Adsorption and Thermal Reaction of Alkanethiols on GaAs(100)

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Reactions to modify a surface are important not only for engineering of surface energy and composition but also for attaching molecules with varied physical and chemical properties. Deposition of self-assembled monolayers (SAM) formed from organosulfur compounds can be formed via bonding of the sulfur atom to various surface. Like adsorption of alkanethiols that occurs on noble metals, a SAM film might be prepared on a GaAs surface that can modify the chemical and physical properties of that surface and become potentially adaptable for such applications as protecting and insulating layers. We report here an investigation of the mechanism of adsorption and decomposition of alkanethiols on a GaAs(100) surface, utilizing temperature- programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS); such spectral examination elucidates pathways of this surface reaction. In principle, the length of the carbon chain of an alkanethiol might exert a significant influence on the thermal stability and reaction mechanism due to the presence of -hydrogen and the interaction between a GaAs surface and an alkyl group. We thus undertook a comparison of thermal reactivity and reaction products for alkanethiols with varied length of alkyl chain (i.e. RSH with R=CH_3, C_2H_5 and C_4H_9), thus probing the formation and thermal stability of alkanethiolate adlayer on a GaAs surface.

The chemical identity of surface species upon adsorption and thermal fragmentation of CH_3SH on a Pt surface is characterized with XPS measurement. Fig 1 shows XPS spectra of S 2p collected from a GaAs(100) surface exposed to CH_3SH at 110 K for varied duration. Three S $2p_{3/2}$ features appear at 162.7, 163.4, and 164.6 eV in order with increasing duration of exposure. The first feature, predominant at small exposures, is attributed to methylthiolate (CH_3S) and the second feature is due to chemisorbed CH_3SH. CH_3S is formed on deprotonation of the sulfhydryl group ($CH_3SH \rightarrow CH_3S + H$) as is observed on other metal surfaces. With duration of exposure greater than 60 s, the intensities of the feature at 164.6 eV increases with exposure, whereas the intensities of that at 162.7 eV due to CH_3S is attenuated. This observation indicates that physisorbed CH_3SH accumulates on the surface with a S 2p binding energy similar to that of chemisorbed CH_3SH. Moreover, an additional S $2p_{3/2}$ feature develops at 164.9 eV in the presence of physisorbed CH_3SH. This feature indicates that a fraction of condensed CH_3SH molecules are assembled with hydrogen bonding that induces the core-level electrons of S 2p to increased binding energy. In contrast, this feature is not present on physisorption of C_2H_5SH and C_4H_9SH. The formation of hydrogen bonding of physorbed alkanethiol depends on the acidity of sulfhydryl group.

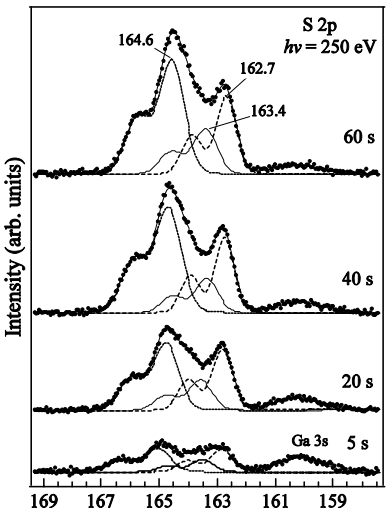

Figure 1. XPS spectra of S 2p taken from a GaAs surface for varied duration of exposure to CH_3SH at 100 K. Dots represent data collected after background subtraction; solid lines are fitted curves, and various components are shown in dashed lines. The photon energy used to collect these spectra is 250 eV.