A Study on the Formation and Thermal Stability of 11-MUA SAMs on Au(111)/Mica and on Polycrystalline Gold Foils

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In this article we present a comprehensive study of 11-mercaptoundecanoic acid self-assembled monolayer (SAM) formation on gold surfaces. The SAMs were prepared in ethanolic solution, utilizing two different substrates: Au(111)/mica and polycrystalline gold foils. Several experimental methods (X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and atomic force microscopy) reveal a well-defined SAM. The main focus of this work, however, was to test the stability of these SAMs by thermal desorption spectroscopy. The spectra show different desorption peaks indicating different adsorption states and/or decomposition products on the surface. The assumed monolayer peak, which can be attributed to desorption of the intact molecule, is detected at 550 K. Further desorption peaks can be found, which result, e.g., from cracking of the S−C bond on the surface, depending on the substrate quality and on the residence time under ambient conditions.

Introduction

There are lots of potential applications for self-assembled monolayers (SAMs), such as for corrosion inhibition, biosensors, lithography, organic electronics, and so forth, as already described comprehensively in several excellent review articles.[1−6] The most frequently used organic molecules for SAM formation are alkane thiols, adsorbed on gold surfaces. The reason is that methyl-terminated, long alkane thiols ($n > 6$) form well-ordered, closely packed monolayers on Au(111).[7] One quite often investigated system in view of applications is mercaptoundecanoic acid (11-MUA, ($HS-(CH_2)_{10}-COOH$)) on gold surfaces, which not only forms well-ordered SAMs, but also provides the opportunity to modify the acid end group by other functionalized groups.[8] Even though this system has already been studied in some detail, there are still a lot of discrepancies and unsolved questions. There is a discussion about the ideal preparation procedure as well as about the alignment of the molecules on the surface.[9−12] Because of the importance of 11-MUA as a precursor for further modifications,[8,13−17] a good understanding of the SAM structure and thermal stability is indispensable.

Various experimental techniques have been used to characterize this system, such as X-ray photoelectron spectroscopy (XPS),[9,10,13,14,16,17] scanning tunneling microscopy (STM)[9,10,18] and Fourier transform infrared spectroscopy (FTIR).[17,19−21] FTIR, even though in principle being one of the most appropriate methods to study SAMs, has the disadvantage of requiring an ideal reference sample. Polarization-modulated infrared reflection−absorption spectroscopy (PM-IRRAS), discarding the need of a reference, was performed by Duevel and Corn[22] for 11-MUA on gold. The resulting spectra suggested a quite wide range of disorder. Also STM has shown that it is difficult to grow good SAMs of 11-MUA on Au(111).[9,10]

With respect to the thermal stability of 11-MUA on gold and to the influence of the substrate structure, however, there is still little information available. In this contribution we focus on these issues. By applying thermal desorption spectroscopy (TDS), in addition to XPS, FTIR, and atomic force microscopy (AFM), we have studied 11-MUA SAMs for three different scenarios: freshly prepared SAMs on Au(111)/mica, 1 month aged SAMs on Au(111)/mica, and SAMs on recrystallized gold foils, which consist of grains with stepped surfaces.

Experiment

SAMs were prepared on gold surfaces ex situ in a 1−3 mM ethanolic solution of 11-MUA. No influence of the concentration in the denoted range on the SAM formation could be noticed. The immersion time was typically 48 h. After removal out of solution,

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