From Order to Disorder of Alkanethiol SAMs on Complex Au (211), (221) and (311) Surfaces: Impact of the Substrate

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In our work, we investigate the impact of the substrate on the structural properties and the morphology of alkanethiol self-assembled monolayers (SAMs) on gold, using first principles calculations and atomistic molecular dynamics simulations. We consider hexadecanethiols on Au(211), Au(221) and Au(311) surfaces which contain few-atom wide terraces separated by monoatomic steps similar to the complex Au surfaces used in experiments. The structure of the SAMs is probed via several structural properties including tilt angles, mean C atom heights from the surface, precession angles, gauche defects, gyration tensors and relative shape anisotropy. Comparing these properties to those of the well-studied SAMs on Au(111), we observe similarities but also striking differences. A clear order to disorder transition is observed by changing the substrate: Well-ordered SAMs on (111) and (211) surfaces become mixed ordered-disordered structures on (311) and fully disordered on (221). The presence of steps on the Au surfaces also results in preferential tilt orientations with long-range order. Our results show that in addition to the expected grafting density dependence, the transition from order to disorder crucially depends on substrate morphology. The onset of ordering behavior is related to the atomic structure of the surface. The key parameter that affects long-range order is the energy for changing the dihedral angle between Au-S-$C_{(1)}$-$C_{(2)}$ of the adsorbed alkanethiol.