Gas-Phase Etching Mechanism of Amorphous Hydrogenated Silicon Nitride by Hydrogen Fluoride: A Theoretical Study

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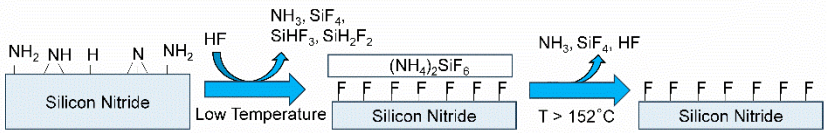
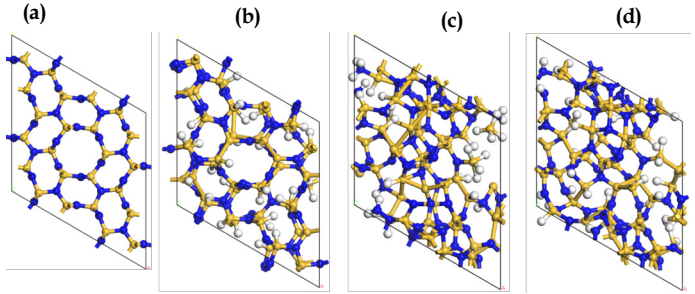
Summary – Reaction Mechanism

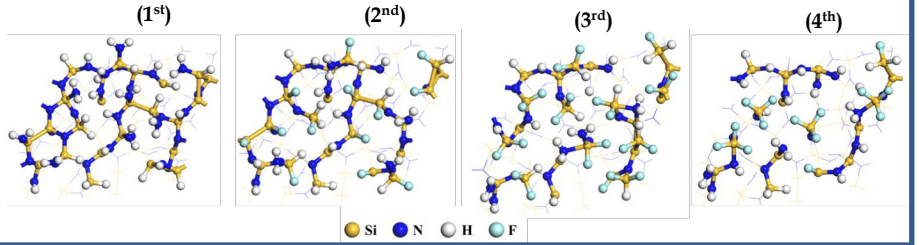


Construction of the amorphous model



a. cr. β-Si_3N_4
b. cr. $SiNH_{0.67}$
c. a-$SiNH_{0.67}$ after melt-quench
d. Final a-$SiNH_{0.67}$

Construction of surface models with different degrees of fluorination



Simulation of Fluorination

a. First Fluorination

Pathway	Reactions	E_{Phy}	ΔE	E_A
P1a	$SiNH_2$* + HF → SiF* + NH_3	-1.09	-0.24	0.45
P1b	SiH* + HF → SiF* + H_2	-0.83	-0.63	2.10
P1c	Si–NH*–Si + HF → SiF* + $SiNH_2$*	-0.91	-1.40	0.02
P1d	Si–N–Si + HF → SiF* + SiNH*	-0.90	-0.97	0.72

b. Second Fluorination

Pathway	Reactions	E_{Phy}	ΔE	Ea
P2a	$Si(NH_2)F$* + HF → SiF_2* + NH_3	-0.54	-0.76	0.68
P2b	SiHF* + HF → SiF_2* + H_2	-0.42	-0.65	1.80
P2c	SiF*–NH*–Si + HF → SiF_2* + $SiNH_2$*	-0.35	-0.24	0.79
P2d	SiF*–N–Si + HF → SiF_2* + SiNH*	-0.51	-0.96	0.75
P2e	Si–N–SiH_2F* + HF → SiH_2F_2 + SiNH*	-0.51	-1.29	0.81
P2f	SiF*–Si + HF → SiF_2* + SiH*	-0.25	-1.31	0.79

c. Third Fluorination

Pathway	Reactions	E_{Phy}	ΔE	Ea
P3a	$Si(NH_2)F_2$* + HF → SiF_3* + NH_3	-0.64	-0.42	0.88
P3b	$SiHF_2$* + HF → SiF_3* + H_2	-0.29	-1.08	1.54
P3c	SiF_2*–NH*–Si + HF → SiF_3* + $SiNH_2$*	-0.37	-0.67	0.74
P3d	SiF_2–N–Si + HF → SiF_3* + SiNH*	-0.30	-0.56	0.90
P3e	Si–N–$SiHF_2$* + HF → $SiHF_3$ + SiNH*	-0.39	-1.13	0.96

d. Fourth Fluorination

Pathway	Reactions	E_{Phy}	ΔE	Ea
P4	Si–NH*–SiF_3* + HF → SiF_4 + $SiNH_2$*	-0.32	-0.77	0.53

Simulation of Salt Formation

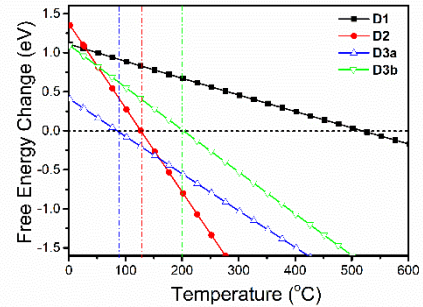
a. Salt Formation

Reaction	Reactions	ΔE	Ea
1	SiF_4 + NH_4F → NH_4^+ + SiF_5^-	-0.06	0.40
2	NH_4^+ + SiF_5^- + NH_4F → 2 NH_4^+ + SiF_6^{2-}	-0.31	0.07

b. Salt Desorption

Pathway	Reaction	E_{des}	T_s
D1	$(NH_4)_2SiF_6$ (surf) → $(NH_4)_2SiF_6$ (g)	1.98	526
D2	$(NH_4)_2SiF_6$ (surf) → 2 NH_3 + 2 HF (g) + SiF_4 (g)	4.79	152
D3a	$(NH_4)_2SiF_6$ (surf) → NH_5F_2 (surf) + NH_3 (g) + SiF_4 (g)	1.97	102
D3b	NH_5F_2 (surf) → NH_3 (g) + 2HF (g)	2.81	200

Simulation of Salt Desorption Temperature



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