

Chemical Characterization and Charge Carrier Behavior
of Alkylated Crystalline Silicon(111) Surfaces
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We present here investigations of the chemical structure and electrical charge carrier properties of alkylated crystalline silicon(111) surfaces in an unprecedented degree of detail. Hydrogen-terminated Si(111) surfaces were alkylated through a two-step chlorination/alkylation procedure with a series of straight-chain hydrocarbons. Chemical characterization was carried out with a number of surface-sensitive techniques. High-resolution X-ray photoelectron spectroscopy with a synchrotron radiation excitation source was used to measure binding energy shifts of Si 2p core electrons to determine the chemical species bonded to surface Si atoms at each step of the chemical preparation. We identified approximately 1 monolayer of H, Cl, and C on the freshly-prepared H-, Cl-, and CH₃-terminated surfaces respectively, and at no point observed any significant growth of silicon oxide species. Surfaces alkylated with bulkier groups such as C₂H₅- or C₆H₅CH₂- showed Si 2p core electron binding energy shifts that suggest that when the Si(111) surface is functionalized with alkyl groups that are too large to fit on every silicon atop atom, the remaining unfunctionalized Si atoms are terminated with H atoms. The methylated Si(111) surface was further characterized using transmission infrared spectroscopy. A CH₃ “umbrella” feature at 1257 cm⁻¹ was observed, indicating the methyl group is perpendicular to the surface. Finally, images of CH₃-Si were obtained by scanning tunneling microscopy at 4.7 and 77 K. The functionalized surface preserved the atomically flat morphology of freshly-etched H-Si(111), and at 4.7 K individual methyl H atoms were clearly resolved for the first time.

Electrical passivation of the alkylated Si(111) surface was investigated through measurement of surface charge carrier recombination velocities (SRV), which are exquisitely sensitive to surface energy trap densities. While unpassivated H- and Cl-terminated surfaces reacted rapidly in an air ambient to yield SRVs of >2000 cm s⁻¹, i.e. instantaneous recombination of surface electron-hole pairs, alkylated surfaces preserved SRVs of <200 cm s⁻¹ even when exposed to air for a period of weeks. We discuss possible reasons for this remarkable electrochemical passivation in air.