Formation and Characterization of Alkylsilane-based Self Assembled Monolayers
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Introduction: Self-assembled monolayers (SAMs) have been used to study adhesion, corrosion, wetting and lubrication of metal surfaces [1]. The most widely studied of these systems is alkanethiols on gold. Recently, hydridosilsesquioxane (H$_8$Si$_8$O$_{12}$) was demonstrated to chemisorb to a freshly evaporated gold surface at room temperature in ultra-high vacuum (UHV) [2, 3]. An extension of the chemistry of SAMs has been achieved through the reaction of alkylsilanes with a gold surface.

Methods and Materials: Hexylsilane (H$_{13}$C$_6$SiH$_3$), octylsilane (H$_{17}$C$_8$SiH$_3$) and octadecylsilane (H$_{37}$C$_{18}$SiH$_3$) were purchased from Gelest, Inc. (Tullytown, PA) and underwent multiple freeze-pump-thaw cycles prior to use. Freshly evaporated gold surfaces were exposed to the alkylsilanes in UHV at room temperature. The resulting layers were investigated using soft x-ray photoemission spectroscopy (XPS) at the National Synchrotron Light Source. Photon energies employed ranged from 160 eV to 400 eV.

Results: For all of the silane-based monolayers, the Si 2p$_{3/2}$ core-level (photon energy = 160 eV) is single-featured and observed at a binding energy of 99.8 eV with a full width at half maximum of 0.4 eV. This width is almost as narrow as that observed for bulk, crystalline silicon, indicating that the silicon atoms in the monolayers are in chemically homogeneous environments. In addition, the binding energy is consistent with the absence of hydrogen bound to the silicon atom. The Au 4f core-levels are observed in all cases, indicating that only a monolayer has formed. The C 1s core-level exhibits a single feature, consistent with that observed for straight chain alkanethiol monolayers on gold. The valence band region exhibits features arising from electrons ejected from Au 5d and 6s orbitals, as well as from C 2s and 2p orbitals. There is a high correlation between the C 2s features observed for the alkylsilane-based monolayers and those observed for straight chain alkanes containing the same number of carbon atoms, indicating the alkyl chains are intact in the monolayers [4]. The silicon and gold core-levels are attenuated to the same degree in each sample, indicating that the silicon and gold are at nearly identical depths within the sample. Film thickness for each of the monolayers has been calculated based upon the attenuation of the gold photoelectrons through the hydrocarbon layer.

Conclusions: The formation of alkylsilane-based SAMs on gold surfaces in UHV occurs through the activation of all three Si-H bonds present in the alkylsilane. The molecules are intact and upright on the surface. The possibility of the formation of multi-layers is excluded by the observation of the gold core-levels and the extremely narrow width of the Si 2p core-level.

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References: