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Thermal behavior of Alkanethiolate Self-Assembled Monolayers on the Cu(111)

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Self-assembled monolayers (SAMs) of alkanethiol have been formed on the Cu(111) surfaces in vacuum. The thermal behavior of octanethiol-based SAMs on the Cu(111) surface have been examined in ultrahigh vacuum. Using X-ray photoelectron spectroscopy (XPS), it is found that the monolayers are stable up to about 500 K in vacuum. Decomposition is signaled by a decrease in the intensity of C 1s peak, accompanied by an increase of the intensity of the Cu 2p peak, However, the intensity of the S 2p peak doesn't change much as a function of annealing temperature. Thermal the decomposition mass spectra show that n-alkene is the predominant species desorbing from the surface in the 500-600 K temperature range. The totality of these data leads to the conclusion that the monolayers decompose through the S-C bond cleavage by hydrogen elimination reaction, resulting in the desorption of hydrocarbon moiety as n-alkene. Following this initial decomposition step. Cu₂S layers are observed on the surface. For comparison, attempts were also made to examine the thermal behavior of octanethiol-based SAMs on the Cu(111) surface in air. It has been shown that the SAMs on the Cu(111) surfaces begin to desorb with the oxidation of the thiolate to sulfonate at 400 K. Upon annealing to 450 K, the monolayer has almost completely desorbed as indicated by the virtual disappearance of the S 2p peak.