

**MOLECULAR LEVEL UNDERSTANDING OF DEPOSITION PROCESSES
ON FUNCTIONALIZED SILICON SURFACES**

by

Jia-Ming Lin

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

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ABSTRACT

The advances in thin solid film research have encountered a formidable challenge: to understand and produce well-defined films and corresponding interfaces at the atomic level. As the layers that make up the device become thinner and thinner, the properties of the interfaces start to affect the performance of the device exponentially. As massive attempts are focused on crafting thinner films, the surfaces involved are being treated as a *reactant* in deposition processes instead of simply a platform where the surface reactions take place. Our group focuses on silicon surface modification and the surface reactions between selected metalorganic precursors and the appropriately functionalized surfaces.

We first observed the differences in the morphology of the copper thin films deposited with Cu(hfac)VTMS on the silicon surface modified with different functionalities including $-H$, $-NH_2$, and $-NH-$ groups. The experimental surface analytical techniques including infrared spectroscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy, and microscopic investigation were supplemented by density functional theory (DFT) studies. We concluded that two major steps are involved in such a reaction: weak adsorption of a metalorganic moiety and hydrogen abstraction by its ligands.

With the help of DFT calculations, we simulated the reactions between metalorganic precursors with various ligands (including alkyl, alkoxide, alkylamide, diketone, amidinate, and cyclopentadienyl ligands) and silicon surfaces; the pros and

cons of these ligands were discussed, and in turn, several suggestions were made for future designs of novel ligands and precursor molecules.

A parallel DFT study focused on the influence from the surface functionalities including $-H$, $-NH_2$, $-NH-$, $-OH$, $-OCH_3$, and $-OCF_3$ groups on the chemisorption process. The predictions indicated that the geometry of the precursor molecule and the basicity of the surface functionalities affect the weak attraction between the precursor molecule and the surface functionalities and the kinetic barrier of the hydrogen abstraction.

In order to further understand the influence of the surface functionalities (i.e., to decouple the electronic and steric effects of the surface functionalities), the reactions between tetrakis(dimethylamido)titanium and the surfaces modified with four different primary amines were studied with an approach combining spectroscopic and theoretical methods. Although the approaches with spectroscopic methods (e.g., MIR-IR) were not conclusive, the results obtained from DFT calculation were encouraging. According to the DFT predictions, the steric effect from the substituents of the primary amines overpowers electronic effect unless the size of the substituents was decreased. In addition, the computational studies of a systematic choice of substituents revealed that the reaction barrier of the hydrogen abstraction process is directly related to the acidity (positive charge) of the proton on the amine functionalities--the more acidic the proton, the lower the barrier would be.

We hope that the molecular level understanding of the surface reactions acquired in this work will shed light on the future investigations and applications of solid substrates and novel deposition processes and materials.

For your convenience, please note:

Chapter 1 introduces the background knowledge, deposition methods, and silicon lattice structures.

Chapter 2 describes the experimental information involved in this work.

Chapter 3 focuses on the influence from the surface functionalities on the morphologies of the deposited films.

Chapter 4 presents the effects from the precursor on the deposition processes.

Chapter 5 addresses, on the other hand, the impact from the surface functionalities on the deposition processes.

Chapter 6 discusses how the electronic and steric effects from the surface functionalities pose influence on the deposition processes.

Chapter 7 concludes the works in this thesis and outlines future works.

Chapter 1

INTRODUCTION

The advances in thin solid film research have stimulated the bloom of applications of cutting-edge devices and designs for microelectronic, sensing, catalytic, and biological technologies. In almost all fields mentioned above, the fierce pursuit of smaller device size has brought the film thickness down to a nanometer scale and kept on going,¹ which encounters one formidable challenge: to produce well-defined films and corresponding interfaces at the atomic level. As the layers that make up the device become thinner and thinner, the properties of the interfaces start to affect the performance of the device exponentially.² Taking integrated circuits as an example, the electrical properties of the layers may be greatly altered because of the chemical composition and structural changes within the layers and corresponding interfaces while downscaling. The evolutionary history of deposition methods have shown us how each method was developed to take on different quests along the way.

For example, for metallic thin film deposition, physical vapor deposition (PVD) is a set of film growth procedures that include vaporization of target metal (for example, by heat, sputtering, plasma), delivery of the metal gas to the desired substrate, and recondensation of the metal onto the substrate under vacuum conditions. PVD offers straightforward, fast, and efficient manufacturing processes for films of micron scale, yet it suffers from limiting coverage for complex topography and fails to provide conformal filling of sophisticated surface features when the film thickness drops to few nanometers.³

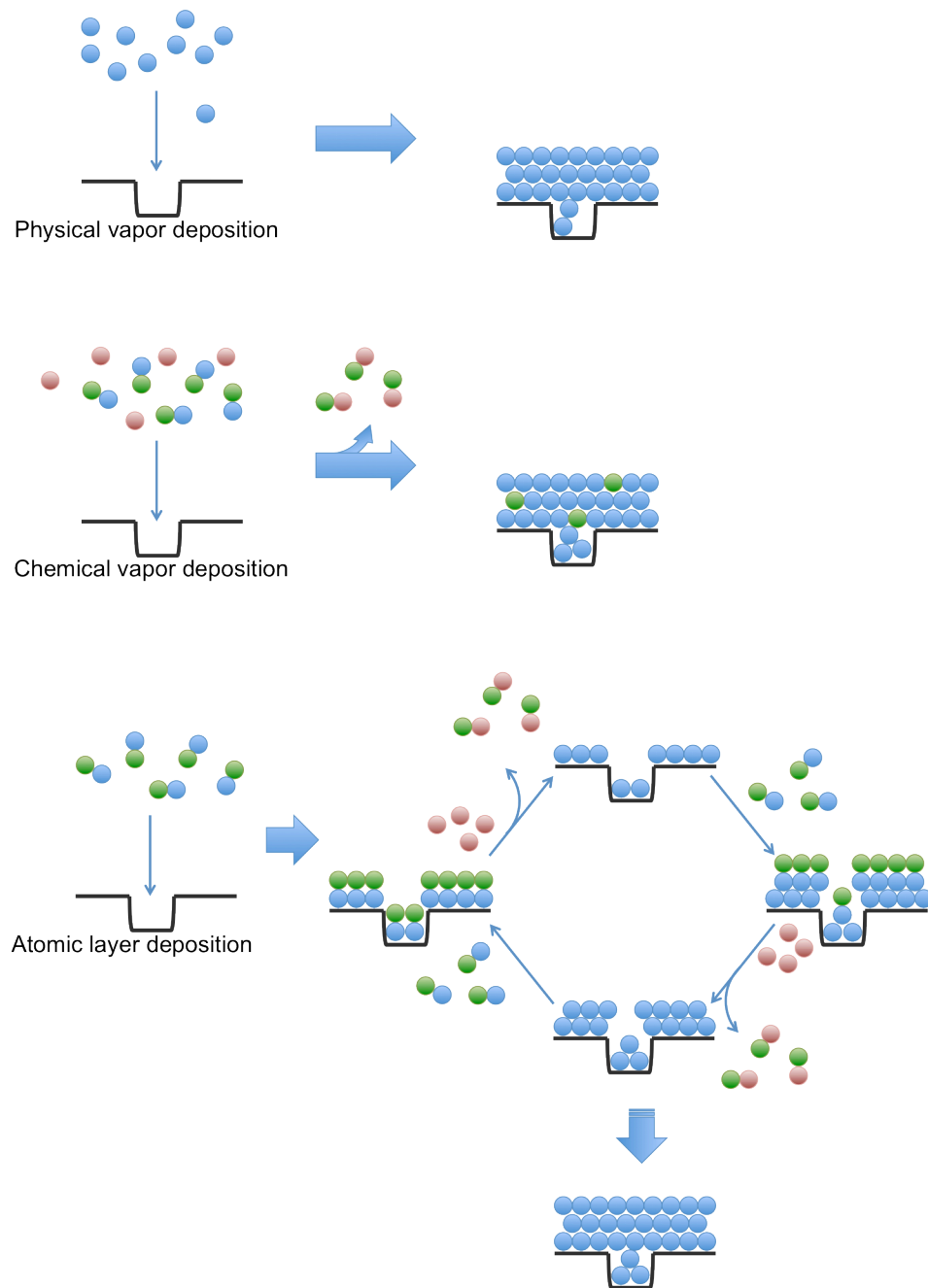


Figure 1.1: Schematic illustrations of PVD, CVD, and ALD methods that indicate the basic differences among these processes.

On the other hand, chemical vapor deposition (CVD) was engineered to fill delicate designs and deliver conformal filling even to a landscape with a high aspect ratio. Instead of vaporizing the target metal directly, CVD employs volatile molecular precursors containing this metal; after transporting these gaseous precursors to the substrate, the film growth relies on the chemical reaction between the precursor and the substrate. However, most of the precursors in the early days of CVD (e.g., metal halides) still had poor volatility, which required high thermal budget, and generated corrosive byproducts during the deposition process⁴ (figure 1.1).

To overcome this shortcoming, metalorganic chemical vapor deposition (MOCVD) was developed. MOCVD utilized metalorganic precursors that gain volatility from their organic ligands. It can be operated at relatively low temperature⁵ and preserves the advantage of conformal filling on complicated morphology, but it is still one step from flawlessness--undesired impurity is easily introduced into the film and at the interface when the organic ligands decompose during the deposition process.⁶

A redesigned deposition procedure termed atomic layer deposition (ALD) was inspired by CVD and discreetly contrived to eliminate contamination from precursor and maintain the advantage of high coverage for complex terrain. ALD is designed to deposit atomic films layer by layer, which is achieved by cycles of sequential exposure of precursors (two or more).⁷ The key characteristics of ALD is a self-limiting surface reaction.⁸

In the MOCVD method, the substrate is usually held at elevated temperatures to initiate the decomposition process of the precursors and to have the desired metal deposited on the substrate while the unwanted ligand is removed. However, the high

temperature can also lead to decomposition of organic ligands and introduce contamination to the as-deposited metal film. In contrast, ALD is usually conducted at lower temperatures. For a two-precursor process at room temperature, the first precursor reacts with the substrate and occupies all available surface sites, and the reaction ceases as no more sites are available and no extra thermal energy is provided (room temperature), then the second precursor reacts with the layer made of the first precursor in the same manner. This is a so-called self-limiting surface reaction--the surface reaction limits itself to the availability of surface reactive sites.

The chemical reaction that leads to the film growth is very important for controlling the chemical composition and structural conformation of the film in both CVD and ALD processes; however, the very first step--the surface reaction between precursors and substrates--is a prerequisite step of the entire deposition process. The surface reaction between precursors and substrates directly determines the quality (chemical composition and sharpness) of the interface between the growing film and the underlying substrate; and, in turn, the interface directly determines the quality of the film and the final device.⁹⁻¹³

It is still not too long ago that the substrate surface was for the first time considered as a *reactant* in surface chemical processes.¹⁴⁻¹⁷ The surface reaction that leads to the film growth used to be treated merely as an opposite to homogeneous process, meaning that the reaction would take place “on the substrate”, with the surface playing a catalytic role, instead of a reaction involving the surface itself as a reagent. However, more and more studies revealed that the properties of the substrate itself (clean or functionalized) influence the surface reactivity that leads to film growth.¹⁸ Although numerous interesting substrates of different materials have

attracted attention for either industrial or research purposes, silicon is still the most studied and utilized semiconductor substrate for several reasons. (1) Natural abundance: Over 90% of the Earth's crust is made of silicon oxide, which makes silicon the second most abundant element after oxygen in the Earth's crust. (2) Ease of handling: Because of silicon's impressive natural abundance, extracting pure silicon from dust or sands is less environmentally hazardous and relatively cheaper; in turn, many mature processes are known to produce high purity silicon with relatively low energy consumption.^{19,20} (3) The bloom of integrated circuit applications: Since silicon was introduced to semiconductor manufacturing, substantial research efforts and funds were supplied into this field. The more multi-tasking electronics become, the faster central processing units (CPU) are desired, and the greater knowledge of silicon chemistry and physics is desired. Because of the utility of silicon chemistry, silicon has been widely used in such diverse fields as solar cells,²¹ sensors,²² and biomedical devices.²³

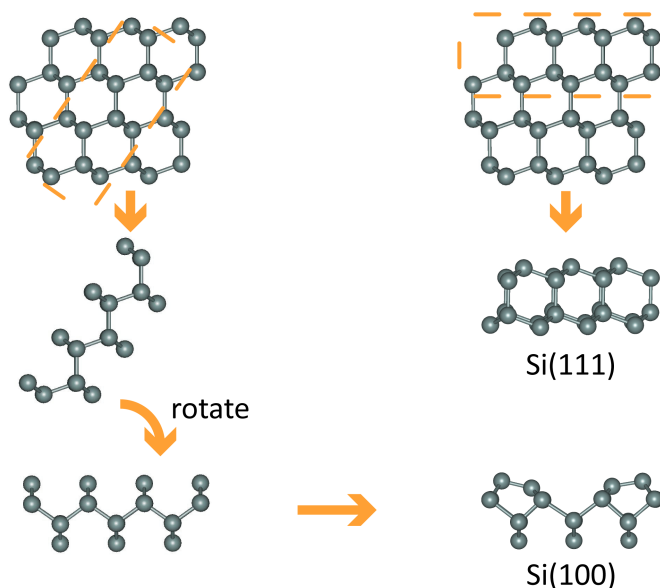


Figure 1.2: The orientation and formation of Si(100) and Si(111) cut from bulk silicon lattice.

The most common silicon surfaces studied are Si(100) and Si(111) surfaces. These two surfaces can be found by cutting the bulk silicon along different directions^{16,24} as shown in figure 1.2.

It was previously found that Si(100) surface exhibits a unique feature of buckled and staggered dimers when the thermal motion is reduced at low temperature around 40 K (denoted Si(100)-c(4x2) surface), and the two Si atoms in one dimer show zwitterionic character²⁵ as illustrated in figure 1.3. Although the 4x2 reconstruction is “defrosted” at room temperature, the zwitterionic character is retained (although the dimers are in a constant thermal motion), which is the origin of the unique activity of Si(100) surface.

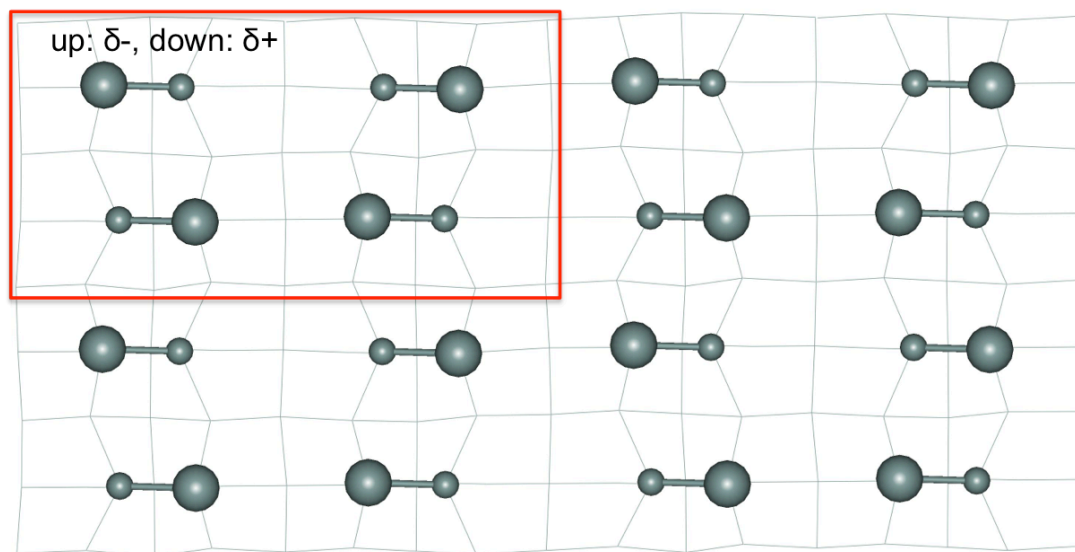


Figure 1.3: The top view of Si(100)-c(4x2) showing the zwitterionic character and the surface unit cell of 4 atoms by 2 atoms.

Si(111) surface, on the other hand, is known to exhibit a complex 7x7 reconstruction, but it is worth noting that Si(111) surfaces can be prepared to be nearly atomically flat, when it is hydrogen or halogen terminated.²⁴ Many novel designs and studies have been conducted based on this structural aspect of Si(111) surface.²⁶⁻²⁸

The studies described in this thesis focus on understanding surface reactions between precursors and silicon surfaces at the molecular level. Here, we start with the analysis of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) visually depicted by natural bonding orbital (NBO) analysis for the surface models and gas-phase reagents. HOMO and LUMO of the precursors and the surface reactive sites are often used as a starting point to reveal how the interaction between the two objects can be initiated, what relative spatial orientation may be required, and which reactive sites are favored.^{29,30} Secondly, steric and electronic effects are taken into consideration. These two effects have long been

the keys to resolving the stability or structure of molecules³¹ or manipulating the thermodynamics or mechanisms of reactions.³² In addition, infrared spectroscopy (IR), temperature programmed desorption (TPD) spectrometry, and density functional theory (DFT) calculations are used to outline the possible mechanisms of the surface reaction.

With all above, this work focuses on the molecular view of modern deposition processes.

Chapter 2

EXPERIMENTAL SECTION

2.1 Ultra-High Vacuum Chamber (UHV chamber)

One of the most crucial issues of studying the surface chemistry of a desired substrate surface is to obtain a clean surface and to maintain the cleanliness for a necessary amount of time to perform experimental analyses, and vacuum is often the answer. The vacuum, high vacuum (HV), and ultra-high vacuum (UHV) are normally referred to pressures of $10^{-3}\sim 10^{-6}$ Torr, $10^{-6}\sim 10^{-9}$ Torr, and below 10^{-9} Torr, respectively.

When a clean surface is surrounded by gas molecules under ambient pressure, molecule-surface collision rate (eq. 2.1) determines how fast the clean surface will be contaminated by the surrounding gas.

$$Rate\left(\frac{molecule}{cm^2 \cdot s}\right) = 3.52 \times 10^{22} \frac{P}{\sqrt{mT}} \quad (2.1)$$

(P: pressure; m: mass; T: temperature)

In general, there are approximately 10^{15} atoms per 1 cm^2 surface area; if every bombardment of the O_2 molecules onto the surface is sufficient for the O_2 molecule to stick to the surface, and the ambient conditions are 298 K and 760 Torr, it takes only 3.7×10^{-9} s for the surface to be fully covered by O_2 molecules. On the other hand, if

the pressure is brought down to 1×10^{-9} Torr, the clean Si surface could survive for about an hour.

Another critical factor is to detect the reactive species such as molecular fragments, electrons, or ions. The mean free path (eq. 2.2) of these species governs how long these reactive species can travel freely before reaching the detector of the instruments.

$$\text{Mean free path} = \frac{k_B T}{\sqrt{2} \pi d^2 P} \quad (2.2)$$

(k_B : Boltzmann constant; T: temperature; d: diameter of the gas particle; P: pressure)

For example, under ambient conditions, a N_2 molecule is able to travel 67 nm between collisions. However, under high vacuum conditions at 10^{-7} Torr, the mean free path of a N_2 molecule increases to 510 m, which is sufficient to be detected by most analytical instruments, such as mass spectrometer.

Thus, in order to satisfy both the requirements for maintaining the cleanliness of the surface for a reasonable time to make a measurement and for being able to detect molecules, ions, and other species, UHV conditions are needed. Ultra-high vacuum conditions are used in many parts of the study described in this thesis and are achieved in two UHV chambers built in the laboratory of Prof. Andrew Teplyakov at the Department of Chemistry and Biochemistry, University of Delaware. These two chambers are dedicated to multiple-internal-reflection infrared spectroscopy (MIR-IR) and temperature programmed desorption (TPD) studies, which are to be explained in detail later.

2.2 Silicon Substrates

The silicon substrates for the two chambers mentioned above were cut into different shapes to fit the individual chamber. Si(100) and/or Si(111) wafers (from University Wafer, p type, single side polished, 100 mm in diameter, 2 mm in thickness) were carefully hand-cut with knife into small circles (9 mm in diameter) to fit the manipulator used for TPD studies. For MIR-IR studies, the wafers (from University Wafer, p type, double side polished, 100mm in diameter, 1 mm in thickness) were cut into $25\text{mm} \times 20\text{mm} \times 1\text{mm}$ trapezoids with 45 degree beveled edges at Hickory Hill Designs.

2.3 Surface Preparation and Cleaning in UHV

The silicon substrates needed to be cleaned before each experiment. Although both substrates in the two individual chambers were to be cleaned under UHV conditions, the procedures are slightly different due to different geometries and equipment of the chambers.

The cleaning procedure for the silicon samples includes cycles of: (1) Argon ion sputtering by an ion sputter gun (Physical Electronics Inc. on MIR-IR chamber; Leybold-Heraeus on TPD chamber) with argon pressure of 3.5×10^{-5} Torr (Matheson, 99.9999%) and beam energy of 2 keV for one hour; (2) Heating up of the silicon substrate with a heater to at least 1000 K (e-beam heater on MIR-IR chamber, McAllister Technical Services; button heater on TPD chamber, Heat Wave Labs) then cooling down (at approximately 2 K/s); (3) Surface elemental analysis by Auger electron spectroscopy (Physical Electronics Inc. and Staib instrumente, respectively). When the surface cleanliness is verified by Auger electron analysis, the last clean cycle is conducted at lower argon ion sputtering pressure (1×10^{-5} Torr), low beam

energy (1 keV), and followed by 20 minutes annealing at 1000 K for the surface reconstruction to take place.

2.4 Multiple-Internal-Reflection Infrared Spectroscopy (MIR-IR)

Infrared spectroscopy is commonly used to study molecular structures by identifying the vibrational modes of the functional groups. In this study, IR spectroscopy was applied to study the surface species in a multiple-internal-reflection configuration (figure 2.1).

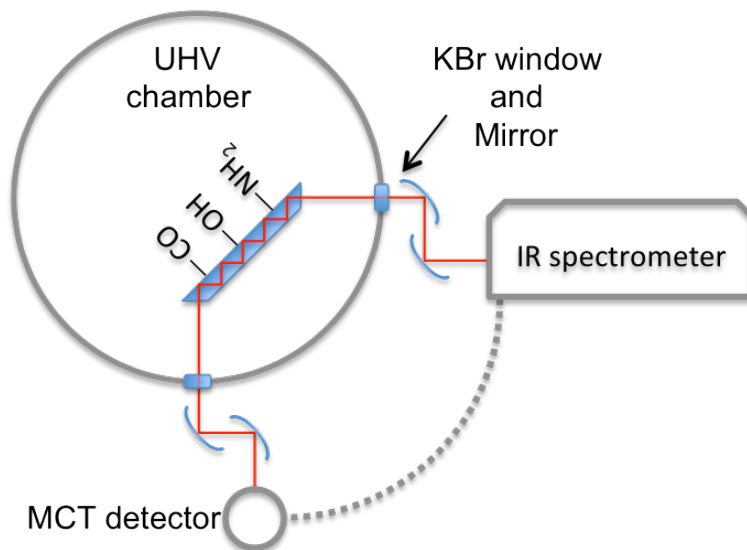


Figure 2.1: Top view of the experimental setup for MIR-IR studies: an infrared beam from the spectrometer (Nicolet Magna-IR 560) was directed into an external MCT detector via the UHV chamber equipped with KBr windows.

An experiment can be described taking the IR studies of copper deposition precursor molecule and amine/imine modified surfaces as the example. After the

cleaning cycle, the trapezoidal substrate was aligned to yield optimal signal intensity. A spectrum of a clean surface was then collected and served as the background for following surface modification experiments (2048 scans, 8 cm^{-1} resolution). Then the substrate was modified with amine ($-\text{NH}_2$) and imine ($-\text{NH}-$) functionalities.

To modify the Si substrate with amine functionality, the clean Si substrate was exposed to ammonia (research purity, Matheson) atmosphere that was intentionally introduced into the UHV chamber through the leak valve without moving the manipulator. The amount of the exposure was quantified in langmuirs (L), defined as second times 10^{-6} Torr ($1\text{ L} = 1\text{ s} \times 10^{-6}\text{ Torr}$). The functionalization was conducted by filling the UHV chamber with ammonia gas to 5×10^{-7} Torr for 200 seconds (total 100 L) at room temperature. Another single beam infrared spectrum was collected and referenced to the background spectrum of clean Si substrate via the spectral math function in OMNIC software (Thermo scientific). The appearance of the Si-H stretching peak around 2070 cm^{-1} was used to confirm the success of amine functionalization, as described in detail below.

The imine functionalization on Si substrate was obtained via further annealing the amine functionalized Si surface at 650 K for 1 minute; after the surface was recooled, an infrared spectrum was collected and referenced to the clean substrate background in the same manner as was done for amine functionalized surface. The blue-shifting of the Si-H signal (to 2100 cm^{-1}) was used to confirm the surface amine groups were transformed into imine groups.

Our previous study shows that ammonia molecules adsorb on Si(100) in a dissociative process with one ammonia molecule breaking into $-\text{NH}_2$ and $-\text{H}$ moieties, and the two moieties bond to two different surface Si atoms in either intra-

or inter-dimer manners.³³ Therefore, the vibrational frequency around 2070 cm⁻¹ (corresponding to the resulting Si-H group) validates the success of amine functionalization. In addition, those studies also indicated that further annealing of the as-prepared -NH₂ functionalized surface at 650 K decomposes -NH₂ groups into -H and -NH- moieties with the -NH- part inserting into the Si-Si bond of either surface dimer or subsurface backbone.³³ Since the vibrational frequency of surface Si-H groups is well known to be very sensitive to the environment,³⁴ when the environment changes from -NH₂ to -NH- groups, the frequency shifts from 2070 to 2100 cm⁻¹ accordingly. Consequently, the blue-shifting of the Si-H signal was treated as the benchmark of transforming -NH₂ groups into -NH- groups.

Copper (hexafluoroacetylacetonato)vinyltrimethylsilane (Cu(hfac)VTMS, CupraSelect, Air Products) was used to react with both -NH₂ and -NH- functionalized surfaces. After this liquid copper deposition precursor was dosed into the chamber and reacted with the modified surfaces, a single beam infrared spectrum was collected again and referenced to the background spectrum of the modified surface; the decrease of Si-H absorption signal revealed the reaction between copper precursor and the surface functionalities. Different amounts of copper precursor exposure on the modified surfaces were systematically studied, and the peak intensities of Si-H signals were analyzed to understand the kinetics and mechanism of the reaction between copper precursor and the two modified surfaces. The results, or data, will be discussed in detail later.

2.5 Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) technique was developed to study the desorbing species from the surface. When a surface is heated with a linear heating

rate, the species that adsorbed on the surface can desorb molecularly or produce molecular products as a result of chemical reaction, which in turn may desorb; the temperature at which the species desorb varies with the nature of the adsorbates and the surface, and the binding energy can be calculated from the desorption temperature. As shown in figure 2.2, the setup is equipped with a button heater controlled by a temperature programmer (Eurotherm, Model 818) that is capable of ramping substrate temperature linearly. During the thermal desorption process, the substrate is brought very close (~ 2 mm) to the mass spectrometer (SRS 200), and a differentially pumped shield is utilized to allow only the species desorbing from the center of the surface to reach the mass spectrometer.

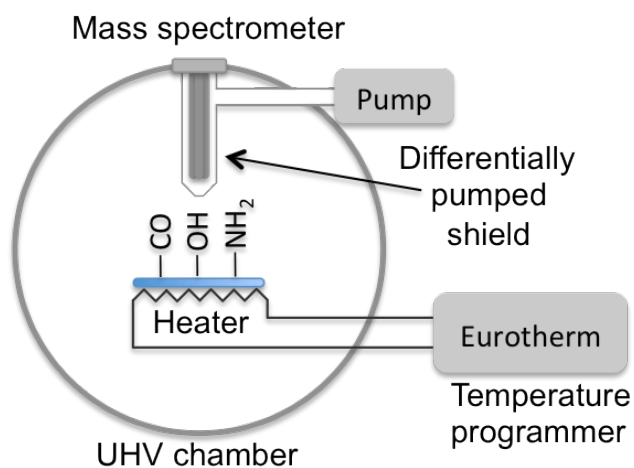


Figure 2.2: Top view of the experimental setup for temperature programmed desorption (TPD) studies.

Again, we take the reaction of Cu(hfac)VTMS and amine/imine-modified surfaces as an example. In the TPD studies, deuterated ammonia (ND₃, ISOTEC, 99%

D purity) was used to modify the Si substrate to avoid the interference from the hydrogen from background. The clean surface was first exposed to 100 L ND₃ at room temperature to be modified with –ND₂ termination, then, brought very close to the mass spectrometer, and linearly (2 K/s) heated from room temperature to 1000 K. All ions corresponding to the expected fragment masses (for example: 2 for D, 4 for D₂, or 18 for ND₂) were followed during TPD analysis by the mass spectrometer with counts vs. time mode. The –ND– modification was introduced to the Si substrate by annealing the –ND₂ modified Si substrate at 650 K for 1 minute and recooling to room temperature. The same TPD analysis was performed for this –ND– modified surface.

TPD analysis does not only provide information of binding energy but also quantitative information. In the studies of the reaction between copper precursor and the amine/imine modified surfaces, TPD method was used to investigate the reaction rate, order, and mechanisms of this system. After the –ND₂ or –ND– modified surfaces were prepared as described previously, systematic exposures of Cu(hfac)VTMS were dosed onto the surfaces (for example: 50, 100, 200, 400, and up to 3000 L). After each trial, the sample was heated linearly (2 K/s) to 1000 K, while the mass spectrometer was set to monitor mass 2 and 4 for deuterium atom and D₂ molecule, respectively. The resulting desorption peaks of deuterium were integrated and used to represent the amount of surface deuterium left after the reaction with copper deposition precursor molecules. The peak integration of the experiment without exposure to copper precursor was treated as 100% deuterium concentration and used to normalize all other peak areas to reveal how copper precursor molecules consumed surface deuterium and to extract the kinetic information about this reaction.

2.6 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy is a surface analytical technique (0.5 to 5 nm depth) that offers quantitative information about surface elemental composition; it applies Auger effect that was discovered independently by Lise Meitner and Pierre Auger in the 1920s. Auger effect refers to a process where an atom is excited and loses one of its core electrons, which causes the electron at outer shell to refill the core orbital; if the relaxation energy is greater than the binding energy of another outer shell electron, that electron can be ejected (Auger electron), as schematically shown in figure 2.3.

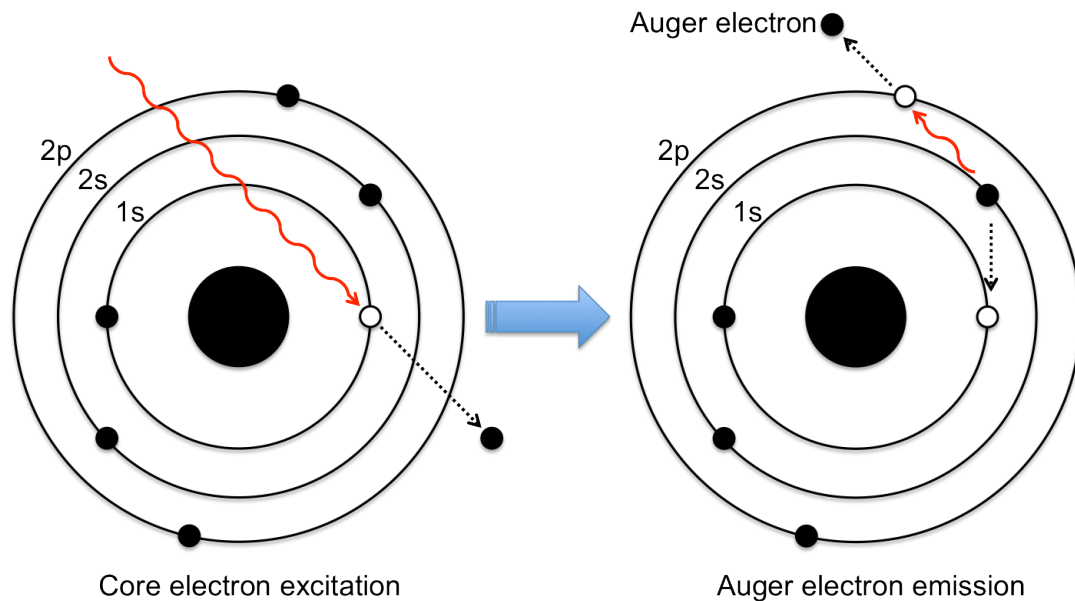


Figure 2.3: Auger effect: a series of internal electron relaxation leading to electron emission.

The Auger electron will carry a certain amount of kinetic energy that comes from a series electron relaxation and is not affected by the excitation source. Taking

figure 2.3 as an example, the kinetic energy of the Auger electron equals the potential energy of 2s and 2p orbitals subtracted from the energy of 1s orbital ($E_k = E_{1s} - E_{2s} - E_{2p}$). Because the energy of the Auger electron is not affected by the excitation source and is determined only by its source element, Auger electron spectroscopy (AES) becomes a reliable surface elemental analysis in microelectronics and other fields.

The Auger spectrometers used in this study were PHI model 25-110 (Physical Electronics Industries) and ESA 100 (Staib Instruments) with their electron gun energies both set to 3000 kV and were installed on MIR-IR chamber and TPD chamber, respectively.

2.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface analytical technique (0 to 10 nm deep) that is very similar to AES discussed above. Instead of using electron beam, XPS utilizes X-ray to excite surface elements and analyzes the kinetic energy of the emitted electrons. As shown in figure 2.4, the core electrons are ejected following X-ray absorption, and their kinetic energy is recorded and analyzed to reveal their original binding energy, type of the source element, and even oxidation state of the source element. XPS data are normally presented in terms of binding energy that is calculated by subtracting the observed kinetic energy and work function of spectrometer from the energy of incoming X-rays ($E_b = E_{xray} - E_k - w$). In addition to the oxidation state information, XPS has one more advantage over AES: XPS offers excellent quantitative accuracy--which makes XPS a very welcome analytical technique in surface science fields.

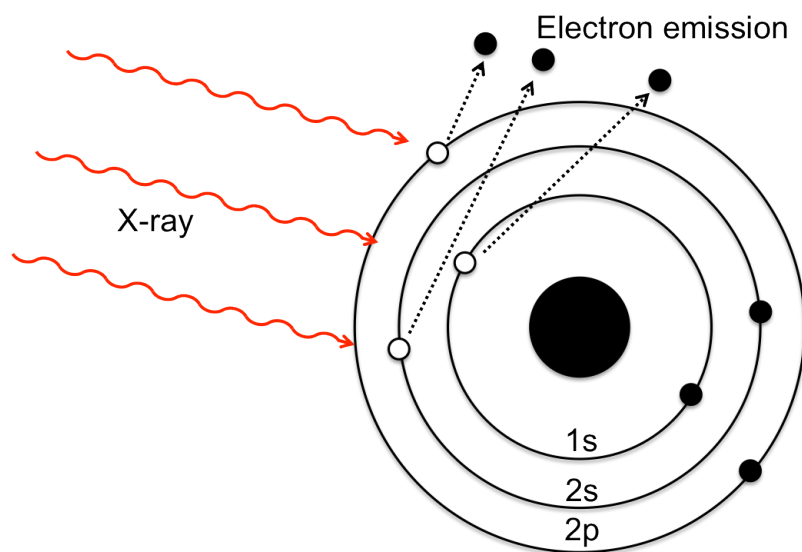


Figure 2.4: Schematic illustration of X-ray photoelectron spectroscopy: The elemental analysis relies on measurements of the kinetic energies of the escaping electrons.

In this study, the XPS data were collected ex situ at a university facility, which made the XPS studies complicated by a possibility of contamination from the ambient when transferring the sample.

There were two XPS instruments used in this study. A PHI 5600 system with a base pressure of 1×10^{-9} Torr with either an Al K α monochromatic X-ray source (1486.6 eV) or Mg K α anode (1253.6 eV) as the X-ray was used in the laboratory of our collaborator, Professor R. Opila at the department of Materials Science and Engineering, University of Delaware. In this system, the analyzer was placed at 45° offset from the sample. For survey spectra, the pass energy of 187.85 eV was set to scan from 0 to 1200 eV with 1.6 eV/step rate and 200 ms/step dwell time. High-resolution spectra were collected at a 46.95 eV pass energy using a 0.1 eV/step and 200 ms/step dwell time. The other XPS instrument was VG ESCA lab 220i-XL

electron spectrometer (VG Scienta, UK), at a base pressure of 10^{-8} Torr, in the Surface Analysis Facility in the Department of Chemistry and Biochemistry, University of Delaware. Spectra were collected with both Al K α X-rays and Mg K α X-rays operated at 15 kV, 8.9 mA, and 120 W using a spot size of 400 μ m. Survey spectra were obtained from 0 to 1200 eV using pass energy of 100 eV. Pass energy was set to 20 eV for high-resolution spectra with 100 ms dwell time. The CASA software was used to perform peak fittings in all cases.

2.8 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) offers excellent high-resolution images at sub-nanometer scale. The probe of AFM includes a cantilever and a tip; when the tip moves around the surface, the force between the tip and the surface affects the position of the cantilever, and this position is detected by a laser deflection, as shown in figure 2.5. A photodiode is utilized to sense the reflected laser and transform the light signals to current, so that morphological information probed by the tip can be detected and recorded.

The AFM images shown in this thesis were collected with a Nanoscope V (Veeco) in the Keck Electron Microscopy Facility at the University of Delaware with tapping mode at 512 lines per scan and Aluminum-coated silicon nitride tips resonating at 300 kHz (Budget Sensors).

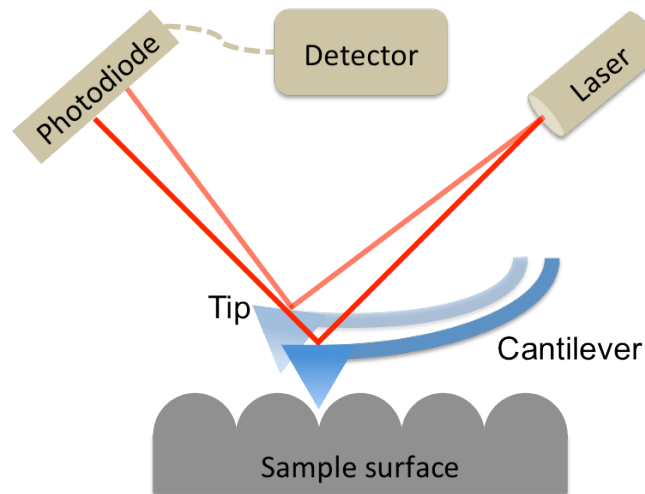


Figure 2.5: Schematic illustration of atomic force microscopy: A photodiode is used to transform the reflected laser to electric signals that carry the morphological information probed by the tip.

2.9 Computational Methods

Density functional theory (DFT) is one of the most popular computational methods used in physics, chemistry, and many other fields. Although the concept of DFT was built on Thomas–Fermi (TF) model^{35,36}, it was not put to a practical use until the two Hohenberg–Kohn theorems (H–K)³⁷ were established. DFT allows the structures of the molecules to be optimized, and the ground state energies and vibrational frequencies of the as-optimized molecules to be predicted with an affordable period of time and resource. The ground state energies can be afterward put together to draw the potential energy diagram along the reaction coordinate, which is helpful in studying reaction mechanism. The comparison of the experimental IR spectra to the predicted vibrational frequencies becomes more and more popular (almost essential) when publishing in the field of surface science. The DFT investigations presented in this thesis were performed with Gaussian 09 suite of programs³⁸ and its graphical interface GaussView 5. The levels of theory used in this study will be specified in each chapter, and a brief introduction to each level of theory is given here:

B3LYP^{39,40}/LANL2DZ⁴¹⁻⁴³ is widely used for transition metals. This basis set simplifies the calculation of core electrons to greatly reduce the calculation expense.

B3LYP/6311+G(d,p)⁴⁴⁻⁵² can be applied from H to Kr. It takes into account both core and valence electrons, polarization of atoms, and diffuse functions of atoms other than H and He (light atoms) in the calculation.

B3LYP/6311++G(d,p)⁵³ further introduces the diffuse functions of H and He atoms to the calculation on top of B3LYP/6311+G(d,p).

B3LYP/cc-pVTZ⁵⁴⁻⁵⁹ is the highest level of theory used in this study. It offers great accuracy but requires enormous computation time.

All the molecules or structures studied here with DFT had no constraint applied on any of the atomic positions with few exceptions that needed constraints to avoid unrealistic distortion of the structure. Detail rationales will be addressed later in the section and in other chapters.

All the energies reported in the potential energy diagrams in the thesis were referenced to the reactant state (the sum of the individual ground state energies of all the reactants before reaction takes place) and converted into kJ/mol (1 hartree = 2625.5 kJ/mol).

Transition states were predicted with synchronous transit-guided quasi-newton (STQN) method^{60,61} and confirmed with the presence of a single negative eigenvector (a negative frequency) in the corresponding frequency calculations.

Natural bond orbital (NBO) analysis was used to visualize the graphical representations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecules or molecular fragments and the clusters representing silicon surfaces, which were then used to rationalize the interaction between molecules and predict the feasible starting point of the reaction.

2.10 Silicon Cluster Models

The cluster models used to represent the natural surface are crucial when studying the reaction of the precursor molecules and surfaces with computational methods. In this thesis, Si(100) and Si(111) surfaces and their functionalized derivatives were simulated with different cluster models.

Base on the crystal structure described previously in the introduction section, a $\text{Si}_{17}\text{H}_{22}$ cluster model was used to represent two neighboring silicon surface atoms on the clean and unreconstructed Si(111) surface with all the silicon atoms representing the subsurface saturated with hydrogen atoms to achieve sp^3 hybridization. Because this two-surface-atom-system visually resembles the dimer system on Si(100) surface, it is often compared to a single Si(100) dimer. When the two topmost silicon atoms (representing the surface layer) were terminated with hydrogen atoms, a $\text{Si}_{17}\text{H}_{24}$ cluster model was created to simulate H-Si(111) surface as shown in figure 2.6.

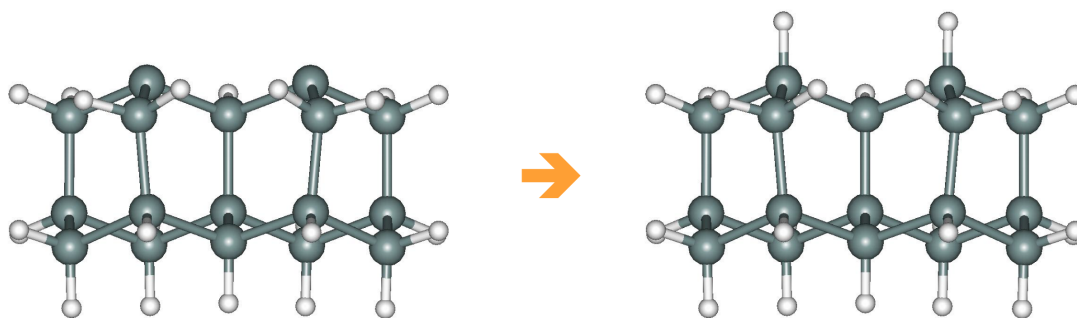


Figure 2.6: The $\text{Si}_{17}\text{H}_{22}$ (left) and $\text{Si}_{17}\text{H}_{24}$ (right) cluster models for clean Si(111) and hydrogen terminated Si(111) surfaces, respectively.

Because of its unique reactivity, Si(100) surface has been studied extensively both experimentally and computationally; consequently, a large number of cluster

models for Si(100) surfaces of different sizes, functionalization, and reconstruction were designed for specific computational studies. The models of Si(100) surface studied in this thesis are categorized as follows.

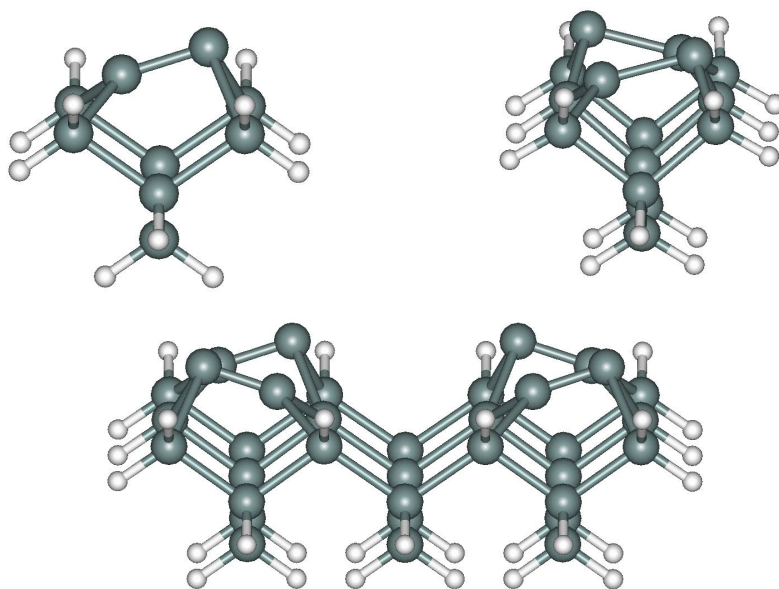


Figure 2.7: Clean Si(100) surface: Si_9H_{14} (top left), $\text{Si}_{15}\text{H}_{20}$ (top right), and $\text{Si}_{35}\text{H}_{40}$ (bottom) cluster models were used to simulate Si(100) surfaces with one, two, or four surface silicon dimer reactive sites.

As shown in figure 2.7, three clusters, Si_9H_{14} , $\text{Si}_{15}\text{H}_{20}$, and $\text{Si}_{35}\text{H}_{40}$, were used to represent a clean Si(100) surface, which correspond to a single dimer, two dimers, and four dimers, with appropriate hydrogen atom termination in the same manner as what has been done for Si(111) clusters. Despite the fact that all the Si(100) cluster models were cut in different sizes, it is important to note that they were constructed according to the lattice structure discussed in the introduction section, and the buckled

architecture of these models structurally featured the zwitterionic behavior of Si(100) surface. With these basic cluster models of clean Si(100) surface, more models of many different functionalities on Si(100) surface were created, as described later in the chapter.

Two different types of hydrogen termination on Si(100) surface were considered in this study: mono-hydrogen and di-hydrogen terminations, which were modeled with Si_9H_{16} and Si_9H_{18} clusters as shown in figure 2.8. According to our previous studies, if the reaction does not involve insertion of functional groups into the sub-layer Si–Si backbone, the predicted results are essentially the same with or without positional constraints. However, the two transition state calculations involving di-hydrogen terminated Si(100) cluster needed constraints on all subsurface atoms (leaving only four topmost hydrogen atoms unconstrained) to avoid unrealistic distortion of the cluster model.

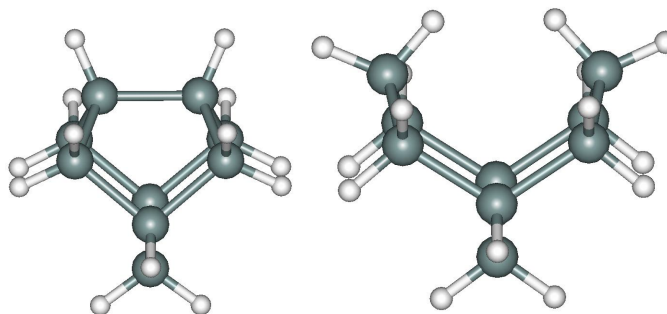


Figure 2.8: Hydrogen-functionalized Si(100) surface: Si_9H_{16} (left) and Si_9H_{18} (right) clusters were used to represent mono-hydrogen and di-hydrogen functionalized Si(100) surface.

Nitrogen-containing functionalities on Si(100) surface were studied experimentally and computationally. There were three cluster models crafted to simulate three different nitrogen-containing functionalities that can be prepared experimentally with ammonia, as shown in figure 2.9. The two imine-terminated clusters were established according to previous understanding that the surface -NH_2 groups can be thermally transformed into imine groups, and the resulting imine group can either insert into the Si-Si bond of the surface dimer or subsurface backbone.

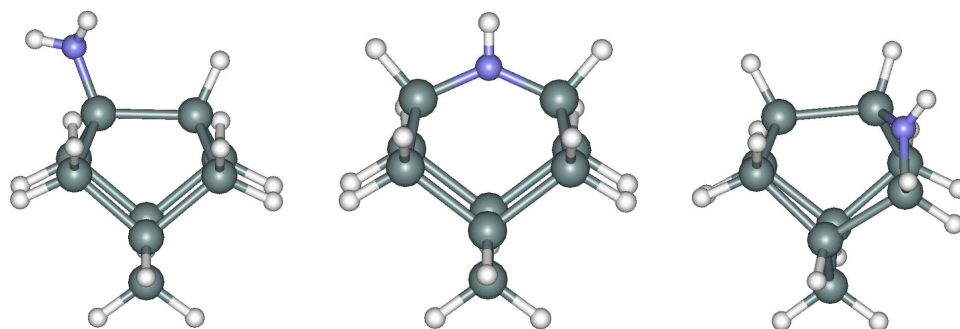


Figure 2.9: Cluster models of amine/imine functionalized Si(100) surfaces: surface amine group (left), bridging imine (center), and backbone-inserted imine (right).

A systematic selection of amines was made to study the electronic and steric effect of the surface functionalities, which includes aniline, cyclohexylamine, fluoroamine, trifluoroethylamine, difluoroethylamine, fluoroethylamine, ethylamine, trifluoromethylamine, difluoromethylamine, fluoromethylamine, and methylamine as shown in figure 2.10.

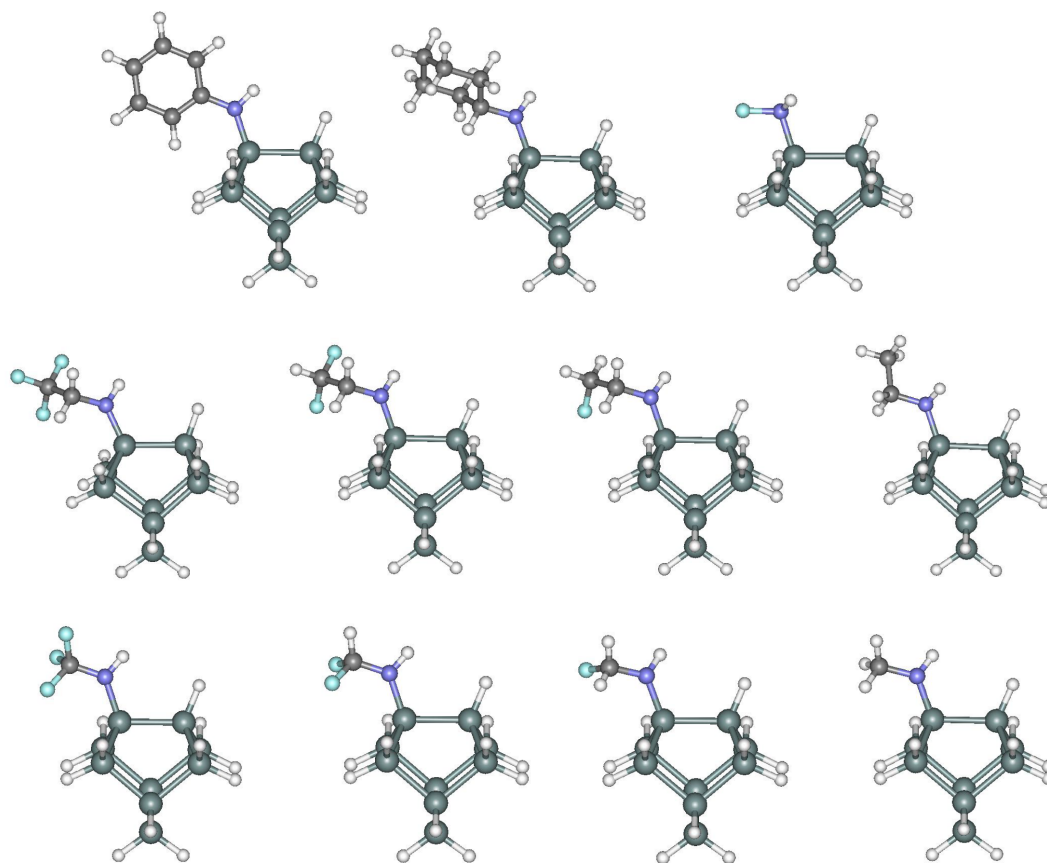


Figure 2.10: Series of amine functionalities with different substituents: (from top left to bottom right) phenyl, cyclohexyl, fluoro, trifluoroethyl, difluoroethyl, fluoroethyl, ethyl, trifluoromethyl, difluoromethyl, fluoromethyl, and methyl groups.

The last class is the oxygen-containing functionalities. Hydroxyl, methoxyl, and trifluoromethoxyl functionalities were chosen as modifiers of the Si(100) surface, and the corresponding cluster models were constructed and shown in figure 2.11.

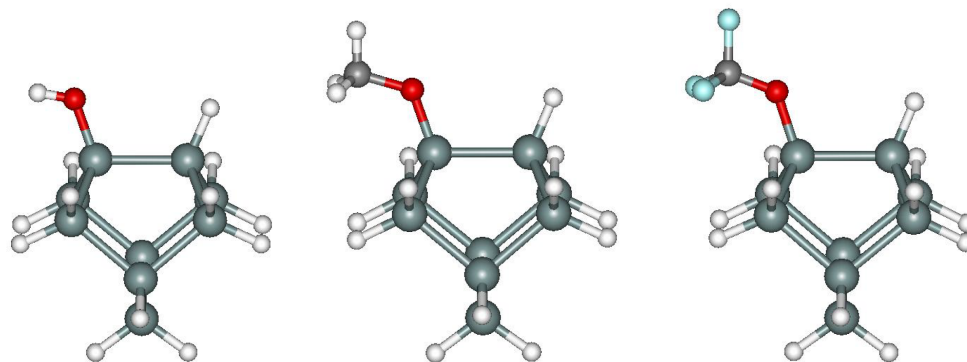


Figure 2.11: Cluster models of Si(100) surface modified with oxygen-containing functionalities: hydroxyl, methoxyl, and trifluoromethoxyl groups.

With the techniques mentioned above, all the data and information obtained from the studies combining MIR-IR, TPD, and DFT designed to understand the kinetics and mechanisms of surface reactions were combined with XPS, AES, and AFM investigations that were used to follow surface morphological and compositional changes, as will be presented and discussed in the following chapters.

Chapter 3

CONTROL OF THE FORMATION OF COPPER NANOPARTICLES ON FUNCTIONALIZED SILICON SURFACES*

3.1 Introduction

Copper is one of the most popular metals used in microelectronics as an interconnect material partially due to its low electrical resistivity. To fulfill the versatile requirements (wires or films, thin or thick), many different deposition processes, such as physical vapor deposition (PVD) or chemical vapor deposition (CVD), have been applied to prepare copper interconnects. Although CVD provides conformal filling to complex topography and is considered superior to PVD methods, the ligands used to increase the volatility of metal precursors for CVD still impede these applications because of organic contamination. Atomic layer deposition (ALD), on the other hand, has been widely studied for its self-limiting character that could provide conformal filling similarly to CVD while minimizing organic contamination. Here we investigate the ALD deposition process involving copper (hexafluoroacetylacetonato)-vinyltrimethylsilane and ammonia-functionalized Si(100) surfaces.

Ammonia-modified silicon surfaces have shown the capability of decreasing interface carbon contamination from the ligand (dimethylamide) of organometallic

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precursors in titanium nitride film deposition.⁶²⁻⁶⁴ As indicated in the experimental description chapter, our previous studies have demonstrated the preparation and thermal transformations of the ammonia-prepared silicon surfaces.³³ In addition to $-\text{NH}_2$ and $-\text{NH}-$ functionalized surface, a surface terminated with a mixture of $-\text{NH}_2$ and $-\text{NH}-$ functionalities was prepared by preheating the silicon substrate to 650 K before exposing it to the ammonia (200 L). Figure 3.1 summarizes the details of functionalized silicon surface preparation.

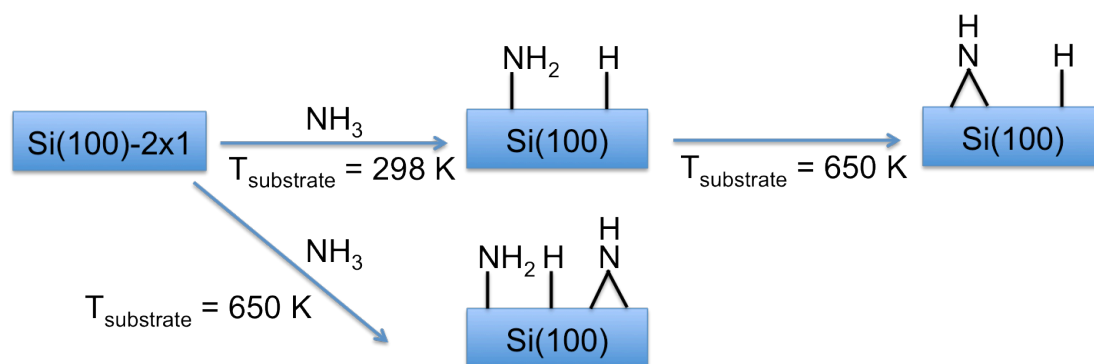


Figure 3.1: Preparation of $-\text{NH}_2$, $-\text{NH}-$, and $-\text{NH}_x$ functionalized $\text{Si}(100)$ surfaces.

Copper(hexafluoroacetylacetonato)vinyltrimethylsilane, $\text{Cu}(\text{hfac})\text{VTMS}$, is a commercially available copper deposition precursor. This copper precursor is engineered to improve its reactivity and volatility with the two ligands--vinyltrimethylsilane (VTMS) and hexafluoroacetylacetonate (hfac). It has been proved that the VTMS ligand is easily removed from the precursor molecule upon adsorption on clean silicon surface^{65,66} or the surface of a thin TiCN film⁶⁷ without posing significant contamination problems; however, the remaining hfac ligand can lead to C,

F, and O contamination,⁶⁸ which is what we hope to overcome by utilizing ammonia-functionalized silicon surfaces.

The proposed deposition processes involving Cu(hfac)VTMS and ammonia-prepared silicon surfaces is a CVD-like process with limited amount of surface reducing agent (Si-H and Si-NH_x groups), which makes the process very similar to an ALD process; that is, the overall amount of copper deposited is restricted because only limited amount of surface reducing agent is available to complete the reaction. The results were also compared to the previous study focused on the reactions of Cu(hfac)VTMS with H-Si(100), H-Si(111), and silicon oxide surfaces to derive the comprehensive understanding of deposition processes involved.⁶⁹

3.2 Methods

This study utilizes MIR-IR, TPD, XPS, AFM, and DFT methods that are previously explained in experimental section. Selected results adapted from previous investigations for comparison were obtained with different surface preparation or analytical investigation techniques, as will be explained in this section.

The silicon substrates with hydrogen or hydroxyl terminations were prepared with modified RCA methods.⁷⁰⁻⁷² The silicon wafers (both Si(100) and Si(111) were from University Wafer, p type, double-side polished, 2 mm in thickness) were placed and cleaned in a Teflon beaker with a 4:1:1 solution of Milli-Q water (≥ 18 M Ω ·cm, Millipore Corporation)/hydrogen peroxide (30%, certified ACS grade, Fisher Scientific)/ammonium hydroxide (29% certified ACS plus grade, Fisher Scientific) in an 80 °C water bath for 10 min, then the wafers were rinsed 3 times with 50 ml Milli-Q water (≥ 18 M Ω ·cm, Millipore Corporation). The native oxide on the silicon surfaces was etched off with a 2 minute dip in buffered hydrofluoric acid (buffer-HF improved

from Transene). Again, the wafers were rinsed 3 times with 50 ml Milli-Q water. A protective oxide layer was grown utilizing a 4:1:1 solution of Milli-Q water (≥ 18 M Ω ·cm, Millipore Corporation)/30% hydrogen peroxide/hydrochloric acid (37.3% certified ACS grade, Fisher Scientific) in an 80 °C bath for 10 min. After rinsing with Milli-Q water, the Si(111) wafers with the protective oxide layer grown at this stage served as the silicon oxide surface for further investigation.⁷³ For hydrogen terminated Si(100) and Si(111) surfaces, the preparation procedure was continued.

In the case of Si(111), the final step was 1 minute buffered hydrofluoric acid (buffer-HF improved from Transene) etch followed by a 6 minute etch in ammonium fluoride (40%, Fluka). On the other hand, 2 min etch in 48% HF (Aldrich, for in situ experiments) was applied to the Si(100) wafer.

Once the substrates were prepared, they were immediately placed in the HV chamber and pumped down to below 1×10^{-5} Torr. The Cu(hfac)VTMS precursor was dosed at a pressure of approximately 2.1×10^{-2} Torr for 2-10 min to saturate the surface at room temperature.

3.3 Results and Discussion

This section will start with AFM analysis. The AFM images of Cu(hfac)VTMS reacting with ammonia-prepared Si(100) surfaces were compared to those of Cu(hfac)VTMS reacting with other surfaces from previous investigations,⁶⁹ as shown in figure 3.2. The NH₂-Si(100) surface functionality^{33,74,75} exhibits the formation of relatively large particles following exposure to Cu(hfac)VTMS. Unlike the NH₂-Si(100) surface, the NH-Si(100) substrate shows the formation of a combination of large and small copper particle growth regimes with an overall narrow size distribution centered around 3 nm in height, which could be attributed to the starting

nonuniform surface containing either bridged -NH- species between Si atoms of a surface dimer or inserted into silicon backbone below surface atoms.^{33,74,75}

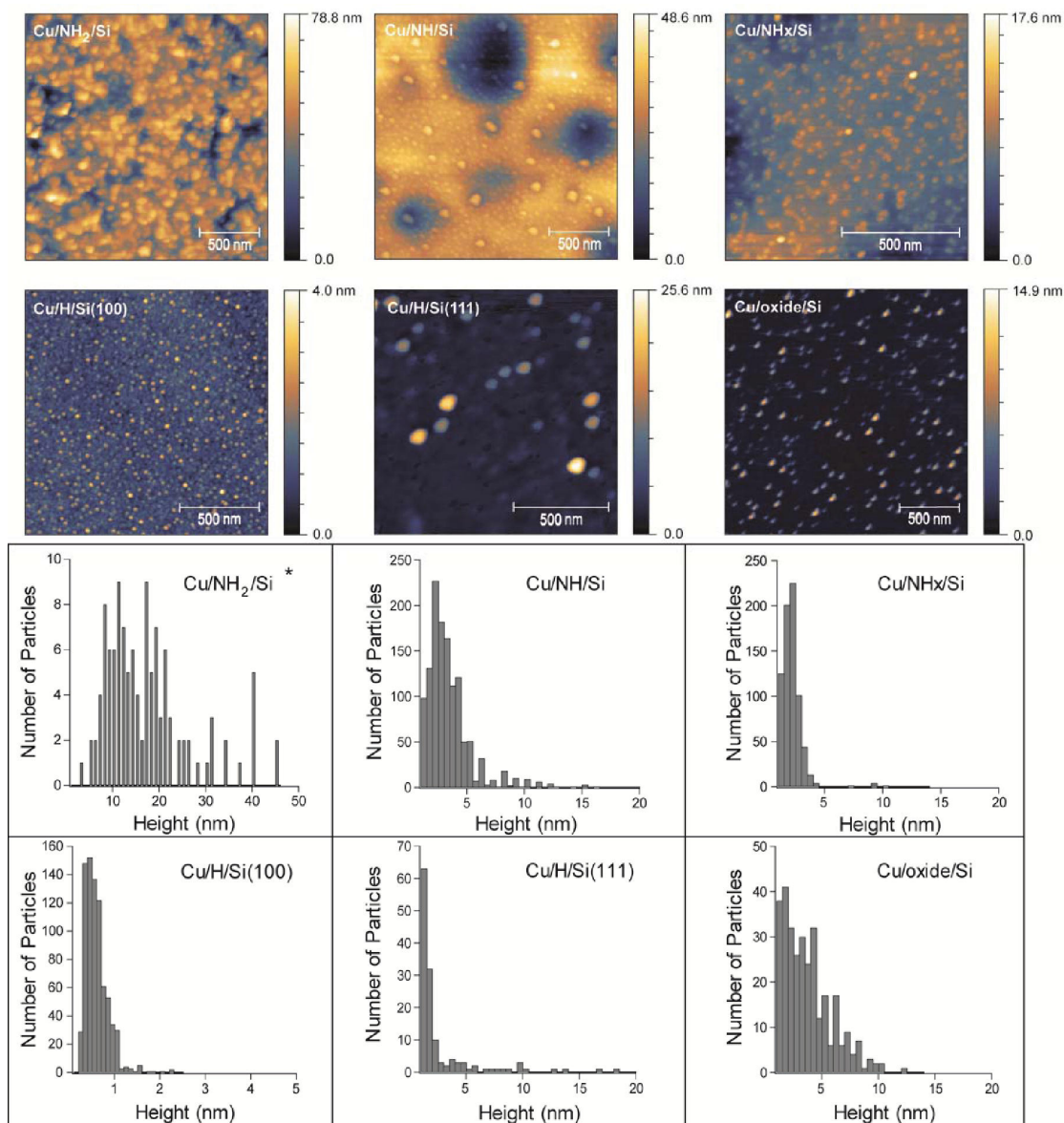


Figure 3.2: AFM images and size distributions of copper nanostructures formed on the functionalized silicon surfaces indicating that the order and functionality of the surface will determine the nanostructure growth. The asterisk (*) denotes that in the case of the Cu/NH₂/Si(100) system, the particle height distribution was difficult to estimate because of high surface roughness that may hide the possibility of film formation instead of particle growth. This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

An even tighter copper nanostructure size distribution centered at 2 nm in height is observed on the $\text{NH}_x\text{-Si(100)}$ surface. These particle size distribution patterns can be compared to those for copper nanostructures formed on hydrogen-terminated silicon surfaces.⁶⁹ Reactions between Cu(hfac)VTMS and the H-terminated silicon surfaces have been suggested previously to initiate at surface defects.⁶⁹ The H-Si(111) surface, when etched with ammonium fluoride, is atomically flat, with a minimum number of surface defects; thus, larger copper particles are formed with a wide size distribution that extends in the similar range as the size distribution on NH-Si(100) surface.

The $\text{NH}_x\text{-Si(100)}$ surface, likely the more defective surface, has copper particle size distribution similar to that of the H-Si(100) surface, suggesting that the reaction on this surface might also begin at defects and lead to a narrower size distribution.⁶⁹ All these are compared to copper deposited on a grown silicon oxide known to be terminated with disordered surface hydroxyl groups.^{70,76} Note that this oxide was prepared ex situ using the RCA cleaning procedure, which results in a 2 nm thick oxide film. Although it is questionable whether the copper precursor reacts with oxygen vacancies or $-\text{OH}$ groups, the copper nanostructure growth on this surface results in the widest particle size distribution, as compared to the ammonia-prepared or H-terminated silicon surfaces. There are two competing processes proceeding on the substrate surface simultaneously--particle nucleation and particle growth. Particle nucleation is determined by the initial reaction rate between Cu(hfac)VTMS and the surfaces, and the particle growth may be governed both by the chemistry of the deposition and by the surface diffusion processes. Particle nucleation is highly dependent on the overall number of surface reactive sites, including defects and minor

functional groups, which makes it straightforward to say: the more reactive sites on the surface, the higher nucleation rate, and thus the tighter particle size distribution. Because of the preparation process for the ammonia-modified surface, the $\text{NH}_2\text{-Si}(100)$ surface is considered to be relatively uniform, followed by $\text{NH-Si}(100)$ then $\text{NH}_x\text{-Si}(100)$ surfaces, so that the size distribution of the particles on these ammonia-prepared surfaces decrease in the order: $\text{NH}_2\text{-Si}(100) > \text{NH-Si}(100) > \text{NH}_x\text{-Si}(100)$. However, the unique morphology formed on $\text{NH}_2\text{-Si}(100)$ might also suggest that $\text{NH}_2\text{-Si}(100)$ surface actually provides a better venue for surface diffusion of copper-containing fragments and, in turn, leads to larger nanoparticle formation.

The AFM analysis shows that different surface modification could lead to diverse surface morphologies, but the elemental composition remains uncertain. With XPS, we are able to not only obtain elemental composition of the copper nanoparticles but also the oxidation state of copper, as shown in figure 3.3.

In figure 3.3, the N 1s region (left) shows peaks with binding energies in the range of 397.9-397.3 eV for all three different ammonia-prepared substrates reacting with $\text{Cu}(\text{hfac})\text{VTMS}$, which is in agreement with recent studies of CVD grown copper nitride (specifically the surface layer of copper nitride) at 397 eV.⁷⁷⁻⁸⁰ However, the larger full width at half maximum value for the $\text{NH}_2\text{-Si}(100)$ and $\text{NH-Si}(100)$ compared to $\text{NH}_x\text{-Si}(100)$ may suggest that more than one type of qualitatively different species are formed on the two surfaces. The N 1s region also shows that no oxidation products involving surface nitrogen occurs on the surface, which would shift the N 1s peaks above 400 eV,⁸¹⁻⁸³ although these samples are exposed to ambient conditions while being transferred to the XPS facility, as mentioned previously in the experimental section. The solid lines underneath the spectra denote the DFT predicted

binding energies. Using the cluster models shown beside the predicted binding energy, the interaction of Cu(hfac)VTMS and ammonia-prepared surfaces was simulated by DFT calculation at the B3LYB/LANL2DZ level of theory, and the calibration of the predicted XPS spectra was performed according to our previous report.⁸¹ The predicted results indicate that the spectral difference between surface -NH_2 and -NH- species is not significant, and that the reaction with Cu(hfac)VTMS shifts the N 1s peaks by less than 2 eV.

The C 1s region (rather complicated as shown in figure 3.3) indicates that several different types of carbon-containing species are present on the surfaces likely due to the exposure to the ambient conditions during transfer, but peaks correspond to hfac ligand are identified according to previous XPS studies,⁸⁴⁻⁸⁶ and the most intense experimental C 1s peak at 284.5 eV is attributed to hydrocarbons or “free carbon” from ambient exposure.⁸⁷ A simple general observation suggests that the ammonia-prepared surfaces show qualitatively different types of surface species present after exposure to Cu(hfac)VTMS. That is, the H-terminated silicon and ammonia-terminated silicon surfaces all exhibit similar C 1s spectral features except for a peak at 282.9 eV that only appears on ammonia-prepared surfaces. There is a possibility that this peak may correspond to the formation of silicon-carbide-like species because the position of this peak is rather unique.⁸⁷⁻⁸⁹ This distinct peak may imply that the reduction process on ammonia-exposed silicon surfaces is different and may result in different types of products compared to hydrogen-terminated silicon.

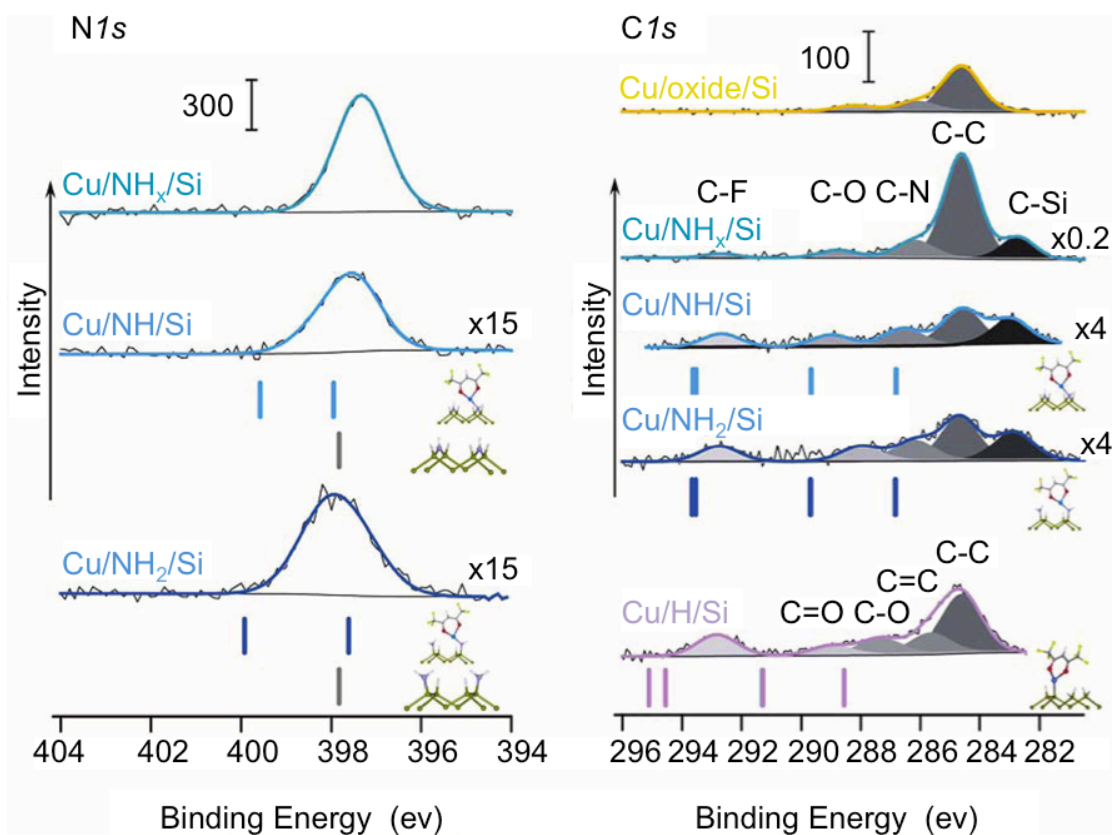


Figure 3.3: XPS binding energies for the N 1s and C 1s regions collected for the functionalized silicon surfaces after reaction with Cu(hfac)VTMS. N 1s spectral regions are not shown for H-terminated silicon surface or silicon oxide surface since no nitrogen is present on these samples. Computational studies for selected surface adsorbates depicted in this figure are shown as solid lines underneath the spectra. This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

It should be noted that the XPS results for silicon oxide surface indicate no CF-containing species present on the surface, and imply that copper deposition processes on oxide-covered silicon surface are very different from those on ammonia- and hydrogen-terminated silicon surfaces.

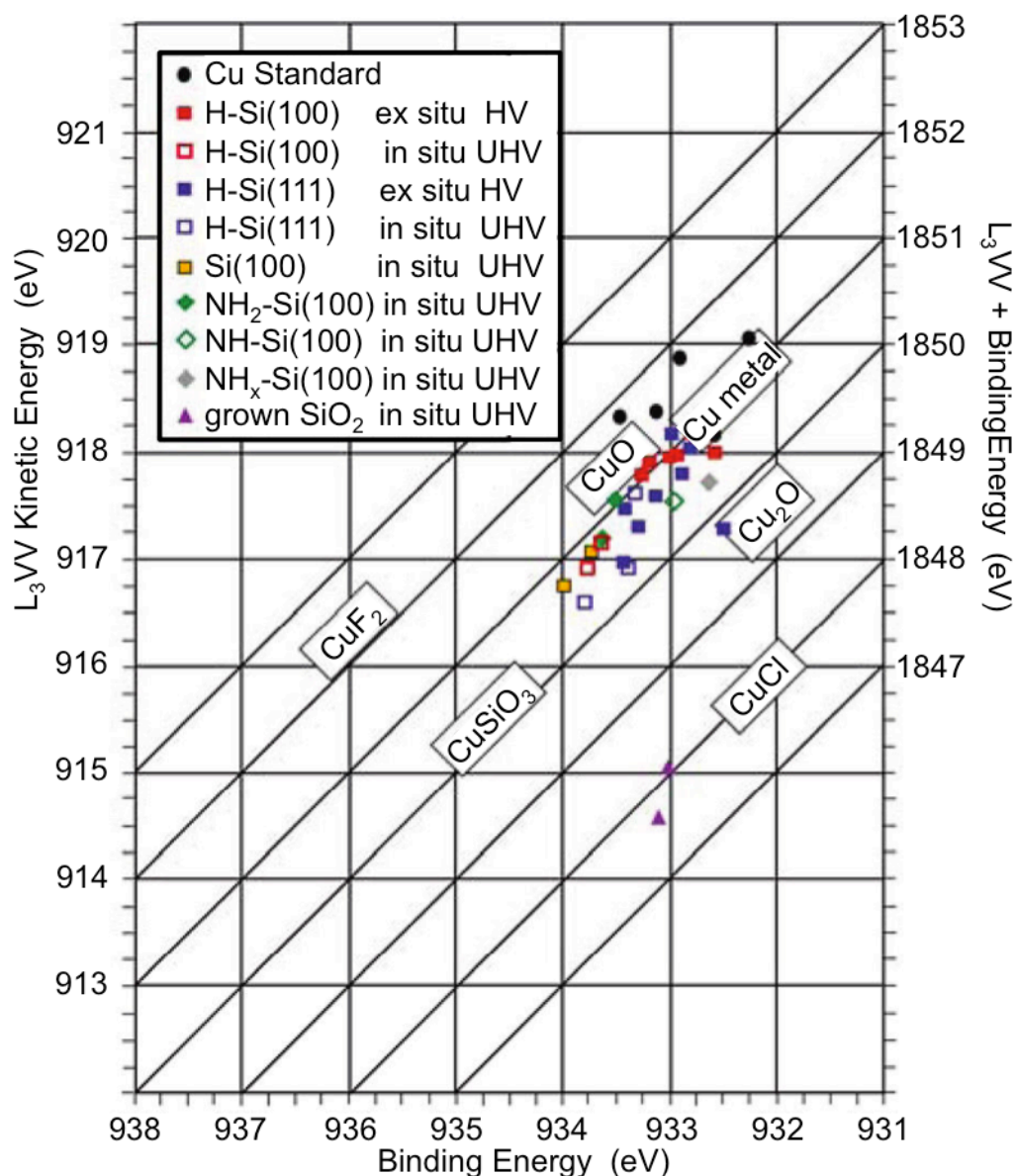


Figure 3.4: The combination of Cu 2p binding energy and the corresponding Cu LMM Auger kinetic energy that were recorded simultaneously on the same XPS spectrometer offers undoubted identification of the oxidation state of the as-deposited copper nanoparticles. This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

The XPS information for copper region is provided by the combination of Cu 2p binding energy and the corresponding Cu LMM Auger kinetic energy that were obtained simultaneously on the same XPS spectrometer, as shown in figure 3.4. XPS analysis is normally sufficient to distinguish Cu^{2+} from Cu^+ and/or Cu^0 oxidation state; however, its sensitivity is not adequate to differentiate Cu^+ and Cu^0 oxidation state, because XPS analyzes elemental information with one electron process.^{69,90} To identify the oxidation state of the as-deposited copper nanoparticles, the more sensitive two-electron Auger process is essential.^{69,90,91} According to figure 3.4, it can be summarized that the majority of the copper deposited the substrates studied here is metallic with the exception of that on silicon oxide surface. It is worth mentioning again that Cu^{2+} oxidation state can be ruled out with typical XPS analysis, and Cu^+ is ruled out with the aid of corresponding Auger analysis.

With AFM and XPS analyses, we realize that $\text{Cu}(\text{hfac})\text{VTMS}$ reacts with differently functionalized silicon surfaces to produce diverse morphologies, but the copper nanoparticles formed on the surfaces are mostly metallic. To further explore the chemistry of the surface reaction of $\text{Cu}(\text{hfac})\text{VTMS}$ and the modified silicon, MIR-IR, TPD, and DFT were combined to study the mechanism and the kinetics of the process. The IR studies are summarized in figure 3.5.

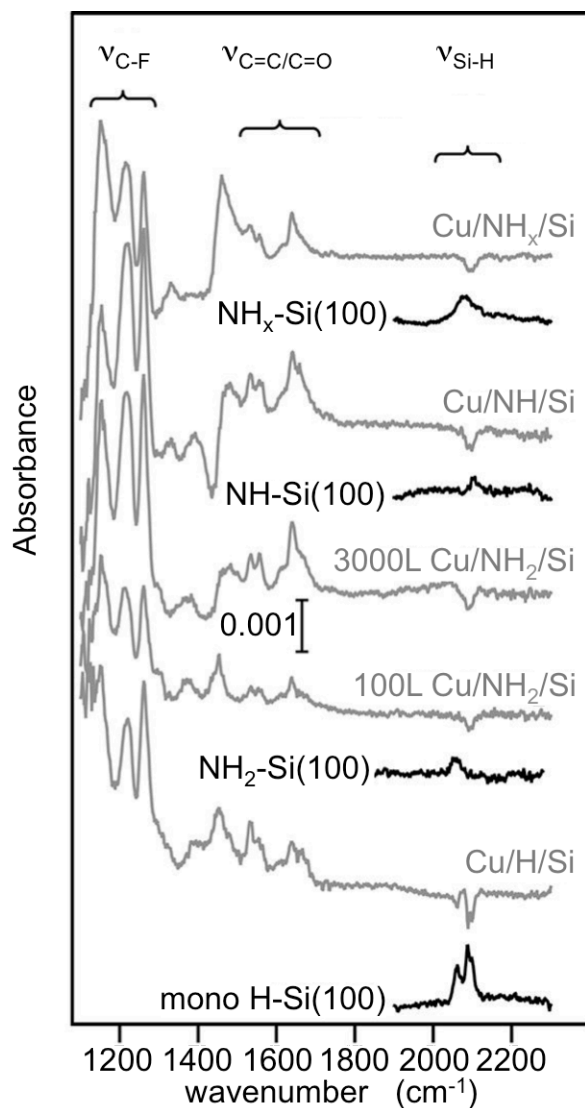


Figure 3.5: The MIR-IR spectra of Cu(hfac)VTMS reacting with differently functionalized silicon surfaces. On the top of the plot, different spectral regions corresponding to C–F, C=C, C=O, and Si–H stretching are denoted. The black curves (only Si–H stretching region shown) are the spectra of the functionalized surfaces before reaction (using a clean Si(100) surface as the background) and will be later used as the background for the spectra of the surfaces after reaction (curves in grey). This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

All the curves in black represent the Si–H stretching region of the spectra of the functionalized surface before the reaction takes place, and it is clearly observed that the shapes and positions of the Si–H stretching bands vary according to the substrate investigated. These spectra in black were in turn used as the background spectra for the spectra (in grey) of the surfaces following reaction with Cu(hfac)VTMS. All the spectra presented in grey show the vibrational signatures of Cu(hfac) fragment including $\nu_{\text{C-F}}$, $\nu_{\text{C=C}}$, and $\nu_{\text{C=O}}$. Although the spectral region of the C–H stretching vibrations (around 3000 cm^{-1}) is not shown in figure 3.5, no additional bands corresponding VTMS ligand are detected, which indicates the elimination of VTMS ligand upon adsorption, as previously reported.⁶⁵⁻⁶⁷ The most important observation ought to be the loss in the intensity of the Si–H stretching bands, which suggests that surface hydrogen is consumed in the reaction between Cu(hfac)VTMS and functionalized surfaces. This is the direct evidence that the surface hydrogen participates in the reaction of Cu(hfac)VTMS and the functionalized surface. Qualitatively, the IR studies point out that after the reaction of Cu(hfac)VTMS and the functionalized surfaces, some hfac ligands still remain on the surface, and the surface hydrogen participates in the reaction and is consumed. However to advance our understanding of the mechanism and kinetics of the reaction, quantitative analysis is required. Figure 3.6 shows the loss of Si–H peak intensity following the reaction between Cu(hfac)VTMS and four differently modified surfaces (left) and the kinetic analyses (right).

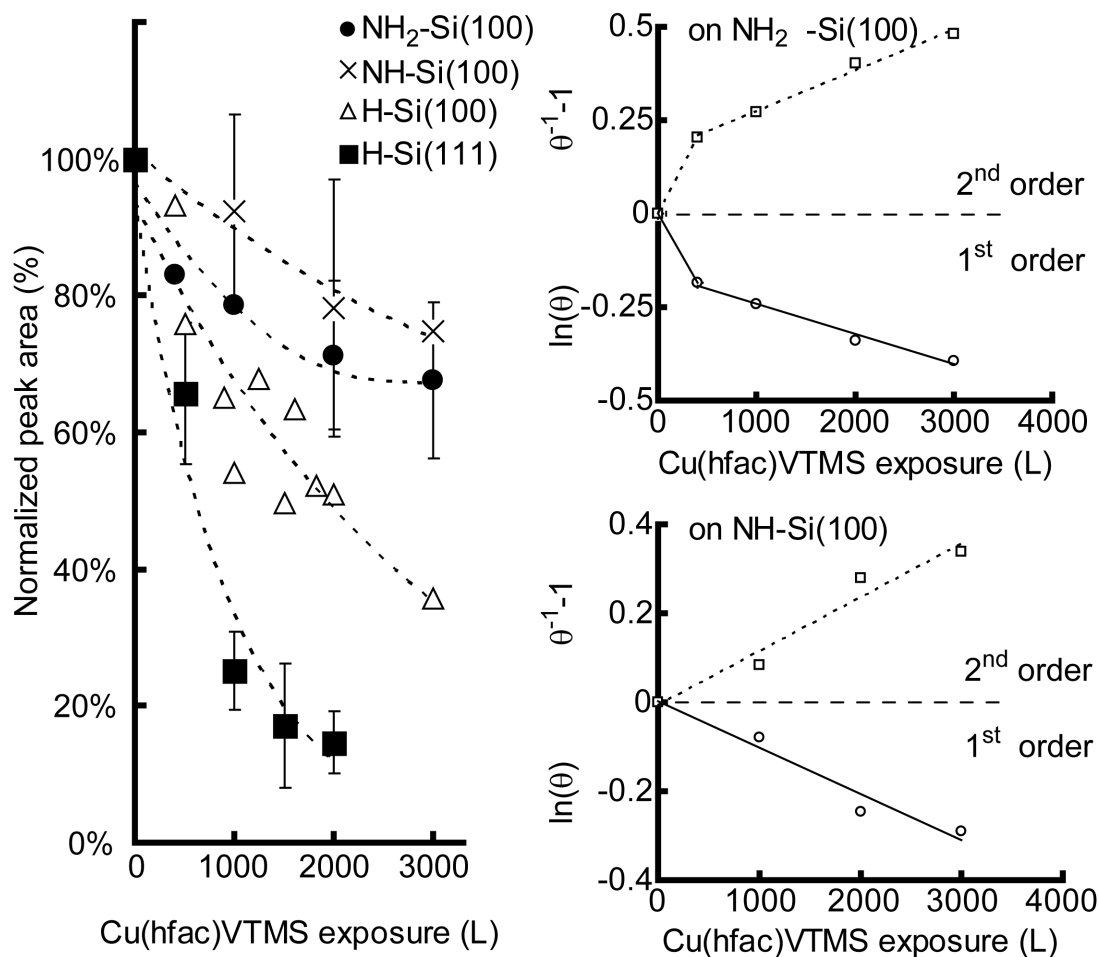
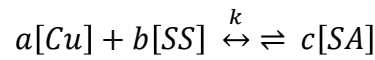


Figure 3.6: Left: room temperature MIR-FTIR studies of the loss of the relative intensity of the Si-H absorption bands against Cu(hfac)VTMS exposures. Dashed lines are provided to guide the eye without any specific fit. Right: kinetic studies of the reaction with NH₂-Si(100) and NH-Si(100) surfaces. This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, 116, 14431. Copyright 2012 American Chemical Society.

It is clearly seen that the hydrogen terminated silicon surfaces yield faster hydrogen consumption rate than ammonia-prepared surfaces. Specifically, H-Si(111) surface is the fastest among the four shown in figure 3.6. In order to extract the kinetic information from this plot, we assumed that (in the reaction between Cu(hfac)VTMS and functionalized surfaces) the reaction is first order in the copper precursor molecules, and either first or second order in surface functionality. Two rate laws for first and second order reaction can be deduced from the following calculation.

Assume the surface reaction proceeds in the form shown below:



[RG] denotes the concentration of Cu(hfac)VTMS
[SS] denotes the concentration of surface reactive sites
[SA] denotes the concentration of surface adducts
a, b, and c are the coefficients of each component
k is the rate constant of the forwarding reaction

So that, the rate law bases on the consumption of surface sites can be written as:

$$-\frac{d[SS]}{dt} = k \cdot [Cu]^a \cdot [SS]^b$$

The concentration of the surface reactive sites is expressed as coverage “ θ ” in this study, so that the rate law can be rewritten and rearranged into:

$$-\frac{d\theta}{dt} = k \cdot [Cu]^a \cdot \theta^b \quad \Rightarrow \quad -\frac{1}{\theta^b} \cdot d\theta = k \cdot [Cu]^a \cdot dt$$

As stated previously, the reaction order for Cu(hfac)VTMS is first order, and that for the surface sites is either first or second order. The integrated form of the rate law can be written as:

$$-\frac{1}{\theta^b} \cdot d\theta = k \cdot [Cu] \cdot dt \Rightarrow \begin{cases} b = 1, & \ln(\theta) = -k \cdot [Cu] \cdot t + \ln(\theta_0) \\ b = 2, & \frac{1}{\theta} = k \cdot [Cu] \cdot t + \frac{1}{\theta_0} \end{cases}$$

θ_0 is the initial coverage of surface reactive sites, which is 100%, so that the equation can be simplified as:

$$\begin{cases} \text{First order,} & \ln(\theta) = -k \cdot [Cu] \cdot t \\ \text{Second order,} & \frac{1}{\theta} - 1 = k \cdot [Cu] \cdot t \end{cases}$$

Here we applied ideal gas law to the concentration copper precursor molecule:

$$PV = nRT \quad \Rightarrow \quad [Cu] = \frac{n_{Cu}}{V} = \frac{P}{RT}$$

V: the volume of the chamber

R: gas constant

T: the reaction temperature

n_{Cu}: the amount of copper precursor in mole

P: the pressure of copper precursor

The equations of the rate laws are transformed into:

$$\left\{ \begin{array}{l} \text{First order, } \ln(\theta) = -k \cdot \frac{P}{RT} \cdot t \\ \text{Second order, } \frac{1}{\theta} - 1 = k \cdot \frac{P}{RT} \cdot t \end{array} \right. \Rightarrow \left\{ \begin{array}{l} \ln(\theta) = -k_{obs} \cdot P \cdot t \\ \frac{1}{\theta} - 1 = k_{obs} \cdot P \cdot t \end{array} \right.$$

As mentioned in experimental section, the exposure of Cu(hfac)VTMS can be quantified by a Langmuir (L), which is defined as 1 second times 10^{-6} Torr (1 L = 1 s $\times 10^{-6}$ Torr). The equations of the rate laws can be then further simplified as:

$$\left\{ \begin{array}{l} \text{first order, } \ln(\theta) = -k_{obs} \cdot \text{exposure} \\ \text{second order, } \frac{1}{\theta} - 1 = k_{obs} \cdot \text{exposure} \end{array} \right.$$

Also note that the rate laws determine the unit of the observed rate constant (k) that is normally different for first and second order rate laws. Since the unit of coverage is percentage (unitless), the units of the rate constant for first and/or second order rate constant are both inverse Langmuir (L^{-1}). With these rate laws, the kinetic information from the IR studies was successfully extracted and the two representative plots are provided in the right panel of figure 3.6.

Upon analysis of the reaction with NH_2 -Si(100) surfaces, first and second order regressions show a possible change of the reaction mechanism around 400 L exposure of the Cu precursor, yet the same trend is absent in the reaction with the NH -Si(100) surface and all other functionalized surfaces. All the rate constants and R^2

values are provided in table 3.1; the R^2 values are used to determine whether a certain reaction is first or second order with respect to the surface reactive sites.

Table 3.1: Estimated kinetic parameters obtained assuming first- and second-order reactions (for surface species) based on initial reaction velocities of Cu(hfac)VTMS deposition on functionalized silicon surfaces calculated from the integrated absorption features corresponding to the Si–H loss (This table is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, 116, 14431. Copyright 2012 American Chemical Society.)

Surfaces	1st order rate constant (L^{-1})		2nd order rate constant (L^{-1})	
	< 400 L	> 400 L	< 400 L	> 400 L
NH ₂ -Si(100)	4.7×10^{-4} ($R^2=1.000$)	8.0×10^{-5} ($R^2=0.984$)	5.1×10^{-4} ($R^2=1.000$)	1.1×10^{-4} ($R^2=0.989$)
NH-Si(100)	1.0×10^{-4} ($R^2=0.956$)		1.2×10^{-4} ($R^2=0.957$)	
NH _x -Si(100)	1.8×10^{-4} ($R^2=0.908$)		2.2×10^{-4} ($R^2=0.894$)	
H-Si(100)	3.3×10^{-4} ($R^2=0.884$)		5.5×10^{-4} ($R^2=0.889$)	
H-Si(111)	1.08×10^{-3} ($R^2=0.850$)		3.59×10^{-3} ($R^2=0.732$)	

As shown in table 3.1, the reaction rates obtained suggest that the reaction with the H-Si(111) surface most likely follows first-order kinetics, but the reaction orders could not be verified for all the other surfaces studied here, since their R^2 values show no substantial differences for the studies presented. However, this approach should be treated as only semi-quantitative, because it assumes that the Si–H vibrational frequencies for all the possible surface species have the same intensity and are unaffected by the presence of a copper deposition precursor, which may not be the

case in these experiments. Consequently, TPD approach was applied to obtain additional quantitative analysis.

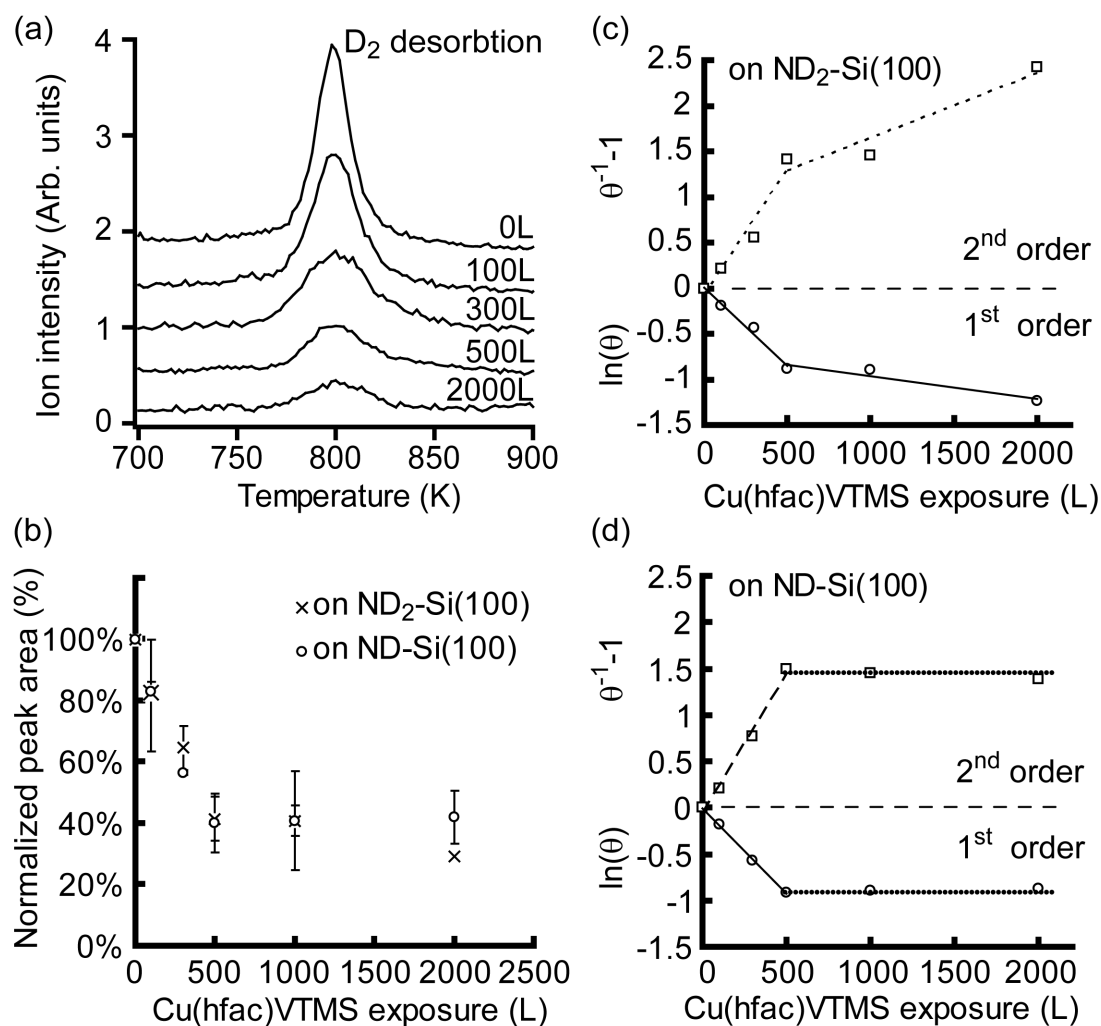


Figure 3.7: Reactivity of ammonia-functionalized silicon surfaces using TPD. (a) Exposure profile of deuterium desorption from the ND_2 -Si(100) surface after a series of doses of Cu(hfac)VTMS. (b) The loss of deuterium on the silicon surface in percentage. (c and d) Plots that estimate rate constants and reaction order parameters. This image is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

Isotopically labeled ammonia, ND₃, was used to create the ND₂-Si(100) and ND-Si(100) surfaces before exposure to Cu(hfac)VTMS, as described in detail in the experimental part. The TPD analysis in this section focuses on the m/z ratios of 2 and 4 (D and D₂ fragments), because Cu(hfac)VTMS would deplete the surface deuterium, regardless of exactly which surface functional group would participate in the reaction. The goal is to understand the amount of deuterium left behind after Cu(hfac)VTMS reacts with the surfaces. It has been shown in multiple previous studies that hydrogen desorbs from silicon single crystals around 800 K,^{92,93} and its amount can be easily estimated based on the area of the TPD peak. The use of ND₃ instead of NH₃ makes such an analysis straightforward, because there is no m/z = 4 (corresponding to D₂) in the background of the UHV chamber within the sensitivity range of the mass spectrometer used. Figure 3.7 (b) shows that the normalized peak area of the deuterium desorption peak of mass 4 around 800 K drops to approximately one-third of its initial value and comes to a saturation plateau on both functionalized surfaces. This suggests that if one Cu(hfac) fragment reacts with a single surface functionality per silicon dimer (for example, -NH₂ group), only two out of three hydrogen atoms of the initial NH₃ molecule are consumed in the reaction. Figure 3.7 (c) and (d) suggest possible mechanism changes for both ND₂-Si(100) and ND-Si(100) surfaces upon 500 L exposure of Cu(hfac)VTMS, which contrasts to the MIR-IR observation that only NH₂-Si(100) surface shows a change of the reaction mechanism with exposure. Furthermore, the initial reaction rate constants appear identical on both surfaces, which is also different from the MIR-IR kinetic studies, as shown in table 3.2. To understand the cause of this difference and more importantly the effect of

surface functionalities on the reaction mechanism, DFT computational approach was utilized.

Table 3.2: Rate constants from TPD kinetic studies based on deuterium loss from ND₂- and ND-functionalized silicon surfaces. (This table is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.)

surfaces	1st order (L ⁻¹)		2nd order (L ⁻¹)	
	< 500 L	> 500 L	< 500 L	> 500 L
ND ₂ -Si(100)	1.7×10^{-3} (R ² =0.985)	2.5×10^{-4} (R ² =0.915)	2.74×10^{-3} (R ² =0.949)	7.2×10^{-4} (R ² =0.912)
ND-Si(100)	1.84×10^{-3} (R ² =0.9999)	0	3.01×10^{-3} (R ² =0.993)	0

DFT was used to predict the reaction of the Cu(hfac) fragment with the functionalized silicon surfaces, as shown in figure 3.8. The VTMS ligand was not considered because the MIR-IR results confirmed that it is eliminated upon initial adsorption. First we consider the adsorption (addition) of Cu(hfac)VTMS onto the functionalized silicon surfaces. The adsorption adduct for NH₂-Si(100) surface is predicted to be thermodynamically favorable by 147.1 kJ/mol, followed by OH-Si(100) at 135.7 kJ/mol and NH-Si(100) surface at 125.6 kJ/mol. Both di-hydride and mono-hydride terminated Si(100) surfaces are predicted to have the least favorable adduct at 110 kJ/mol. Once these adducts are formed, there are two possible mechanism to reduce Cu⁺ to Cu⁰ by oxidizing the hfac ligand to hfacH via hydrogen abstraction from the surface, since there are two hydrogen sources on the surface--from the functionalities or from the surface Si-H groups. As illustrated in figure 3.8,

among nine different processes, only di-hydride terminated Si(100) and H-Si(111) surface produce thermodynamically favorable products. However, the more important information can be obtained from the predicted barriers for each process, which are given in table 3.3.

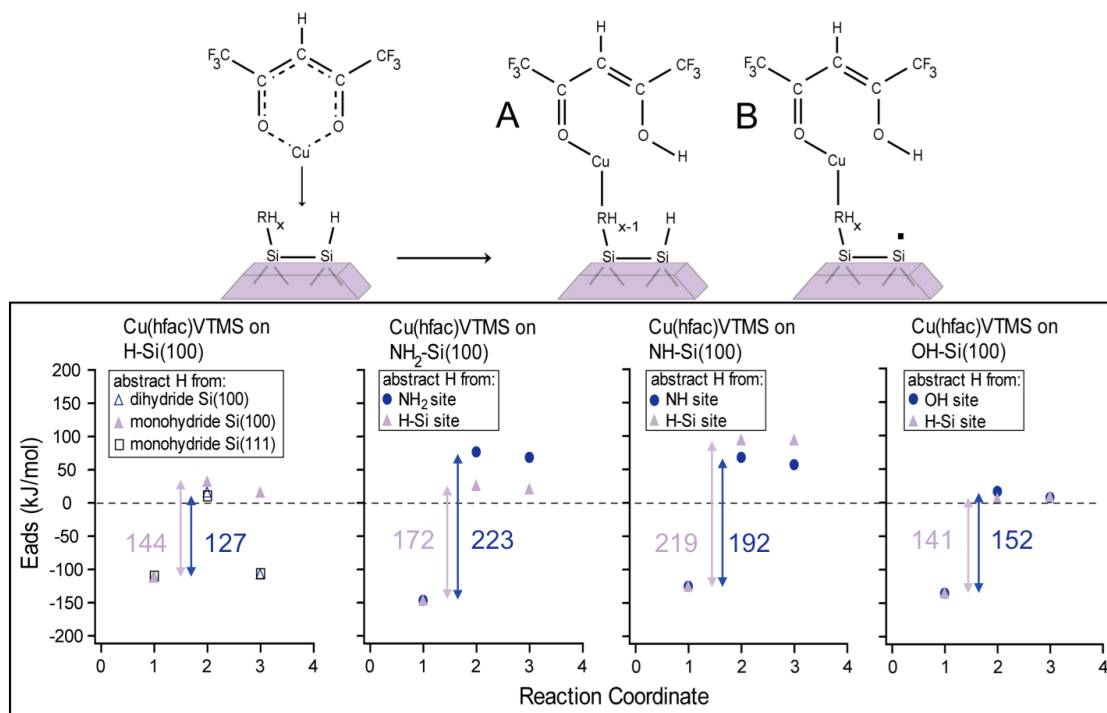


Figure 3.8: DFT barrier predictions for Cu(hfac) to abstract hydrogen from the surface as either (A) a hydrogen from the surface functionality or (B) hydrogen from the surface Si-H. The B3LYP/LANL2DZ level of theory was used to compute adsorption energies and transition states. Note that for the H-terminated silicon surfaces, the RH_x represents a dangling bond. Both di-hydride and mono-hydride surface species are considered for the H-Si(100) surface, and the corresponding barriers of selected processes are marked on the plots as well as summarized in table 3.3. This image is adapted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.

Table 3.3: Predicted energy barriers (in kJ/mol) for hydrogen abstraction from either the Si–H surface species or the functionality itself (This table is reprinted with permission from Perrine, K. A.; Lin, J.-M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431. Copyright 2012 American Chemical Society.)

surface	H from functionality (kJ/mol)	H from silicon (kJ/mol)
NH ₂ -Si(100)	223.3	172.4
NH-Si(100)	192.4	219.1
H-Si(111)	--	120.7
diH-Si(100)	--	127.3
monoH-Si(100)	--	144.1
OH-Si(100)	151.8	140.8

As shown in table 3.3, the energy barriers for hydrogen abstraction from the surface Si–H groups on OH-functionalized or ammonia-functionalized surfaces increase in the following order: OH-Si(100) < NH₂-Si(100) < NH-Si(100), which is in accordance with the MIR-IR observation for ammonia-functionalized surfaces. However, the predicted barriers for hydrogen removal from the N-containing functional groups (–NH₂ and –NH– groups) show the opposite trend; that is, the barrier for H removal from the –NH– functionality is smaller than that from –NH₂ species. These opposite trends are the origins of the experimentally observed difference between the reaction rate constants obtained by TPD and by FTIR for NH₂-Si(100) and NH-Si(100) functionalities. As discussed above, once the Cu(hfac) fragment adsorbs on the surface, there are two pathways of hydrogen abstraction--from the functionalities or from the surface Si–H groups. It seems that for a Cu(hfac) fragment adsorbed onto an NH₂-covered silicon surface, it is substantially easier to abstract a hydrogen atom from a surface Si–H group. Conversely, if the Cu(hfac) fragment is initially adsorbed onto a silicon surface with –NH– functionality, the

removal of a hydrogen from this functionality is a preferred reaction pathway. Because TPD method allows us to follow the overall amount of hydrogen left on the surface following its reaction with the incoming copper precursor molecules, both -NH_2 and -NH- functional groups seem to lead to the same amount of hydrogen left on the surface at saturation exposure. However, in the case of MIR-IR studies, we exclusively followed the amount of hydrogen removed from the surface Si-H groups (as opposed to, for example, the N-containing functionality), making it possible to discern the mechanistic differences between the reactions happening on two ammonia-prepared surfaces.

Here, we would like to propose a reaction mechanism for Cu(hfac)VTMS . First, when a Cu(hfac)VTMS molecule approaches the functionalized surface, the VTMS ligand leaves the molecule upon adsorption. Second, the remaining Cu(hfac) fragment then adsorbs on a surface reactive site, which can be viewed as the nucleophilic attack of the surface reactive species onto the copper center of the Cu(hfac) fragment. Thus, the kinetics of this step should be determined by the reactivity of the surface functional group in donating its electron to copper. This rationale is supported by the above DFT predictions that the initial reaction of the Cu(hfac) fragment with the surface functionalities is more favorable on the more basic $\text{NH}_2\text{-Si(100)}$ surface as compared to the less basic H-Si(100) surface. A similar rationale for the reactivity of surface amino groups with respect to the Ti-containing deposition precursor molecule was described in detail earlier.¹⁸ Third, the surface Cu(hfac) fragment then reacts via hydrogen abstraction to pick up a hydrogen from either the functionalities or from the surface Si-H groups and removes hfac ligand as hfacH molecule. The rate of the third step is determined by how easy it is to abstract

that hydrogen; in other words, the easier the transfer of a hydrogen atom from the silicon surface to hfac, the faster the rate of the surface reaction. Because the adsorption process (the second step) is expected to have a very low or no barrier, the energy barrier of the third step of the reaction is likely governing the overall surface reaction rate. This statement is supported by DFT and MIR-IR studies. In table 3.3, it is shown that the energy barriers of the reaction on hydrogen-terminated surfaces (mostly around 120 kJ/mol) are substantially lower than those on ammonia-exposed surfaces (around 200 kJ/mol), which reflects the faster hydrogen depletion rates of the reactions on hydrogen-terminated surfaces than those on ammonia-prepared surface. Although the factors that affect the reaction barriers of the third step still remain unclear, several effects can be taken into account: the steric effect of the surface (from the surface and the functionalities), the steric effect of the incoming precursor molecule (from the ligands and molecular geometry), the electronic effect of the surface (substrate material and the electron donating/withdrawing ability of the functionalities), and the electronic effect of the precursor molecule (lone pair on the ligand and the nature of the metal).

3.4 Conclusions

The functionalization of the starting surface has a tremendous influence on the copper nanoparticle growth on silicon, similarly to growth processes on metal oxides.⁹⁴ In a copper deposition process based on Cu(hfac)VTMS, the basicity of the functional group defines the rate of the initial attachment, but it is the difficulty of hydrogen abstraction from the surface chemical functionalities or from the surface Si-H groups, following the adsorption of a Cu(hfac) fragment, that determines the rate of the overall reaction.

Out of all the functionalized surfaces studied here, the $\text{NH}_2\text{-Si}(100)$ surfaces not only possess high reactivity toward metalorganic precursors but are also well-defined from dissociative adsorption of ammonia on the $\text{Si}(100)\text{-}2 \times 1$ surface, making them ideal for designing interfaces with high reactivity and efficient nanostructure formation. The recent work on producing well-defined structured H-terminated^{95,96} and NH-terminated⁹⁷ silicon surfaces by wet chemistry methods should aid in further work on manipulating the formation of nanostructures on silicon. This work suggests that tuning surface properties through chemical functionalization can help design interfaces with unique properties, including nanostructure formation for applications in modern electronics, surface catalysis, and materials chemistry.

Chapter 4

COMPETING REACTIONS DURING METALORGANIC DEPOSITION: LIGAND-EXCHANGE VERSUS DIRECT REACTION WITH THE SUBSTRATE SURFACE*

4.1 Introduction

In the previous chapter, with the aid from a combination of MIR-IR, TPD, and DFT, we concluded that the energy barrier of the hydrogen abstraction from either the surface chemical functionalities or from the surface Si–H groups could govern the overall reaction rate of the surface reaction of Cu(hfac)VTMS and selected chemically modified surfaces. Furthermore, the studies indicated that the hydrogen abstraction by Cu(hfac) fragment show preferential reactivity toward different surface reactive sites on ammonia-prepared surfaces (e.g., Cu(hfac) fragment prefers surface Si–H groups when reacting with NH₂-Si(100) surface but –NH– functionalities when reacting with NH-Si(100) surface), yet the cause of these differences needs more investigation for general understanding. In this section we designed a series of DFT calculations to inspect the chemistry of six different representative deposition precursors for their preference in reactivity and surface reactions on a functionalized surface.

As described in the first chapter, as the lateral size of modern microelectronics keeps decreasing, the deposition schemes have evolved into the process that is capable

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of producing sharp film/substrate interfaces at subnanometer scale and films with nominally zero level of contamination; i.e., atomic layer deposition (ALD). ALD is known to deliver better control over impurities introduction and film thickness achieved by designing specific surface chemistry that can rely on highly selective ligand-exchange reactions--the reactions that exchange surface functionalities and the ligands of the incoming precursor molecule to remove the precursor ligands cleanly and anchor the metal-containing fragment on the surface.^{7,10,63,98-103}

In spite of the high level of control achieved during deposition, in some systems the levels of contamination are still high, especially during the first stages of deposition (the so called transient or incubation regime), where the reactions leading to film growth are determined by non-uniformities of the underlying substrate surface.⁹⁻¹³ Thus, even though ALD is based on controlled ligand-exchange reactions (hereafter denoted as “desired” reactions), several uncontrolled (“undesired”) reactions will take place during the transient regime and can also occur throughout the deposition process, as the growing film is likely to feature diverse surface reactive sites. Although there are numerous investigations highlighted in the literature for the design of the ligand-exchange reactions to be used in ALD,¹⁰⁴⁻¹¹² undesired reactions where a ligand is not eliminated but attached to the surface, have received less attention, in spite of their decisive role in film determining the purity of the film deposited.^{64,66,98,113-116}

In this chapter, both desired and undesired reactions are compared for the most common groups of deposition precursors. Alkyl-, alkoxide-, alkylamide-, diketonate-, amidinate-, and cyclopentadienyl-based metalorganic compounds are represented in this work by $\text{Al}(\text{CH}_3)_3$ (trimethylaluminum), $\text{Ti}[\text{OC}_3\text{H}_7]_4$ (titanium isopropoxide),

Hf[N(CH₃)₂]₄ (tetrakis(dimethylamido)hafnium), Cu(acac)₂ (copper acetylacetonate), Ni[ⁱPr-amd]₂ (nickel isopropylamidinate) and Hf(Cp')₂(CH₃)₂ (bis(methyl-η⁵-cyclopentadienyl)dimethyl hafnium).

On the other hand, OH-terminated Si(100) surface and bare Si(100) surface are chosen to be the platforms to test the desired and undesired reaction routes for those selected precursors, because OH-terminated Si(100) surface has been employed to simulate the ALD growth of metal oxides with water as one of the precursors,^{110-112,117-121} and the undesired reactions between metalorganic compounds and the clean Si(100) surface have been investigated extensively.^{66,98,113-116} Since deposition processes considered in this work focus on general chemical characteristics of the precursor molecules, we will target general aspects of the process that are relevant for other systems.

4.2 Assessment of the Deposition Processes and Targets of Investigation from a Computational Perspective

This study is restricted to the chemical processes controlling the deposition of metal-containing thin solid films by DFT methods. Additional important factors expected to affect the outcome of such processes (including fluidics of the precursor inside the deposition chamber, effects of additional precursors and/or carrier gases, pre- and post-treatment methods, etc.) are beyond the scope of this investigation, but have been covered to some extent in the literature.^{4,7,10,103,122} To limit the extent of our simulations and to construct a set of chemical processes most relevant to controlling the chemistry of deposition, the following assumptions are made:

1. Precursors approach the surface intact, without undergoing gas-phase reactions before adsorption. This is a fundamental prerequisite in ALD and

- is a common assumption for CVD, although in several cases these gas-phase reactions may be behind the deposition of contaminants.¹²³
2. Only monomeric species are considered, although several metalorganic precursors are known to oligomerize (such as metal alkyls¹²⁴⁻¹²⁶ and metal alkoxides⁶).
 3. Reactions involving complete decomposition of surface species are not pursued, as they usually involve changes in oxidation states (e.g., during Cu deposition using copper diketonates^{84,127,128}), the release of fragments from the precursor itself into the gas-phase (e.g., ethylene desorption from ethyl ligands via β -hydride elimination¹²⁹⁻¹³¹), and other processes.
 4. We will focus on two types of decomposition reactions: through scission of the metal-ligand bond, and through scission of a C–H bond. These two types of bonds are common to all metalorganic compounds considered and comparisons across groups of precursors can be made. Other bonds (e.g., N–C, O–C, C–C) are explored in selected cases, as it will be mentioned throughout the chapter.
 5. In the case of the OH-terminated surface, the desired ligand-exchange reaction will be simulated only on the –OH surface sites, since this is the basis for several ALD processes. The surface Si–H group will not be considered, although it has been observed to participate in several deposition processes.^{69,118,132}
 6. The simulation of a surface reaction using DFT methods offers information regarding the energy of initial, transition and final states during a reaction. In the case that the energy of the final state is more negative than that of

the initial state, the reaction will be described as thermodynamically favorable. If, in addition, the difference between initial and transition state (the activation barrier) is relatively small, the reaction will be described as kinetically feasible. When an activation barrier is large (regardless of the stability gained) a reaction will be said to be under kinetic control, and it will occur only at temperatures sufficiently large to allow overcoming the activation barrier. When an activation barrier is small, the reaction will proceed to the most stable state and it will be said to be under thermodynamic control. Notice that these terms are used in a physical-chemical context and not in terms of the overall deposition process.

7. In order to effectively establish practical comparisons, a general scheme of reactions, based on the reactivity trends of the isolated precursors, is considered for all the precursors tested. However, this does not mean that different deposition pathways are not possible on the surface of the growing film. Actually, we hope that this work will stimulate further investigations where other reaction pathways will be considered, based on the reactivity trends of a particular surface and a particular precursor.

These are necessary assumptions that will help us avoid an exceedingly complicated and lengthy investigation; at the same time, this will make establishing general trends possible. Ultimately, this set of investigations will lay the groundwork for further studies of processes constituting film growth.

4.3 Surface Reactions of $\text{Al}(\text{CH}_3)_3$ as an Example of Metal Alkyl Chemistry

The family of alkyl-based compounds is arguably the most common set of precursors for ALD-based deposition of Al-containing films; particularly, the

deposition of Al_2O_3 using $\text{Al}(\text{CH}_3)_3$ as the metal precursor has become a test reaction^{10,101,133-140} and, due to its reliability, it has been scaled up to the industrial level.^{141,142} As has been described in Chapter 2 (experimental section), NBO calculation was applied to visualize the HOMO and LUMO of the precursor molecule, fragment of the precursor, or the surface cluster and to rationalize the interaction between the species.

According to figure 4.1, the HOMO of an alkyl aluminum molecule involves the C atoms that are attached to the metal center. However, a nucleophilic attack initiated at these carbon-containing groups is unlikely due to the lack of free electrons on the carbon atom. On the other hand, the LUMO clearly involves the metal atom, which indicates that it can be easily attacked by a surface nucleophile, especially considering that in this case the metal center is unsaturated (since it has only three bonds and can accept an extra electron pair, in compliance with the so-called octet rule). In addition, the geometry of this precursor might also facilitate a direct interaction of the metal and a surface site.

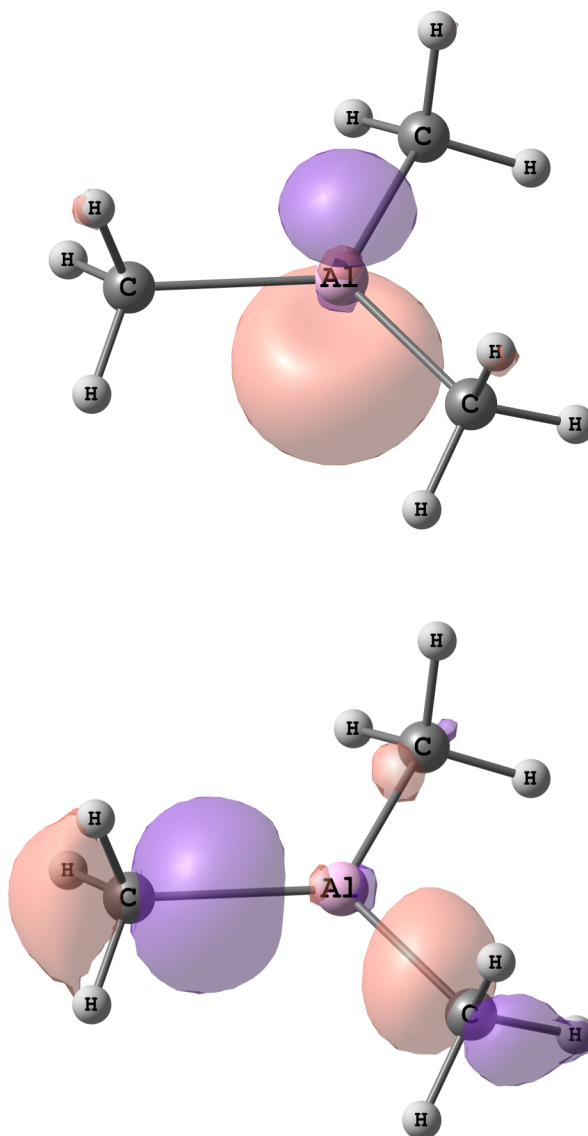


Figure 4.1: LUMO (top) and HOMO (bottom) of $\text{Al}(\text{CH}_3)_3$ as the representative of the metal alkyl family. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

54 kJ/mol; other calculations using various hydroxylated models have predicted values within the 30-60 kJ/mol range.^{119,143-145} Upon elimination of methane, the resulting surface structure gains a stability of ~200 kJ/mol. The by-product (methane) is very inert and has a low sticking coefficient on most surfaces, and therefore does not readsorb on the surface during film deposition.

On the other hand, the adsorption on a bare (non-functionalized) silicon surface results in the formation of a weak Si-Al bond (structure A), since Si is not as efficient an electron donor as O. Evidence of this weak interaction has been observed on other substrates, such as GaAs.¹⁴⁶ Dissociation of a metal-ligand bond in this case features a modest kinetic requirement (8 kJ/mol) and results in a very stable dissociated state (structure M, with a thermodynamic gain of ~240 kJ/mol), suggesting that dissociative adsorption can take place at low temperatures. Indeed, other metal alkyls have been observed to dissociate at 250 K.¹⁴⁷ However, it is important to stress that structure A has a nearly equal chance to either dissociate to form structure M or to desorb reversibly into the gas phase, because the energy of the transition state between structure A and M is very close to the reactant level. This phenomenon implies that in the presence of both types of reactive sites (bare and hydroxylated), the occurrence of ligand-exchange reactions will be more favored than the undesired reaction of dissociative adsorption, even though both pathways are thermodynamically feasible. This observation explains the success of metal alkyls in ALD schemes, where reactions are under kinetic control (i.e., at temperatures that are sufficiently low to favor only the pathway with the lowest barrier). At high temperatures, the fact that the dissociated structure M is more stable than the product of ligand-exchange (structure E) indicates that under thermodynamic control (i.e., at temperatures sufficiently high

to overcome local kinetic barriers and reach the most stable state) the undesired reaction will be favored.

The dissociated state (structure M) can undergo further transformations leading to ligand decomposition. This process can take place through the scission of a C–H bond, which is kinetically demanding ($E_a \sim 200$ kJ/mol), as is expected since such bonds are particularly strong.¹⁴⁸⁻¹⁵² The formation of a Si–H bond and a methylene ($\text{H}_2\text{C}=\text{}$) ligand, structure H, can evolve rapidly into structure C (with stabilization energy of 380 kJ/mol) through a barrierless process in which rehybridization of the methylene group occurs and a stable Si–C linkage is formed. The large kinetic requirement to decompose the alkyl ligand indicates that this reaction will only take place under thermodynamic control. Indeed, evidence of methyl decomposition from the metal alkyl $\text{Al}(\text{CH}_3)_3$ has been observed only at temperatures above 600 K;¹⁵³ similar observations have been reported for $\text{Ga}(\text{CH}_3)_3$.^{154,155}

For $\text{Al}(\text{CH}_3)_3$, in spite of the impressive stability gain achieved by the formation of Si–C bonds (e.g., in structures M and C), the combined kinetic barriers likely preclude this pathway from being a major one in the surface transformations of $\text{Al}(\text{CH}_3)_3$ if hydroxyl-terminated (or other strong nucleophilic) surface sites are available. Under moderate deposition temperatures the undesired pathway can be suppressed, which contributes to the nearly perfect behavior of metal alkyls as deposition precursors in ALD.

4.4 Surface Reactions of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ as an Example of Metal Alkylamide Chemistry

The alkylamide precursors have received significant attention for the deposition of nitrides and oxides of group IV metals (Ti, Zr, Hf), as well as those of W and Ta.^{6,99,103,156-161} Although these volatile and relatively easy-to-handle precursors have dominated the field of diffusion barrier film deposition for nearly three decades,¹⁰³ a substantial disadvantage of using these molecules in CVD-like processes is carbon contamination, which is not easily controlled.^{64,83,98,114-116} Fortunately, contamination has been reduced with the use of ALD schemes (with water or ammonia as secondary precursors for the respective growth of oxides and nitrides); various post-treatment methods have also led to dramatic improvements of the deposited films.^{160,162-165}

Hafnium alkylamides (for example, tetrakis(dimethylamido)hafnium, $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$) have a set of remarkable properties as the precursors of depositing a variety of Hf-containing films,^{11,161,166-172} including hafnium dioxide, a high-k dielectric material with a wide range of current and potential applications.^{172,173}

The analysis of the frontier molecular orbitals of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ (figure 4.3) demonstrates that the LUMO is localized on the Hf atom indicating that nucleophilic attacks of the surface sites onto the metal center should play a major role in determining the mechanism of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ reactions. In contrast to the planar geometry of the $\text{Al}(\text{CH}_3)_3$ precursor, the tetrahedral geometry of the hafnium alkylamide precursors suggests that a direct attachment of the metal to the surface may be hindered sterically.

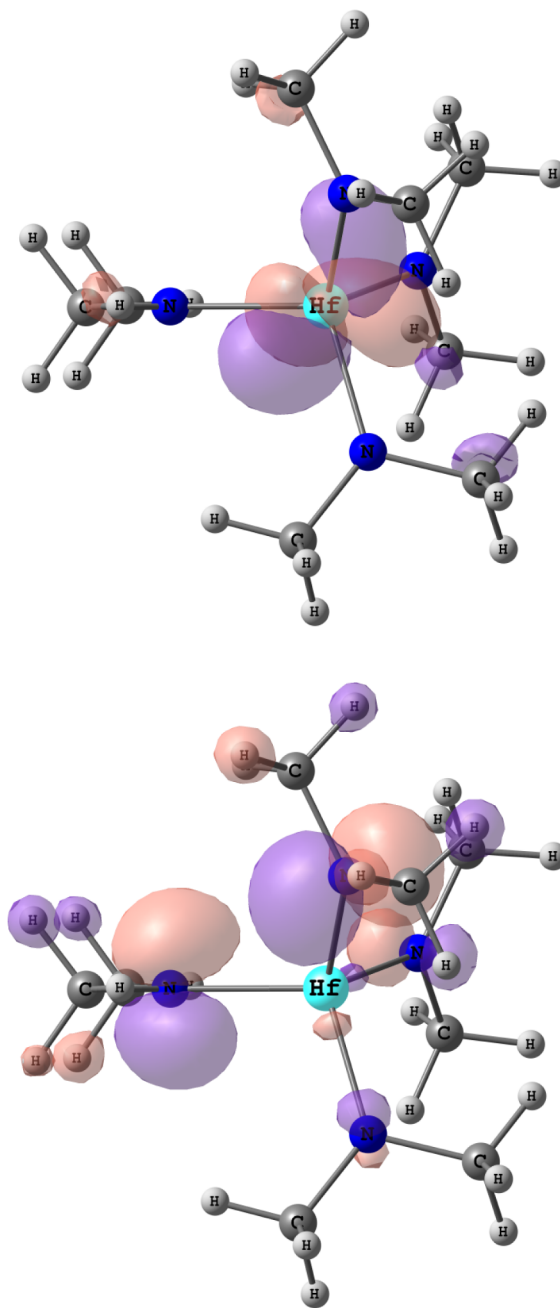


Figure 4.3: LUMO (top) and HOMO (bottom) of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ as the representative of the family of alkylamide precursor. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

On the other hand, the HOMO is largely localized around nitrogen atoms of the alkylamide ligands, which is not surprising considering that N can be regarded as having an available lone pair of electrons (although the geometry of the ligand suggests that the bond with the metal could be described as a N=M double bond¹¹⁴). Thus, as this precursor molecule approaches a surface, a nucleophilic attack of the N lone pair onto an electron-deficient surface site is possible. In addition, the HOMO extends towards a C–H bond of each methyl group; this is a consequence of the so-called Bohlmann effect, which leads to the weakening of C–H bonds in aliphatic amines and amides.¹¹⁴ Due to the presence of relatively weak C–H bonds, ligand decomposition through scission of these bonds will receive additional consideration below.

The reaction of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ with a hydroxyl-terminated surface is very favorable, as shown in figure 4.4. As the precursor approaches the surface, the interaction between the hydroxyl group and the N atom on one of the dimethylamido ligands stabilizes the system by 43 kJ/mol (structure D) and makes the Hf atom accessible for a nucleophilic attack by the oxygen atom despite the steric hindrance mentioned earlier. The produced surface species is stable thermodynamically (by 140 kJ/mol) and the kinetic requirements for the ligand-exchange reaction are negligible, which suggests that low temperatures can be used to deposit films in alkylamide-based ALD schemes. An essentially barrierless process and a similar energy gain have also been simulated by Kelly et al.⁵³ In practical application schemes, temperatures as low as 200 °C have been reported.^{161,171} It is important to mention that the by-product (dimethylamine) features a lone pair that can effectively compete with the Hf precursor for electron-deficient surface sites.⁶² Although purging periods between

ALD cycles are expected to eliminate the by-products, this competition is still a potential drawback during the ALD process.

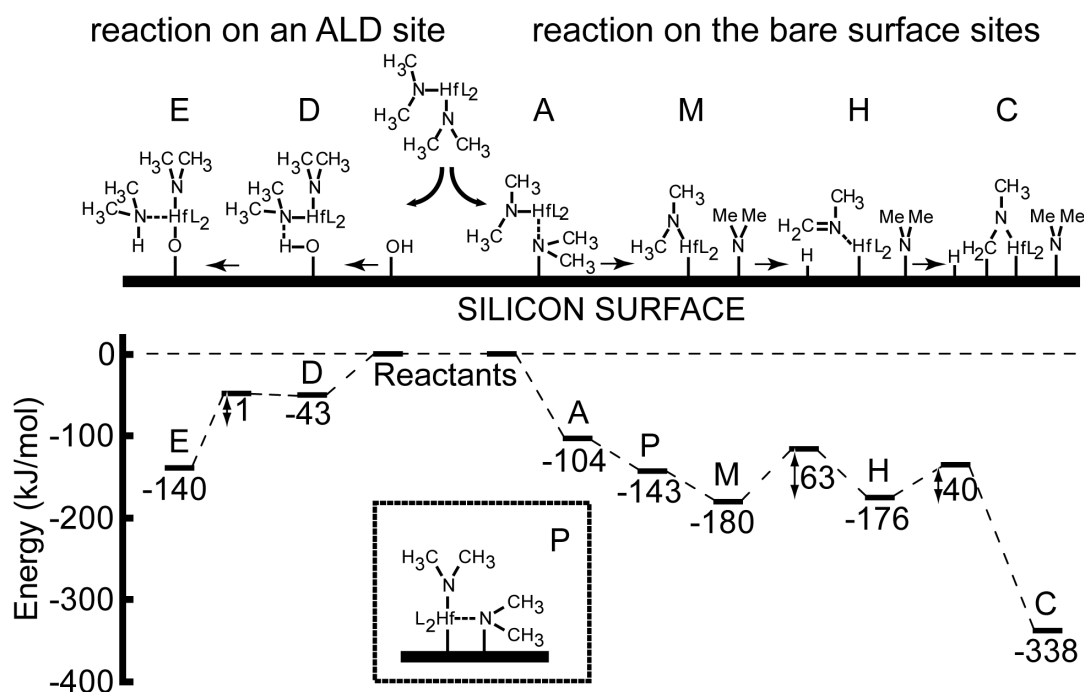


Figure 4.4: Energy diagram for the reactions of $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ reacting with a hydroxyl-terminated surface site (left) and with a bare silicon surface (right). The numbers on the right of the two-way arrows represent the barrier of corresponding processes. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

On the bare Si surface, the Hf atom does not participate in an initial interaction, partially due to steric effects and/or partially because a Si atom is not as efficient an electron donor as the O atom of a hydroxyl site. Indeed, our attempts to simulate a molecularly adsorbed structure via a Hf–Si bond formation (by changing

the overall geometry of the precursor from tetrahedron to trigonal bipyramid) systematically led to a structure with a dative N–Si bond (structure A) instead of a Hf–Si bond. Since the frontier molecular orbital analysis indicates that the HOMO of the precursor is centered around the N atoms, this dative bond is not unexpected. The resulting molecularly adsorbed structure A is thermodynamically stabilized by 104 kJ/mol, which is substantially larger than structure D (the desired pathway). The adsorption process is predicted to be barrierless, since this reaction only involves the formation of a Si–N bond, without any energetically demanding bond scission processes taking place. This Si–N dative bond facilitates the attack of the neighboring Si atom onto the Hf atom (structure P); no bond scission is required, since Hf is a large atom that can easily expand its coordination number and form a penta-coordinate geometry, which has been reported previously.¹¹² In structure P, the N atom attached to the surface is tetra-coordinated; thus, scission of the N–Hf bond is favorable because it leads to the stable coordination states for both N (three) and Hf (four). These processes are found to be essentially barrierless and lead to a very stable surface species (structure M, stabilized by 180 kJ/mol).

When both hydroxylated and bare silicon sites are present on the surface, in spite of the fact that both pathways in figure 4.4 are predicted to be barrierless, the reaction on the bare surface is thermodynamically more favored than the ligand-exchange process. Unlike in the case of $\text{Al}(\text{CH}_3)_3$, where low temperature could be applied to favor the desired ligand-exchange reaction, undesired reaction will be more feasible in the case of alkylamides, since both pathways are barrierless.

The possibility of C–H bond scission during deposition (mentioned in the analysis of the HOMO orbitals above) is also considered. Starting with structure M,

the precursor can undergo C–H bond scission to form a Si–H bond and an imido ($\text{CH}_3\text{--N=CH}_2$) ligand (structure H); the kinetic barrier that needs to be overcome is relatively small (~ 63 kJ/mol), especially with respect to the barrier required to break the C–H bond in metal alkyls (~ 200 kJ/mol in figure 4.2). This supports the observation that the C–H bond in this alkylamide is weakened because of its involvement in the HOMO; additional evidence of this reaction is the detection of $\text{CH}_3\text{--N=CH}_2$ during thermal decomposition of dimethylamides from $\text{Ti}^{113,115}$ and As^{174} alkylamides. Although the formation of structure H does not gain additional stability, further attachment of this imido ligand through the methylenic, =CH_2 , carbon (forming a C–Si bond) can lead to a dramatic increase in stability (structure C, over 300 kJ/mol with respect to the reactant level). Due to the presence of several kinetic barriers required to reach structure C, the reaction is expected to occur at high temperatures and induce carbon contamination to the as-deposited films.¹⁷⁵

In summary, both desired and undesired pathways are likely to occur on a surface with both types of reactive sites available, which means carbon contamination could be introduced into the deposited film, because the Bohlmann effect weakens the C–H bond of alkylamide ligands and stimulates thermal decomposition of the ligand. The best approach to exclude this contamination should likely be focused on eliminating possible surface reactive sites leading to the bond scission by surface passivation or other treatments.

4.5 Surface Reactions of $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ as an Example of Metal Alkoxide Chemistry

Metal alkoxides have been employed as precursors for depositing metal oxides, mainly those of Ti, Zr, Hf, V and Nb.^{99,156,176-178} The alkoxide ligand was one of the first to be modified to increase the volatility of the precursor.¹⁷⁶ Ti alkoxides have been used to deposit not only TiO_2 ,^{177,179-182} but also ternary materials such as SrTiO_3 , which could be used as a dielectric material in microelectronics.⁹⁹

The alkoxide ligand is reminiscent of the alkylamide ligand, both featuring a heteroatom with available lone pairs of electrons. Not surprisingly, the chemistry of these compounds is similar in many aspects, as it can be understood from the analysis of the frontier molecular orbitals in figure 4.5. The LUMO is centered around the metal atom, once again indicating that nucleophilic surface sites can promote an attack onto titanium. The HOMO is centered around the oxygen, which indicates that $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ can form ligand-surface dative bonds, similarly to alkylamide precursors. The Bohlmann effect on C–H moieties is known to be less pronounced in oxygen-containing compounds than in their nitrogen counterparts; therefore, C–H scission is expected to be more energetically demanding in the case of alkoxides.

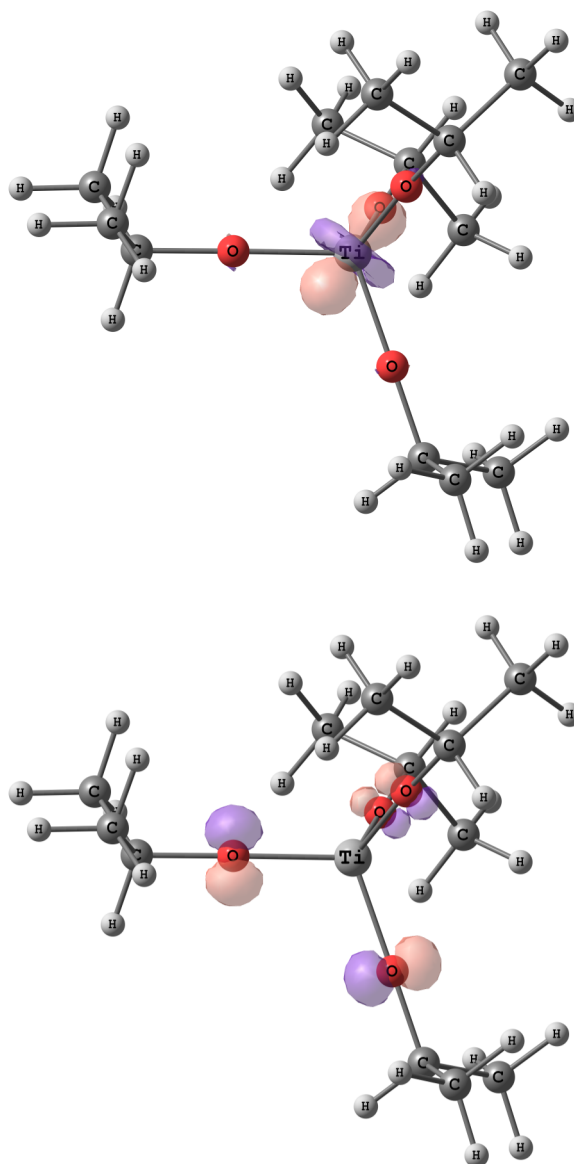


Figure 4.5: LUMO (top) and HOMO (bottom) of $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ as the representative of the family of alkoxide precursor. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

The reaction of $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ (or TTIP) with a hydroxyl-covered surface (summarized in figure 4.6) is predicted to start with a weak interaction between the precursor ligand and the surface hydroxyl groups, which allows the system to gain stability as soon as the precursor approaches the hydroxyl site (structure D). However, the ligand-exchange reaction features a transition state with energy very close to that of the reactant level; therefore, the adsorbed precursor has comparable chances to proceed to the desired product of ligand-exchange reaction or desorb into the gas phase, which can create efficiency problems for ALD schemes.

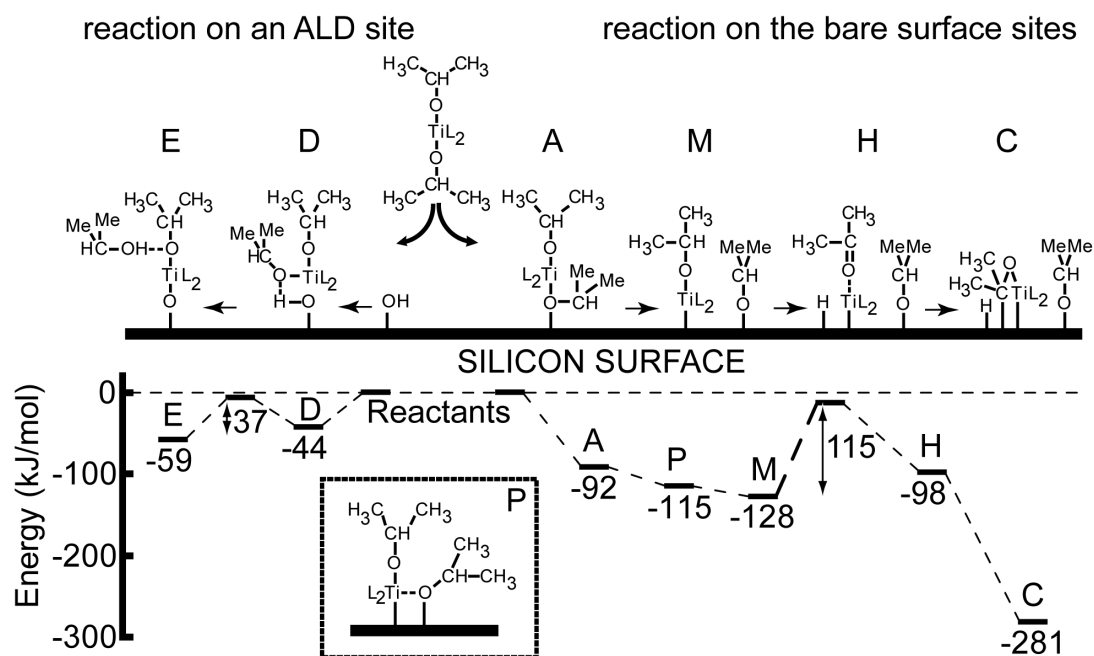


Figure 4.6: Energy diagram for the reactions of $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ reacting with a hydroxyl-terminated surface site (left) and with a bare silicon surface (right). The numbers on the right of the two-way arrows represent the barrier of corresponding processes. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, 31, 021401. Copyright 2013 American Vacuum Society.

Indeed, TTIP has been shown to involve a lower growth rate than when TiCl_4 is employed.¹⁸³ Different from the cases of ligand-exchange reactions of $\text{Al}(\text{CH}_3)_3$ and $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$, where the product of the exchange was stabilized by more than 100 kJ/mol, in the case of TTIP the product of the ligand-exchange reaction (structure E) is only stabilized by ~ 60 kJ/mol; in other words, this reaction does not gain substantial thermodynamic stability. Some of these complications have been avoided in practice by using strong oxidants, such as ozone and hydrogen peroxide.^{7,100,179,184}

The adsorption of TTIP on a bare silicon surface closely resembles that for alkylamides. A dative Si–O bond (structure A) confers a great stability to the system, and further induces the dissociation of a ligand-metal bond and the formation of a Si–Ti bond (structure M, stabilized by 128 kJ/mol). As shown in figure 4.6, the reaction between TTIP and the bare silicon surface exhibits a barrierless pathway and forms a more thermodynamically favorable product, which is clearly more advantageous to the undesired pathway. Consequently, in the presence of both hydroxylated and bare silicon surface sites, the alkoxide precursor will preferentially bind to the latter, opening a path for uncontrolled reactions leading to contamination. Under practical conditions, the best solution is to decrease the number of defect sites (i.e., to increase the extent of hydroxylation on the surface), for example, by extending the water pulse during ALD.¹⁸⁵

As mentioned earlier, the Bohlmann effect is weaker in alkoxides than in alkylamides; consequently, ligand decomposition through scission of the central C–H bond features a kinetic barrier of 115 kJ/mol, almost twice as large as the one observed in the case of Hf alkylamide, which indeed demonstrates that the C–H weakening effect of alkoxide precursors is less pronounced than for alkylamides.¹¹⁴

Upon C–H scission, the ligand is transformed into acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, which has been observed during CVD using TTIP.¹⁸² In addition to the scission of a C–H bond in alpha-position with respect to O, scission of the terminal C–H bond (from CH_3) can also take place. This possibility (figure 4.7) would lead to the formation of propene, which has also been observed during the CVD processes.^{180,186}

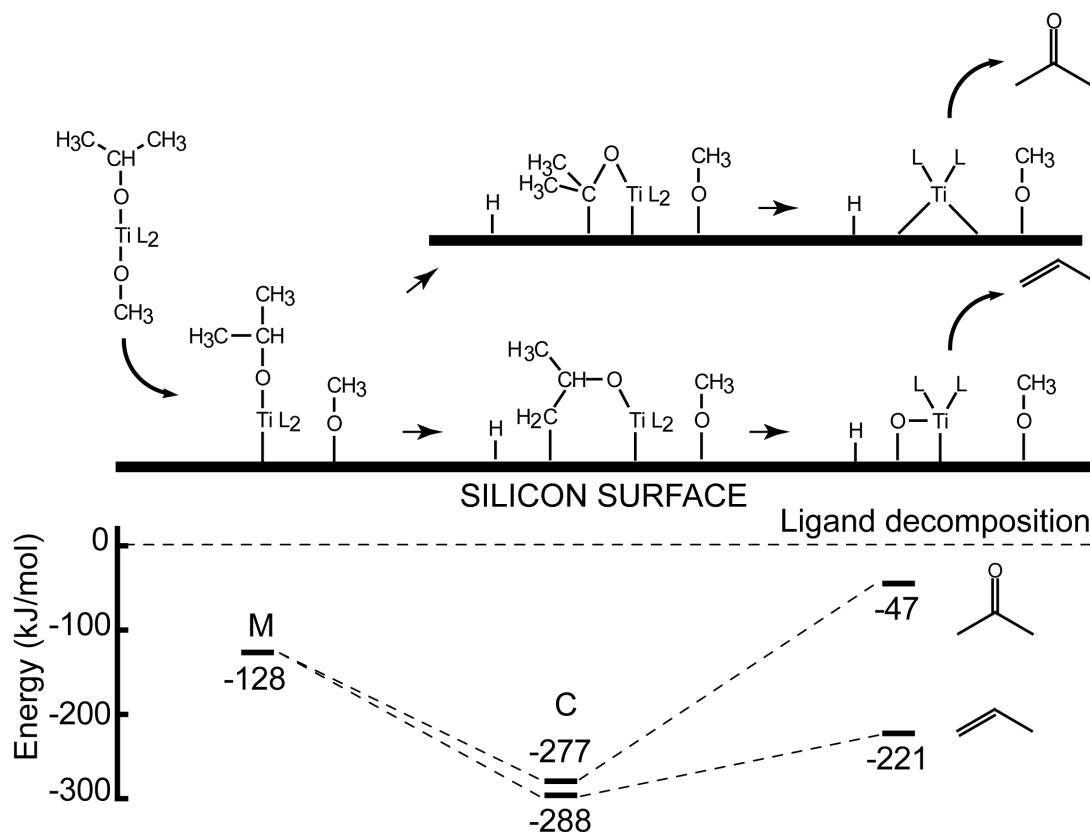


Figure 4.7: Ligand decomposition possibilities of an isopropoxy ligand (B3LYP/LANL2DZ): A simplified molecule where three of the isopropoxy ligands on TTIP were replaced with methoxy (CH_3O) ligands was employed; the remaining isopropoxy group was used to investigate the elimination of both acetone and propene. Notice that propene elimination is more favorable thermodynamically than acetone elimination.

In spite of the low stability that the dehydrogenated structure H gains (98 kJ/mol below the reactant level), the following formation of a Si–C bond enhances dramatically the stability of the system, indicating that ligand decomposition through C–H scission is thermodynamically favorable, and it is expected to take place at high temperatures, where the thermal energy is sufficient to overcome the barrier between structure M and H. Indeed, temperatures as low as 550 K are sufficient to decompose TTIP during ALD processes,¹⁷⁹ and CVD processes on Si surfaces at ~650 K lead to the formation of Si–C bonds.¹⁸⁷

In summary, the desired ligand-exchange pathway is impeded by the transition state with predicted energy close to that of the reactant level, which means that the reaction has a propensity to follow the undesired pathway under kinetic control (low temperature). Even if high deposition temperature is utilized, the more thermodynamically favored ligand decomposition reaction (undesired pathway) will still dominate. As mentioned earlier, to avoid an undesired pathway, the best solution is to decrease the concentration of surface defect sites.

4.6 Surface Chemistry of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ in Examining the Role of Cyclopentadienyl Ligand

Cyclopentadienyl (Cp) compounds have been known for a long time; however, not until relatively recently have these organometallic compounds been employed as precursors for film deposition. Their main advantage over alkylamides and alkoxides is high thermal stability which allows temperatures above 400 °C.^{100,188-191} Their thermal stability and volatility have been tuned through a careful modification of the ligands, which has led to a wide range of available cyclopentadienyl-based precursors.¹⁹¹⁻¹⁹³ Choosing among this myriad of compounds, we will focus on

$\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ (Cp' stands for methyl- η^5 -cyclopentadienyl ligand), as the combination of cyclopentadienyl and methyl ligands is often used in transition metal deposition,¹⁸⁹ specifically, for deposition of HfO_2 films.^{188,191} Interestingly, substituted Cp rings seem to lead to films with lower carbon contamination compared to unsubstituted ones,¹⁹⁰ thus expanding the precursor design capabilities even further.

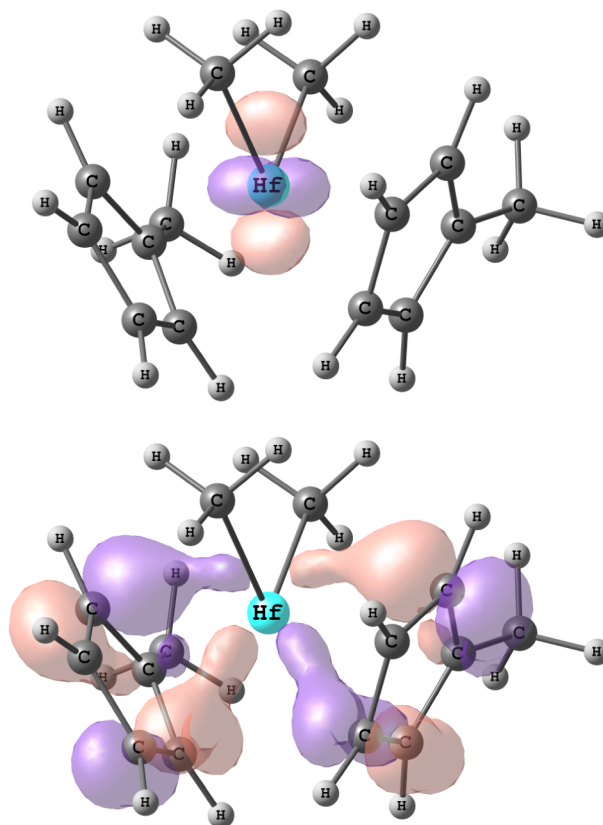
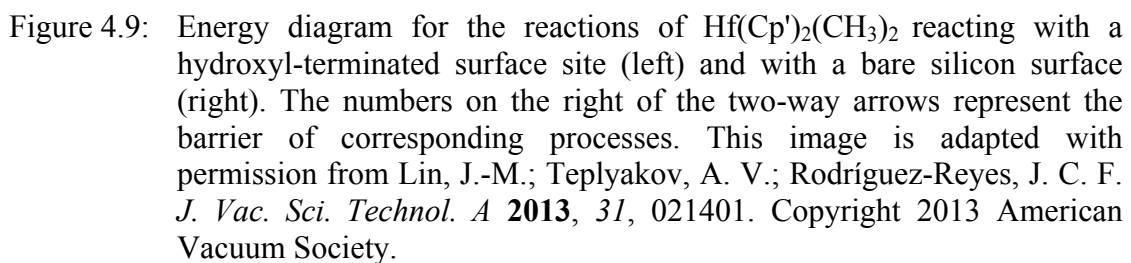


Figure 4.8: LUMO (top) and HOMO (bottom) of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ as the representative of the family of cyclopentadienyl-based precursor. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

The analysis of the frontier molecular orbitals of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ summarized in figure 4.8 indicates that the most electrophilic portion (the LUMO) corresponds to the Hf center. Thus, Hf is expected to be susceptible to a nucleophilic attack by electron-rich species such as surface hydroxyl sites. Different from previous cases, where the HOMO was centered predominantly around a single atom (e.g., O in alkoxides and N in alkylamides), the HOMO of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ encompasses the cyclopentadienyl rings. The dispersion of electronic density in this case can lead to a relatively low ability of a ligand to attack electron-deficient surface species, which is expected to be beneficial for decreasing the number of pathways for surface contamination.

As shown in figure 4.9, the reaction of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ with a hydroxyl surface site is predicted to start with a rather weak interaction between the precursor and the surface (structure D, stabilized by 11 kJ/mol), especially compared to our alkylamide and alkoxide models, which were stabilized by more than 40 kJ/mol. Different from those previous cases, where additional stabilization originated from weak interaction between the surface hydroxyl groups and the electron-rich atom of the precursor ligands, in the case of the cyclopentadienyl precursor, only the interaction between the surface $-\text{OH}$ group and the Hf atom (probably weakened by steric hindrance) is observed. Noticing that the ligand-exchange reaction can take place using either a Cp' or a CH_3 ligand, we will focus on the first option, since it is more relevant to the type of ligand under investigation. The elimination pathway involving the methyl (CH_3) ligand produces methane as by-product^{194,195} (figure 4.10).



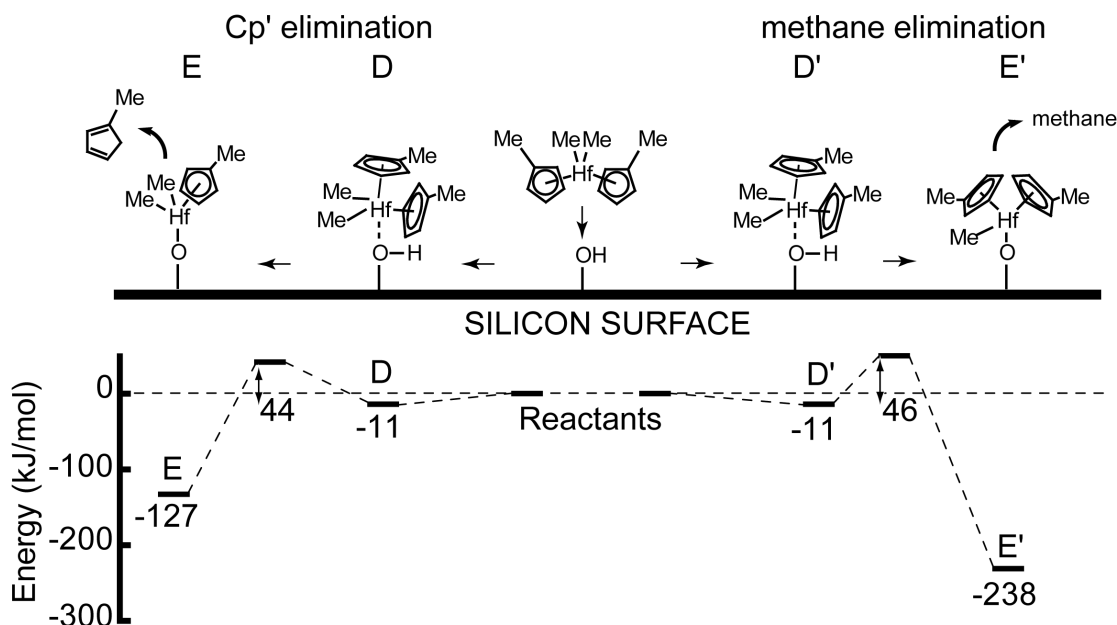


Figure 4.10: Two ligand-exchange reactions of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ on hydroxylated silicon surface (B3LYP/LANL2DZ): Although the barriers for both pathways are comparable, methane elimination is predicted to lead to a more stable surface species.

The ligand-exchange reaction involving the Cp' ligand occurs by overcoming a barrier of 44 kJ/mol, which places the transition state for this transformation above the level of the reactants. This indicates that desorption of the precursor back into the gas phase is more likely than the ligand-exchange reaction, even though the product of the ligand-exchange reaction is very stable (structure E in figure 4.9, stabilized by 127 kJ/mol). In fact, this kinetically unfavorable barrier might explain the low growth rate of HfO_2 films deposited with water and $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ comparing to the processes utilizing a more aggressive co-reactant, ozone.¹⁹¹

The initial interaction of $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ with a bare Si surface outlined in figure 4.9 does not lead to a significant increase in stability either. The precursor

approaches and weakly interacts with the surface through one of the cyclopentadienyl ligands (structure A, stabilized by 8 kJ/mol). This interaction was predicted to be weak, because the electrons on Cp' ligand cannot effectively form a dative Si–C bond. Cyclopentadienyl-type ligands are known to coordinate to the metal center with three bonds, which means all six π -electrons are used on coordination bonds (notice that in the case of alkylamides and alkoxides electrons are available as lone pairs). Furthermore, dissociation of the cyclopentadienyl-metal bond requires overcoming a transition state higher than the reactant level (a barrier of 31 kJ/mol) similar to that of the ligand-exchange reaction, which means that the molecularly adsorbed precursor is more likely to desorb than to dissociate, even though the reaction is driven towards dissociation thermodynamically (structure M, stabilized by 109 kJ/mol).

In a scenario where two types of surface sites (hydroxyl-terminated and bare) are presented, although both desired and undesired pathways feature a kinetic barrier above reactant level, the product of ligand exchange (structure E) is thermodynamically more stable than that of the undesired reaction (structure M) by ~ 20 kJ/mol. This prediction makes $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ significantly different from other precursors considered here, because only $\text{Hf}(\text{Cp}')_2(\text{CH}_3)_2$ exhibits a more thermodynamically favorable ligand-exchange pathway, which makes cyclopentadienyl-based precursors robust candidates for ALD processes.

In addition, the simulation of ligand decomposition through C–H bond scission further extends the set of attractive qualities of the cyclopentadienyl ligand. The product of C–H bond scission is extremely stable (structure C, stabilized by 269 kJ/mol); however, the kinetic requirements to break the C–H bond in the cyclopentadienyl ligand are very high (181 kJ/mol), especially as compared to those

for alkylamides and alkoxides (63 and 115 kJ/mol, respectively). Due to the stability of the ligands, decomposition reactions during ALD using cyclopentadienyl precursors have been only observed above ~650 K.¹⁹⁵

Our results suggest that cyclopentadienyl precursors are superior to other types of precursors considered here in the following aspects: (1) their inefficiency of molecular adsorption onto bare silicon surface, and 2) their kinetic hindrance towards ligand decomposition. However, more enhancements need to be done to ease the kinetic requirements towards the ligand-exchange pathway.

4.7 Surface Reactions of Cu(acac)₂ as an Example of a Metal Diketonate Chemistry

Diketonate ligands gained popularity at the end of the last century, when copper replaced aluminum in metallization schemes, and Cu diketonates were among the few precursors available to deposit this metal by CVD.¹⁹⁶⁻¹⁹⁸ In addition to copper, diketonate ligands can also be used to form volatile metalorganic compounds with alkaline-earth and rare metals.^{199,200} Although these ligands initially suffered from several drawbacks, such as their tendency to decompose and relatively low volatility of the corresponding metalorganic compounds, the volatility was improved by using several substituents, including the use of fluorine.^{6,127,197-199} Chemically, the concern related to the use of these compounds was the introduction of contaminants (first carbon and oxygen, later also fluorine) in the as-deposited film during CVD. The deposition of metallic films often requires the use of hydrogen to protonate the ligand and reduce copper to its metallic state.²⁰¹ The deposition of oxides with diketonate-based precursors by ALD has rarely employed water and/or hydroxyl sites; instead, it relies more often on strong oxidizing agents, such as ozone.^{100,190} This fact has been

associated with the unusual strength of the metal-ligand bond due to chelating effects.^{106,202,203} In addition, it has been proposed that the strength of the ligand-metal bond ultimately causes the heavy carbon contamination.¹⁰⁶

Although Cu(acac)₂ has been broadly used for deposition of Cu films, as is the case with other metal diketonates, the use of this precursor has been hampered by multiple uncontrolled reactions that lead to film contamination.⁸⁴

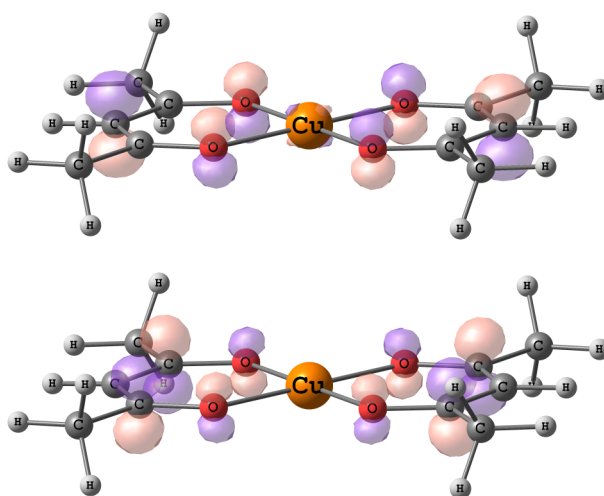


Figure 4.11: LUMO (top) and HOMO (bottom) of Cu(acac)₂ as a representative of the family of diketonate-based precursor. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

The predicted frontier molecular orbitals are shown in figure 4.11. Both the HOMO and the LUMO are spread along the skeleton of the ligands, which suggests that the reactivity of this molecule will mostly involve the interactions between surface and the ligands. The fact that the LUMO is not centered around the metal atom

indicates that the attack from an electron-rich surface species will not be very favorable. In addition, since the HOMO is spread along the skeleton of the ligands, the nucleophilic attack onto electron-deficient surface sites can occur not only through the O atom, but also, for example, through a C atom, as will be shown below.

The calculations involving $\text{Cu}(\text{acac})_2$ and a bare Si surface site lead to an immediate dissociation of the Cu–O bond of the $\text{Cu}(\text{acac})_2$ molecule and a dissociative adsorption across the silicon-silicon dimer, likely because the planarity of the molecule allows the simultaneous approach for both O and Cu, as shown in figure 4.12.

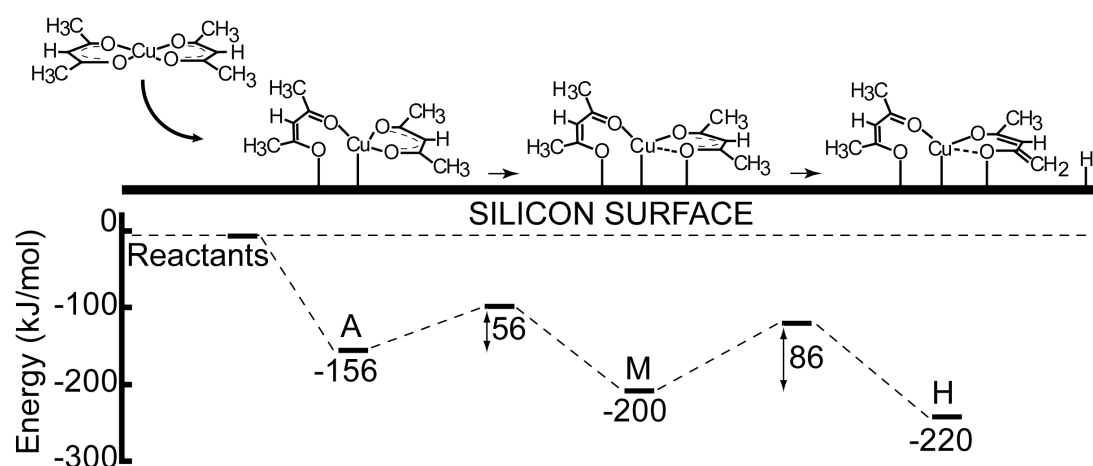


Figure 4.12: Dissociative adsorption of $\text{Cu}[\text{acac}]_2$ molecule on the Si(100) surface (B3LYP/LANL2DZ). The numbers on the right of the two-way arrows represent the barrier of corresponding processes.

The second ligand is able to approach the surface forming an additional Si–O bond with a rather large (yet feasible to overcome) energy barrier of 56 kJ/mol. Scission of a C–H bond of a methyl group is also predicted to be kinetically feasible

(86 kJ/mol), and further stabilizes the structure (by 220 kJ/mol). Notice that in this case the increase in stability is possible without forming a Si–C bond, because the ligand can stabilize the resulting CH₂ moiety by forming a C=C double bond. However, since the goal of this section is to explore the reactivity of the ligands following initial adsorption of the intact metalorganic entities, the immediate dissociation of the Cu–O bond is avoided by “capping” one of the surface silicon atoms with a hydrogen atom; that is, on a Si(100) cluster model that represents two neighboring silicon dimers, one of the surface silicon atom was terminated with a hydrogen atom, leaving the remaining three open to a reaction. When simulating the reaction between Cu(acac)₂ molecule and this cluster, the reaction was restrictively initiated on the half-occupied dimer, which is described as structure A in figure 4.13.

Cu(acac)₂ adsorbs molecularly through the formation of a dative O–Si bond (structure A, stabilized by 71 kJ/mol) and proceeds to a more stable structure (structure M, stabilized by 139 kJ/mol) via the formation of a dative bond between a bare Si atom (on the neighboring dimer) and the central CH portion in the skeleton of the other acac ligand. Since this carbon atom was originally unsaturated (it formed part of the resonance structure) no bond scission is involved; consequently, only geometric adjustments are necessary to reach this state and the process is essentially barrierless. This is in agreement with the conclusion drawn from the NBO analysis that the HOMO distributes along the ligand skeleton, as shown in figure 4.11. Scission of the C–H bond at the carbon attached to the surface takes place upon overcoming a barrier of 77 kJ/mol. Although it does not lead to an increase in stability in this case, scission of this bond has been observed even at room temperature on other surfaces.⁸⁴ The prediction of this pathway is of importance because it highlights an exclusive set

of reactions (not available for the other precursors considered), where stable structures are obtained: (1) without attaching the metal to the surface, and (2) without a substantial kinetic barrier impeding carbon attachment. This finding adds to a previous computational study suggesting that scission of ligand skeleton is facile in diketonates.¹⁰⁶ Thus, one of the main drawbacks of diketonate-based deposition is the kinetically viable adsorption of ligands on a surface, in particular through direct carbon attachment.

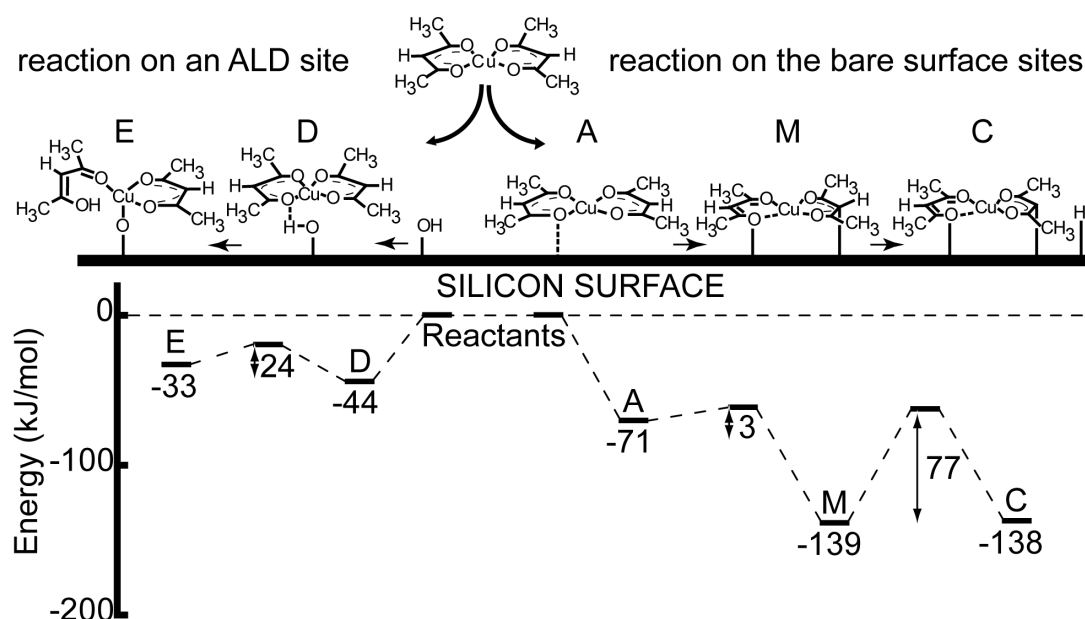


Figure 4.13: Energy diagram for the reactions of $\text{Cu}(\text{acac})_2$ reacting with a hydroxyl-terminated surface site (left) and with a bare silicon surface (right). The numbers on the right of the two-way arrows represent the barriers of corresponding processes. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

On the hydroxyl-terminated surface, the initial interaction of the precursor with the hydroxyl group stabilizes the system through the interaction between the ligand and the surface hydroxyl group (structure D in figure 4.13, stabilized by 44 kJ/mol). Although the barrier for proceeding the ligand-exchange reaction (24 kJ/mol) is rather small, the final product is predicted to be less stable than the D state (structure E, stabilized by 33 kJ/mol), which means that the reaction is not favorable thermodynamically.¹⁰⁵ This is in agreement with the fact that the LUMO is not centered around the Cu atom; therefore, the nucleophilic attack onto Cu atom is not expected to be very favorable. Not surprisingly, ALD schemes involving diketonate precursors often require strong oxidants, such as ozone, rather than water. Due to chelating effect, the acac ligand remains attached to the Cu atom, which is detrimental for deposition schemes, since the protonated ligand is held close to the surface instead of being eliminated.

With respect to the undesired pathway established on a bare Si surface, the ligand-exchange reaction of $\text{Cu}(\text{acac})_2$ is clearly not favorable. The need for a more aggressive co-reactant during ALD processes (e.g., ozone) agrees with the limitation of $\text{Cu}(\text{acac})_2$ to efficiently eliminate its ligands.

4.8 Surface Chemistry of $\text{Ni}[\text{Pr-amd}]_2$, as an Illustration of Metal Amidinate Properties

The use of amidinates as deposition precursors was established only recently.^{102,201,204-209} These compounds garnered substantial attention, because they improved the performance shown by diketonates, especially for Cu and Ni deposition. Amidinates featured an improved thermal stability, higher vapor pressure and, more importantly, produced films that were practically free of contamination.²⁰¹ The ability

to synthesize amidinate complexes of a large portion of the transition metal list has also helped introduce this family as promising precursors for several deposition schemes¹³² (for example, La^{210} and Ni^{211}). In this section, special emphasis is placed on comparing the results for amidinates with those for diketonates.

Amidinate-based precursors, such as those of Co and Ni, can feature a tetrahedral or a square planar geometry, with steric effects playing an important role in the preferred configuration.²¹¹ Previous calculations indicate that the most stable state for $\text{Ni}[\text{}^i\text{Pr-amd}]_2$ precursor molecule has the tetrahedral geometry;^{211,212} oppositely, our calculations indicate that the planar geometry is the most stable geometry. It should be noted that the previously reported calculations utilized computational methods of higher level than those discussed here, but our investigation focuses on the role of the ligands in the chemical transformations of the adsorbed metalorganic compounds, and, for consistency, we proceeded with the geometry predicted by B3LYP/LANL2DZ. It is indeed possible that realistic surface transformations of the adsorbed $\text{Ni}[\text{}^i\text{Pr-amd}]_2$ precursor are more complicated than described here and could potentially involve subtle changes in the electronic state of central nickel atom. Nevertheless, the emphasis here will be placed on the reactions of the ligands that follow the initial adsorption, and a simple comparison with the other compounds considered will be performed.

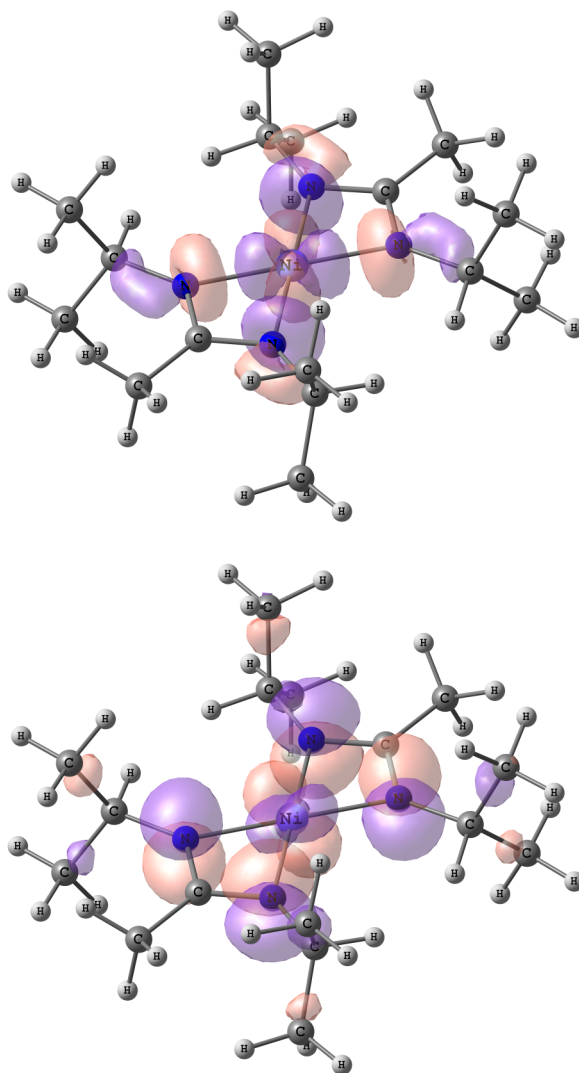


Figure 4.14: LUMO (top) and HOMO (bottom) of $\text{Ni}[\text{Pr-amd}]_2$ as the representative of the family of amidinate-based precursor. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, *31*, 021401. Copyright 2013 American Vacuum Society.

In general, although amidinate precursors structurally resemble diketonates, the frontier molecular orbitals shown in figure 4.14 are significantly different, specifically due to the fact that both the HOMO and the LUMO are centered around the metal atom (notice that in the case of the diketonate the electronic density was spread around the ligand skeleton). This fact suggests that a ligand attachment through C atoms is impeded; indeed, our attempts to simulate this scenario systematically converged to other structures, described later. It should be pointed out that if a tetrahedral geometry is considered instead of the planar one here; qualitatively, the structures of HOMO predicted are very similar.

LUMO orbitals also exhibit substantial similarity; however, in the case of tetrahedral geometry, they do stretch out to the unsaturated carbon in the ligand skeleton. Further studies are needed to understand all the details of the $\text{Ni}[\text{Pr-amd}]_2$ precursor molecule reactions with a surface. In particular, the possibility of the surface directly bonding to a carbon atom similarly to the case of diketonates should be considered.

The initial interaction of the $\text{Ni}[\text{Pr-amd}]_2$ precursor with a hydroxyl-terminated surface stabilizes the system through the interaction between the approaching ligand and the surface hydroxyl group (structure D in figure 4.15, stabilized by 47 kJ/mol). The completion of the H transfer to protonate an amidinate ligand requires overcoming a transition state above reactant level with a barrier of 51 kJ/mol, which means that the desorption of the precursor molecule back to gas phase is more likely to take place instead of ligand-exchange reaction, even though the product of ligand-exchange reaction is thermodynamically favored with a stabilization energy of 90 kJ/mol. Notice that in the case of diketonates the ligand-exchange

reaction was not favored thermodynamically, which indicates that a mild co-reactant may be sufficient to drive the reaction to completion, such as water; in fact, it has been reported that La[Pr-meAMD] can be protonated even with background water during ALD.¹³²

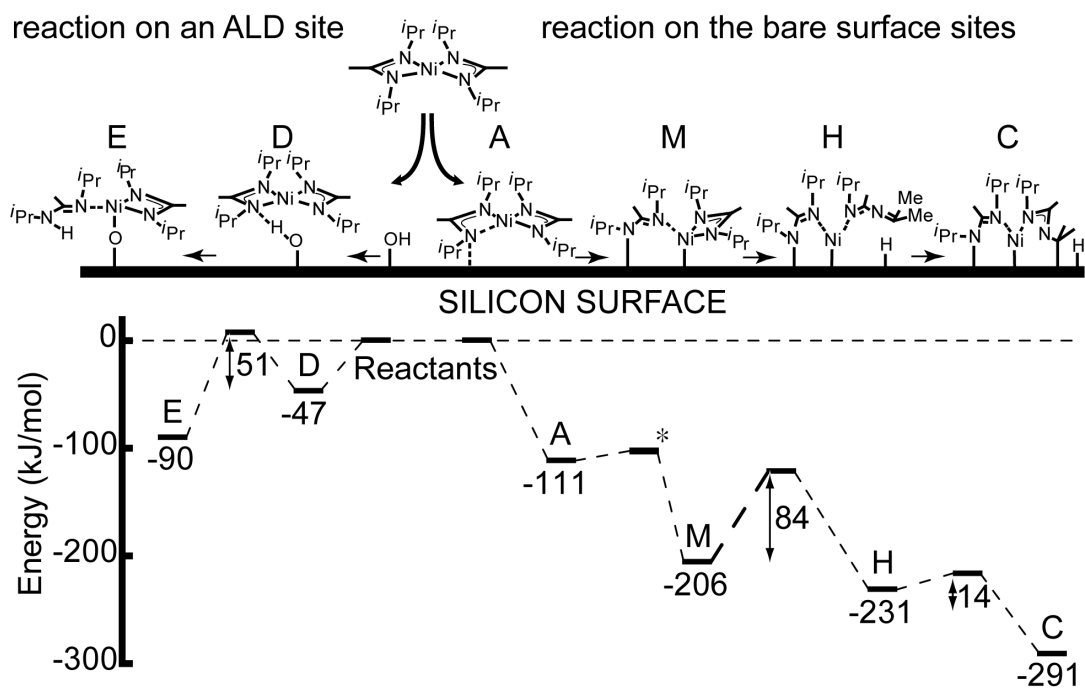


Figure 4.15: Energy diagram for the reactions of $\text{Ni}[\text{iPr-amd}]_2$ reacting with a hydroxyl-terminated surface site (left) and with a bare silicon surface (right). The numbers on the right of the two-way arrows represent the barrier of corresponding processes. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V.; Rodríguez-Reyes, J. C. F. *J. Vac. Sci. Technol. A* **2013**, 31, 021401. Copyright 2013 American Vacuum Society.

On the other hand, adsorption on a bare Si surface site takes place through a N atom that nucleophilically attacks an electron-deficient site (structure A, stabilized by

111 kJ/mol). Different from the case observed for diketonates, no additional constraints were necessary to ensure a molecular adsorption, which is an indication of the enhanced stability offered by amidinates with respect to diketonates. The dissociation of one of the N–Ni bonds stabilizes the system by 206 kJ/mol (structure M), indicating that thermodynamically this process is favorable. Unfortunately, the precise kinetic barrier involved in this dissociation step was not calculated here, due to the difficulty in describing multiple rotational motions involved in the transformation. However, since the only cases in which the kinetic barrier surpasses the level of reactants were predicted when the molecularly adsorbed states were not sufficiently stable (e.g., for the alkyl- and cyclopentadienyl-based precursors), we can safely assume that in this case the dissociation of the metal-ligand bond is not kinetically hindered.

Upon further reaction, the dissociation pathway involves the scission of a C–H bond at the central atom of the isopropyl group and requires overcoming a kinetic barrier of 84 kJ/mol and then leads to the stable structure H (stabilized by 230 kJ/mol). If this imine moiety ($\text{N}=\text{CMe}_2$) approaches the silicon surface and forms a Si–C bond, the system will be further stabilized (structure C, 1291 kJ/mol). Thus, surface decomposition of the amidinate ligand seems to be rather facile; in fact, $\text{La}[\text{Pr-MeAMD}]_3$ has been observed to undergo surface decomposition at low temperatures,¹³² and a Cu amidinate has been observed to incorporate carbon upon exposure to a nickel surface at temperatures as low as 400 K.²⁰⁸

In the event that an amidinate approaches a surface featuring both hydroxylated and bare surface sites, the undesired pathway is more feasible than the ligand-exchange pathway, because precursor desorbs into the gas phase and hinders

the desired reaction. In contrast, the great stability obtained upon formation of molecularly adsorbed structure A in figure 4.15 facilitates the transition to the dissociated structure M and ultimately to structure C without substantial kinetic requirements. In conclusion, this undesired pathway of amidinate precursors can be detrimental for the purity of films in a fashion that is both kinetically feasible and thermodynamically favorable.

4.9 Summary

This chapter has outlined possible surface reactions in the presence of hydroxylated and bare silicon surface sites. The simulation of similar reaction pathways using the same surface models and levels of theory allows for a comparison of the thermodynamics and kinetics across a wide range of precursor types. In all, there are three types of reactions that are involved in the deposition processes discussed.

4.9.1 Ligand-exchange reaction

This pathway is the basis of ALD process and eventually leads to a complete elimination of unwanted ligands. It is clearly seen that alkyl, alkylamide and cyclopentadienyl precursors react with OH-terminated silicon surface and produce thermodynamically favorable products; in contrast, the products produced by alkoxide, diketone, and amidinate precursors are not as stable (especially if they are compared to the products of the competing, undesired reactions). However, it is important to remember that due to the low temperatures usually employed in ALD, the ligand-exchange reaction is under kinetic control. Consequently, cyclopentadienyl precursors would perform rather poorly, since its ligand-exchange reaction needs to

overcome a transition state above the reactants level; therefore, desorption back into the gas phase is more favorable. Using this criterion, only alkyl and alkylamide precursors seem to have an efficient uptake, since reverse process (desorption) does not compete with the ligand-exchange mechanisms. Interestingly, these are the precursors that often utilize mild co-reactants, such as water.

4.9.2 “Undesired” reaction

This mechanism is potentially detrimental to deposition processes, because it allows the ligands to attach to the surface and form very stable species, which makes the reverse reaction virtually impossible. Thermodynamically, the reactions are favorable in all cases. The cases of alkyl and cyclopentadienyl precursors, however, deserve to be highlighted, because their ligand dissociation steps feature a transition state either close to or above the level of reactants; therefore, this undesired process competes with molecular desorption back into the gas phase. On the other hand, the reactions are almost barrierless in all the other cases, which suggests that once the precursor molecule attaches to the bare silicon surface, the undesired reaction takes place easily and irreversibly.

4.9.3 Decomposition of ligand on bare silicon surface

The last process to be considered is the decomposition of ligands. In order to compare a set of different precursors, the scission of the C–H bond in all cases (common to most ligands) has been followed as the initial process of ligand decomposition and carbon incorporation. Thermodynamically, this reaction is favored in all cases (structure H in all cases, if applicable) and leads to the formation of carbon-surface bonds (structure C in all cases). Although this means that this reaction

is unavoidable at high temperatures, some of the reactions can be suppressed at lower temperatures, depending on the kinetic requirements needed to overcome the barrier for C–H scission, such as in the cases of alkyl, alkoxide, and cyclopentadienyl precursors. It is important to mention that Bohlmann effect significantly reduces the kinetic requirement for alkylamide precursors to undergo C–H scission to 63 kJ/mol, which is the lowest barrier among all six types of precursors investigated.

4.9.4 Suggestions for the design of metalorganic precursors

Ligand design and modification are critical not only for the improvement of physical properties (e.g., volatility, thermal stability), but also for tuning the surface chemistry involved in the deposition process. The suggestions for novel designs of precursor ligands, as appropriate for specific deposition process, can be summarized as follows: (1) avoid atoms with lone pairs, since they can form dative ligand-surface bonds of great stability; (2) avoid heteroatoms that can induce Bohlmann effect to weaken C–H bonds, since scission of C–H bond might lead to carbon contamination; (3) avoid chelating ligands, since these ligands cannot be easily eliminated even after protonation.

With all the investigations described above, we have examined six common precursor ligands for their reactivity and selectivity towards different surface reactive sites on the basis of electronic effect (e.g., lone pairs to form dative bonds to the surface) and steric effect (e.g., molecular geometry). Next we shall proceed to the examination of the electronic and steric effects of the surface reactive sites.

Chapter 5

COMPUTATIONAL INVESTIGATION OF SURFACE REACTIVITY OF FUNCTIONALIZED SILICON SURFACES IN DEPOSITION PROCESSES*

5.1 Introduction

In recent years, silicon surface functionalization has evolved from understanding how multifunctional molecules would react with silicon to finely-tuned manipulation of surface stability, electronic properties, and chemical functionality.^{16,24,213} While we recognize that it would be impossible to investigate all the available functionalized silicon surfaces in this work, we chose three groups of functionalized silicon surfaces to illustrate their reactivity and provide the roadmap for further pathways for modification of silicon surfaces: (1) silicon surfaces with hydrogen termination, (2) silicon surfaces with nitrogen-containing (amine) termination, and (3) silicon surfaces with hydroxyl (or alkoxy) termination. The representative surfaces of every type mentioned above have been prepared experimentally^{24,33,64,69,137,214-217} and the chemical termination has been shown to play major role in our ability to efficiently form an interface between silicon and the thin solid film grown on silicon surfaces with such functionalities.^{137,214,216-218} In addition, these types of surface terminations are amenable to produce the interfaces required to grow the metal-based films that also include oxygen,¹³⁷ nitrogen, and carbon,^{64,216} that

* Adapted in part with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, *132*, 1.

are most commonly needed to interface with silicon. Thus, we will use a computational approach to explore the formation of Si–O–M, Si–C–M, Si–N–M, and Si–M bonds (where M is a metal, specifically Al or Ti in these studies) in a chemical reaction of functionalized silicon surface with metalorganic deposition precursors and the viability of surface reaction pathways to eliminate the corresponding ligands to yield a well-defined and impurity-free interface between silicon and a solid film.

In the previous chapters and in the previous work, we followed a number of surface reactions of metalorganic deposition precursor molecules with different surface functionalities.^{18,24,29,64,69,98,216} These works ranged from experimental microscopic and spectroscopic analysis to computational investigations of reaction mechanisms. Selected results of these studies will be referred to in the discussion section below to serve as useful illustrations for understanding the role of chemical functionality in defining surface reaction pathways on functionalized silicon.

One of our most recent investigations focused on six different families of ligands and their competing reactions with different functionalities on Si(100) surface using density functional theory (DFT).²⁹ Specifically, we compared the reactions of surface –OH group and the interaction of precursor molecules with bare silicon surfaces to explore the effect of ligand structure on the possibility to form an impurity-free interface. Here, we will expand this approach to understand the effect of surface functionality on the surface reaction mechanisms to highlight the role of surface functionalization in altering the thermodynamic and kinetic requirements for creating well-defined interfaces. To demonstrate the viability of this analysis as a general approach to designing the required interface, we chose two different types of deposition precursors: trimethylaluminum (TMA) and

tetrakis(dimethylamido)titanium (TDMAT). TMA will allow us to use simple initial frontier orbital analysis to evaluate possible surface reactions within a limited number of options (since only Al–C and C–H bonds can undergo surface dissociation). TDMAT will allow us to explore more complicated effects, as its interactions with the surface could result in Ti–N, N–C, and N–H dissociation and can also be profoundly affected by steric effects. Both compounds have been previously investigated experimentally and computationally on a variety of surfaces,^{18,64,137,219,220} TDMAT has been the focus of a number of studies in our group.^{18,24,64,83,98,221,222} These previous works will provide good starting points and comparators for our analysis.

5.2 Computational Methods and Surface Models

All the DFT calculations were conducted with Gaussian 09 suite of programs, as was explained in Chapter 2--experimental section. The B3LYP/ LANL2DZ and B3LYP/6-311+G(d,p) levels of theory were applied to all calculations involving trimethylaluminum molecule, and single point calculations at the B3LYP/6-311++G(d,p) and B3LYP/cc-pVTZ level of theory were applied to test selected results. In the cases involving TDMAT molecule, all calculations were performed using B3LYP/LANL2DZ level of theory, and selected results were further tested with B3LYP/ 6-311+G(d,p). A comparison and validity of such an approach will be discussed below.

A Si₁₇H₂₄ cluster was used to represent two neighboring silicon surface atoms on the unreconstructed Si(111) surface, as was described in Chapter 2. Si₉H₁₂ cluster was used to simulate the unmodified Si(100) surface as the basis for further functionalization. On the unmodified Si(100) cluster, the top two silicon atoms (the dimer) were functionalized with the following sets of functionalities: –H and –H,

-H and -NH₂, -H and bridging -NH-, -H and -OH, -H and -OCH₃, -H and -OCF₃. All the atoms in the clusters were not constrained, as was discussed in detail in Chapter 2; however, the only two exceptions presented in this chapter are the transition state calculations described below as reactions R2B and R11B, where cluster atoms representing subsurface silicon atoms had to be constrained at their positions to avoid unrealistic distortion.

All the energies reported here were referenced to the sum of the individual energies of corresponding reactants (the precursor molecules and the silicon clusters with different functionalities) in kJ/mol, and the barriers refer to the difference in energy between the transition state and the weak (molecular) adsorption configurations.

Transition states were determined using the synchronous transit-guided quasi-Newton (STQN) method. The presence of a single negative eigenvector in these calculations confirms the convergence to a transition state. Natural bond orbital (NBO) analysis is used to retrieve the visual representations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the precursor molecules and the silicon clusters.

5.3 Results

In order to apply the frontier molecular orbital approach to analyze possible surface reactions of metalorganic precursors with functionalized silicon surfaces, one must first illustrate the appropriateness of this approach by exploring the structure of HOMOs and LUMOs of the chosen molecules. Figure 5.1 shows the schematic representations of TMA and TDMAT molecules and the corresponding HOMO and LUMO structures.

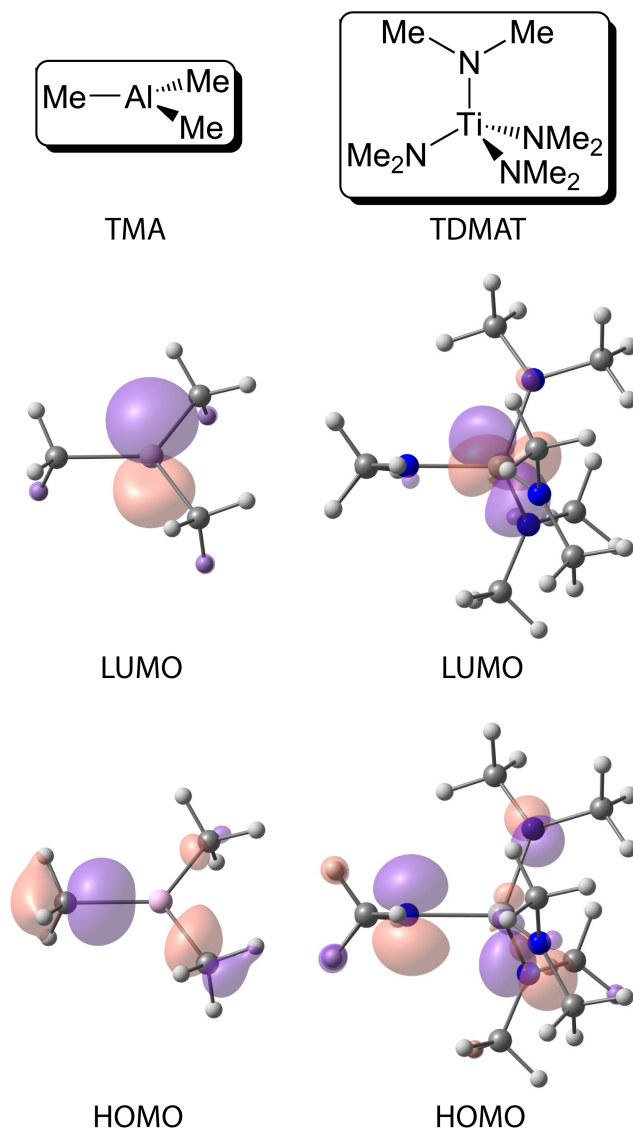


Figure 5.1: Visual representations of HOMO and LUMO (as indicated) of the two metalorganic precursors predicted with natural bond orbital (NBO) analysis. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, 132, 1.

It is immediately apparent that in both cases the LUMOs are centered at the metal atom and the HOMOs are spread out towards the ligands. It must be mentioned that because of the symmetry of the molecules, there are several very closely related molecular orbitals with similar energies that can be predicted; however, their geometrical description still conforms to the same statement: The nature of the LUMOs is determined by the center atom, and the nature of the HOMOs is defined by the ligands. Recall from Chapter 4, although this statement doesn't apply to the two precursors with chelating ligands--Cu(acac)₂ and Ni[ⁱPr-amd]₂, the statement describes TMA and TDMAT molecules appropriately.

To determine the appropriate reaction pathways, a set of analyses similar to what is described above for molecular structures, should be performed on the cluster models representing functionalized silicon surface. Among the classes of the surfaces described in this chapter, H-terminated silicon is probably the easiest to investigate. Despite structural differences for the three types of H-terminated silicon surfaces investigated, the HOMO/LUMO analysis presented in figure 5.2 suggests that for all those surfaces HOMO and LUMO orbitals predominantly involve surface silicon atoms. Thus the initial interaction of the surface species with a corresponding LUMO or a HOMO of the incoming metalorganic molecule is expected to involve surface Si-H or Si-Si bond.

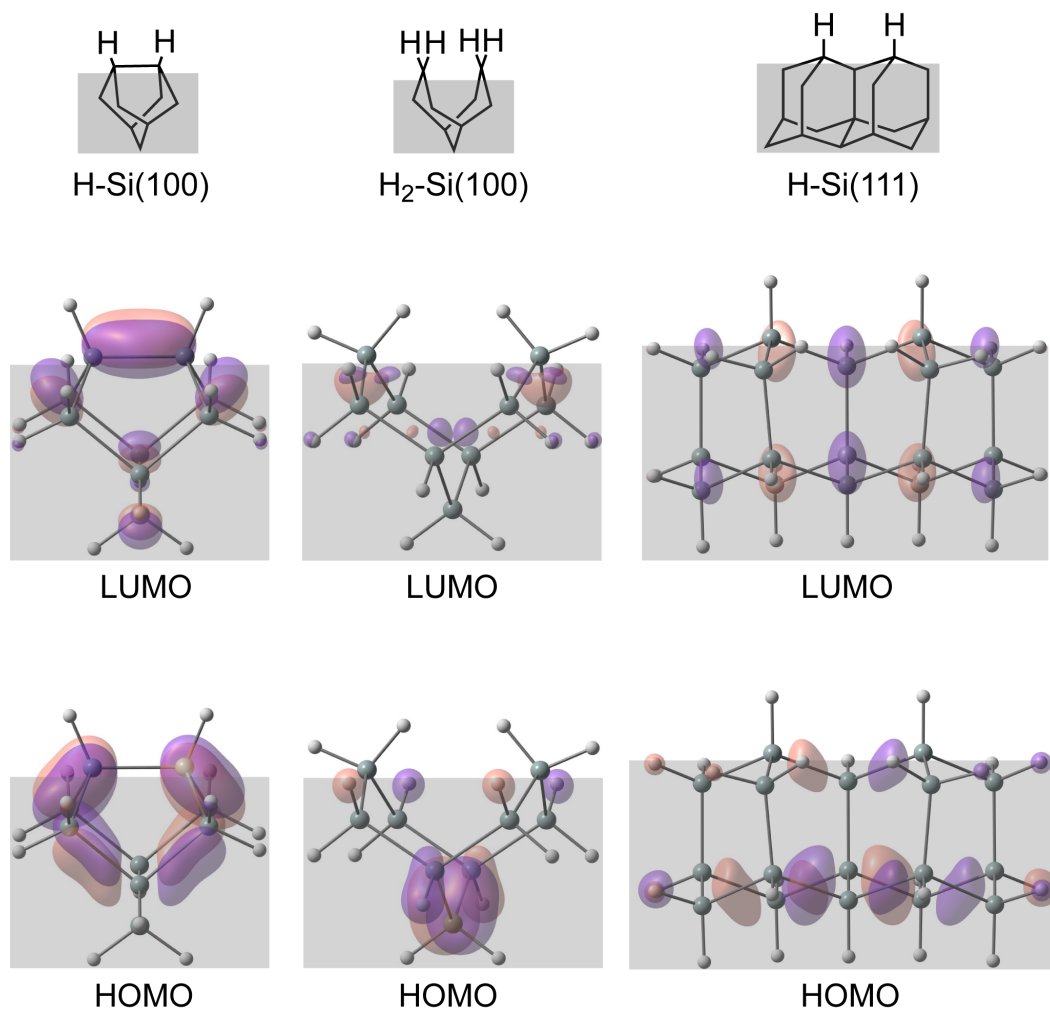


Figure 5.2: Visualized HOMO and LUMO orbitals of hydrogen-terminated silicon surfaces (as indicated in the figure). The shaded area represents the bulk (subsurface) silicon lattice beneath the surface layer. In all three clusters, only the two silicon atoms and their terminations on the top (surface layer) were considered in the surface reactions with metalorganic precursors. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, 132, 1.

The story seems to be much more complex for surface -NH_x species described in figure 5.3. As expected, nitrogen atom is involved substantially in any HOMO orbitals; however, the LUMOs can involve surface hydrogen (Si-H) or Si-Si bonds. This is what makes this class of functionalized surfaces so interesting. The initial interaction of a metalorganic molecule with a surface functionality very likely involves nitrogen, but since in most reactions investigated below, the next step is a removal of a hydrogen atom to eliminate a corresponding ligand from a precursor molecule, it is becoming important to understand if this hydrogen is provided by the surface (Si-H) or by the functionality (N-H).

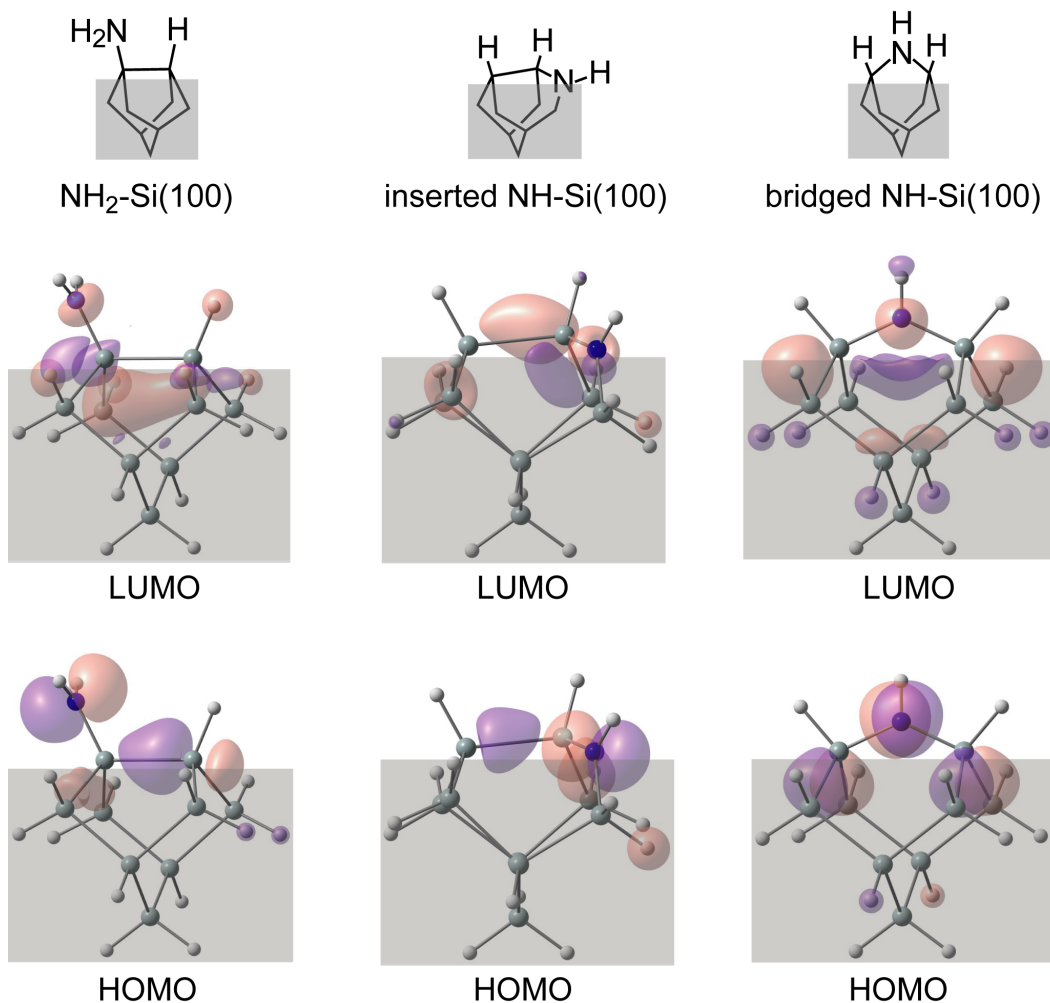


Figure 5.3: Visualized HOMO and LUMO orbitals of silicon surfaces with nitrogen-containing termination. The shaded area represents the bulk (subsurface) silicon lattice beneath the surface layer. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, *132*, 1.

Finally, exploring the reactivity within the group of -OH , -OCH_3 , and -OCF_3 surface species should yield several additional pieces of information. The initial interaction very likely should involve the oxygen atom of each functional group, since as illustrated in figure 5.4, it is involved in the HOMOs and LUMOs. Based on a number of previous studies, it is expected that the hydrogen atom of the surface -OH group should be very reactive compared to the Si-H .

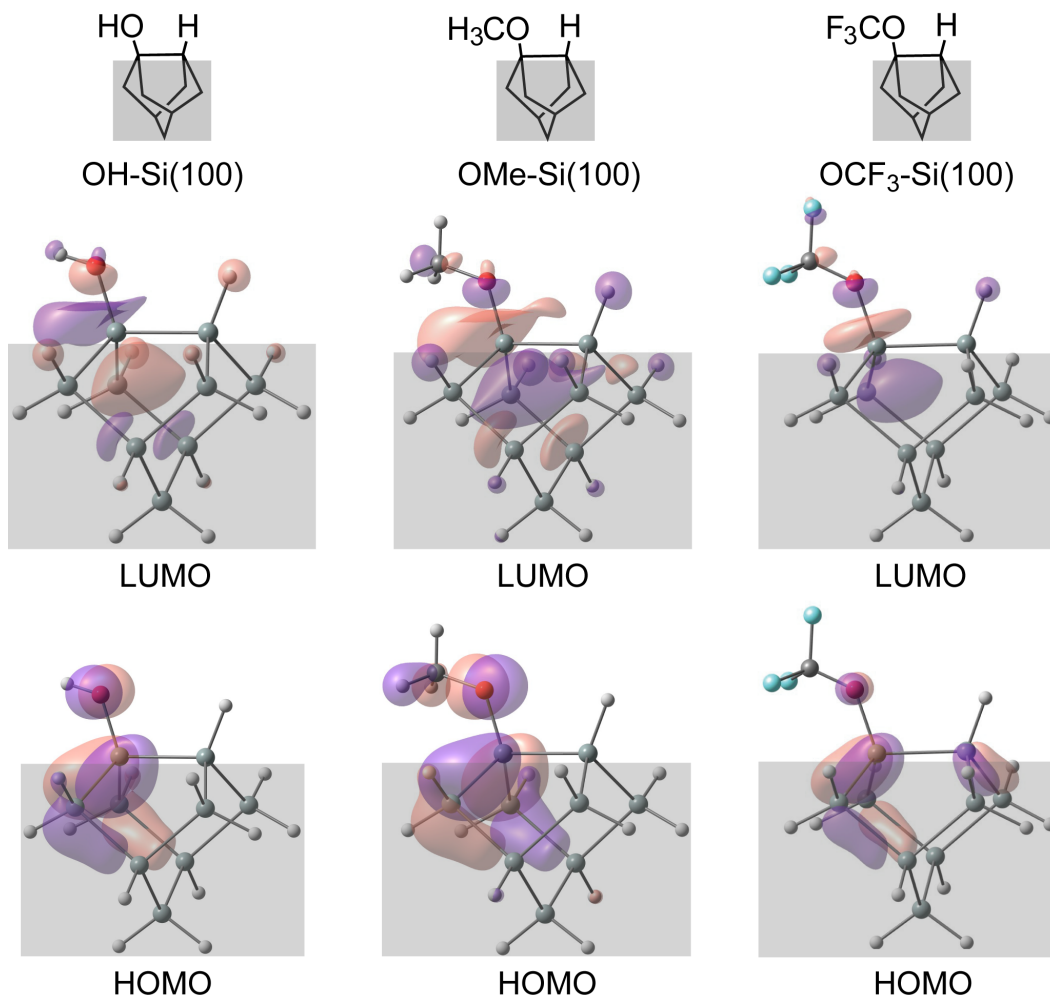


Figure 5.4: Visualized HOMO and LUMO orbitals of silicon surfaces terminated with water, methanol, and trifluoromethanol. The shaded area represents the bulk (subsurface) silicon lattice beneath the surface layer. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, 132, 1.

On the other hand, according to the simple analysis in figure 5.4, the hydrogen of the surface Si-H functionality is preeminent in the LUMOs for every one of the models involved and thus is expected to be very reactive following the initial adsorption. In addition, unlike in the case of structurally different -NH_x functionalities described in figure 5.3, the surface entities presented in figure 5.4 are all very much structurally similar, causing the overall geometric similarities of the HOMOs and LUMOs for all the structures described. At the same time, it is expected that the electronegativity of the fluorine atom will influence the reactivity of the -OCF_3 entity tremendously compared to the -OCH_3 group. This effect will be compared below with the previous studies of surface “basicity” of N-containing functional groups in reactions with metalorganic precursor molecules.

All the reactions investigated basically involve two steps: adsorption of a metalorganic precursor molecule onto a functionalized silicon surface and chemisorption following a ligand removal.^{29,104,118} In case of TMA this means methane elimination,^{29,219,223} while in case of TDMAT this process follows dimethylamine desorption.^{64,220} The final step in all the cases is the formation of a surface species with a participation of a metal center and a complete removal of the byproduct (methane or dimethylamine) into the gas phase. Of course, the main question in understanding all these surface reactions is the thermodynamic stability of the products and the kinetic viability of the processes. However, one more very important point is the source of the hydrogen atom for ligand removal: Is it provided by the surface (Si-H) or by the functionality (C-H, O-H, or N-H)? Table 5.1 summarizes all the findings obtained using B3LYP/LANL2DZ. The observed trends will be analyzed below in the discussion section.

Table 5.1: Thermodynamic and kinetic data predicted using LANL2DZ basis set for all the reactions described in this chapter. This table is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, *132*, 1.

Entry	Surface reactions	Stabilization energy of weak (molecular) adsorption/structure A	Energy of the transition state (barrier compared to structure A given in parenthesis)	Energy of the product of hydrogen abstraction corresponding to structure B and/or C
R1		-0.8	134.1 (134.9)	B -50.7
R2		-0.8	167.8 (168.6) 147.3 (148.1)	B -44.6 C -39.2
R3		-2.9	138.2 (141.1)	B -46.3
R4		-71.2	39.9 (111.1) 132.3 (203.5)	B -113.7 C -110.4
R5		-37.5	52.0 (89.5) 148.7 (186.2) 135.4 (172.9)	B -104.0 C -34.0 D -49.7
R6		-5.7	53.7 (59.4) 150.1 (155.8)	B -102.2 C -33.3

Table 5.1 continued.

Entry	Surface reactions	Stabilization energy of weak (molecular) adsorption/structure A	Energy of the transition state (barrier compared to structure A given in parenthesis)	Energy of the product of hydrogen abstraction corresponding to structure B and/or C
R7		-86.0	-32.4 (53.6) 124.2 (210.2)	B -201.3 C -125.2
R8		-72.6	152.9 (225.5) 66.6 (139.2)	B -31.1 C -124.2
R9		-16.3	119.9 (136.2)	B -80.5
R10		-0.9	61.8 (62.7)	B 32.9
R11		-1.2	88.7 (89.9) 70.9 (72.1)	B 68.9 C 54.3
R12		-1.1	61.6 (62.7)	B 46.1

Table 5.1 continued.

Entry	Surface reactions	Stabilization energy of weak (molecular) adsorption/structure A	Energy of the transition state (barrier compared to structure A given in parenthesis)	Energy of the product of hydrogen abstraction corresponding to structure B and/or C
R13		-8.9	77.2 (86.1) 62.0 (70.9)	B -23.7 C 31.2
R14		-3.0	78.8 (81.8) 77.7 (80.7) 64.7 (67.7)	B 3.0 C 59.0 D 33.5
R15		-9.3	86.0 (95.3) 80.9 (90.2)	B 3.3 C 60.9
R16		-34.3	-32.2 (2.1) 52.0 (17.7)	B -128.4 C 22.1
R17		-6.6	185.3 (191.9) 67.8 (74.4)	B 97.2 C 27.1
R18		-0.5	34.9 (35.4)	B 14.1

5.4 Discussion

5.4.1 Viability of the computational approach and robustness of the basis sets

Before analyzing the reaction trends, it is important to address the validity of the entire cluster model approach to assessing the surface reactions of metalorganic compounds on silicon.

The interaction of organic molecules on hydrogen-terminated silicon cluster models representing single crystalline silicon has been studied for about two decades. This approach proved its worth by comparison with spectroscopic data including infrared spectroscopy and X-ray photoelectron spectroscopy predictions.^{81,97,216} It also proved useful in understanding the mechanisms of surface adsorption processes for multifunctional compounds and the subsequent thermal decomposition.^{64,98,216} There are some indications that in modeling the chemical properties of clean silicon surfaces, it may be important to use a large cluster as a model (such as in understanding the exact mechanism of ammonia reaction,^{224,225} for example); however, for the most part, the results of simple cluster calculations are in a complete agreement with slab models and rarely exhibit profound dependence on the cluster size, especially for functionalized silicon surfaces.^{219,223}

That said, it is important to choose a cluster commensurate with the type of surface reaction investigated. For example, limiting the cluster size to represent a single Si–Si dimer of the Si(100)-2x1 surface excludes the possibility to investigate adsorption on multiple dimers⁷⁵ and interaction with dimers on the neighboring rows,²²⁶ which may be very important. In the investigation presented in this chapter, however, we only focus on the interaction with a single surface reaction site, and understanding the involvement of neighboring dimers in this interaction is not the

target of this chapter. Again, while it is indeed important to use substantially larger clusters when mimicking surface reactions of clean silicon surfaces,^{224,225} the type of investigation presented here does not require such an increase because of a much more localized nature of these interactions, as justified by the frontier orbital analysis described in the previous section. Of course, during the course of these studies, the geometric arrangement of atoms in adsorbed structures and especially in the transition states for surface reactions should make physical sense and the geometry of all the structures has been followed closely to not introduce any artifacts related to the surface representation.

We have previously used relatively small clusters to represent chemical reactions of metalorganic molecules on silicon.^{29,216} However, another concern may be related to the use of a relatively short LANL2DZ basis set. We have previously successfully utilized this basis set to predict stability of surface organic and metalorganic species,^{27,216,227,228} to investigate the pathways for rather complex surface reactions,^{29,216} and to produce a number of spectroscopic observables to compare with the experimental results.^{27,216,227,228} However, in the present investigation that involves the studies of metalorganic precursor molecules and a hydrogen transfer as the final step, it is important to recognize the limitations of the DFT approach. For example, the initial step in every reaction summarized in table 4 is a weak (molecular) adsorption of the precursor molecule onto a functionalized surface. In many cases, the numbers corresponding to the surface mediated adsorption are very small (R1, R2, R18), as our model may not adequately describe weak interactions,²¹⁹ especially without inclusion of van der Waals interactions.^{120,223,229} However, what is more important is to recognize that the thermodynamics of the overall process can be compared using this

approach for a variety of surface processes to analyze the trends in surface reactivity. The advantage of using the shorter basis set is a dramatic decrease of the computational time that allowed us to truly explore a multidimensional reaction space and a multitude of reactants to produce the trends in reactivity. In order to demonstrate that the thermodynamic and kinetic parameters can be reliably predicted by our B3LYP/LANL2DZ approach, a set of computations describing the process of adsorption and reaction of TMA with H-terminated and NH₂-modified Si(100) surfaces has been performed including the use of 6-311+G(d,p), 6-311++G(d,p), and cc-pVTZ basis sets. These results are summarized in figures 5.5 and 5.6.

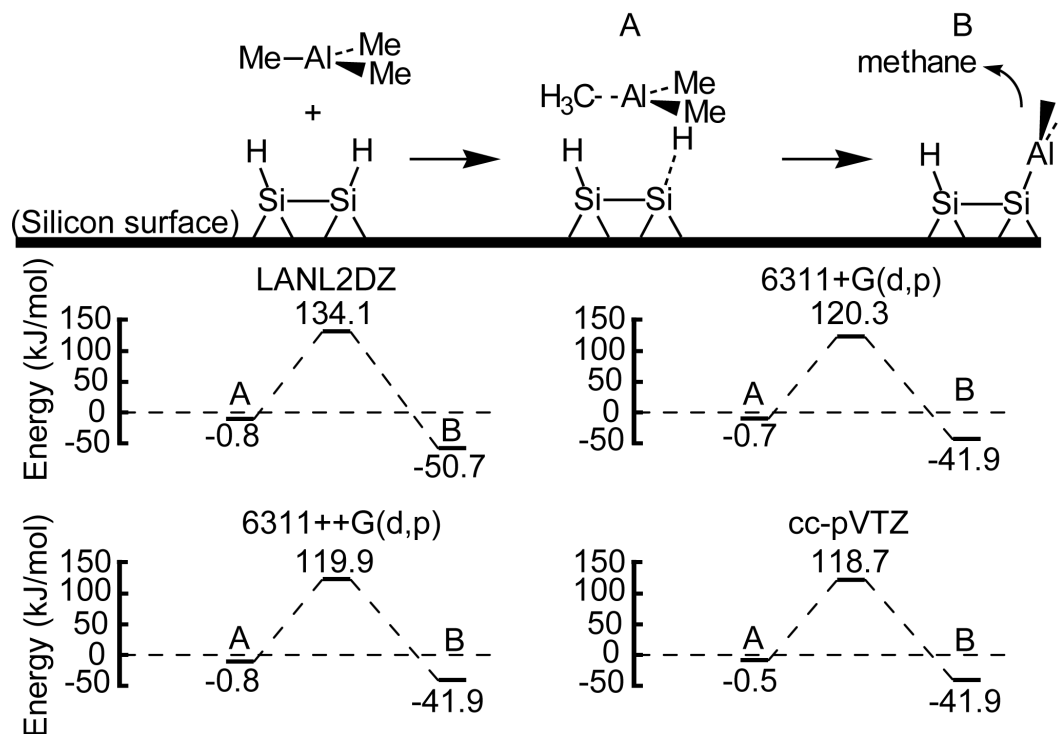


Figure 5.5: Thermodynamic predictions for the reaction of TMA and H-terminated Si(100) surface using B3LYP and four different basis sets. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, 132, 1.

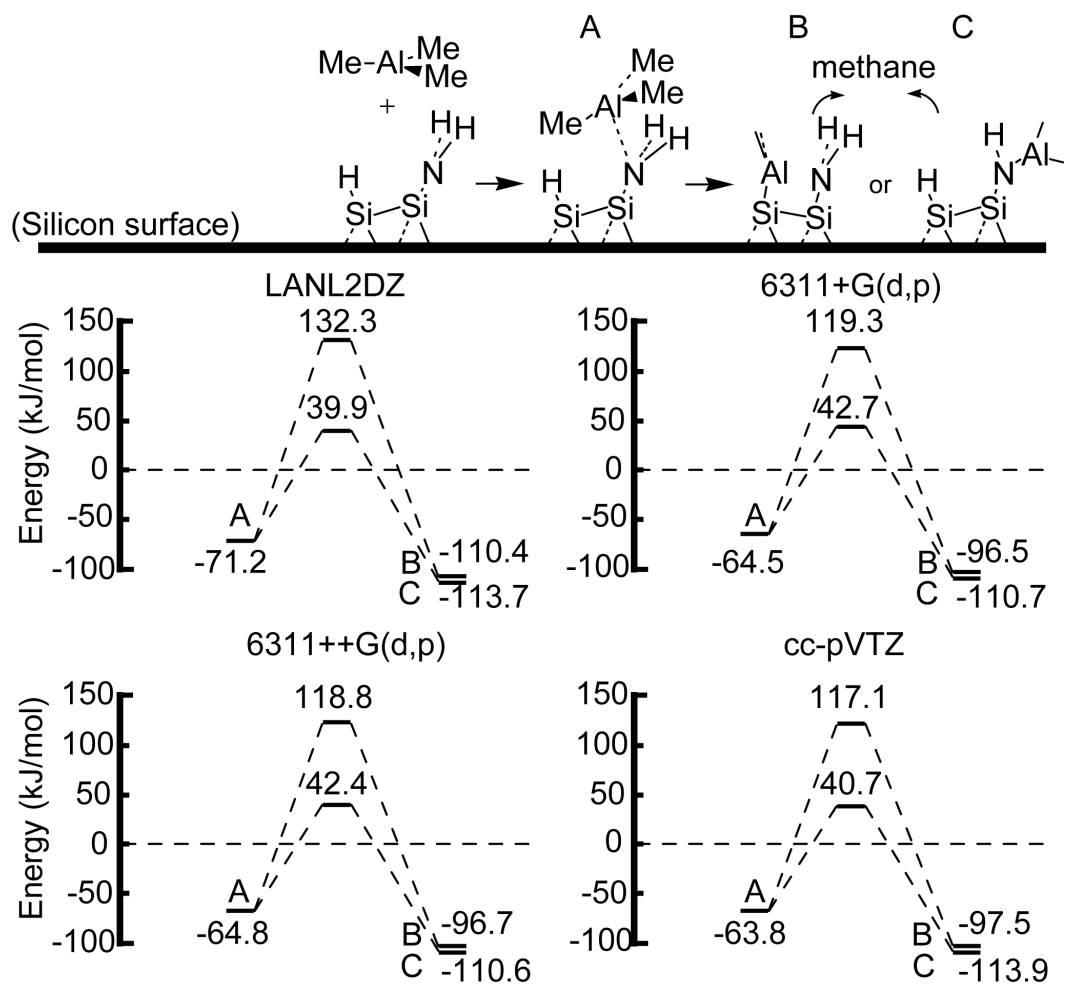


Figure 5.6: Thermodynamic predictions for the reaction of TMA and NH₂-Si(100) surface using B3LYP and four different basis sets. This image is adapted with permission from Lin, J.-M.; Teplyakov, A. V. *Theor. Chem. Acc.* **2013**, 132, 1.

As can be clearly seen from this comparison, the use of a shorter and more efficient LANL2DZ basis set gives the same exact trends as observed in all the cases. Thus, we used the B3LYP/LANL2DZ for the main trend predictions summarized in this chapter.

In addition, in order to evaluate the contribution of van der Waals interactions and possible effects of the use of cluster models as opposed to slabs, one can compare our results for TMA interaction with a Si(100) surface reacted with water molecule resulting in Si-H and Si-OH surface species with much more complex study of the same system by Kim et al.²¹⁹ That study reported on a set of slab calculations of a TMA molecule reacting with H- and OH-terminated Si(100) surfaces, performed with VSAP code using dispersion-corrected DFT (DFT-D2) approach. The energies and trends of the reactions observed in that case are in complete agreement with the observations reported here (although the initial adsorption leads to a more stable structure by including dispersion interactions). The transition state structures are essentially the same and only minor differences can be found in two approaches (table 5.2). Thus, overall our approach is efficient and sufficiently robust to explore a number of trends in interaction of metalorganic precursor molecules with functionalized silicon surfaces.

Table 5.2: The thermodynamic and structural comparison of the reaction between TMA and water terminated Si(100) surface calculated with a cluster model (B3LYP/LANL2DZ in this chapter) and with a slab model (Kim *et al.*²¹⁹)

Stage	Property	Cluster model	Slab model
Weak (molecular) adsorption	Energy	-86.0 kJ/mol	-96.5 kJ/mol
	Distance between Al and O	2.03 Å	2.06 Å
Transition state	Reaction barrier	53.6 kJ/mol	59.8 kJ/mol
	Distance between Al and O	1.93 Å	1.89 Å
	Distance between Al and the C of the leaving CH ₃	2.19 Å	2.07 Å
	Distance between O and H of the surface -OH group	1.16 Å	1.41 Å
	Distance between C (-CH ₃) and H (-OH)	1.52 Å	1.42 Å
Hydrogen abstraction	Energy	-201 kJ/mol	-150.5 kJ/mol
	Distance between Al and O	1.73 Å	1.72 Å

5.4.2 Surface reactions on hydrogen-terminated silicon surfaces (R1-R3, R10-R12)

The cluster models shown in figure 5.2 describe the three most common types of silicon H-termination that can be prepared experimentally: monohydride and dihydride surface reactive sites that are observed on differently prepared Si(100) surfaces²⁴ and ideal H-terminated Si(111) surface that has been a gold standard in a large number of experimental^{97,230,231} and computational²³²⁻²³⁴ studies.

Although frontier molecular orbital analysis suggests that the initial interaction between test metalorganic precursors and hydrogenated silicon surface should involve the surface Si-H or Si-Si bonds, it should also be mentioned that the surface silicon atoms are already electronically saturated according to the octet rule. Silicon is generally considered to be a poor electron donor to donate an electron to the precursor, and in addition, the potential place to accept such electrons, the LUMO of TDMAT, is shielded by the organic ligands. Consequently, the stability of the weakly bound molecularly adsorbed TMA or TDMAT on all the H-terminated silicon surfaces is predicted to be very low. Nevertheless, even our simplistic approach to describe these interactions indicates a slightly exothermic process.

Following the initial weak (molecular) adsorption, the second step of chemical interaction between metalorganic precursors and H-covered silicon is the cornerstone of the ALD process: “deposition” of the metal-containing entity (formation of a strong chemical bond between the metal and a surface) and elimination of at least one of the ligands. In both test cases described here, this means hydrogen transfer from the surface to form methane from TMA and dimethylamine from TDMAT. Interestingly, the energy barriers for hydrogen abstraction by TDMAT system (R10-R12) are almost half as low as those for the TMA (R1-R3), and the products in the TMA system are

thermodynamically stable, while the reactions of TDMAT are slightly endothermic. This general statement is in a complete agreement with the predictions of Musgrave group for interaction of TDMAH (tetrakis(dimethylamido)hafnium) with -OH^{118} and -NH-^{104} terminated Si(100) as compared to H-termination.

The transition state calculations for TMA on H-terminated silicon in all cases (R1-R3) indicate the breaking of Al-CH_3 and Si-H bonds and the formation of $\text{Me}_2\text{Al-Si}$ surface species and $\text{H}_3\text{C-H}$ that occur essentially at the same time. This observation also agrees with the previous studies.^{219,223} In the TDMAT system (R10-R12), only $\text{Me}_2\text{N-H}$ bond forming and bond breaking of Ti-NMe_2 and Si-H were observed to contribute substantially to the transition state, which implies that the energy barrier should depend mostly on how well the ligand interacts with the surface hydrogen. Obviously, amido ligands are expected to interact with the surface hydrogen stronger than alkyl ligands do, and in turn facilitate hydrogen abstraction.

The bulky organic ligands of TDMAT clearly shield its metal center from initial interaction with the functional groups of a surface, but they also introduce additional steric strain to the surface species produced, and this decreases thermodynamic stability of the final product of the reaction between TDMAT and the functionalized surfaces. On the other hand, the thermodynamically favorable reaction products of TMA reaction with the same surfaces (R1-R3) basically result from the planar geometry of TMA that makes the metal center easily accessible and does not lead to introduction of any additional strain effects following the reaction. It can be added that on a dihydride-Si(100) surface (with SiH_2 functionality, R2 and R11), the geometry of a simple cluster model studied here implies a possibility of two different reaction pathways involving the transfer of either one of the two geometrically

different surface hydrogen atoms. This would not have been the case if a periodic structure calculation approach were used; however, the differences between these two pathways in this section are small, and all the observed trends are consistent for all the models studied, again highlighting the robustness of our computational approach.

5.4.3 Surface reactions on silicon surfaces with nitrogen-containing functional groups (R4-R6, R13-R15)

With a renewed interest in carbon-free interfaces, a number of studies focused on silicon surfaces that can be prepared by exposure to ammonia.^{33,74,235,236} This study will focus on the models of surfaces that can be prepared by dosing ammonia on a clean and well-ordered Si(100)-2x1 surface in vacuum and subsequent treatments. The room temperature adsorption leads to N-H dissociation, and further annealing yields -NH- functionality inserted either into the Si-Si bond of the surface dimer or into a silicon backbone, as shown in figure 5.3.^{33,74,237} These models will allow us to investigate the adsorption processes and also to follow the hydrogen transfer step to determine if its source is the Si-H group or the nitrogen-containing functionality.

The weak (molecular) adsorption of TMA onto the -NH₂ functionality of the silicon surface (R4A) is, as expected, based on the interaction of the LUMO of TMA (empty orbital on Al atom) and the HOMO of the surface (lone pair of N atom). A similar interaction is observed between TMA and inserted -NH- functionality (R5A). However, because of the steric hindrance and lower accessibility of the inserted -NH- group, the interaction between the TMA molecule and the -NH- functionality is much weaker compared to the open and easily accessible -NH₂. The steric effect is even more noticeable in the case of TDMAT interaction with the same surface functionalities. Here, as was already discussed above, the HOMO orbital of the

metalorganic precursor is shielded by the organic ligands. However, unlike in the case of TMA, weak interactions that may not be adequately described by the computational methods used here will play a more substantial role in the adsorption of TDMAT because of the presence of hydrogen bonding, described in more detail below for OH-terminated silicon surface.

According to the results in table 5.1, the energy barriers for hydrogen abstraction from the surface Si-H by TDMAT (R13C, R14C-D, R15C) are lower than those in similar reactions with TMA (R4C, R5C-D, and R6C). Surprisingly, the energy requirements for TMA to pick up the hydrogen from either -NH₂ or -NH- surface functionalities are substantially lower and in certain cases (R6B vs. R15B) even lower than the corresponding pathway for TDMAT. These barriers are expected to depend on how well the precursor ligands interact with the hydrogen to be abstracted. In fact, the simplest analogy of this process is acid-base neutralization. The organic ligand can be viewed as a base not only when it coordinates to a metal but also in its interaction with the surface hydrogen to be abstracted. In other words, the acidity of the surface hydrogen participating in hydrogen transfer step is essential in determining the kinetics of the surface reaction. Thus, it is the combination of the basicity of the organic ligand participating in the deposition process (methyl for TMA and dimethylamido for TDMAT) with the acidity of the surface hydrogen that defines the overall reaction barrier.

The electron-rich nitrogen-containing functionalities also influence the thermodynamic stability of the surface reaction products. Compared to the reactions with H-terminated silicon described in the previous section (R10-12), the chemical transformations of TDMAT on amino-functionalized silicon are much more

thermodynamically accessible (R13B, R14B, R15B). In fact, the reaction of TDMAT and -NH_2 functionality is exothermic (R13B). Thus, in the test cases presented here, if Si-H and N-H groups are both present on the silicon surfaces, it is clear that the hydrogen abstraction from N-H should always occur prior to that from Si-H-containing surface functional groups. It must, however, be noted that every reaction should be investigated separately, as in the reactions of Cu(hfac)VTMS (copper(hexafluoroacetylacetonato)vinyltrimethylsilane) with mixed -NH_2 , -NH- , and Si-H surface functionalities, the precise mechanism and source of hydrogen for hfacH elimination were found to vary depending on surface preparation leading to different nanostructuring of deposited copper.²¹⁶

5.4.4 Surface reactions on silicon surfaces with hydroxy- or alkoxy-termination (R7-R9, R16-R18)

Based on a comparison of structures presented in figures 5.3 and 5.4, it can be expected that the interaction of TMA and TDMAT with amino-functionalized silicon and surfaces with hydroxyl (or alkoxy) termination will proceed in a similar fashion. As shown in table 5.1, TMA adsorbs on surfaces with hydroxyl (or alkoxy) termination by a formation of a relatively strong bond (R7-R9). As would also be expected, the strongest bond is formed with a hydroxyl group (R7A) and the weakest bond is formed with -OCF_3 functionality (R9A) because the highly electronegative F atoms withdraw the electron density from the oxygen and thus diminish the interaction between Al and O atoms.

The initial adsorption of TDMAT on -OCH_3 and -OCF_3 functionalities on silicon results in a rather weak interaction (R17A, R18A), mostly because of shielding of the metal center with organic ligands, similarly to the other cases described above.

However, TDMAT interaction with a hydroxyl group on a surface is worth considering in more detail (R16A). So far we mostly considered interaction of the HOMO of a surface species with a LUMO of the metalorganic precursor molecule. In case of TMA, this is obviously the most straightforward way to evaluate its interaction with oxygen-containing surface species. However, TDMAT can actually form a hydrogen bond between its ligands and such functionalities as -NH_2 or -OH on a surface. Although the computational method used in this study is not completely suitable for predicting such weak interactions, the optimized geometry exhibiting hydrogen bond was captured, and the distance between a nitrogen of the TDMAT ligand and a hydrogen of the surface hydroxyl group was found to be 1.73 Å at the B3LYP/LANL2DZ level of theory (1.93 Å by B3LYP/6-311+G(d,p)). This bond length is in agreement with the formation of a hydrogen bond.²³⁸⁻²⁴⁰

Thus, the electron-donating ability of the precursor ligands and the acidity of the targeted surface hydrogen atom are once again taken into account to explain the trends in the reaction barriers. The electron-rich amido ligands of TDMAT promote the reactions between this organometallic precursor molecule and the surface (R16-R18) leading to lower energetic barriers compared to those for TMA (R7-R9, with only -CH_3 ligands available) in corresponding reactions. At the same time, the acidity of the hydrogen of the surface -OH group leads to the lower kinetic requirements compared to those involving the dissociation of a surface Si-H bond (R7B vs. R7C and R16B vs. R16C). This is in accord with the common use of hydroxyl-functionalized surfaces and water exposure step in a number of ALD processes leading to metal oxide formation.^{171,241,242}

Overall, the trends in thermodynamic stability of the products of the reactions involving TMA or TDMAT hydroxyl- and alkoxy-modified silicon surfaces closely parallel those including nitrogen-containing functionalities described above. One reaction that has to be mentioned is a potential pathway involving hydrogen abstraction from the surface methoxy group (R8B, R17B). As expected, this pathway involved very high energy barriers both for TMA and for TDMAT (225.5 and 191.9 kJ/mol, respectively) inferring that these reactions do not play any major roles in the deposition processes on -OCH_3 functionalized silicon.

5.5 Summary

The study in this chapter used frontier orbital analysis to explore interactions of common organometallic precursor molecules, TMA and TDMAT, with functionalized silicon surfaces. A robust and efficient computational approach based on cluster models representing specific surface reactive sites and functionalities was applied to explore the electronic and steric effects of the surfaces and the ligands of participating metalorganic precursor molecules on adsorption and initial reactions. Despite the apparent simplicity, the results of the study are in complete agreement with advanced computational analysis of some of the selected systems. The trends in adsorption process and surface reactivity were explored for silicon surfaces terminated with hydrogen and also for previously experimentally prepared silicon surfaces with $-\text{NH}_2$, $-\text{NH}-$, $-\text{OH}$, $-\text{OCH}_3$, and $-\text{OCF}_3$ functionalities. The hydrogen-terminated silicon surfaces and Si-H functional group in the presence of other functionalities investigated proved to be the least reactive with respect to both organometallic precursors investigated.

We have learned that the electronic and steric effects from the surface (e.g., the acidity of the hydrogen on surface functionalities and the structural hindrance from the surface, respectively) could tremendously affect the thermodynamics and kinetics of the surface reaction involved in the deposition processes, but systematically fine tuning the reactivity of the surface functionalities is still difficult to achieve. In order to do that, it is essential to differentiate the electronic and steric effects of the surface functionalities, which is what we attempt to do in next chapter.

5.6 Conclusions

Based on the frontier orbital approach, the interactions between organometallic precursor molecules and functionalized silicon surfaces can be understood to provide a set of benchmarks for designing better deposition schemes, surface functionalities, and precursor molecules.

The initial adsorption of the organometallic precursor molecules on functionalized silicon produced only very weak bonding on H-terminated silicon, but the strength of the bond formed was increased substantially on O- and N-containing functional groups, with steric factors (such as shielding of the metallic center of TDMAT by dimethylamido ligands) playing as important role as the electronic interactions. Formation of a hydrogen bond between a ligand and a surface functionality proved to be important if the steric hindrance prevented the direct interaction of the HOMO of a surface group with the LUMO of the metal center.

In following interactions of TMA and TDMAT with different functional groups, it was predicted that overall Si-H entities are less likely to provide hydrogen for clean ligand elimination compared to the functionalities containing N-H or O-H bonds. Thus, it is important to understand the trends in the basicity of the surface functional groups similarly to the previously published investigations,^{18,243} but it is also required to evaluate the acidity of the surface hydrogen to be transferred from the surface during ligand elimination step.

Chapter 6

COMPUTATIONAL STUDIES OF ELECTRONIC AND STERIC EFFECTS ON SURFACE REACTIONS OF METALORGANIC PRECURSORS

6.1 Introduction

Steric and electronic effects have long been the guides for explaining the stability and geometry of molecules³¹ or for manipulating the thermodynamics or kinetics of chemical reactions.³² For numerous demands such as to maximize the yield of the synthetic process, to elongate the lifetime of the catalysts, or to better control the enantioselectivity of the reactions, the interaction/combination of steric and electronic effects has been well studied and reviewed for classic synthesis,²⁴⁴ catalytic synthesis,^{245,246} synthesis of biomedical compounds^{247,248} and molecular switches.^{249,250}

While major efforts focused on optimizing the combination of steric and electronic effects for selected reactions,^{244,245,247-249} substantial attention has also been directed at differentiating the role of these effects in a number of processes.^{246,251,252} In 2001, Pophristic and Goodman reported that by removing hyperconjugation interaction (electronic effect), the “eclipsed” ethane in its preferred conformation was successfully predicted with or without steric hindrance.²⁵³ The long-advocated textbook explanation has been challenged.

In addition to homogeneous conditions, growing attempts have been made to demystify steric and electronic effects in surface reactions,^{254,255} since treating a surface as a (macro-)molecular reagent has been successful in a number of

applications, including organic modification of semiconductors^{97,216,256} and heterogeneous catalysis.^{243,257,258} However, the surface adds another dimension to differentiating these two effects.

Surfaces may be involved in a surface reaction both in steric and electronic aspects, because the surface itself not only restricts the geometry but also affects the electronics of chemical transformation, not to mention that the influence from the ligands or substituents needs to be taken into account. To differentiate steric and electronic effects is challenging in homogeneous processes,^{253,259} to do so on surfaces is even more difficult.^{260,261}

A practical approach to evaluate steric and electronic factors is rooted in a concept of acidity vs. basicity of functional groups on solid surfaces,^{29,30} and one of the recent studies applied this concept to evaluate reactivity of the amino-functionalized surfaces toward adsorption and following surface transamination reactions of metalorganic compounds with amino-based ligands.¹⁸ In this report, tetrakis(dimethylamido)titanium (TDMAT) was used as a probe to estimate the ability of the lone pair on a nitrogen atom (of surface functionality) to nucleophilically attack the electrophilic site of TDMAT, and then the ability of the produced surface species to transfer hydrogen to eliminate appropriate ligands was considered within the context of overall acidity or basicity of the chemical groups involved. However, even in the best-case scenario, it appeared that steric and electronic factors interplayed in the overall process, and distinguishing them would be nearly impossible.

The goal of this project is to combine experimental and computational studies to uncover the role of one type of the effects without the presence of the other, thus splitting the mechanistic reasoning behind surface transformations involving amine

functionalities into two main groups. The dominance of one group or the other will define the approaches that can be used in the future to direct a wide variety of surface processes and can be further applied to other functionalities.

6.2 Experimental Section

The research techniques involved in this project include: MIR-IR, DFT, and NBO methods, while the basic information of these techniques have been introduced in the experimental section, some supplemental details will be provide below.

After the Si(100) substrates were cleaned and their cleanliness and structure were validated with the procedure described in the experimental section, multiple-internal-reflection infrared spectroscopy was applied to study the Si(100) substrates modified with trifluoroethylamine (Acros, 99.5%), cyclohexylamine (Acros, 99%), and aniline (Acros, 99.8%); both aliphatic- and aromatic-substituted amines adsorb on clean Si(100) surface by dissociating one N–H bond; the R–NH and H moieties then bond to the surface silicon atoms similarly to the ammonia dissociative adsorption³³ described in Chapter 2 (experimental section) as well as other studies.^{64,150,151,224,262-268} The use of MIR-IR focused on monitoring the vibrational signatures of the surface functionalities before and after the functionalized silicon surface would be exposed to TDMAT (Acros, 99.99%) precursor. Spectra of different amounts of TDMAT (controlled as exposure) onto modified silicon substrates were analyzed to reveal the reactivity of the surface functionalities and the kinetics of the corresponding reactions.

All the DFT and NBO calculations were performed using Gaussian 09 suite of programs at B3LYP/6311+G(d,p) level of theory, and all the cluster models have been discussed previously in the experimental section. In this project, NBO calculations

were used to not only provide graphical representation of the HOMOs and LUMOs but also to understand the charge distribution within the molecules and cluster models.

6.3 Results and Discussion

Based on the previous results obtained by XPS, AES, and MIR-IR,¹⁸ when TDMAT was dosed onto ethylamine and aniline modified silicon surfaces, only on ethylamine Si(100) surface was titanium metal deposited. The results were attributed to either the bulky phenyl ring of aniline posing steric hindrance towards TDMAT or the electron withdrawing nature of phenyl ring weakening the nucleophilic attack of the N-H group onto TDMAT or the combination of both effects that prohibited the surface reaction of TDMAT and the modified surface. However, it was difficult to further decouple these two effects, since ethylamine and aniline functionalities formed on the Si(100) surface were both sterically and electronically different.

In order to solve this puzzle, we intended to modify Si(100) surface with trifluoroethylamine (structurally resembles ethylamine but shows very different electronic character) and expose this trifluoroethylamine modified surface to TDMAT to compare the surface reaction to the reaction on ethylamine modified Si(100) surface; the results are shown in figure 6.1. The spectrum of the trifluoroethylamine modified Si(100) surface shows clear vibrational signature of Si-H stretching that is used to confirm the dissociative adsorption of amine species onto clean Si(100) surface. In addition, the C-F stretching bands indicate the presence of trifluoroethylamine functionality, although the intensity of C-H stretching bands (2940 cm^{-1}) is weak, and no vibrational band was detected in N-H stretching region likely due to band broadening of N-H absorptions.

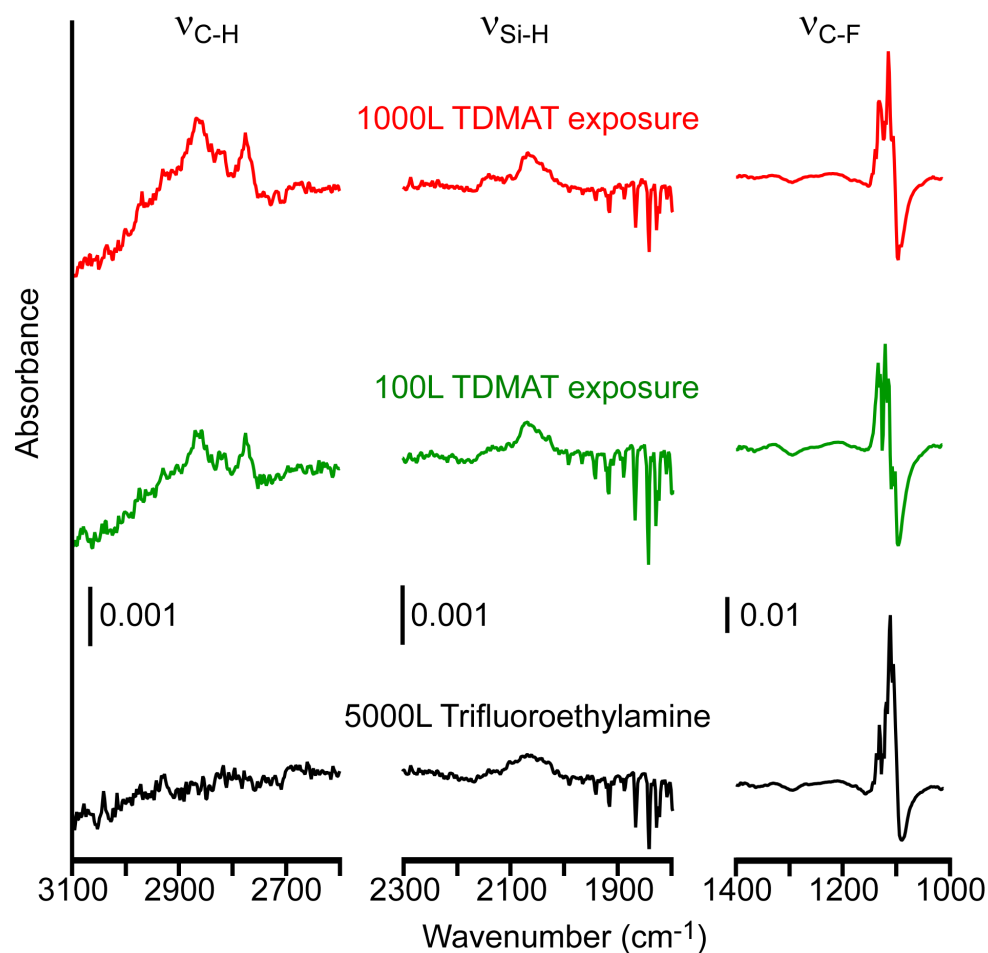


Figure 6.1: The MIR-IR studies of the trifluoroethylamine modified Si(100) surface (in black, bottom), after being exposed to 100 L of TDMAT (in green, center), and after being exposed to 1000 L of TDMAT (in red, top). The bottom spectrum was referenced to the spectrum of the clean Si(100) surface, and the other two spectra were referenced to the spectrum of trifluoroethylamine-modified Si(100) surface.

After the surface modification was confirmed by MIR-IR studies, the prepared surface was exposed to 100 L of TDMAT and inspected with MIR-IR as well, as shown in figure 6.1. It is clearly seen that the C–H stretching signature was observed for the methyl groups of dimethylamido ligands, which resulted from the reaction between TDMAT and the surface. The change in the shape of the Si–H stretching band implies the variation of the surface features, since we have previously shown that the Si–H band is very sensitive to its environment (Chapter 3). Additional TDMAT (total 1000 L) was dosed onto the modified Si(100) surface to assure that the surface was saturated (another 1000 L of TDMAT was dosed, but the spectra are not shown because no further changes were detected). Although MIR-IR studies confirmed the success of the surface modification and the reaction between TDMAT and modified surface, it is important to acquire elemental information of the deposited film; here we utilized AES to investigate the elemental composition of the surface.

Figure 6.2 shows the change in elemental composition of the clean surface and the treated surface. It is clearly seen that titanium metal was deposited on the surface accompanied with carbon and nitrogen signals from the surface functionality or the dimethylamido ligand of the precursor. Considering that TDMAT deposited Ti metal via a reaction with trifluoroethylamine- and ethylamine-modified silicon surfaces rather than aniline-modified surface, a preliminary conclusion can be made: it is more likely that the steric effect prohibits TDMAT from reacting with the surface N–H functionalities. However, the surface Si–H sites produced by the dissociative adsorption of the primary amines could serve as the alternative reactive sites for TDMAT deposition (as explained in Chapter 3); more understanding of the reaction mechanism is needed.

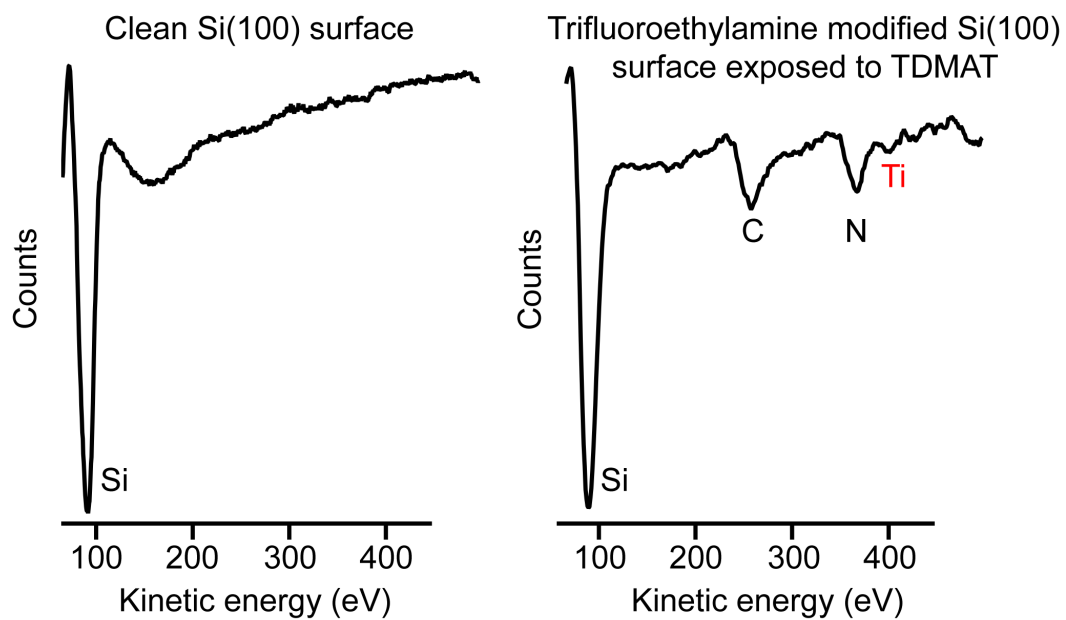


Figure 6.2: The AES analyses of the clean Si(100) surface (left) and the surface after the deposition process including first surface functionalization with 5000 L trifluoroethylamine and then exposure to 2000 L of TDMAT.

In Chapter 5, we have utilized computational methods to study the surface reaction between TDMAT and $\text{NH}_2\text{-Si(100)}$ surface and revealed that the deposition process might include two steps: (1) the weak attraction between the precursor molecule and the surface and (2) the hydrogen abstraction from two different surface hydrogen sources. As summarized in figure 6.3, TDMAT molecule approaches the modified surface without significant stabilization (3.6 kJ/mol) unlike in the case of hydroxyl-modified surface that forms hydrogen bond with dimethylamido ligand (explained earlier in Chapter 5). Because there are two possible sources of proton on the surface, TDMAT can perform hydrogen abstraction to eliminate dimethylamine via two different routes. Although the hydrogen abstraction from $-\text{NH}_2$ functional group is predicted to be thermodynamically favorable, both pathways feature similar kinetic barriers.

In order to evaluate the influence of the electronic and steric effects from the substituents on both weak attraction and hydrogen abstraction steps described above, we applied DFT computation on the reaction between TDMAT and two sets of primary amines; one set includes ethylamine and trifluoroethylamine, and the other one with cyclohexylamine and aniline. The goal of this selection is to group the amines that feature similar steric effects but extremely different electronic effects in one set; at the same time, an amine from one set can also be compared with a specific amine of similar electronic effect (but different steric hindrance) from another set.

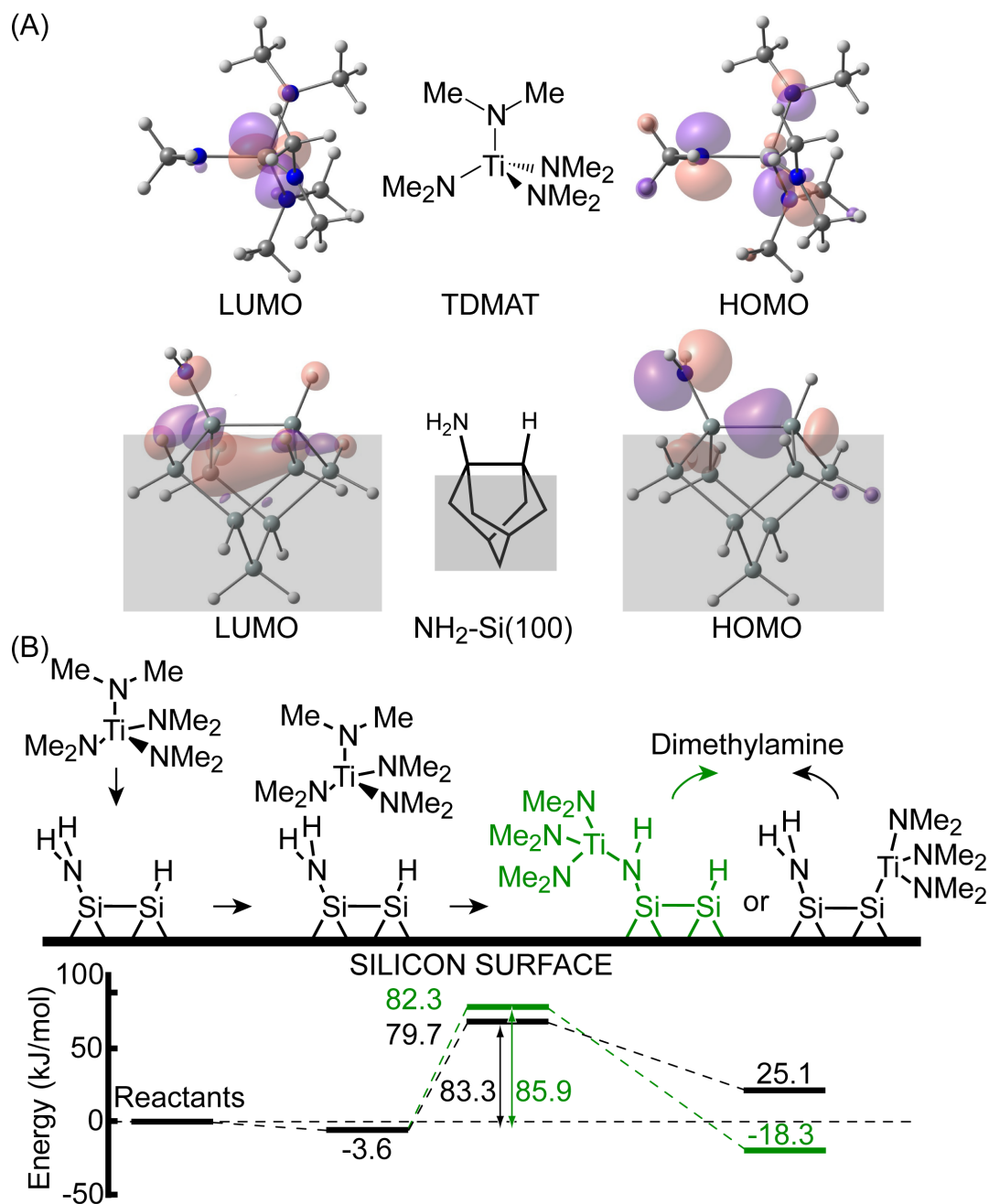


Figure 6.3: DFT and NBO results at B3LYP/6311+G(d,p) level of theory. (A) HOMO and LUMO of TDMAT precursor and NH₂-Si(100) cluster model predicted with NBO analysis. The shaded area represents the bulk silicon lattice. (B) The potential energy diagram of the reaction between TDMAT and NH₂-Si(100) cluster model. The numbers adjacent to the two-way arrows denote the barriers of the corresponding pathways.

Starting with NBO studies, the HOMOs and LUMOs of the four primary amines are compared in figure 6.4. According to these results, the HOMOs in all four cases localize around the N atom on the surface, making the N atoms open for electrophilic interaction. Although the HOMOs also reach out to the carbon-hydrate substituents, these substituents are less likely to interact with the precursor molecule by electron donation. In fact, because of the steric hindrance from the dimethylamido ligands and the tetrahedral geometry of TDMAT, the LUMO of TDMAT molecule is protected by the ligands (figure. 6.3A) and nearly impossible to accept any electron even though a surface nitrogen is capable of a nucleophilic attack. Moreover, the LUMOs of the four surface models mainly surround the surface hydrogen atoms (Si-H) instead of the hydrogen atoms on the amines, causing the formation of hydrogen bonding from N-H to the dimethylamido ligand to be difficult unlike in the case of the water-modified Si(100) surface in Chapter 5.³⁰ Consequently, the weak adsorption of the precursor molecule onto the modified surfaces seems to be insignificant; indeed, this step is predicted to gain limited stability in all four cases, as shown in figure. 6.5.

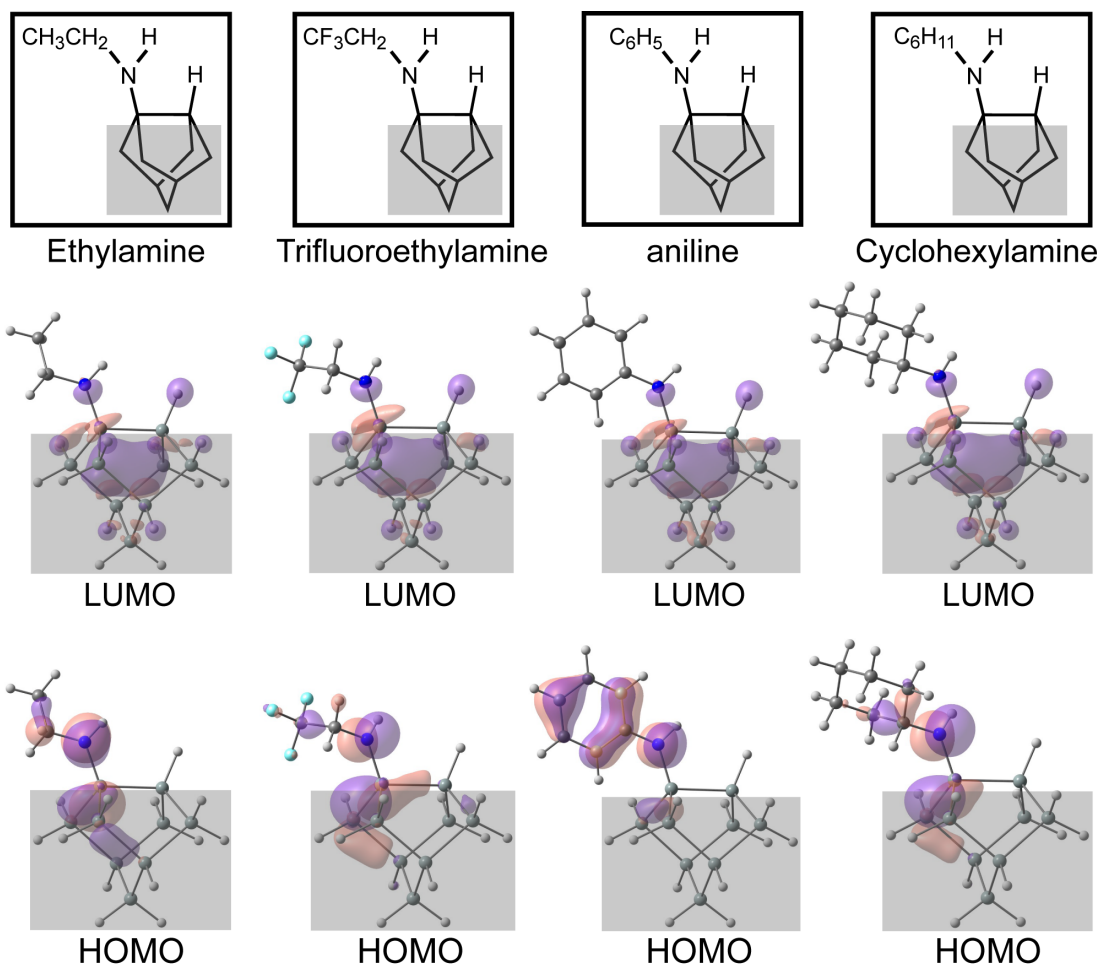


Figure 6.4: HOMOs and LUMOs of the Si(100) cluster models modified with four primary amines (as indicated) predicted with natural bond orbital (NBO) analysis (B3LYP/6311+G(d,p)). The shaded area represents the bulk (subsurface) silicon lattice beneath the surface layer.

In figure 6.5, it is clearly seen that the weak adsorption in all four cases leads to only small gains in respective stabilities. However, in addition to the similarity in the first step, the overall reactions between TDMAT and all four surface amine functionalities exhibit remarkable similarity not only in the reaction trends but also the thermodynamics. First the energy barriers for abstracting hydrogen from the N–H sites are, in all cases, considerably higher than those from the corresponding surface hydrogen sites (Si–H). Conversely, the products formed after TDMAT picks up a hydrogen from N–H sites are more stable than those from Si–H sites; nevertheless, the product formations are predicted to be slightly exothermic in all eight pathways. Third, most of the predicted energies of the transition states or the product show no significant difference. For example, following the Si–H pathway, the energies of transition states range from 79.4 to 84.6 kJ/mol, and the products of the same pathway range from 21.9 to 28.3 kJ/mol. Although these results may not be unexpected, since the substituents are too far away to affect the surface Si–H sites in all cases, the energies of the products following N–H path still do not respond to the variance in substituents (2.6 to 15.0 kJ/mol). The only noticeable difference is found in the predicted energies of the transition states following N–H dissociation pathway (92.6 to 146.6 kJ/mol).

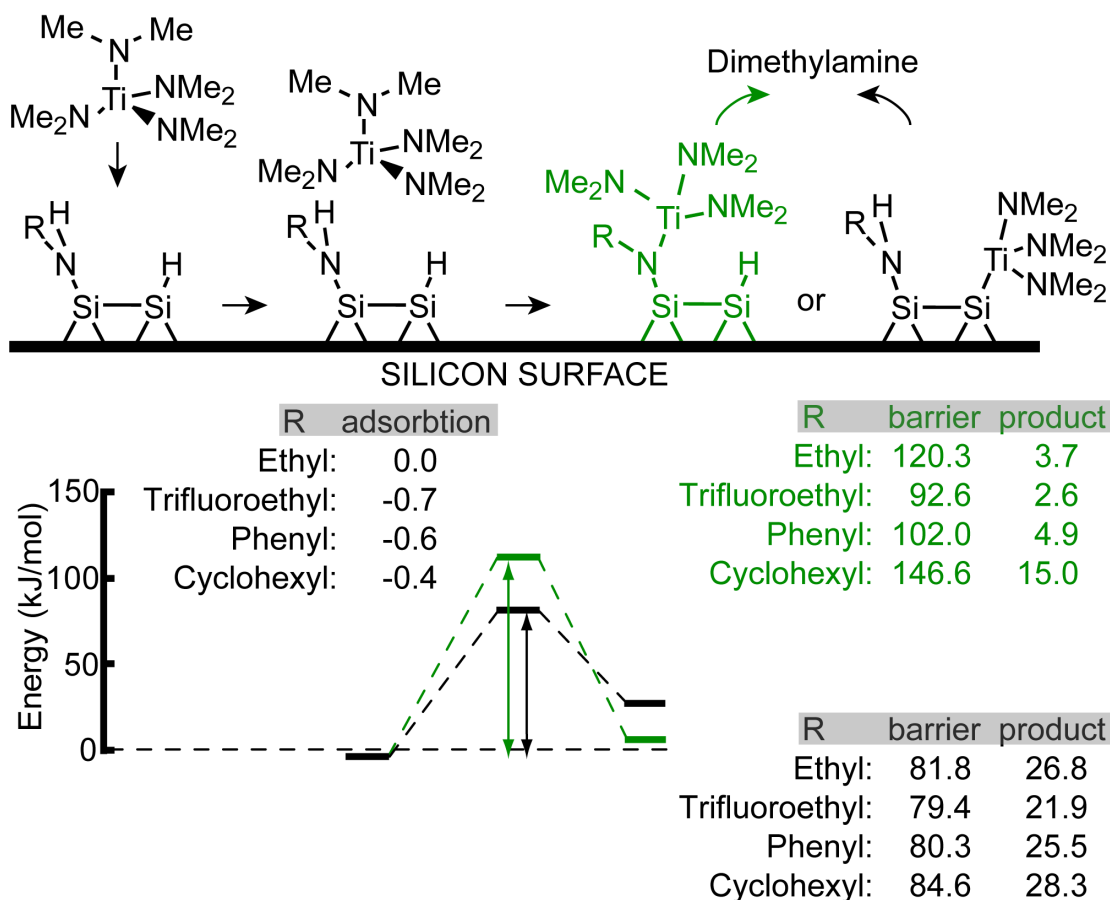


Figure 6.5: The potential energy diagram following the reaction of TDMAT and four amine-modified surfaces at B3LYP/6311+G(d,p) level of theory.

However, recall the results predicted for TDMAT reacting with ammonia-modified Si(100) surface summarized in figure 6.3. Although the energies predicted for Si-H route are nearly identical to those of primary amine cases, the thermodynamics of N-H route is of significant difference. Unlike the cases of the primary amines, the energy barrier is only slightly higher along the N-H route, which implies that all four different substituents might pose steric hindrance on the N-H pathways and alter the corresponding thermodynamics consistently. This might mean

that the steric hindrance for these four surface amine substituents is too high and overpowers any possible electronic effects from the substituents. In order to diminish the steric effect from the substituents and to focus on the electronic factors, we performed a computational comparison between ammonia and fluoroamine-modified surfaces.

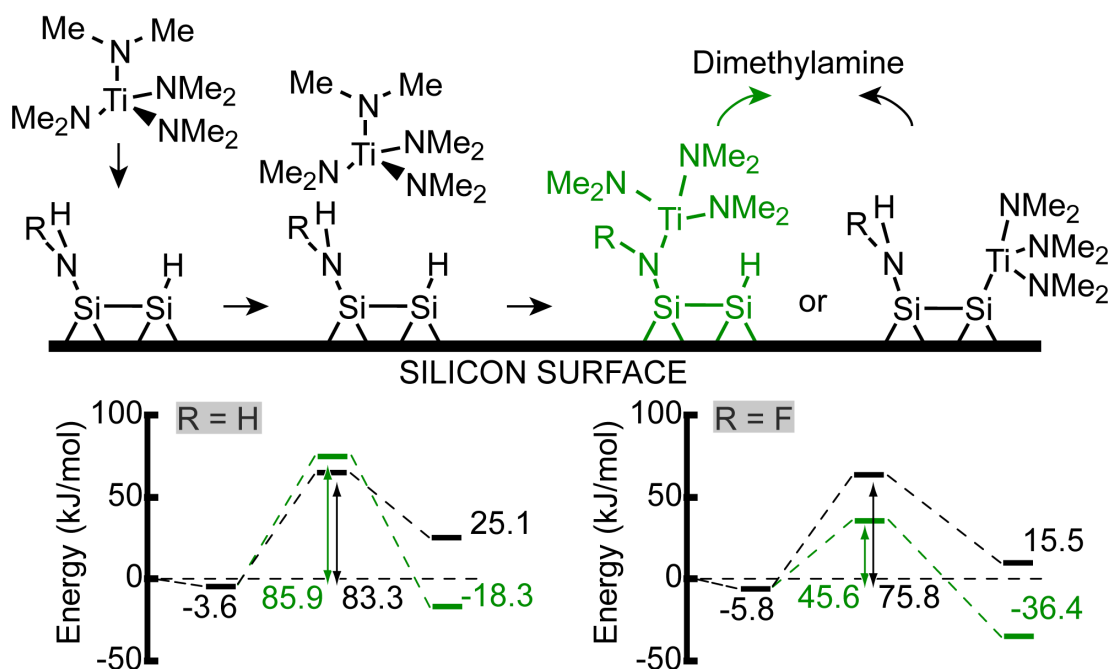


Figure 6.6: The potential energy diagrams of TDMAT reacting with ammonia- and fluoroamine-modified Si(100) surfaces at B3LYP/6311+G(d,p) level of theory. The numbers adjacent to the two-way arrows denote the barriers of the corresponding pathways.

As shown in figure 6.6, the difference between the two potential energy diagrams is striking. While the Si-H pathways in two cases are still predicted to be similar (also similar to those of the previous four primary amines in figure 6.5), the

N–H route of abstracting hydrogen from fluoroamine site presents an energy barrier that is, as the first case, lower than that of the corresponding Si–H route in all six systems presented so far. Thus, without the steric effect from bulky substituents, the electronic effect from the electron withdrawing fluorine atom emerges. In addition to change in the kinetic barrier, it is also worth pointing out that the first step (weak adsorption) in either example remains at low stability, as was predicted for the four primary amines.

These observations do not mean that the electronic or steric effects from the substituents have no impact on the weak adsorption stage; on the contrary, this phenomenon is the consequence of the geometry of the precursor molecule, which prohibits the LUMO of TDMAT from interacting with surface functionalities. In fact, substantial stability was gained for the interaction between the LUMOs of the surface amine/imine groups and the “unblocked” HOMO of the trigonal-planar trimethylaluminum molecule in Chapter 5.³⁰

Based on these interpretations, we assume that when the substituents of the primary amines occupy substantial space, the steric effect screens the electronic effect and results in higher energy barrier and lower stability of the products. Although the electronic effect emerges when the sizes of the substituents are minimized, a more clear relationship between electronic effect and the thermodynamics of the reactions needs more examination. To do so, we purposed a series of calculations based on a systematic selection of primary amines including three groups. The first group consists of cyclohexylamine, ethylamine, methylamine, and –NH_2 functionalities as the steric series. The second group is represented by ethylamine, fluoroethylamine, difluoroethylamine, and trifluoroethylamine to study electronic effect. Lastly, the third

group contains methylamine, fluoromethylamine, difluoromethylamine, and trifluoromethylamine to compare with the second groups to understand the interplay between electronic and steric effects.

In figure 6.7, the DFT-predicted energy barrier (A) for TDMAT to abstract the hydrogen from surface amine sites and NBO estimated charge (B) on the hydrogen atom of amine functionalities are plotted against the size of the substituents (steric effect) and number of fluorine atoms on the substituents (electronic effect).

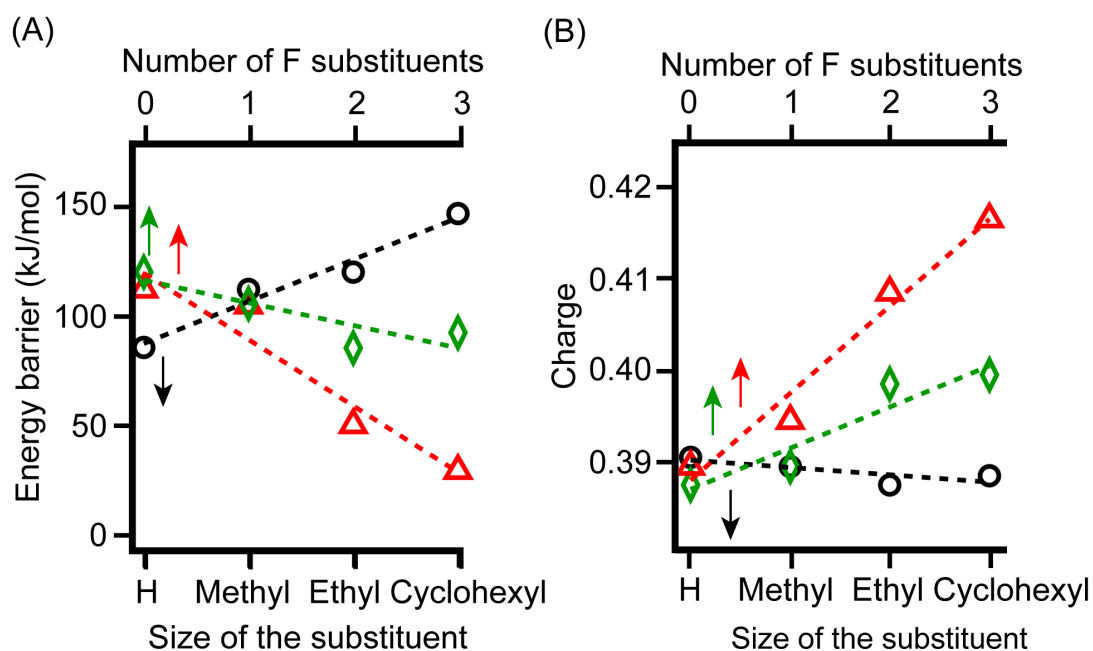


Figure 6.7: The plots of energy barriers for TDMAT abstracting hydrogen from surface amine groups (A) and the charge on the hydrogen of surface amines (B). ○: the steric series; ◇: the electronic series of ethylamine; △: the electronic series of methylamine. The dashed lines are provided to guide the eye without any specific fit. The colored arrows direct plots of the same color to the corresponding axis.

The plot of black circles (steric series) in figure 6.7 clearly shows that the energy barrier increases with the size of the amine substituents, while the charge on the hydrogen atom slightly decreases due to the electron donating nature of these substituents (methyl, ethyl, and cyclohexyl). On the other hand, the energy barrier of the two electronic series (red and green in figure 6.7) drops when more and more fluorine atoms are added to the substituents, not to mention the charge on the hydrogen atom becomes more positive because of the strong electron withdrawing ability of fluorine. In addition, the decreased slope for ethylamine series compared to the methylamine series likely results from the shorter distance from the fluorine atoms to the hydrogen in the methylamine series (α carbon for methylamine; β carbon for ethylamine). These two plots not only display the influences of electronic and/or steric effects but also point out that the barrier is actually inversely related to the acidity of the proton on the surface amine group, which conforms to the conclusions we stated in Chapter 5.

Knowing that both steric and electronic effects alter the kinetic barriers of the hydrogen abstraction suggests that kinetic study with spectroscopic methods may provide experimental confirmation of the computational results and shed light on tuning surface reactivity via electronic and steric effects. The first attempt was performed with MIR-IR to investigate the reaction between TDMAT and cyclohexylamine-modified Si(100) surface. Unlike in the case of trifluoroethylamine-modified surface, cyclohexylamine displays intense C–H stretching bands, as shown in figure 6.8; however, the N–H stretching absorption bands are still difficult to identify because of the low signal-to-noise ratio or the interference from O–H signals in this region (not shown here). In addition to the C–H stretching signal, Si–H signal

at 2080 cm^{-1} indicates the typical dissociative adsorption of amines onto clean Si(100) surface. To this as-prepared surface, different amounts of TDMAT were dosed; it is clearly seen that the intensity of C–H stretching bands of TDMAT rises as more and more TDMAT is dosed; at the same time, gradual decrease of intensity in the Si–H stretching region appears as well, which means surface hydrogens are consumed. The same analyses were conducted for clean Si(100) surface and aniline modified surface to evaluate the differences among all these surfaces.

Recall that we followed the decrease in the intensity of Si–H bands in Chapter 3 for Cu(hfac)VTMS reacting with amine/imine modified surface, but there are actually two sources of hydrogen for the precursors to react with, as we have discussed in Chapters 4 and 5. In order to extract the kinetic information from these MIR-IR spectra, the integration of C–H stretching signal of TDMAT on different surfaces is plotted against the exposure of TDMAT, as shown in figure 6.9.

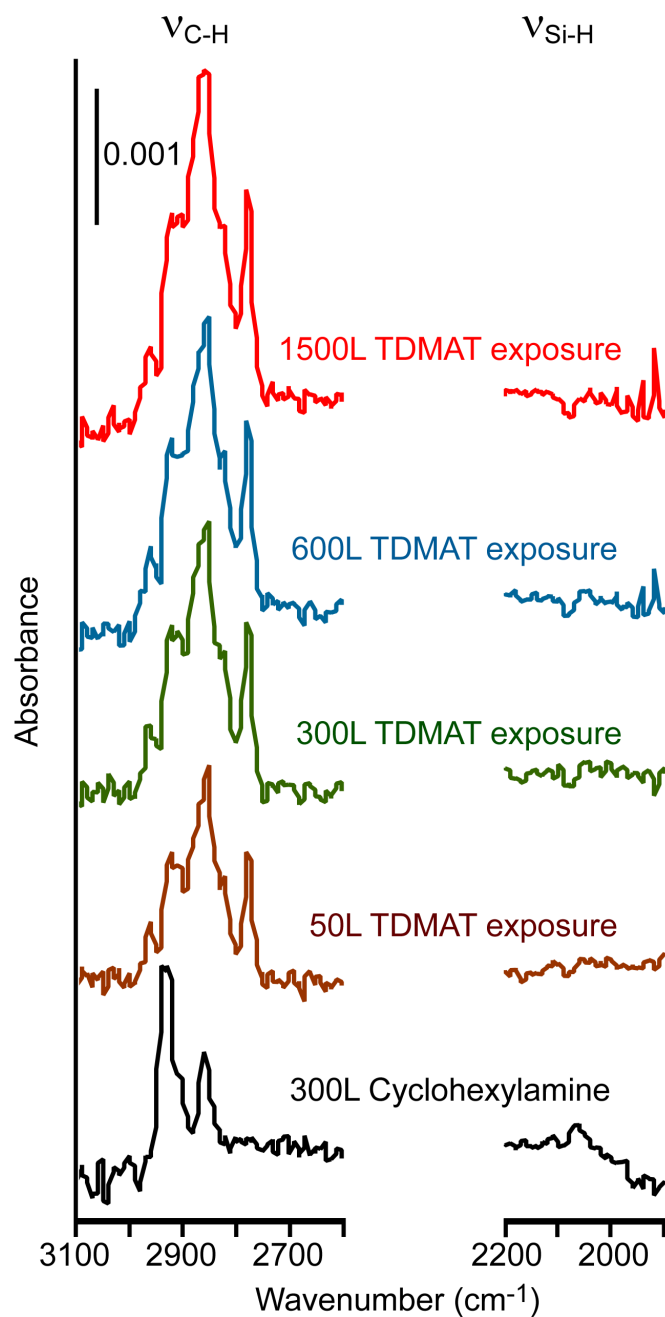


Figure 6.8: MIR-IR spectra of TDMAT reacting with cyclohexylamine-modified surface. The bottom spectrum was collected when the surface was exposed to 300 L cyclohexylamine using a spectrum of clean Si(100) as the background, and the bottom spectrum was then used as the background for the rest of the spectra.

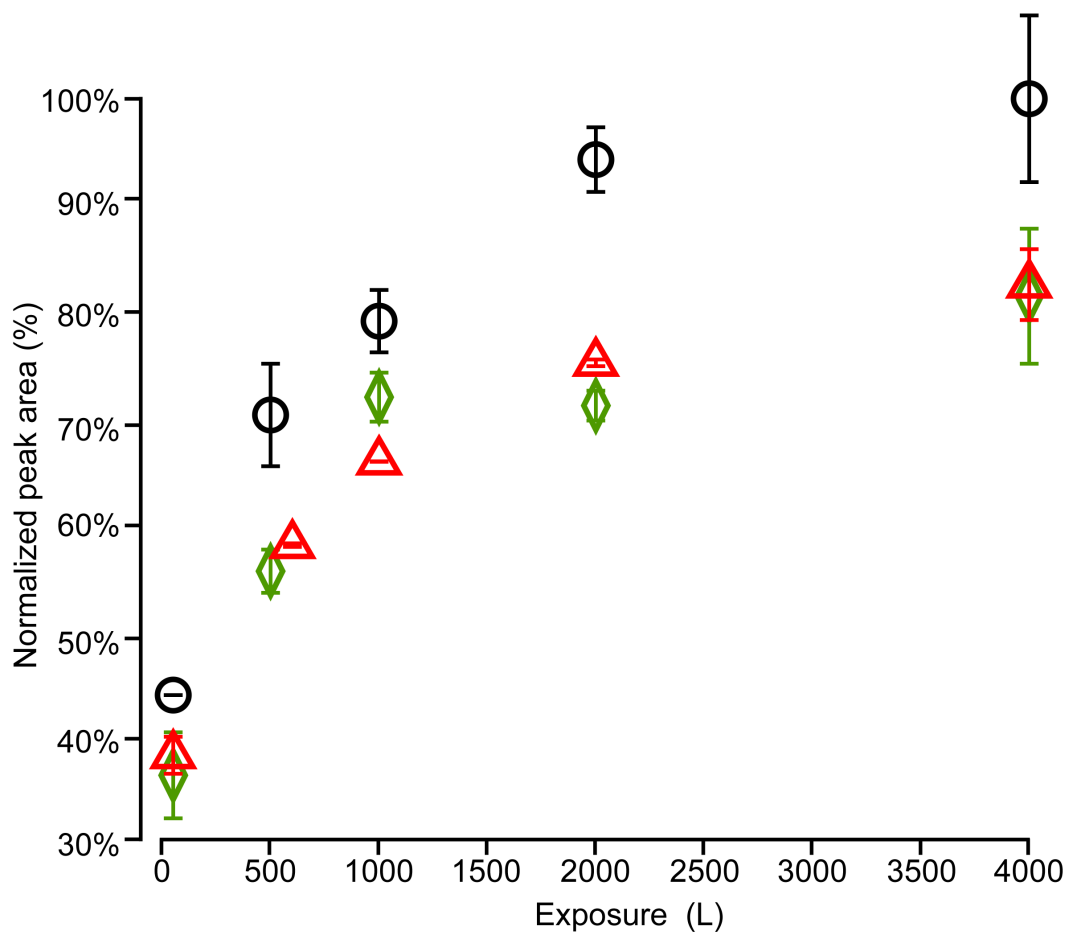


Figure 6.9: The exposure profiles of TDMAT reacting with clean (○), cyclohexylamine-modified (△), and aniline-modified (◇) surfaces. the integration of C–H band from the reaction of 4000 L TDMAT with clean Si(100) surface was used to normalize all other integrations (other points). Assuming that 4000 L of TDMAT saturates clean Si(100) surface, which means 100% coverage, all other normalized integrations were plotted against TDMAT exposure, so that the relationship between TDMAT exposure and surface saturation can be deduced with the plot.

It should be noted that although the most intense signal was treated as 100%, the reaction of TDMAT with clean Si(100) surface is different from those in the cases of primary amine modified surfaces, since there is no hydrogen on clean silicon surface. According to figure 6.9, with the increasing TDMAT exposure, the coverage of both cyclohexylamine and aniline modified Si(100) surfaces reaches about 80%, and these two plots show no significant difference in curvature, which implies that these experiments might not successfully provide useful information. Moreover, according to the previous results,¹⁸ the reaction of TDMAT with aniline-prepared Si(100) surface was impeded by the surface amine functionality; however, it is evidently shown that TDMAT reacts with aniline-prepared surface even with low dosage (50 L). Resolving this discrepancy will be a part of future work.

6.4 Conclusions

With the help from DFT and NBO calculations, we have simulated the reactions of TDMAT towards a systematic selection of primary amines, and according to the observations, several conclusions can be obtained. First, changing the substituents of the surface amine group results in insignificant effect on the first step (weak adsorption) of the reaction between TDMAT and functionalized surfaces, which might be due to the shielding effect from the ligands because of the molecular geometry of TDMAT. Next, steric effect dominates the influence of substituents on the reaction thermodynamics as long as the substituent occupies substantial space. Third, with the trends of the energy barrier increasing with the size of the substituents and decreasing with the number of F atoms, we clearly decouple steric and electronic effects; furthermore, we proved that the acidity of the hydrogen to be abstracted by the

precursor molecule is the key factor in the transamination of TDMAT with surface amine functionalities.

On the other hand, the AES studies of the trifluoroethylamine-prepared surface reacting with TDMAT indicate that titanium metal was deposited on the surface, which consequently suggests that steric effect might be responsible for the discrepancy observed in our previous studies;¹⁸ however, the initial kinetic studies with MIR-IR did not deliver conclusive results. A different set of experiments needs to be designed to address this discrepancy in the future.

Chapter 7

CONCLUSIONS AND FUTURE WORKS

Specific surface reactions involving different deposition precursors and various surface reactive sites were investigated both experimentally and computationally to obtain a comprehensive view at a molecular level. The surface reactions studied in this work for metalorganic precursor reactions with functionalized silicon surfaces were proposed to proceed via two steps: (1) the weak attraction of the precursor molecule on a functionalized surface and (2) the hydrogen abstraction from a surface hydrogen source. The factors that could potentially affect the reactions include electronic and steric effects that were analyzed for both the surface and the precursor molecule.

In the first step, the interaction between the surface and the precursor molecule determines the stability of the initial adsorbate (weak attraction). The interaction we have discussed is based on HOMO/LUMO interaction.

Surface reactive sites such as O–H and N–H groups can form a bond with the precursor ligand and, in turn, pull the precursor molecule close to the surface for further reaction; for example, the bonding between surface O–H group and the dimethylamide ligand of tetrakis(dimethylamido)titanium molecule or the isopropoxide ligand of titanium isopropoxide molecule stabilizes the systems by 34.3 and 44 kJ/mol, respectively. However, the structurally similar N–H groups do not form hydrogen bond in the same manner plausibly due to the smaller electronegativity of nitrogen, which is rooted in the electronic effect from the surface functionalities. In

fact, surface O–H groups do form bonds with dimethylamide, isopropoxide, acetylacetonate, and amidinate ligands, as we discussed in Chapter 4.

The weak attraction caused by the interaction between the HOMO and LUMO of the surface or the precursor molecule can be treated as a coordination bond if it results from the nucleophilic attack of a HOMO of the surface functionality onto the LUMO of the precursor metal center. This can be observed for trimethylaluminum molecule reaction with surface amine, imine, and alkoxides. In this interaction, both steric and electronic effects affect the stability of the bond formed. For example, reactions R5 and R6 in Chapter 5 describe similar interactions between TMA and surface imine group, but the stability of the weak attraction between TMA and bridged –NH– group (R6) is significantly smaller likely due to the steric hindrance from the surface that can be thought of as a macro-molecular substituent. Nevertheless, the interactions of TMA with surface hydroxyl and trifluoromethoxyl group illuminate the electronic effect. TMA coordinates to the surface O–H group and gains 86 kJ/mol stability; however, this molecule binds to the fluorine atom of the trifluoromethoxyl group instead of oxygen atom and gains only 16 kJ/mol, which corresponds to the strong electron withdrawing ability of fluorine pulling away the electron density on oxygen atom. Conversely, steric influence from the precursor molecule altering this coordinative interaction can also be obtained when TMA and TDMAT react with a surface amine site (Chapter 5, R4 and R13). The surface –NH₂ group coordinates to the aluminum center and gains 71.2 kJ/mol stability, while the steric hindrance of the dimethylamide ligands shields the titanium center and impedes its ability to interact with surface functional groups.

In addition to the coordinative attraction, one more HOMO/LUMO interaction can be studied for the cases involving bare (clean) Si(100) surface dimer (Chapter 4). Because of the zwitterionic nature of the dimer, many precursors adsorb on the clean surface via the interaction between the HOMO of the precursor (mostly located on the electron-rich element of the ligand) and the LUMO of the surface dimer (the partially positive Si atom) including titanium isopropoxide, tetrakis(dimethylamido)hafnium, copper acetylacetonate, and nickel isopropylamidinate. Thus, the influence of steric and electronic factors on the weak attraction step of the deposition reaction is explained, and the next step, hydrogen abstraction, can be considered.

For the second step of the chemisorption process, the hydrogen abstraction from two different sources was discussed. Although the electronic and steric effects from both the precursor and the surface can affect the reaction, only the effects from the surface part were investigated here. Surface Si-H site as one of the hydrogen sources offers hydrogen to the precursors (TDMAT and TMA, Chapter 5) in a similar manner, which features energy barriers ranging from 120 to 150 kJ/mol for TMA and 50 to 80 kJ/mol for TDMAT reactions. Since manipulating the electronic and steric effects of Si-H sites is relatively restricted even computationally, most of the interpretations focus on hydroxide and amine functionalities.

In Chapter 6, a systematic study concludes that steric effect overwhelms electronic effect, when the substituent of the surface amine site occupies substantial space. However, if a smaller substituent (e.g., methyl) is selected the electronic effect can be clearly identified, when the number of fluorine substituents increases. Moreover, the acidity of the hydrogen to be abstracted undoubtedly governs the

energy barrier of the corresponding hydrogen abstraction step--the more acidic the hydrogen is, the lower the energy barrier will be.

Although the electronic and steric effects from the precursor in the second step were not systematically inspected in the desired ligand-exchange reaction discussed in Chapters 3 to 6, the combined influence from the precursor ligand on the overall mechanism and on the mechanism of the undesired reaction on bare (clean) silicon surface was considered in Chapter 4. The results suggest avoiding incorporating unhindered atoms with lone pairs in precursor ligands, for example, heteroatoms that can induce Bohlmann effect, and chelating ligands to novel precursor designs.

Although we have obtained experimental evidence that the surface modification could alter the morphology of the deposited film in Chapter 3, a new design of experiment is needed in the future to uncover the fundamental chemistry that causes these differences, since the preliminary experimental investigation did not lead to conclusive results. The future work should also include a systematic selection of precursor ligands to study electronic and steric effects from the ligand itself, not only surface functionalities.

REFERENCES

- (1) International Technology Roadmap for Semiconductors, 2013, <http://www.itrs.net/reports.html>.
- (2) Rickerby, J.; Steinke, J. H. G. *Chem. Rev.* **2002**, *102*, 1525.
- (3) Doppelt, P. *Coordin. Chem. Rev.* **1998**, *1998*, 1785.
- (4) Choy, K. L. *Prog. Mater. Sci.* **2003**, *48*, 57.
- (5) Malandrino, G.; Fragala, I. L. *Coordin. Chem. Rev.* **2006**, *250*, 1605.
- (6) Jones, A. C.; Aspinall, H. C.; Chalker, P. R. *Surf. Coat. Tech.* **2007**, *201*, 9046.
- (7) Puurunen, R. L. *J. Appl. Phys.* **2005**, *97*, 121301.
- (8) Zaera, F. *J. Mater. Chem.* **2008**, *18*, 3521.
- (9) Deshpande, A.; Inman, R.; Jursich, G.; Takoudis, C. *J. Vac. Sci. Technol. A* **2004**, *22*, 2035.
- (10) George, S. M. *Chem. Rev.* **2010**, *110*, 111.
- (11) Ho, M. T.; Wang, Y.; Brewer, R. T.; Wielunski, L. S.; Chabal, Y. J.; Moumen, N.; Boleslawski, M. *Appl. Phys. Lett.* **2005**, *87*, 133103.
- (12) Kim, J. H.; Kim, J. Y.; Kang, S. W. *J. Appl. Phys.* **2005**, *97*, 093505.
- (13) Lim, J. W.; Park, H. S.; Kang, S. W. *J. Electrochem. Soc.* **2001**, *148*, C403.
- (14) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N. *Acc. Chem. Res.* **2000**, *33*, 617.
- (15) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879.

- (16) Leftwich, T. R.; Teplyakov, A. V. *Surf. Sci. Rep.* **2008**, *63*, 1.
- (17) Ciampi, S.; Harper, J. B.; Gooding, J. J. *Chem. Soc. Rev.* **2010**, *39*, 2158.
- (18) Bent, S. F.; Kachian, J. S.; Rodriguez-Reyes, J. C.; Teplyakov, A. V. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 956.
- (19) Rao, G. M.; Elwell, D.; Feigelson, R. S. *J. Electrochem. Soc.* **1980**, *127*, 1940.
- (20) De Mattei, R. C.; Elwell, D.; Feigelson, R. S. *J. Electrochem. Soc.* **1981**, *128*, 1712.
- (21) Bergmann, R. B. *Appl. Phys. A* **1999**, *69*, 187.
- (22) Bergveld, P. *Sens. Actuators, B* **2003**, *88*, 1.
- (23) Katz, E.; Willner, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 6042.
- (24) Perrine, K. A.; Teplyakov, A. V. *Chem. Soc. Rev.* **2010**, *39*, 3256.
- (25) Yoshinobu, J. *Prog. Surf. Sci.* **2004**, *77*, 37.
- (26) Zhang, X. C.; Antonopoulos, I. H.; Kumar, S.; Chen, J.; Teplyakov, A. V. *Appl. Surf. Sci.* **2009**, *256*, 815.
- (27) Zhang, X. C.; Teplyakov, A. V. *Langmuir* **2008**, *24*, 810.
- (28) Liu, Y.; Chen, J.; Teplyakov, A. V. *Langmuir* **2012**, *28*, 15521.
- (29) Lin, J. M.; Teplyakov, A. V.; Rodriguez-Reyes, J. C. F. *J. Vac. Sci. Technol., A* **2013**, *31*, 021401.
- (30) Lin, J.-M.; Teplyakov, A. *Theor. Chem. Acc.* **2013**, *132*, 1.
- (31) Kemp, J. D.; Pitzer, K. S. *J. Chem. Phys.* **1936**, *4*, 749.
- (32) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
- (33) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *Phys. Rev. B.* **2007**, *76*, 075348.
- (34) Michalak, D. J.; Amy, S. R.; Aureau, D.; Dai, M.; Esteve, A.; Chabal, Y. J. *Nat. Mater.* **2010**, *9*, 266.

- (35) Thomas, L. H. *Math. Proc. Cambridge*. **1927**, 23, 542.
- (36) Fermi, E. *Z. Phys.* **1928**, 48, 73.
- (37) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, 136, B864.
- (38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. In *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT Wallingford CT, 2009.
- (39) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (40) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (41) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270.
- (42) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, 82, 284.
- (43) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.
- (44) Wachters, A. J. *J. Chem. Phys.* **1970**, 52, 1033.
- (45) Hay, P. J. *J. Chem. Phys.* **1977**, 66, 4377.
- (46) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650.
- (47) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, 72, 5639.
- (48) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, 91, 1062.
- (49) Binning, R. C.; Curtiss, L. A. *J. Comput. Chem.* **1990**, 11, 1206.
- (50) McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, 94, 511.

- (51) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J. P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.
- (52) Blaudeau, J. P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016.
- (53) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. *J. Comput. Chem.* **1983**, *4*, 294.
- (54) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (55) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (56) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
- (57) Peterson, K. A.; Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 7410.
- (58) Davidson, E. R. *Chem. Phys. Lett.* **1996**, *260*, 514.
- (59) Wilson, A. K.; vanMourik, T.; Dunning, T. H. *THEOCHEM-J. Mol. Struc.* **1996**, *388*, 339.
- (60) Peng, C. Y.; Schlegel, H. B. *Isr. J. Chem.* **1993**, *33*, 449.
- (61) Peng, C. Y.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.
- (62) Okada, L. A.; George, S. M. *Appl. Surf. Sci.* **1999**, *137*, 113.
- (63) Elam, J. W.; Schuisky, M.; Ferguson, J. D.; George, S. M. *Thin Solid Films* **2003**, *436*, 145.
- (64) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Phys. Chem. C* **2007**, *111*, 16498.
- (65) Pirolli, L.; Teplyakov, A. V. *J. Phys. Chem. B* **2005**, *109*, 8462.
- (66) Pirolli, L.; Teplyakov, A. V. *Surf. Sci.* **2006**, *600*, 3313.
- (67) Pirolli, L.; Teplyakov, A. V. *Surf. Sci.* **2007**, *601*, 155.
- (68) Ni, C.; Zhang, Z.; Wells, M.; Beebe Jr., T. P.; Pirolli, L.; Mendez de Leo, L. P.; Teplyakov, A. V. *Thin Solid Films* **2007**, *515*, 3030.

- (69) Perrine, K. A.; Teplyakov, A. V. *Langmuir* **2010**, *26*, 12648.
- (70) Queeney, K. T.; Fukidome, H.; Chaban, E. E.; Chabal, Y. J. *J. Phys. Chem. B* **2001**, *105*, 3903.
- (71) Chabal, Y. J.; Higashi, G. S.; Raghavachari, K.; Burrows, V. A. *J. Vac. Sci. Technol., A* **1989**, *7*, 2104.
- (72) Zhang, X.; Garfunkel, E.; Chabal, Y. J.; Christman, S. B.; Chaban, E. *E. Appl. Phys. Lett.* **2001**, *79*, 4051.
- (73) Takeda, S.; Fukawa, M.; Hayashi, Y.; Matsumoto, K. *Thin Solid Films* **1999**, *339*, 220.
- (74) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *Phys. Rev. B* **2008**, *78*, 165314.
- (75) Bowler, D. R.; Owen, J. H. G. *Phys. Rev. B* **2007**, *75*, 155310.
- (76) Chabal, Y. J. *Phys. Rev. B* **1984**, *29*, 3677.
- (77) Depla, D.; Haemers, J.; De Gryse, R. *Plasma Sources Sci. Technol.* **2002**, *11*, 91.
- (78) Fallberg, A.; Ottosson, M.; Carlsson, J. O. *Chem. Vap. Deposition* **2009**, *15*, 300.
- (79) Fallberg, A.; Ottosson, M.; Carlsson, J. O. *J. Cryst. Growth* **2010**, *312*, 1779.
- (80) Lu, Q.; Zhang, X.; Zhu, W.; Zhou, Y.; Zhou, Q.; Liu, L.; Wu, X. *phys. status solidi A* **2011**, *208*, 874.
- (81) Leftwich, T. R.; Teplyakov, A. V. *J. Electron. Spectrosc. Relat. Phenom.* **2009**, *175*, 31.
- (82) Perrine, K. A.; Leftwich, T. R.; Weiland, C. R.; Madachik, M. R.; Opila, R. L.; Teplyakov, A. V. *J. Phys. Chem. C* **2009**, *113*, 6643.
- (83) Rodríguez-Reyes, J. C. F.; Ni, C. Y.; Bui, H. P.; Beebe Jr., T. P.; Teplyakov, A. V. *Chem. Mater.* **2009**, *21*, 5163.
- (84) Girolami, G. S.; Jeffries, P. M.; Dubois, L. H. *J. Am. Chem. Soc.* **1993**, *115*, 1015.

- (85) Hampden-Smith, M. J.; Kodas, T. T. *Polyhedron* **1995**, *14*, 699.
- (86) Mezhenny, S.; Lyubinetsky, I.; Choyke, W. J.; Yates, J. T. *J. Appl. Phys.* **1999**, *85*, 3368.
- (87) Besling, W. F. A.; Goossens, A.; Meester, B.; Schoonman, J. *J. Appl. Phys.* **1998**, *83*, 544.
- (88) Kang, H.-K.; Kang, S. B. *Mater. Sci. Eng. A* **2006**, *428*, 336.
- (89) Perry, S. S.; Somorjai, G. A. *J. Vac. Sci. Technol., A* **1994**, *12*, 1513.
- (90) Barr, T. L. *Modern ESCA : the principles and practice of x-ray photoelectron spectroscopy*; Boca Raton ; London : CRC Press, **1994**.
- (91) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. *Handbook of x-ray photoelectron spectroscopy*; 1st ed.; Perkin-Elmer Corp.: Eden Prairie, MN., **1979**.
- (92) Flowers, M. C.; Jonathan, N. B. H.; Morris, A.; Wright, S. *J. Chem. Phys.* **1998**, *108*, 3342.
- (93) Flowers, M. C.; Jonathan, N. B. H.; Liu, Y.; Morris, A. *J. Chem. Phys.* **1993**, *99*, 7038.
- (94) Cuenya, B. R. *Thin Solid Films* **2010**, *518*, 3127.
- (95) Aldinger, B. S.; Gupta, A.; Clark, I. T.; Hines, M. A. *J. Appl. Phys.* **2010**, *107*.
- (96) Gupta, A.; Aldinger, B. S.; Faggin, M. F.; Hines, M. A. *J. Chem. Phys.* **2010**, *133*.
- (97) Tian, F. Y.; Taber, D. F.; Teplyakov, A. V. *J. Am. Chem. Soc.* **2011**, *133*, 20769.
- (98) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *Chem. Eur. J.* **2007**, *13*, 9164.
- (99) Leskela, M.; Ritala, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 5548.
- (100) Niinisto, L.; Paivasaari, J.; Niinisto, J.; Putkonen, M.; Nieminen, M. *phys. status solidi A* **2004**, *201*, 1443.

- (101) George, S. M.; Ott, A. W.; Klaus, J. W. *J. Phys. Chem.* **1996**, *100*, 13121.
- (102) Seitz, O.; Dai, M.; Aguirre-Tostado, F. S.; Wallace, R. M.; Chabal, Y. *J. J. Am. Chem. Soc.* **2009**, *131*, 18159.
- (103) Kim, H. *J. Vac. Sci. Technol. B* **2003**, *21*, 2231.
- (104) Xu, Y.; Musgrave, C. B. *Appl. Phys. Lett.* **2005**, *86*, 192110.
- (105) Elliott, S. D. *Surf. Coat. Technol.* **2007**, *201*, 9076.
- (106) Holme, T. P.; Prinz, F. B. *J. Phys. Chem. A* **2007**, *111*, 8147.
- (107) Xu, Y.; Musgrave, C. B. *Chem. Phys. Lett.* **2005**, *407*, 272.
- (108) Xu, Y.; Musgrave, C. B. *Surf. Sci.* **2005**, *591*, L280.
- (109) Widjaja, Y.; Musgrave, C. B. *J. Chem. Phys.* **2002**, *117*, 1931.
- (110) Widjaja, Y.; Musgrave, C. B. *Appl. Phys. Lett.* **2002**, *81*, 304.
- (111) Widjaja, Y.; Musgrave, C. B. *Appl. Phys. Lett.* **2002**, *80*, 3304.
- (112) Mui, C.; Musgrave, C. B. *J. Phys. Chem. B* **2004**, *108*, 15150.
- (113) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V.; Brown, S. D. *Surf. Sci.* **2010**, *604*, 2043.
- (114) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Appl. Phys.* **2008**, *104*, 084907.
- (115) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Phys. Chem. C* **2008**, *112*, 9695.
- (116) Rodríguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Phys. Chem. C* **2007**, *111*, 4800.
- (117) Hu, Z.; Turner, C. H. *J. Phys. Chem. C* **2007**, *111*, 5756.
- (118) Kelly, M. J.; Han, J. H.; Musgrave, C. B.; Parsons, G. N. *Chem. Mater.* **2005**, *17*, 5305.
- (119) Ghosh, M. K.; Choi, C. H. *Chem. Phys. Lett.* **2006**, *426*, 365.

- (120) Halls, M. D.; Raghavachari, K. *J. Phys. Chem. B* **2004**, *108*, 4058.
- (121) Hu, Z.; Turner, C. H. *J. Am. Chem. Soc.* **2007**, *129*, 3863.
- (122) Gates, S. M. *Chem. Rev.* **1996**, *96*, 1519.
- (123) Creighton, J. R.; Wang, G. T.; Breiland, W. G.; Coltrin, M. E. *J. Cryst. Growth* **2004**, *261*, 204.
- (124) Gow, T. R.; Lin, R.; Cadwell, L. A.; Lee, F.; Backman, A. L.; Masel, R. I. *Chem. Mater.* **1989**, *1*, 406.
- (125) Strongin, D. R.; Comita, P. B. *J. Phys. Chem.* **1991**, *95*, 1329.
- (126) Bulanin, K. M.; Kong, M. J.; Pirolli, L.; Mathauser, A. T.; Teplyakov, A. V. *Surf. Sci.* **2003**, *542*, 167.
- (127) Irven, J. *J. Mater. Chem.* **2004**, *14*, 3071.
- (128) Jain, A.; Chi, K. M.; Hampden-Smith, M. J.; Kodas, T. T.; Farr, J. D.; Paffett, M. F. *J. Mater. Res.* **1992**, *7*, 261.
- (129) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Vac. Sci. Technol. A* **1988**, *6*, 1920.
- (130) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634.
- (131) Forbes, J. G.; Gellman, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 6277.
- (132) Kwon, J.; Dai, M.; Halls, M. D.; Langereis, E.; Chabal, Y. J.; Gordon, R. G. *J. Phys. Chem. C* **2009**, *113*, 654.
- (133) Dillon, A. C.; Ott, A. W.; Way, J. D.; George, S. M. *Surf. Sci.* **1995**, *322*, 230.
- (134) Elliott, S. D.; Scarel, G.; Wiemer, C.; Fanciulli, M.; Pavia, G. *Chem. Mater.* **2006**, *18*, 3764.
- (135) Ott, A. W.; Klaus, J. W.; Johnson, J. M.; George, S. M. *Thin Solid Films* **1997**, *292*, 135.
- (136) Frank, M. M.; Chabal, Y. J.; Wilk, G. D. *Appl. Phys. Lett.* **2003**, *82*, 4758.

- (137) Frank, M. M.; Wang, Y.; Ho, M. T.; Brewer, R. T.; Moumen, N.; Chabal, Y. J. *J. Electrochem. Soc.* **2007**, *154*, G44.
- (138) Lu, P.; Demirkan, K.; Opila, R. L.; Walker, A. V. *J. Phys. Chem. C* **2008**, *112*, 2091.
- (139) Rahtu, A.; Alaranta, T.; Ritala, M. *Langmuir* **2001**, *17*, 6506.
- (140) Wind, R. A.; George, S. M. *J. Phys. Chem. A* **2010**, *114*, 1281.
- (141) Lundin, W. V.; Sakharov, A. V.; Tsatsul'nikov, A. F.; Zavarin, E. E.; Besyul'kin, A. I.; Fomin, A. V.; Sizov, D. S. *Semiconductors* **2004**, *38*, 678.
- (142) van Hemmen, J. L.; Heil, S. B. S.; Klootwijk, J. H.; Roozeboom, F.; Hodson, C. J.; van de Sanden, M. C. M.; Kessels, W. M. M. *J. Electrochem. Soc.* **2007**, *154*, G165.
- (143) Blitz, J. P.; Diebel, R. E.; Deakyne, C. A.; Christensen, J. M.; Gun'ko, V. M. *J. Phys. Chem. B* **2005**, *109*, 5667.
- (144) Lu, H. L.; Chen, W.; Ding, S. J.; Xu, M.; Zhang, D. W.; Wang, L. K. *J. Phys.: Condens. Matter* **2005**, *17*, 7517.
- (145) Widjaja, Y.; Han, J. H.; Musgrave, C. B. *J. Phys. Chem. B* **2003**, *107*, 9319.
- (146) Kuramochi, H.; Cui, J.; Iwai, H.; Ozeki, M. *J. Vac. Sci. Technol. B* **2000**, *18*, 2072.
- (147) Lam, H. T.; Vohs, J. M. *Surf. Sci.* **1999**, *426*, 199.
- (148) Cao, X. P.; Hamers, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 10988.
- (149) Carman, A. J.; Zhang, L. H.; Liswood, J. L.; Casey, S. M. *J. Phys. Chem. B* **2003**, *107*, 5491.
- (150) Mui, C.; Wang, G. T.; Bent, S. F.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *114*, 10170.
- (151) Mui, C.; Han, J. H.; Wang, G. T.; Musgrave, C. B.; Bent, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 4027.
- (152) Cao, X. P.; Hamers, R. J. *J. Vac. Sci. Technol. B* **2002**, *20*, 1614.

- (153) Hill, J. J.; Aquino, A. A.; Mulcahy, C. P. A.; Harwood, N.; Jones, A. C.; Jones, T. S. *Surf. Sci.* **1995**, *340*, 49.
- (154) Zhu, X. Y.; White, J. M.; Creighton, J. R. *J. Vac. Sci. Technol. A* **1992**, *10*, 316.
- (155) Creighton, J. R.; Bansenauer, B. A.; Huett, T.; White, J. M. *J. Vac. Sci. Technol. A* **1993**, *11*, 876.
- (156) McElwee-White, L. *Dalton Trans.* **2006**, 5327.
- (157) Becker, J. S.; Suh, S.; Wang, S. L.; Gordon, R. G. *Chem. Mater.* **2003**, *15*, 2969.
- (158) Becker, J. S.; Gordon, R. G. *Appl. Phys. Lett.* **2003**, *82*, 2239.
- (159) Maeng, W. J.; Kim, H. *Electrochem. Solid-State Lett.* **2006**, *9*, G191.
- (160) Musschoot, J.; Xie, Q.; Deduytsche, D.; Van den Berghe, S.; Van Meirhaeghe, R. L.; Detavernier, C. *Microelectron. Eng.* **2009**, *86*, 72.
- (161) Hausmann, D. M.; Kim, E.; Becker, J.; Gordon, M. S. *Chem. Mater.* **2002**, *14*, 4350.
- (162) Kim, J. Y.; Seo, S.; Kim, D. Y.; Jeon, H.; Kim, Y. *J. Vac. Sci. Technol. A* **2004**, *22*, 8.
- (163) Kaloyeros, A. E.; Chen, X.; Lane, S.; Frisch, H. L.; Arkles, B. *J. Mater. Res.* **2000**, *15*, 2800.
- (164) Lim, B. K.; Park, H.-S.; See, A. K. H.; Liu, E. Z.; Wu, S. H. *J. Vac. Sci. Technol. B* **2002**, *20*, 2219.
- (165) Park, S.-G.; Kim, D.-H. *Jpn. J. Appl. Phys.* **2004**, *43*, 303.
- (166) Fix, R. M.; Gordon, M. S.; Hoffman, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 7833.
- (167) Fix, R. M.; Gordon, M. S.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138.
- (168) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1990**, *2*, 235.
- (169) Becker, J.; Kim, E.; Gordon, R. G. *Chem. Mater.* **2004**, *16*, 3497.

- (170) Horii, S.; Yamamoto, K.; Asai, M.; Miya, H.; Kaneko, I.; Ishihara, T.; Hayashi, S.; Niwa, M. *Jpn. J. Appl. Phys.* **2004**, *43*, 6963.
- (171) Kukli, K.; Pilvi, T.; Ritala, M.; Sajavaara, T.; Lu, J.; Leskela, M. *Thin Solid Films* **2005**, *491*, 328.
- (172) Liu, X.; Ramanathan, S.; Longdergan, A.; Srivastava, A.; Lee, E.; Seidel, T. E.; Barton, J. T.; Pang, D.; Gordon, R. G. *J. Electrochem. Soc.* **2005**, *152*, G213.
- (173) Wong, H.; Iwai, H. *Microelectron. Eng.* **2006**, *83*, 1867.
- (174) Cui, J.; Ozeki, M.; Ohashi, M. *Appl. Phys. Lett.* **1997**, *71*, 2659.
- (175) Dezelah, C. L.; El-Kadri, O. M.; Kukli, K.; Arstila, K.; Baird, R. J.; Lu, J.; Niinisto, L.; Winter, C. H. *J. Mater. Chem.* **2007**, *17*, 1109.
- (176) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.
- (177) Alen, P.; Vehkamäki, M.; Ritala, M.; Leskela, M. *J. Electrochem. Soc.* **2006**, *153*, G304.
- (178) Yokoyama, Y.; Zhu, S. Y.; Nakajima, A. *Jpn. J. Appl. Phys., Part 1* **2006**, *45*, 7091.
- (179) Aarik, J.; Aidla, A.; Uustare, T.; Ritala, M.; Leskela, M. *Appl. Surf. Sci.* **2000**, *161*, 385.
- (180) Ahn, K. H.; Park, Y. B.; Park, D. W. *Surf. Coat. Technol.* **2003**, *171*, 198.
- (181) Farm, E.; Kemell, M.; Ritala, M.; Leskela, M. *J. Phys. Chem. C* **2008**, *112*, 15791.
- (182) Weber, A.; Poeckelmann, R.; Klages, C. P. *Microelectron. Eng.* **1997**, *33*, 277.
- (183) Ritala, M.; Leskela, M.; Niinisto, L.; Haussalo, P. *Chem. Mater.* **1993**, *5*, 1174.
- (184) Putkonen, M.; Niinistö, L.; Fischer, R. *Top. Organomet. Chem.* **2005**, *9*, 125.
- (185) Matero, R.; Rahtu, A.; Ritala, M.; Leskela, M.; Sajavaara, T. *Thin Solid Films* **2000**, *368*, 1.

- (186) Fictorie, C. P.; Evans, J. F.; Gladfelter, W. L. *J. Vac. Sci. Technol. A* **1994**, *12*, 1108.
- (187) Karlsson, P. G.; Richter, J. H.; Blomquist, J.; Uvdal, P.; Grehk, T. M.; Sandell, A. *Surf. Sci.* **2007**, *601*, 1008.
- (188) Black, K.; Aspinall, H. C.; Jones, A. C.; Przybylak, K.; Bacsa, J.; Chalker, P. R.; Taylor, S.; Zhao, C. Z.; Elliott, S. D.; Zydor, A.; Heys, P. N. *J. Mater. Chem.* **2008**, *18*, 4561.
- (189) Codato, S.; Carta, G.; Rossetto, G.; Rizzi, G. A.; Zanella, P.; Scardi, P.; Leoni, M. *Chem. Vap. Deposition* **1999**, *5*, 159.
- (190) Niinisto, J.; Putkonen, M.; Niinisto, L. *Chem. Mater.* **2004**, *16*, 2953.
- (191) Niinisto, J.; Putkonen, M.; Niinisto, L.; Song, F. Q.; Williams, P.; Heys, P. N.; Odedra, R. *Chem. Mater.* **2007**, *19*, 3319.
- (192) Losurdo, M.; Giangregorio, M. M.; Capezzuto, P.; Bruno, G.; Malandrino, G.; Fragala, I. L.; Armelao, L.; Barreca, D.; Tondello, E. *J. Electrochem. Soc.* **2008**, *155*, G44.
- (193) No, S. Y.; Eom, D.; Hwang, C. S.; Kim, H. J. *J. Appl. Phys.* **2006**, *100*.
- (194) Elam, J. W.; Pellin, M. J.; Elliott, S. D.; Zydor, A.; Faia, M. C.; Hupp, J. T. *Appl. Phys. Lett.* **2007**, *91*.
- (195) Niinisto, J.; Rahtu, A.; Putkonen, M.; Ritala, M.; Leskela, M.; Niinisto, L. *Langmuir* **2005**, *21*, 7321.
- (196) Shin, H. K.; Chi, K. M.; Farkas, J.; Hampdensmith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424.
- (197) Becht, M.; Gerfin, T.; Dahmen, K.-H. *Chem. Mater.* **1993**, *5*, 137.
- (198) Ekerdt, J. G.; Sun, Y. M.; Szabo, A.; Szulczewski, G. J.; White, J. M. *Chem. Rev.* **1996**, *96*, 1499.
- (199) Barreca, D.; Gasparotto, A.; Maragno, C.; Tondello, E.; Bontempi, E.; Depero, L. E.; Sada, C. *Chem. Vap. Deposition* **2005**, *11*, 426.
- (200) Turnipseed, S. B.; Barkley, R. M.; Sievers, R. E. *Inorg. Chem.* **1991**, *30*, 1164.

- (201) Li, Z. W.; Rahtu, A.; Gordon, R. G. *J. Electrochem. Soc.* **2006**, *153*, C787.
- (202) Jones, A. C. *J. Mater. Chem.* **2002**, *12*, 2576.
- (203) Orimoto, Y.; Toyota, A.; Furuya, T.; Nakamura, H.; Uehara, M.; Yamashita, K.; Maeda, H. *Ind. Eng. Chem. Res.* **2009**, *48*, 3389.
- (204) Brazeau, A. L.; Barry, S. T. *Chem. Mater.* **2008**, *20*, 7287.
- (205) Lee, B.; Choi, K. J.; Hande, A.; Kim, M. J.; Wallace, R. M.; Kim, J.; Senzaki, Y.; Shenai, D.; Li, H.; Rousseau, M.; Suydam, J. *Microelectron. Eng.* **2009**, *86*, 272.
- (206) Li, H.; Farmer, D. B.; Gordon, R. G.; Lin, Y.; Vlassak, J. *J. Electrochem. Soc.* **2007**, *154*, D642.
- (207) Li, Z. W.; Barry, S. T.; Gordon, R. G. *Inorg. Chem.* **2005**, *44*, 1728.
- (208) Ma, Q.; Guo, H. S.; Gordon, R. G.; Zaera, F. *Chem. Mater.* **2010**, *22*, 352.
- (209) Paivasaari, J.; Dezelah, C. L.; Back, D.; El-Kaderi, H. M.; Heeg, M.; Putkonen, M.; Niinisto, L.; Winter, C. H. *J. Mater. Chem.* **2005**, *15*, 4224.
- (210) Lim, B. S.; Rahtu, A.; de Rouffignac, P.; Gordon, R. G. *Appl. Phys. Lett.* **2004**, *84*, 3957.
- (211) Li, J. Y.; Wu, J. P.; Zhou, C. G.; Han, B.; Lei, X. J.; Gordon, R.; Cheng, H. S. *Int. J. Quantum Chem.* **2009**, *109*, 756.
- (212) Wu, J. P.; Li, J. Y.; Zhou, C. G.; Lei, X. J.; Gaffney, T.; Norman, J. A. T.; Li, Z. W.; Gordon, R.; Cheng, H. S. *Organometallics* **2007**, *26*, 2803.
- (213) Heath, J. R. *Annu. Rev. Mater. Res.* **2009**, *39*, 1.
- (214) Lim, S. W.; Mo, R. T.; Pianetta, P. A.; Chidsey, C. E. D. *J. Electrochem. Soc.* **2001**, *148*, C16.
- (215) Leftwich, T. R.; Madachik, M. R.; Teplyakov, A. V. *J. Am. Chem. Soc.* **2008**, *130*, 16216.
- (216) Perrine, K. A.; Lin, J. M.; Teplyakov, A. V. *J. Phys. Chem. C* **2012**, *116*, 14431.

- (217) Brewer, R. T.; Ho, M. T.; Zhang, K. Z.; Goncharova, L. V.; Starodub, D. G.; Gustafsson, T.; Chabal, Y. J.; Moumen, N. *Appl. Phys. Lett.* **2004**, *85*, 3830.
- (218) Frank, M. M.; Chabal, Y. J.; Green, M. L.; Delabie, A.; Brijs, B.; Wilk, G. D.; Ho, M. Y.; da Rosa, E. B. O.; Baumvol, I. J. R.; Stedile, F. C. *Appl. Phys. Lett.* **2003**, *83*, 740.
- (219) Kim, D. H.; Baek, S. B.; Kim, Y. C. *Appl. Surf. Sci.* **2011**, *258*, 225.
- (220) Xie, Q.; Jiang, Y. L.; Detavernier, C.; Deduytsche, D.; Van Meirhaeghe, R. L.; Ru, G. P.; Li, B. Z.; Qu, X. P. *J. Appl. Phys.* **2007**, *102*, 6.
- (221) Miller, T.; Lin, J. M.; Pirolli, L.; Coquilleau, L.; Luharuka, R.; Teplyakov, A. V. *Thin Solid Films* **2012**, *522*, 193.
- (222) Perrine, K. A.; Rodriguez-Reyes, J. C. F.; Teplyakov, A. V. *J. Phys. Chem. C* **2011**, *115*, 15432.
- (223) Kim, D. H.; Baek, S. B.; Seo, H. I.; Kim, Y. C. *Appl. Surf. Sci.* **2011**, *257*, 6326.
- (224) Widjaja, Y.; Musgrave, C. B. *Surf. Sci.* **2000**, *469*, 9.
- (225) Widjaja, Y.; Musgrave, C. B. *J. Chem. Phys.* **2004**, *120*, 1555.
- (226) Chung, O. N.; Kim, H.; Chung, S.; Koo, J. Y. *Phys. Rev. B* **2006**, *73*, 033303.
- (227) Tian, F. Y.; Ni, C. Y.; Teplyakov, A. V. *Appl. Surf. Sci.* **2010**, *257*, 1314.
- (228) Perrine, K. A.; Skliar, D. B.; Willis, B. G.; Teplyakov, A. V. *Surf. Sci.* **2008**, *602*, 2222.
- (229) Ghosh, M. K.; Choi, C. H. *Chem. Phys. Lett.* **2006**, *426*, 365.
- (230) Thissen, P.; Peixoto, T.; Longo, R. C.; Peng, W. N.; Schmidt, W. G.; Cho, K. J.; Chabal, Y. J. *J. Am. Chem. Soc.* **2012**, *134*, 8869.
- (231) Tian, F. Y.; Yang, D.; Opila, R. L.; Teplyakov, A. V. *Appl. Surf. Sci.* **2012**, *258*, 3019.
- (232) Dai, M.; Wang, Y.; Kwon, J.; Halls, M. D.; Chabal, Y. J. *Nat. Mater.* **2009**, *8*, 825.

- (233) Wang, X. L.; Xu, X. *J. Phys. Chem. C* **2007**, *111*, 16974.
- (234) Yuan, S. L.; Zhang, Y.; Li, Y.; Xu, G. Y. *Colloids Surf. A* **2004**, *242*, 129.
- (235) Tian, F. Y.; Teplyakov, A. V. *Langmuir* **2013**, *29*, 13.
- (236) Owen, J. H. G. *J. Phys.: Condens. Matter* **2009**, *21*, 443001.
- (237) Kim, J. W.; Yeom, H. W. *Surf. Sci.* **2003**, *546*, L820.
- (238) Dunitz, J. D.; Taylor, R. *Chem. Eur. J.* **1997**, *3*, 89.
- (239) Warren, I. D.; Wilson, E. B. *J. Chem. Phys.* **1972**, *56*, 2137.
- (240) Buckton, K. S.; Azrak, R. G. *J. Chem. Phys.* **1970**, *52*, 5652.
- (241) Hausmann, D. M.; Kim, E.; Becker, J.; Gordon, R. G. *Chem. Mater.* **2002**, *14*, 4350.
- (242) Gordon, R. G.; Hausmann, D.; Kim, E.; Shepard, J. *Chem. Vap. Deposition* **2003**, *9*, 73.
- (243) Liu, X. Y.; Madix, R. J.; Friend, C. M. *Chem. Soc. Rev.* **2008**, *37*, 2243.
- (244) Karmakar, R.; Yun, S. Y.; Wang, K.-P.; Lee, D. *Org. Lett.* **2013**, *16*, 6.
- (245) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 1871.
- (246) Poater, A.; Falivene, L.; Cavallo, L.; Llobet, A.; Rodriguez, M.; Romero, I.; Sola, M. *Chem. Phys. Lett.* **2013**, *577*, 142.
- (247) Wu, Z.; Berhal, F.; Zhao, M.; Zhang, Z.; Ayad, T.; Ratovelomanana-Vidal, V. *ACS catal.* **2013**, *4*, 44.
- (248) Gao, D.; Canard, G.; Giorgi, M.; Vanloot, P.; Balaban, T. S. *Eur. J. Inorg. Chem.* **2014**, *2014*, 279.
- (249) Siewertsen, R.; Strube, F.; Mattay, J.; Renth, F.; Temps, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15699.
- (250) Perrier, A.; Maurel, F.; Jacquemin, D. *J. Phys. Chem. C* **2011**, *115*, 9193.

- (251) Ananikov, V. P.; Szilagyi, R.; Morokuma, K.; Musaev, D. G. *Organometallics* **2005**, *24*, 1938.
- (252) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Eur. J. Inorg. Chem.* **2007**, 5390.
- (253) Pophristic, V.; Goodman, L. *Nature* **2001**, *411*, 565.
- (254) Xiang, J.; Xie, Z.; Hoang, M.; Ng, D.; Zhang, K. *J. Membr. Sci.* **2014**, *465*, 34.
- (255) Saha, U.; Jaiswal, R.; Singh, J.; Goswami, T. *J. Nanopart. Res.* **2014**, *16*, 1.
- (256) Miller, T.; Teplyakov, A. V. *Langmuir* **2014**, *30*, 5105.
- (257) Gong, J.; Mullins, C. B. *Acc. Chem. Res.* **2009**, *42*, 1063.
- (258) Gao, J.; Teplyakov, A. V. *J. Catal.* **2013**, *300*, 163.
- (259) Mo, Y. *J. Org. Chem.* **2010**, *75*, 2733.
- (260) Sonnenberg, J.; Pichugin, D.; Coombs, N.; Morris, R. *Top. Catal.* **2013**, *56*, 1199.
- (261) Szöllösi, G.; Hermán, B.; Felföldi, K.; Fülöp, F.; Bartók, M. *Adv. Synth. Catal.* **2008**, *350*, 2804.
- (262) Kugler, T.; Ziegler, C.; Göpel, W. *Mater. Sci. Eng. B* **1996**, *37*, 112.
- (263) Bitzer, T.; Alkunshalie, T.; Richardson, N. V. *Surf. Sci.* **1996**, *368*, 202.
- (264) Rummel, R.-M.; Ziegler, C. *Surf. Sci.* **1998**, *418*, 303.
- (265) Cao, X.; Coulter, S. K.; Ellison, M. D.; Liu, H.; Liu, J.; Hamers, R. J. *J. Phys. Chem. B* **2001**, *105*, 3759.
- (266) Kim, A.; Filler, M. A.; Kim, S.; Bent, S. F. *J. Phys. Chem. B* **2005**, *109*, 19817.
- (267) Wang, G. T.; Mui, C.; Tannaci, J. F.; Filler, M. A.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. B* **2003**, *107*, 4982.
- (268) Widjaja, Y.; Mysinger, M. M.; Musgrave, C. B. *J. Phys. Chem. B* **2000**, *104*, 2527.

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Online Publication Date	Jan 7, 2013
Volume number	31
Issue number	2
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