Ammonia modification of oxide-free Si(111) surfaces

Tatiana Peixoto Chopra, Roberto C. Longo, Kyeongjae Cho, Yves J. Chabal*

Department of Materials Science and Engineering, University of Texas at Dallas, Richardson,
Texas 75080, USA

Abstract

Amination of surfaces is useful in a variety of fields, ranging from device manufacturing to biological applications. Previous studies of ammonia reaction on silicon surfaces have concentrated on vapor phase rather than wet chemical processes, and mostly on clean Si surfaces. In this work, the interaction of liquid and vapor-phase ammonia is examined on three types of oxide-free surfaces-- passivated by hydrogen, fluorine (1/3 monolayer) or chlorine -- combining infrared absorption spectroscopy, X-ray photoelectron spectroscopy and first-principles calculations. The resulting chemical composition highly depends on the starting surface; there is a stronger reaction on both F- and Cl-terminated than on the H-terminated Si surfaces, as evidenced by the formation of Si-NH₂. Side reactions can also occur, such as solvent reaction with surfaces, formation of ammonium salt by-products (in the case of 0.2 M ammonia in dioxane solution), and nitridation of silicon (in the case of neat and gas phase ammonia reactions for instance). Unexpectedly, there is formation of Si-H bonds on hydrogen-free Cl-terminated Si(111) surfaces in all cases, whether vapor phase or neat liquid ammonia is used. First principles modeling of this complex system suggests that step edge surface defects may play a key role in enabling the reaction under certain circumstances, despite the endothermic nature for Si-H bond formation.

Keywords

Silicon modification; Ammonia; Characterization; FTIR; XPS; DFT

Introduction

Surface amination has become more important for applications in microelectronics,[1-4] biotechnology,[5-8] and nanotechnology.[1, 6, 9, 10] Ammonia has been widely used to achieve surface nitridation and amination, particularly on silicon surfaces. Early work examined adsorption and dissociation of gas phase ammonia on clean, reconstructed Si(100) 2x1[11-17] or

Si(111) 7x7 [14, 18-20] surfaces; only recently has the attention been placed on ammonia reactions with passivated surfaces, such as H-terminated silicon surfaces. Examples of work involving modified Si surfaces include the stepwise NH_3 vapor dissociation on H-terminated Si(111) surfaces,[21] and ammonia/amine reactions on Cl-terminated Si (100) and Si(111) surfaces using both vapor[22-24] and wet chemical[24-27] conditions. In this work, new questions arise, highlighting the need for fundamental understanding of the reaction mechanisms. In particular, the reaction of neat liquid ammonia on passivated silicon remains completely unexplored. Neat liquid ammonia with its high molecular density, can provide a faster and cheaper route of amination and nitridation of silicon surfaces.

The interaction of liquid-phase ammonia on passivated silicon surfaces was therefore systematically examined using well-defined, atomically flat and oxide-free Si(111) surfaces to minimize side reactions at steps and defect sites. In the case of silicon, it has been shown atomically flat H-terminated Si(111) surfaces can be prepared [28-30] and used to graft alkene-terminated molecules by hydrosilylation.[5, 6] Starting from this H-terminated surface, complete chlorination can be achieved, using either wet chemistry (PCl_5) or gas phase chlorination, without roughening the surface.[24, 32, 33] Fluorination of silicon is more difficult as fluorine easily etches silicon surfaces. However, starting from an atomically flat H-terminated Si(111) surface, Michalak *et al.*[31] have developed a method to produce a mixed surface with 1/3 ML F- and 2/3 ML H-termination (where ML stands for monolayer), remaining atomically flat and stable through numerous wet chemical steps. Because the Si-F bond is surrounded by a ring of six Si-H bonds, this is an excellent model surface to compare the relative reactivity of amines with Si-F and Si-H surface groups. On the premise that Si-F reacts faster than Si-H with amines,[23] yet less readily than Si-Cl (halogen reactivity increases with increasing atomic number), this model surface is ideal to study reactions with the isolated Si-F groups.

The present work is directly motivated by the need to achieve amination by wet chemical methods because they are more compatible with most applications. However, liquid phase processes with ammonia are complex (e.g. partial Si oxidation), so the study of gas phase ammonia has also been performed in order to unravel and confirm mechanistic details. In both cases, we have used H-, Cl- and F-terminated Si(111) model surfaces. Overall, we find that ammonia reactivity is highest for Cl-terminated, less reactive on the 1/3 ML F-terminated, and

virtually absent on H-terminated Si (111) surfaces. In all cases, there is some oxidation of the silicon surface, varying in degree. The 0.2M ammonia in dioxane solution also produces surface salts, particularly on the 1/3 ML F- and Cl-terminated surfaces, although similar surface reactions are observed irrespective of the surface termination. Neat liquid ammonia reacts with both on 1/3 ML F- and Cl-terminated Si(111) surfaces, as evidenced by IR and XPS data, but not with H-terminated Si(111) surfaces.

The possibility of the beginning of nitridation and formation of a Si-NH-Si linkage is also discussed based on the resulting infrared spectrum and XPS energies. Unexpectedly, we also observe the formation of Si-H bonds on Cl-terminated Si(111) surfaces for all forms of amine exposure along with complete removal of all Si-Cl bonds. Computational modeling of this complex system suggests that despite the endothermic nature of formation, step edge surface defects may play a key role in the Si-H formation under certain circumstances.

Methods

Experimental Details

The following chemicals were purchased from Sigma-Aldrich: anhydrous methanol (CH_3OH , 99.8%), anhydrous 0.5M ammonia solution in dioxane (NH_3), phosphorus pentachloride (purum p.a. PCl_5 , $\geq 98.0\%$), and anhydrous toluene ($\text{C}_6\text{H}_5\text{CH}_3$, 99.8%); before being opened the chemicals were placed inside a $\text{N}_2(\text{g})$ -purged glovebox. Aqueous ammonium fluoride (40 wt %) and aqueous hydrofluoric acid (49 wt %) used for creation of a hydrogen surface termination were obtained from J.T. Baker. Aqueous hydrogen peroxide (30 wt %) and concentrated (18 M) sulfuric acid used for piranha cleaning were obtained from Fisher Scientific. All deionized H_2O was obtained from a Millipore Advantage A10 water filtration system, characterized by a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$. The substrate used for the experiments consisted of N-type (phosphorus-doped, resistivity of $24\text{--}34 \text{ }\Omega\cdot\text{cm}$) float-zone (FZ) double-side polished Si(111) wafers, cut into $1.5 \text{ cm} \times 3.8 \text{ cm}$ pieces for infrared transmission and XPS measurements.

Organic contamination on native oxide silicon samples was chemically removed using a piranha solution (3:1 concentrated (18 M) H_2SO_4 /30% $\text{H}_2\text{O}_2(\text{aq})$) for 30 min at 80°C . The three surface terminations were prepared as follows:

1) **H-termination**: Si(111) samples were H-terminated by a 30 s dip in 10–20% $\text{HF}(\text{aq})$ followed by a 2.5 min dip in 40% $\text{NH}_4\text{F}(\text{aq})$, and a final rinse in H_2O for 10 s.[34] This latter

procedure produces an atomically smooth surface for tens to hundreds of nanometers depending on the sample miscut. Since atomically flat surfaces could be achieved repeatedly with the same Si(111) sample, samples were reoxidized by piranha cleaning then re-etched with the HF/ NH₄F solutions.

2) **F-termination**: A partially fluorinated (1/3 ML Si-F) termination on H-terminated Si(111) samples, henceforth referred to as the 1/3 ML F-termination, was achieved using the method of Michalak *et al.*[31] based on intermediate methoxylation in methanol followed by deoxygenated 49 wt % HF immersion.

3) **Cl-termination**: The chlorine-termination was achieved following the method described in literature by Bansal *et al.*,[32, 35] by reacting a H-terminated Si(111) surface with a 14 mL solution of ~0.6M phosphorus pentachloride (PCl₅) in chlorobenzene and ~40 mg of benzoyl peroxide radical initiator, added prior to the sample introduction. The reaction was conducted at 90°C for 45 mins, then cooled 10 mins prior to a sequential rinsing of chlorobenzene and acetonitrile and drying under inert conditions.

Once the oxide-free Si(111) surfaces were passivated by H, F and H, or Cl, further functionalization was performed either inside a nitrogen glovebox using 14mL of a 0.2 M ammonia in dioxane solution in a glass vial for 30 min at room temperature, followed by a dioxane solvent rinse; or using a glass vial attached to a Schlenk line under argon, with N₂(liq)-liquefied ammonia gas kept under a dry ice/acetone bath for a 30 min reaction with the respective surface termination. After reaction with liquid ammonia, the surface was rinsed with 20 mM 2-methylimidazole in toluene solution, followed by toluene rinsing and immediate N₂(g) drying.

Alternatively, vapor phase experiments were conducted in a stainless steel chamber with a base pressure of ~10⁻⁶ torr, with an ammonia pressure of 2 Torr for 3 min, followed by N₂(g) purge for 200 s.

IR absorption data for solution and liquid ammonia experiments were obtained with a Fourier-transform infrared (FTIR) spectrometer (Nicolet 6700) located in a N₂(g)-purged glovebox. Spectra were recorded with a nominal 4 cm⁻¹ resolution between 400 and 4000 cm⁻¹ in transmission, at an angle of incidence of 74° with respect to the silicon surface normal, averaging 1500 single beam spectral scans for each sample. Reference spectra were obtained on the respective starting surfaces, such as H-, 1/3 ML F- or Cl-termination and on the original

oxidized surfaces. *In-situ* infrared measurements were performed for vapor phase experiments, in a chamber equipped with KBr windows and spectral measurements taken at 80 °C for all vapor phase experiments.

XPS analysis was performed *ex-situ* with a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA) spectrometer equipped with a concentric hemispherical analyzer under ultrahigh vacuum conditions (10^{-9} mbar) and an Al K α X-ray source (15 keV, filament current 20mA). Spectra were recorded at a 45° takeoff angle with respect to the surface. A sample area of 100 $\mu\text{m} \times 100 \mu\text{m}$ was analyzed using a pass energy of 29.25 eV for the detailed elemental scans. The spectra obtained were analyzed using the CASA XPS software, with the spectral peaks calibrated to the C 1s peak of adventitious carbon, set at 285 eV. The monolayer coverage of particular surface groups (Φ_{ov}) on the Si(111) surface was calculated using the simplified method outlined by Haber *et al*[36]:

$$\Phi_{ov} = \left(\frac{\lambda \sin \theta}{a_{ov}} \right) \left(\frac{SF_{Si}}{SF_{ov}} \right) \left(\frac{\rho_{Si}}{\rho_{ov}} \right) \left(\frac{I_{ov}}{I_{Si}} \right) \quad (1)$$

This equation assumes $\lambda_{Si} \approx \lambda_{ov} = \lambda$, with λ being the escape depth of the photoelectrons. The quantity ρ_{Si} is the density of the silicon substrate (2.33 g/cm³) and ρ_{ov} the density of the atoms of interest in the overlayer (N=0.808 g/cm³, Cl=1.5625 g/cm³, F=1.505 g/cm³, with reported values for the liquid phase of each diatomic element). I is the integrated area of the overlayer and substrate peaks, θ is the XPS take-off angle (45°), and the sensitivity factor (SF) of each element (0.283, 0.477, 1, and 1.77 for Si, N, F, and Cl respectively) used can be found in the MultiPak Version 6.0 software (supplied by Physical Electronics). The atomic diameter, a_{ov} , of the species in the overlayer estimated from their liquid state (N=0.31 nm, Cl=0.34 nm, F=0.28 nm) is calculated using equ 2:

$$a = \sqrt[3]{\frac{A}{\rho N_{Av}}} \quad (2)$$

where a is the atomic diameter, A is the molecular weight of the atom, ρ the density of atoms in liquid phase, and N_{Av} is Avogadro's number (6.022×10^{23} atoms/mol).

The approximation for $\lambda_{Si} \approx \lambda_{ov} = \lambda$ is valid because the kinetic energy (in eV) of the overlayer atoms (F 1s, Cl 2p, N 1s) and the Si(111) substrate (Si 2p) are similar. Therefore, the escape depth of silicon atoms ($\lambda_{Si}=\lambda$) on a well-defined, fully chlorinated surface is used in the monolayer calculations of eq 1. The escape depth is approximated using the empirical equation

$$\lambda = 0.41a^{1.5}E^{0.5} \quad (3)$$

where E is the Si kinetic energy in eV, λ the attenuation length (in nm), a the diameter of the Cl atoms (0.34 nm). Using eq 3, λ_{Si} is calculated to be 3.0 nm.

The 102-103 eV binding energy region of the XPS Si 2p core level was used to estimate the percentage of surface nitridation/oxidation. The percentage was calculated as a ratio of the fitted peak area in the 102-103 eV region to the overall fitted area of the Si 2p core level.

For each of the surface terminations, the error bars associated with the estimated coverages were calculated by taking the standard deviation resulting from analysis of three independent sets of measurements.

Computational Details

Ab initio calculations were performed using density-functional theory (DFT) within the Projector-Augmented Wave (PAW) approach,[37] as implemented in the Vienna *Ab initio* Simulation Package (VASP).[38, 39] The total energy calculations were performed using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) functional,[40] and the electronic wave functions were expanded into plane waves up to a kinetic energy of 400 eV. The supercell used in this work consists of 8 atomic layers of H- or Cl-terminated Si(111) surface plus adsorbed molecules and a vacuum region equivalent to 16 atomic layers. The 7 uppermost layers of Si as well as the adsorbates degrees of freedom were allowed to relax without any constraint to a tolerance of 10^{-4} eV in the total energy and 0.01 eV/Å in the forces on every atom. For all the structures considered, a Brillouin zone sampling with a 4x4x1 k -point mesh within the Monkhorst-Pack scheme[41] was used to ensure a convergence of 1 meV/unit cell.

Eigenmodes and vibrational frequencies were obtained with the force-constant (FC) approach, diagonalizing the mass-weighted second derivative matrix (Hessian) in case of the adsorbed species and the top Si layer. The restriction to the atoms of the top layer and the adsorbed species is legitimate because the Eigenmodes of these atoms do not overlap with the Eigenmodes of the bulk material. The kinetic barriers, transition states and reaction pathways were obtained using the climbing image-nudged elastic band method (CI-NEB).[42] This method has previously been shown to be reliable in obtaining the minimum energy path (MEP) between a set of two different states, where the reaction path is divided into a set of images “connected

with a spring”. During the relaxation, the initial and final states are kept frozen while the images move according to the constraint of the “elastic band”. The MEP is then found when the components of the forces perpendicular to the “elastic band” vanish, the relative positions of the images and the barrier being determined by the parallel components of the forces.[43, 44]

Results

a. Reaction of 0.2 M ammonia-dioxane solution with H-, 1/3 ML F-, and Cl-terminated Si(111) surfaces

The focus on dilute ammonia was motivated by a recent study by Tian *et al.*,[27] who examined the reaction of ammonia in a tetrahydrofuran (THF) solution on Cl-terminated Si(111) surfaces. This work showed that a complete removal of chlorine occurs at room temperature, with only the formation of Si-NH-Si bonds observed; there was no spectroscopic evidence for Si-NH₂ formation (i.e. no detectable NH₂ stretch and deformation modes), with only three infrared regions shown: 1500-1660 cm⁻¹, 2020-2140 cm⁻¹, and 3100-3600 cm⁻¹. While the reactions reported by Tian *et al.* had well controlled temperatures, the concentration of ammonia in the THF solution was unknown. Since dioxane is a molecule similar to tetrahydrofuran and ammonia/dioxane solutions are available with known concentrations, we have studied the reaction of 0.2 M ammonia in a dioxane with the three model surfaces (H-, 1/3 ML F- and Cl-terminated Si(111) surfaces); we also expand on the infrared regions reported by Tian *et al.* in order to carefully explore the surface composition after ammonia exposure. Figure 1 summarizes the i) IR and ii) XPS data for all three surfaces (A: Cl-, B: 1/3ML F-, and C: H-terminated), described sequentially below.

Figure 1 i) Infrared spectra of the reaction of 0.2 M ammonia in dioxane solution with A) Cl-terminated Si(111) surface, B) 1/3 ML F-terminated Si(111) surface, and C) H-terminated Si(111) surface. The 750-1800 cm^{-1} and 2400-4000 cm^{-1} infrared region are referenced to their respective H-termination, and the 1850-2400 cm^{-1} region referenced to the silicon oxide termination. ii) XPS N1s core level for the reaction on A) Cl-terminated Si(111) surface, B) 1/3 ML F-terminated Si(111) surface, C) H-terminated Si(111), showing amine attachment, molecular ammonia and charged/ oxidized amine on the surface terminations.

The first observation is the presence of strong sharp bands at $\sim 3050 \text{ cm}^{-1}$ and $\sim 3150 \text{ cm}^{-1}$ along with a mode at $\sim 1410 \text{ cm}^{-1}$, most clearly seen on the 1/3 ML F- and Cl-terminated silicon surfaces (Figure 1i: A-B). These features are directly associated with ammonium salt stretch and bending vibrations.[45] Note that the H-terminated Si surface (Figure 1i: C) contains almost no ammonium salt infrared vibrations; as a result weak bands associated with the $\nu(\text{N-H})$ stretch vibrations appear at higher frequency, located at 3160 cm^{-1} and 3345 cm^{-1} , with a significantly weaker $\delta(\text{NH}_4^+)$ band at 1410 cm^{-1} . The peaks at 402.3 eV, 401.9 eV, and 402.2 eV for the H-, 1/3 ML F-, and Cl-terminated surfaces, respectively, in the XPS N1s core level spectra (Fig. 1ii) are consistent with surface charging or ammonia dative bonding, which supports the ammonium salt assignment. The amount of ammonium surface salts trapped at the surface appears to correlate with surface polarity, with the lowest salt amount observed on the non-polar H-terminated Si(111) surfaces and the highest amount observed on the polar Cl-terminated Si(111) surfaces. Note that spectral features associated with the dioxane solvent are also observed on all three surfaces: there are IR absorption bands in the $\nu(\text{C-H})$ stretch ($2800\text{-}3000 \text{ cm}^{-1}$) and CH_x deformation ($1000\text{-}1450 \text{ cm}^{-1}$) regions, which we attribute to dioxane physisorbed on the surface.

The second main observation is that molecular NH_3 can also be detected in some cases, possibly due to the presence of the ammonium salts of the surface. For instance, the IR spectra in Figure 1i of all three surfaces contain IR bands at 1660 cm^{-1} and 1600 cm^{-1} , attributed to the asymmetric bending mode of ammonia multilayers in a solid-like state[46, 47] and physisorbed ammonia gas,[18, 48, 49] along with a band at 880 cm^{-1} , attributed to the ammonia umbrella mode, $\delta(\text{NH}_3)$. [48] The observation of N1s core levels at 400 eV, 400.4 eV, and 400.3 eV in the XPS of the H-, 1/3 ML F-, and Cl-terminated surfaces, respectively, is consistent of the presence of molecular ammonia as well[18, 19, 50].

Finally, the data also indicates ammonia reacted, i.e. grafting of NH_2 on some of these surfaces. This reaction is most easily identified by the appearance of the $\delta(\text{NH}_2)$ deformation mode, typically in the $1530\text{-}1600 \text{ cm}^{-1}$ region. For 0.2 M ammonia in dioxane, a shoulder at $\sim$

1550 cm^{-1} is observed on all three surfaces, initially assigned to the $\delta(\text{NH}_2)$ mode. Supporting evidence of ammonia dissociation is provided by the N1s core level spectra in XPS (Figure 1 ii). All surface terminations have a peak in the 398.3-399 eV region associated with NH_2 species.[11, 18, 19, 50]

By measuring the area of this peak and using the equation outlined in the methods section, an estimated NH_2 monolayer surface coverage is obtained: $24 \pm 6\%$ for the H-terminated Si(111) surface (N1s peak at 398.5 eV), $21 \pm 4\%$ on the 1/3 ML F-terminated Si(111) surface (N1s peak at 398.4 eV), and $24 \pm 8\%$ on the Cl-terminated Si(111) surface (N1s peak at 399.0 eV); with the error bars of the estimates dominated by experimental reproducibility considerations from three independent measurements.

Another evidence for ammonia dissociation is the presence of a $\nu(\text{Si-N})$ mode in the infrared spectra, as a small peak at $\sim 810 \text{ cm}^{-1}$ for the 1/3 F- and Cl-terminated Si(111) surfaces, and a weak shoulder on the H-terminated Si(111) surface, in good agreement with the 781 cm^{-1} calculated $\nu(\text{Si-N})$ mode (Table 4). While the $\nu(\text{Si-N})$ mode is usually reported at $835\text{-}850 \text{ cm}^{-1}$ in molecules,[18, 21] it has also been reported in the $790\text{-}817 \text{ cm}^{-1}$ region for ammonia vapor dissociation on reconstructed Si(100) 2×1 and Si(111) 7×7 surfaces. [12, 18]

Besides the reaction of ammonia to form NH_2 , unexpected IR spectra features are present on the Cl-terminated surfaces, namely the formation of Si-H species. On H- and 1/3 ML F-terminated silicon surfaces, the original Si-H stretch modes at 2083 and 2092 cm^{-1} , respectively, are weakened and red-shifted to 2077 and 2073 cm^{-1} , respectively, as is typical for a partial reaction or deterioration of the initial Si-H termination. On both surfaces, a small component appears at $2245\text{-}2250 \text{ cm}^{-1}$, corresponding to the formation of trace amount of subsurface oxide (H-Si-O_x) or oxynitride ($\text{H-Si-O}_x\text{N}_y$). The combined integrated area of the SiH bands with and without backbonded oxide result in an estimated Si-H coverage of: $45 \pm 4\%$ ML for the H-terminated surfaces, and $68 \pm 3\%$ ML (compared to the initial $66 \pm 3\%$ ML) Si-H coverage of for the 1/3 ML F-terminated Si(111) surface. Surprisingly, on the initially hydrogen-free Cl-terminated Si surface, Si-H appears in the form of two clear $\nu(\text{Si-H})$ absorption bands at 2070 cm^{-1} and 2250 cm^{-1} after exposure to 0.2 M ammonia in dioxane solution. This behavior is similar to what we recently observed upon diamine reaction with Cl-terminated Si surfaces[51] and will be discussed in the discussion section.

The main conclusion for the interaction of 0.2M ammonia in dioxane is that there is accumulation of salts, mostly on the Cl- and F-terminated surfaces and some oxidation of all surfaces. In all cases, the solvent (dioxane) interacts with the surface, contaminating the final result. Table 1 summarizes the data presented above for 0.2M ammonia in dioxane.

Table 1 Summary of 0.2 M ammonia in dioxane reaction results on the modified Si(111) surfaces. The SiH (with, $\text{Si-H}+\text{O}_x\text{Si-H}$, and without, Si-H, backbond oxidation) and estimated NH_x monolayer coverages (NH_x component of XPS N 1s peak in 398-399 eV range), and % ratio of oxidized XPS Si 2p peak have their peak location in parenthesis.

Surfaces	<u>$\nu(\text{N-H})$ IR</u> <u>mode, cm^{-1}</u> ($\delta(\text{N-H})$, cm^{-1})	<u>% ML</u> <u>Si-H</u> (cm^{-1})	<u>% ML</u> <u>Si-H+O_xSi-H</u> (O _x Si-H cm^{-1})	<u>XPS NH_x</u> <u>% ML</u> (eV)	<u>XPS Si 2p</u> <u>% Ratio of</u> <u>Si^{3+,4+}/Si⁰</u> (eV)
H-Si(111)	3160, 3345 (1410)	44 ± 4 (2077)	45 ± 4 (2245)	24 ± 6 (398.5)	11 ± 4 (102.8)
1/3 ML F-Si(111), 2/3 ML H-Si(111)	~3050, ~3150 (1410)	49 ± 4 (2073)	68 ± 3 (2250)	21 ± 4 (398.4)	9 ± 4 (103.3)
Cl-Si(111)	~3050, ~3150 (1410)	21 ± 4 (2070)	29 ± 1 (2250)	24 ± 8 (399.0)	15 ± 2 (102.7)

b. Liquid ammonia reaction on H-, 1/3 ML F- and Cl-terminated Si(111) surfaces

In an attempt to avoid ammonium salt formation and remove oxygen-containing solvents from the ammonia solution, which may have fostered surface oxidation/nitridation, immersion in neat liquefied ammonia was studied. Ammonia gas was liquefied using the methods outlined in the methods section and kept liquid at a temperature below -33°C using an acetone/dry ice bath. After the liquid ammonia treatment, the surfaces were sequentially rinsed in a solution of 20 mM 2-methylimidazole in toluene followed by neat toluene, all at room temperature, in order to limit molecular ammonia physisorption, then quickly dried with $\text{N}_2(\text{g})$.

The absence of vibrational bands at $\sim 3050 \text{ cm}^{-1}$ and $\sim 3150 \text{ cm}^{-1}$ associated with $\nu(\text{NH}_4^+)$ and $\sim 1410 \text{ cm}^{-1}$ associated with $\delta(\text{NH}_4^+)$, confirm the absence of ammonium salt deposition on all three surfaces from the IR spectra of Figure 2. Instead, there are signatures for NH species, characterized by NH stretch modes at higher frequencies (3160 cm^{-1} to 3500 cm^{-1}). For instance, for liquid ammonia reacted on H-terminated Si(111) surfaces, the $\nu(\text{NH})$ IR bands are found at $\sim 3160 \text{ cm}^{-1}$ and $\sim 3370 \text{ cm}^{-1}$, with a shoulder at $\sim 3490 \text{ cm}^{-1}$. On 1/3 ML F-terminated Si(111)

surfaces, the modes are located at $\sim 3150\text{ cm}^{-1}$ and $\sim 3340\text{ cm}^{-1}$, with a shoulder at $\sim 3480\text{ cm}^{-1}$. On the Cl-terminated surfaces, the $\nu(\text{NH})$ modes are shifted to $\sim 3170\text{ cm}^{-1}$ and 3320 cm^{-1} (as a shoulder). Also, amine hydrohalide vibrations[45, 52] are observed on the Cl-terminated surfaces: $\nu(\text{NH}_3^+)$ and $\nu(\text{NH}_2^+)$ bands at $\sim 3100\text{ cm}^{-1}$ and $\sim 2700\text{ cm}^{-1}$, respectively, and $\delta(\text{NH}_3^+)$ bending modes at $\sim 2500\text{ cm}^{-1}$ and 2400 cm^{-1} .

In addition to NH species, XPS reveals the presence of molecular ammonia. The component of the N1s level at $\sim 400\text{ eV}$ is associated with molecular ammonia. There is also a component at $\sim 401\text{ eV}$, which we tentatively attribute to charged species, although it could also be attributed to other species as described below.

The low reaction temperature of liquid ammonia leads to easy condensation during the post-reaction rinsing, adsorbing the 2-methylimidazole rinsing molecule on the surface, as evidenced by characteristic signatures in both the IR and XPS spectra. Infrared vibrations associated with the imidazole molecule[53, 54] are observed in the $2800\text{-}3000\text{ cm}^{-1}$ region for $\nu(\text{C-H})$, at $\sim 1750\text{ cm}^{-1}$ for $\nu(\text{C=N})$, and at 1660 cm^{-1} and 1600 cm^{-1} attributed to imidazole ring vibrations. These observations suggest that this solvent quickly adsorbs on the cold surface and cannot be fully removed by the subsequent toluene wash. Although these modes could also be attributed to solid and gas-phase ammonia as in the previous section, since the $\delta(\text{NH}_3)$ umbrella mode at 880 cm^{-1} is also present in the infrared spectra, the strong modes observed at $\sim 1100\text{ cm}^{-1}$ and $\sim 1170\text{ cm}^{-1}$ are most likely associated with the imidazole molecule. These strong bands make it difficult to unravel the possible presence of vibrational bands at $\sim 1180\text{ cm}^{-1}$ associated with Si-NH-Si bonds or $\delta(\text{N-H})$, and bands at $\sim 880\text{-}900\text{ cm}^{-1}$, associated with Si-N-Si phonon modes.[21, 45]

Evidence for Si-NH₂ formation is not straightforward in either IR or XPS spectra because of other contributions, requiring some analysis. In the IR spectra, there is a discernible $\delta_{\text{scissor}}(\text{NH}_2)$ bending mode at 1545 cm^{-1} on the 1/3 ML F-terminated Si(111) surface, which appears as a shoulder at $\sim 1560\text{ cm}^{-1}$ in the H- and Cl-terminated Si(111) surfaces, all consistent with ammonia dissociation (Figure 2). In the XPS spectra, we must first take into account the observation of physisorbed 2-methylimidazole, characterized by two kinds of nitrogen species: the C=N species giving rise to a N1s core level peak at 398.1 eV and the C-NH-C species with a peak at 401 eV .[53-55] If there are only physisorbed (i.e. intact) 2-methylimidazole molecules, we should expect to see a 1:1 ratio between the two peak areas. Assuming that the whole of the

401 eV peak belongs to the imidazole moiety (since no vibrations belonging to oxidized amines such as hydroxylamine or charged nitrogen species are observed using IR), [25, 56] we then subtract its area from the area of the ~398 eV peak (imidazole C=N species). Any remaining intensity will then be associated with NH_x species. Using this method, the NH_x coverages are estimated to be $1 \pm 10\%$ on the H-terminated Si(111) surface (398.1 eV), $20 \pm 7\%$, on the 1/3 ML F-terminated Si(111) surface (398.5 eV), and $42 \pm 11\%$ on the Cl-terminated Si(111) surface (398.3 eV). Note that since we know from IR spectroscopy that there are charged amine species on the Cl-terminated Si(111) surface, the above method underestimates the amine coverage of the Cl-terminated Si(111) surface; i.e. the 401 eV peak area in this case is due to the presence of both amine charging and the methylimidazole molecule. When the 401 eV peak area of the Cl-terminated Si(111) surface is subtracted from the measured peak area at 398 eV, removing not only the methylimidazole area contribution but also area associated with the NH_x coverage, leading to a lower calculated amine coverage.

Figure 2 i) IR absorption spectra showing the reaction of liquid ammonia on a A) Cl-terminated Si(111) surface, B) 1/3 ML F-terminated Si(111) surface, and C) H-terminated Si(111) surface. All surfaces are referenced to their previous surface termination, the 1850-2400 cm^{-1} region referenced to the silicon oxide termination. ii) XPS N1s core level for the reaction on A) Cl-terminated Si(111) surface, B) 1/3 ML F-terminated Si(111) surface, C) H-terminated Si(111), showing possible amine attachment, imidazole species and charged (or possibly oxidized) amine on the different surface terminations.

A band at $\sim 750 \text{ cm}^{-1}$ is tentatively assigned to the Si-N stretch vibration, providing further evidence for the formation of amines; note that it is partially obscured in the spectrum of the Cl-terminated surface due to the presence of the imidazole out-of-plane bending mode at 740 cm^{-1} . The frequency of this mode is slightly lower than the value usually reported in the 820-850

cm^{-1} range for Si-N, which could be due to the presence of NH_3 instead (symmetric NH_3 bending vibration), or be associated with the Si-H bending vibration of a step-edge Si-NH-Si bridging structure.[21]

In summary, liquid ammonia clearly reacts with F- and Cl-terminated silicon surfaces. Its effect on existing Si-H bonds, however, was less clear. For H-terminated Si(111) surfaces, $97 \pm 3\%$ of the starting Si-H ($\text{H-Si-O}_x + \text{Si-H}$ without oxide) was preserved, with most of the Si-H stretch band remaining at 2083 cm^{-1} (only a weak band developed at $\sim 2262 \text{ cm}^{-1}$, associated with backbonded $\text{H-Si-O}_x/ \text{H-Si-O}_x\text{N}_y$ stretch modes). The presence of a Si 2p peak located at 103.2 eV in the XPS spectra suggests that some oxidation and/or nitridation occurs during the process, making up $11 \pm 5\%$ of the overall Si 2p peak. For 1/3 ML F-terminated surfaces, $69 \pm 6\%$ of the 2/3 ML Si-H bonds remained on the surface with its main IR absorption band at 2077 cm^{-1} and a smaller band at $\sim 2260 \text{ cm}^{-1}$, associated with backbonded $\text{H-Si-O}_x/ \text{H-Si-O}_x\text{N}_y$ stretch modes. Again, the presence of O or N backbonds is supported by XPS with a component at 103.3 eV making up $14 \pm 4\%$ of the XPS Si 2p peak. For Cl-terminated Si(111) surfaces, ammonia reacted to form Si-H, as evidenced by the appearance of a new $\nu(\text{Si-H})$ band located at $\sim 2090 \text{ cm}^{-1}$ (note that there is also a weak band at $\sim 2245 \text{ cm}^{-1}$, associated with backbonded $\text{H-Si-O}_x/ \text{H-Si-O}_x\text{N}_y$ stretch modes) yielding an estimated $24 \pm 7\%$ Si-H coverage. In this case, examination of the Si 2p spectrum at 102.9 eV reveals that this oxidized/nitridized component constitutes $6 \pm 3\%$ of the overall XPS Si 2p spectrum. Data highlights for the important values found are tabulated in Table 2 below.

Table 2 Summary of liquid ammonia reaction results on the modified Si(111) surfaces. The SiH (with, $\text{Si-H}+\text{O}_x\text{Si-H}$, and without, Si-H, backbond oxidation) and estimated NH_x monolayer coverages (NH_x component of XPS N 1s peak in 398-399 eV range), and % ratio of oxidized XPS Si 2p peak have their peak location in parenthesis.

Surfaces	<u>$\nu(\text{N-H})$ IR mode,</u> <u>cm^{-1}</u> ($\delta(\text{N-H})$, cm^{-1})	<u>% ML</u> <u>Si-H</u> (cm^{-1})	<u>% ML</u> <u>Si-H+O_xSi-H</u> (<u>O_xSi-H</u> cm^{-1})	<u>XPS NH_x</u> <u>% ML</u> (eV)	<u>XPS Si 2p</u> <u>% Ratio of</u> <u>Si^{3+,4+}/Si⁰</u> (eV)
H-Si(111)	$\sim 3160, \sim 3370$, shoulder 3490 (shoulder ~ 1560)	82 ± 10 (2083)	97 ± 3 (2262)	1 ± 10 (398.1)	11 ± 5 (103.2)
1/3 ML F-Si(111), 2/3 ML H-Si(111)	$\sim 3150, \sim 3340$, shoulder 3480	62 ± 10 (2077)	69 ± 6 (2260)	20 ± 7 (398.5)	14 ± 4 (103.3)

	(1545)				
Cl-Si(111)	~3100, ~3170, shoulder 3320 (shoulder ~1560)	18 ± 1 (2090)	24 ± 7 (2245)	42± 11 (398.3)	6 ± 3 (102.9)

c. Vapor phase ammonia reaction on the Cl-terminated Si(111) surface

In the previous sections, the analysis of ammonia reaction has been hindered by a number of factors that make it difficult to draw conclusions on the bonding configuration, such as the presence of charged amine species, a $\delta(\text{NH}_2)$ vibration that is hard to distinguish, and the presence of the physisorbed imidazole. To eliminate potential spectral contributions from the solvent and to better understand the chemical attachment on Cl-terminated surfaces, treatment in vapor phase ammonia (2 Torr) was studied as a function of substrate temperature. As summarized in supplementary information (Figure S1), ammonia gas begins to react on the Cl-terminated Si(111) surface at 250°C, as evidenced by two weak bands at 1000 cm^{-1} and 880 cm^{-1} associated with the Si-N TO_{asym} and Si-N TO_{sym} modes respectively, and a weak $\delta(\text{NH}_2)$ mode at 1540 cm^{-1} . All these fingerprint bands increase in intensity with temperature and are well defined in Figure 3 after a 3 min NH_3 exposure at 275°C. To minimize contamination by physisorbed contaminants (e.g. hydrocarbons), the sample was preannealed at 250°C for 3 min in vacuum prior to NH_3 exposure.

Figure 3 Vapor phase infrared spectroscopy and XPS spectra of the ammonia reaction on a Cl-terminated Si(111) surface at a sample temperature of 275°C. Infrared spectrum is referenced to the 250°C pre-annealed Cl-terminated Si(111) surface prior to ammonia exposure.

The infrared spectrum in Figure 3, referenced to the preannealed sample, is characterized by $\nu(\text{N-H})$ modes at $\sim 3260 \text{ cm}^{-1}$ and $\sim 3330 \text{ cm}^{-1}$ along with a sharp $\delta(\text{NH}_2)$ deformation vibration at 1540 cm^{-1} , a weak $\delta(\text{NH}_2)$ twisting vibration at 1340 cm^{-1} , and modes at $\sim 1170 \text{ cm}^{-1}$, $\sim 1130 \text{ cm}^{-1}$, $\sim 1080 \text{ cm}^{-1}$, and $\sim 990 \text{ cm}^{-1}$ attributed to the $\delta(\text{N-H})$ of the Si-NH-Si vibration, Si-N LO mode, Si-O stretch vibration, and Si-N TO_{asym} , respectively. There is also a sharp band at 825 cm^{-1} , assigned to $\nu(\text{Si-N})$, providing further evidence for NH_3 reaction. The single peak in the XPS N1s spectrum located at 398.4 eV in Figure 3 is attributed to the formation of NH_x ($x = 1$ or 2) and oxynitride species, yielding an estimated N coverage of $\sim 106 \pm 10\%$ ML. Here, a monolayer (ML) is defined as $7.8 \times 10^{14} \text{ atoms/cm}^2$ on the flat Cl-terminated Si(111) surface, ideally with no defect sites. As will be further discussed in the discussion section, attachment at defect sites and oxynitride formation is believed to roughen the surface and generate more defect sites, causing the N coverage estimate to become over a 100% ML.

Interestingly, surface Si gets hydrogenated in the process, as evidenced by weak $\nu(\text{Si-H})$ absorption bands at $\sim 2070 \text{ cm}^{-1}$ and 2210 cm^{-1} . The latter arises from $\text{O}_2\text{Si-H}/\text{O}_x\text{N}_y\text{Si-H}$ species due to subsurface oxidation/nitridation, consistent with the observed Si-N LO/TO modes and Si 2p core level at 102.7 eV, characterized by a $4 \pm 1\%$ concentration of the overall XPS Si 2p spectrum. Importantly, as shown in the supplementary information, the appearance of Si-H follows that of NH_2 , suggesting that NH_2 is a necessary intermediate for Si-H formation.

A summary of the results discussed above is displayed in Table 3.

Table 3 Summary of vapor ammonia reaction results on the Cl-terminated Si(111) surface. The SiH and estimated NH_x monolayer coverages (NH_x component of XPS N 1s peak in 398-399 eV range), and % ratio of oxidized XPS Si 2p peak have their peak location in parenthesis.

Surfaces	<u>$\nu(\text{N-H})$ IR mode, cm^{-1}</u> ($\delta(\text{N-H})$, cm^{-1})	<u>% ML Si-H</u> (cm^{-1})	<u>% ML Si-H+O_xSi-H</u> (O _x Si-H cm^{-1})	<u>XPS NH_x % ML</u> (eV)	<u>XPS Si 2p % Ratio of Si^{3+,4+}/Si⁰</u> (eV)
Cl-Si(111)	$\sim 3260, \sim 3330$ (1540)	3 ± 2 (~ 2070)	7 ± 2 (2220)	106 ± 10 (398.4)	4 ± 1 (102.7)

Discussion

a. NH_2 surface attachment

We start this discussion with the reaction of liquid ammonia, drawing on results from vapor phase processing as needed. The case of ammonia in solution is more complex and discussed later.

The formation of a $\delta(\text{NH}_2)$ band in the $1540\text{-}1600\text{ cm}^{-1}$ range gives a clear spectroscopic indication that ammonia chemisorption occurs. For liquid phase ammonia processing, ammonia chemisorption is most clearly observed for the $1/3\text{ ML}$ F-terminated Si(111) surface with the appearance of the $\delta(\text{NH}_2)$ band at 1545 cm^{-1} , the frequency of which is in good agreement with the calculated frequency of 1533 cm^{-1} reported in Table 4. This band is also present for the Cl-terminated Si(111) surface, appearing more as a shoulder than a well-defined vibration.

Overall, the observed reactivity of liquid ammonia follows the predictions of DFT calculations: negligible reaction on the H-terminated Si(111) surface and most ($\sim 42\%\text{ ML}$) on the Cl-terminated Si(111) surface as shown in Table 2. These two reactions on the flat Si(111) terrace sites are modeled by DFT as shown in Figure 4 and the total energy and reaction barriers summarized in Table 4. The first step of ammonia dissociation on H- and Cl-terminated Si(111) surfaces is slightly thermodynamically exothermic (-0.011 eV) for H-Si(111) and slightly endothermic for Cl-Si(111) (0.385 eV), which appears contrary to observations. However, as shown below the reactivity is controlled by the kinetic barrier, not the total energy.

Figure 4 DFT final configurations for the different NH_3 adsorption reactions on flat surface terrace sites considered in this work (see Table 4 for the reaction energies). Yellow spheres represent Si atoms; white, H; turquoise, Cl and blue spheres N atoms, respectively.

This higher reactivity on the Cl-terminated surfaces can be explained by DFT modeling. As reported in Table 4 and schematically shown in Figure 5, there is a difference in the Si-NH_2 formation kinetic barriers for H- and Cl-terminated Si(111) surfaces. These barriers are 0.3 eV lower on the Cl-terminated than on the H-terminated Si(111) surface, leading to much better reaction on Cl-terminated surfaces. A similar finding has also been reported in a recent work for ethylenediamine reaction on the same Si(111) surface terminations.[51]. Therefore, there is no reaction on H-terminated silicon surfaces, even though the product configurations (NH_2) are thermodynamically slightly more favorable (0.39 eV, Table 4) than for Cl-terminated silicon surfaces. These results indicate that the reaction on the Cl-terminated Si(111) surface is kinetically driven even if thermodynamically less favorable.

Table 4 Reaction energies, kinetic barrier and infrared frequency modes for the adsorption of NH_3 on Si(111) flat terrace sites for H- and Cl-terminated surfaces.

Flat Si(111) Terrace Sites

H-terminated Si(111)	Reaction energy (eV)	Kinetic Barrier (eV)	IR modes (cm⁻¹)
Si-NH ₂ + H ₂	-0.011	1.5	$\delta_{\text{scissor}}(\text{NH}_2)$ -1533 $\delta_{\text{rock}}(\text{NH}_2)$ -798 $\nu(\text{Si-N})$ -781
Si-N-Si + 2H ₂ (backbond)	2.417		
Si-NH-Si + 2H ₂ (surface)	2.799		
Si-NH-Si + 2H ₂ (subsurface)	2.675		
Cl-terminated Si(111)			
Si-NH ₂ + HCl	0.385	1.2	
Si-N-Si + HCl + H ₂ (backbond)	2.899		
Si-NH-Si + 2HCl (surface)	3.623		
Si-H, Si-NH ₂ + Cl ₂	2.671		$\nu(\text{Si-H})$ -2070 $\delta_{\text{scissor}}(\text{NH}_2)$ -1530 $\nu(\text{Si-N})$ -819 $\delta_{\text{rock}}(\text{NH}_2)$ -799 $\delta(\text{Si-H})$ -602

Table 4 also shows that subsequent decomposition of the ammonia molecule into Si-NH-Si on either surface is not thermodynamically favorable; Si-NH-Si bond formation is calculated to be endothermic by ~2.7 eV for the H-terminated surface and ~3.6 eV for the Cl-terminated Si(111) surface. Again, the total energy may not dictate the final configuration, and a mixture of Si-NH₂ and Si-NH-Si bonds may form, as discussed below.

Figure 5 Kinetic barrier for the dissociative adsorption of NH₃ on the Cl-terminated Si(111) surface (left) and H-terminated Si(111) surface (right). The insets show the initial, transition and final states, respectively. Yellow spheres represent Si atoms; white spheres, H atoms; turquoise spheres, Cl atoms; and blue spheres N atoms, respectively.

The strongest evidence of further NH₂ dissociation comes from the observed IR absorption band at $\sim 1180\text{ cm}^{-1}$ attributed to the Si-NH-Si stretch vibration[21] and the theoretically calculated shift in the Si-N stretch mode from 781 (Table 4) to 752 cm^{-1} (Table 5) in going from NH₂ to NH. For vapor phase ammonia on Cl-terminated Si(111) surfaces, two clear IR bands are observed at $\sim 1170\text{ cm}^{-1}$, assigned to the $\delta(\text{N-H})$ of the Si-NH-Si vibration, and 825 cm^{-1} , assigned to the Si-N stretch vibration. For the liquid ammonia reaction on the Cl-terminated surface, the mode at $\sim 1170\text{ cm}^{-1}$ is present but the $\nu(\text{Si-N})$ stretch vibration is shifted to $\sim 750\text{ cm}^{-1}$, supporting the conclusion that Si-NH-Si species formed on the surface. An explanation for the formation of Si-NH-Si bonds is shown in Figure 6 for Si step edge reactions. DFT calculations in Table 5 suggest that with an exothermic reaction of -0.001 eV for H-termination and -1.937 eV for Cl-termination, Si-NH-Si species could easily occur at silicon defect sites. Furthermore, the calculated Si-NH-Si IR vibrations of $\delta(\text{N-H})$ at 1154 cm^{-1} , $\nu_{\text{asym}}(\text{Si-N})$ at 838 cm^{-1} , and $\nu_{\text{sym}}(\text{Si-N})$ at 755 cm^{-1} , in Table 5 for the Cl-terminated surface are in good agreement with the liquid and vapor phase IR results.

The case of 0.2 M ammonia in dioxane is more complex. As illustrated in Table 1, there is spectroscopic evidence for ammonia chemisorption on the different surface terminations: first, there is a shoulder at $\sim 1550\text{ cm}^{-1}$ observed on all three surfaces, in good agreement with the calculated $\delta(\text{NH}_2)$ bending mode of 1533 cm^{-1} in Table 4; second, the characteristic $\nu(\text{Si-N})$ vibration at 810 cm^{-1} is also detectable, in agreement with the calculated $\nu(\text{Si-N})$ mode at 781

cm⁻¹ and the calculated $\delta_{\text{rock}}(\text{NH}_2)$ mode at 798 cm⁻¹ (Table 4). The N 1s core level observed at ~398.5 eV by XPS for each of the surfaces is also consistent with chemisorption, although this component could have two origins: 1) Si-NH₂ formation, as reported in the literature in the range of 398.5- 399 eV,[11, 17] or 2) oxidation of nitrogen in Si-Si backbonds, i.e. oxynitride formation, which is also characterized by a N 1s core level in this binding energy region.[26, 56] Table 1 shows similar (~20% ML) nitrogen coverage for all three surface terminations, in contrast to the surface termination coverage dependence of the liquid phase ammonia reaction (Table 2) and preferential Cl-terminated reaction by DFT calculations (Figures 4-6 and Tables 4-5). It is possible the dioxane solvent surface interaction caused surface roughening and introduction of new defect sites, thus lowering the reaction barrier and enabling surface reactions and/or oxidation to occur. Curiously, the oxide/oxynitride % ratio of the 0.2M ammonia in dioxane reactions is also similar for the three surface terminations. The correlation between the calculated N coverage and oxide/oxynitride % ratio, lead to the conclusion that the calculated nitrogen coverage in this case, may primarily be due to the formation of oxynitride species on the surface along with some Si-NH₂ formation.

b. Si-H formation on Cl-terminated Si(111) surfaces

As was suggested in the previous section, the experimental data and calculations point to the formation of Si-NH-Si bonds *at defect sites*. As shown in Figure 6, the defect site also contains a neighboring Si-H bond, which could also explain the mechanism for Si-H bond formation on the previously H-free Cl-terminated Si(111) surfaces. Surprisingly, the amount of newly formed Si-H bonds on the Cl-terminated Si(111) surfaces is similar regardless of the liquid treatment (~25% ML, Table 1-2); it is believed the vapor phase ammonia treatment had a lower concentration of Si-H (~7% ML, Table 3) since the exposure temperature used (275°C) was between the temperatures shown in Figure S1 to have no visible Si-H formation (250°C) and visible Si-H formation (300°C). The temperature of 275°C was chosen with the goal of chemisorbing the maximum ammonia amount while trying to minimize surface nitridation.

Figure 6 DFT final configurations for the different NH_3 adsorption reactions on surface step edge sites considered in this work (see Table 5 for the reaction energies). Yellow spheres represent Si atoms; white, H; turquoise, Cl and blue spheres N atoms, respectively.

Therefore, two different mechanisms are considered for Si-H bond formation on the Cl-terminated Si(111) surface. First, on the atomically flat Cl-terminated Si (111) surface, Figure 5 and Table 5 show that dissociative adsorption of NH_3 leads to the formation of Si-NH_2 and Si-H surface species and the release of Cl_2 . The reaction energy for this mechanism is 2.67 eV (Table 4, Si-H, NH_2), *i.e.*, it is an endothermic process that needs to overcome a moderately large thermodynamic barrier (and, obviously, a much larger kinetic barrier). Second, on a stepped Cl-terminated Si(111) surface (modeled in Figure 6), the adsorbed NH_3 molecule can form a Si-NH-Si, bridge between the step edge atom and the neighboring Si atom on the bottom terrace, releasing 2 HCl molecules or one HCl and one Cl_2 molecules in two consecutive adsorption processes. This second mechanism for hydrogenation at the step edge is thermodynamically more favorable (exothermic by -1.94 eV for release of 2 HCl, as Si-NH-Si in Table 5; and slightly endothermic by 0.226 eV for release of HCl and Cl_2 , as Si-H, Si-NH-Si in Table 5) and is therefore much more favorable than on flat surfaces. Although the Cl-terminated surface may start out with few defect sites, further surface roughening can occur and create more defect sites

through surface oxidation and molecular attachment at the defect sites. This is evident for the ammonia liquid phase reaction, where the observed $\nu(\text{Si-H})$ in this case occurs at $\sim 2090 \text{ cm}^{-1}$ and is in good agreement with the calculated vibration at 2108 cm^{-1} for the Si-H in the Si-H, Si-NH-Si bridge configuration.

In contrast, the vapor phase ammonia on the Cl-terminated surface has a $\nu(\text{Si-H})$ band $\sim 2070 \text{ cm}^{-1}$, although there is also evidence for Si-NH-Si formation. This band exactly matches the calculated vibration in Table 4 for the Si-H, Si-NH₂ DFT configuration in Figure 4, suggesting that Si-H can be formed on terrace sites as well, for substrates at 275°C (i.e. thermally activated process). Note that the vapor phase reactions were conducted at a temperature (275°C) chosen to reduce the amount of Si-NH-Si and nitridation formation, leading to hydrogenation on the terrace sites prior to the creation of new defect sites. This behavior can be observed in Figure S1, with the first Si-H vibration observed $\sim 2080 \text{ cm}^{-1}$ at 300°C then shifting to $\sim 2090 \text{ cm}^{-1}$ at 350°C . In both cases, the NH₃ adsorption terminates with Si-H surface species.

Table 5 Reaction energies and infrared frequency modes for the adsorption of NH₃ on Si(111) step edge sites for H- and Cl-terminated surfaces.

Surface Step Sites		
H-terminated Si(111)	Reaction energy (eV)	IR modes (cm ⁻¹)
Si-NH ₂ + H ₂	0.088	$\delta_{\text{scissor}}(\text{NH}_2)$ -1535 coupled $\nu_{\text{asym}}(\text{Si-N, Si-H})$ -895 $\delta_{\text{rock}}(\text{NH}_2)$ -798 coupled $\nu_{\text{sym}}(\text{Si-N, Si-H})$ -745
Si-NH-Si + 2H ₂	-0.001	$\delta(\text{NH})$ -1147 $\nu_{\text{asym}}(\text{Si-N})$ -843 $\nu_{\text{sym}}(\text{Si-N})$ -752
Cl-terminated Si(111)		
Si-NH ₂ + HCl	0.035	
Si-NH-Si + 2HCl	-1.937	
Si-H, Si-NH-Si + HCl + Cl ₂	0.226	$\nu(\text{Si-H})$ -2108 $\delta(\text{NH})$ -1154 $\nu_{\text{asym}}(\text{Si-N})$ -838 $\nu_{\text{sym}}(\text{Si-N})$ -755

c. Surface salt formation

Processing in 0.2 M ammonia in dioxane reaction led to the stabilization of ammonium salts at the surface, characterized by vibrations at $\sim 3050\text{ cm}^{-1}$ and $\sim 3150\text{ cm}^{-1}$ (Table 1), the amount of which is correlated to the surface polarity for the 1/3 ML F- to the Cl-terminated Si(111) surfaces. The H-terminated Si(111) surface however, did seem to contain ammonium salts (very low surface polarity), having N-H vibrations (3160 cm^{-1} and 3345 cm^{-1}) at higher wavenumbers indicative of a less H-bonded, constrained surface vibration. It is believed the dioxane solvent actually stabilized salt adsorption on the silicon surfaces instead of removing it, similarly to what has been observed on Si_3N_4 surfaces after HF etching.[4] The F 1s peak was observed at 687.3 eV instead of 685.6 eV[31] and the Cl $2p_{3/2}$ peak at 199.6 eV instead of 199.0 eV[32, 35] after the ammonia reaction. The shift of these positions to higher binding energies indicate that the silicon-halogen bonds have become more covalent, i.e. closer to what is characteristic for hydrohalide salts, known to form during amine-halide reactions.[52, 57-59] Due to the shared charged between the hydrogen halide and the amine, these species are highly affected by the polarity of the nitrogen environment. The N 1s peak attributed to the ammonium species is found $\sim 402\text{ eV}$ for all the three surface terminations, and is in reasonable agreement with the reported binding energy of NH_4Cl salt at 401 eV.[23] It is possible that the presence of physisorbed ammonia molecules on the surface could also increase the salt binding energy. As shown in Table 6, the 1/3 ML F- and Cl-terminated Si(111) surfaces retained $\sim 70\%$ of their halogen peak area, however, due to the peak shifts discussed above, this halogen estimate is not attributed to the original silicon-halogen termination but to the surface hydrohalide salt formation observed via IR and XPS. The possibility that the dioxane solvent also chemisorbed on the surface cannot be ruled out, especially on the Cl-terminated surface where literature speculates similar molecules such as THF may undergo a ring opening reaction and attach on the surface.[35]

The situation is different for processing in liquid ammonia. While there was no sign of salt formation in the IR spectra of the H- and F-terminated Si(111) surfaces, several charged vibrations (NH_2^+ and NH_3^+) were observed on the Cl-terminated surface after ammonia reaction, much like after ethylenediamine processing of the same Cl-terminated surface.[51] The ammonia-processed 1/3 ML F- and Cl-terminated Si(111) surfaces are characterized by halide binding energies similar to those of processed in ammonia dioxane solution: the F 1s peak at 687.9 eV and the Cl $2p_{3/2}$ at 199.9 eV. The main difference between liquid ammonia and

ammonia in dioxane is shown in Table 6: only $4 \pm 3\%$ of the fluorine and $33 \pm 8\%$ of the chlorine area remains on the surface as a salt, much less than after ammonia in dioxane processing. This indicates that while the 2-methylimidazole rinse caused some solvent physisorption on the silicon surface, it is also more efficiently removed the halogen salts. For completeness, we note that imidazole rinsing is unlikely to affect the surface during wet processing, because the position of the N 1s core level is consistent with the expected energies (398 eV and 401 eV) for unreacted imidazole molecules. The vapor phase ammonia reaction at 275°C on the Cl-terminated surface further confirms the remaining halogen content from wet chemical processing is a salt formation. After gas phase ammonia exposure, a small Cl 2p_{3/2} peak is observed at 199.2 eV (only $4 \pm 4\%$ ML), attributed to a remnant of the starting chlorine termination (not a salt). The amount of remnant Cl depends on the substrate temperature: at 250°C ~20% ML remains; at 300°C there is no Cl 2p signal detected, although silicon nitride forms as evidenced by Si₃N₄ phonon absorption in the IR spectra.

Table 6 Comparison of fluorine and chlorine removal depending on ammonia surface treatment.

	<u>0.2M Ammonia in Dioxane</u>		<u>Liquid Ammonia</u>		<u>Vapor Ammonia</u>
	% Fluorine Remaining	% Chlorine Remaining	% Fluorine Remaining	% Chlorine Remaining	% Chlorine Remaining
1/3 ML F-Si(111), 2/3 ML H-Si(111)	70 ± 7	-----	4 ± 3	-----	-----
Cl- Si(111)	-----	70 ± 5	-----	33 ± 8	4 ± 4

Conclusion

In summary, we show that the ultimate surface composition after amination depends on the initial termination of oxide-free silicon surfaces and the ammonia reaction method used. Specifically, liquid ammonia reacts more strongly on Cl-terminated Si surfaces, then F-terminated Si surfaces, with negligible chemisorption on H-terminated Si(111) surfaces. The NH₂ spectral fingerprint is most clearly seen on the 1/3 ML F-terminated Si(111) surface and observed on Cl-terminated Si(111) surfaces as a shoulder. Using both XPS and IR absorption spectra, vapor phase ammonia reaction on Cl-terminated Si(111) surfaces, have strong evidence

that a mixture of Si-NH₂ and Si-NH-Si surface species are formed, with the neat liquid ammonia reaction on Cl-terminated Si(111) surfaces supporting the surface nitridation/ oxynitride formation also observed in vapor phase. An unexpected hydrogenation of the initially fully Cl-terminated Si(111) surface is also observed regardless of the ammonia exposure method used, and is attributed to a reaction mechanism involving the formation of Si-NH-Si species bridging the edge Si atom and the neighboring terrace Si atom at the bottom of the step. This understanding provides a basis for optimizing ammonia modification of oxide-free surfaces, opening new options for the processing of new silicon-based devices.

Author Information

*Corresponding Author
chabal@utdallas.edu

Notes

The authors declare no competing financial interest.

Supporting Information

Infrared spectra of vapor phase NH₃ reaction on Cl-terminated Si(111) surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Graphical Abstract

Ammonia

H-, 1/3 ML F- or Cl-terminated Si(111)

Si-NH₂

Si-NH-Si