Supporting Information

Role of Trimethylaluminum (TMA) in Low Temperature Atomic Layer Deposition of Silicon Nitride

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Determination of nitrogen monolayer sensitivity in XPS using an amine-terminated self-assembled monolayer (SAM)

To calibrate the nitrogen (N) coverage in XPS measurements, we prepared a surface with a well-defined N coverage. To do so, we start with an atomically flat H-terminated Si(111) surface, prepared by etching with 49% HF for 1 min 30 s, followed by 15 min in 40% NH_4F. An ester terminated monolayer was prepared using standard Schlenk line techniques by immediately inserting the freshly etched Si wafer into neat, dried ethyl undecylenate at 200 ^oC and left overnight (~ 10 h) under nitrogen flow. After hydrosilylation, the sample is removed from solution, rinsed three times with ethyl ether, then heated in boiling dichloromethane for 1-2 min and dried under N_2. The ester-terminated SAM was transformed into a carboxylic acid functional group by subsequent immersion in 0.25 M potassium tert-butoxide in DMSO (2 min), neat DMSO (30s), 2 M HCl (1 min), and H_2O.[1] Nitrogen was then introduced by grafting ethylene-diamine to the carboxylic acid group in a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) buffered in 2-(N-morpholino)ethanesulfonic acid (MES)[2] using well known EDC coupling techniques at room temperature resulting in amine termination. This process attaches two N per molecule to the surface. We estimate that with a maximum SAM coverage is ~66%[2], which corresponds to 1.3 monolayers worth of nitrogen due to the two N attached with the EDA molecule.

XPS spectra of the N1s core level were measured for both the amine terminated SAM (with 1.37 N coverage), as well as a silicon substrate after 1 pulse of di-sec-butylaminosilane (DSBAS) (Figure S1). For the amine-terminated SAM, the integrated area of the peak centered at ~400 eV in the SAM spectrum (within the 396 to 404 eV spectral range) is 1356 counts. To estimate our sensitivity in the bottom spectrum obtained after DSBAS exposure, we require that a detectable feature must have an integrated area at least 2x larger than that of the noise to emerge from the baseline. We estimate the error in measuring a peak area by varying the baseline in the region between 396 - 404 eV in the DSBAS spectrum; this error is ~4.0 counts. Therefore, we require ≥ 8 counts for N detection. Since 1356 counts corresponds to 1.37 monolayers, then our lower limit of detection is ~0.8% of a monolayer of nitrogen, which we round up to 1% of a monolayer.

1. Seitz, O.; Dai, M.; Aguirre-Tostado, F. S.; Wallace, R. M.; Chabal, Y. J. Copper−Metal Deposition on Self Assembled Monolayer for Making Top Contacts in Molecular Electronic Devices. *J. Am. Chem. Soc.* **2009**,

131, 18159-18167.

2. Nguyen, H. M.; Seitz, O.; Aureau, D.; Sra, A.; Nijem, N.; Gartstein, Y. N.; Chabal, Y. J.; Malko, A. V. Spectroscopic Evidence for Nonradiative Energy Transfer between Colloidal CdSe/ZnS Nanocrystals and Functionalized Silicon Substrates. Appl. Phys. Lett. 2011, 98, 161904/1–3.

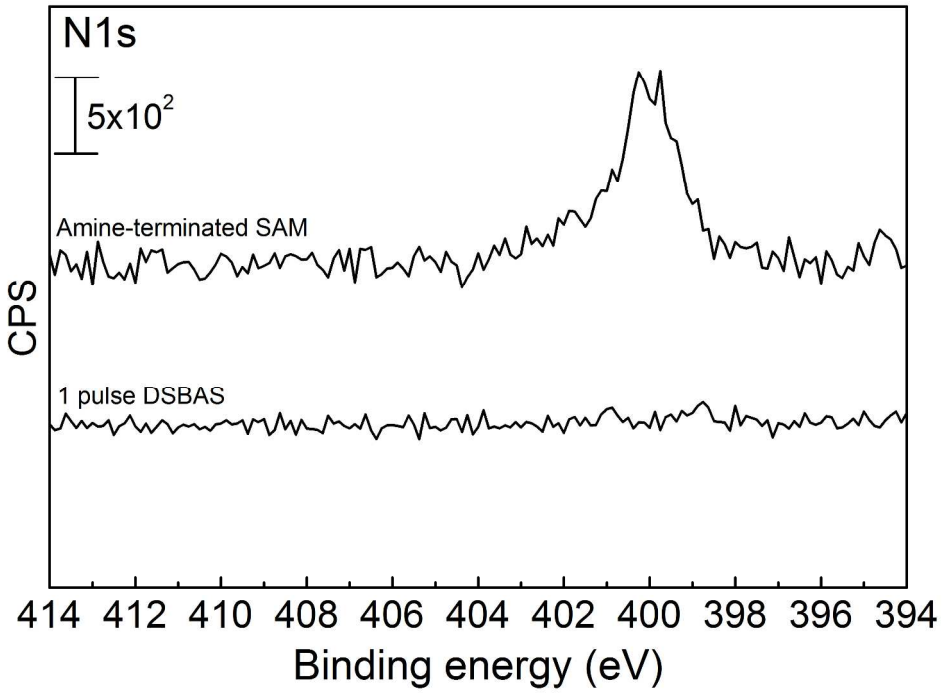


Figure S1. N1s XPS spectra of an amine-terminated SAM and OH-terminated silicon following 1 pulse of DSBAS.

Film Thickness determination from X-ray Photoelectron Spectroscopy (XPS)

The Si_3N_4 thickness was determined by measuring the attenuation of the substrate Si 2p core level intensity (overlayer attenuation model):

$$I_s = I_0 e^{-\frac{d}{(\lambda sin\theta)}} \qquad \textbf{(Eqn. S1)}$$

where I_s is the photoelectron yield with overlayer, I_o is the photoelectron yield w/o overlayer, d is the overlayer thickness, λ is the electron inelastic mean-free path, and θ is the XPS take-off angle (45^o in our case).

High resolution XPS spectra of the Si2p region (Figure S2) were taken of the as-deposited film, as well as the bare Si substrate obtained after sputtering with 3 kV Ar^+ ions to remove the film. From these spectra, the intensity of the bulk Si 2p core level at ~99eV was determined with and without the film. To estimate the inelastic mean free path (IMFP, λ) for electrons in the film (that unfortunately gets partly oxidized during transport to the XPS system), two limiting cases are considered, purely SiO_2 and purely Si_3N_4 films. The respective inelastic mean free paths, λ_{SiO2} = 3.772 nm and λ_{SiN} = 3.673 nm, are obtained from NIST Electron Inelastic-Mean-Free-Path Database: Version 1.2[1] for an electron kinetic energy of 1387 eV for electron from bulk Si (x-ray source energy - binding energy of bulk Si). Using λ_{SiO2} would describe a system where the Si_3N_4 film is completely oxidized, while using λ_{SiN} would describe a system with proper stoichiometry.

For the two limiting case, Eqn. S1 yields film thicknesses of 0.95 and 1.03 nm for SiO_2 and Si_3N_4, respectively.

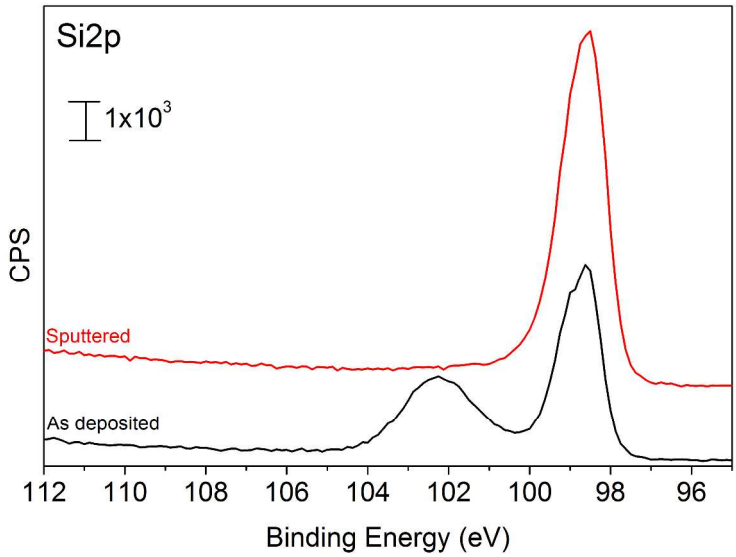


Figure S2. High resolution Si2p XPS spectra of the film as deposited and after being fully removed by 3 kV Ar^+ ion sputtering.

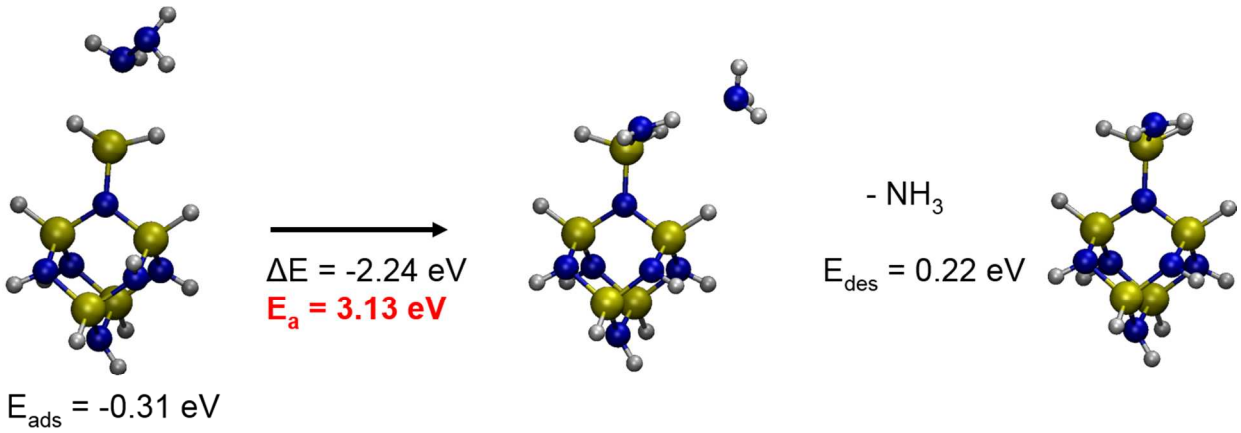
λ	I_s	I_o	$D_{Si_3N_4}$
λ_{SiO_2}	4818	14361	0.95 nm
λ_{SiN}	4818	14361	1.03 nm

Table S1. Parameters inserted into overlayer model for film thickness calculations

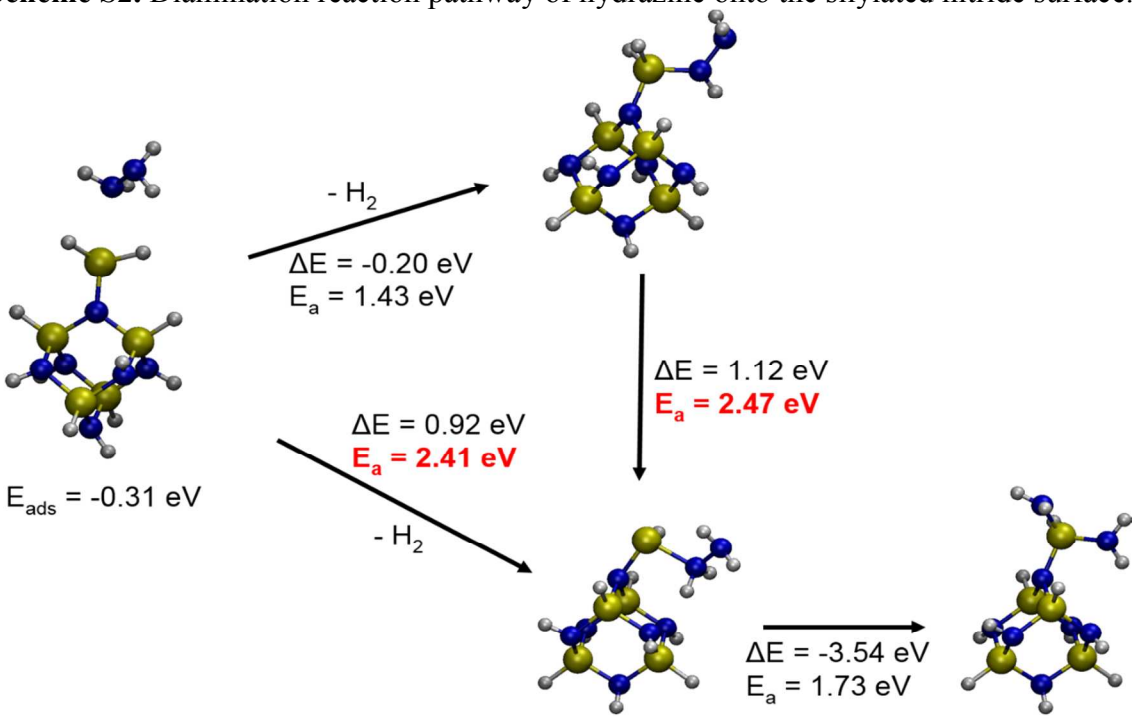
1. https://www.nist.gov/srd/nist-standard-reference-database-71

Hydrazine reactivity with Si-model surface (no Al)

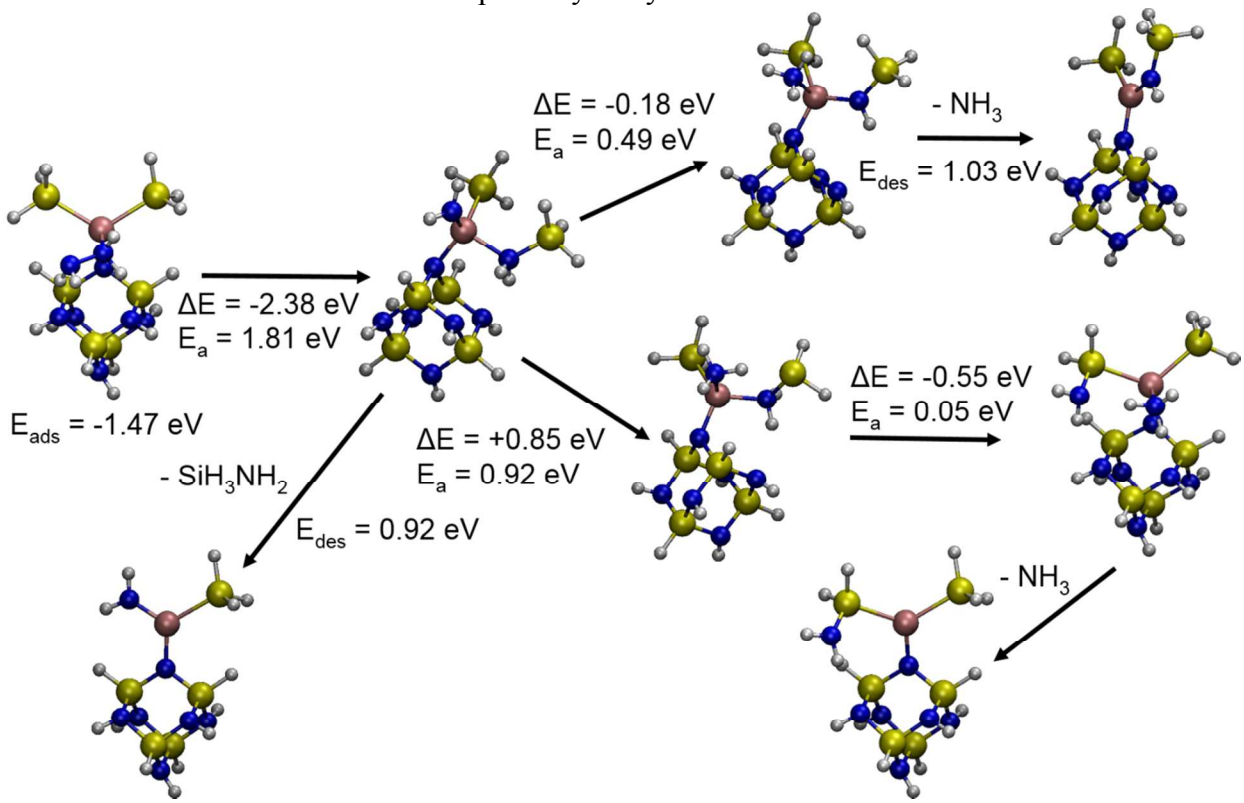
Scheme S1. Monoamination reaction pathway of hydrazine onto the silylated nitride surface.



Scheme S2. Diamination reaction pathway of hydrazine onto the silylated nitride surface.



Scheme S3. Monoamination reaction pathway of hydrazine onto the aluminum-activated surface.



Scheme S4. Monoamination reaction pathway of hydrazine onto the aluminum-activated surface.