Chapter 7 Conclusion

In this thesis, the binding of chemical functionalities onto silicon surfaces was investigated using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), high-resolution electron energy loss spectroscopy (HREELS) and density functional theory (DFT) calculations. Experimental and theoretical calculation results are summarized as follows.

(1) Acetyl cyanide ($CH_3COC{\equiv}N$) produces both ketenimine-like species and a tetra-σ adduct on Si(100)-2×1. Methyl methacrylate [$CH_2{=}CH(CH_3)COOCH_3$] and methyl propiolate ($CH{\equiv}C{-}COOCH_3$) were found to undergo a [4+2]-like cycloaddition through C=C-C=O and a [2+2]-like reaction via C≡C, respectively. The different reaction pathways of these three molecules are caused by the reactivity of various functional groups, as well as the reactive sites on Si(100)-2×1.

(2) Formic acid (HCOOH) chemisorbs dissociatively on Si(111)-7×7 to form a monodentate formate species on adatom and H atom on the adjacent rest atom. For the unsaturated methacrylic acid [$CH_2{=}CH(CH_3)COOH$], the OH dissociative reaction is favored over the competing cycloaddition reactions. However, Methyl methacrylate [$CH_2{=}CH(CH_3)COOCH_3$], the ester of methacrylic acid, was found to undergo a [4+2]-like cycloaddition across the C=C-C=O group. These results suggest that the reactivity of OH, C=C, C=O groups on Si(111)-7×7 is in the order of OH dissociation > [4+2]-like cycloaddition via C=C-C=O > [2+2]-like cycloaddition through C=C or C=O. The different reaction mechanisms of MAA and MMA on Si(111)-7×7 also demonstrate that the substitution groups play an important role in determining the surface reaction

pathways of multifunctional molecules on Si(111)-7×7, offering a greater flexibility in organic modification of silicon surfaces.

(3) For the adsorption of N-methylallylamine [CH_2=CH-CH_2-NH(CH_3)] on Si(111)-7×7, an N-H dissociative reaction is preferred over a [2+2]-like cycloaddition via C=C. However, the methyl-protected N,N-dimethylallylamine [CH_2=CH-CH_2-N(CH_3)$_2$] reacts with the Si surface in a [2+2]-like addition through the C=C group. The great impact of substitution groups on the attachment behaviors of unsaturated chain amines on the silicon surface was discovered.

(4) Chemisorbed glycine [NH_2CH_2COOH] and L-cysteine [$NH_2CH(CH_2SH)COOH$] both dissociate to yield two surface intermediates on Si(111)-7×7 through the breakage of O-H and N-H groups. The selective adsorption of L-cysteine on Si(111)-7×7 demonstrates that the reactivity of carboxylic acid, amino and thiol groups on the Si surface is in the order of –COOH > -NH_2 > -SH.

A detailed understanding of the competition and selectivity of multifunctional molecules on silicon surfaces, as well as the impact of substitution groups on the attachment behavior can be obtained from this thesis, making it possible to control the selectivity in the initial surface reaction. In addition, the information obtained from glycine/Si(111)-7×7 and L-cysteine/Si(111)-7×7 would be helpful for further studies of more complicated systems including protein/Si and peptide/Si. It is concluded that silicon surfaces can be efficiently modified by covalent attachment of chemical functionalities, creating fundamental molecular interface for the fabrication of new organic/silicon hybrid devices.