

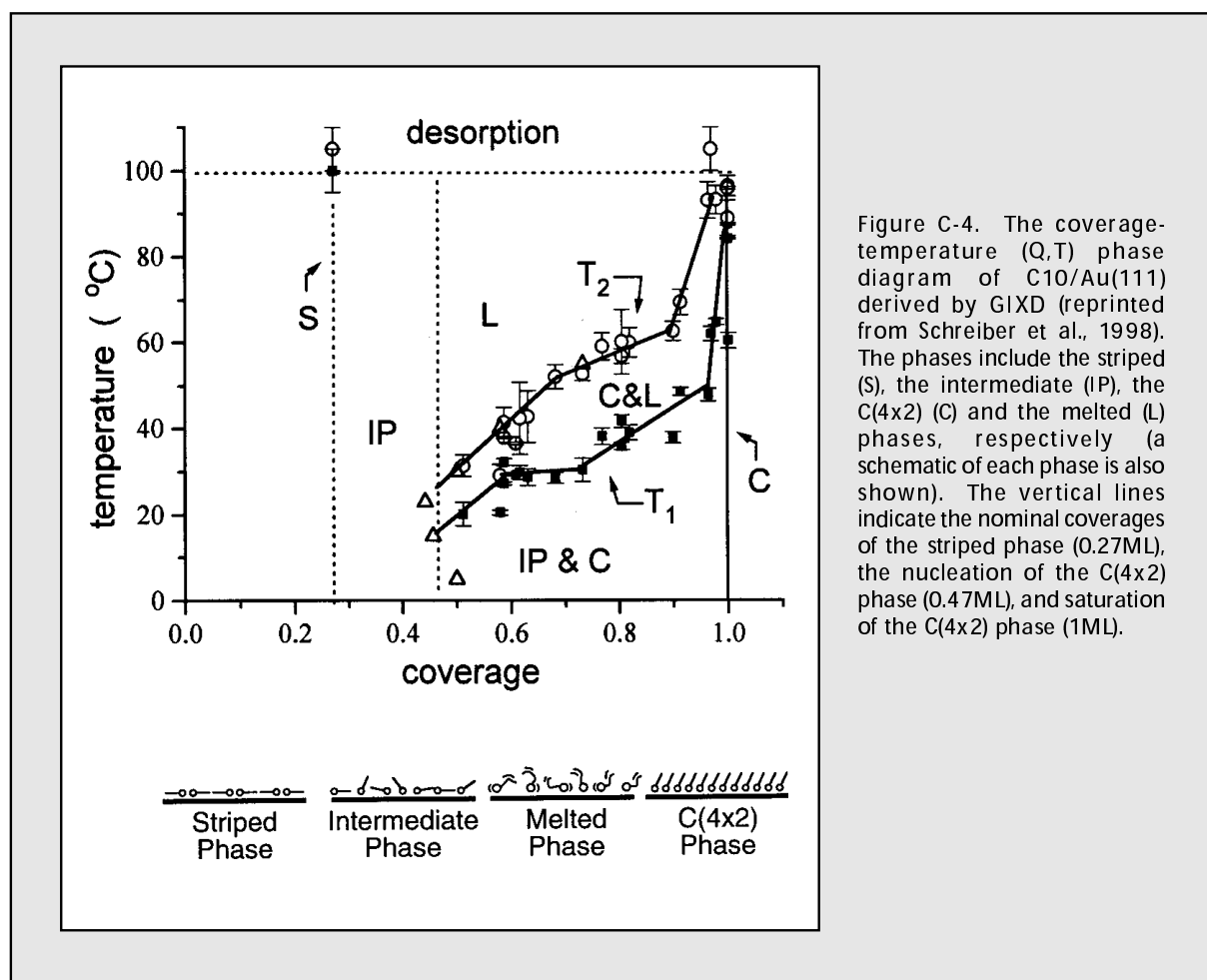
# Using X-Ray "Vision" to Understand Self-Assembly

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## INTRODUCTION

The concept of "self-assembly" (SA) is derived from biological systems and can be defined as a process by which molecules having many internal degrees of freedom are able to form ordered supermolecular structures utilizing weak interactions such as van der Waals forces or hydrogen bonding<sup>[1]</sup>. Monolayers of alkyl-thiols grown on Au(111) surfaces are special among the many self-assembling systems because this system is widely considered as prototypical and has many potential technical

applications. In this system the gold-sulfur bond is strong enough to anchor the molecules to the surface, yet at the same time this interaction leaves sufficient lateral mobility to allow the inter-chain van der Waals interaction to drive the system toward the formation of a stable well-ordered monolayer. Here we review some of the phenomena that we have uncovered using x-ray scattering techniques to study the growth of decanethiol (C10) on Au(111) surfaces from the vapor phase (for details of sample preparation, etc., see references<sup>[2, 3, 4]</sup>).



## PHASE BEHAVIOR OF SAMS

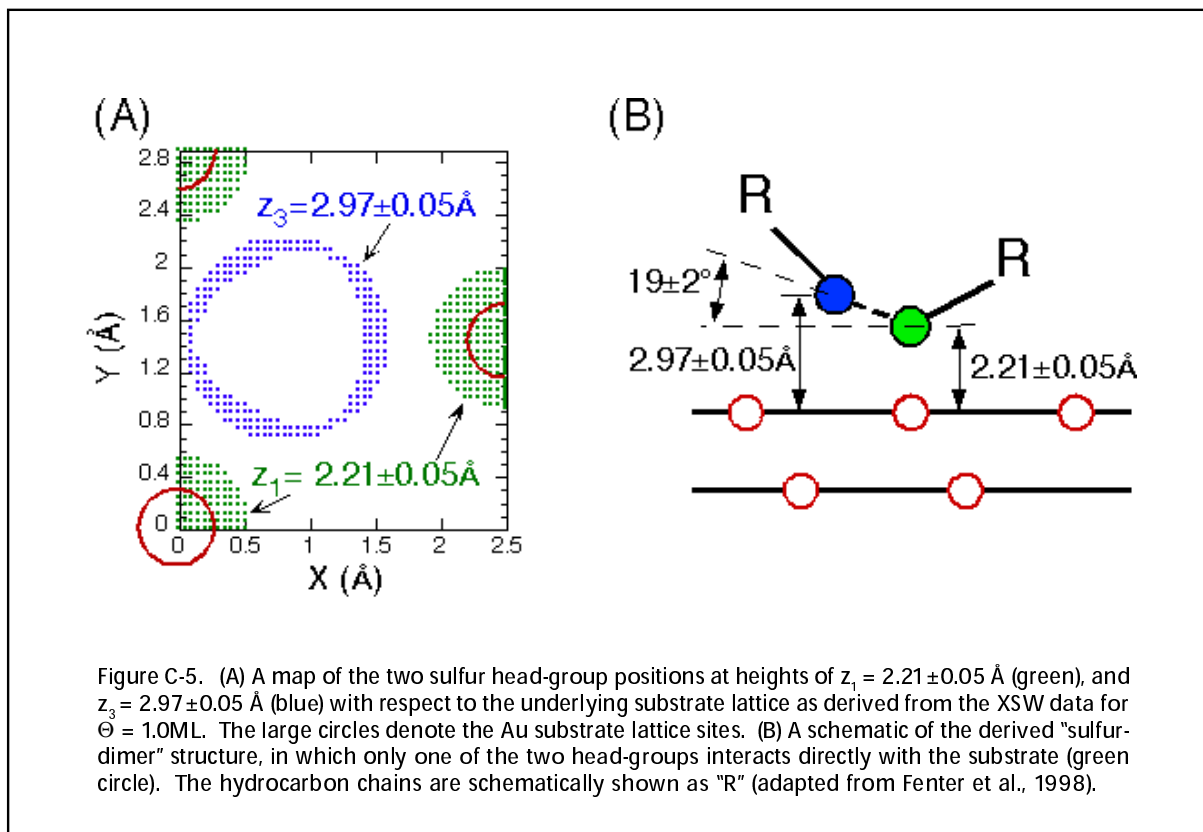
The first complexity that must be overcome is to understand the different equilibrium structures that are present during growth. Early growth studies have interpreted SAM growth as a continuous process by which the alkyl chains within the monolayer collectively transform from a disordered to an ordered configuration<sup>[5]</sup>. Instead, through a combination of X-ray, He atom diffraction and scanning tunneling microscopy, it has been shown that there are a number of distinct phases present during the growth process<sup>[3, 6]</sup>. In addition to the densely packed "standing up" C(4x2) phase at saturation coverage ( $\Theta = 1$  ML =  $4.6 \times 10^{14}$  molecules/cm<sup>2</sup>), at low coverages a lying down "striped" phase ( $\Theta = 0.27$  ML) has been observed. By mapping out the temperature and coverage dependence of these two ordered phases using grazing incidence x-ray diffraction (GIXD), we have delineated<sup>[3]</sup> the equilibrium phase behavior of this system (shown in **Figure C-4**). In addition to these two ordered phases there are at least two other *disordered* phases. There is an "intermediate" phase which is found at coverages intermediate between the C(4x2) and the striped phases (for  $T < 15^\circ\text{C}$ , with a nominal coverage of  $\Theta = 0.47$  ML), and a melted phase which apparently exists at all coverages for sufficiently elevated temperatures. Thus, at

equilibrium, the growth proceeds primarily through the *coexistence* of these distinct phases<sup>[3]</sup>.

A remarkable feature is that while a complete monolayer melts at  $\sim 90^\circ\text{C}$ , at  $\Theta \sim 0.5$  ML the SAM melts at  $\sim 15^\circ\text{C}$  (even though both phases are chemisorbed!). This dependence of  $T_m$  with  $\Theta$  is one of the essential keys to understanding the SAM's ability to assemble into highly ordered structures<sup>[3]</sup>. When growing in the presence of the melted phase ( $T > 15^\circ\text{C}$ ) the order in the SAM (as measured by the average domain size) is substrate limited which is suggestive of significant diffusivity and Ostwald ripening of the growing islands. At lower temperatures ( $< 15^\circ\text{C}$ ) the final SAM is significantly less ordered and the domain size evolution during growth is consistent with a fixed number of islands suggesting a loss of diffusivity at these temperatures<sup>[3]</sup>.

## THE HEADGROUP-SUBSTRATE INTERFACE STRUCTURE AT THE BURIED INTERFACE

How can we understand the combination of high thermal stability coupled with an ability to assemble at, and even *below*, room temperature? This issue is closely related to the nature of the S-Au bond. While the vast majority of studies on these systems assume that the sulfur



headgroup bonds to the Au surface in an hexagonal  $\sqrt{3}\times\sqrt{3}$  mesh with a S-S spacing of 5 Å<sup>[7]</sup>, our 2D crystallography results found that while the chain-chain spacing was indeed ~5 Å, the sulfur headgroups were instead arranged as sulfur dimers with a S-S spacing of ~2.2 Å<sup>[8]</sup>.

To resolve the ensuing controversy, we performed X-ray standing wave (XSW) measurements to directly probe the S/Au interface structure for this system<sup>[2]</sup>. XSW is one of the few techniques which can directly and quantitatively probe a buried interface structure containing a low Z element such as sulfur by probing its XSW induced photoelectron yield near a substrate Bragg condition. The results (summarized in **Figure C-5**) reveal a highly detailed picture of the S-Au interface structure and directly contradict the widely assumed hexagonal S

mesh. We find that the two distinct S headgroup locations within the unit mesh each have a distinct height and lateral position<sup>[2]</sup>. By combining these results with the information derived with GIXD<sup>[8]</sup>, we find that the S dimer is bound to the Au substrate through only one of the two S atoms with the presumed S-S bond being inclined by  $19^\circ \pm 2^\circ$  with respect surface plane. The derived Au-S-S angle is consistent with the tetrahedral angle and therefore provides a natural context in which to understand the S-Au interface structure. The existence of a sulfur *dimers* species (which presumably interacts more weakly with a gold surface than a sulfur monomer) provides a simple yet plausible explanation for the observation of both a melted phase and significant surface diffusivity for these chemisorbed species at temperatures as low as 15°C.

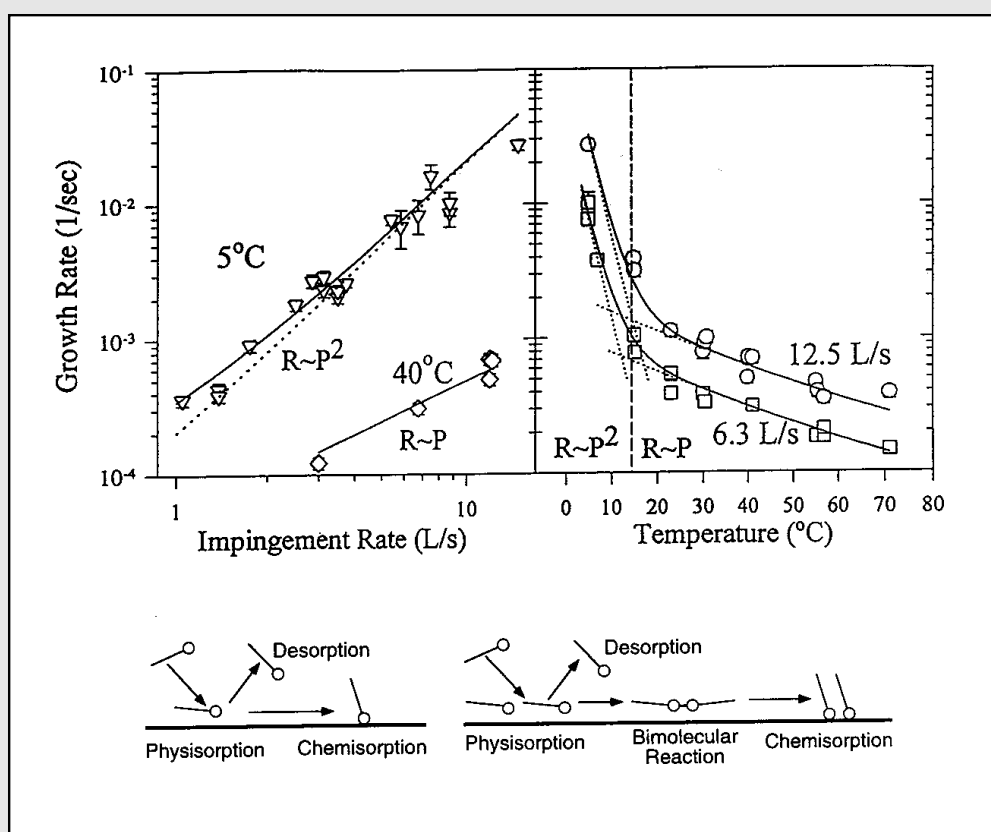


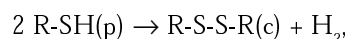
Figure C-6. The C(4x2) growth rate is plotted as a function of impingement rate for two representative temperatures, and as a function of temperature for two impingement rates (reprinted from Eberhardt et al., 1998). At 40°C the dependence is linear, but at 5°C the growth rate increases *quadratically* with the impingement rate. Also shown is a schematic of the uni- and bi-molecular adsorption processes.

## ADSORPTION MECHANISMS IN SELF-ASSEMBLY

In this system, SA proceeds in a two-step fashion<sup>[2,3]</sup>, of which the second step is associated with the formation of the C(4x2) phase and the final “assembly” of the monolayer. We have made use of the simple proportionality between the GIXD integrated intensity and the coverage of a particular phase (the C(4x2) phase) to follow the growth kinetics *in situ* and in real-time, as a function of the thiol impingement rate and the substrate temperature<sup>[4]</sup>. The data (**Figure C-6**) clearly show that there are two distinct adsorption processes, each having a distinct dependence upon temperature and pressure. From the decrease of the growth rate vs. increasing temperature in both processes, we can directly conclude that the molecules adsorb as a physisorbed precursor phase and thermalize before either chemisorbing or desorbing from the surface (i.e., physisorption mediated chemisorption)

A unique feature of these data is that while the high temperature process varies *linearly* with the impingement rate, the low temperature process varies *quadratically* with this quantity<sup>[4]</sup>. While a linear variation is ubiquitous in surface adsorption and can be understood phenomenologically as the result of a uni-molecular process (i.e., each molecule adsorbs or desorbs independently of other molecules), the quadratic variation can be understood as an associative adsorption process, whereby the rate-limiting step is a *bimolecular reaction* in

the physisorption well:



where “p” and “c” denote physisorbed and chemisorbed species, respectively. This bimolecular adsorption process is very unusual and may ultimately be the result of the peculiar adsorption energetics of this system<sup>[9]</sup>.

## CONCLUSIONS

X-ray scattering techniques have allowed us to unravel many of the molecular-level aspects of SA of C10 on Au(111). We conclude that the growth of this system can be understood in terms of its phase behavior, bonding, and adsorption mechanisms, and the complexity of this system is *not* a direct result of the molecular structure (e.g., as a result of chain entanglement), although chain entanglement is expected to be important for longer aliphatic molecules (e.g., polymer brushes). In work presently in progress<sup>[9]</sup>, we are testing our level of understanding of the SA process by probing the behavior of molecules that have two headgroups (e.g., hexanedithiol) and by investigating the influence of the molecular backbone rigidity. ■

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