Since the 80's, the reactions of organic and organometallic compounds with group IV semiconductors and on II-VI substrates have been of great interest both from fundamental and from practical applications points of view. Two basic approaches focused on either UHV surface functionalization of clean single crystals or on the reactions of H-terminated substrates. Most recently, the focus of our research has been in preparing the surface functionalities normally achievable in UHV but using wet chemistry approaches. In addition, we question the effect of surface preparation on its physical properties. For example, by using HF treatment method, the H-terminated Si (111) surface produced relatively long charge-carrier lifetime and low surface recombination velocity (<200 cm s\(^{-1}\)), but poor chemical properties with multiple surface H-containing species formed. In contrast, an alternative method (the RCA procedure) produced a chemically well defined monohydride silicon surfaces with relatively poor electrical properties. The discussion will bring up the use of multiple spectroscopic and microscopic techniques and DFT calculations to investigate the functionalization and passivation of semiconductors with the primary emphasis on nitrogen-containing compounds. The differences and similarities of reaction mechanisms in vacuum and in ambient will also be addressed.