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Theoretical Evaluation of Thermal Decomposition of Dicholosilane for Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride: The Important Role of Surface Hydrogen

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Table S1. Selected geometric parameters of the hexagonal β-Si_3N_4 unit cell using different dispersion corrections compared to experimental values[1].

	Volume (Å^3)	a (Å)	c (Å)	$d_{Si\text{-}N}$ (Å)
DFT	149.1	7.666	2.929	1.74
DFT-D3	148.0	7.647	2.922	1.74
DFT-D3BJ	146.3	7.617	2.910	1.73
experimental[1]	145.81	7.6093	2.9079	1.729

The lattice parameters of the β-Si_3N_4 unit cell were optimized using a hexagonal primitive unit cell, while all atoms were fully relaxed until residual force were below a tolerance of 10^{-3} eV/Å. Periodic boundary conditions were imposed in all three directions. Geometric parameters obtained from standard DFT are compared to the method of Grimme (DFT-D3)[2] and the improved method including Becke-Johnson damping (DFT-D3BJ)[3]. The predicted crystal lattice parameters were found to agree with previous DFT-GGA[4] and experimental studies[1]. Interestingly, the lattice parameters predicted via DFT-D3BJ were very close to the experimentally measured values, despite the expected overbinding from the combination of the PBE functional and the DFT-D3BJ method[3].

The choice of dispersion correction is most important in the estimation of the binding strength in the molecularly adsorbed configuration. E_b for a molecularly adsorbed DCS in the lowest-energy configuration was found to be 0.59 eV via DFT-D3BJ, close to E_b = 0.54 eV obtained via DFT-D3. The activation barrier E_a = 0.27 as predicted via DFT-D3BJ while DFT-

D3 predicted a slightly higher E_a of 0.32 eV. The results presented in this work were obtained from the DFT-D3BJ method as our primary interest will be E_a determined by the energy of the molecularly adsorbed state and the transition state where non-covalent interactions will be significant.

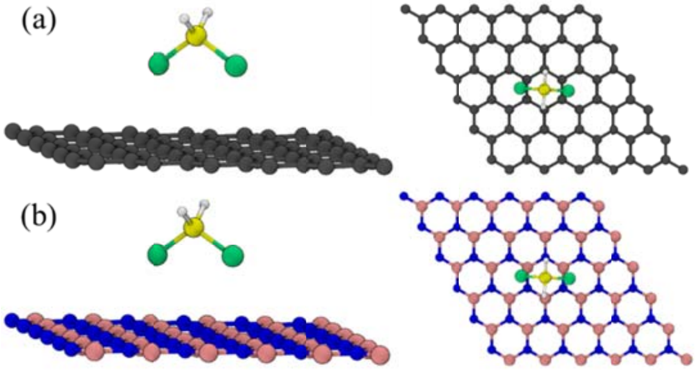


Figure S1. Side (left panels) and top (right panels) views for molecularly adsorbed DCS in the lowest energy configuration on graphene [(a)] and hexagonal boron nitride [(b)]. Green, yellow, white, black, blue, and pink balls represent Cl, Si, H, C, N and B atoms, respectively.

Two dimensional materials, particularly graphene (a = 2.466 Å via DFT-D3BJ) and hexagonal boron nitride (a = 2.508 Å), serve as single atomic layer thickness materials, providing a model where the magnitude of the dispersion correction (through E_b) can be predicted without considering the convergence as a function of slab thickness. A 6 × 6 supercell of each material was prepared utilizing a 4 × 4 × 1 Γ-centered k-point mesh and 15Å of vacuum to separate periodic sheets. E_b was predicted to be 0.25 eV in both cases.

Table S2. Binding strength (E_b) of DCS molecularly adsorbed on the (2 × 2) H/NH_2-terminated N-rich surface and dispersion correction energy (E_{disp}) for varying slab thicknesses as predicted via DFT-D3BJ.

Layers	E_b (eV)	E_{disp} (eV)
3	0.59	-0.61
4	0.58	-0.62
5	0.60	-0.62

DFT-D3BJ predicts a correction to the dispersion energy based on pair-wise interactions between each atom. It is thus necessary to use a slab with enough depth so that the adsorbed species interacts with a sufficient number of atoms in the regime of significant attractive dispersion forces to approximate a bulk surface. E_b was compared against varying slab thickness of a 2 × 2 β-Si_3N_4 slab featuring the H-saturated N-rich surface to ensure that the slab models included an adequate number of layers. The contribution of the DFT-D3BJ method (E_{disp}) to E_b is presented alongside E_b in Table S2. Both converged within 4 slab layers, thus the slab models used in this study included 3 bulk layers for all calculations. Three slab layers correspond to a slab thickness of 5.3 Å; this would indicate that the pairwise dispersion interactions decline to a negligible strength within this maximum distance.

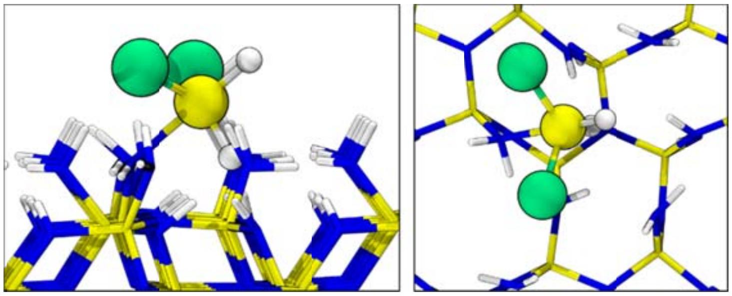


Figure S2. Side (left) and top (right) views of the transition state (E_a = 0.3 eV) Green, yellow, and white balls represent Cl, Si, and H atoms, respectively.

Table S3. Selected geometric parameters of the transition state as predicted via DFT-D3BJ (DFT).

	d (Å)		Angle
Si-NR	2.1 (2.5)	∠H-Si-H	97.5° (103.4°)
NR-H	1.0 (1.0)	∠Cl-Si-Cl	114.9° (116.3°)
Si-H	1.5 (1.5)	∠Si- NR-Si	137.5° (106.4°)
Si-Cl	2.1 (2.1)		

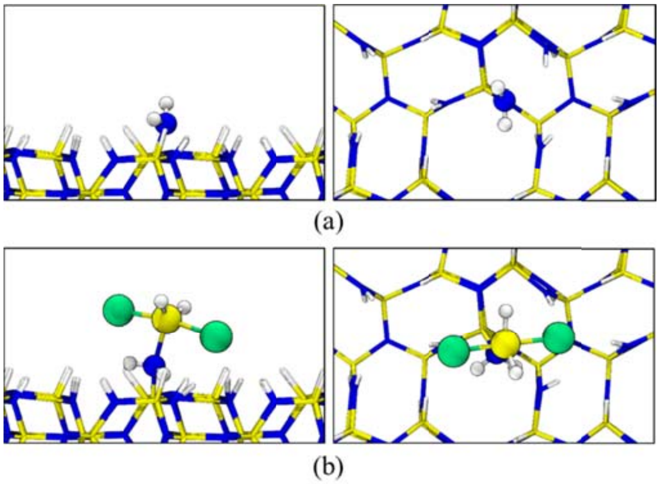


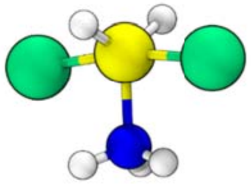
Figure S3. Side (Left) and top (right) views of (a) the alternative surface created by replacing all NH_2 groups with H and (b) the DCS-amine adduct on the surface. Green, yellow, blue, and white balls represent Cl, Si, N, and H atoms, respectively.

Table S4. Selected geometric parameters of the DCS-amine adduct on the surface as predicted via DFT-D3BJ.

	d (Å)		Angle
Si-N^R	1.93	∠H-Si-H	129.1°
N^R-H	1.02	∠Cl-Si-Cl	169.4°
Si-H	1.47		
Si-Cl	2.24		

Table S5. Selected geometric parameters of the gas-phase DCS-NH_3 adduct as predicted via DFT-D3BJ (DFT).) Green, yellow, blue, and white balls represent Cl, Si, N, and H atoms, respectively.

	d (Å)		Angle
Si-N^R	1.93 (1.93)	∠H-Si-H	129.1° (129.1°)
N^R-H	1.02 (1.02)	∠Cl-Si-Cl	169.4° (169.4°)
Si-H	1.47 (1.47)		
Si-Cl	2.24 (2.24)		



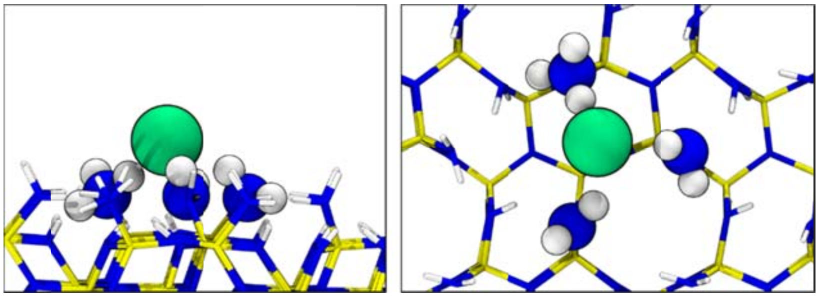


Figure S4. Side (left) and top (right) views of the ammonium complex on the N-rich β-Si_3N_4 (0001) surface. Green, blue, and white balls represent Cl^-, N, and H atoms, respectively, in –NH_3^+ and –NH_2.

Table S6. Selected geometric parameters of the ammonium complex (in Fig. S4) as predicted via DFT-D3BJ.

	d (Å)		Angle
H-Cl	1.89 (1.90)	∠Cl-H-N	173° (173°)
N-H	1.09 (1.09)	∠H-N-H	105° (105°)
N-Si	1.83 (1.83)		

The distance between H (of ammonium) and the chlroide anion of 1.89 Å demonstrates a distinct elongation compared to the distance between H and Cl of HCl(g), 1.28 Å as predicted via DFT-D3.

References

1 P. Yang, H. K. Fun, I. A. Rahman and M. I. Saleh, Two phase refinements of the structures of α-Si_3N_4 and β-Si_3N_4 made from rice husk by Rietveld analysis, *Ceram. Int.*, 1995, **21**, 137–142.

2 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.*, 2010, **132**, 0–19.

3 S. Grimme, S. Ehrlich and L. Goerigk, Effect of damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, 2011, **32**, 1456-1465.

4 L. Huang, B. Han, B. Han, A. Derecskei-Kovacs, M. Xiao, X. Lei, M. L. O'Neill, R. M. Pearlstein, H. Chandra and H. Cheng, Density functional theory study on the full ALD process of silicon nitride thin film deposition via BDEAS or BTBAS and NH3, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18501–18512.