

# Real time *in situ* studies of the self-assembly of octadecyltrichlorosilane monolayers

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## Introduction

Self-assembly of molecular monolayers from solution is a powerful way to make organized, stable (chemically bonded) arrangements of functionalized molecules. Although *ex situ* self-assembled films have been extensively studied, the process of self-assembly is poorly understood. In the simplest and most-studied system, octadecyltrichlorosilane (OTS) adsorbed on silicon, there is not even qualitative agreement about what happens at intermediate stages of growth [e.g. refs. 1-4]. We have therefore looked at self-assembly *in situ* and in real time using X-ray reflectivity.

## Methods and Materials

We studied the self-assembly of OTS from dilute solutions in heptane onto polished Si(111) substrates. Heptane was chosen because it has a relatively low density and so produces a significant (although small) electron density contrast at the monolayer-liquid interface. We used a transmission cell [5] adapted and simplified from designs used for electrochemical studies [6].

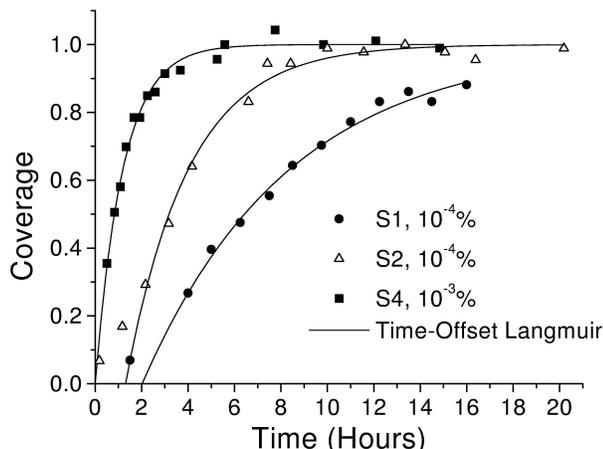


Fig. 1: Coverage as functions of time for three samples, obtained from fitting real-time X-ray reflectivity data. The curves follow Langmuir kinetics, but for the low concentration solutions, a time offset is required. [From ref. 7]

## Results

In earlier work performed at NSLS [5], we found that the best fits to reflectivity curves at all intermediate stages of growth were obtained with electron density distributions representing a monolayer of varying density but a *constant* thickness corresponding to the molecular length. This was inconsistent with the findings of Tidswell et al [2], who had reported (using interrupted-growth, i.e. the partially-deposited films are removed from the solution for reflectivity studies) that the molecules were more tilted at first and became less tilted as more molecules were adsorbed.

Because of intensity limitations, our studies at NSLS were performed at micromolecular concentrations to slow down the growth. Typically, monolayers are deposited from higher-concentration solutions. At APS, we studied the deposition process at various solution concentrations [7]; we found that at all concentrations studied, the molecules were vertical when deposited. The coverage as a function of time could always be fitted with a Langmuir adsorption curve (Fig. 1), but for the more dilute solutions, a time offset was needed for a good fit [7]. A similar time offset has been reported by Schwartz and coworkers [8] for another self-assembling system, using atomic force microscopy.

We also established that the discrepancy between our results and those of Tidswell et al. [2] were not due to unquantified variations in experimental conditions; rather, they resulted from the use of interrupted-growth measurements as stand-ins for *in situ* measurements. We studied partially deposited monolayers *ex situ*, and our results were quite consistent with those of Ref. 2. The process of removing a monolayer from the deposition cell causes irreversible changes, so that the interrupted-growth method does not give a true indication of what is happening *in situ* [7].

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