Connecting the Chemistry of Silanes and Silicon Surfaces with Radical-based Mechanisms

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Integrating molecules with silicon is of great interest for applications in molecular electronics, for passivation of silicon surfaces for solar fuel generation, and yet further miniaturization of feature sizes of transistors on silicon into the sub-10 nm regime.[1] The formation of silicon-carbon bonds via hydrosilylation is a practical and commonly used approach to chemically functionalize the surface of silicon due to the stability of the Si-C bond. There is a surprisingly diverse array of distinct mechanisms, and hence reaction conditions, that can be harnessed to enable this chemistry.[2] Research over the past two decades has shown, however, that the mechanisms in operation are far more diverse, and the chemistry much richer, than initially believed. The underlying electronics of the silicon play an important role in enabling the chemistry of the surface, and under many circumstances, can dominate.[3] We will discuss the latest developments in the surface chemistry of silicon that provide practical avenues for exquisitely precise integration of molecules with silicon surfaces. From the use of surface plasmons to bonding via exotic elements (such as Si-S,Si-Se, Si-Te bonds), silicon continues to surprise.

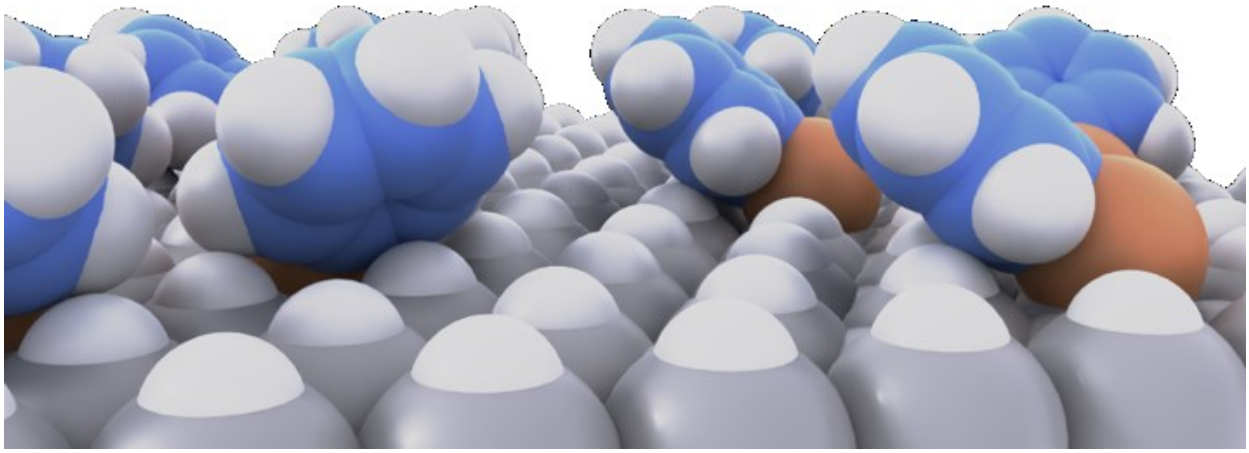

Figure 1. Model of phenyl chalcogenide groups bound to a Si(111)-H-terminated surface through ≡Si-E bonds (E = S, Se, Te).

[1] Buriak, J. M.; Sikder, Md D. From Molecules to Surfaces: Radical-Based Mechanisms of Si-S and Si-Se Bond Formation on Silicon. *J. Am. Chem. Soc.,* **2015,** *137,* 9730–9738.

[2] Buriak, J. M. Illuminating Silicon Surface Hydrosilylation: An Unexpected Plurality of Mechanisms. *Chem. Mater.*, **2014,** *26,* 763-772.

[3] Hu, M.; Hauger, T. C.; Olsen, B. C.; Luber, E. J.; Buriak, J. M. UV-Initiated Si-S, Si-Se and Si-Te Bond Formation on Si(111): Coverage, Mechanism, and Electronics. *J. Phys. Chem. C,* **2018,** ASAP (invited/Prashant V. Kamat Festchrift; DOI: 10.1021/acs.jpcc.8b00910).