Nanopatterned surfaces are of central importance to a variety of areas and applications, such as computer chip architectures, tissue interfacing, biosensors, light management and plasmonics, among others. One of the most important materials for a myriad of functions is silicon, as the functionalization of silicon surfaces is of interest for computing applications, water splitting, batteries, on-chip sensing, molecular electronics, and solar energy conversion, amongst many others. Typically, the various approaches to nanopatterning of surfaces, including silicon, are broken into two major classes: top-down methods such as photolithography, e-beam lithography and scanning force microscopy variants, and bottom-up synthetic techniques, including self-assembly. Since lithography is the single most expensive step in computer chip manufacturing, the use of self-assembled block copolymers (BCPs) templates on surfaces is being seriously considered by the semiconductor industry to pattern, sub-20 nm features on a semiconductor surface; the Industry Technology Roadmap for Semiconductors (ITRS) terms this development ‘directed self-assembly’, or DSA. Here we will describe how self-assembly of BCPs can be used to produce useful nanopatterns on technologically relevant surfaces, and in some cases, bypassing native equilibrium structures to form higher density patterns, and forms of higher complexity. We will end by showing how BCP patterns can be both conceptually and physically separated from the surface they are intended to pattern through a plasmonic approach. Via the use of gold nanopatterns, produced via BCP self-assembly (DSA), localized silicon surface chemistry, a form of nanolithography, can be enabled upon illumination of light to excite the plasmons of gold, leading enhanced local electric fields that drive proximal silicon-carbon bond formation on the silicon surface. This chemistry, plasmon-assisted silicon surface chemistry, represents a new approach to the discovery of new reactivity, and sub-20 nm nanolithography, on a range of surfaces.