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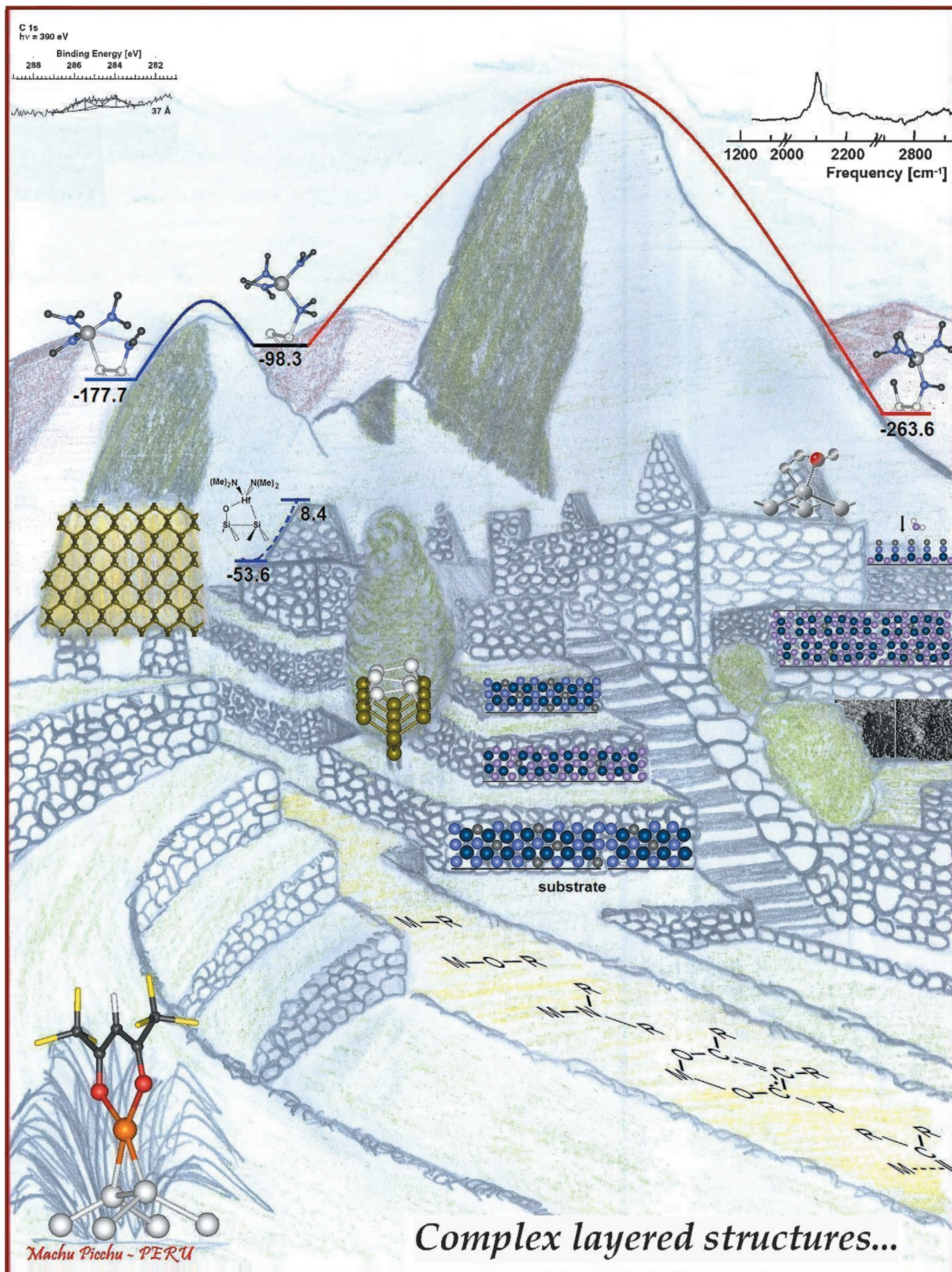

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Chemistry of Organometallic Compounds on Silicon: The First Step in Film Growth

Juan Carlos F. Rodríguez-Reyes and Andrew V. Teplyakov*[a]

Abstract: The continuous decrease in size of electronic devices has reached a critical point at which the molecular-level understanding of chemical processes is imperative. Metal-containing films, an important part of every circuit, are currently deposited from a myriad of organometallic compounds, in order to control the first stages of film growth and ultimately produce an atomically defined interface. This article outlines recent molecular-level investigations on reactions of organometallic compounds with silicon surfaces. The role of surface structure and chemical state is placed in a framework of future challenges and opportunities for applications in electronics.

Keywords: organometallic compounds • reaction mechanisms • silicon • surface chemistry • thin films

Introduction

In microelectronics, complex layered structures are deposited on a semiconductor surface to transmit intelligent electronic signals, forming an integrated circuit. A variety of materials, from conductors to insulators, are used as components to build these structures. Their properties and deposition procedures have long been established and as a result there has been continuous improvement to the performance of electronic devices over the last sixty years, when the development of the integrated circuit marked the blooming of the microelectronics age. However, as the size of layered structures approaches the atomic-level scale, a new set of problems have to be solved before substantial advances can be made.[1,2] With the introduction of organometallic compounds as film precursors, the future of microelectronics no longer depends only on the search for more efficient materials and techniques to deposit them. Formation of structures on the atomic scale requires an atomic- and molecular-level understanding of the reactions occurring during this process. The pressing need for the formation of sharp, well-defined interfaces is quickly rising and, in this context, surface chemistry will be decisive for the future development of microelectronics.[3] Far from being intended to be a comprehensive review of techniques and processes for thin film growth, this article is focused on the reactions of organometallic precursors with ordered, well-defined silicon surfaces. Since this article is focused on the chemical processes designed to deposit metal-containing films onto silicon substrates, the complexities of the hydrosilylation chemistry catalyzed by organometallics, described in detail by Buriak,[4] will be avoided. The first section briefly describes the most important deposition techniques and explains the need for organometallic compounds as film precursors. The second section introduces the ordered silicon surfaces that will be discussed in this article. The third section describes some of the recent advances toward the chemical understanding of reactions of organometallics on silicon surfaces, and the most relevant concepts involved in this field are highlighted in the fourth section. Finally, the challenges and future opportunities for surface chemistry of organometallic compounds are discussed in last section.

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The Deposition Techniques and Their Chemical Basis

There is a variety of ways to deposit thin films on surfaces. Deposition of atoms ejected from a solid source is known as physical vapor deposition (PVD), while deposition of gaseous compounds is known as chemical vapor deposition (CVD). In spite of the purity and high density obtained by PVD, this technique fails in producing uniform films on complex surface structures, such as deep trenches, or vias, used in microelectronics. In contrast, CVD produces uni-

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form films, but the use of somewhat complex volatile compounds often leads to impurities incorporated throughout the film and specifically at the interface with the silicon substrate. A number of deposition schemes designed for metal-containing film growth by CVD utilize metal halides and a co-dosing agent (e.g. $TiCl_4$ and NH_3 for TiN films), and corrosive by-products (halides and salts) often contaminate the film. In addition, temperatures needed for this type of CVD are usually substantially higher than those used in circuit processing. The use of organometallic precursors instead of halides proves to be more successful in certain aspects: lower temperatures are needed, corrosive compounds are absent in the resulting film, and ligands can be formed by elements that are expected to be present in the film, so no co-dosing agent may be needed. This variation of CVD (sometimes called metallorganic CVD, MOCVD) became an important technique for film growth, and is schematically shown in Figure 1. However, a new problem appeared: ligands are usually complex and leave other sources of contamination, such as carbon, nitrogen, oxygen, or fluorine, as was shown in several examples in our group.[5,6] Lower levels of contamination can be obtained if a co-dosing agent is used. One of the more recently developed methods, atomic layer deposition (ALD), consists of a series of self-limiting reactions with two compounds. Here, thin films are grown in a layer-by-layer fashion by alternating between the two precursors, as shown in Figure 1.[7–9] This technique allows the use of lower temperatures for decomposition and gains the feasibility of controlling the film thickness at the subnanometer scale (at a molecular level), but the films are usually not dense and contamination is still an issue.

These four techniques (PVD, CVD, MOCVD, and ALD) have received considerable attention lately, in order to solve the inherent problems that each technique possesses. However, as the film thickness approaches the atomic scale and high temperatures compromise the performance of smaller components, it seems that the future of thin film growth depends particularly on organometallic-based ALD and CVD. In this context, regardless of the deposition technique, specific surface chemistry defines the deposition process and in this sense a unified protocol for thin film deposition cannot possibly exist, as for every single deposition scheme, it will have to be analyzed separately. Although a large number of precursors have been tested, they usually can fall in one of the categories shown in Scheme 1, which covers all the compounds that will be discussed in this article. Some of the newest precursor molecules, such as amidinates and cyclic polyenes,[8,9] will not be discussed here because, to the best of our knowledge, their reactions with silicon surfaces have not yet been explored from the mechanistic perspective.

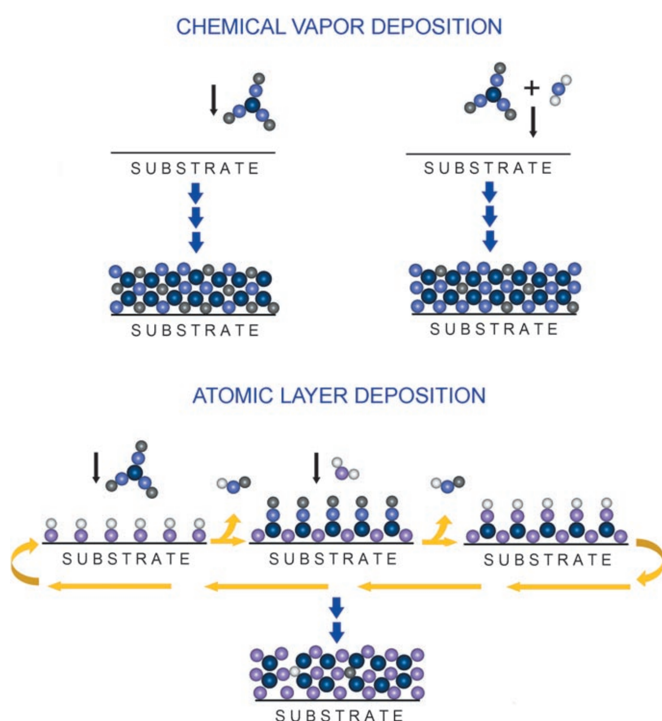
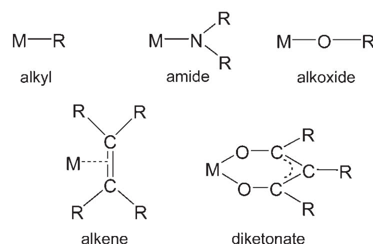


Figure 1. Organometallic-based deposition techniques, showing schematically the nature of the film produced. Dark blue: metal, grey: carbon, white: hydrogen, light blue and purple: non-metals (e.g. nitrogen and/or oxygen). Chemical vapor deposition (CVD) without a co-dosing agent (top left) produces films with high levels of carbon contamination. This is improved if a co-dosing agent is used (top right). In both cases, a dense film is deposited. Atomic layer deposition (ALD) consists of successive self-limiting cycles of deposition. Note that, in contrast to CVD, in ALD ligands do not have to consist of the elements expected in the final product. The film produced has lower levels of contamination than CVD films but it may have lower density as well.



Scheme 1. Most frequent types of organometallic precursors used for film deposition.

In industry, film deposition is normally performed under low pressures at temperatures above 500 K. In contrast, to investigate surface reactions relevant for this process, ultra-high vacuum (UHV) conditions (for which the background pressure is held below 10^{-8} torr or 10^{-11} atm) and lower temperatures are used. Extremely low pressures are necessary to avoid surface contamination, especially if the surface is highly reactive in air, as it is the case for silicon surfaces. In addition, most analytical techniques have to be surface sensitive in that they should be able to detect small quantities of surface species, the signals of which are much smaller than that of the surroundings. Since high temperatures result in the immediate formation of a film, low temperatures are often employed to investigate the first stages of adsorption and decomposition processes.

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Thus, a combination of these deposition schemes that is sufficiently robust for industrial applications with novel precursor molecules amenable to molecular-level control of the deposition processes is needed to address the formation of sharp and well-defined interfaces in the future.

Characteristics and Importance of Si(100) and Si(111) Surfaces

Silicon is one of the most important substrates in semiconductor industry. Therefore, its surface has been analyzed and studied extensively. In particular, surfaces with defined crystallographic orientations have been used not only in microelectronics, but also in such fields as molecular electronics, biological sensor design and surface self-assembly.[10–12] The most commonly used surface is Si(100), but the (111) orientation has received substantial attention as well, especially for reactions in aqueous environments. These surfaces are shown in Figure 2. In this article, we will be focusing mostly on the Si(100) structure, and readers interested in learning more details about the silicon surface structures and preparation procedures as well as in their chemical properties can refer to recent reviews on this topic.[13]

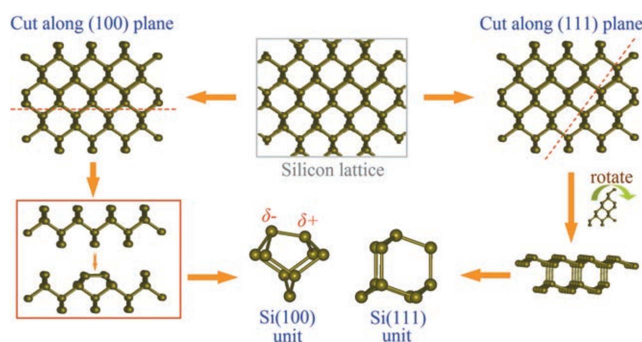

Figure 2. Structure of ordered silicon surfaces. The diamond-like silicon lattice can be cut along the (100) plane (left) or along the (111) plane (right). Since surface atoms in Si(100) are bonded to only two silicon atoms in the second layer, the 2×1 reconstruction allows the formation of a dimer structure. The buckling of a silicon dimer results in the acquisition of a zwitterionic character. Surface atoms in Si(111) are bound to three silicon atoms in the second layer, adopting a trigonal pyramidal structure. This surface undergoes a more complicated (7×7) reconstruction, which is described in reference [16]. The units shown for Si(100) and Si(111) contain nine and ten silicon atoms, respectively. If, with exception of the topmost atoms, the silicon atoms are terminated with hydrogen, the resulting clusters, Si_9H_{12} and $Si_{10}H_{16}$, are the smallest models for computational calculations.

While in the bulk each Si atom is bound to four other atoms, on a clean Si(100) surface the topmost silicon atoms are bonded to only two atoms located in the second layer. The coordination of the silicon surface atoms is increased by arranging them into dimers (known as the 2×1 reconstruction) as shown in Figure 2. The buckling of the dimers, observed in the same figure, creates a difference in electronic density between the dimer silicon atoms, which further stabilizes the surface. Thus, the Si(100)-2×1 surface can be described as an array of dimer rows, in which each dimer has a zwitterionic character,[14] although the π-bonding character has often been highlighted as well, especially when surface reactions with organic molecules are investigated.[11,12] Despite the stabilization, the Si(100)-2×1 surface still has an exceptionally high reactivity, allowing for the possibility of decorating the surface with diverse organic fragments or organic functionalization of semiconductor substrates.[11,12,13] Since surface reactions often take place on this surface without breaking the Si–Si dimer bond, a controlled organization of adsorbates on Si(100) can often be achieved. Thus, the Si(100)-2×1 surface has extended its realm to emerging areas such as molecular electronics and surface self-assembly, for which a high degree of order in the surface structure is imperative.[10,15] Clean Si(111) surfaces can also undergo substantial stabilization by a rather complex 7×7 reconstruction. This process is described in detail elsewhere.[13] If the desired reaction between the silicon substrate and an organometallic precursor molecule can utilize H-terminated silicon, both (100) and (111) surfaces can be hydrogenated, as described in a recent review by Mayne et al.[16]

Approaches to Understanding Organometallic Deposition

The urgent need for understanding the interactions of organometallic compounds with surfaces has motivated the development of important research directions. Several approaches were followed to mechanistically understand surface processes, including the studies of 1) gas-phase transformations, 2) ligand precursors on surfaces, 3) organometallic compounds on clean surfaces, and 4) organometallic compounds on functionalized surfaces. Since the last two approaches involve directly the organometallic–surface interaction, this article will focus mostly on these directions. Although the study of gas-phase reactions is important, as the occurrence of these reactions would produce a new set of molecules deposited on the surface (especially when the deposition is done at high temperatures), this approach is beyond the scope of this concept paper and will not be covered. It is important to highlight that an essential amount of research is done in the formation of metal-containing films, but focused in the development of strategies to improve the properties of the resulting film. Some important reviews centered on this aspect of thin-film research have been published recently.[7,17,18] In particular, surface pre-treatment as a means to reduce contamination at the interface has been investigated. For example, Brewer et al. has used NH_3 to prevent interfacial oxide formation[19] and Karlsson et al. have used O_2 to prevent interfacial carbon formation.[20]

Surface reactions of precursor ligands: In an attempt to modify the reactivity of silicon surface, organic functionalization reactions (such as adsorption of alkenes, alcohols, amines, and ketones) were vigorously investigated due to

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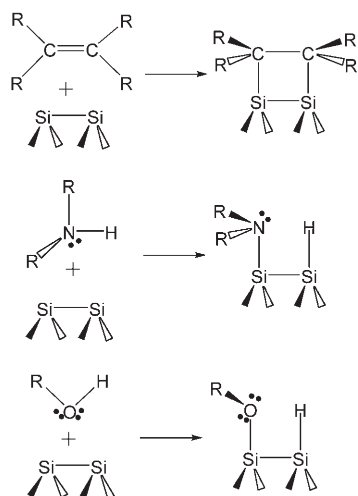
the potential applications of these surfaces in molecular electronics, surface self-assembly and other developing fields.[4,11,12,14,21] However, it was soon realized that the study of functionalization reactions can offer some insight into the molecular-level understanding of deposition processes (note that alcohols, amines, and diketones can be described as hydrogenated forms of alkoxide, amide, and diketonate ligands, respectively). Ligands are often present in the dosing gas in their hydrogenated forms, so understanding their reactivity is necessary to identify sources of film contamination. Examples of reactions of the Si(100) surface with alkenes, amines and alcohols are shown in Scheme 2.



Scheme 2. Reaction of the Si(100)-2×1 surface dimer with alkenes (top), amines (middle), and alcohols (bottom).

Alkenes are known to adsorb through surface cycloadditions. Cycloaddition chemistry is also characteristic of dienes and ketones.[11] At the same time, amines and alcohols were observed to adsorb dissociatively on the surface, through a mechanism that involves the formation of a dative bond through the lone pair of N or O, followed by dissociation of the molecule that allows the electronegative atom to retain its usual coordination. Diketones have shown a complex chemistry of adsorption, due to the multiple reaction pathways available due to keto–enol tautomerism. In the gas phase, the enolic form is more stable thermodynamically and can be condensed in multilayer films at cryogenic temperatures.[22,23] However, even considering only the enolic isomer, adsorption on the Si(100) surface is possible through [2+2] and [2+4] cycloadditions with the C=C double bond, through formation of dative bonds with the ketonic O, or through dissociative adsorption of the O−H group.

Even though these investigations were successful in offering pathways towards surface functionalization, a direct analogy between the chemistry of a ligand precursor and the organometallic compound was often difficult to achieve, because of the different reactivity of the hydrogenated organic ligands and corresponding organometallic compounds. We will show in the next section that, despite the difference in reactivity, there are indeed substantial parallels between the adsorption chemistry of an organometallic compound to that of its ligand. In addition, the recognition of spectroscopic signatures corresponding to the ligand by itself is useful in tracking its behavior as a part of the organometallic compound.

Reactions of organometallic compounds with bare silicon: Metal alkyls were one of the first groups of organometallic compounds for which the adsorption on silicon was investigated. A large number of these investigations has been published over the last two decades. Particular focus was placed on aluminum, due to the wide use of this metal as conducting material in the past decade. In addition, due to the relative simplicity of aluminum alkyls (AlR_3), some surface techniques not often available for the study of more complex organometallic compounds were used, as described below. Since tricoordinate aluminum alkyls are known to form dimers,[24] trimethylaluminum (TMA), dimethylaluminum hydride (DMAH) and diethylaluminum hydride (DEAH) were observed to adsorb as dimers at cryogenic temperatures.[25–27] In the case of TMA, heating to 300–400 K initiates dimer dissociation, but higher temperatures are needed to start the decomposition reactions. Vibrational spectroscopy shows that, between 400 and 600 K, $Al(CH_3)_3$ can undergo methane elimination to form surface-bound $CH_2{=}AlCH_3$ species. This species finally decomposes, first into Al and CH_X groups at 600 K, and after hydrogen desorption (700–900 K) into surface aluminum and carbon.[25] The description of this process shows the two likely pathways that are available for almost every organometallic compound on the surface: elimination of ligands versus their incorporation into the surface. As it was stated previously, carbon is one of the major sources of film contamination, and its presence is usually considered deleterious. In spite of the efficient methane elimination reported, TMA decomposes leaving significant amounts of carbon on the surface. A similar compound, $(CH_3)_2AlH$ or DMAH, follows the same trend as TMA: molecular adsorption at low temperatures, followed by decomposition at high temperatures.[26] This molecule is one of the few organometallic compounds that has been studied in detail using scanning tunneling microscopy, as shown in Figure 3. Mitsui et al. identified seven different configurations upon room temperature adsorption, all of them involving molecularly adsorbed DMAH. Upon heating above 550 K the molecule decomposes into Al, H, and CH_x groups. If the adsorption is performed on a surface at 400–575 K, the amount of carbon that is incorporated into the surface is lowered, possibly due to the pyrolysis of the molecules before they interact strongly with the surface. This exemplifies the role of gas-phase reactions in thin-film deposition. Our group has studied the chemistry of a similar organoaluminum hydride, $(CH_3CH_2)_2AlH$ (DEAH).[27] Interestingly, we found that after low-temperature adsorption, heating the surface to high temperatures leads to relatively carbon- and alumi-

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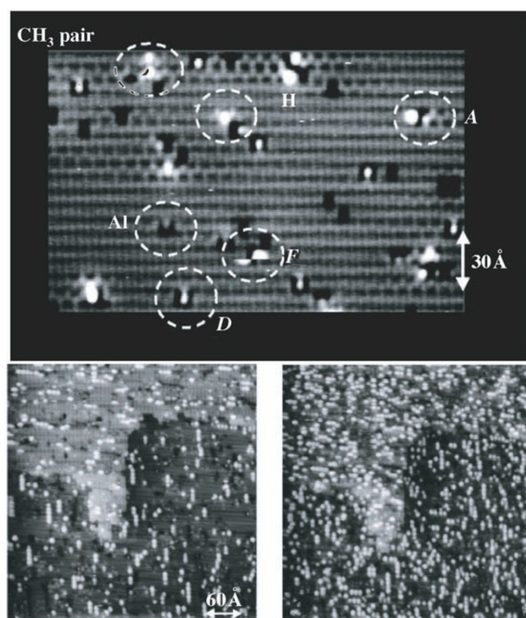
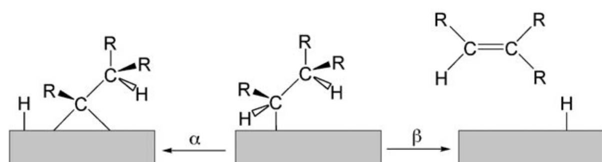


Figure 3. STM images for DMAH on Si(100). The top image shows surface species after room temperature adsorption followed by heating to 525 K. Only three out of seven initial configurations are still visible, and decomposition products (CH_3, H, Al) are detected. The two bottom images correspond to the adsorption of DMAH at 757 K, showing the difference between low exposures (left) and high exposures (right). Bright spots are aluminum dimers on the surface. Reprinted with permission from reference [26]. Copyright 2007 American Physical Society.

num-free surfaces. The spectroscopic detection of desorbing ethylene at 650 K is indicative of β-elimination,[24] which is favored over α-elimination. Both mechanisms are shown in Scheme 3. While β-elimination mechanism leads to a clean surface, α-elimination results in a carbon-rich surface.[3]



Scheme 3. Possibilities for alkyl decomposition: alpha and beta eliminations.

Although aluminum is an important conducting material for the semiconductor industry, currently the preferred conducting material is copper, and therefore several organocopper precursors have been analyzed. To deposit this metal, organocopper compounds with two different oxidation states are used. While Cu^{II} compounds generally have two diketonate ligands, Cu^{I} compounds consist of one diketonate ligand and one alkene, such as in (hexafluroacetylacetonato)(vinyltrimethylsilane)copper(I) [Cu(hfac)(vtms)]. Our group has studied the adsorption of this compound on Si-(100), and comparison of the spectroscopic features of this compound to those corresponding to its isolated ligands (Figure 4) offers important insight into its chemistry.[22,28,29] Infrared spectroscopy shows that upon adsorption of [Cu(hfac)(vtms)] at 100 K the characteristic features of both

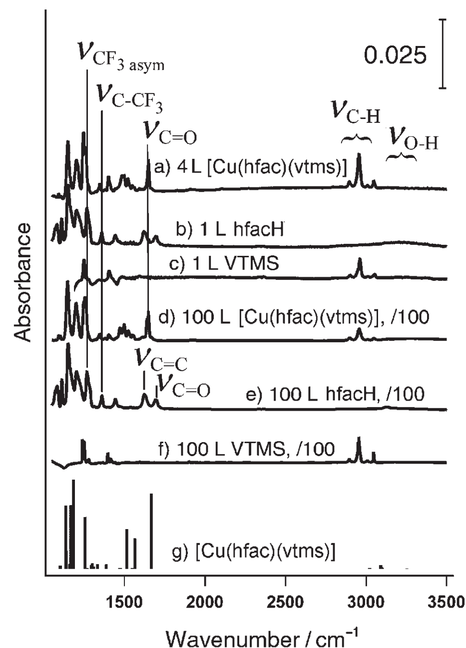


Figure 4. Infrared spectra corresponding to cryogenic adsorption of [Cu(hfac)(vtms)] and its ligand precursors, VTMS and hfacH at various exposures, expressed in Langmuirs (L, for which $1\,L = 10^{-6}$ torr$\,s^{-1}$). Characteristic features for each ligand are labeled, and they agree with the features of the organometallic compound. For comparison, predicted vibrational frequencies [B3LYP/6–311+G(d,p) level of theory] for [Cu-(hfac)(vtms)] in gas phase is included at the bottom. Reproduced with permission from reference [29]. Copyright 2007 Elsevier B. V.

ligands are observed. However, heating the surface to 200 K decreases the C–H features dramatically, which indicates that VTMS desorbs from the surface. Adsorption at room temperature shows no vibrational features corresponding to the VTMS ligand, indicating that it has desorbed. Recently, our group has used theoretical models based on density functional theory to study the stability of likely intermediates and also to compare predicted vibrational frequencies to experimental values. This approach was used to investigate the different possibilities for adsorption of the {Cu(hfac)} fragment, as shown in Figure 5. In this case, predicted vibrational features of structure I, containing a {$(Si)_2$Cu(hfac)} surface species, match closely with the experimental features. Dissociation of the metal–diketonate bonds leads to two possible structures, depending on the orientation of the ligand. While structure III is less stable than the original structure I, structure II is highly stable. However, vibrational features corresponding to this structure are not observed as major components of the IR spectrum. This indicates that cleavage of the Cu–vtms bond is a kinetically favored process, while the cleavage of the Cu–hfac bonds may require substantially higher temperatures. The significance of this work is that it demonstrates the “perfect” be-

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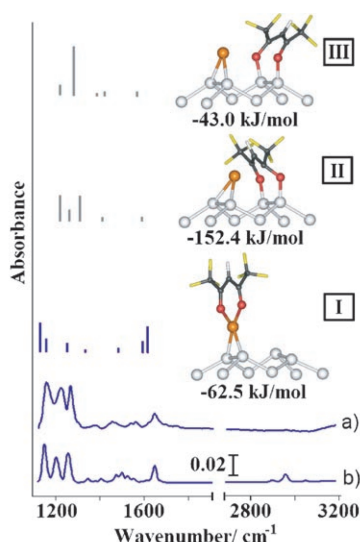

Figure 5. a) Infrared spectrum corresponding to the adsorption of [Cu(hfac)(vtms)] on Si(100) at 300 K. b) Infrared spectrum of a condensed layer of [Cu(hfac)(vtms)] at 100 K. Since no features corresponding to VTMS are observed, structures I, II, and III are considered as adsorption models and both their relative stability (defined as the stability of the structure less the energy of the free organometallic less the energy of the empty cluster plus the energy of free VTMS) and their vibrational frequencies are calculated at the B3LYP/LANL2DZ level of theory. White: silicon, orange: copper, red: oxygen, dark grey: carbon. Yellow and white sticks represent fluorine and hydrogen, respectively. Adapted from reference [29].

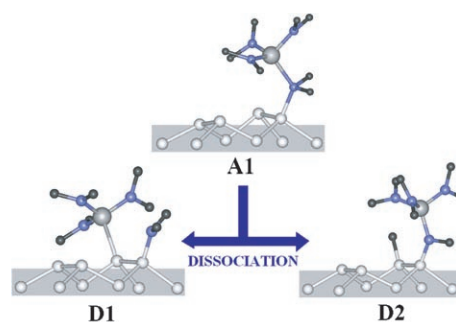

Figure 6. The amine-like interaction of TDMAT with the Si(100) surface. Upon molecular adsorption (A1), two dissociation pathways are possible: through scission of the N-Ti bond (D1) and through scission of the N−C bond (D2). White: silicon, light grey: titanium, blue: nitrogen, dark grey: carbon. Hydrogen terminations of methyl groups have been omitted for visualization purposes. Adapted from reference [30].

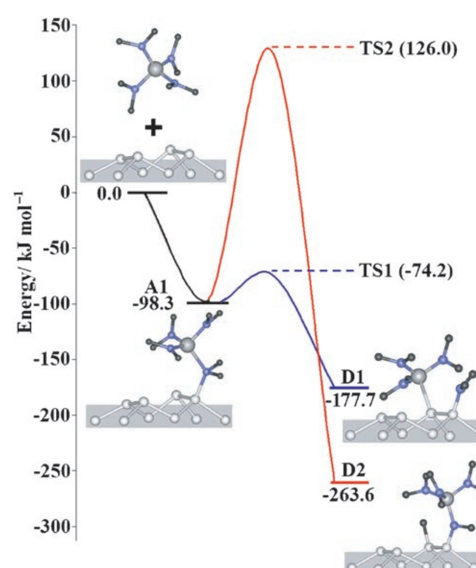

Figure 7. Potential-energy diagram corresponding to the possible dissociation pathways for TDMAT on Si(100), with respect to the isolated surface and TDMAT in gas phase. TS1 and TS2 are the transition states for the reactions A1→D1 and A1→D2, respectively. Density functional calculations done at the B3LYP/LANL2DZ level of theory. White: silicon, light grey: titanium, blue: nitrogen, dark grey: carbon. Hydrogen terminations of methyl groups have been omitted for visualization purposes. Adapted from reference [30].

havior of VTMS as a ligand: it stabilizes the Cu atom in the gas phase, but once it is on the surface, it desorbs cleanly, without any noticeable decomposition. Thus, the only source of contamination during the growth of Cu films from [Cu(hfac)(vtms)] is the diketonate ligand.

A similar combination of experimental and computational techniques has been recently used in our group to understand the chemistry of metal alkylamides on Si(100).[30] Metal alkylamides constitute an important group of precursors for metal nitride deposition. These materials are used as diffusion barriers between silicon and the conducting material such as aluminum or copper, because the metallic film deposited on silicon can degrade to metal silicides. We have recently proposed that, in analogy to amines, metal alkylamides adsorb molecularly through the nucleophilic attack of the nitrogen lone pair in one of the ligands onto a Si surface atom; this process can be followed by dissociation, as indicated in Figure 6. The alkylamide used was tetrakisdimethylamidotitanium ([Ti{N(CH$_3$)$_2$}$_4$], TDMAT)[30] and its amine-like behavior was analyzed using density functional calculations, as shown in Figure 7. Although the possibilities for dissociation through either N−Ti or N−C scission are thermodynamically feasible, as they produce structures that are more stable than the molecularly adsorbed state, there is a crucial difference between these two reaction pathways. While dissociation through N−Ti scission requires a predicted energy barrier of only 24 kJ mol^{-1} and the product is 178 kJ mol^{-1} more stable with respect to reactants, dissociation through N−C bond requires an energy barrier of 224 kJ mol^{-1} and the product is 264 kJ mol^{-1} more stable than reactants. This indicates that at temperatures substantial enough to overcome both kinetic barriers the most stable dissociation product (D2) is favored. However, at low temperatures, when the kinetic barrier of N−C scission is difficult to overcome, formation of structure D1 is preferred. The different conditions for these two dissociation pathways exemplify the presence of two regimes of adsorption: the kinetically controlled regime, for which the pathway with the lowest energy barrier is favored, and the thermodynamically controlled regime, for which the pathway that leads to

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the formation of the most stable product is preferred. Infrared spectroscopy was used to follow these possibilities, as summarized in Figure 8. In particular, a characteristic C–H stretch feature, referred to as the Bohlmann band, was analyzed. This feature is normally observed in amines at unusually low wavenumbers (below 2800 cm^{-1}) and is attributed to the interaction of the N lone pair with the C–H bond in an antiperiplanar position. This interaction weakens the C–H bond, therefore redshifting the C–H stretch vibration. For a physisorbed multilayer of TDMAT condensed at 100 K, the Bohlmann band is recorded at 2764 cm^{-1}, but adsorption at 300 K results in a shift of the Bohlmann band to 2779 cm^{-1}. We predicted the frequencies corresponding to adsorbed and dissociated states computationally, as shown in Figure 7. While the molecularly adsorbed state A1 shows a Bohlmann band at 2810 cm^{-1}, structure D1 shows two Bohlmann bands: a low-intensity one due to the Si–$N(CH_3)_2$ moiety and a more intense absorption, from the Si–Ti{$N(CH_3)_2$}$_3$ moiety. These two bands are located at 2762 and 2790 cm^{-1}, respectively. Structure D2 also exhibits two bands, but in this case the more intense one, corresponding to the intact ligands, is located at 2764 cm^{-1} and a less intense one, from the Si–$N(CH_3)$–Ti moiety is observed at 2790 cm^{-1}. The origin of these shifts has been explained in terms of the differences of the electron donation from N to the metallic center, since a higher donation to the metallic center (such as in structure A1 and D1) weakens the antiperiplanar interaction of the lone pair with the C–H bond. On the other hand, structure D2 shows no significant change in the metallic center (which is still bonded to four tricoordinate nitrogen atoms), and its predicted frequencies correlate closely with those for TDMAT in the gas phase. Further evidence of the N–Ti bond scission comes from the fact that the predicted core level energies (C1s) for structure D2 result in two signals, separated by approximately 1.0 eV. Such a difference would be easily observed in an XPS spectrum. However, experimental data show that the C1s feature has only one component.[25] Although structures D1 and A1 also have two predicted C1s features, they are separated by only 0.3 eV, which would not be sufficient to resolve them experimentally. This previous XPS study suggested that adsorption at room temperature might lead to other pathways of decomposition and that the formation of C=N bonds is possible at this temperature, while adsorption at 580 K produced Si–CH_x surface species.[31] Another set of XPS investigations has observed that the CH_x groups are incorporated into the film especially during the first stages of deposition.[32] These results confirm our theoretical prediction that high temperatures favor the scission of N–C bond. In addition, our vibrational spectroscopy data show a small ν_{Si-H} absorption feature upon room-temperature adsorption of TDMAT, which indicates that a minor channel involving C–H scission occurs and supports the chemical transformation of ligands at room temperature.[5]

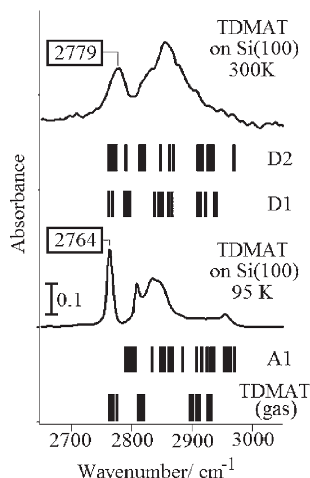

Figure 8. Infrared spectra corresponding to the adsorption of TDMAT on Si(100) at 100 K and at 300 K. The position of the Bohlmann band, originally at 2064 cm^{-1}, shifts toward higher wavenumbers when the reaction takes place at 300 K. Predicted spectra corresponding to TDMAT in gas phase, the molecularly adsorbed state A1 and both possible dissociation products (D1 and D2) are included for comparison. Density functional calculations of frequencies performed at the B3LYP/LANL2DZ level of theory. Adapted from reference [30].

Metal alkoxides are similar to alkylamides in the fact that both groups of precursors have ligands with elements bearing lone pairs. According to our proposed model, adsorption of metal alkoxides on Si(100) should take place through a nucleophilic attack of the oxygen lone pair onto one silicon atom, followed by dissociation. Most likely, both kinetically controlled (scission of oxygen–metal bond) and thermodynamic controlled (scission of oxygen–carbon bond) regimes are present. Several investigations have already been conducted in the thermodynamically controlled regime. For example, Karlsson et al. have followed the deposition of zirconium oxide from zirconium tetrabutoxide (ZBTO), [Zr{OC-$(CH_3)_3$}$_4$], on Si(100) and Si(111) at 673 K.[33] This investigation exemplifies the different reactivity of these silicon surfaces. Figure 9 shows that on both surfaces, the thinnest film (approximately 0.5 nm) shows significant differences in the nature of carbon species. While on the Si(100) surface the main components are Si–C-containing species, on Si(111) the carbon is present mostly as a part of butoxide ligands, and the amount of carbon incorporated onto the surface is minimal. It is worth highlighting the existing differences in reactivity of different silicon surfaces with organic and organometallic compounds, which has been reviewed recently.[13] Thus, the design of deposition schemes should take these differences into account.

Returning to the adsorption of ZTBO on the Si(100) surface, both the abundant presence of Si–C-containing species and the absence of O–C-containing species agree with what is expected in a thermodynamically controlled regime. The presence of methyl groups is observed only along the interface, suggesting that the products of ligand decomposition are stabilized by silicon atoms. Evidence of a kinetically controlled pathway will be obtained in the future by studying the low-temperature adsorption of metal alkoxides.

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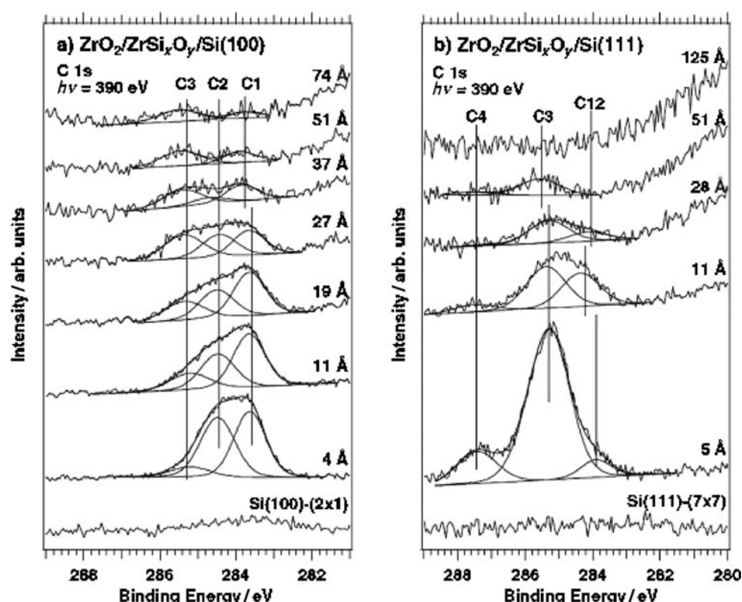

Figure 9. C1s XPS spectra corresponding to the adsorption of Zr[OC-$(CH_3)_3]_4$ (ZTBO) on Si(100) and on Si(111) surface. For each surface, the spectra corresponding to the clean surface and the thinnest film are the most informative for our purposes. C1 and C2: peaks associated with C attached to the silicon (Si−C and Si-C-C-Si). C3 and C4: CH_3 groups in butoxy ligands (C−CH_3 and C−O species). C12: silicon carbide. Reproduced with permission from reference [33]. Copyright 2007 Elsevier B. V.

The adsorption of a similar compound, titanium tetraisopropoxide, has been studied theoretically by Palma et al.[34] Their results suggest that the adsorption of this alkoxide on an unreconstructed Si(100) surface at 600 K occurs through scission of the C−H bond, forming a structure containing Si−H and Si−C surface bonds. This pathway is certainly possible at elevated temperatures, especially considering that steric hindrance may not be a problem during the scission of the C−H bond on the surface, as opposed to the O−C bond obstructed by a bulky isopropoxide ligand. However, computational studies of a more realistic, reconstructed substrate are necessary to make this assumption practical.

Reactions of organometallic compounds with functionalized surfaces: Since UHV conditions are not always available, passivation of the silicon surface, for example through hydrogenation, is often important to avoid undesirable reactions. Despite the fact that oxidation may sometimes be needed to form currently used silicon oxide, the passivation approach is very important for developing the chemistry for depositing materials with high dielectric constant (high-*k* dielectrics). These materials are called upon to replace SiO_2, as once the SiO_2 film reaches a thickness of only a few nanometers quantum mechanical tunneling across the film commences and the possibility of failure in several applications is present.[1,2] Among the most promising candidates are the oxides of aluminum and hafnium, which would be deposited on clean, passivated silicon surfaces. The simplest method of silicon-surface passivation is HF or fluoride etching at a variety of conditions.[16] This process removes oxide layers and terminates the surface atoms with hydrogen, conferring an extraordinary stability to the surface. Figure 10

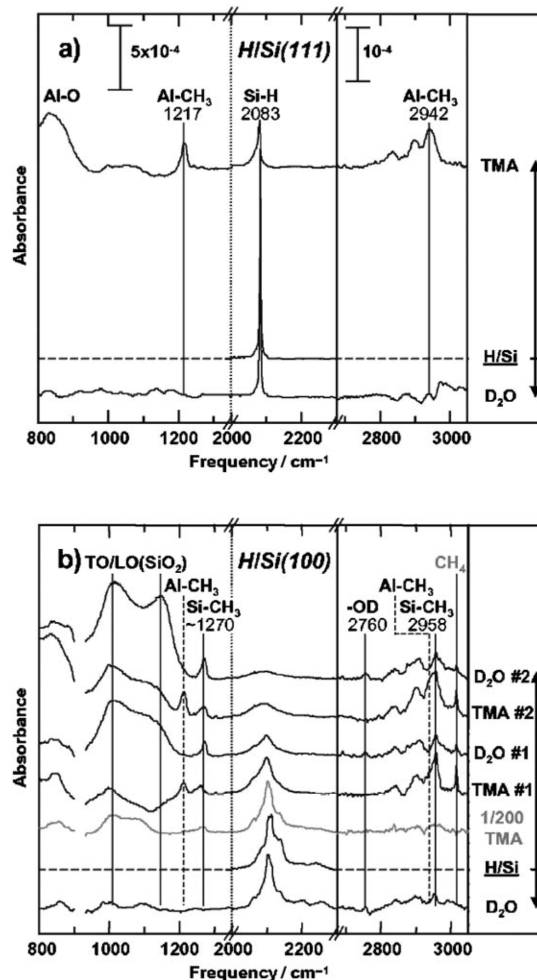

Figure 10. Infrared spectra showing hydrogen-terminated Si(100) and Si(111) before and after exposure to TMA. Notice that the bottom spectra show the Si−H vibrational signature obtained upon etching, which is narrower for Si(111) than for Si(100). Exposure of these surfaces to D_2O at 573 K does not change significantly the spectroscopic features. The effect of TMA on the vibrational features can be observed, particularly the signals attributed to Al-CH_3. Reproduced with permission from reference [35]. Copyright 2007 The American Institute of Physics.

shows infrared spectra corresponding to hydrogen-terminated Si(100) and Si(111).[35] The sharp Si−H signal for Si(111) indicates that there is only one type of hydrogenated species, (Si)H. On the Si(100) surface, fluoride etching results in the formation of (Si)H, $(Si)H_2$, and $(Si)H_3$, as can be deduced from the broad Si−H signal with several easily observable signature features.

Aluminum oxide can be deposited by ALD using $Al(CH_3)_3$ (TMA) and H_2O as precursors.[9] Frank et al. have reported the adsorption of TMA on both Si(100) and Si(111) hydrogenated surfaces.[35] The reaction, carried out at 573 K, was followed by infrared spectroscopy (Figure 10).

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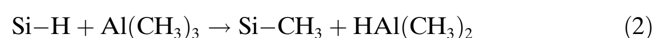
In both cases the main indication of the occurrence of a reaction is the decrease of intensity of the Si–H signal. However, while on the Si(111) methyl groups are observed to be attached to Al, on Si(100) some $Si-CH_3$ bonding is observed. As previously highlighted, this observation indicates that there is a significant difference in the reactivity of these surfaces. Figure 10 shows that, surprisingly, both hydrogenated surfaces are rather inert upon exposure to deuterated water at 573 K and, therefore, hydroxylation or oxidation of the surface is not a major reaction. However, applying a water dose to hydrogenated surfaces pre-covered with TMA leads to the formation of silicon oxides. This indicates that aluminum promotes the oxidation of the passivated surface. Two computational studies have shown the inertness of these surfaces towards water and the catalytic effect of aluminum for oxygen incorporation.[36,37] Halls et al. conducted a very thorough computational study using several cluster models simulating the Si(111) surface to investigate steric effects during the adsorption. Focusing on the single-surface-site model (Figure 2), three likely processes were investigated using this model [Eqs.: (1)–(3)].

$$Si{-}H + H_2O \rightarrow Si{-}OH + H_2 \qquad (1)$$



$$Si{-}H + Al(CH_3)_3 \rightarrow Si{-}CH_3 + HAl(CH_3)_2 \qquad (2)$$

$$Si{-}H + Al(CH_3)_3 \rightarrow Si{-}Al(CH_3)_2 + CH_4 \qquad (3)$$

Transition states corresponding to these reactions are shown in Figure 11, and the calculated barriers are 158.3, 140.2, and 118.7 $kJ\,mol^{-1}$, for reactions (1)–(3), respectively. The fact that reaction (3) is observed experimentally indicates that on a hydrogenated surface the reactions at 673 K are still under the kinetically controlled regime (notice that similar temperatures on clean silicon were sufficient to promote the thermodynamically controlled regime).[36] Theoretical studies using a Si(100) model have considered reactions (1) and (3), finding kinetic barriers of 176.1 and 98.7 $kJ\,mol^{-1}$, respectively, which agrees with experimental observations and the theoretical investigation mentioned above.[37] Hu et al. also considered the mechanism of hydroxylation, reaction (1), when a TMA molecule is close to the surface. In this case, the barrier for reaction (1) is 113.0 $kJ\,mol^{-1}$ (approximately 63 $kJ\,mol^{-1}$ lower than that in absence of TMA), offering theoretical support for the observation that aluminum catalyzes the hydroxylation and oxidation of the silicon surface.[37] Both theoretical studies agree that the products of reaction (1) are thermodynamically more favorable than the products of reactions (2) and (3), and therefore once the kinetic barriers are lowered, the preferred reaction will be the oxidation of the surface.

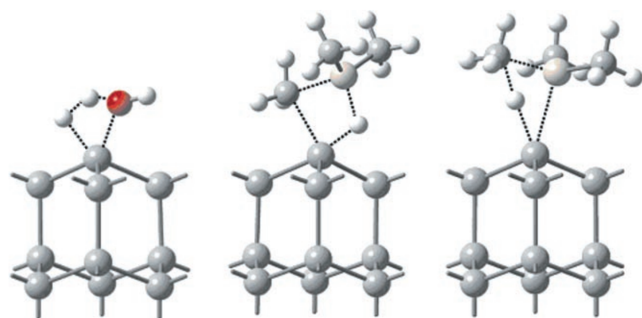


Figure 11. Transition states geometries for reactions (1)–(3), from left to right. The model surface represents a Si(111) site initially hydrogenated. The results of reactions (1)–(3) are (Si)OH, $(Si)CH_3$ and $(Si)Al(CH_3)_2$ surface species, respectively. Calculations done at the B3LYP/dzdp level of theory. Reproduced with permission from reference [36]. Copyright 2007 The American Chemical Society.

Hafnium oxide films deposited on hydrogen-terminated Si surfaces by ALD with metal alkylamides and oxygen-containing precursors have recently been investigated.[38,39] In particular, the adsorption of tetrakisdimethylamidohafnium, $[Hf\{N(CH_3)_2\}_4]$ or TDMAH, on a hydrogen terminated Si(100) surface has been studied by a combination of experimental and theoretical methods.[39] A room-temperature reaction is observed, but only to a limited extent and by using large doses of TDMAH. The ALD performed at 523 K with TDMAH and water shows that Si–H species are present on a surface even after 100 reaction cycles at this temperature. Both results agree well with the known inertness of the passivated surface. Still, the reaction is observed to occur to some extent, which can be attributed to contaminants that may facilitate the reaction. The proposed explanation for this is that remaining water from the fluoride solution or from an ALD step can be sufficient to hydroxylate/oxidize the surface. Thus, the inclusion of hydroxyl groups as a contaminant is important when model systems are studied. Kelly et al. have investigated two pathways for the interaction of TDMAH with a surface dimer terminated by –OH and –H groups, as shown in Figure 12.[39] In particular, the pathway involving elimination of dimethylamine through hydrogen loss of the surface hydroxyl group is found to be favorable. A second pathway, considering the combination of one ligand with surface Si–H species, results in a less favorable process, with a barrier of 34.3 $kJ\,mol^{-1}$. In contrast to this, hydrogen loss from a hydrogenated Si(100) surface (not shown) is predicted to have a barrier of 70.3 $kJ\,mol^{-1}$. However, the model employed in these calculations uses an ideal monohydride surface, which does not represent the realistic structure (as observed from Figure 10) as the Si(100) surface is a mixture of mono-, di-, and trihydrides and even small patches of hydrogen-terminated Si(111), as reviewed in reference [16].

Although the previous result was significant in demonstrating that impurities such as hydroxyl groups may have a significant impact in the possibilities for adsorption, the reactions under investigation by Kelly et al. can be placed into another framework: it represents the first ALD cycle for HfO_2 on Si(100). Upon H_2O adsorption on the clean Si(100) surface, this molecule dissociates to form (Si)OH and (Si)H moieties[14] (in analogy to alcohol adsorption in Scheme 2) and exposure of TDMAH to this surface completes the very first ALD cycle. From this point of view, these computational results show that the occurrence of this process should be

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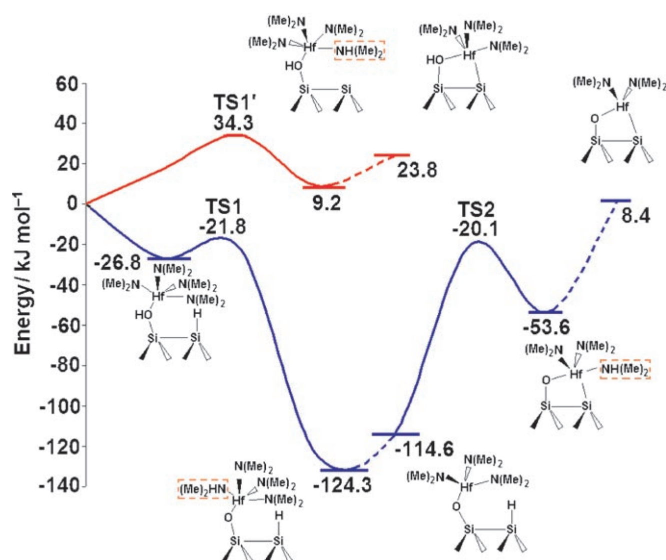

Figure 12. Potential-energy diagram corresponding to the interaction of TDMAH with a hydroxylated Si(100) surface. The pathway marked with a blue line is the most favorable and consist of the adsorption of TDMAH by scission of an O-H surface bond. The pathway marked with a red line is not favorable, and takes place through scission of the Si–H bond. Leaving dimethylamine molecules, $HN(CH_3)_2$, are shown in squares, and their elimination (dashed lines) leads to structures with a slightly decreased stability. Density functional calculation performed at the used B3LYP/LANL2DZ, 6–311++G(d,p) level of theory. Adapted from reference [39].

possible at low temperatures, since all the barriers are below rectants level. We have studied a similar possibility considering the adsorption of TDMAT on an NH_3-covered surface (NH_3 dissociates into (Si)NH_2 and (Si)H species,[14] similarly to amines in Scheme 2). Our spectroscopic results indicate that the prompt reaction of TDMAT with this functionalized surface occurs through elimination of one ligand after recombining with a hydrogen atom from the amine species, while the Si–H bonds seem to be unreactive.[40] Xu and Musgrave have anticipated the occurrence of this reaction by using hafnium dimethylamide instead of titanium dimethylamide.[41] Their calculations indicate that the process is thermodynamically favorable, but might present some kinetic restrictions, since a barrier of 66 kJ mol^{-1} was predicted.

As it has been discussed earlier, the reactions of organometallic compounds with functionalized surfaces are important because they reflect a more realistic environment, in which defects and impurities can affect the course of the deposition. The use of low temperatures and the incorporation of metal atoms into an ordered, functionalized surface is also possible: the recent work of Haran et al. in adsorption of TDMAT on a Si(100) surface covered by alkyltrochlorosilane self-assembled monolayers is an example of the promising use of organic/inorganic materials.[42] Thus, deposition techniques are being taken to a new level: they are meeting molecular electronics, a promising field that involves the use of molecules as devices for transmission of electronic signals.

Selected Concepts Related to Organometallic Deposition

Characteristics of the produced film: The quality of deposited films for the semiconductor industry usually depends on the following characteristics: purity, density, and structure of a well-defined interface. The purity of the film is crucial because small amounts of contaminants can lead to failure of its electronic properties. Usually, the most deleterious materials are halides (because of their corrosive character), carbon (because of its ability to increase resistivity), and oxygen (because most metals tend to form highly stable oxides). High density is desired to reach structural integrity of the bulk material and also to behave as an effective barrier against the introduction of contaminating agents. A well-defined interface is important, since as the thickness of deposited films decreases the interface between the substrate and the film has to conform to the same aspect ratio. A film with low levels of contamination, high density, and with a sharp interface is the ultimate goal for most deposition processes. Rather than a luxury, the molecular-level control of these processes, which requires a complete understanding of surface chemical reactions, is becoming a necessity as microelectronics approaches the challenging sub-nanometer scale.

Surface structure-reactivity relations: Although a complete comparison of surface reactivity of Si(100) and Si(111) was not performed here, some significant pieces of information have been recounted. While the reaction of $[Zr\{OC(CH_3)_3\}_4]$ with Si(100) leads to ligand decomposition and Si–C species formation, most ligands remain intact upon the same reaction on Si(111). In a similar manner, the interaction of $Al(CH_3)_3$ with hydrogen-terminated Si surfaces leads preferentially to the formation of Al–CH_3 groups on Si(111) and Si–CH_3 groups on Si(100). These examples indicate clearly that the Si(100) surface is more reactive than the Si(111) surface, with the difference in reactivity of both silicon surfaces due to the higher thermodynamic stability of Si(111). For this reason, Si(111) can form almost-perfect, atomically flat terraces, whereas Si(100) is atomically rougher, with a higher density of defect sites. Although a highly reactive surface is desired for lower temperature reaction conditions, reactive surfaces are also more easily contaminated. Methods to passivate/manipulate the surface have been developed and are improved continuously. Thus, the reactivity of the silicon surface can be tuned by selecting a crystallographic orientation and a surface treatment (such as organic functionalization, hydrogenation, or surface modification) prior to deposition. As more insight is gained into the techniques to control the structure and reactivity of the silicon surface, the technological applications of this versatile substrate will increase in the coming years.

Precursor reactivity: Despite the fact that contaminants may be incorporated from the surroundings, the primary source of detrimental elements is the precursors themselves, together with their possible decomposition products. Effects such

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as disproportionation, oligomerization, and other gas-phase decomposition reactions have to be considered prior to the inclusion of an organometallic compound as potential precursor for deposition. However, in addition, a significant source of contamination arises from surface mechanisms of ligand decomposition and therefore the nature of the ligand plays an important role in the formation of the deposited film. For this reason, choosing the appropriate organometallic precursor (i.e., the appropriate ligand) is of capital importance for the formation of a high-quality film. In particular, two ligands cited in this article have shown an interesting behavior: VTMS in [Cu(hfac)(vtms)] and ethyl ligand from DEAH. In the case of VTMS, its ability to desorb from the surface at low temperatures is exceptional for deposition of metallic films, for which it is desired that the totality of ligands desorbs from the surface. The possibility of β-elimination in DEAH allows the elimination of hydrocarbon chains, which is crucial for most deposition techniques due to the detrimental character of carbon. Drawbacks of these ligands include a poor stabilization of the metal ion (VTMS) and the excessive size of the precursor that diminish the saturation level of reactive sites on the surface (hydrocarbon-based ligands). Thus, it can be deduced that a detailed analysis of reaction pathways for organometallic compounds by themselves, as well as with surface sites, is fundamental to understanding and optimizing the deposition process. To optimize the desired reactions and block pathways that lead to contamination, a clear understanding of the conditions for every reaction is necessary.

Thermal regimes and their mechanisms: A didactic example of different pathways of adsorption and decomposition is shown in Figure 7 for the reaction of $[Ti\{N(CH_3)_2\}_4]$ with Si(100). At low temperatures, in the kinetically controlled regime, there are two mechanisms involved: adsorption through the formation of dative bonds and dissociation through metal–ligand scission. These mechanisms are barrierless or involve only a low barrier. At high temperatures, however, the favored mechanism is the decomposition of ligands and the formation of Si−C bonds, because these mechanisms drive the reaction toward more stable species. Although different types of organometallic precursors have been shown here, they seem to follow the same behavioral trend in these thermal regimes. Thus, it is possible to infer that carbon incorporation, the main drawback of the use of organometallic compounds, is inherent to the thermodynamically controlled regime (high temperatures), because the formation of Si−C species stabilizes the surface tremendously. An immediate conclusion is that carbon incorporation during most deposition processes can be lowered by lowering the deposition temperature to the kinetically controlled regime. The generally lower contamination levels obtained from ALD with respect to CVD can be explained as follows: while the low-temperature regime normally is self-limiting (in the sense that once the surface sites are occupied no further adsorption is possible), the high-temperature regime leads to the decomposition of ligands producing reactive sites on the surface to guarantee a continuous growth. Thus, ALD processes, for which the adsorption of compounds has to be self-limiting and the expected reaction occurs through scission of the metal–ligand bond, is a deposition process that falls into the kinetically controlled regime. On the other hand, a CVD process, for which the adsorption of compounds is expected to form reactive sites to ensure the continuous growth of the film, is predominantly a thermodynamically controlled process.

The boundaries of these two regimes depend on the nature of the surface and on the organometallic compounds used, as outlined in the two previous sections. Thus, by taking advantage of surface structure, design of organometallic compound, and appropriate thermal conditions, molecular-level control of the deposition process can indeed be possible.

Final Remarks

A complete understanding of the mechanisms of organometallic adsorption on silicon can lead to the development of strategies for controlling the nature of the surface structures. In the last decade, an increased interest in organic functionalization of surfaces marked a new direction in silicon surface research and, as was outlined above, the reactions of organometallic compounds with these functionalized surfaces have begun to receive substantial attention. In this context, the direct metal–organic functionalization of the silicon surface (that is, the controlled formation of metal-containing structures directly attached to the semiconductor surface) is a direction that is worth exploring. The high reactivity of the metal–ligand bond has been observed to result in structures in which the metal is directly attached to silicon; this offers interesting possibilities for the metallization of the surface at the atomic level.

The main aspiration of this concept paper is to convey the realization that, due to the inherent limitations of each deposition technique, the future hardly holds the promise for the development of a universal, near-perfect protocol for producing thin films. For each set of materials intended for a specific purpose, a suitable technique will be developed. Numerous materials are currently used and others are being developed, and for each one the reactions of precursors with the surface are to be tamed in order to achieve the desired molecular-level control. Once the reactions of organometallic compounds are understood on an ordered substrate, the insight obtained for this reaction can be applied to more complex surfaces, as demonstrated in our study of [Cu(hfac)(vtms)] on TiCN films.[6,43,44] Having entered the nanoscale age for film deposition and with molecular electronics emerging as a promising field to continue the improvement of electronic devices, chemistry is called upon to be the center of attention for its capacity to understand, design, and control the reactions involved in the formation of electronic devices at the atomic scale.

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