Etching of Silicon Oxynitride Films in Supercritical CO_2

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Outline

- Introduction
  - silicon oxynitride materials
  - supercritical fluid processing
- Experimental method
  - processing
  - characterization
- Results
  - etching rate
  - surface characterization
  - reaction scheme
- Conclusion

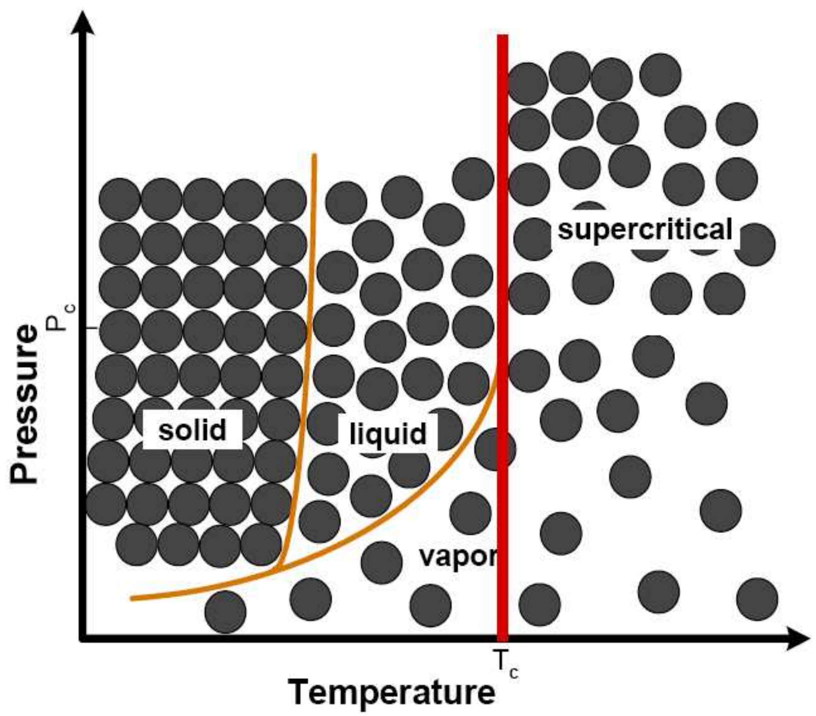
Introduction - Silicon oxynitride

- Amorphous, insulating films of the form SiO_xN_y
- Material properties intermediate between Si_3N_4 and SiO_2
- Transparent in the visible and near infrared regions
  - variable refractive index values
- Compared to SiO_2
  - reduced interfacial defects
  - increased resistance to boron diffusion
  - higher dielectric breakdown
- Current SiO_xN_y processing techniques
  - aqueous HF solutions
  - fluorine plasma

Introduction - Supercritical fluid processing

- Supercritical fluid
  - liquid-like densities (~ 0.6 g/mL)
  - gas-like mass transport (diffusivity ~ 10^{-3} cm^2/s)
  - zero surface tension and low viscosity

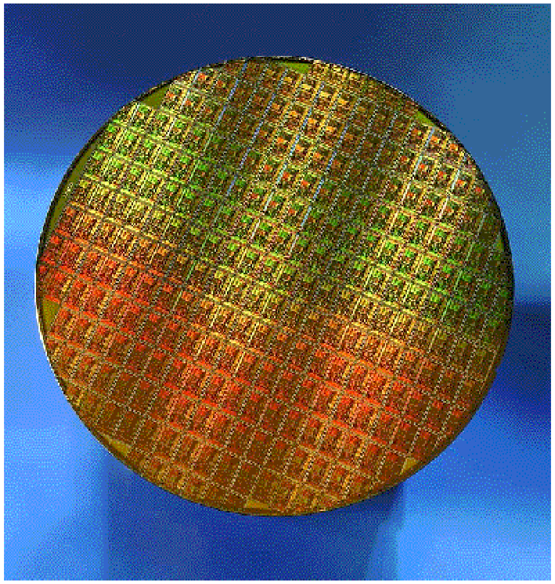
- Carbon dioxide
  - moderate critical parameters
  - nontoxic
  - nonflammable
  - low cost
  - recycle/recovery potential



Introduction - Supercritical fluid processing

- Considerations
  - high pressure equipment
  - nonpolar solvent

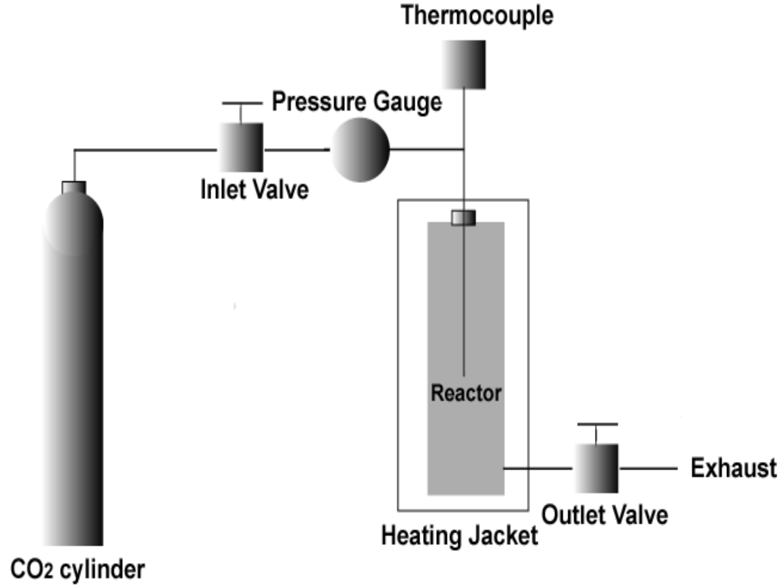
- Microelectronics processing
  - photoresist
    - drying
    - development
  - low k films
    - synthesis
    - repair
  - Cu metal
    - deposition
    - etching



www.cstl.nist.gov

Experimental Method

- Materials
  - SiO_xN_y samples
    - CVD with silane and N_2O
    - 422 nm layer
    - 50% Si 40% O 10% N
  - 70% HF/pyridine complex (Sigma Aldrich)
  - 99.5% CO_2
- High pressure reactor
  - batch style
  - 50 mL capacity



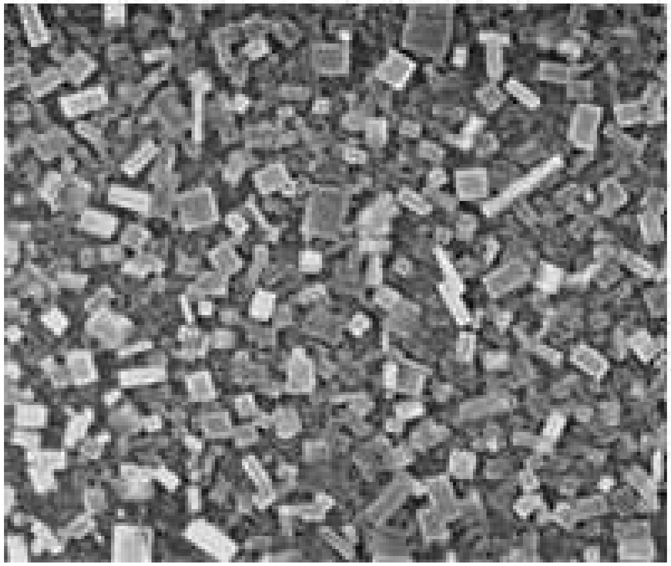
Experimental Method

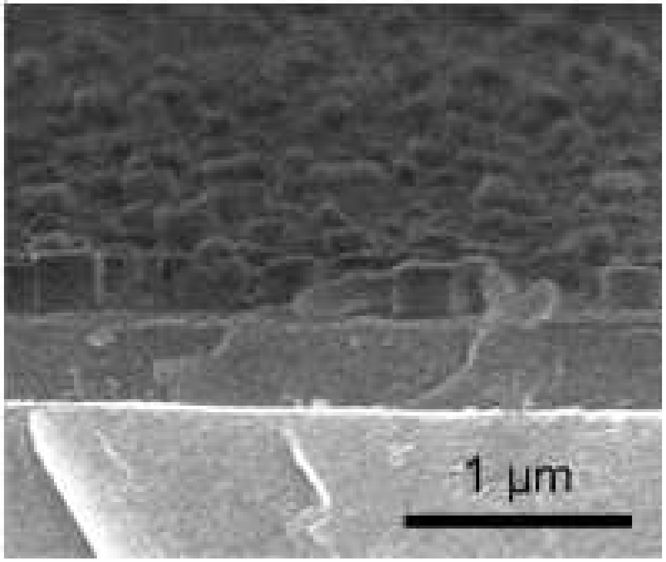
- Processing
  - 0 - 22.4 mM etchant concentration
  - 50 - 75℃ processing temperature
  - 160 ± 10 bar processing pressure
  - 17 minute reaction time

- Characterization
  - field emission SEM
  - AFM
  - FTIR
  - XPS
  - ellipsometry
    - rinsed salt layer prior to analysis

Results – $(NH_4)_2SiF_6$ formation

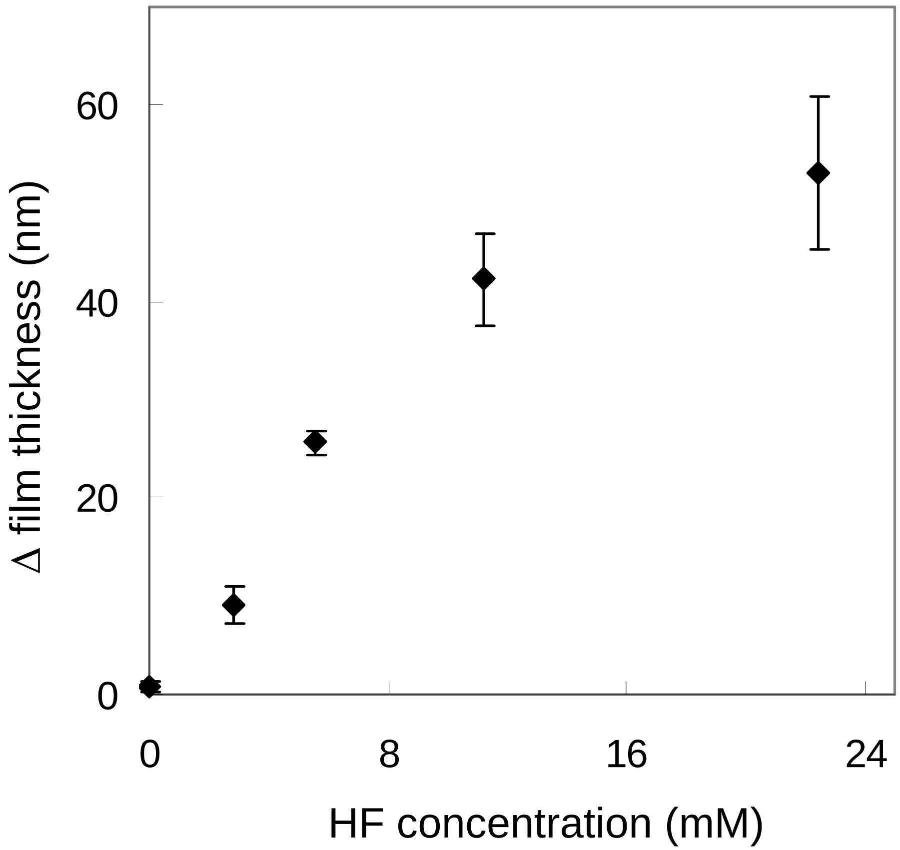
- Reaction formed inorganic etch product identified as $(NH_4)_2SiF_6$
  - water soluble
  - ΔG_f = -2366 kJ/mol





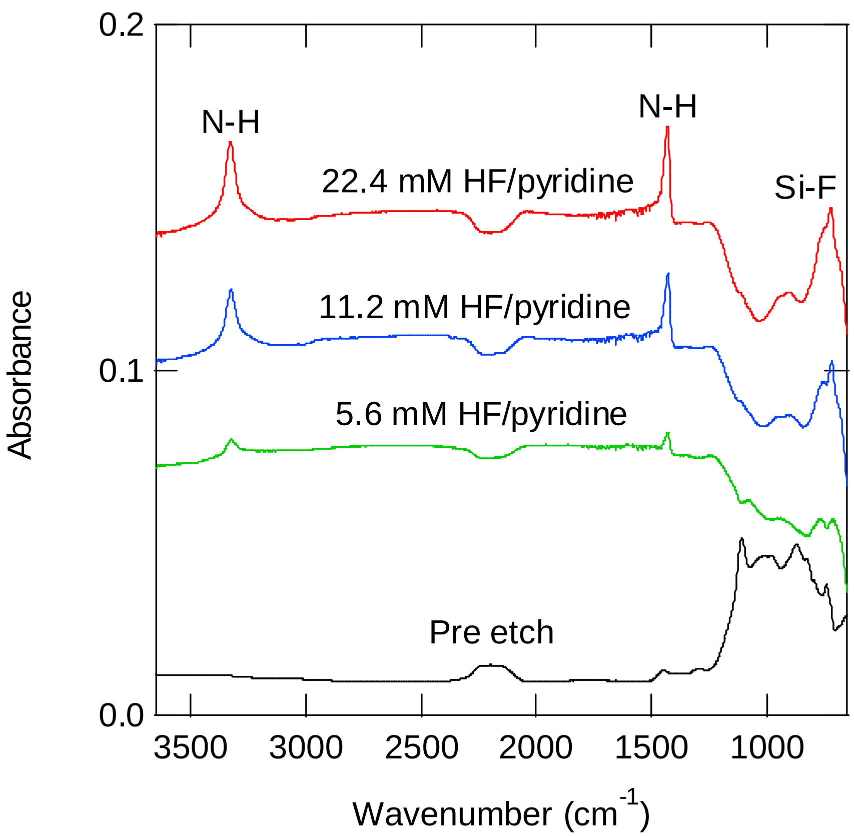
Results - Etching rate

- Etch rate increased with increasing HF concentration
- Maximum etch rate of 3.1 nm/min
- Reaction order decreased at higher concentrations
- Salt layer
  - hindered etch rate
  - prevented uniform removal



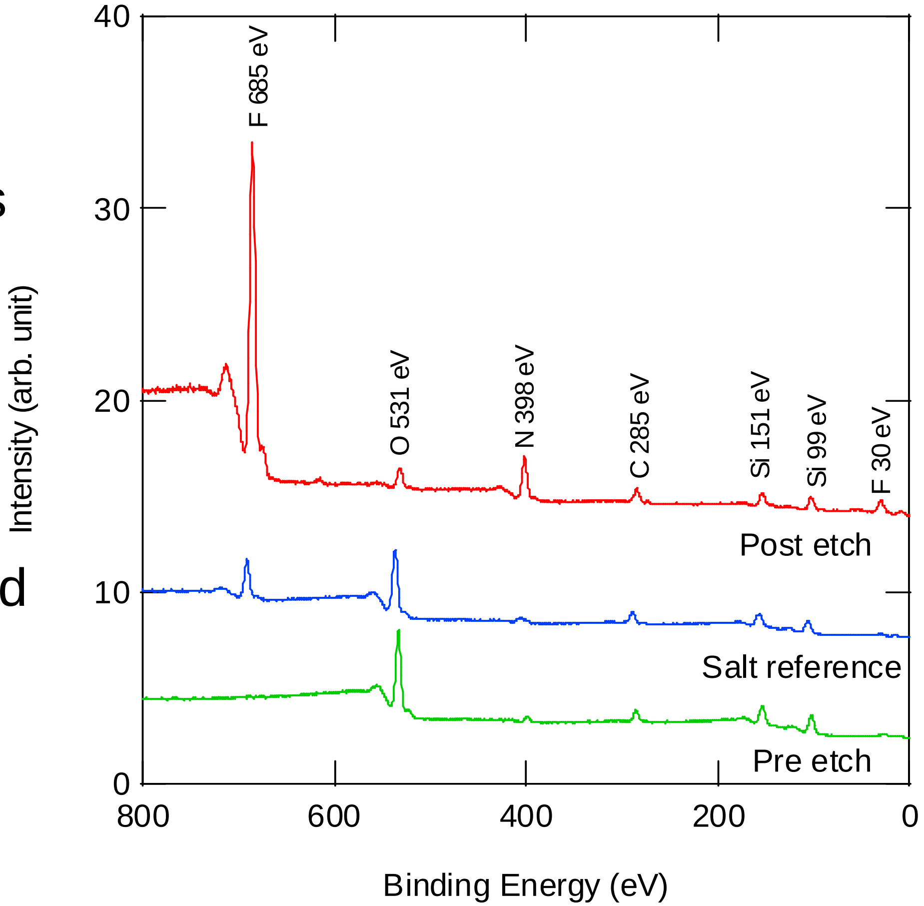
Results – FTIR characterization

- As-received film
  - 1200 – 800 cm^{-1} Si-O and Si-N vibrations
  - 2195 cm^{-1} Si-H stretching
- After etching
  - 1433 cm^{-1} N-H bending
  - 3327 cm^{-1} N-H stretching
  - 715 cm^{-1} Si-F modes
- Decreasing intensity of SiO_xN_y absorbances
- Increasing intensity of $(NH_4)_2SiF_6$ modes



Results – XPS characterization

- As-received film
  - Si, O, N, adventitious C
- After etching
  - appearance of F 1s and 2s peaks
  - increase in N intensity
  - decrease in O intensity
- Salt reference sample
  - O presence due to exposed SiO_xN_y
  - used to determine experimental sensitivity factors



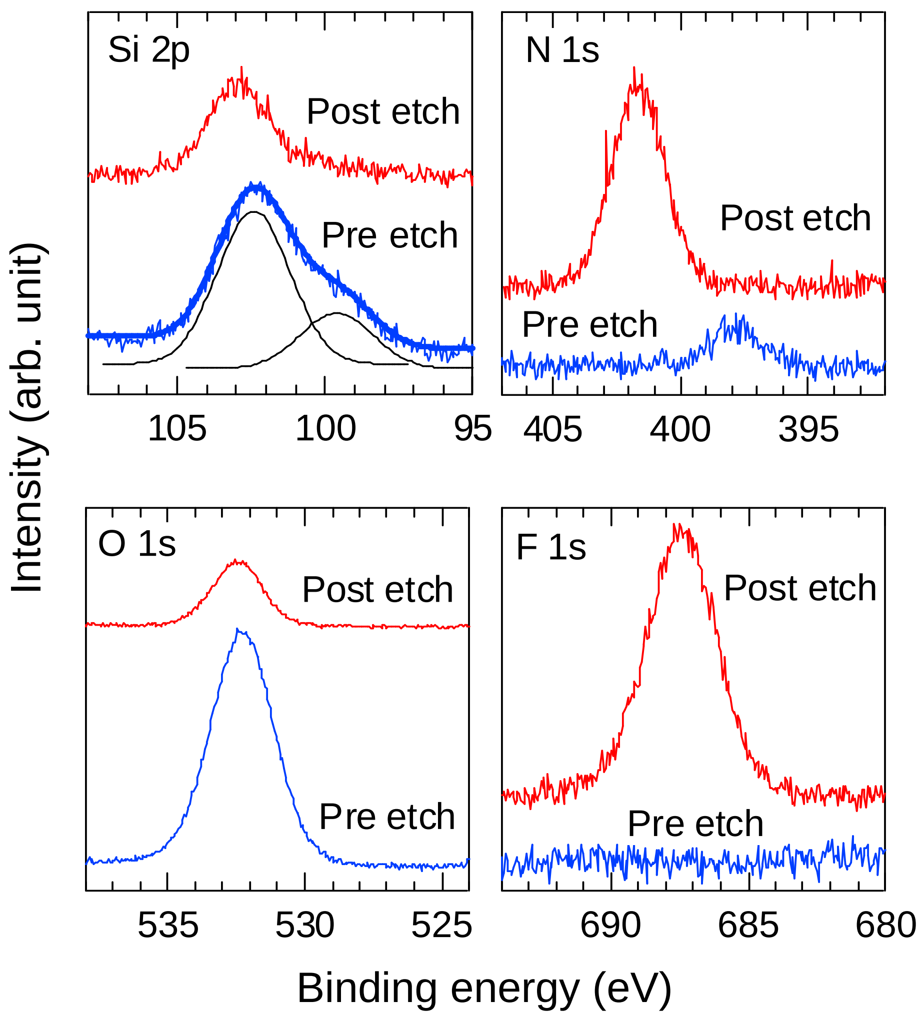
Results – XPS characterization

Element	S.F.	Salt composition (%)	
		Calculated	Stoichiometric
Si	0.21	9.0	11.1
N	0.18	25.3	22.2
F	1.00	65.7	66.7

$$C_i = \frac{area_i / S.F._i}{\sum area_i / S.F._i}$$

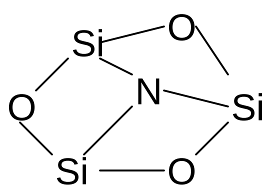
Results – XPS characterization

- Pre etch
  - silicon 99.6 & 102.4 eV
    - Si metal & SiO_xN_y
  - nitrogen 397.9 eV
    - N-Si in O rich matrix
  - oxygen 532.4 eV
    - O-Si bonding
- Post etch
  - silicon 102.9 eV
  - nitrogen 401.7 eV
- Si and N shift to higher binding energy after processing

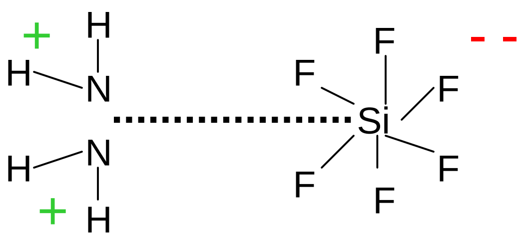


Results – XPS characterization

amorphous silicon oxynitride



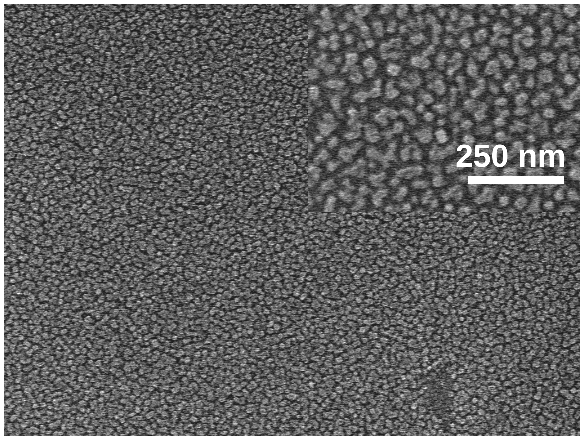
ammonium hexafluorosilicate



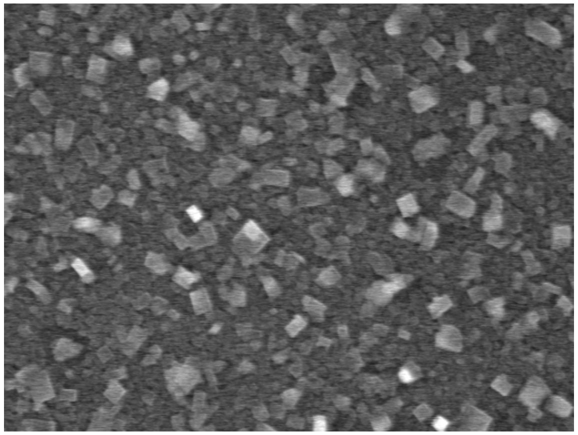
	Nitrogen	Silicon
Matrix effect	$SiO_xN_y \rightarrow NH_4^+$ ↑	$SiO_xN_y \rightarrow SiF_6^{-2}$ ↓
Bonding effect	N-Si → N-H	Si-O, Si-N → Si-F ↑
Binding energy shift	3.8 eV ↑	0.5 eV ↑

Results - Salt morphology

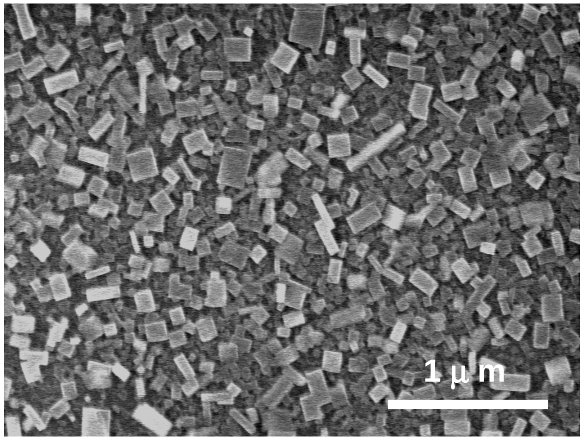
- Formed as 3-D nanoscale crystals
  - parallel to surface, no preferred lateral orientation
  - cubic shape: isometric hexoctahedral packing
- Higher HF concentration
  - increased coverage and crystal size



5.6 mM HF



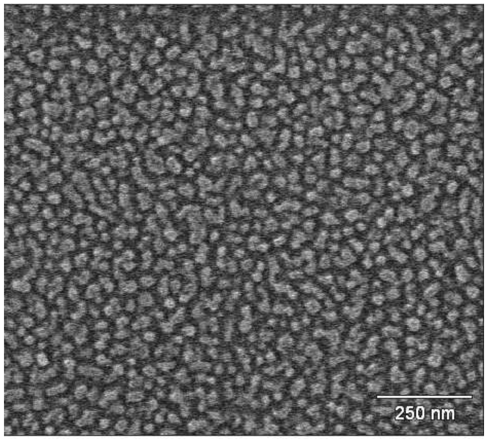
11.2 mM HF

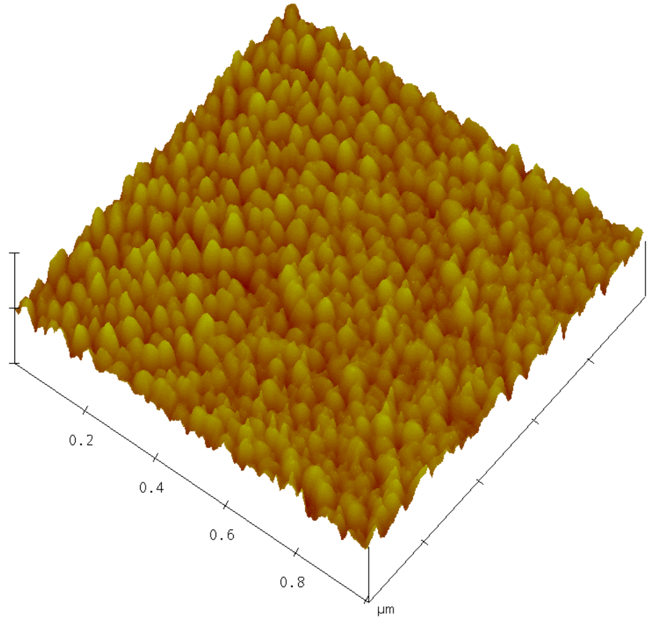


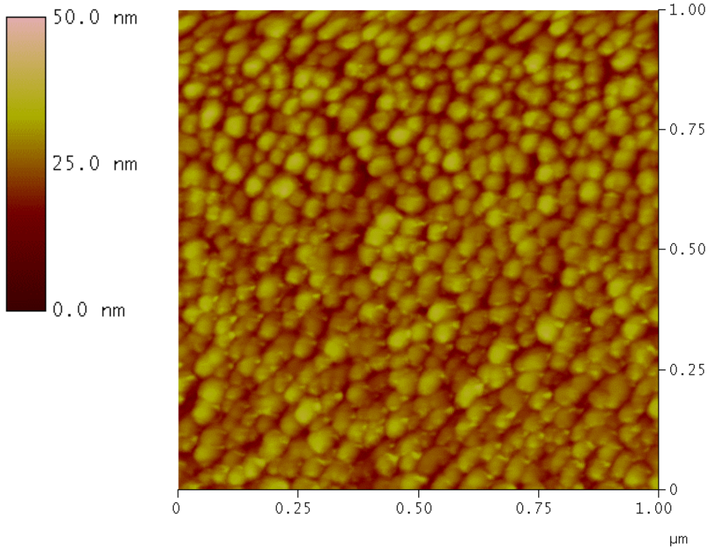
22.4 mM HF

Results – Salt morphology

- AFM
  - confirmed 3-D structure
  - approx height = 35 nm

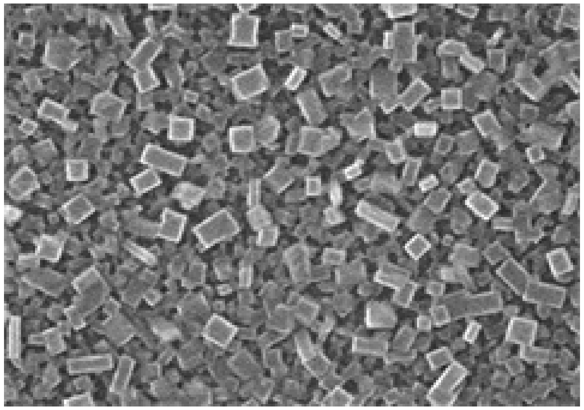




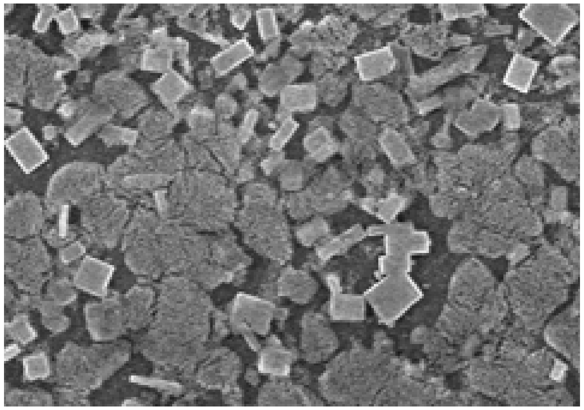


Results – Salt morphology

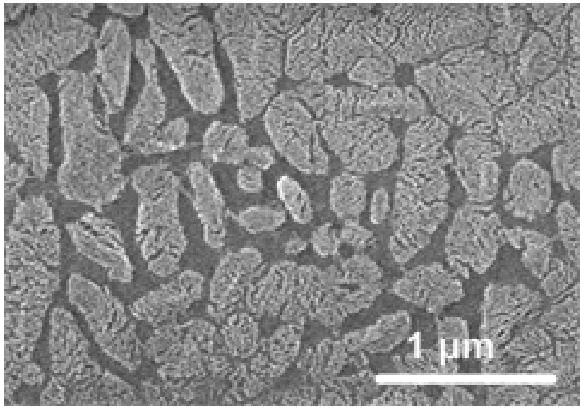
- Temperature effect
  - 50 - 57℃: 50 – 100 nm crystals
  - above 70℃: powder morphology
    - commonly reported form
  - no change in chemical composition



T = 57℃



T = 70℃



T = 75℃

Results – Reaction scheme

- HF reaction with Si-O and Si-N bonds

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

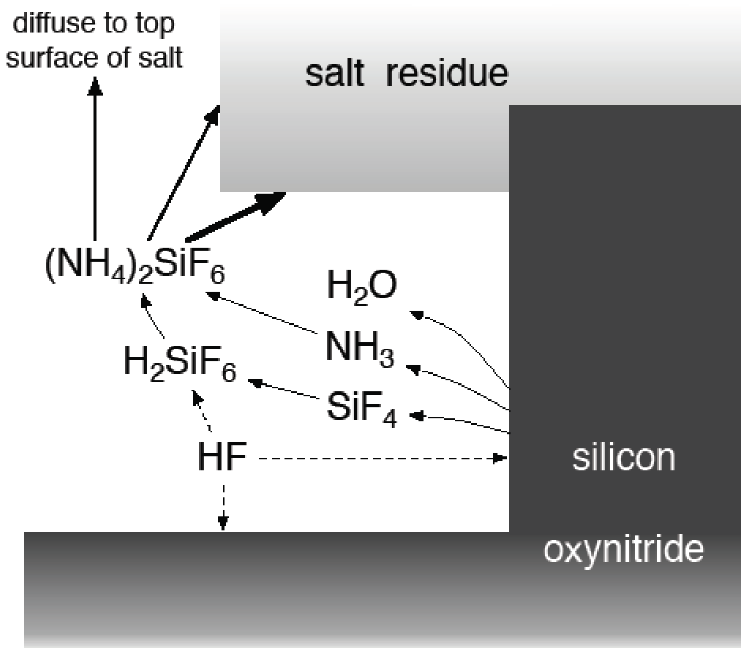
$Si_3N_4 + 12HF \longrightarrow 3SiF_4 + 4NH_3$

- HF reaction with SiF_4 product

$SiF_4 + 2HF \longleftrightarrow H_2SiF_6$

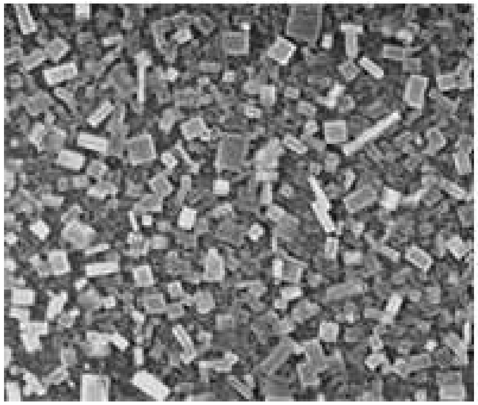
- H_2SiF_6 with NH_3 product

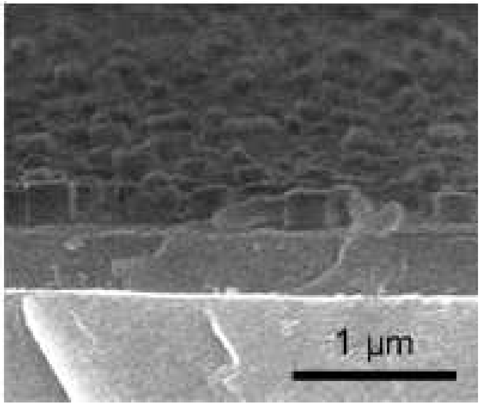
$H_2SiF_6 + NH_3 \longrightarrow (NH_4)SiF_6$



Results – $(NH_4)_2SiF_6$

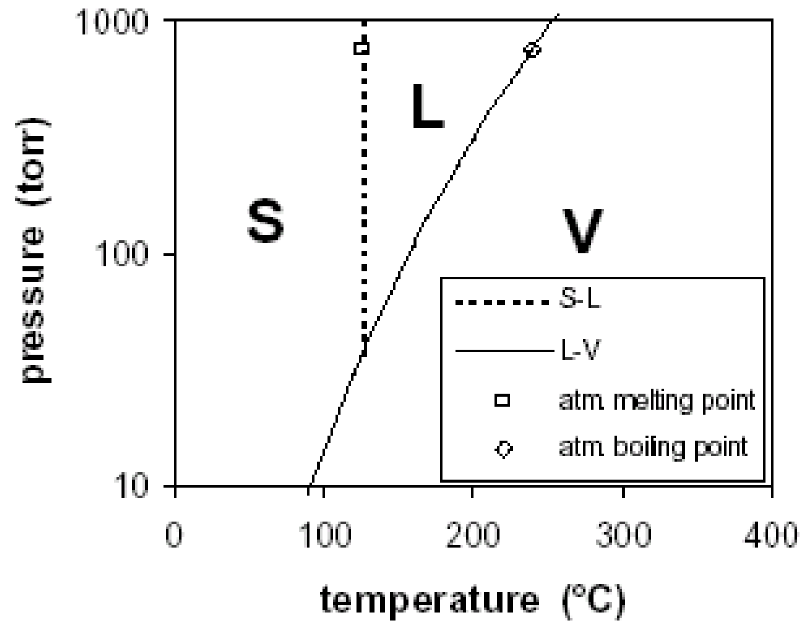
- Occurrence in semiconductor manufacturing
  - Si vapor etching with HNO_3/HF
    - S. Kalem, Appl. Surf. Sci. (2004)
  - gas phase HF etching of SiO_2/Si_3N_4 stacks
    - B. D. Bois *et al*, Proc. Sensor Tech. (2001)
  - plasma etching of Si_3N_4 with F plasmas
    - W. Knolle *et al*, J. Electrochem. Soc. (1988)
  - liquid SiO_2 etching with NH_4 buffered HF
    - M. Niwano *et al*, Appl. Phys. Lett. (1993)





Results – Salt removal

- Water rinse
  - negates benefits of using nonaqueous etching techniques
- Ambient heating
  - salt layer may form into a liquid melt and damage fine features
- Vacuum heating
  - allows for sublimation of salt product



Du Bois *et al*, National Dutch Sensor Conference, 2006

Conclusions

- Etching SiO_xN_y in $HF/scCO_2$
  - bulk removal of the film
  - formation of $(NH_4)_2SiF_6$ etch product
  - salt layer hindered etch rate
    - lower HF concentrations
    - small structures

- $(NH_4)_2SiF_6$ surface characterization
  - nanoscale, cubic shaped crystals
  - characteristic N-H and Si-F infrared vibrations
  - full scan XPS matched salt composition
  - shift to higher binding energy for Si and N relative to SiO_xN_y

Conclusions

- Proposed reaction scheme
  - reaction byproducts combined with excess HF
    - formation of hexafluorosilicic acid
  - salt grew from bottom interface
    - highest precursor concentrations

- Salt removal
  - water rinse
  - heating
  - sublimation

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