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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, TX 75080, USA

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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-NH_2. 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 of neat liquid ammonia is used. The 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.

1. 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) 2×1 [11–17] or Si(111) 7×7 [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 0.2 M 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-

* Corresponding author.
E-mail address: chabal@utdallas.edu (Y.J. Chabal).

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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.

2. Methods

2.1. Experimental details

The following chemicals were purchased from Sigma-Aldrich: anhydrous methanol (CH_3OH, 99.8%), anhydrous 0.5 M ammonia solution in dioxane (NH_3), phosphorus pentachloride (purum p.a. PCl_5, ≥98.0%), and anhydrous toluene($C_6H_5CH_3$, 99.8%); before being opened, the chemicals were placed inside a N_2(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 MΩ•cm. The substrate used for the experiments consisted of N-type (phosphorus-doped, resistivity of 24–34 Ω•cm) float-zone (FZ) double-sided polished Si(111) wafers, cut into 1.5 cm × 3.8 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% H_2O_2(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% HF(aq) followed by a 2.5 min dip in 40% NH_4F(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/NH_4F 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 ~0.6 M phosphorus pentachloride (PCl_5) 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 min, then cooled 10 min 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 14 mL 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 N_2(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 N_2(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 N_2(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 N_2(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 Kα X-ray source (15 keV, filament current 20 mA). Spectra were recorded at a 45° takeoff angle with respect to the surface. A sample area of 100 μm × 100 μm 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]:

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

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/cm^3) and ρ_{ov} the density of the atoms of interest in the overlayer (N = 0.808 g/cm^3, Cl = 1.5625 g/cm^3, F = 1.505 g/cm^3, 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 takeoff 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 Eq. (2):

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

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

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

where *E* is the Si kinetic energy in eV, λ is the attenuation length (in nm), and *a* is 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.