Influence of Surface Morphology and Substrate on Thermal Stability and Desorption Behavior of Octanethiol Self-Assembled Monolayers

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The formation and thermal desorption behaviors of octanethiol (OT) SAMs on single crystalline Au (111) and polycrystalline Au, Ag, and Cu substrates were examined by X-ray photoelectron microscopy (XPS), thermal desorption spectroscopy (TDS), and contact angle (CA) measurements. XPS and CA measurements revealed that the adsorption of octanethiol (OT) molecules on these metals led to the formation of chemisorbed self-assembled monolayers (SAMs). Three main desorption fragments for dioctyl disulfide (C8SSC8+, dimer), octanethiolate (C8S+), and octanethiol (C8SH+) were monitored using TDS to understand the effects of surface morphology and the nature of metal substrates on the thermal desorption behavior of alkanethiols. TDS measurements showed that a sharp dimer peak with a very strong intensity on single crystalline Au (111) surface was dominantly observed at 370 K, whereas a broad peak on the polycrystalline Au surface was observed at 405 K. On the other hand, desorption behaviors of octanethiolates and octanethiols were quite similar. We concluded that substrate morphology strongly affects the dimerization process of alkanethiolates on Au surfaces. We also found that desorption intensity of the dimer is in the order of Au > >Ag > Cu, suggesting that the dimerization process occurs efficiently when the sulfur-metal bond has a more covalent character (Au) rather than an ionic character (Ag and Cu).

Keywords: Alkanethiol, Self-Assembled Monolayer, Substrate Dependence, Thermal Desorption Behaviors