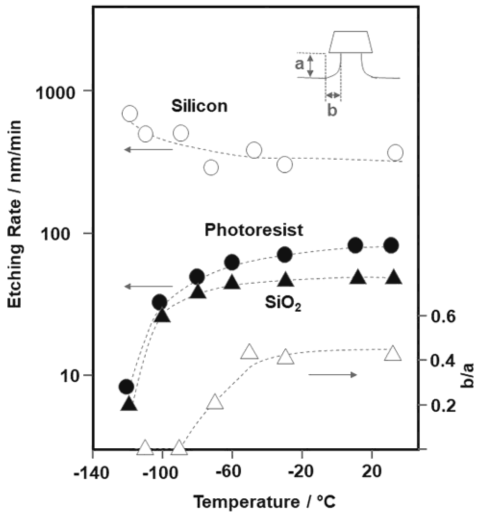
Benefits of low temperature etching for HAR dielectric memory etching

- Faster etch rate
- Reduced Aspect Ratio Dependent Etching
- Better profile
- Better mask morphology



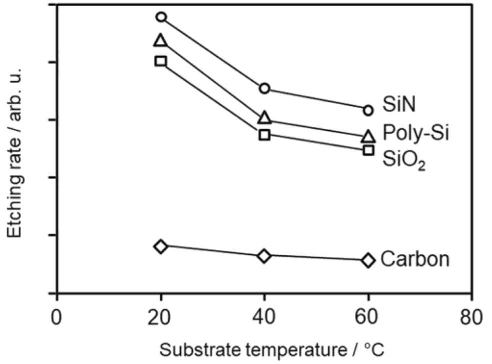
Shen et al., Japanese Journal of Applied Physics 62, SI0801 (2023)

Literature data confirming increasing etching and deposition rates at lower temperatures



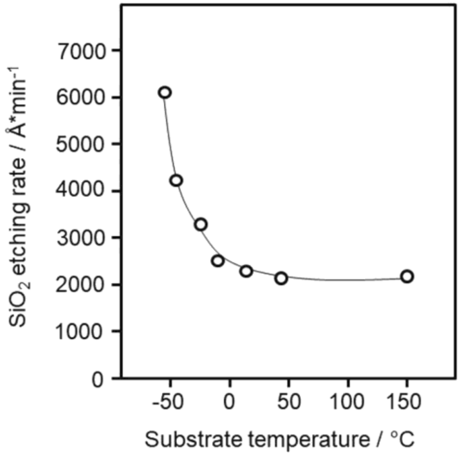
Si etch with SF_6

Tachi et al., Appl. Phys. Lett. 52, 616 (1988)



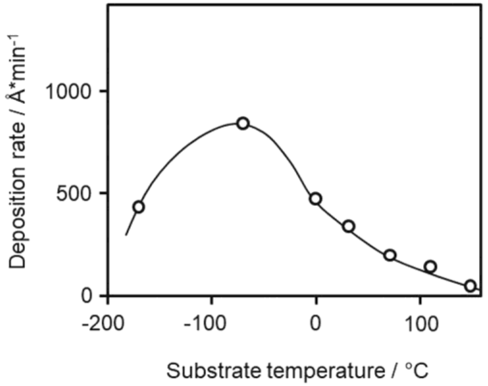
Si, SiO_2, SiN etch with C_xF_y/HBr

Iwase et al., Jpn. J. Appl. Phys. 57, 06JC03 (2018)



SiO_2 etch with CHF_3

Ohiwa et al., Jpn. J. Appl. Phys. 31, 405 (1992)

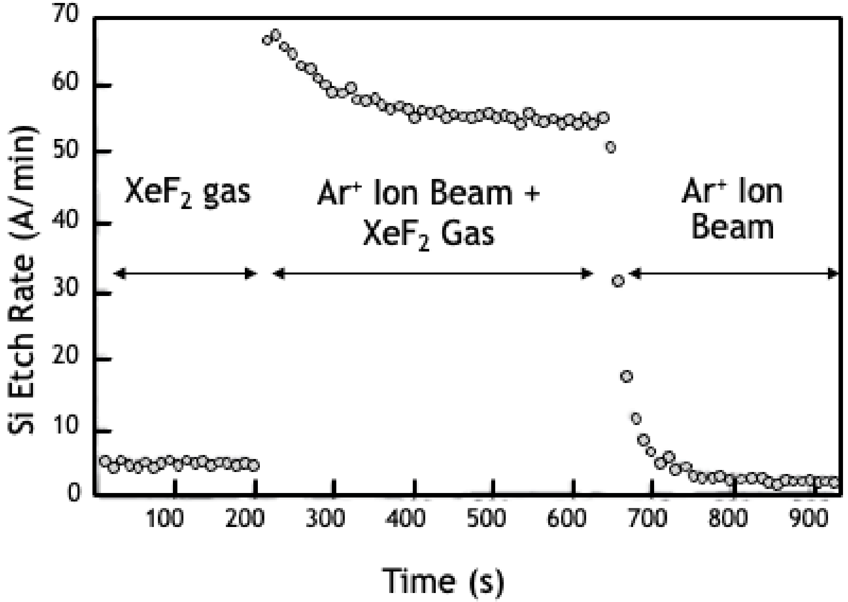


C_xF_y deposition

Ohiwa et al., Jpn. J. Appl. Phys. 31, 405 (1992)

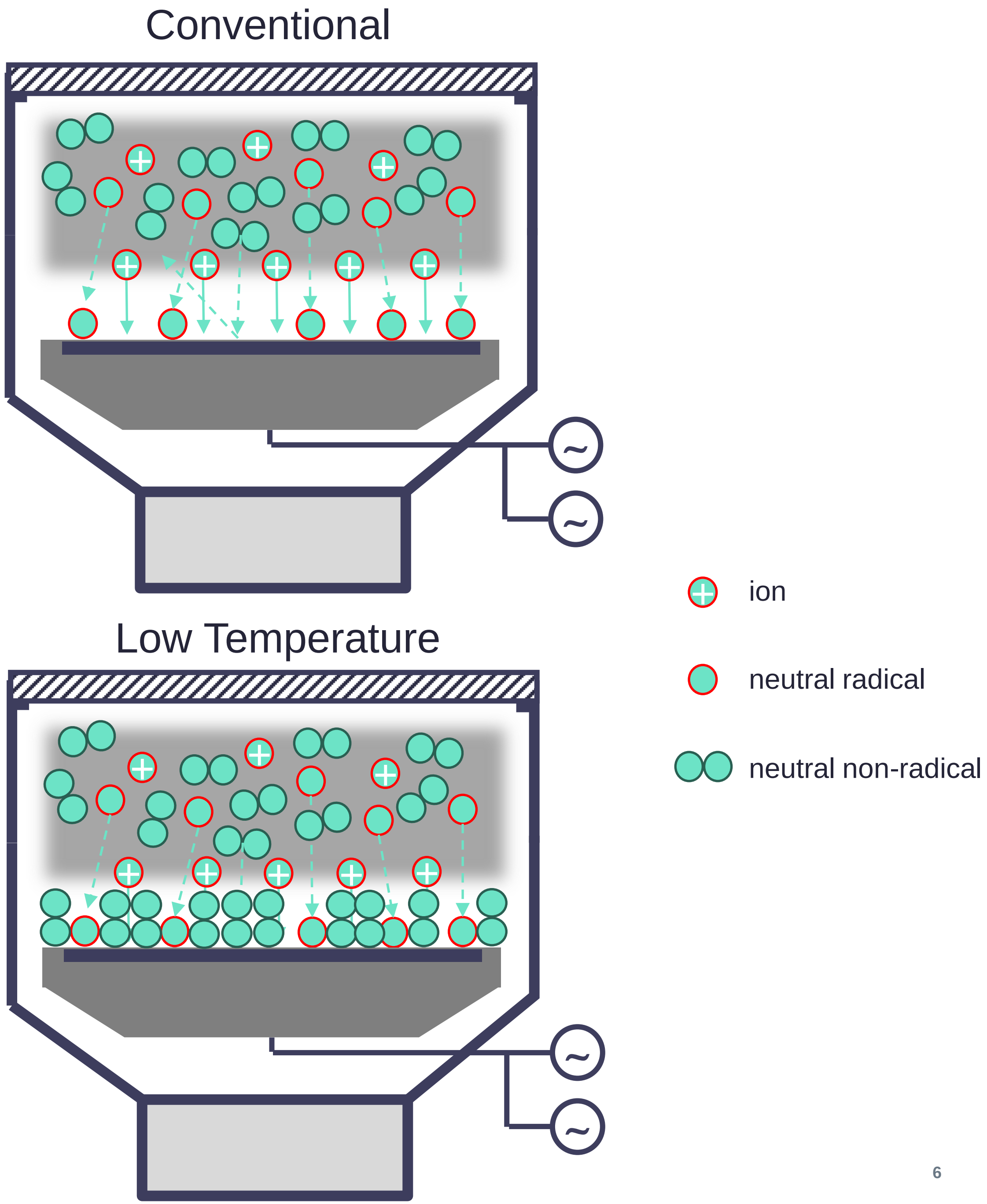
Hypothesis for High Etching Rate at Lower Temperature

Seminal experiment demonstrating ion – neutral synergy

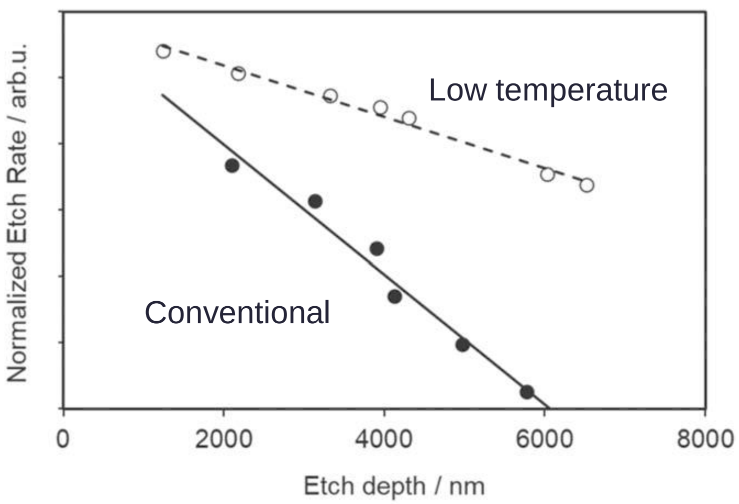


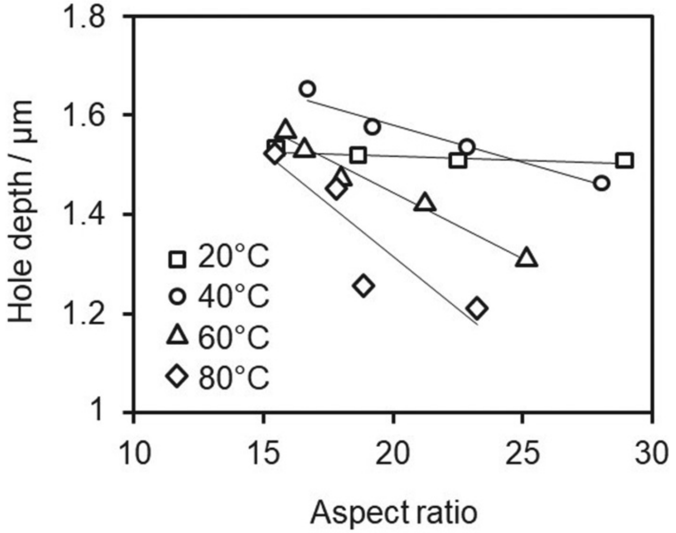
J.W. Coburn, H.F. Winters, J. Appl. Phys. 50, 3189 (1979)

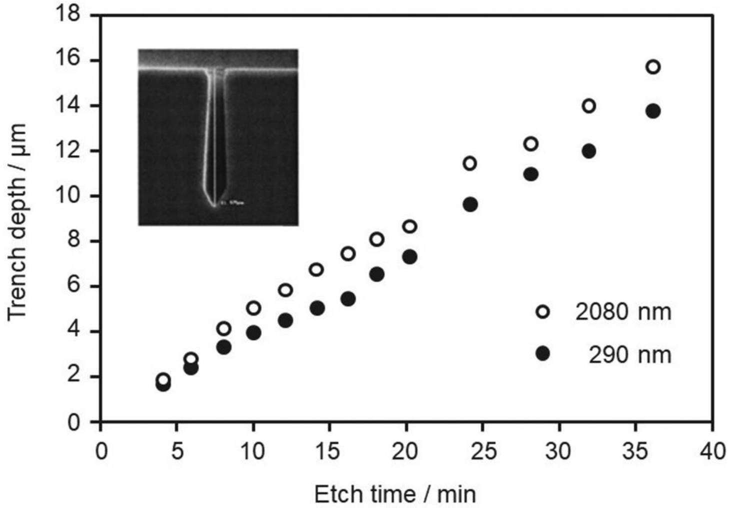
Reactive Ion Etching uses ions and reactive neutrals in a synergistic way. Conventionally, only radicals which are formed via plasma dissociation adsorb at the surface. The surface coverage can be increased by one to two orders of magnitude at low temperatures when non-dissociated species can physisorb.



Literature data confirming reduced ARDE at lower temperatures







ONON / Fluorine based chemistry

ONON / C_xF_y, HBr

Si / SF_6, O_2

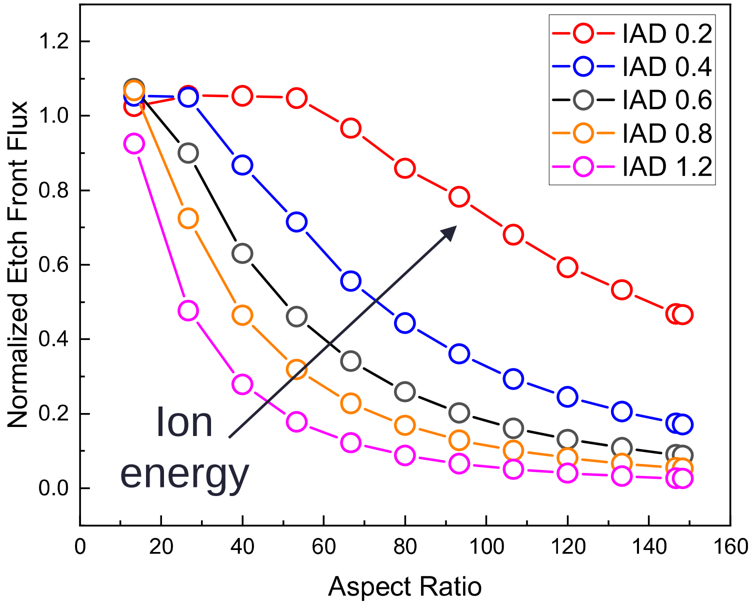
Shen et al., Jpn. J. Appl. Phys. 62, SI0801 (2023)

Iwase et al., Jpn. J. Appl. Phys. 57 06JC03 (2018)

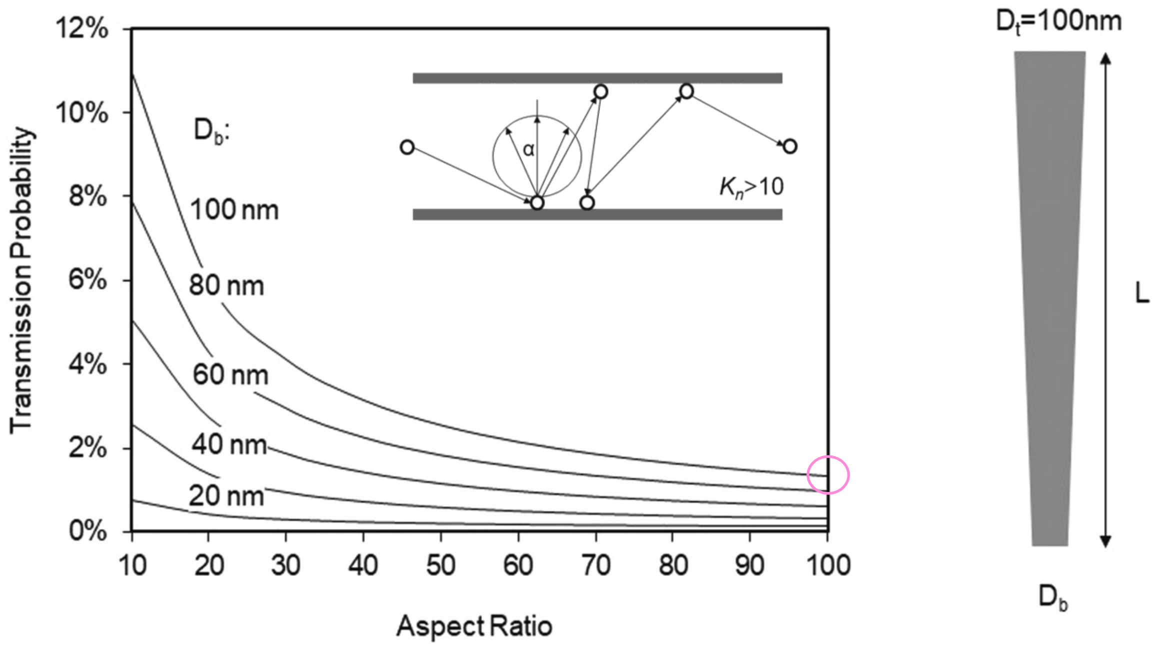
Blauw et al., J. Vac. Sci. Technol. B 18, 3453 (2000)

Aspect ratio dependence of ion and neutral fluxes

$$ER = \frac{\nu E_i J_i}{1 + \nu E_i J_i / (\nu_n s J_n)}$$



Simulated normalized ion fluxes at the etch front flux for the evolution of a perfect cylinder profile. IADs are assumed to follow a Gaussian distribution with 1σ specified.

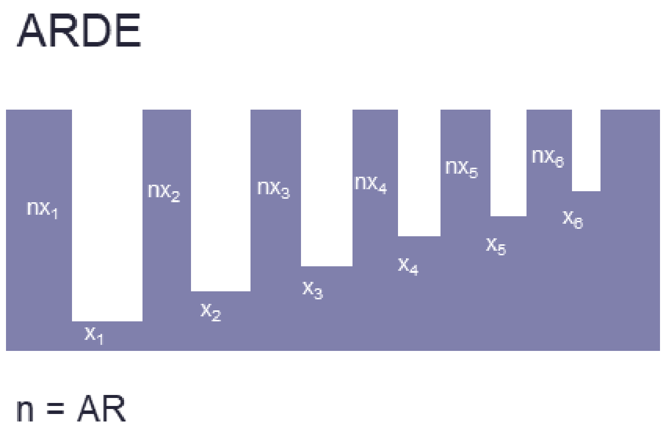


Transmission probability for straight and tapered cylinders as a function of the aspect ratio and bottom diameter. No sticking on the sidewall, complete consumption at etch front.

Shen et al., Jpn. J. Appl. Phys. 62, SI0801 (2023)

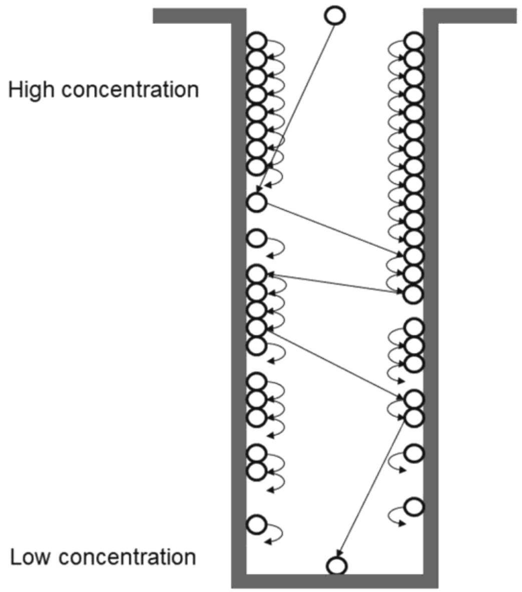
Panagopoulos, Lill, J. Vac. Sci. Technol. A 41, 033006 (2023)

Hypothesis for Reduced Aspect Ratio Dependent Etching



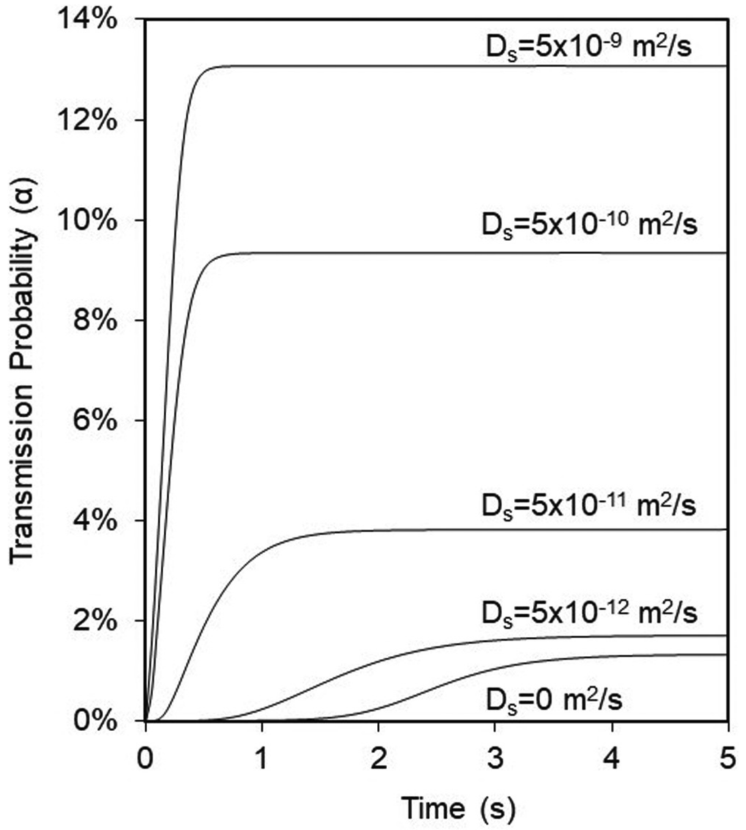
ARDE – Aspect Ratio Dependent Etching:

Smaller features etch slower. The final aspect ratio is independent on the opening size.
The etching rate slows down as the etch proceeds deeper (higher cost, limit for how deep can be etched).
The root cause is the attenuation of ion and neutral fluxes vs. depth.
Since neutrals don't have a preferred direction, they are more attenuated. It is of critical importance to enhance neutral transport.



Neutral Transport:

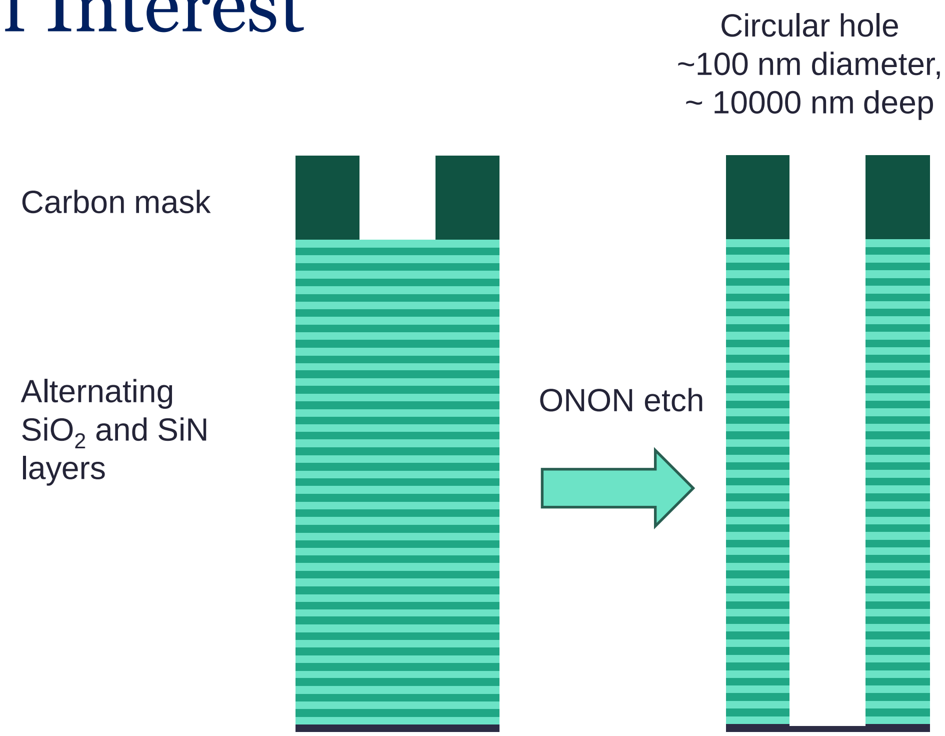
At the pressures and feature sizes we are operating in, neutrals reach the bottom of the feature via. Knudsen transport.
For 100:1 aspect ratio, only 1.3% of the species entering the feature reach the bottom. The rest is reflected.
We are proposing a synergistic transport model combining Knudsen transport and surface diffusion.



Modeling showed impact of surface diffusion:

Transmission probabilities as a function of time and surface diffusion coefficient D_s for cylindrical holes considering adsorption, desorption, and surface diffusion. The initial sticking coefficient is 0.1, and the desorption rate constant is 50 s^{-1}. The aspect ratio is 100. The pressure is 7.5 mTorr.

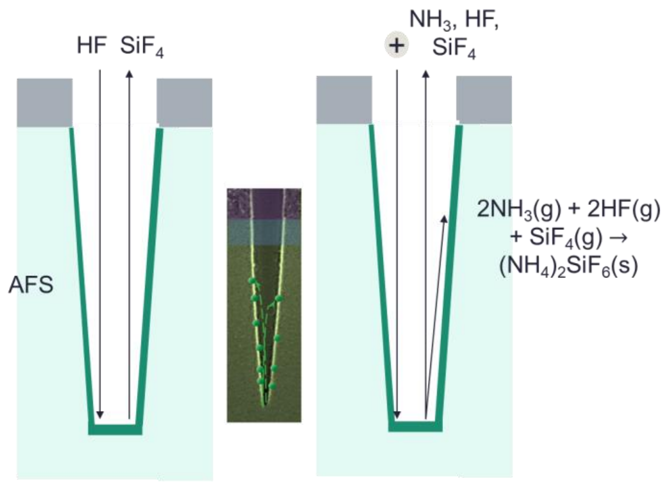
Etching Application of Interest



- Industry is ramping 2xx layers and roadmaps to 5xx SiO_2/SiN layers have been announced. Aspect ratios are approaching 100.
- The latest etching process uses HF and “cryo” temperatures. The real wafer surface temperature is higher than the chiller set-point because of plasma heating. It is around 0 to 10℃.
- The etching rate is about double that of conventional processes (C_4F_8).

Role of AFS in Cryo Etching with HF: Intrinsic ONON sidewall protection

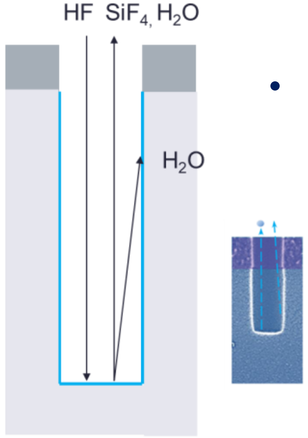
HF reaction w. SiN **Ion removal**



$Si_3N_4(s) + 16HF(g) \rightarrow 2(NH_4)_2SiF_6(s) + SiF_4(g)$

$(NH_4)_2SiF_6(s) \xrightarrow{\text{ions}} 2NH_3(g) + 2HF(g) + SiF_4(g)$

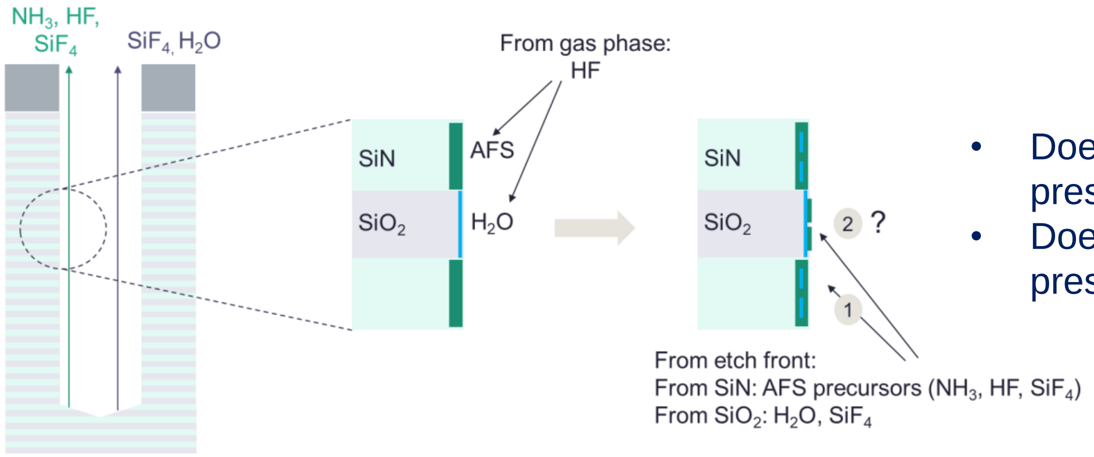
Hsiao et al., *ACS Appl. Electron. Mater.* 2023, 5, 12, 6797−6804



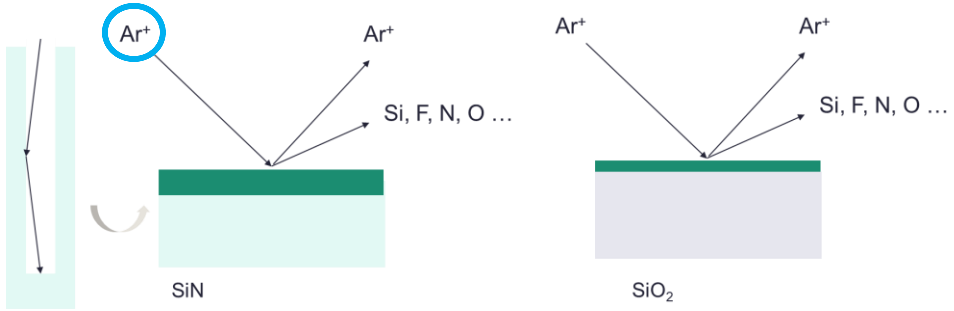
- No sidewall protection on SiO2

$SiO_2(s) + 4HF(g) \rightarrow SiF_4(g) + 2H_2O\ (l,g)$

Hattori et al Jpn. J. Appl. Phys. 62 (2023) SI1001
Lee et al., J. Electrochem. Soc., 143 (1996) 1099
Kim et al., ACS Omega 6 (2021) 16009



- Does AFS form on SiO_2 in the presence of NH_3 and SiF_4?
- Does AFS form on SiO_2 in the presence of NH_3 and SiF_4?



- What is the scattering and sputtering yield of AFS?

- What is the selflimting thickness if AFS on SiN?
- At what thickness does AFS stop isotropic etching of SiO_2?

SiN Etch Mechanism: Salt Formation

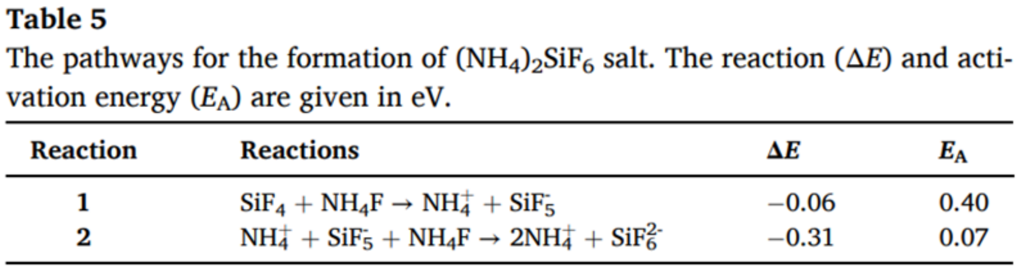


Table 5
The pathways for the formation of $(NH_4)_2SiF_6$ salt. The reaction (ΔE) and activation energy (E_A) are given in eV.

Reaction	Reactions	ΔE	E_A
1	$SiF_4 + NH_4F \rightarrow NH_4^+ + SiF_5^-$	−0.06	0.40
2	$NH_4^+ + SiF_5^- + NH_4F \rightarrow 2NH_4^+ + SiF_6^{2-}$	−0.31	0.07

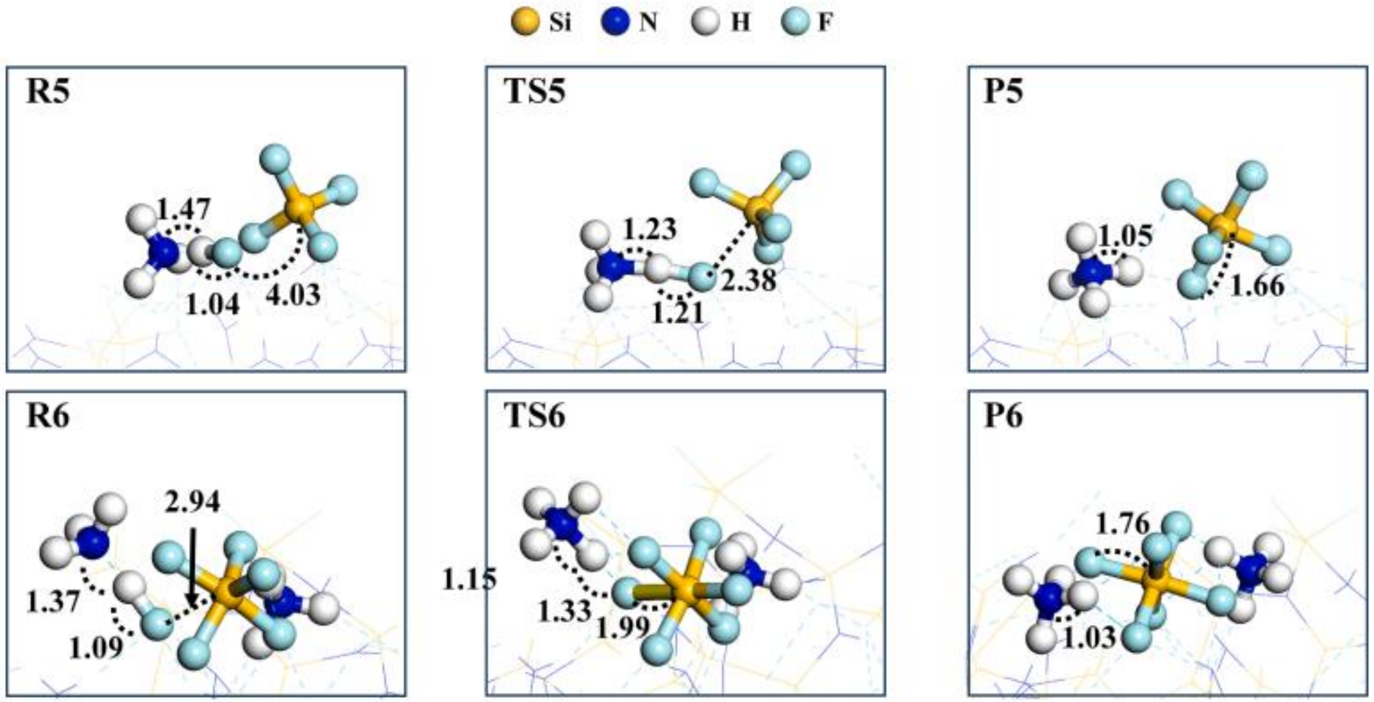


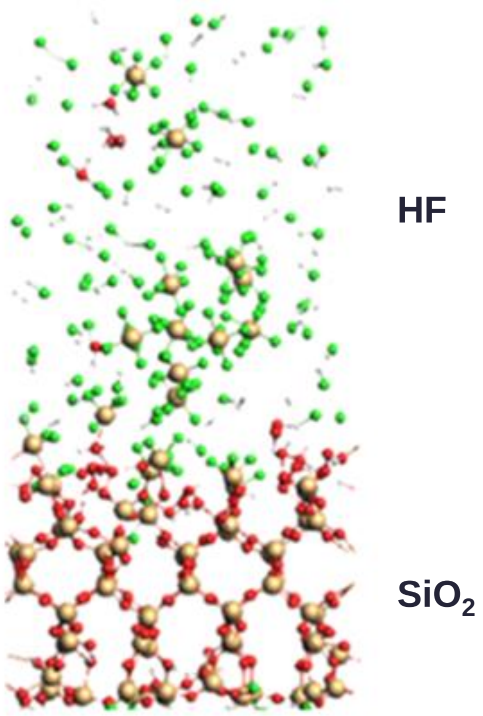
Fig. 9. The changes in atomistic structures for salt formation. The dashed lines represent the interatomic distances, which are given in Å.

DFT (Dmol) calculations show reaction pathway where two NH_4F molecules react with SiF_4.

Khumaini et al., Applied Surface Science 654 (2024) 159414

Alternative SiO_2 Etch Mechanisms

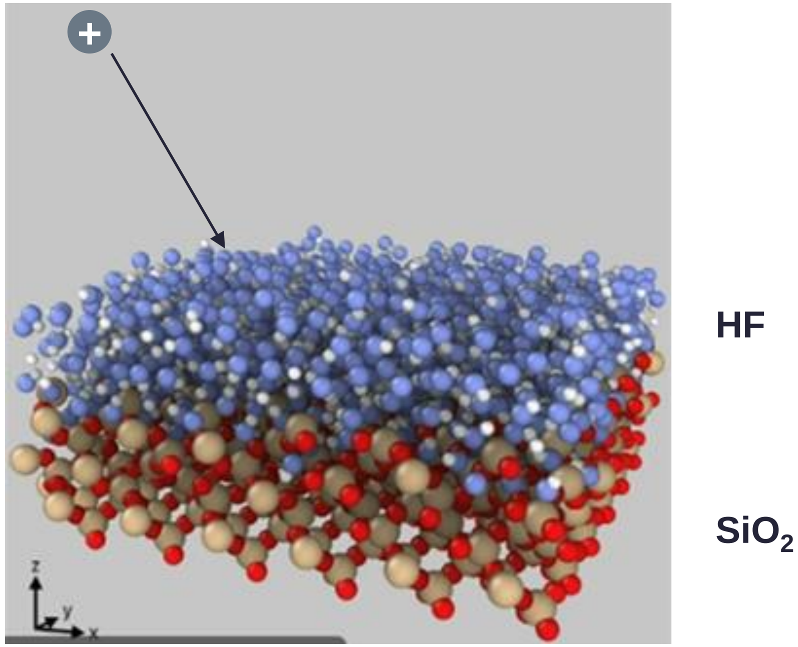
Mechanism A



Fast HF with a few 10 eV etching SiO_2 spontaneously

Kim et al., ACS Omega 6 (2021) 16009

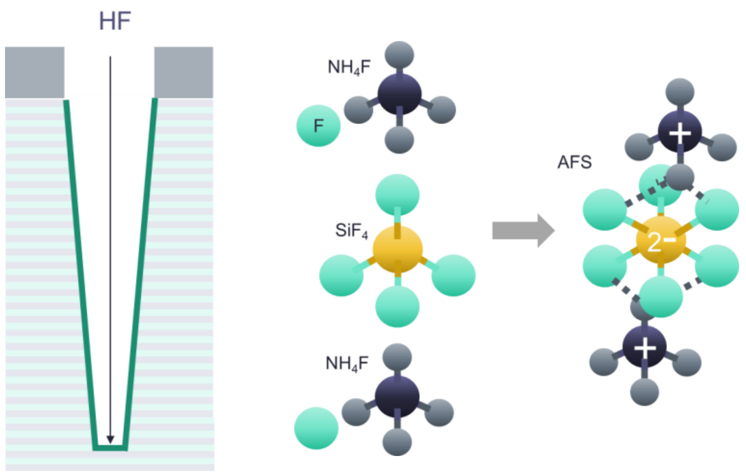
Mechanism B



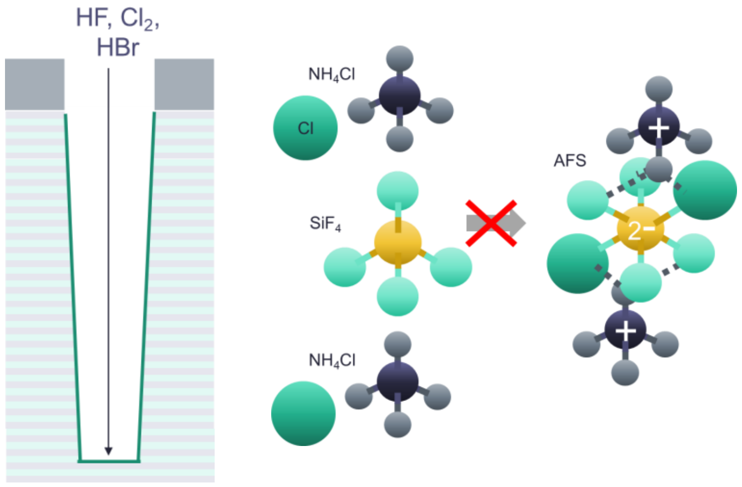
Ion bombardment activates physisorbed HF

Possibly both mechanisms proceed simultaneously.

Role of AFS in Cryo Etching with HF: Isothermal Thickness Control

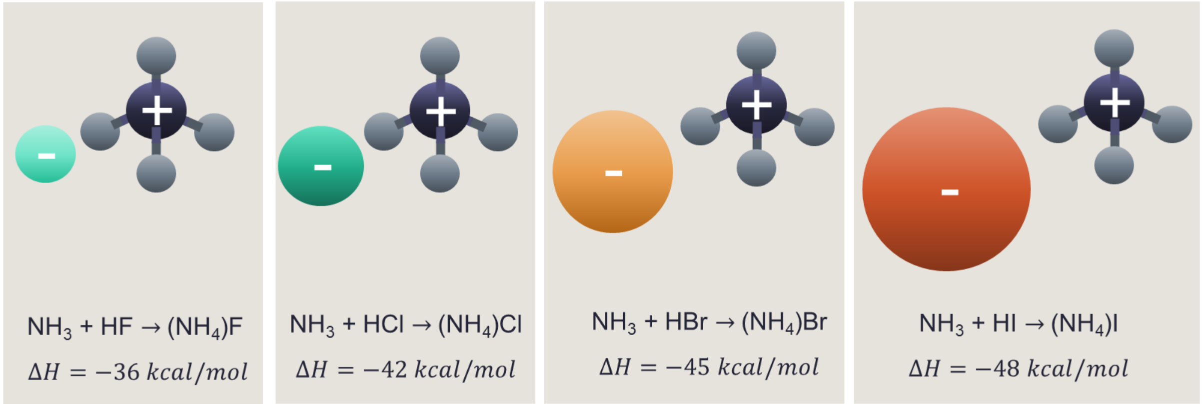


Khumaini et al., Applied Surface Science 654 (2024) 159414



AFS thickness tuning using other halogen gases

Hypothesis explaining experimental results



$NH_3 + HF \rightarrow (NH_4)F$

$\Delta H = -36\ kcal/mol$

$NH_3 + HCl \rightarrow (NH_4)Cl$

$\Delta H = -42\ kcal/mol$

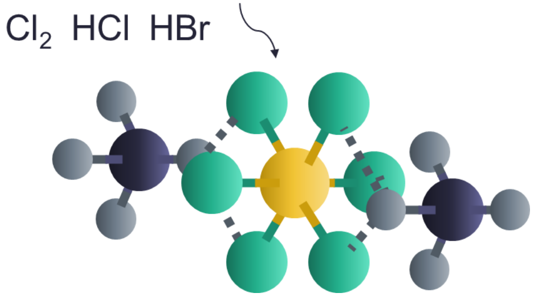
$NH_3 + HBr \rightarrow (NH_4)Br$

$\Delta H = -45\ kcal/mol$

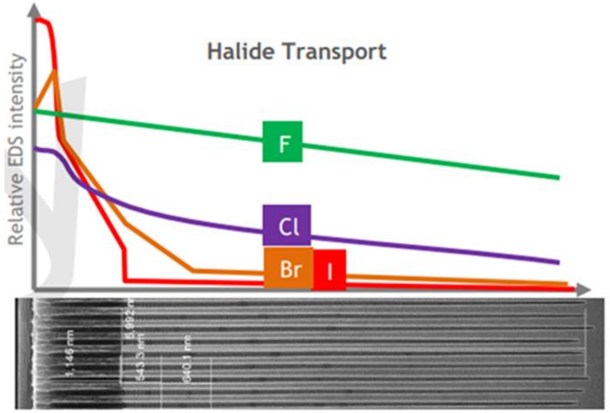
$NH_3 + HI \rightarrow (NH_4)I$

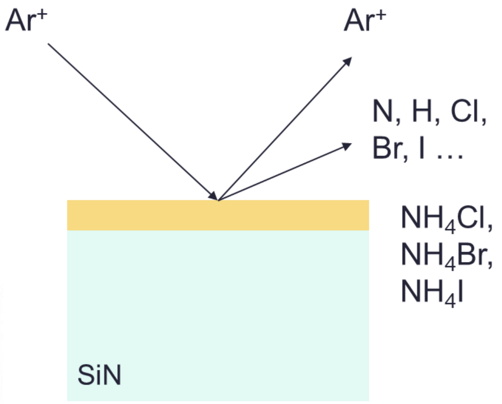
$\Delta H = -48\ kcal/mol$

Formation enthalpy of ammonium halides increases with atomic number



Do chlorine, bromine and iodine containing gases break up AFS once it is formed ?





- Ammonium halides have useful deposition profile
- Are they good for sidewall protection?

Summary of important gaps in understanding

- Does adsorption of H2O or HF weaken AFS?
- Does AFS form on SiO2 in the presence of NH3 and SiF4 from etching of SiN?
- Properties of AFS as sidewall passivation (scattering and sputtering under oblique incidence)
- Reaction of AFS with Cl2, HBr, bromine containing gases: Do they really suppress AFS formation? Do they break up AFS?
- Properties of ammonium halides as sidewall passivation (scattering and sputtering under oblique incidence)
- Reaction of HF with AFS on SiO_2 and SiN: Minimum AFS thickness to be barrier against HF etching SiO_2 and further AFS formation on SiN