The interfacial structure of silicon/dielectric and silicon/metal systems is particularly amenable to analysis using a combination of surface spectroscopies together with a variety of chemical structures of Si/SiO₂, Si/SiO₂/Si₃N₄, Si/Si₂N₂O, Si/SiO₂/Al, and Si/Native Oxide interfaces using high resolution (0.350 eV FWHM) X-ray photoelectron spectroscopy. The general structure of these dielectric interfaces entails a monolayer chemical transition layer at the Si/dielectric boundary, which consists of specific distributions of the intermediate oxidation states of silicon (Si⁺, Si⁺₂, and Si⁺₃), which appear to be related to local morphology of the silicon substrate. Amorphous Si substrates show a wide variety of hydrogenated Si and Si(OH)ₓ states that are not observed in thermal oxidation of single crystal material. Extended SiO₂ layers greater than 8 Å in thickness are shown to be stoichiometric SiO₂, but to exhibit a wide variety of local network structures. In the nitrogen-containing systems, we see an approach to stoichiometric oxynitride compounds with interesting impurity- and electron-trapping properties. In native oxides, we find substantial topographical non-uniformity in oxide thickness and composition (e.g., a nominal 25 Å oxide can be shown to have 4 different areal distributions of SiO₂ ranging in thickness from 12 to 165 Å). Analysis of metal/oxide interfacial layers is accomplished by analytical removal of the Si substrate by UHV XeF₂ dry etching methods. The general question of the importance of the chemical state of the starting silicon surface to the final dielectric/silicon interface composition will be addressed in a series of experiments using covalent silicon surface substitution. Finally, the modification of silicon surface bonding and hybridization in the presence of sub-monolayer levels of transition metals will be examined from the perspective of a modification in interfacial reactivity.