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Silicon Surface Functionalization Targeting Si–N Linkages

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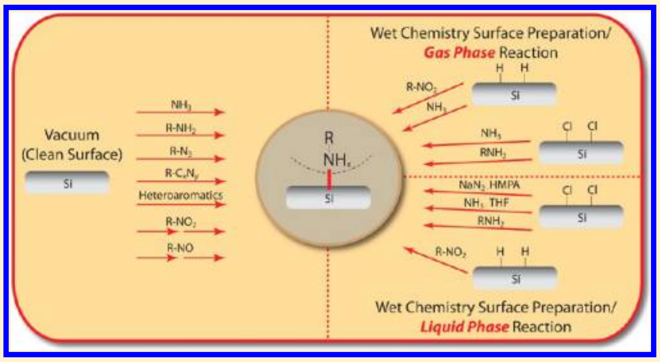

ABSTRACT: Silicon substrates have been a fascinating topic of fundamental and applied research for well over 50 years. They have attracted even more attention over the last couple of decades with advances in chemical functionalization that made oxide-free silicon surfaces a reality. Fundamentally new electronic properties and chemical reactivity became available, and the focus of chemical research turned more toward targeting specific chemical bonds and functionalities on silicon. Although thermodynamics clearly drives most processes under ambient conditions toward the formation of an oxide layer, kinetic control of the oxidation processes and thermodynamic tricks based on gaining stability of surface monolayers with high-density assembly have allowed for the formation of stable Si–C bonds and Si–O–C linkages on oxide-free silicon crystals. This feature article targets recent advances in making Si–N linkages on the same oxide-free single crystals. It covers the range of chemical approaches to achieving this goal and offers possible chemistry that can take advantage of the systems produced. The present status of the field and the future directions of its development will be considered.

1. INTRODUCTION

Silicon substrates have been the foundation of the microelectronics industry and the focus of fundamental and applied research for over 50 years. Of course, this attention brought up a number of new applications, including optoelectronics, biosensors, and photovoltaics. In particular, the nearly perfect atomically flat interface between the Si(100) face of a silicon single crystal and the native oxide layer has been the driving force in most of the current applications of silicon, and the chemical surface modification targeted SiO_x as a reagent. Fundamentally, the applications of the Si/SiO_x systems have a very well determined limit because the minimal thickness of the silicon dioxide required for practical applications without leakage currents prevents further miniaturization of silicon-based components. Thus, novel oxide-free interfaces were targeted and in many instances built for alternative applications of silicon platforms. Our group has been investigating semiconductor surface modification and functionalization for well over a decade, including surface reactions in ultrahigh vacuum, wet chemistry approaches, and density functional theory studies. In this feature article, we will mostly focus on the recent progress in building and understanding hybrid interfaces between silicon and organic materials and try to place the work of our group within the context of the development of the entire multifaceted field.

Two main problems with oxygen-free silicon-based hybrid interfaces are (1) for practical applications they must be oxygen-free, otherwise the electronic properties of the target layers suffer from charge traps even on silicon with only a few percent surface oxide, and (2) all of the chemical modification steps have to be directed toward making stable covalent bonds on a silicon surface and not on a convenient SiO_x platform. And therein lies the biggest concern: thermodynamically, SiO_x is extremely stable, even compared to silicon nitride or silicon carbide. A heat of formation of −910.86 kJ/mol for silica (quartz)[1] compared to very modest values for silicon carbide (−73.22 kJ/mol)[2] and silicon nitride (approximately −851 kJ/mol depending on the polymorph[3] but only one-third of that if normalized per silicon atom) should clearly drive any chemistry for surface modification that forms an organic interface for oxidation as soon as the surface is exposed to oxygen-containing species, making it virtually impossible to use thermodynamics to achieve the goal of oxide-free silicon interfaces. Another way to compare the stability of targeted interfaces is based on the energies of corresponding chemical bonds. Average bond dissociation enthalpies for Si–O are approximately 460 kJ/mol, but this number is only 318 kJ/mol for Si–C and 355 kJ/mol for Si–N.[4] On top of that, the bond energy for a Si–Si single bond is around 222 kJ/mol, making it thermodynamically unstable compared to most organic alternatives.

So what can be done to produce a stable oxide-free interface between silicon and organic materials? In terms of using thermodynamics as a driving force, the formation of Si–N or Si–C linkages should be compensated for by other stabilization energies to avoid their oxidation, leading to the formation of stable silicon oxide species. This can be achieved by using high-density assembly, for example (with energy stabilization

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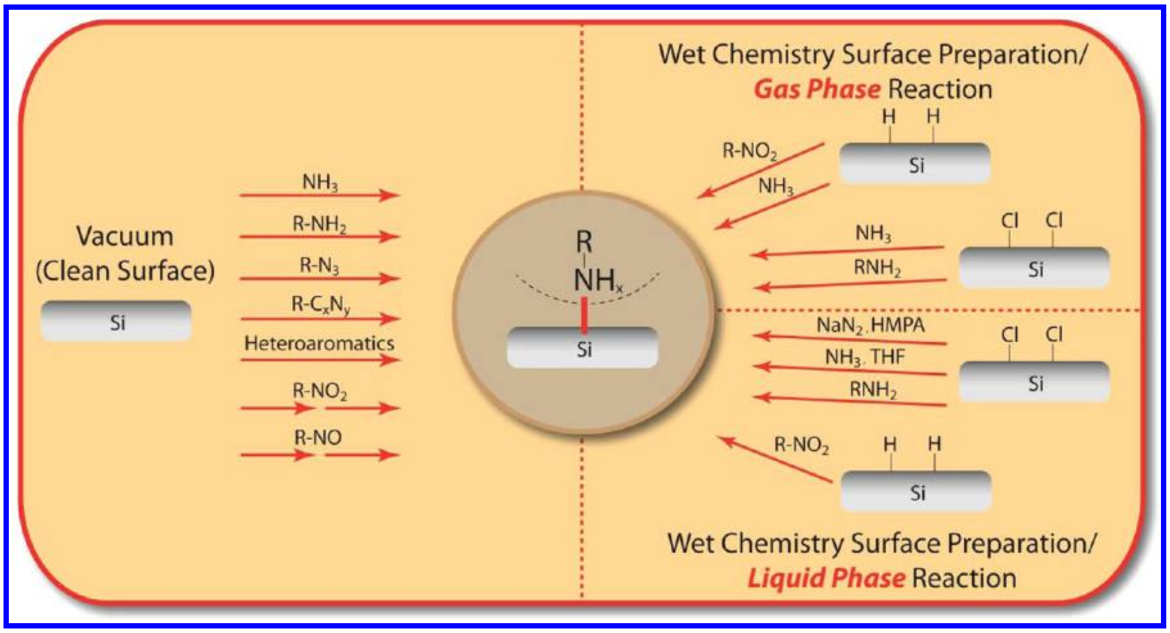

Figure 1. Summary of the approaches to form a Si−N bond on silicon surfaces with N-containing compounds, including ammonia, alkyl or aryl amines, nitro-, nitroso-, and azido compounds, starting from clean, H-terminated, and Cl-terminated Si surfaces by vacuum or wet-chemistry methods. The substituent R group could be a hydrogen, alkyl, or aryl functionality. $x = 0, 1, 2$. Selected reactions will be explained in detail in the following sections.

achieved by intermolecular interactions compensating for the unfavorable thermodynamics of the linkage formation). This will also affect the kinetics of diffusion of oxidizing reagents toward the interface formed. Alternatively, purely kinetic handles could be employed, as described below, but then care must be taken either not to expose the produced linkages to ambient conditions or to make sure that the kinetics of oxidation can be slowed down so substantially that it would not make any difference during the lifetime of a component (such as in single-use biosensors).[5] Because some of the systems described below involve well-ordered structures, the entropic factor can sometimes contribute greatly to the free-energy change. However, within the scope of this article, we will primarily focus on the enthalpic contribution. Further studies will need to address the contribution of order to the overall energy landscape.

Over the last two decades, the art of formation of oxide-free interfaces based on Si−C linkages has been nearly perfected, and a variety of organic monolayers with very attractive properties have been produced. Instead of recounting the most exciting advances in this field and speculating on its further development, we will direct the reader to a recent feature article in Langmuir that was dedicated specifically to this topic.[6] Here we will target primarily oxide-free hybrid interfaces between organic layers and silicon crystals that are based on Si−N bonds. This field is much younger compared to more traditional Si−C-based monolayers on silicon, but it really has taken off in recent years for several reasons. First, the thermodynamic stability of the Si−N bond compared to that of the Si−C bond allows for a robust interface amenable to thermal treatment. Second, the presence of carbon at the organic−silicon interface is not always desirable. If the targeted interface is used for inorganic thin film deposition or silicon nitride formation, then the presence of carbon is actually detrimental to the electronic properties of the interface produced. Finally, because Si−C-based monolayers usually require high density to produce an additional thermodynamic driving force by molecular assembly, most of the monolayers for practical applications require relatively long alkyl chains present between the silicon surface and the functionality on the tail of the organic molecule. Thus, the electronic properties of the monolayer produced can be tuned only by the clever use of unsaturated or aromatic linkers between the reactive head, which is normally the terminal alkene group and the functional tail amenable to further chemical modification.[7] However, only a very limited number of these designed chains allow for the formation of a well-ordered dense layer following this modification step. The use of saturated alkyl groups is much better in making such an ordered monolayer, but then the electronic properties of the interface produced are very different. As will be shown below, using Si−N linkers to form the hybrid organic−silicon interface allows one to place the desired functionality as close to the silicon surface as needed while maintaining the integrity of the monolayer.

Despite being in its infancy, silicon functionalization based on Si−N linkages has already brought about a number of interesting observations and possible practical applications. Further advances in this field will benefit tremendously from the basic knowledge collected over the last few decades on silicon surface preparation and the formation of organic monolayers on semiconductors in general. Below we outline several modern approaches to making such interfaces, raise several issues that are still a subject of controversy, and outline possible venues for the further development of this field.

2. PREPARATION OF SI−N LINKAGES ON OXIDE-FREE SILICON SINGLE CRYSTALS

2.1. General Approaches to Selective Silicon Termination. The preparation of selectively terminated silicon single-crystal surfaces normally starts either with a clean silicon surface exposed to selected reactive compounds under ultrahigh vacuum (UHV) conditions or with hydrogen-terminated silicon

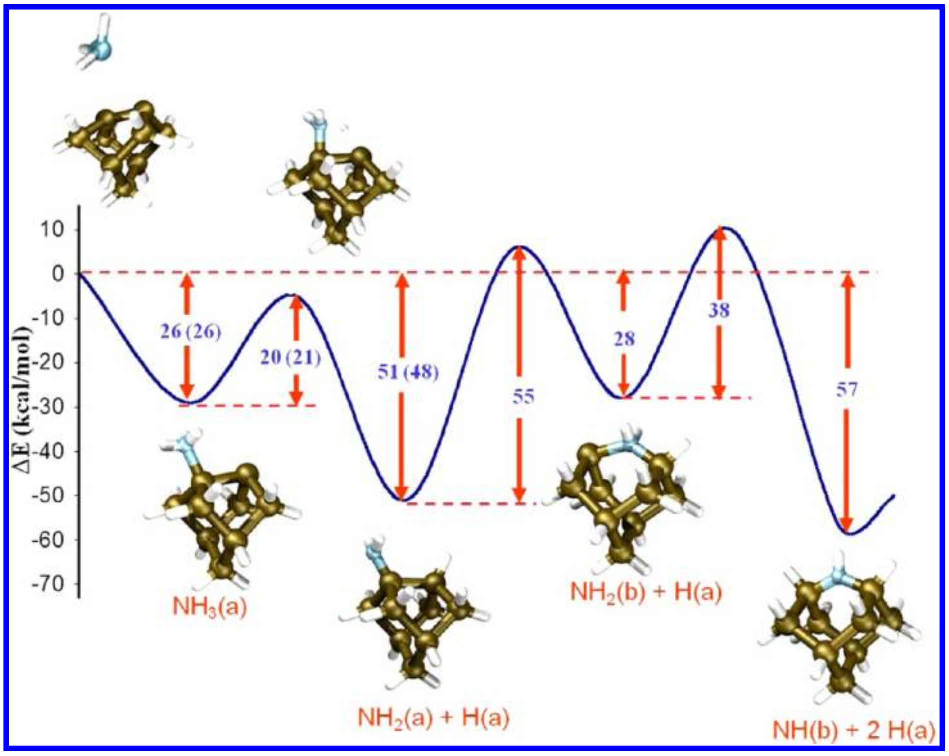

Figure 2. Reaction pathway of NH_3 on Si(100)-(2 × 1) and the predicted potential energy surface of the initial growth of silicon nitride by ab initio studies (with selected experimental TPD results[29] shown in parentheses). The brown, light blue, and white atoms represent silicon, nitrogen, and hydrogen atoms, respectively. This figure, courtesy of Professor C. Musgrave, is based on the data in ref 20.

samples prepared by wet-chemistry methods and further reacted with a target compound in a gas phase or in solution. Most commonly used silicon surface modification procedures start with H-terminated silicon that can be produced under both UHV and solution-phase conditions and also could lead to the formation of many useful linkages, including Si−C,[8] Si−P,[9] Si−halogen (−Cl, −Br, and −F),[10,11] and Si−NH_x (x = 0 to 3).[12] H-terminated silicon single-crystalline surfaces, including Si(100) and Si(111), can be reliably produced by modified RCA or piranha HF etching wet-chemistry methods[13] or by exposing a clean silicon surface to gas-phase hydrogen in the presence of a hot tungsten filament at elevated surface temperature in UHV.[14] Following this initial surface preparation, selective silicon terminations can be prepared by a number of reactions, including hydrosilylation, cyclocondensation, electrochemical grafting, and alkylation by Grignard reagents.[14−16] However, all of these approaches have already been described and reviewed previously. In this article, on the basis of recent work, we are going to focus mostly on the preparation of Si−N linkages starting from clean, H-terminated, and Cl-terminated silicon surfaces in UHV or through wet-chemistry methods, as summarized in Figure 1.

2.2. Si−N Linkages on Clean Silicon in Vacuum. As has been mentioned above, there are a large number of silicon surface reactions leading to the formation of the Si−N bond in UHV. Although we do not intend to review all of those possibilities, it is worth learning some of the general trends in these reactions and the key issues in Si−N bond formation on a surface by briefly exploring the chemistry of ammonia, amines, and a few other compounds on clean silicon.

2.2.1. Ammonia on Clean Silicon in UHV. From a fundamental perspective, the reaction of ammonia with a clean Si(100)-2 × 1 surface can help us to understand the main steps and problems associated with the Si−N-based interface formation. The clean and reconstructed Si(100)-2 × 1 surface can be best described as rows of Si−Si dimers with one Si atom (down-Si) carrying a partial positive charge and the other one (up-Si) with a partial negative charge. This system at room temperature is in dynamic equilibrium, meaning that the buckling of the dimer and charge distribution constantly change, making this silicon surface very reactive. One of the consequences of this structure, which has this zwitterionic character, is that it can act as a good electron acceptor, favoring the reaction with nucleophilic reagents such as NH_3. This seemingly simple reaction has been a subject of intense study. In general, there are three main steps in this process: adsorption, dissociation, and insertion.[14,17] The first step is the least controversial: an NH_3 molecule adsorbs on the electron-deficient "down" atom of the surface silicon dimer and forms a dative bond.[18] This process results in a decrease in electrophilicity on the neighboring Si dimer and can extend to the next-nearest dimer. This effect (also known as an induced electronic effect) influences the adsorption of the next ammonia molecules on this surface. Widjaja et al. have demonstrated that this nonlocal effect was mainly directed along the dimer row and not across the trench separating the rows.[19] The datively bonded NH_3 subsequently dissociates to Si−NH_2 and Si−H on adjacent silicon atoms of the same dimer, as predicted by detailed DFT investigations[18,20,21] and observed by XPS,[21−24] STM,[25,26] FTIR,[18,27] and HREELS.[24] The XPS studies conducted by Mathieu et al.[21] confirmed that ammonia dissociated into NH_2 and H on the neighboring atoms of the Si−Si dimer but not across the trench because the intrarow reaction would induce N 1s peak splitting of ~0.4 eV whereas the cross-trench H-bonding pattern would be expected to increase the splitting to 0.7 eV. In addition, Kim et al.[28]

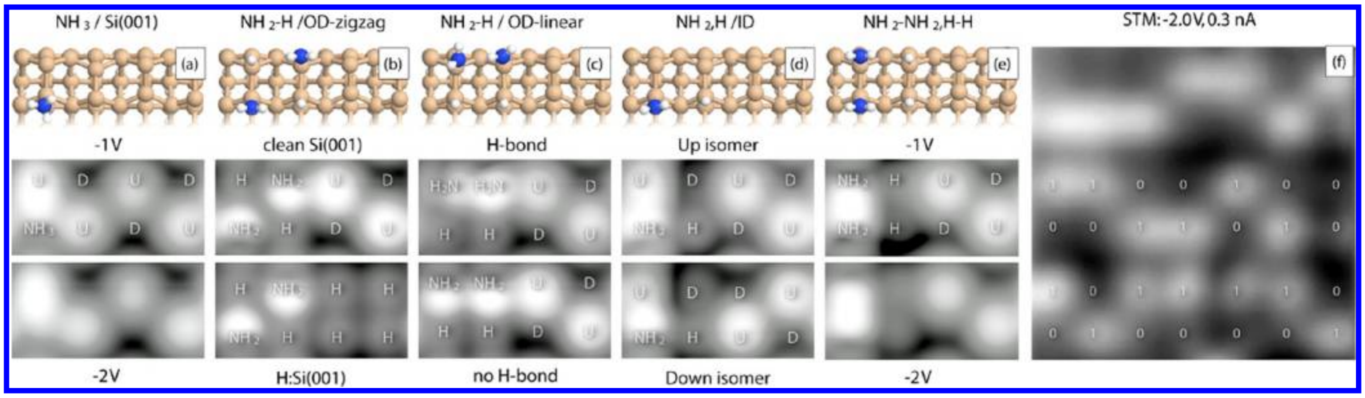

Figure 3. Simulated STM images showing a Si surface with absorbed NH_3, NH_2, and H configurations at bias voltages of between −1 and −2 V: (a) A single NH_3 molecule adsorbed on a Si surface with the up Si atom, which is on the same dimer with the NH_3 molecule, is brighter than the other up atoms. NH_2−H on-dimer (OD) with (b) zigzag and (c) linear configurations: the NH_2 group is brighter than the H atom but darker than the up Si atom on clean dimers. For in-dimer (ID) structures d and e, the dimer with NH_2 adsorbed is brighter than the dimer with the H atom in both cases. (f) Section of an STM image of the saturated surface taken at −2 V, 0.3 nA as a comparison. This figure is reprinted with permission from ref 26. Copyright (2007) by the American Physical Society.

suggested that hydrogen bonding between the surface species (Si−H and Si−NH_2) and the impinging NH_3 molecules played an important role in NH_3 surface adsorption. This is where some of the initial challenges with the correct description of ammonia adsorption have emerged. The adsorption of ammonia induced a buckling effect on the silicon dimer. This effect propagated along the dimer row to cause ammonia adsorption and subsequent dissociation on the neighboring silicon dimer to produce the on-dimer (OD) zigzag patterns confirmed by STM[25,26] and NEXAFS.[21] The linear configurations of NH_3 + NH_2 along the dimers of the neighboring dimer rows (Si−Si(NH_3) and (NH_2)Si−SiH) and opposing NH_2 + H in the same dimer row (shown in Figure 3b) were also confirmed by vibrational spectroscopy.[18] Figure 2 summarizes the reaction path for ammonia dissociation on a single Si−Si surface dimer, and Figure 3 immediately suggests that this process is affected by the reaction on neighboring dimers. Because of the high reactivity of the surface and because of the relatively short-length electronic effect produced by an adsorption of a single ammonia molecule, the observed zigzag patterns are only a few dimers long. However, there is indeed an effect of the neighboring dimers and the chemical reactions involving them on the reactivity of the rest of the surface. This effect is even more profound for the nitrogen insertion step.

With the surface temperature increasing to 450 K, surface Si−NH_2 species start to convert to ═NH by the insertion of a N atom into a silicon substrate.[20,23,25,27,30] The Si−N bond length for the species formed was found to be 1.75 Å with a Si−N−Si planar angle of 10° with respect to the surface normal, and the bond length of N−H was 1.05 Å.[31] One of the questions is whether N−H inserts into the Si−Si dimer to form a Si−N−Si bridging bond or into the silicon back bonds (toward the second layer, as schematically summarized in Figure 4) and how this affects the interaction of the incoming NH_3 molecules with species that are already formed on the silicon surface.

Answering this question is especially important for understanding the initial stages of silicon nitride formation. Theoretical studies suggested that NH insertion into the Si−Si surface dimer was thermodynamically more favorable than into Si back bonds;[20,27] however, this process was hindered by a very substantial energy barrier making the back-bond diffusion more favorable.[27] By analogy to the compensation effect of the neighboring silicon dimers on ammonia adsorption and dissociation, Rodriguez-Reyes et al.[30] proposed the surface strain concept to explain the insertion process. In other words, because of the effect of several neighboring silicon dimers occupied by ammonia on the nitrogen insertion process, the insertion occurs in such a way that it alleviates the surface strain, and in this case, the lowest energy barrier for N subsurface insertion was found to be similar to that for surface insertion.

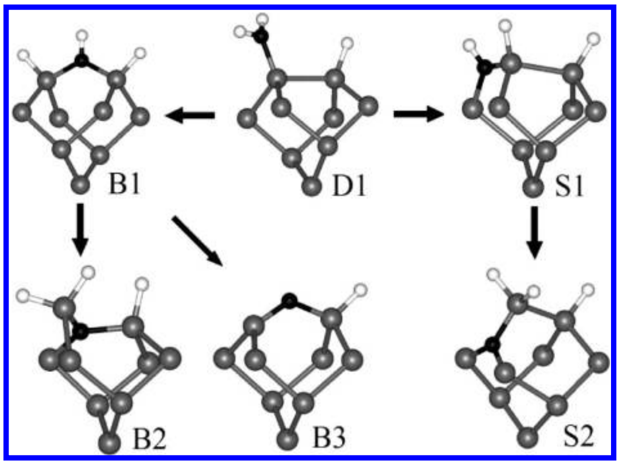

Figure 4. Proposed pathways for the decomposition of dissociative adsorbed species: D1 → B1 → B2 (B3) represents the surface insertion pathway. D1 → S1 → S2 represents the subsurface insertion pathway. Black, nitrogen; gray, silicon; white, hydrogen. This figure is reprinted with permission from ref 27. Copyright (2007) by the American Physical Society.

Following the initial stages of ammonia reaction with Si(100)-2 × 1, if the surface temperature is increased to 800 K, then silicon nitride is formed.[20,23] Kubler et al.[22,23] pointed out that the thick nitride layer could be formed only at higher NH_3 pressure/exposure (>200L) and at higher temperature (600−800 °C); otherwise, heterogeneous Si_3N_4 islands would be formed.

The general trends for ammonia reaction with the Si(100)-2 × 1 surface can help us to understand similar reactions on other silicon faces. For example, the clean Si(111) surface forms a well-characterized 7 × 7 reconstruction with adatom and rest-

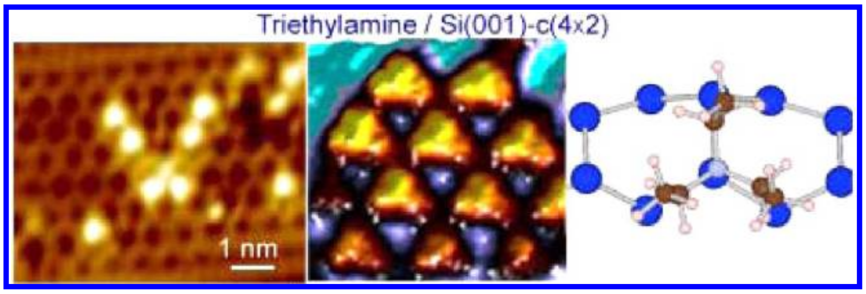

Figure 5. High-resolution STM image of triethylamine (TEA) on a Si(100) surface taken at room temperature (left): at saturation coverage, datively bonded TEA molecules self-assembled into *c*(4 × 2) domains with ternary symmetry. The eclipsed conformer (right) was confirmed by STM, although both eclipsed and staggered geometries were calculated with same adsorption energy by DFT. This figure is reprinted with permission from ref 43. Copyright (2012) by the American Chemical Society.

atom reactive sites that are basically similar to the up (electron-rich) and down (electron-deficient) silicon atoms of the silicon dimer on the Si(100)-2 × 1 surface. Similar to the ammonia reaction with Si(100)-2 × 1, the adsorption and dissociation of NH_3 on Si(111) are temperature-dependent;[32,33] however, the distribution of surface species is more complex than for Si(100)-2 × 1. On Si(111)-7 × 7, the adsorbed NH_3 molecule dissociates to form both NH_2 and NH species at temperatures that are as low as 70 K. NH_2 formation is quite similar to the process on Si(100)-2 × 1, but there is another reaction pathway available on Si(111): immediate dissociation of ammonia to Si−NH−Si and two adsorbed hydrogen atoms, which is quite different from the NH_3 behavior on the Si(100) surface.[34] The local structures of dissociated NH_2, NH, and H on Si(111)-7 × 7 drew substantial attention. Most NH_2 species (87.9%[35] of N-containing surface species) were bound to silicon rest atoms with a Si−N bond length of 1.71 ± 0.02 Å, whereas only a small fraction of NH_2 occupied the adatom atop Si sites.[32,34,36] Wang et al.[37] explained why dissociated NH_2 was mostly adsorbed on the rest atom Si site and not on the adatom silicon by following the effect of the charge transfer between adatoms and corresponding rest atoms following ammonia adsorption. The charge transfer between adatom and rest-atom sites caused by adsorbed species made the rest-atom sites better electron acceptors and also influenced the adsorption of the following NH_3 molecule.[34] The natural bond orbital (NBO) analysis of Kohn−Sham wave functions in the NH_3/Si(111) system also indicates the charge transfer from the rest-atom site to the adatom site when the ammonia molecule approaches the rest atom.[38] In the subsequent NH_x ($x = 1, 2$) insertion process, the NH insertion is most feasible for adatom silicon back bonds followed by H transfer, as verified by LEED, XPS, and STM.[34−37]

The description of ammonia adsorption and reaction on silicon surfaces brings up a number of general points that have to be considered when dealing with the Si−N linkages formed in UHV on clean silicon surfaces:

(1) The initial adsorption is a nucleophilic attack of the nitrogen lone pair on a suitable surface electrophilic site.

(2) The initial adsorption process affects the reactivity of the neighboring sites, which can potentially lead to the formation of adsorption patterns, but this is not a long-range effect (at most, the second-closest silicon dimer on the Si(100)-2 × 1 surface is affected substantially).

(3) The high reactivity of the silicon surface leads to N−H dissociation in a reaction with ammonia, providing additional surface functionality (Si−H) that has to be taken into account when designing further chemical and thermal transformations of the functionalized surface.

(4) The produced Si−N linkage is stable at room temperature in vacuum, and further thermal transformations of the surface species depend drastically on the surface arrangement of adsorbates and the effects of the neighbors.

2.2.2. Amines on Clean Silicon in UHV. A parallel between the chemistry of ammonia and the adsorption and reactions of amines on clean silicon surfaces leads to highly versatile amine-based functionalities whose reactivity can be easily tuned by changing the substituent groups (for example, from electron-withdrawing to electron-donating to affect the reactivity of the nitrogen atom) on an amine compound. This approach can be used to alter the desired chemical reactivity of amino-functionalized silicon substrates for a wide range of applications, from diffusion barriers in microelectronics to biosensors. Probably the most informative is a comparison between the adsorption and reactions of tri- and dimethylamines on clean silicon surfaces. The chemisorption of tri- and dimethylamine (TMA and DMA) on Si(100) and Si(111) surfaces in UHV was investigated by STM, XPS, FTIR, and DFT modeling on the atomic level.[39,40] TMA forms a very strong dative bond on both Si(100) and Si(111) surfaces via the Si−N linkage (with electron density on the neighboring surface sites strongly affected by this adsorption). At very high exposures, another reaction pathway involving C−H dissociation was uncovered. Similarly, the dative bond was also formed when the DMA molecule adsorbed on both silicon surfaces; however, this dative complex increased the electron density on the N atom, which also weakened the N−H bond available in this compound. Consequently, DMA dissociated into $Si{-}N{-}(CH_3)_2$ and Si−H on a Si−Si dimer on the Si(100) surface or $Si{-}N(CH_3)_2$ on the adatom site and Si−H on either the adatom or rest-atom site when dissociation occurred on the Si(111)-7 × 7 surface. The most important finding from this comparison is that in amines with an available N−H bond (primary and secondary amines) this bond is the first to dissociate on clean silicon. The N−C bond is so much stronger that its dissociation is energetically prohibitively expensive. In fact, C−H dissociation has also been reported for TMA only at extremely high exposures. This makes tertiary amines a very promising target for future studies because they not only form a very strong dative linkage with silicon but also provide a venue for adsorption that avoids introducing additional functionalities (such as Si−H) onto silicon substrates. A direct comparison of the chemisorption behavior of primary, secondary, and tertiary amines on the Si(100) surface is given in a series of experimental and theoretical works from the groups of Bent, Hamers, and Musgrave.[40−42] Unfortunately, the attachment of tertiary amines to clean silicon surfaces is also not quite as simple at practical conditions of high coverage. The electron transfer upon attachment of a tertiary amine to the dimer of the Si(100)-2 × 1 surface results in lower electrophilicity of the neighboring Si dimer (nonlocal electronic effect)[19] that in turn influences the adsorption of incoming amine molecules and results in a lower saturation coverage. A recent study investigated the adsorption of triethylamine (TEA) on a Si(100) surface in UHV at room temperature. XPS results indicated that some of the TEA molecules formed dative bonds on this surface, which induced static buckling of the Si−Si surface dimers and led to the self-assembly of TEA molecules into *c*(4 × 2) domains with a ternary symmetry pattern observed by STM and illustrated in Figure 5.[43] The rest of the TEA molecules dissociated to Si−N(CH_2CH_3)$_2$ and Si−CH_2CH_3 at the same silicon dimer.[43]

Compared to aliphatic amines, aromatic amines have several reaction pathways based on the aromatic functionality. In addition, aromaticity influences the reactivity of the amine functionality. A number of aromatic amines of various structures have been investigated on the Si(100) surface in UHV including aniline,[44−47] 1,4-phenylenediamine,[44] pyrrole,[45,48] 3-pyrroline,[45] and pyrrolidine.[45,48] Among all of these compounds, the adsorption and reaction of aniline is probably the most informative because it can involve both the phenyl ring and the primary amine group. In addition, the structure of this compound can potentially lead to the formation of molecular chains on silicon. Following aniline's reaction with the Si(100) surface, the phenyl ring in the produced surface species remains intact and coplanar with the amino group, and the product is tethered to the silicon surface through Si−N−C (the carbon from the aromatic ring) linkages with the hydrogen atom on the neighboring silicon dimer site. Also, the maximum coverage of aniline on the Si(100) surface is 0.5 aniline molecule per Si−Si dimer, with the surface energy gap increased by 154.4 kJ/mol following aniline chemisorption. Thus, aromatic functionality can be retained in a reaction of aromatic amines with clean silicon surfaces in vacuum. Of course, a wide variety of aromatic amines can indeed produce a variety of surface products. Some of them lead to the formation of a Si−N−C linkage, others may go through N−H cleavage or cycloaddition processes that break up aromaticity, and some may also form the Si−N dative bond.[45] An example of a low-coverage STM study that compares the reaction of an aromatic ring in pyridine to the formation of a Si−N dative bond on Si(100) is given in Figure 6. However, in principle, the retention of aromaticity in a reaction of aromatic compounds with the silicon surface and the formation of aromatic surface species upon this reaction have been found to be the main driving forces determining the distribution of surface products.[15,38,45,48,49] Elaborate chemical schemes that may involve partial blocking of the surface reactive sites with hydrogen (as in studies of aromatic amines on H-covered Si(100)[50]) or, on the contrary, may promote multiple surface reactions of substituted heteroaromatics with clean silicon[38,49,51] that can in principle lead to stable Si−N linkages as well; however, these schemes generally produce low-coverage Si−N linkages and complex product distributions and are outside the main focus of this article.

Finally, the reactions of the same amines on the surfaces of group IV elemental semiconductors can help us to understand the general requirements for Si−N bond formation. For example, the proton affinity of the topmost layer of the Si(100) surface is stronger than that of the Ge(100) surface, which means that the electron density on Ge(100) is lower than that on the Si(100) surface.[42,46,48] Thus, compared to Si(100), Ge(100) is more favorable for forming dative bonds between surface atom and N from either aromatic or aliphatic amines.

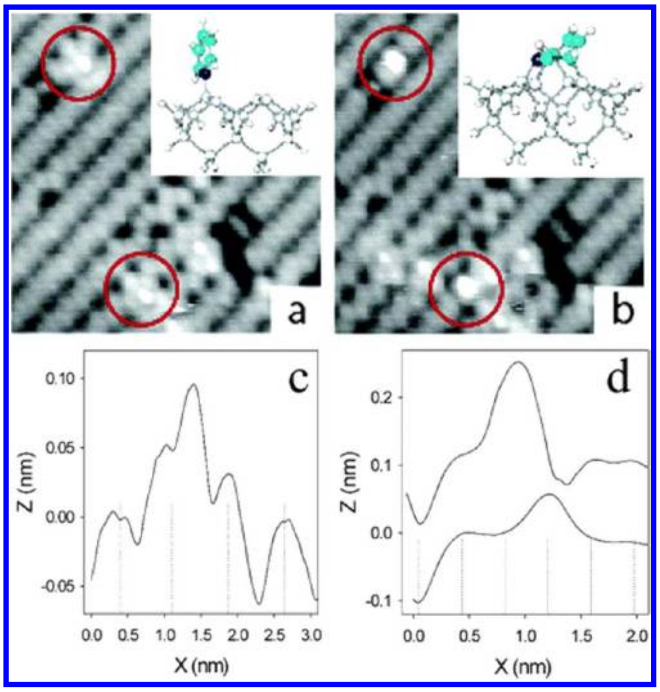

Figure 6. Occupied-state STM images (7 × 7 nm^2, −2 V, 40 pA) during pyridine dosing on Si(100). (a) Two datively bonded adducts are highlighted and are observed to relax to the "tight-bridge" configuration in image b. The insets show model bonding geometries for the dative and tight-bridge configurations, respectively. A cross section (perpendicular to the dimer row) through the highlighted datively bonded pyridine in the top left-hand corner is shown in plot c. The dashed lines indicate the center of the dimer rows. Cross sections (along the dimer row) for this same molecule (bottom) before and (top) after conversion are shown in plot d. The deep depression on the left is due to a surface defect and is used to register the two profiles. The dashed lines indicate the position of the dimers along the adjacent row. This figure is reprinted with permission from ref 50. Copyright (2005) by the American Chemical Society.

In addition to the important points suggested by the analysis of the ammonia reaction on clean silicon, on the basis of the reactions of amines,

(1) in a reaction of primary and secondary amines on clean silicon in vacuum, the chemistry is dominated by N−H dissociation;
(2) if the N−H dissociation channel is not available (such as in tertiary amines), then a strong dative Si−N bond can be formed; however, this process is more complex at very high exposures (and high coverages) and further studies are needed to control it for practical applications;
(3) the presence of multiple chemical handles in the form of functional groups provides a wide variety of tuning knobs both for varying the reactivity of the amine group and for controlling the structure and reactivity of the ultimate layer produced.

2.2.3. Reactions of Other Nitrogen-Containing Functional Groups with Clean Silicon in UHV. This section will focus on using multistep chemical modification schemes (mostly on Si(100)-2 × 1) to produce the target Si−N linkage. Our group has been working on this approach for over a decade. We initially focused on the reactions of nitroalkanes, including nitroethane and nitromethane, on a clean Si(100)-2 × 1 surface[52] in UHV. Both nitroethane and nitromethane undergo a 1,3 cycloaddition reaction on this surface at room temperature, and this initial attachment is followed by subsurface oxygen migration that can be promoted at elevated temperatures. The formed monolayer is very stable, with the nitrogen and oxygen coverages remaining essentially unchanged even after annealing to 900 K; however, in the case of nitroethane, 50% of the carbon was released from the surface as ethylene following hydrogen elimination. Despite the retention of the N−C bond following nitroalkane reactions with clean silicon, we were not initially certain as to how the linkage to the surface was formed following subsurface oxygen migration. Nevertheless, the nitro group was proven to possess high reactivity toward silicon, and we continued the study with nitrobenzene. The adsorption of nitrobenzene on the Si(100) surface in UHV is a similar 1,3 dipolar cycloaddition reaction[53] through a nitro group with a modest energy barrier. Detailed investigations of Si−O−N−O−Si five-membered ring formation (two Si atoms from the same dimer) suggested that this surface species can exist only at cryogenic temperatures. As the surface temperature is raised to 160 K, oxygen atoms start to insert into either the Si−Si dimer or the Si back bonds; however, the phenyl ring remains intact and is bonded to the Si(100) surface through the nitrogen atom. This system proved to be remarkably stable, even following brief annealing to 1000 K. Detailed computational studies[54] follow all of the intricate details of the initial stages of subsurface oxygen migration. To control the spacial distribution of the produced Si−N linkers (even though the side product of the nitro-group reaction with clean silicon is subsurface oxygen), we also studied the molecular patterning based on the coadsorption of ethylene and nitrobenzene on a clean Si(100) surface in UHV.[55] The Si surface was initially covered by a half monolayer of ethylene, which occupied every other surface silicon dimer, and then exposed to nitrobenzene at room temperature. Following this coadsorption, the surface temperature was increased until all ethylene molecules were desorbed, whereas the strongly bound nitrobenzene remained on a surface. Future STM studies will be needed to confirm that the remaining nitrobenzene molecules occupied every other surface silicon dimer, but a compelling argument that this is indeed the case was made on the basis of a detailed computational DFT investigation.

In addition to $-NO_2$, the nitroso ($-N{=}O$) group is also a good anchor for tethering an aromatic ring to a silicon surface. The absorption of nitrosobenzene on clean Si(100) in UHV is a [2 + 2] cycloaddition process at room temperature. Initially, a four-membered ring (Si−N−O−Si) is formed on the same Si−Si dimer. In the subsequent reaction, the oxygen atom migrates into silicon back bonds with the phenyl ring remaining intact through the Si−N−Si group. This phenylnitrene adduct structure was confirmed as the main surface species by N 1s high-resolution XPS studies.[56] As expected, the migration of the oxygen atom subsurface and the formation of a Si−N−Si structure with a phenyl ring linked to the amine functionality can be stimulated by thermal annealing. Although the reactions of nitro and nitroso compounds on clean silicon surfaces in vacuum do not produce oxygen-free interfaces, as will be shown below, the amount of oxygen can be reduced drastically in cyclocondensation processes with the same compounds.

Using the azide ($-N_3$) group to deliver an aromatic ring onto the Si surface is the cleanest approach that does not lead to any oxygen contamination on the surface. The chemisorption of phenylazide and benzylazide on a clean Si(100) surface in UHV was investigated by both spectroscopy and DFT studies.[57,58] Phenylazide undergoes a 1,3 addition reaction followed by nitrogen elimination above room temperature (315 K), and benzylazide adsorption occurs predominantly via a 1,2 addition process with a gas-phase nitrogen molecule evolved from the surface as shown in Figure 7 at approximately 400 K.

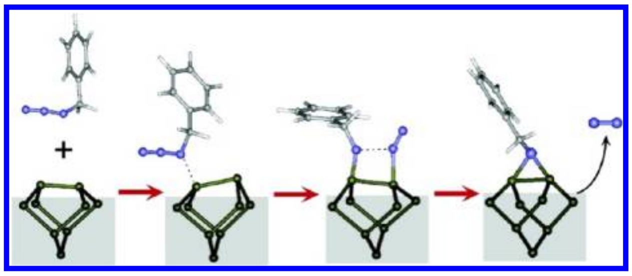

Figure 7. Surface reaction pathway for the chemisorption of benzylazide on a Si(100)-2 × 1 surface represented by a Si_9H_{12} cluster. The benzylazide molecule initially adsorbed on the Si(100) surface by forming a dative bond, followed by the attachment of two nitrogen atoms on the neighboring Si atom of the same dimer. Finally, a stable surface product on a Si−Si−N cyclic entity was formed with nitrogen molecule elimination. Green, silicon; blue, nitrogen; gray, carbon; white, hydrogen. This figure is reprinted with permission from ref 57. Copyright (2006) by the American Chemical Society.

A nice spectroscopic signature predicted computationally for the product of the 1,2 cycloaddition of benzylazide allowed for a precise identification of this reaction pathway. These studies focused on the detailed mechanistic understanding of the azide reaction on clean silicon; however, regardless of the specific mechanism, this multistep process leaves the nonoxidized Si−N(R)−Si structure as its only outcome in vacuum.

Additional information on the multistep reactions leading to the formation of the Si−N linkages could be gathered from studies of other N-containing compounds such as cyano derivatives,[15] isonitrile,[47] N_2H_4,[59] NO,[60] and hydrazoic acid (HN_3)[38,60] on clean silicon surfaces in UHV; however, a full description of these studies is beyond the scope of this article, and the work summarized above is sufficient to provide the key observations for the multistep chemical approach to the formation of Si−N linkages on silicon.

The multistep reactions on clean silicon in UHV can clearly yield the desired Si−N linkages. The main problem is the presence of multiple surface species following most reaction schemes and the presence of side products (such as subsurface oxygen) that may have properties detrimental to the potential applications of this strategy. Nevertheless, in the reactions of azides, both issues are overcome, and in the future, the design of alternative multistep chemical processes for Si−N linkages is a realistic possibility. In addition, the lessons learned from this analysis can be applied to the further design of surface modification schemes that help us to avoid undesired side products, as will be described in the next section.

2.3. Preparation of Si−N Linkages by Reacting H-Terminated Silicon Single Crystals with the Desired

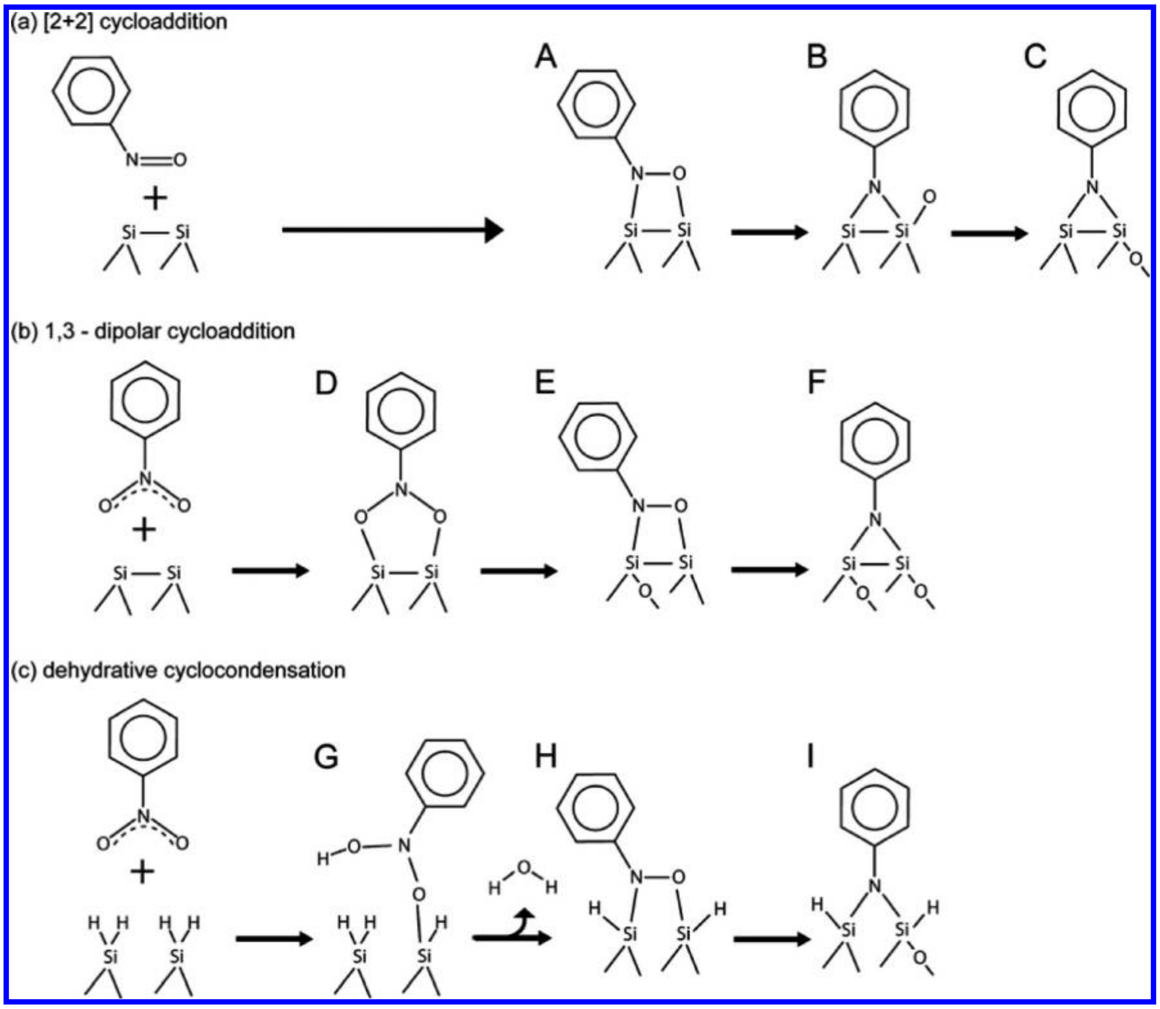

Figure 8. Proposed surface reaction pathways for the chemisorption of nitro- and nitrosobenzene componds on selected silicon surfaces: (a) [2 + 2] cycloaddition of nitrosobenzene with Si(100)-2 × 1. (b) 1,3 dipolar cycloaddition of nitrobenzene with Si(100)-2 × 1. (c) Dehydrative cyclocondensation of nitrobenzene with hydrogen-terminated Si(100). Structures A, E, and H show the nitrosoadduct, structures B, C, F, and I exhibit the phenylnitrene adduct, structure D shows the nitroadduct, and structure G is a stable intermediate. This figure is reprinted with permission from ref 56. Copyright (2009) by the American Chemical Society.

Reactants. As discussed above, H-terminated silicon surfaces can be prepared under both vacuum and ambient conditions and remain stable for a short period of time. In addition to providing the necessary barrier for surface oxidation, surface hydrogen (or, more specifically, SiH_x functional groups) can be used to design chemical processes utilizing its reactivity. Our group has conducted a number of studies involving nitrobenzene on H-terminated Si(100) and Si(111) surfaces in UHV.[61] Figure 8 draws parallels between cycloaddition processes described in the previous section and the cyclocondensation reaction between nitrobenzene and H-covered silicon substrates. The [2 + 2] cycloaddition of nitrosobenzene on Si(100)-2 × 1 in Figure 8a goes through species A and B ultimately to form phenylnitrene product C following oxygen atom migration. Similarly, the 1,3-cycloaddition of nitrobenzene on the same surface occurs via the D and E sequence to form an adduct that is essentially the same as C following the migration of two oxygen atoms into the silicon back bonds. Those two approaches require UHV conditions to maintain the cleanliness of the original Si(100)-2 × 1 surface, and at the end, the targeted chemical functionality comes at the expense of producing subsurface oxygen. Thus, achieving the same chemical functionality starting with H-terminate silicon would be preferred. This is exactly the approach described in Figure 8c (for a reaction involving surface SiH_2 groups). Refluxing H-terminated silicon crystals in neat nitrobenzene at elevated temperature allow one to avoid UHV conditions and decrease the amount of subsurface oxygen by a factor of 2 compared to that in the nitrobenzene reaction with clean Si(100)-2 × 1. The byproduct of the cyclocondensation reaction, water, does not seem to have any measurable effect on the chemistry of the process. In our experiments, the surface partial coverage of phenyl rings was monitored by vibrational spectroscopy. The infrared absorbance of the Si—H stretching region around 2100 cm^{-1} was used to monitor the surface reaction as a function of time and temperature, and the results were very similar to those obtained for nitroalkanes reacting in the same fashion with the H-covered Si(100) surface prepared in vacuum.[62] The next step in designing cyclocondensation processes should be based on the complete removal of oxygen atoms with the byproducts. For example, one can think of using nitrosobenzene instead of nitrobenzene, which in reality is more complicated than it sounds because nitrosobenzene is a solid at room temperature.

Cyclocondensation is not the only way to produce Si—N linkages on H-terminated silicon. In 2009, Dai et al.[12] exposed atomically flat mono- and dihydride-stepped H—Si(111)

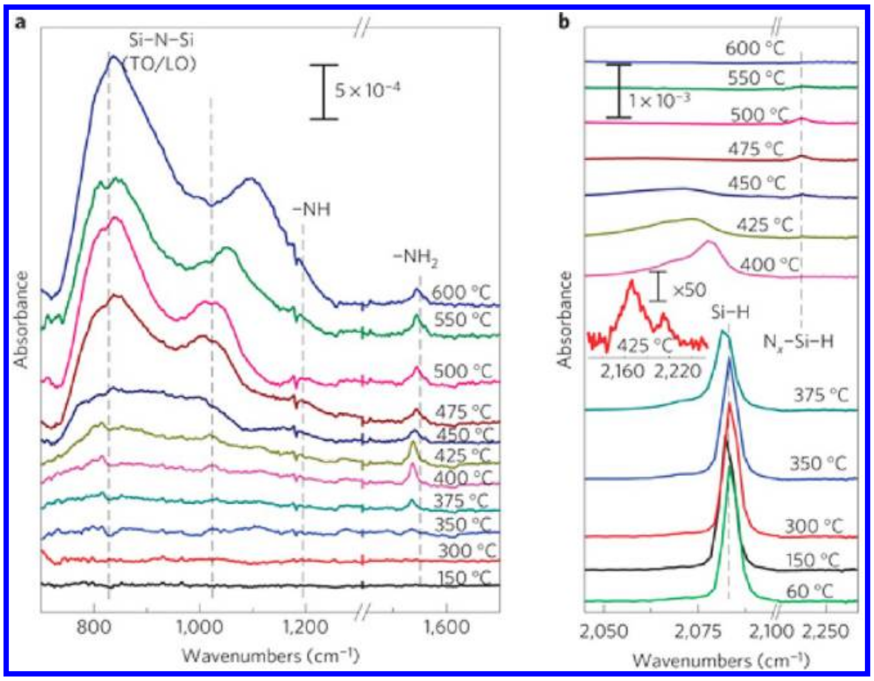

Figure 9. Infrared absorption spectra showing surface nitrodation on an H-terminated Si(111) surface by annealing in gas-phase NH_3 at various temperatures: (a) Si−N−H_x bending region, (b) Si−H and N_x−Si−H stretching regions, where the inset in plot b shows the N_x−Si−H stretching mode observed after annealing at 425 °C. Starting from 350 °C, the NH_2 bending mode peak appeared at 1535 cm^{-1}, and the peak intensity of the Si−H stretching mode started decreasing, which indicated that the initial surface reaction involved Si−H to form Si−NH_2. This figure is reprinted with permission from ref 12. Copyright (2009) by Nature.

surfaces to gas-phase ammonia under several Torr of pressure and investigated the temperature-dependent nitridation process (shown in Figure 9) by using in situ FTIR combined with DFT computational studies. For atomically flat H−Si(111) and monohydride-stepped H−Si(111) systems, −NH_2 groups would be formed starting from 350 °C, and with the temperature increased to above 400 °C, the surface was covered with a complex mixture of Si−NH_x species and regenerated Si−H. However, the dihydride-stepped H−Si(111) formed a bridging step-edge H−Si−NH−Si silazane structure. Dihydride-stepped H−Si(111) species in the $[\bar{1}12]$ direction react with NH_3 by forming H−Si−NH−Si bridging structures.

A recent computational work compared the activation energies for reactions of gas-phase ammonia with clean Si(100), H-terminated Si(100), and halogen-terminated Si(100).[63] The reaction of ammonia on a clean Si(100) surface requires noticeable activation energy. On the H-terminated Si(100), the reaction has an even higher energy barrier of 160.25 kJ/mol. In other words, to react gas phase ammonia with H-terminated silicon successfully, the temperature of the substrate has to be increased to the point where other surface processes start being dominant. This comparison explains why so few successful surface modification procedures by ammonia have been designed for H-terminated silicon substrates. The same work also pointed out that the overall activation energy barriers for ammonia reactions with Cl− or Br−Si(100) surfaces are much lower than for H-terminated silicon, which indicates that both of those surfaces have better reactivity toward ammonia and other nucleophilic reactants.

Finally, azide coupling with H-terminated silicon has been considered by Wang et al.,[64] who investigated the reaction of azido compounds on H-terminated porous silicon under microwave irradiation in the presence of benzoyl peroxide or under UV illumination that leads to the formation of Si−N linkages. This work focused predominantly on the use of porous silicon for biological applications, for example, protein (bovine serum albumin) attachment, but it did suggest a viable surface reaction mechanism. Further work with more controlled silicon surfaces and an oxygen-free environment is required to elucidate the details of this mechanism.

2.4. Preparation of Si−N Linkages by Reacting Cl-Terminated Silicon Single Crystals with Ammonia and Amines in the Gas Phase. As mentioned above, the Cl-terminated Si surface has a lower activation energy barrier for ammonia reactions compared to that of H-terminated silicon. The Cl-terminated Si surface can be obtained by heating a native-oxide-covered Si surface to 1250 K and then exposing the resulting surface to a saturation dose of Cl_2 (gas) at 300 K in UHV.[60,65] Alternatively, the wet-chemistry approach[10] based on the reaction of the H-terminated silicon surface with PCl_5 in chlorobenzene with a trace amount of benzoyl peroxide as an initiator can be used. Further modifications of the produced chlorinated surfaces can be done by either gas-phase reagents or by wet chemistry methods. The solution-phase processes will be discussed in the next section. In this part, we will focus on the gas-phase reactions, for example, the chemisorption of gas-phase ammonia or amines on a Cl-terminated Si(100) surface in a vacuum chamber. Finstad et al.[66] investigated the adsorption and dissociation of gas-phase NH_3 on the Cl-terminated Si(100) surface in UHV by XPS. The possible mechanism of this reaction at room temperature involved the removal of the HCl molecule as a side product and the formation of surface Si−NH_2 species. When the temperature increased to 500−700 K, the Si−NH−Si bridging structure was observed. However, a set of parallel theoretical studies suggested that this reaction is endothermic and that the surface product is expected to be Si−$NH_3^+Cl^-$, not Si−NH_2.[63,67] The more recent ab initio computational studies[68] were consistent

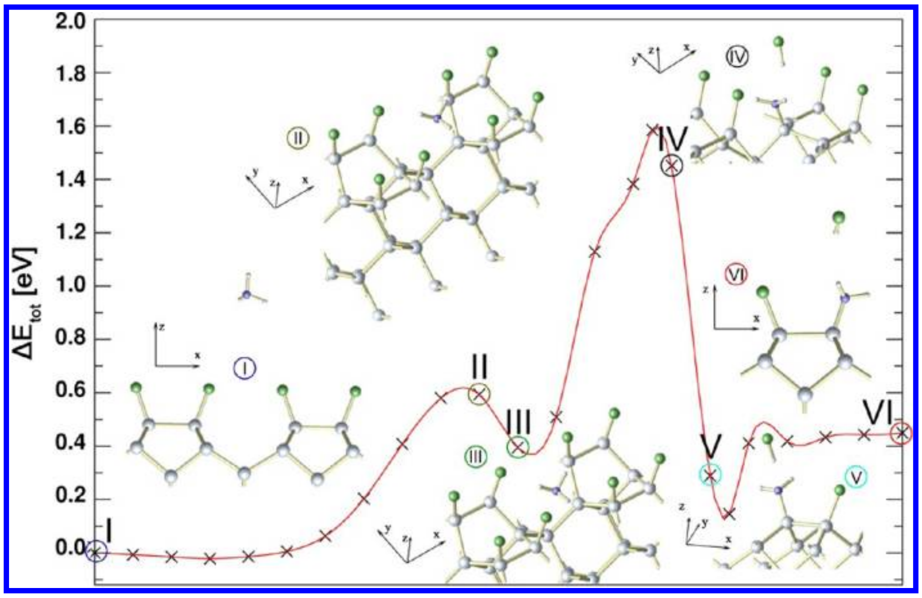

Figure 10. Reaction pathways for the adsorption of NH_3 on a Cl-terminated Si(100) surface. The simulations were performed on the gradient-corrected density functional theory (DFT-GGA) level with the Vienna ab initio simulation package (VASP). Green, chlorine; gray, silicon; blue, nitrogen; white, hydrogen. This figure is reprinted with permission from ref 67. Copyright (2008) by Elsevier.

with the experiments confirming that the lone-pair electrons on a nitrogen atom of ammonia molecule nucleophilically attacked the Si atom with HCl desorbing from the surface. However, further reaction leading to the formation of the Si−NH−Si bridge across the same silicon surface dimer concurrently with the desorption of the second HCl molecule was found to be prohibitively expensive kinetically, as summarized in Figure 10, which is in contrast to Finstad's XPS observations.[66] Instead, the second NH_3 adsorbed on the neighboring Si dimer site resulted in additional stabilization because of the N−H interaction with the neighboring Cl atom. In a separate effort, Zhu et al.[65] investigated the CVD process of gas-phase aniline and alkyl amines (butylamine and octylamine) on a Cl-terminated Si(100) surface in vacuum by XPS supported by molecular modeling. Amine molecules were chemisorbed on the silicon surface via a Si−N−Si bridging structure. The phenyl rings in aniline-derived adducts remained intact even at temperatures of as high as 750 K. However, alkyl amines started dissociating to carbide and nitride below 750 K.

In general, this approach seems to work and produce the desired Si−N linkages while keeping the rest of the functionalities in amines available for further surface modification. It still leads to a wide distribution of surface products, including secondary amines, tertiary amines, and oxide species, and requires vacuum systems for the amine reaction step. More importantly, only the first step of this reaction is understood reasonably well, and the following transformations require additional investigations. Undoubtedly, local surface arrangements, effects of neighbors, impurities, defects, possible surface reconstructions, and many other factors have to be considered to understand this chemical modification method fully. Perhaps gas-phase reactions with chlorine-terminated Si(111) that involve simple amines and ammonia under UHV conditions could shed some light on the mechanism of the entire surface modification.

2.5. Preparation of Si−N Linkages by Wet Chemistry Reactions with Cl-Terminated Silicon Single Crystals.

Compared to performing silicon modification reactions in vacuum, wet chemistry is very convenient, reliable, and widely accessible and can be easily scaled up for most practical applications. A perfect substrate for the studies of "complete" wet-chemistry formation of Si−N linkages starting with halogenated silicon is the monochloride-covered Si(111) surface. A reliable approach to obtaining this surface by solution chemistry was proposed by Bansal et al.[10] When it is used, a 99% surface coverage of chlorine can be reached by PCl_5/chlorobenzene with a benzoyl peroxide approach. This work opened the door for generating a Si−N linkage on a chlorinated silicon surface through wet chemistry.

The first published study of liquid-phase amine reactions with a Si−Cl surface bond was presented by Bergerson et al.[65] They started with H-terminated porous silicon (PSi) to obtain chlorine termination in deoxygenated chlorobenzene/PCl_5 at 100 °C for 1 h and then reacted the freshly prepared Cl-terminated PSi with butylamine at 80 °C for 24 h. Following this reaction, the surface was characterized by XPS and FTIR. Alkylamine was chemically tethered to the surface through a Si−N−Si bridge bond, and the formed organic layer was thermally stable; however, its stability under ambient conditions has to be studied further. Several years later, azide functional groups were produced directly on Si(111) surfaces through wet chemistry.[69] This study used a chemically well defined, H-terminated Si(111) surface as a starting point and then exposed it to PCl_5/chlorobenzene solution with benzoyl peroxide as the initiator in a 110 °C oil bath for 1 h to obtain well-ordered Cl-terminated Si(111). After that, the Cl-terminated surface was treated with NaN_2 in HMPA (hexamethylphosphoramide, a polar aprotic solvent) or methanol for 5 min or 3 h, respectively. Each modification step was monitored with XPS and STM. HMPA was found to be a better solvent for the azidation process: an azide surface coverage of around 55% was reached after exposure to NaN_2/HMPA solution. In contrast, exactly the same reaction in MeOH as a solvent provided a lower coverage of only 35% even after 3 h. Even though these were only preliminary studies of the azide modification, they proved that the $-N_3$ group is present on a surface and that the functionalized surface is stable.

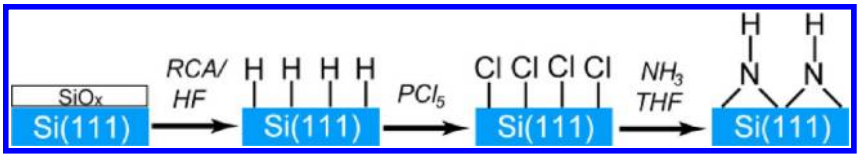

Figure 11. Schematic representation of the preparation steps in forming a Si(111) surface with Si−NH−Si as the functional group. This figure is reprinted with permission from ref 70. Copyright (2011) by the American Chemical Society.

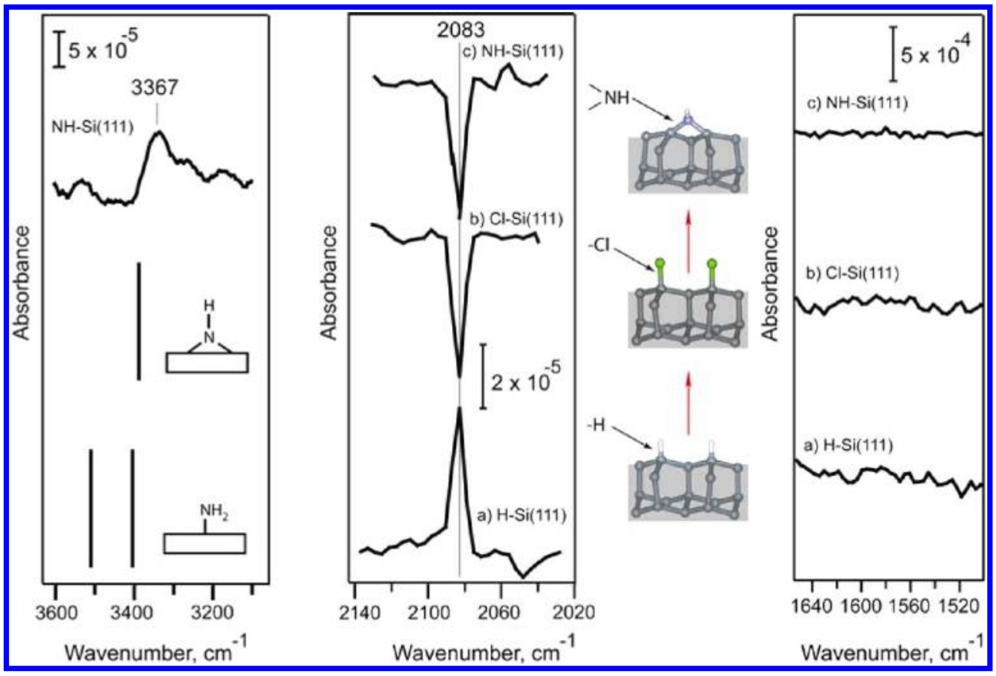

Figure 12. Infrared vibrational spectra of the Si(111) surface after every modification step. The Si−H stretching and $-NH_2$ bending spectral regions are presented for (a) a Si(111) surface terminated with hydrogen, (b) a Cl-terminated surface prepared by exposure to PCl5 in the presence of benzoyl peroxide initiator, (c) a Si−NH−Si-terminated silicon surface prepared by the exposure of Cl-terminated Si(111) to NH_3/THF. Spectra a use a clean silicon wafer covered with thermal oxide as a background. Spectra b and c use a single-beam spectrum collected in spectra a as a background. Schematic representations of the proposed surface structures are provided on the basis of a computational cluster representing two neighboring surface silicon atom sites. The left panel presents the N−H stretching-region spectrum obtained on the basis of averaging five different experiments for a better signal-to-noise ratio. The expected vibrational frequencies for surface −NH− and $-NH_2$ species obtained from computational models are presented as solid bars (frequencies were scaled by a common scaling factor of 0.965). Gray, silicon; green, chlorine; white, hydrogen; blue, nitrogen. This figure is reprinted with permission from ref 70. Copyright (2011) by the American Chemical Society.

Recently, our group demonstrated a new approach to generating Si−N linkages on silicon by reacting a chemically well-defined Cl-terminated Si(111) surface with ammonia in THF solution, as illustrated in Figure 11.[70] The use of a solvent (rather than condensed ammonia, for example) allows one to vary the reaction conditions and run this process at or above room temperature, which is needed to overcome a kinetic barrier; it also avoids potential contamination of the surface and interface by co-reagents. After 1 h of reaction at room temperature, the −NH− termination was formed on the Si(111) surface as confirmed by several analytical tools, including IR, XPS, and ToF-SIMS, and supported by our DFT computational investigations. Several representative vibrational features were observed in infrared spectra. For example, the presence of the N−H stretch and the absence of $-NH_2$ wagging vibrations, together with the confirmation of hydrogen removal (complete disappearance of the Si−H stretch vibration following chlorination step), were consistent with the successful reaction of ammonia with the chlorine-covered Si(111) surface. Selected results are shown in Figure 12. Meanwhile, the surface coverage of N was measured to be approximately 55% of the initial chlorine coverage on the basis of high-resolution N 1s and Si 2p regions, confirming that every ammonia molecule replaces two surface chlorine atoms during this modification. The XPS studies helped us to rule out the possibility of oxidation or nitride formation on the silicon surface. The high sensitivity ToF-SIMS also confirmed that the final product on the surface was a secondary amine species and not the primary amine. Finally, DFT studies investigated the possible mechanisms for the ammonia reaction with the Cl-terminated Si(111) surface and the possible surface reaction products. Similar to some of the previous investigations, the initial step of the proposed reaction leading to HCl release and the formation of the $Si-NH_2$ surface group is very slightly endothermic but is certainly possible at room temperature, and the barrier for this step is not substantial. The issue is that the simple proposed Si−N−Si bridged structure was found to be absolutely thermodynamically unstable. Thus, the formation of the secondary amine group on this silicon surface is probably accompanied by complex surface reconstruction, and only the average coverage of nitrogen corresponds to the replacement of two chlorine atoms by one ammonia molecule. Further computational and microscopy studies are needed to support this hypothesis. Regardless of the specific long-range surface

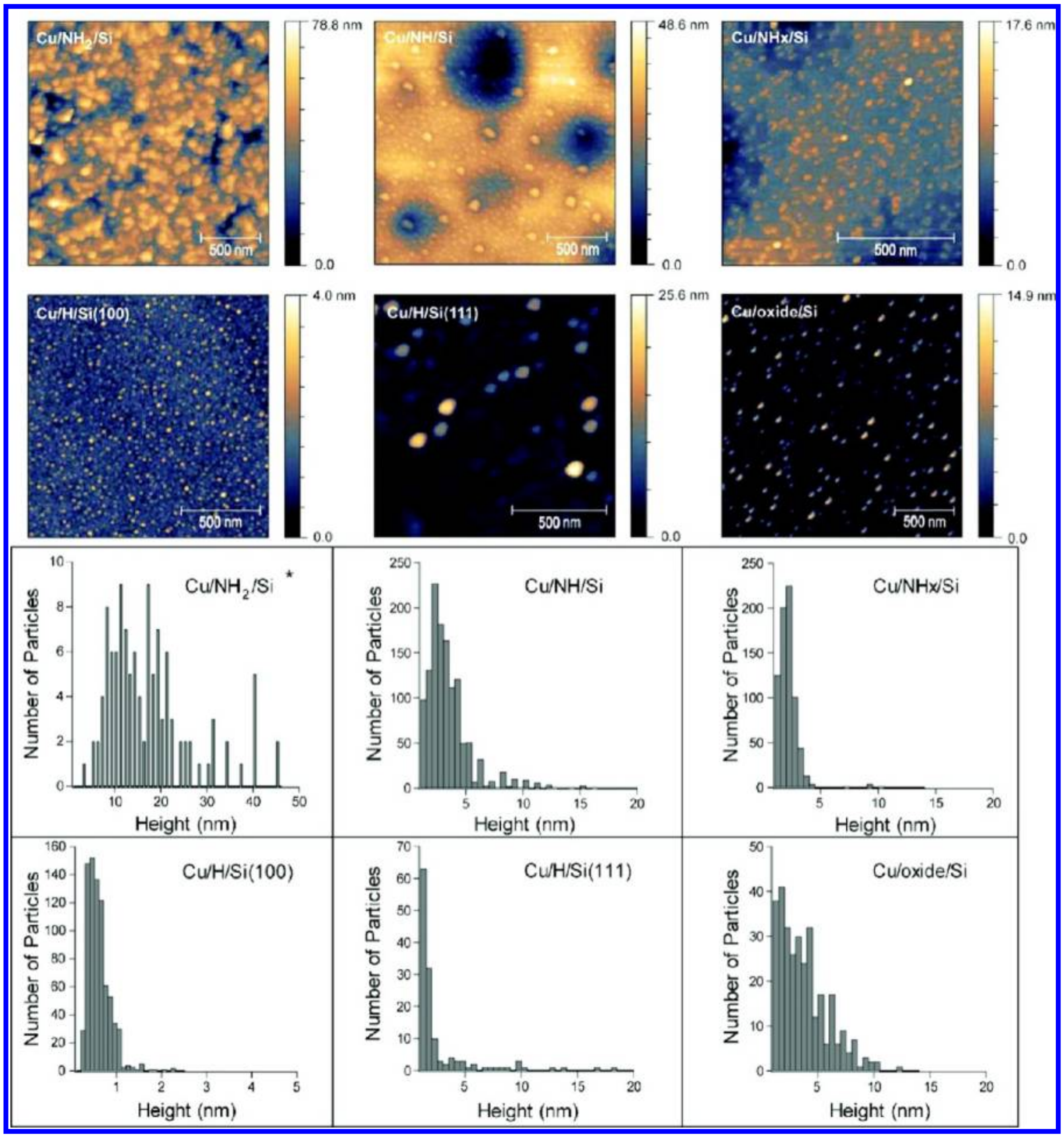

Figure 13. (Top) AFM images and (bottom) size distributions of Cu nanoparticles on selective functionalized silicon surfaces. The asterisk (*) scenario corresponded to Cu/NH$_2$/Si(100), for which it was difficult to estimate the particle height distribution and particle growth process because of the high surface roughness. The AFM studies indicated that the Cu nanostructure growth was influenced by the order and functionality of the surfaces. This figure is reprinted with permission from ref 79. Copyright (2012) by the American Chemical Society.

structure, the produced functionalized silicon substrate is stable under anhydrous THF for days, which makes this preparation procedure extremely attractive for practical applications.

3. PROPERTIES AND STABILITY OF THE SI–N LINKAGES

Silicon surface with stable Si–N linkages will have a number of important applications. Despite the fact that most of the approaches to make these linkages have been studied only recently, some of the functionalized silicon surfaces produced in these studies have already warranted some attention as platforms for further reactions.

One of the most attractive features of ammonia-reacted silicon substrates is the absence of both surface oxidation products and also the absence of surface carbon following the appropriately crafted modification procedures. The $-NH_x$ monolayer on the silicon surface can be used as a starting point for metal, metal oxide, or metal nitride deposition and may even work as a diffusion barrier during these processes. In the chemical vapor deposition (CVD) of Ti-based thin films, tetrakis(dimethylamino)titanium ($Ti[N(CH_3)_2]_4$, TDMAT) is one of the most important and common metal–organic precursors. On clean silicon surfaces, the initial stages of the chemistry of this compound resemble those of amines. The first step on Si(100)-2 × 1 involves the nucleophilic attack of the nitrogen of one of the dimethylamino groups on the electron-deficient atom of the silicon surface dimer. Of course, following this initial formation of the dative bond, the presence of N–Ti bonds in TDMAT makes the chemistry much more complex than for amines.[71] To assess the potential of S–N linkages in

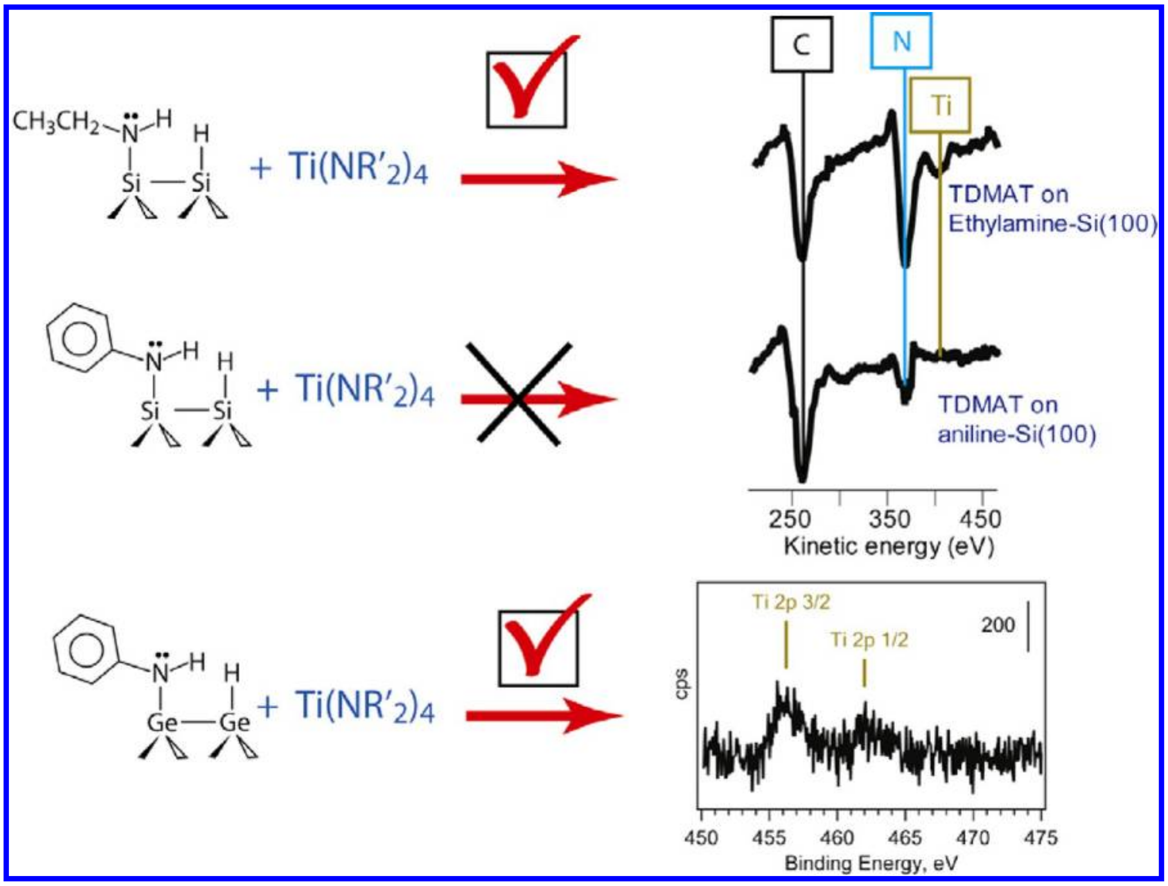

Figure 14. AES studies of a transamination reaction of TDMAT on both ethylamine- and aniline-functionalized Si(100)-2 × 1 surfaces (top two) and Ti 2p high-resolution XPS spectrum showing TDMAT chemisorbed on an aniline-covered Ga(100)-2 × 1 surface. This figure is reprinted with permission from ref 46. Copyright (2011) by the Proceedings of the National Academy of Sciences of the United States of America.

reducing carbon contamination from ligands of the TDMAT molecule, we introduced $-NH_x$ ($x = 2$ or 1) termination on the Si(100) surface by saturated dose of gas-phase ammonia on a clean Si(100) surface in UHV. The adsorption of TDMAT on NH_x-terminated Si(100) at room temperature was investigated by in situ IR, TPD, and DFT modeling.[72] The main surface reaction is a transamination process with TDMAT reacting with surface $-NH_x$ and dimethylamine eliminated concurrently. Further computational studies[73] based on density functional theory confirmed that other processes included the dissociation of C−N and C−H as a result of the formation of surface Ti−N bonds, which weakened the C−N bonds. Following the initial stages of the TDMAT reaction with modified silicon surfaces, thermally controlled TiCN and TiN film deposition on the Si(100) surface becomes possible.[74] The chemical vapor deposition of TDMAT on a clean Si(100) surface in UHV can generate a TiCN thin film, and by leaving this film in the gas-phase ammonia environment at 900 K for 10 min (exposure = 6000 L) to eliminate most carbon, the TiN film is formed. Following this nitridation step, if the surface of the film is required to have the reactivity of TiCN (which is rather different from that of TiN), then the exposure of this system to ethylene can be used to make this possible. Temperature programmed desorption (TPD), ex situ characterization by XPS, TEM, and AFM, and density functional calculations were used to study and confirm these reactions and changes in surface morphology. Besides TDMAT, the adsorption and decomposition of other metal alkylamine precursors, such as tetrakis(dimethylamido)zirconium, $Zr[N(CH_3)_2]_4$, tetrakis(dimethylamido)hafnium, $Hf[N(CH_3)_2]_4$, pentakis(dimethylamido)tantalum, $Ta[N(CH_3)_2]_5$, and bis(*t*-butylimido)-bis(dimethylamido)tungsten, $[(CH_3)_3CN]_2W[N(CH_3)_2]_2$, were also investigated by computational calculations.[75] Wang et al.[76] studied hafnium oxide deposition by dosing metal alkylamine precursor tetrakis(ethylmethylamino)hafnium, $Hf[N(CH_3)(C_2H_5)]_4$ (TEMAH), and D_2O on various functionalized Si surfaces. Silicon nitride worked as a good diffusion barrier film for HfO_2 atomic layer deposition (ALD), and the reactivity toward TEMAH was even better than those of H-terminated and Cl-terminated silicon surfaces.[77,78]

Not only can continuous films be formed following this general approach. Recently, our group demonstrated a new method for designing a highly reactive interface with controlled nanostructure formation by growing metallic copper nanostructures using Cu(hfac)VTMS as a metalorganic precursor on various functionalized Si surfaces, including H-, OH-, NH-, and NH_2-terminated silicon.[79] The reaction was followed by in situ FTIR, TPD, ex situ XPS, and AFM and supported with DFT computations. Among all samples, NH_2-terminated Si(100) presented the highest activity with respect to CVD of copper nitride, which was verified by detailed TPD and FTIR analysis. AFM studies summarized in Figure 13 showed the largest copper nanostructures on the NH_2-terminated Si(100) surface, especially compared to our previous work of deposition of Cu(hfac)VTMS on H-terminated Si(111) and Si(100).[80] In addition, NH_2-terminated Si(100) was calculated to be thermodynamically most favorable toward Cu(hfac) fragment reaction with a hydrogen abstraction energy barrier of 147.1 kJ/

mol. Further studies in this direction will be focused on the stability of the interfaces produced and on the specific mechanism of hydrogen-transfer processes. In a set of preliminary studies, the monolayer of $-NH_x$ functional groups seems to act as a perfect diffusion barrier between copper and silicon even after annealing to 600 K. However, further studies are needed to confirm this possibility.

So how does the functionalization with different amines help us to understand and fine tune the deposition processes? A recent example shows that amino-functionalized silicon surfaces with amino groups of different bacisities can be used to influence the electron-transfer process during nucleophilic reactions with such surfaces. In a set of studies summarized in Figure 14, the seemingly similar reactions of ethylamine and aniline produce surface amino functionalities with different basicities (depending on the effect of the substituent aryl or ethyl groups). The reactivity of these two surfaces in a reaction with TDMAT is drastically different. Ethylamine-modified silicon is very efficient in TDMAT adsorption but the strong electronic effect of the phenyl group in similar reaction precludes any adsorption at room temperature. Taken one step further, the amino-functioanlization process on the Ge(100) surface instead of Si(100) works regardless of whether the substituent is phenyl or ethyl. Thus, the effect of the surface itself becomes important, and the electron-transfer processes have to be understood very well in the context of a specific surface reaction. Of course, further studies have to be performed to sort out the geometric effects, and they are currently underway. However, it is undoubtedly extremely useful to have an additional chemical handle for fine tuning surface reactivity by varying a substituent group in surface amines.

4. SUMMARY AND OUTLINE OF FUTURE RESEARCH DIRECTIONS

The development of robust chemical functionalization protocols leading to the formation of stable Si−N-based interfaces still lags behind similar approaches to obtaining layered structures involving Si−O or Si−C bonds. Nevertheless, simple thermodynamic analysis suggests that further work on the Si−N interfaces is necessary because they are expected to be more stable and versatile compared to Si−C, have several electronic properties that could be more attractive than Si−O, and also provide a number of chemical handles to control the surface reactivity. The lessons learned from the decades-long research of Si−O and Si−C interfaces should shorten the time required to achieve similar understanding and control over Si−N-based films and layers. Recent rapid advances in making Si−N bonds on silicon surfaces using multifunctional compounds in vacuum and under ambient conditions, with all of the available tools for gas-phase reactions and for liquid-phase functionalization, promise that this field will undergo a substantial surge over the next 5 to 10 years. Potential practical applications for this field include photoelectrochemistry, photovoltaics, biosensing, electrocatalysis, solar energy conversion, optoelectronics, and many others. Factors such as the mechanisms of addition, condensation, and insertion processes, the production of a singular type of target surface species, controlling the geometric arrangement of these species, designing tunable chemical functionalities attached to the surface based on Si−N bonds, and increasing the thermal and chemical stability of the interfaces produced undoubtedly will be studied much more in the future. Among specific types of functionalization, robust ambient and solvent-based methods will yield approaches to practical and easy to scale up applications. However, for these schemes to be successful, it is imperative to continue fundamental studies of the mechanisms of surface reactions, both in vacuum and under ambient conditions in gas-phase and in liquid-phase modification schemes. Similarly to many other applications of silicon substrates, in addition to well-defined single crystals, future functionalization schemes will target more complex substrates, including porous silicon, silicon nanotubes and nanorods, composite silicon-based materials, and many more. Finally, for future developments to be successful, a good effort should be directed toward the use and control of the interfaces obtained. Most straightforwardly, electronic properties of the Si−N-based interfaces will have to be controlled at the highest level, and chemical functionalities placed on a surface with the help of the reactions outlined above will have to be tested for reactivity and stability under practical conditions.

Thus, this promises to be a very exciting time in developing new chemical approaches and optimizing the available ones that lead to silicon functionalization based on Si−N bonds.

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Notes

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