

# Structure-Dependent Change of Desorption Species from *n*-Alkanethiol Monolayers Adsorbed on Au(111): Desorption of Thiolate Radicals from Low-Density Structures

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The coverage dependence of desorption behavior of *n*-alkanethiol monolayers on Au(111) has been studied using thermal desorption spectroscopy (TDS) together with scanning tunneling microscopy (STM) to investigate the molecule–substrate interactions. STM observations indicated four different phases during the growth. We present for the first time evidence for a drastic coverage-dependent change of desorption species, which is parallel with a structure change from a low-density phase to a denser phase: while the thiols in the latter phase bimolecularly desorb as disulfides, those in the former phase unimolecularly desorb as thiolate radicals.

Self-assembled monolayers (SAMs) on solid surfaces have attracted considerable attention because they are potentially useful for a wide range of technological applications.<sup>1</sup> In particular, *n*-alkanethiol SAMs on Au(111) have been profoundly studied as a prototype system for the fundamental understanding of the self-assembly phenomena because of their simplicity, stability, and high ordering.<sup>2–4</sup> So far, fundamental aspects of alkanethiol SAMs such as structures and adsorption processes have been studied in some detail with a variety of techniques. For example, recent beam diffraction studies<sup>5–7</sup> and scanning tunneling microscopy (STM) studies<sup>8–10</sup> have shed light on the molecular arrangements of the highly ordered structures and adsorption mechanisms of the alkanethiol SAMs. The consensus from these studies is that the adsorption of thiols exhibits a two-stage process in which an initial low-density monolayer, which is called “striped” phase, is rapidly formed, followed by a much slower evolution to a saturated monolayer with a commensurate rectangle unit cell, which can be described as a  $c(4 \times 2)$  superlattice of a  $(\sqrt{3} \times \sqrt{3})R30$  hexagonal arrangement. And also, it is widely accepted that the bonding state is, in all cases, in the form of a Au-thiolate.<sup>2,11–13</sup> Despite the progress of the understanding of the adsorption-related aspects, however, as for the desorption phenomena, only a limited number of studies have been reported.<sup>11,14</sup> According to these studies, surface thiols associatively desorb as disulfides, while the thermal desorption data for an alkanethiol monolayer formed on Au(100) suggested that it desorbs molecularly as thiols.<sup>15</sup>

Herein, we report the desorption behavior of hexanethiol ( $\text{CH}_3(\text{CH}_2)_5\text{SH}$ ; C6) monolayer on Au(111), which is one of the most thoroughly characterized SAM systems, and its relation to the coverages (hence structures) of C6 SAM by using thermal desorption spectroscopy (TDS) and STM. We observed for the first time that the desorption species drastically changes depending on the coverage, which is parallel with a structure change from the striped phase to a higher density phase: the

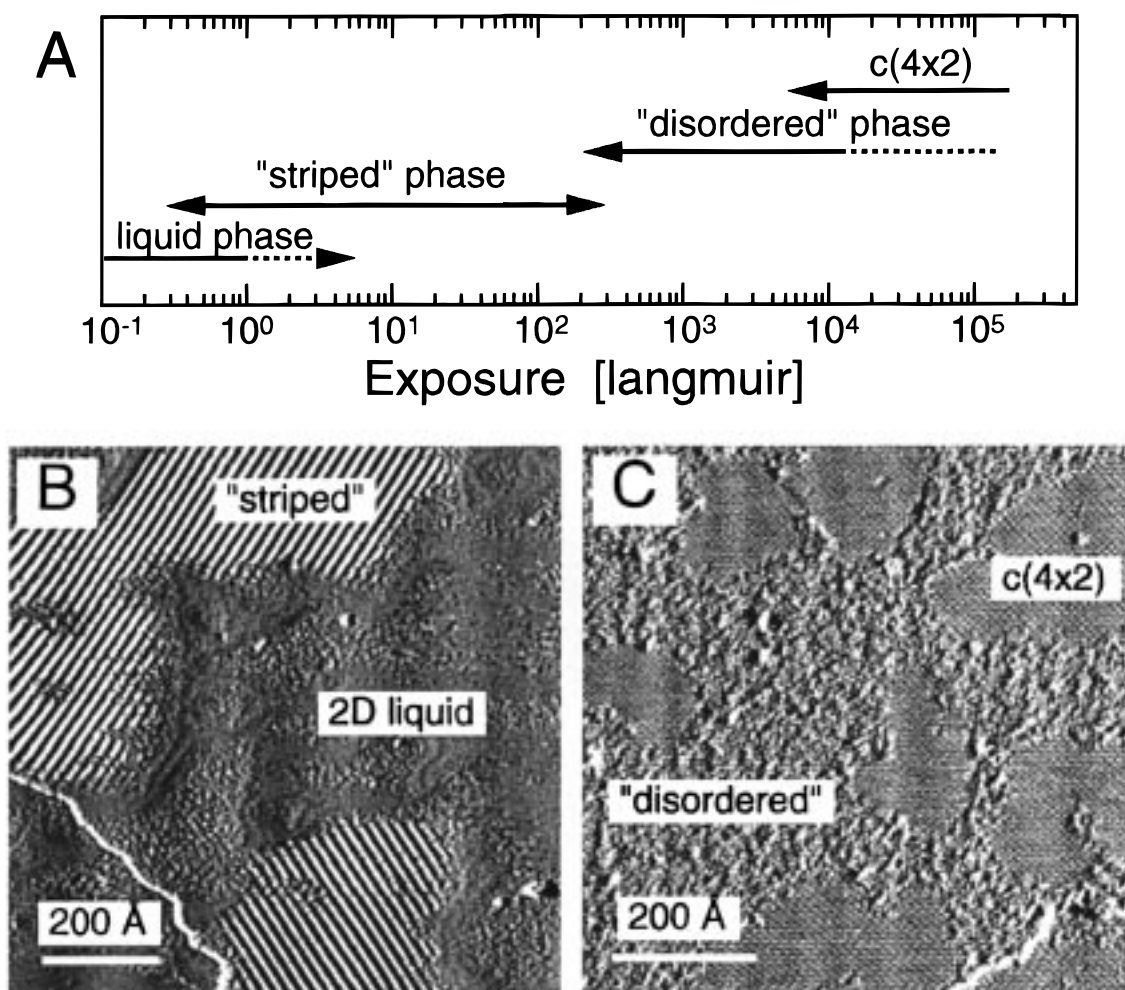
thiols in the former structure desorb as thiolate radicals, while those in the latter one as disulfides. To our best knowledge, such a drastic switching of the desorption species depending on the structure has not been reported so far.

The experiments were performed using an ultrahigh-vacuum STM system (JEOL, JSTM-4500XT), which is equipped with facilities for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and TDS. The Au(111) surface was cleaned by  $\text{Ar}^+$  sputtering and annealing. Cleanliness and ordering were confirmed by AES, LEED, and STM. The “herringbone” structure due to the  $23 \times \sqrt{3}$  reconstruction of clean Au(111)<sup>16</sup> was clearly observed by STM. The clean Au(111) surfaces were exposed to gaseous hexanethiol at room temperature.<sup>17</sup> STM observations were carried out at room temperature using electrochemically prepared tungsten tips. TDS measurements were performed with a multiple mass spectrometer at a heating rate of 9 K/s.

To provide an outline of the whole growth processes, we performed a STM observation of the C6 monolayers on Au(111) with increasing exposure from  $10^{-1}$  to  $10^5$  langmuirs (1 langmuir =  $10^{-6}$  Torr·s; 1 Torr = 133 Pa). High-resolution STM images have revealed that four different phases appear during the growth to a saturated monolayer as shown in Figure 1A. At low exposures less than 5 langmuirs, a striped phase and a two-dimensional liquid phase coexist on the surfaces (see Figure 1B).<sup>18</sup> Exposing the surface to more than 5 langmuirs results in complete covering of the surface with the striped phase. However, exposure to more than 200 langmuirs causes appearance of a “disordered” phase again, of which the region grows with exposure at the expense of the striped-phase islands. This disordered phase completely covers the whole surface at around 300 langmuirs. Further exposure to more than 5000 langmuirs of C6 results in nucleation and growth of an ordered phase with the  $c(4 \times 2)$  periodicity (see Figure 1C). The  $c(4 \times 2)$  structure is the saturated structure and identical to the monolayer structure when prepared by the dipping method.<sup>6,8,9</sup>

Figure 2A shows TD spectra of C6 disulfide ( $\text{C}_6\text{H}_{13}\text{SSC}_6\text{H}_{13}$ ; 234 amu) for C6-SAM-covered Au(111) surfaces

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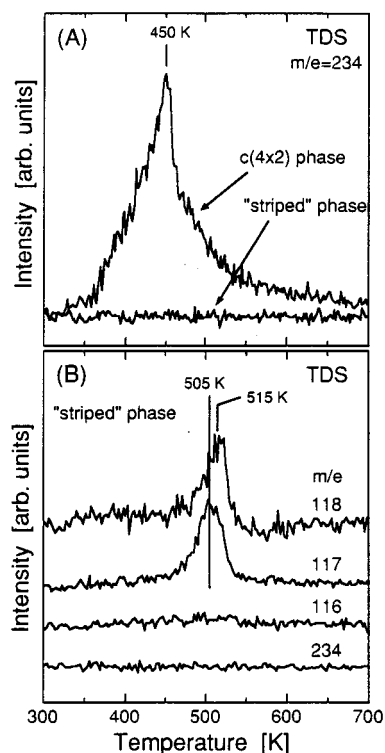
**Figure 1.** (A) Overview of the growth of the hexanethiol (C6) monolayers on Au(111) as a function of exposure obtained from STM observations. (B), (C) STM images of Au(111) surfaces after exposing to 0.5 and 5250 langmuirs of C6, respectively. At 0.5 langmuirs, a striped phase appears as islands and a small amount of a herringbone-like features are observed (mostly around the center). The other areas are filled with an obscured structure that is associated with a two-dimensional liquid phase. At 5250 langmuirs islands of a  $c(4 \times 2)$  phase and a disordered phase are observed.

with exposures of 95 (lower) and 117 800 (upper) langmuirs. STM observations indicated that these surfaces were covered with the striped phase and the  $c(4 \times 2)$  phase, respectively. While no desorption feature is observed for the striped phase, a prominent desorption peak of C6 disulfide is seen at 450 K for the  $c(4 \times 2)$  phase, which indicates that the desorption of the disulfide occurs only for the  $c(4 \times 2)$  phase and not for the striped phase.

To investigate desorption species from the striped phase, TD spectra of several mass numbers were measured for a striped-phase covered Au(111) surface as shown in Figure 2B. The TD spectrum for C6 thiol (118 amu:  $p$ ) exhibits a desorption peak at 515 K. A similar peak is also observed with a comparable intensity at 505 K in the desorption trace for  $p - 1$  (117 amu), while no apparent desorption feature is seen in the spectrum for  $p - 2$  (116 amu). It should be noted that this fragmentation ratio is completely different from that of C6 thiol measured with our mass spectrometer, i.e.,  $I_{118}:I_{117}:I_{116} = 1:0.03:0.07$ . This discrepancy shows that the desorbed species is not C6 thiol. Since there is no desorption feature in the 234-amu spectrum, the desorption features observed in the 117- and 118-amu spectra are not associated with C6 disulfide. We propose to attribute this species to a C6 thiolate radical ( $\text{CH}_3(\text{CH}_2)_5\text{S}^\cdot$ : 117 amu) on the basis of the observed fragmentation ratio ( $I_{118}:I_{117} \approx 1:1$ ). It is known that a desorption peak of a radical with a mass number  $n$  tends to be accompanied by a desorption

peak of the  $n + 1$  species with a comparable intensity via hydrogen-abstraction reaction on the walls inside the chamber.<sup>19</sup> The  $n + 1$  peak is observed at a slightly higher temperature (i.e., at a slightly delayed time). This is probably because multiple collisions with the surfaces are required for the hydrogen abstraction. An alternative explanation for the origin of the 118-amu peak is surface hydrogenation of the C6 thiolates and subsequent desorption as C6 thiols. This can be excluded, however, since surface hydrogen atoms on gold readily desorb at a very low temperature (115 K).<sup>20</sup> These facts suggest that all the thiolates in the striped phase desorb as thiolate radicals at around 510 K.

A series of TD spectra for C6-SAM-covered surfaces with a series of exposures (not shown) has revealed that there is a critical exposure (around 300 langmuirs) where the desorption of the disulfide starts. This critical point almost coincides with the start of the formation of the "disordered" phase (see Figure 1A): at lower exposures before formation of the "disordered" phase (i.e., for the liquid and the striped phases), only the desorption of the thiolate radicals was observed. Thus, the desorption mode drastically varies from a unimolecular desorption to a bimolecular one at the critical exposure that corresponds to the structure transformation from the striped phase to the disordered phase.<sup>21</sup> This remarkable difference should be related to a difference in molecular density and/or a



**Figure 2.** Thermal desorption spectra (TDS) for C6 SAMs on Au(111). (A) TD spectra of mass/charge ( $m/e$ ) = 234 amu (C6 disulfide) for surfaces after exposing to 95 (lower) and 117 800 (upper) langmuirs. These surfaces are covered with the striped phase and the  $c(4 \times 2)$  phase, respectively. Only the high-density  $c(4 \times 2)$  phase gives desorption of disulfides. (B) TD spectra for a Au(111) surface after exposing to 8 langmuirs of C6. This surface is covered with the striped phase. The TD spectra exhibit a clear desorption peaks for  $m/e = 117$  and 118 amu at around 510 K, while apparent features are observed neither for  $m/e = 116$  nor 234 amu. These spectra strongly suggest that the desorption species is not a disulfide but a thiolate radical (see text).

difference in bonding of the molecule–substrate interface. Further experiments to elucidate the mechanism are now underway.

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- (17) The vapor of hexanethiol was introduced onto the Au(111) surfaces via a variable leak valve with a nozzle (hole diameter, 0.5 mm; nozzle length, 200 mm; distance from sample, 10 mm). Here, since the local pressure at the sample position during the exposure could not be precisely calibrated, we use readings of a pressure gauge located 200 mm underneath the sample as apparent gas pressures.
- (18) At 0.5 langmuirs, a small amount of herringbone-like features still remain on the surface, and these features completely disappear at slightly higher exposures (0.6 langmuirs). Surface areas other than the herringbone-like features and striped islands are filled with obscure domains, which we attributed to a "2D liquid" phase since these domains have no ordered structure and their domain boundaries are fluctuating. The details of the growth processes will be reported elsewhere. Kondoh, H.; Kodama, C.; Sumida, H.; Nozoye, H. To be submitted.
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