

Molecular Chemistry on Silicon Surfaces

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Literature Seminar

January 23, 1997

The study of silicon surfaces has recently attracted much attention because of its technological importance in the semiconductor and electronics industries. The structure of the bare Si surface has been thoroughly investigated. However, the interaction of molecules with its surface is not well understood. Much work has been done on how atoms are adsorbed onto silicon surfaces under ultrahigh vacuum (UHV), but there is only a small amount of literature devoted to silicon's molecular surface chemistry in solution.¹

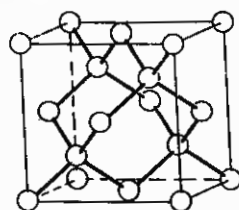
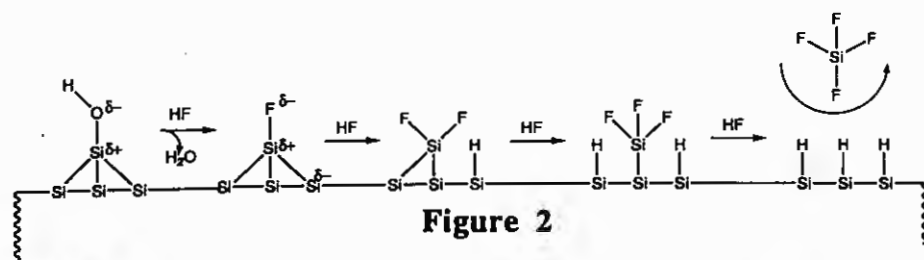


Figure 1

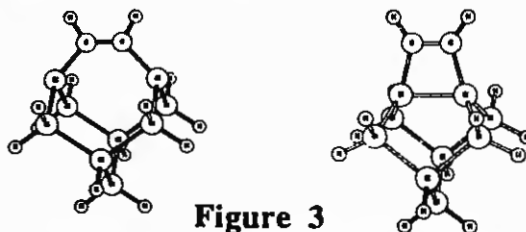
Bulk silicon adopts the diamond lattice structure (Figure 1). Silicon surfaces are generated by cleaving the bulk crystal along one of its lattice planes breaking Si-Si bonds and reducing the bulk four-fold coordination. Each covalent bond breakage leaves silicon with an unpaired electron, termed a dangling bond. When bulk silicon is truncated along the (100) face each surface silicon contains two dangling bonds; cleavage in the (111) direction results in silicon atoms with either one or three unpaired electrons. The surface structure is most stable when it contains a minimum number of dangling bonds. Therefore surface silicon atoms will reconstruct by bonding with unpaired electrons on adjacent silicon atoms in an effort to increase the coordination number and lower the overall surface energy.² The Si(100)-(2x1) reconstruction reduces the number of dangling bonds in the unreconstructed surface by 50%.³

STM images of clean silicon surfaces provide conclusive evidence of their surface structure and bonding.⁴ Images of the reconstructed Si(100) surface confirm the dimer model originally proposed by Schlier and Farnsworth⁴ which shows a strong σ interaction and a weak π interaction between the silicon atoms comprising the dimer. A fluxional dimer model whereby localized charge is transferred between silicon atoms is also supported by STM. Such charge transfer can explain the reactivity of the Si(100) surface.

Many chemical reactions on silicon start with H-passivation of the surface. The adsorption of H on Si(100) and Si(111) has been studied extensively.⁵⁻⁸ Under UHV exposure to atomic hydrogen, Si(100) forms a 2x1 monohydride, a 1x1 dihydride, or a 3x1 mixed mono- and dihydride structure whose stability depends on the concentration of atomic hydrogen.⁶ H-passivation of the Si(100) surface via chemical HF etching yields a microscopically rough surface structure. When Si(111) is exposed to an HF etching solution buffered with NH_4F , an ideally passivated surface is obtained where each surface dangling bond is saturated with an H atom oriented normal to the Si surface.⁸ The mechanism of H-passivation by HF has recently been elucidated by infrared spectroscopy.⁹ Due to the stability of the Si-F bond it was previously thought that F termination was responsible for the chemical passivation of the silicon surface during etching. However, infrared spectroscopy studies show silane formation on the surface during the HF cleaning process leading to the conclusion that etching proceeds via H passivation of the surface with the generation of SiF_4 (Figure 2).



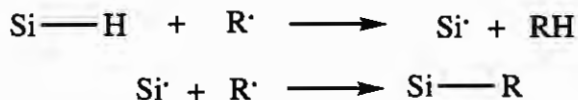
Studies on the chemical interactions between molecules and the Si(100)-(2x1) surface have mostly been carried out under UHV. The interaction of organic molecules and the Si(100) surface is important for the role it plays in the formation of Si-C films. Acetylene, a prototype of organic molecules chemisorbed on Si(100), interacts with the Si surface by aligning its π system with that of the silicon dimer (Figure 3).¹⁰ Whether or not the Si-Si σ bond remains intact is still under debate.



The first example of the use of cluster complexes to study and control reactions with silicon is that of spherosiloxanes on Si(100)-(2x1).¹¹ Using photoemission spectroscopy, Banaszak Holl shows that these cluster compounds ($H_8Si_8O_{12}$, $H_{12}Si_{12}O_{18}$, and $H_{14}Si_{14}O_{21}$) undergo an Si-H addition across the Si-Si dimer bond. The cluster is chemisorbed on to one Si atom of the dimer by one vertex via a Si-Si bond while the H is chemisorbed on the remaining dimeric Si.

Another example of cluster molecules on Si(100) is that of diborane, B_2H_6 , and the larger cluster, $B_{10}H_{14}$. At room temperature, borane molecules or molecular fragments aggregate on the surface in an orderly fashion. At elevated temperatures boron is incorporated into the second atomic layer of the silicon lattice modifying the surface Si dimer structure.¹²

The first example of a chemical reaction on a H-passivated silicon surface was the formation of an alkyl monolayer on Si(111) and Si(100) prepared by the pyrolysis of diacyl peroxides, $[CH_3(CH_2)_nC(O)O]_2$.^{13a} Linford and Chidsey also prepared alkyl monolayers on H-passivated Si(111) by reaction with 1-alkenes.^{13b} A free radical reaction mechanism is proposed whereby the H terminated surface reacts with a radical, R^\cdot , generating a surface dangling bond which combines with a second radical to form a Si-C bond. Cleland et. al.



also report the functionalization of H-passivated Si(111) by its reaction with various alcohols such as ferrocene methanol.¹⁴ It is claimed that the chemisorption of these alcohols forms stable monolayer structures on the silicon surface.

More recently Bansal et. al. reported the alkylation of Si surfaces via a Grignard reaction.¹⁵ Si crystals prepared by etching in HF solution were then exposed to PCl_5 forming surface Si-Cl bonds which were then exposed to alkyl-Li or alkyl-Grignard reagents. Infrared spectroscopy shows a highly crystalline alkane environment. The alkyl layer deposited on the Si surface was shown to provide significant resistance to surface oxidation.

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