Reactions on the Silicon (100)-2x1 Surface:

Characterization of Oxygen Insertion and the Amino Acid Deposition using Electronic Structure Theory

Glen Allen Ferguson
Raghavachari Group
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Introduction:

The Silicon (100)-2x1 surface is one of the most technologically relevant materials. It is ubiquitous in the semiconductor industry as the preferred material for use in semiconductor devices. This popularity makes the surface an exciting and rich material for scientific investigation. The research in this report centers on two aspects of silicon surface chemistry. The first aspect looks at the initial reactions of oxygen with the silicon surface with the goal of improving the existing silicon technology. The second addresses the question of how biomolecules react with the surface to form novel materials.

Oxygen Insertion:

The growth of silicon oxide by wet-oxidation has recently been the subject of increasing interest[1]. One of the major driving forces behind this intense interest is the importance of silicon/silicon oxide interface to the semi-conductor industry. Silicon oxide has been widely used as the gate dielectric layer in many microelectronic devices, such as the field effect transistors. To improve these important devices, it is important to characterize and understand the formation of the silicon oxide monolayers on silicon surfaces at the microscopic level. Only then will the devices continue to achieve the criterion set by Moore's Law[2].

Moore's Law states the number of transistors per square inch on an integrated circuit doubles every year. In order to adhere to this ideal the feature size on semi-conductor devices must be reduced. One promising way to reduce the size of

microelectronics devices is to reduce the thickness of the dielectric layer. If the current trend continues future generations of semiconductors may require the dielectric layer to be a few molecular layers[3] thick. In order to further the use of silicon oxide as a viable dielectric layer, it is important to understand methods the mechanism of oxygen insertion into the silicon surface. For these reasons the Si/SiO_2 interface has been extensively studied both experimentally[4-6] and theoretically[7,8].

These studies show some interesting qualities of oxygen insertion reactions. The initial reaction of oxygen with the silicon surface during wet oxidation is known to occur in a multi-step process. The oxygen insertion occurs only after water decomposition on the clean Si(100)-(2x1) surface. This process has been thoroughly characterized in previous studies and is well understood[9]. Hybrid density-functional studies indicate the water disassociation and adsorption occur essentially without barrier[10]. The water disassociates homolytically to form a hydroxyl and monohydride which bind to a single silicon addimer. The resulting surface contains addimer silicon atoms which are all either bond to a hydrogen atom or a hydroxyl group. This step is followed by oxygen insertion into either the dimer bond or the backbond. It is this next reaction we are concerned with in the present study. Control of the reaction can be accomplished by either a thermal mechanism or by the generation of free radicals using atomic hydrogen.

Thermal control is accomplished by annealing the water exposed surface. The surface heating provides enough energy thermal energy to overcome the barrier for oxygen insertion. The thermodynamic stability of the oxygen insertion in the dimer and the backbond has been well characterized in several studies. These studies by

Stevanov and Raghavachari[11] and Teraishi *et al.*[12] indicate the dimer bond is more thermodynamically favorable then backbond, indicating the dimer insertion would be observed more then the backbond insertion. The studies further implied the thermodynamic stability of the backbond product increased after dimer bond insertion. The increased stability resulted in the formation of multiply oxygenated species. Since the creation of a homogenous surface composed of a singled oxygenated dimer species is the desired pathway, the multiple oxygen insertions are an obvious failing of the annealing process. An alternative method, which can alleviate these failings, is desirable in order to maintain the improvement of semi-conductor technology.

The second means is using chemical control which is has been accomplished by catalyzing the reaction at low temp using atomic hydrogen. The atomic hydrogen drives the reaction of the hydroxyl group with the silicon surface by creating free radicals on the surface followed by a surface reconstruction. In recent studies by Weldon *et al*[13-14] surface infrared spectroscopy as well as density functional cluster calculations s were used to characterize the annealed and atomic hydrogen exposed surfaces. There was an excellent agreement between the theoretical and experimental results[7]. The study indicates a preference for dimer bond insertion over backbond insertion, observed experimentally using external transmission infrared geometry[12]. While this observation is significant, it did not provide a mechanism for the initial oxygen insertion but gives significant insight as to the possible mechanism.

Since the microscopic mechanism of chemically controlled oxygen absorption has not yet been demonstrated we proposed in this study we to examine the initial atomic hydrogen-controlled oxygen insertion of wet-oxidized silicon using

a density functional theory. Each of the possible paths was mapped in order to demonstrate the possible methods of oxygen insertion. The most probable pathway was then compared to the experimental data and other theoretical studies. Finally a presentation of the most probable pathway as determined by the energy barrier was determined.

Peptide Deposition:

In recent years a great deal of reach has been focused on nanoscale phenomena. Some reasons for this are increases in technology allowing more accurate measurements as well as the increase in computer speeds which have allowed larger theoretical calculations to be performed. These advances can be readily seen in the research on the silicon surface. More recently research on the silicon surface has begun to examine other areas beyond inorganic modification of the silicon surfaces.

One important area is organic modification of silicon surfaces. This area has been the subject of recent attention[16-22]. Some possible uses for the novel materials created by organic modification are improved microelectronic devices, DNA Chips, and chemical sensors[23-25]. The formation of these organic monolayers can provide novel properties, which have the possibility of leading to advances in silicon surface based technologies. One example is the use of organic molecules to replace existing dielectric materials in microprocessors[26]. Most of the recent research has focused on the fundamentals of bonding organic molecules to the surface and the organization of organic monolayers. Following is an overview of the areas being examined to date.

The different types of research on organic modification of silicon surfaces are in three distinct categories[19]. Organic modification has focused on modification to the clean silicon surface under ultrahigh vacuum conditions (UHV)[26-31], modification of hydrogen terminated surfaces under either UHV conditions or wet conditions[17,22,25,32,33], and halogenated surfaces with under either UHV conditions or wet conditions[34-36]. Research conducted using the clean surface is restricted to UHV due to the large number of dangling bonds present on the unpassivated silicon surface. These dangling bonds result in an extremely reactive surface on which to carry out organic functionalization. The problem with such a surface is that it is difficult to prepare under conditions which are favorable for organic molecules. The use of hydrogen-terminated surfaces is attractive due to the excellent stability of the surface. In order to make the surface reactive to organic modification under UHV conditions several different strategies have been employed. It is possible to selectively remove a terminating hydrogen using an STM tip [22,37] or UV light. The vacancy results in a surface dangling bond that will react with organic molecules in much the same way as organosilanes. Free radicals reactions have also been implicated in the chain reactions of some organic molecules along rows of bonds on the Si(001) surface [37-40]. The wet chemistry has focused on the use of metallic catalysts in organic solutions. The final area of halogenation-terminated surfaces has not been exploited to any great extent. Hammers and coworkers[36] have carried out modification of iodine terminated surfaces using UV light. The reactions of chlorinated surfaces have centered on Grignard and alkyllithium reactions[22]. Each of these areas presents interesting

challenges to researchers. A different area of research focuses not on what type of surface is being reacted but the type of molecule being attached to the surface.

The current focus is surface modification is to react the surface with a small organic molecules or long alkyl chains then functionalize either the alkyl groups or organic molecules respectively. The attachment of biomolecules to the silicon surface is a new and promising area to study in organic functionalization of silicon. These molecules provide interesting challenges to chemists. They can have more then one functional group to react with the surface, competing reactions are possible, and the molecules can have many different conformers to react with the surface. Recent work by Qu and coworkers[41] was focused on elucidating these different reactions for glycine reaction with a clean Si(100)-2x1, using electronic structure theory. The study examined a single unit cell reaction to determine the competition between functional groups and a double unit cell to examine the cross dimer reactions. The results of the study indicated that silicon-oxygen bond formation was favored over the silicon-nitrogen or silicon-carbon bond formation[41]. Another study by Schmidt and coworkers[42-43] focused on the nucleic acid, uracil. These results show promise for further exploration of organic modification of silicon surfaces.

In this report we have examined the analogous backbone reactions of glycine, cystine, tyrosine, and serine. The reactions of the peptide backbones with the silicon surface are investigated using Hartree-Fock theory to compare the reactions of the various peptides with the surface.

Computational Details:

Oxygen Insertion:

The cluster model used in this study was developed by Stefanov and Raghavachari[15] and has been shown to give reasonable results. A cluster model was chosen for this study since they have been shown to give reasonably accurate results but keep the computational cost to an affordable level.

The $Si_9H_{12}HOH$ model was representative of an excised reaction center for oxygen insertion on the Si(100)-(2x1) surface. The cluster was layered to contain the surface reconstruction of a silicon dimer adatoms, and the first through third layers. The layers are composed of four silicon atoms, two silicon atoms and one silicon atom for the first through third layers respectively. The model was further refined to include terminating hydrogen atoms at the sites of unsaturated valences (dangling bonds). By terminated the sites with hydrogen atoms any problems of excess charge or spin were avoided. Additionally the termination maintains the sp^3 hybridization of the silicon atoms, which is the hybridization present in the extended surface. The hydrogen termination does much to ensure the cluster is close to the surface.

The final technique used to avoid unphysical relaxations was the constraint of the third and fourth layer silicon and hydrogen atoms. This technique holds the constrained atoms ridged during the optimization, while allowing the remaining atoms of the cluster to relax.

This study examined the difference in the initial oxygen insertion reaction in the silicon surface when a dangling bond is formed using atomic hydrogen. Only the

pathways that can lead to the experimentally products were examined. The structures of the reacting structures, the product structures, and the transition states were used to determine the kinetics of the initial reactions. The four possible sites for an atomic hydrogen to react and form a dangling bond were examined to determine what products would predominate.

The energetics of the reactions were determined using the gradient corrected density functional calculations using B3LYP method[45]. The B3LYP method combines Becke's gradient corrected 3-parameter exchange functional[45] with the Lee, Yang, and Parr electron correlation functional[46]. The basis sets used on the unconstrained atoms was the 6-31G** [47] and the basis set used on the constrained atoms was the 6-31G[47]. This level of theory has been shown in the past to give reasonable results[14]. The initial reaction were examined with second order Møller-Plessant perturbation theory with CCSD(T) single point calculations to ensure the validity of the B3LYP results. In addition calibration was performed using a model system with the QCISD(T) and 6-31+G*[47]basis set to find any necessary correction factors to the B3LYP energies.

Transition state optimizations were used to locate the transition states for each reaction. Difficult structures were determined with the using QST2, QST3, or relaxed potential energy surface scans. The resulting transition states were then optimized.

To determine if the transition states were first-order saddle points second-order differentiation of the energy minima, with respect to the nuclear coordinates, were used. These calculations also verified structures were at a minimum on the

potential energy surface and generated the zero-point correction factor to the correlation energy.

Animations of the frequencies were used to determine if the structures were intermediate between the reacting and product structures and IRC was also used to confirm transition states when the animation of the imaginary frequencies where not perfectly clear. All calculations were performed with GAUSSIAN-03[45] suite of programs.

The relative energies were calculated by computing the energy difference of the optimized reacting structures and the energy of the transition state or products. The resulting difference between the relative energy of the transition state and reacting structure was classified as the energy barrier (E_a).

Peptide Deposition:

The same Si_9H_{12} cluster model was used to the reactions on the amino acids. Identical constraints were included to mimic the extended surface.

The reactions of the amino acid backbone and the silicon surface were characterized using enthalpies. The three reactions examined were that of the amine group with the surface to form a silicon nitrogen bond, the reaction of the carboxyl group with the surface to form a silicon oxygen bond and reaction of the carboxyl carbon and oxygen to form the 2 + 2 cycloaddition product.

The energetics of the reactions were determined using the B3LYP gradient corrected density functional[46] with the 6-31G[48] basis set. The B3LYP method

combines Becke's gradient corrected 3-parameter exchange functional[46] with the Lee, Yang, and Parr electron correlation functional[47].

All transition states were located by optimization followed by calculation of second derivatives. The single imaginary frequencies were visualized to determine if they corresponded to the correct transition state. No ambiguous reactions were observed. To determine if the transition states were first-order saddle points second-order differentiation of the energy minima, with respect to the nuclear coordinates, were used. All reported energy values are zero-point corrected.. All calculations were performed with GAUSSIAN-03[45] suite of programs.

The relative energies were calculated by computing the energy difference of the optimized reacting structures and the energy of the reacting complex, the transition state and products respectively. The differences were used as the reaction barriers without entropic or dynamic correction.

Results and Discussion:

Oxygen Insertion:

Oxygen insertion into the wet-oxidized silicon (100)-(2x1) surface can follow several paths which are not equal in utility. The two possible pathways are the insertion of oxygen into the backbond or dimer bond on the silicon surface. The pathway for insertion into the dimer bond can proceed with only one possible product while insertion into the backbond has two equivalent paths. An inhomogeneous surface will result in the need to increase the number silicon oxide layers to achieve a viable dielectric layer. If the initial oxygen insertion is isolated to reactions involving only the dimer bond will result in a homogenous surface. Therefore dimer insertion is preferred of the silicon oxide layer must be precisely controlled.

Previous studies of the exposure of wet oxidized Si(100)-(2x1) to atomic hydrogen the oxygen insertion by Weldon *et al.*[13-14] This infrared spectroscopy measurement helped to elucidate several important aspects of the reaction mechanism. The oxygen insertion was observed to primarily occur in the dimer bond. This data indicates oxygen bridging of the monohydride silicon dimer atoms. Other observed products included single and double oxygen insertion into the backbonds of the silicon dimer atoms. The relative intensity of the different vibrational modes indicates a preference for insertion into the dimer bond. Furthermore the authors suggest a reasonable mechanism for preferential insertion into the dimer bond[12]. The suggested mechanism was the initial abstraction of the hydroxyl hydrogen followed by the preferential insertion of the oxygen radical into the dimer bond. This mechanism

requires the breaking of the oxygen-hydrogen bond creating a dangling bond. The dangling bond is then free to insert into either the dimer bond of the backbond. The next step was the insertion of the oxygen into the dimer bond creating a dangling bond on the dimer silicon which was formerly attached to the hydroxyl group. The final step is the passivation of the dangling bond with free atomic hydrogen. The logic behind this proposed mechanism assumes that the activation barrier for dimer bond insertion must be lower then for backbond insertion. While this is a very sound mechanism it is only one of several possible mechanisms which lead to dimer hydrogen insertion.

Other novel mechanisms not before proposed include abstraction of the hydrogen atoms from the silicon dimer atom resulting in a dangling bond which forms on the surface. This mechanism can also lead to the dimer insertion product and would be equally likely if the reaction is controlled by the kinetics of oxygen insertion or by the thermodynamic stability of the products. The second novel mechanism that can lead from this path is the transfer of the hydroxyl hydrogen to the dimer silicon dangling bond. This hydrogen-hopping mechanism results in the dangling bond on the oxygen atom. The reaction can then proceed by the above stated mechanism. Therefore the hopping mechanism is a bridge between the mechanisms that result in a dangling bond on the oxygen or a dangling bond on the hydrogen. There are several other possible mechanisms that need to be addressed for completeness.

Two other possible pathways are the elimination of water and the formation of dihydride silicon atoms. The first of these pathways begins with atomic hydrogen

attacking the hydroxyl group, forming an oxygen hydrogen bond. The mechanism finishes with elimination of water from the surface with passivation of the dangling bonds by atomic hydrogen. The second reaction is the attack of the dimer silicon by atomic hydrogen. The reaction then completes a series of hops to form the final structure. Both of these mechanisms would be possible side reactions, but the do not agree well with the experimental observations. They may be possible side reactions that occur at a much slower rate then the dominate reactions.

In transition state theory it would be expected that at low temperature the above described reaction mechanisms would be controlled by there respective kinetic barrier as opposed to the thermal stability. In out present work we seek to explain the why the single oxidized coupled monohydride predominates under condition of atomic hydrogen exposure, by examining the reaction barrier for the above reactions.

The discussion is organized in the following manner. The different pathways will all be discussed in detail and potential energy surfaces will be presented. The different pathways are then discussed in relation to one another and the competing pathways are compared in detail. Finally, the mechanism best supported by the data is presented and compared to the thermodynamic pathway of insertion.

Oxygen Insertion Reaction Paths

Water Elimination Reaction

A possible side reaction of hydrogen attack at the hydroxyl oxygen was explored in order to ensure it will not seriously compete with the primary reaction. The starting structure for the reaction is the wet-oxidized silicon cluster, $Si_9H_{13}OH$, and atomic hydrogen. The reaction proceeds in a two step mechanism. The first mechanism is the concerted breaking of the silicon oxygen bond and the formation of a hydrogen oxygen bond. The second step in the mechanism is the passivation of the dangling bond on the silicon to form a very stable passivated Si(100)-2x1 surface. The reaction path is shown in figure 1 with the energetics in table 1. The partially formed and partially broken bonds in the transition states are shown with dashed lines. The first water forming step of the reaction is 0.58 eV higher then the separated reacting structures, showing a significant energy barrier to the reaction. The resulting separated products are -.0375 eV lower in energy then the separated reactants. Passivation then occurs without barrier to form the final product. The overall reaction is found to be exothermic by -3.875 eV. Comparison with the other reacting structures shows the reaction is the least exothermic with an initial reaction barrier 0.34 eV higher then the next highest barrier. The reaction is believed to occur infrequently in comparison to the other investigated pathways.

Hydroxyl Hydrogen Abstraction

The reaction of the atomic hydrogen with the hydroxyl oxygen was examined as a potential pathway for oxygen insertion into the dimer and backbonds. Wet oxidized silicon (100)-2x1, modeled using the $Si_9H_{13}OH$ cluster model was used as the starting structure. The reaction consists of a multi-step process in which the hydroxyl oxygen is abstracted producing a free radical. The pathway then has a bifurcation into two separate paths. One path leads to the formation of the dimer inserted oxygen product. The second path results in an oxygen insertion in the backbond. The potential energy surface is shown in figure 2 with the energetics reported in table 1.

The abstraction of the hydroxyl hydrogen is the first step in the reaction path. The reaction proceeds with a bond formation between the hydroxyl hydrogen and the atomic hydrogen and a breaking of the bond between the oxygen and the hydroxyl hydrogen, forming atomic hydrogen and a dangling bond on the oxygen. The kinetic barrier is 0.24 eV higher then the enthalpy of the reacting structures and the products are exothermic by -.0.24 eV.

The reaction then has the possibility of two different competing reactions. Oxygen is free to either insert into the dimer bond or one of two back bonds. The dimer insertion pathway is a concerted mechanism in which the oxygen with the dangling bond breaks the silicon-silicon dimer bond creating a dangling bond on one of the dimer silicon atoms. The reaction is -0.10 eV lower then the combined reacting structures and 0.13 eV higher then the hydrogen abstraction products. Overall the reaction is very exothermic compared to the combined reacting structures by -2.24 eV.

The insertion reaction path is completed when the dangling bond on the silicon combines with atomic hydrogen without an activation barrier. The final structure is very exothermic being -5.84 eV lower in energy then the combined reacting structures and -3.61 eV lower then the dimer insertion product.

The second possible reaction is the insertion of the oxygen into the dimer back bond. While two possibilities exist the symmetric nature of the molecule indicates both paths will be identical. The backbond insertion occurs when the dangling bond on the oxygen reacts with a second layer silicon atom to form an oxygen bridge between the first and second rows. The transition is -0.10 eV lower then the combined reaction structures and 0.13 eV higher then the reacting structure. The final structure is -5.41 eV lower then the combined reacting structures and -3.58 eV lower then the products of the insertion reaction.

The two reactions are very similar from an energetic standpoint. The reaction relative enthalpies were calculated to be extremely close for either insertion reaction. The only difference in the calculated profile of the potential energy surface is the greater stability of the dimer insertion product, with both the radical products and the final products differing by 0.3 eV.

The initial hydrogen abstraction from the hydroxyl oxygen was investigated with MP2 in order to examine the appropriateness of B3LYP for the hydrogen abstraction reaction. The MP2 energy of 1.01 eV is 0.77 eV higher then the B3LYP energies. A CCSD(T) single point was carried out giving an energy of 1.03 eV, which is not a significant difference from the MP2 energies. The large difference in the MP2 and B3LYP energies indicates a significant failing of the density functional theory for

this class of reactions. While it is now necessary to reoptimize the entire reaction path with MP2 sufficient time was not available before the publication of this report.

Dimer Hydrogen Attack

Hydroxyl Hydrogen Abstraction

The reaction of the atomic hydrogen with the monohydride silicon was examined. The wet oxidized Si(100)-2x1, modeled using the $Si_9H_{13}OH$ cluster model was used as the starting structure. The reaction consists of a multi-step process in which the hydrogen is abstracted from the surface producing a dangling bond on the silicon and molecular hydrogen. In order to complete the reaction the oxygen can insert into the dimer bond followed by hydrogen transfer from the oxygen to a dangling bond on one of the adjacent silicon atoms and finally passivation by free atomic hydrogen. A second possible path results in an oxygen insertion in the backbond followed by hydrogen transfer and passivation. The potential energy surface is shown in figure 3, with the energetics reported in table 1.

The abstraction of the silicon monohydride hydrogen is the first step in the reaction path. The reaction proceeds with a bond formation between the silicon monohydride hydrogen and the atomic hydrogen followed by the breaking of the bond between the silicon and hydrogen. Molecular hydrogen and a silicon dangling bond are formed as the intermediate. The kinetic barrier is the same as the enthalpy of the reacting structures and the products are exothermic by -.1.075 eV.

The reaction then has the possibility of two different competing reactions. The hydroxyl group is free to either insert into the dimer bond or one of two backbonds.

The dimer insertion pathway is a concerted mechanism in which the hydroxyl group breaks the silicon-silicon dimer bond creating dangling bonds on both of the dimer silicon atoms. The reaction is 0.525 eV higher then the combined reacting structures and .6133 eV higher then the hydrogen abstraction products. The transfer of atomic hydrogen from the oxygen to the dimer silicon has a barrier of 0.722 eV. Overall the reaction is exothermic compared to the combined reacting structures by -2.24 eV. The insertion reaction path is completed when the dangling bond on the silicon combines with atomic hydrogen without barrier. The final structure is very exothermic being -5.85 eV lower in energy then the combined reacting structures.

The second possible reaction is the insertion of the hydroxyl into the backbond. The backbond insertion occurs when the hydroxyl group reacts with a second layer silicon atom to form a hydroxyl bridge between the first and second rows. The transition state is 1.0 eV higher then the combined reaction structures. A hydrogen transfer then occurs from the hydroxyl group to the dimer silicon. The barrier for the hydrogen transfer is 1.1 eV above the energy of the combined reacting products. The reaction is completed by free hydrogen passivation of the remaining silicon dangling bond. The final structure is -5.51 eV lower then the combined reacting structures.

The initial hydrogen abstraction from the hydroxyl oxygen was investigated with MP2 in order to examine the appropriateness of B3LYP for the hydrogen abstraction reaction. The MP2 energy of 0.480 eV is 0.48 eV higher then the B3LYP energies. A CCSD(T) single point was carried out giving an energy of 0.50 eV, which is not a significant difference from the MP2 energies. The large difference in the MP2

and B3LYP energies indicates a significant failing of the density functional theory for this class of reactions. While it is now necessary to reoptimize the entire reaction path with MP2 sufficient time was not available before the publication of this report.

In order to understand the full extent to which B3LYP fails in the reaction a model system was explored using highly accurate quantum chemical methods. The model system consisted of a hydrogen abstraction from a silane molecule by atomic hydrogen to form a silane radical and molecular hydrogen. The energetics the reactions are reported in table 2. The energetics for the transition state indicate close agreement between the MP2 and QCISD(T) energies, a difference of 0.03 eV, indicate MP2 is an appropriate level of theory to describe the reaction. However the difference of 0.61 eV between the MP2 and B3LYP energies indicate a severe underestimate of the barrier heights by B3LYP. The reaction energetics must therefore be corrected by either optimizing the structures at the MP2 level of theory or by carefully developing correction factors for the B3LYP energies.

Hydrogen Hopping Mechanism

The hydrogen hopping mechanism is a possible link between the two reactions after the initial hydrogen abstraction from the monohydride silicon. The link occurs after hydrogen abstraction from the monohydride silicon by atomic hydrogen. There is a possibility the hydrogen will transfer from the hydroxyl group to the silicon dimer quenching the dangling bond on the silicon and creating a new dangling bond on the hydroxyl group. The energetics for the reaction is reported in table 1. The barrier for the transition state of the hop is 1.00 eV above the separated reactants.

This is 0.50 eV higher then the dimer insertion reaction which follows the monohydride abstraction. The energy is almost the same for the backbond insertion following a monohydride abstraction. The large difference between the dimer and backbond insertion energies indicated this will not be a significant side reaction leading to undesired products.

Comparison of reactions

The reactions thus far characterized indicate competition between the products of the monohydride and hydroxyl hydrogen abstractions. The lower kinetic barrier of the monohydride abstraction indicates the reaction will occur at a great rate then the hydroxyl abstraction. However, the overall lower energy of the hydroxyl abstraction makes it seem like a more favorable reaction pathway. Since the experimental evidence[13] indicates the dimer bond is preferred, an as yet unexplained part of the reaction must be resulting in an avoidance of the monohydride abstraction products to react on the surface. However more calculations at higher levels of theory are needed to understand the entirety of the reaction.

Peptide Deposition

The deposition of amino acids onto the clean silicon (100)-2x1 surface, when the backbone is the assumed reaction site, can occur by a three mechanisms. The possible reactions, seen in figure 4, are the hydrogen transfer reactions of the amino and carboxyl functional group with a surface silicon dimer, and the cycloaddition reaction of the carboxyl functional group. Reactions of the various R-groups with the

surface also present an interesting area that was not explored in this report. If the surface is selective for a single functional group then a homogenous monolayer of with available functional groups could be formed.

The previous study by Qu *et. al.* has found the both thermodynamic and kinetic selectivity for the hydroxyl dissociation on the surface[41]. The study examined both the reaction between dimmers and the reactions on single dimmers. In both cases the same result was indicated. This study was corroborated by a recent experimental study by Lopez *et. al.*[47], in which the authors used thermodynamic calculations as well as high-resolution electron loss spectroscopy (HREELS) to study the initial reaction of glycine on the Si (100)-2x1 surface. This study also indicated a selective bonding of the hydroxyl bond to the exclusion of any other detectable type of bonding.

The discussion is organized in the following manner. The three different types of pathways for each amino acid will be pathways will all be discussed and the differences in-between each will be examined.

Peptide Deposition Reaction Paths

Amine Functional Group Reactions

The reaction of the amino group with the clean silicon surface proceeds via a hydrogen transfer reaction. The reaction occurs by first forming a complex between the amino nitrogen and a dangling bond on the silicon dimer. The weakly bound complex then reacts in a concerted mechanism to form a bond between the silicon and the amine group. Simultaneously an amine hydrogen dissociates and forms a bond

with the adjacent silicon dangling bond. The resulting structure can be seen in figure 4.

The effects of the R-group on the energetics of the reactions are not significant. As can be seen in table 2, the complexation energies for glycine, cystine, tyrosine, and serine are -33.91 kcal/mol, -28.29 kcal/mol, -32.75 kcal/mol, and -30.07 kcal/mol form the separated reactants respectively. The differences between these do not represent any significant effects of the R-group when the reaction occurs on one dimer. A similar trend can be seen in the transition state and product energies. All energies are below the vacuum level which indicates the reactions would occur overall without any barrier.

An attempt was made to obtain the glycine nitrogen dissociation results reported by Qu *et. al.*[41]wever at the time of printing the methodology had not yet been elucidated. It is possible the conformation used in the reaction differed significantly from our calculations. Future work on this project will include determination of the energetics of different conformers.

Carboxyl Functional Group Reactions

The reaction of the carboxyl group with the clean silicon surface proceeds via a hydrogen transfer reaction. The reaction occurs by first forming a complex between the hydroxyl group of the carbonyl and a dangling bond on the silicon dimer. The weakly bound complex then reacts in a concerted mechanism to form a bond between the silicon and the hydroxyl group. Simultaneously the hydroxyl hydrogen dissociates

and forms a bond with the adjacent silicon dangling bond. The resulting structure can be seen in figure 4.

The effects of the R-group on the energetics of the reactions are not significant. As can be seen in table 2, the complexation energies, transition states, and products for glycine, cystine, tyrosine, and serine are relatively close in energy. All are below the energy of the combined reacting structures indicating overall the reactions occur without barrier. The differences between these do not represent any significant effects of the R-group when the reaction occurs on one dimer.

One trend with separates the Carboxyl dissociation from the other reaction are the nonexistent reaction barriers of the hydrogen dissociation. It would be expected that the hydrogen transfer would have some barrier. However it is possible Hartree-Fock theory is e\underestimating the energy. If the barrier is small and composed mostly of correlation energy the barrier would be missed. To test this hypothesis the reaction must be characterized at a higher level of theory.

Carboxyl [2+2] Cycloaddition Reactions

A second reaction of the carboxyl group with the clean silicon surface proceeds via a [2+2] cycloaddition. The reaction occurs by first forming a complex between the carbonyl oxygen doubly bonded to the carbon of the carbonyl and a dangling bond on the silicon dimer. The weakly bound complex then reacts in a concerted mechanism to form a bond between the silicon and the oxygen, which loses its double bond character. Simultaneously the carbon loses double bond character and

forms a bond with the adjacent silicon dangling bond. The resulting structure can be seen in figure 4.

The effects of the R-group on the energetics of the reactions are not significant in most cases. As can be seen in table 2, the complexation energies, transition states, and products for glycine, cystine, tyrosine, and serine are relatively close in energy, with the exception of the cystine complexation energy. A slight difference in the binding energy indicates a slight effect of the cystine sulfide group. It is also possible it is merely an unfavorable conformation of the amino acid. Further investigation is needed to examine this conjecture. All energies are below the energy of the combined reacting structures indicating overall the reactions occur without barrier.

Conclusion

We have investigated the reactions of amino acids on silicon surfaces and oxygen insertion reactions of wet oxidized silicon. The support for the mechanism of oxygen insertion is not yet complete. Further characterization of the mechanism using more accurate quantum chemical methods are needed before final determination of the mechanism can be made.

The deposition of amino acids has been investigated. While more accurate model chemistries are necessary several things can be concluded from the preliminary study. The conformation of the amino acid may be significant in determining the energy of the system and the R-groups most likely do not significantly affect the energetics.

Figures and Tables

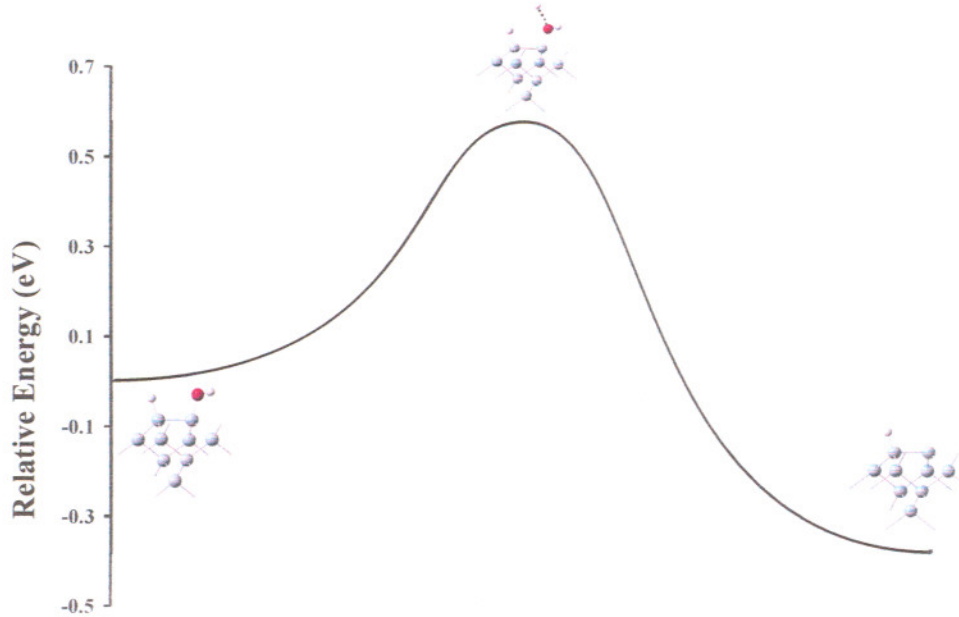

Figure 1. The reaction initial reaction of water elimination from the reaction of atomic hydrogen with the wet oxidized silicon surface.

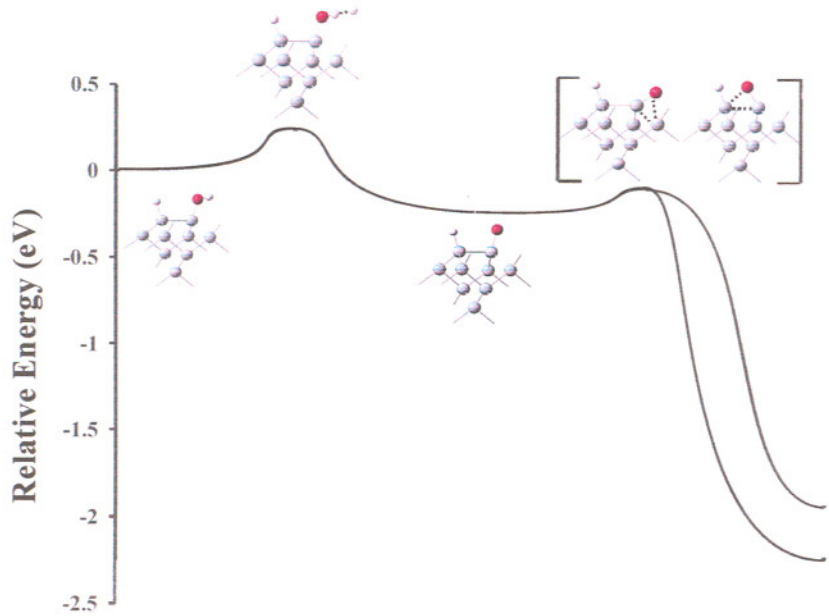

Figure 2. The reaction path of the hydrogen abstraction from the hydroxyl group followed by oxygen insertion into either the dimer bond or the backbond.

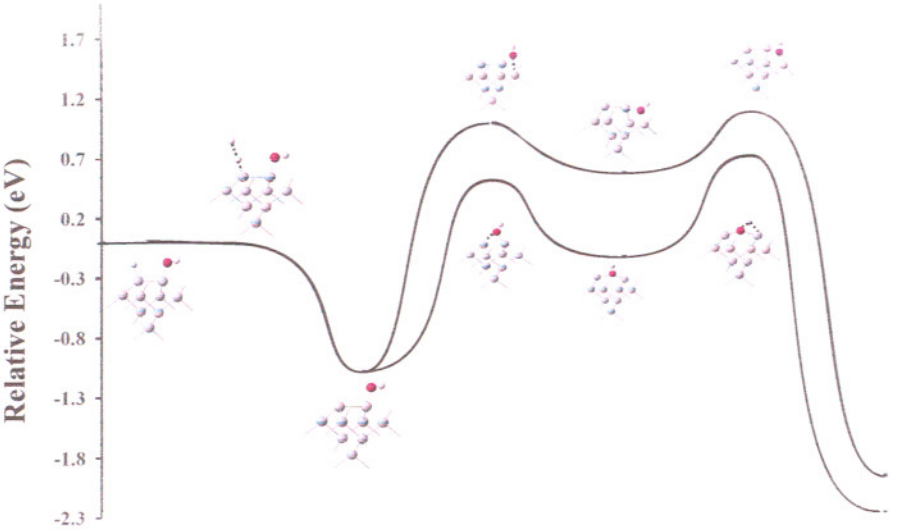

Figure 3. The reaction path of the hydrogen abstraction from the monohydride silicon followed by oxygen insertion into either the dimer bond or the backbond.

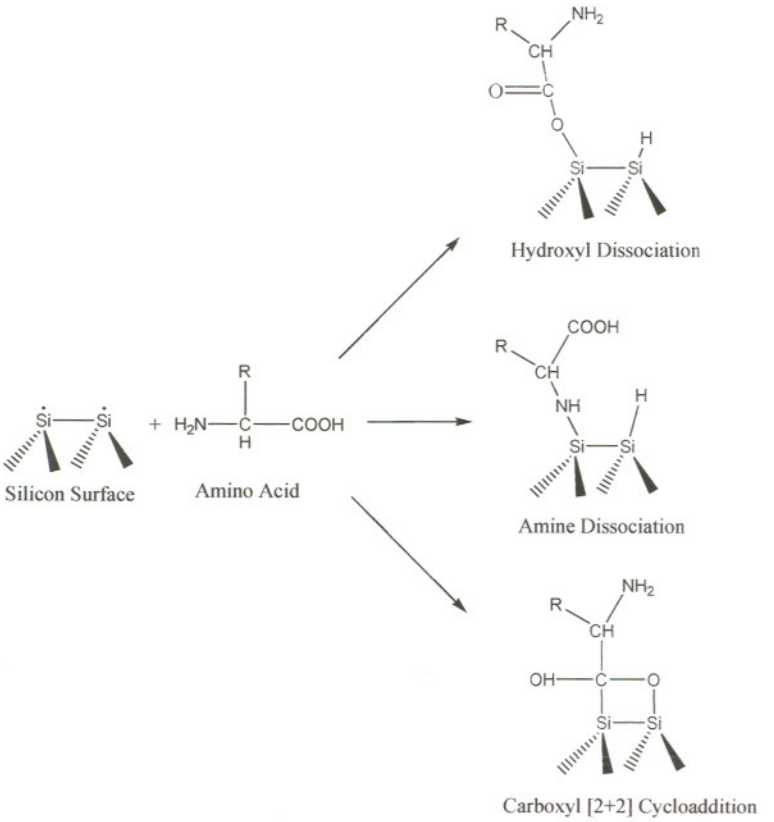

Figure 4.The three reaction studied for glycine (R=hydrogen), cystine (R=sulfide), tyrosine (R=phenol), and serine (R=hydroxyl).

Table 1. The energetics of the oxygen insertion reactions.

Reaction	Coordinate	Stoichiometry	Relative Energies, eV
Dimer Hydrogen Abstraction/Dimer Insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H--H--Si-Si-OH	-0.001
	Intermediate 1	H• + H2 + *Si-Si-OH	-1.075
	Transition State 2	H• + H2 + *Si--OH-Si	0.525
	Intermediate 2	H• + H2 + *Si-OH-Si*	-0.113
	Transition State 3	H• + H2 + *Si-O--H--Si*	0.722
	Intermediate 4	H• + H2 + *Si-O-Si-H	-2.237
	Product	H2 + H-Si-O-Si-H	-5.846
Dimer Hydrogen Abstraction/Backbond Insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H--H--Si-Si-OH	-0.001
	Intermediate 1	H• + H2 + *Si-Si-OH	-1.075
	Transition State 2	H• + H2 + *Si-Si-OH--(Si)	1.003
	Intermediate 2	H• + H2 + *Si-Si*-OH-(Si)	0.589
	Transition State 3	H• + H2 + *Si-Si*--H--O-(Si)	1.091
	Intermediate 4	H• + H2 + *Si-Si(H)-O-(Si)	-1.937
	Product	H2 + H-Si-Si(H)-O-(Si)	-5.515
Dimer Hydrogen Abstraction/Hydrogen Hop/Dimer insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H--H--Si-Si-OH	-0.001
	Intermediate 1	H• + H2 + *Si-Si-OH	-1.075
	Transition State 2	H• + H2 + *Si--H--O-Si	1.007
	Intermediate 2	H• + H2 + H-Si-Si-O*	-0.237
	Transition State 3	H• + H2 + H-Si--O*--Si	-0.103
	Intermediate 4	H• + H2 + H-Si-O-Si*	-2.237
	Product	H2 + H-Si-O-Si-H	-5.846
Dimer Hydrogen Abstraction/Hydrogen Hop/Backbond insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H--H--Si-Si-OH	-0.001
	Intermediate 1	H• + H2 + *Si-Si-OH	-1.075
	Transition State 2	H• + H2 + *Si--H--O-Si	1.007
	Intermediate 2	H• + H2 + H-Si-Si-O*	-0.237
	Transition State 3	H• + H2 + H-Si-Si--O*--(Si)	-0.109
	Intermediate 4	H• + H2 + H-Si-Si*-O-(Si)	-1.937
	Product	H2 + H-Si-Si(H)-O-(Si)	-5.515
Oxygen Hydrogen Abstraction/Dimer insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H-Si-Si-O--H--H	0.237
	Intermediate 1	H• + H-Si-Si-O* + H2	-0.237
	Transition State 2	H• + H-Si--O*--Si + H2	-0.103
	Intermediate 2	H• + H-Si-O-Si* + H2	-2.237
	Product	H-Si-O-Si-H+ H2	-5.846
Oxygen Hydrogen Abstraction/Backbond insertion			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H-Si-Si-O--H--H	0.237
	Intermediate 1	H• + H-Si-Si-O* + H2	-0.237
	Transition State 2	H• + H-Si-Si-O*--(Si) + H2	-0.109
	Intermediate 2	H• + H-Si-Si*-O-(Si) + H2	-1.937
Water Elimination			
	Reactants	2H• + H-Si-Si-OH	0.000
	Transition State 1	H• + H-Si-Si--H--OH	0.575
	Intermediate 1	H• + H-Si-Si* + H2O	-0.378
	Product	H-Si-Si-H + H2O	-3.875

Table 2. The energetics of the reaction of silane and atomic hydrogen with different model chemistries.

Level of Theory	Coordinate	Relative Energies, kcal/mol
DFT/6-31+G*	Reactants	0.00
	Transition State	19.19
	Product	-16.78
MP2/6-31+G*	Reactants	0.00
	Transition State	33.34
	Product	-7.31
QCISD/6-31+G*	Reactants	0.00
	Transition State	34.10
	Product	-5.94

Table 3. The energetics of the amino acid backbones with the silicon surface.

Reaction	Coordinate	Relative Energies, kcal/mol
Glycine		
N-H Dissociation	Reactant	0
	Complex	-33.91
	Transition State	-10.82
	Product	-63.24
COOH Dissociation	Reactant	0
	Complex	-37.33
	Transition State	-38.21
	Product	-74.60
COOH [2+2] Cycloaddition	Reactant	0
	Complex	-22.082
	Transition State	-18.34
	Product	-39.48
Cystine		
N-H Dissociation	Reactant	0
	Complex	-28.29
	Transition State	-6.99
	Product	-62.86
COOH Dissociation	Reactant	0
	Complex	-34.58
	Transition State	-35.75
	Product	-74.08
COOH [2+2] Cycloaddition	Reactant	0
	Complex	-17.27
	Transition State	-15.32
	Product	-38.45
Tyrosine		
N-H Dissociation	Reactant	0
	Complex	-32.75
	Transition State	-8.12
	Product	-62.47
COOH Dissociation	Reactant	0
	Complex	-36.05
	Transition State	-36.74
	Product	-75.09
COOH [2+2] Cycloaddition	Reactant	0
	Complex	-20.55
	Transition State	-17.41
	Product	-39.44
Serine		
N-H Dissociation	Reactant	0
	Complex	-30.07
	Transition State	-7.14
	Product	-61.59733168
COOH Dissociation	Reactant	0
	Complex	-34.82456585
	Transition State	-36.13664552
	Product	-74.50569964
COOH [2+2] Cycloaddition	Reactant	0
	Complex	-19.29853967
	Transition State	-18.54723884
	Product	-38.43997165

References:

[1] Z. Massound, E. H. P., C. R. Helms. "Proceedings of the 1st-3rd International Symposium on the Physics and Chemistry of SiO_2 and the Si/SiO_2 Interface", 1988-1996, Pennington, NJ.
[2] Morre, G. In *IEDM Tech*, 1975; Vol. Digest 11.
[3]al., G. T. e. In *IEDM Tech. Dig.*, 1997; pp 930.
[4]Andersohn, L.; Kohler, U. *Surface Science* **1993**, *284*, 77.
5 Chander, M.; Li, Y. Z.; Patrin, J. C.; Weaver, J. H. *Physical Review B* **1993**, *48*, 2493.
[6] Struck, L. M.; Eng, J.; Bent, B. E.; Flynn, G. W.; Chabal, Y. J.; Christman, S. B.; Chaban, E. E.; Raghavachari, K.; Williams, G. P.; Radermacher, K.; Mantl, S. *Surface Science* **1997**, *380*, 444.
[7] Raghavachari, K.; Chabal, Y. J.; Struck, L. M. *Chemical Physics Letters* **1996**, *252*, 230.
[8] Konecny, R.; Doren, D. J. *Journal of Chemical Physics* **1997**, *106*, 2426.
[9] P. A. Thiel, T. E. M. *Surface Science Reports* **1987**, *7*, 211.
[10] Konečný, R. and Doren, D. J. *Journal of the American Chemical Society*. **1997**, 6, 2426.
[11] Stefanov, B. B.; Raghavachari, K. *Surface Science* **1997**, *389*, L1159.
[12] Teraishi, K.; Takaba, H.; Yamada, A.; Endou, A.; Gunji, I.; Chatterjee, A.; Kubo, M.; Miyamoto, A.; Nakamura, K.; Kitajima, M. *Journal of Chemical Physics* **1998**, *109*, 1495.
[13] Weldon, M. K.; Queeney, K. T.; Gurevich, A. B.; Stefanov, B. B.; Chabal, Y. J.; Raghavachari, K. Ibid.**2000**, *113*, 2440.
[14] Weldon, M.K.; Stefanov, B.B.; Raghavachari, K.; and Chabal, Y.J. *Physical Review Letters* **1997**, 79, 15, 2851.
[15] Stefanov, B. B.; Raghavachari, K. *Applied Physics Letters* **1998**, *73*, 824.
[16] Lu, X., and Lin, M.C. (2002). Reactions of some [C,N,O]-containing molecules with Si surfaces: experimental and theoretical studies. International Reviews in Physical Chemistry *21*, 137-184.
[17].Bent, S.F. (2002). Organic functionalization of group IV semiconductor surfaces: principles, examples, applications, and prospects. Surface Science *500*, 879-903.
[18].Yates, J.T. (1998). A New Opportunity in Silicon-Based Microelectronics. Science *279*, 335-336.
[19].Filler, M.A., and Bent, S.F. (2003). The surface as molecular reagent: organic chemistry at the semiconductor interface. Progress in Surface Science *73*, 1-56.
[20].Bent, S.F. (2002). Attaching Organic Layers to Semiconductor Surfaces. Journal of Physical Chemistry B *106*, 2830-2842.
[21].Buriak, J.M. (2002). Organometallic chemistry on Siliocn and Germanium Surfaces. Chemical Reviews *102*, 1271-1308.
[22].Wayner, D.D.M., and Wolkow, R.A. (2002). Organic modification of hydrogen terminated silicon surfaces. Journal of the Chemical Society-Perkin Transactions 2, 23-34.
[23].Patole, S.N., Pike, A.R., Connolly, B.A., Horrocks, B.R., and Houlton, A. (2003). STM study of DNA films synthesized on Si(111) surfaces. Langmuir *19*, 5457-5463.
[24].Lin, Z., Strother, T., Cai, W., Cao, X.P., Smith, L.M., and Hamers, R.J. (2002). DNA attachment and hybridization at the silicon (100) surface. Langmuir *18*, 788-796.
[25].Sieval, A.B., Linke, R., Heij, G., Meijer, G., Zuilhof, H., and Sudholter, E.J.R. (2001). Amino-terminated organic monolayers on hydrogen-terminated silicon surfaces. Langmuir *17*, 7554-7559.
[26].Loh, K.P., Kingsley, C.R., Foord, J.S., and Jackman, R.B. (1995). The Interaction of Azomethane with Si(100). Surface Science *341*, 92-102.
[27].Zhu, X.Y., Mulder, J.A., and Bergerson, W.F. (1999). Chemical vapor deposition of organic monolayers on Si(100) via Si-N linkages. Langmuir *15*, 8147-8154.
[28].Mulcahy, C.P.A., Carman, A.J., and Casey, S.M. (2000). The adsorption and thermal decomposition of dimethylamine on Si(100). Surface Science *459*, 1-13.
[29].Mui, C., Wang, G.T., Bent, S.F., and Musgrave, C.B. (2001). Reactions of methylamines at the Si(100)-2x1 surface. Journal of Chemical Physics *114*, 10170-10180.
[30].Cao, X.P., and Hamers, R.J. (2002). Formation of a surface-mediated donor-acceptor complex: Coadsorption of trimethylamine and boron trifluoride on the silicon (001) surface. Journal of Physical Chemistry B *106*, 1840-1842.

[31].Wu, J.B., Yang, Y.W., Lin, Y.F., and Chiu, H.T. (2004). Adsorption and decomposition studies of t-butylamine, diethylamine, and methylethylamine on Si(100)-(2 x 1). Journal of Physical Chemistry B *108*, 1677-1685.
[32].Cerofolini, G.F., Galati, C., Reina, S., and Renna, L. (2003). Functionalization of the (100) surface of hydrogen-terminated silicon via hydrosilation of 1-alkyne. Materials Science & Engineering C-Biomimetic and Supramolecular Systems *23*, 253-257.
[33].Sieval, A.B., Vleeming, V., Zuilhof, H., and Sudholter, E.J.R. (1999). An improved method for the preparation of organic monolayers of 1-alkenes on hydrogen-terminated silicon surfaces. Langmuir *15*, 8288-8291.
[34].Bansal, A., Li, X.L., Yi, W.H., Lauermann, N.S., Yi, S.I., and Weinberg, W.H. (1996). Alkylation of Si Surfaces Using a Two-Step Halogenation Grignard Route. Journal of the American Chemical Society *118*, 7225.
[35].Bansal, A., Li, X.L., Yi, S.I., Weinberg, W.H., and Lewis, N.S. (2001). Spectroscopic Studies of the Moification of Crystalline Si(111) Surfaces with Convalently Attached Alkyl Chains Using a Chlorination/Alkylation Method. Journal of Physical Chemistry B *105*, 10266.
[36].Cai, W., Lin, Z., Strother, T., Smith, L.M., and Hamers, R.J. (2002). Chemical Modification an Patterning of Iodine Terminated Silicon Surfaces Using Visible Light. Journal of Physical Chemistry B *106*, 2656.
[37].Qu, Y.Q., and Han, K.L. (2004). Theoretical studies of benzonitrile at the Si(100)-2 x 1 surface. Journal of Physical Chemistry B *108*, 8305-8310.
[38].Lopinski, G.P., Wayner, D.D.M., and Wolkow, R.A. (2000). Self-Directed Growth of Molecular Nonowires on Silicon. Nature *406*, 48-51.
[39].Sieval, A.B., van den Hout, B., Zuilhof, H., and Sudholter, E.J.R. (2000). Molecular Modeling of Alkyl Monolayers on the Si(111) Surface. Langmuir *16*, 2987-2990.
[40].Cho, J.H., Oh, D.H., and Kleinman, L. (2002). One-dimensional Molecular Wire on Hyrogenated Si(001). Physical Review B *65*, 081310(R).
[41].Qu, Y.Q., Wang, Y., Li, J., and Han, K.L. (2004). Quantum chemical study of surface reactions of glycine on the Si(100)-2 X 1 surface. Surface Science *569*, 12-22.
[42].Seino, K., and Schmidt, W.G. (2004). Reflectance anisotropy of uracil covered Si(001) surfaces: Ab initio predictions. Surface Science *548*, 183-186.
[43].Seino, K., Schmidt, W.G., and Bechstedt, F. (2004). Organic modification of surface electronic properties: A first-principles study of uracil on Si(001). Physical Review B *69*.
[44] M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople. GAUSSIAN 03, REVISION B.02, Gaussian, Inc., Pittsburgh PA, 2003.
[44]Becke, A. D. *Journal of Chemical Physics* **1993**, *98*, 5648.
[45] Lee, C. T.; Yang, W. T.; Parr, R. G. *Physical Review B* **1988**, *37*, 785.
[46] W. J. Hehre, L. R., P. V. R. Schleyer, J. A. Pople *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
[47] Lopez, A. Heller, T. Bitzer, T. Richardson, N.V. Chem. Phys. 277 (2002) 1.