Irregularities in the Synthesis of an Undecylenic Acid Methyl Ester (UDAME) Monolayer on a Silicon(111) Substrate

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Abstract

Recent research suggests that ultraviolet illumination is essential for the creation of monolayers of Undecylenic Acid Methyl Ester (UDAME), as it is believed that the UV illumination initiates the radical-chain polymerization. Samples created without UV illumination, however, also show signs of a monolayer. In this study, samples were analyzed using atomic force microscopy and X-ray reflectivity to ascertain the characteristics of the film. A two-hour dark exposure, as opposed to two-hour UV illumination, showed the characteristics of a film expected from the UV treatment. A sample prepared with a total exposure of five minutes to UDAME also showed signs of a film, though not a monolayer. This suggests that further work is necessary to fully understand UDAME monolayer formation.

Introduction

Most of the industrialized world now has at least some understanding of the potential impact of nanoscale research. This technology will have widespread applications, including disease, biological, and chemical detection, which in turn will have an enormous impact on disease prevention and diagnostics. Ultimately, novel sensors will have recognition and signal transduction, based on an understanding of processes occurring on sub-100 nanometer features. Developing patterning technologies that give access to this length scale is one of the largest hurdles currently facing nanotechnology. While this challenge is the main deterrent to the advancement of these detectors, the solution will have a significant impact on a number of other disciplines.

In the quest to solve these issues, and in an effort to reduce production time, perhaps too much faith is placed in the existing methods to create the basic materials. It is often assumed that the current processes to manufacture initial samples are the most efficient and most current, but taking the opportunity to improve the primary steps can challenge these assumptions.

Such is the case with the creation of an Undecylenic Acid Methyl Ester (UDAME) monolayer on a silicon(111) substrate. UDAME ($CH_2CH(CH_2)_8COOCH_3$) is a bifunctional molecule in that it can attach itself to the substrate and be functionalized on the other end by various other potential terminations such as DNA.

Background

The scientific community is very interested in the development of nanoscale technology. Of specific interest is the creation of monolayers of unsaturated carbon compounds on a hydrogen-terminated silicon(111) surface. Silicon (111) is an enticing starting point for the synthesis of these monolayers, as research shows it capable of functionalizing its hydrogen silicon bond at the surface. Recent studies attempted to analyze the most effective method of accomplishing this task in a systematic way.[1] Researchers sought to show that the generation of densely packed hydrocarbon films of molecular thickness depended on illumination of the sample with ultraviolet light. By doing so, they suggest that the H-Si bond adds across the unsaturated bond in a manner similar to hydrosilylation, which is known for small-molecule

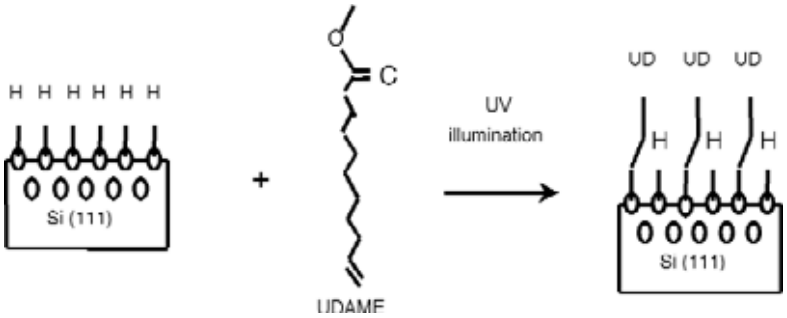

Figure 1: Attachment of a UDAME monolayer on a Si(111) surface. Note that the UDAME molecule is too large to occupy every H-Si position, which means 100% film coverage is not possible.

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Table 1. Results on Dark-Exposed UDAME

Sample	ρF (e^-/Å^3)	T (Å)	σS (Å)	σI (Å)	(°)
H-Si(111)	0	0	-	4.0	-
UV-UDAME	0.35	12.2	2.3	3.2	35
Dark-UDAME	0.29	12.4	3.1	3.6	34

ρF: Film-electron-density
T: Film-thickness
σI: Si-Film interface-roughness
σS: Film-Air interface-roughness
α: Molecular tilt-angle

chemistry that produces adsorbates covalently bonded to the surface. The key assertion is that these molecules react as a result of a radical-chain mechanism initiated by ultraviolet illumination that then causes photodesorption of the hydrogen.

Recent experiments performed at Northwestern University, however, cast doubt on the necessity of ultraviolet illumination to initialize the radical-chain mechanism. In this study, samples of silicon(111) were hydrogen passivated (as explained later in this article) and covered in UDAME for two hours without ultraviolet illumination. To eliminate any extraneous contaminants, the sample was placed in a nitrogen-rich environment and covered in aluminum foil to avoid any exposure to ambient light. According to previous research, no film should be present in such a sample, and the spectra from a hydrogen-passivated silicon surface can be obtained. Results obtained using an 18KW X-ray reflectivity machine, however, showed that there was a film present on the sample prepared under these conditions. Subsequent analysis of this data concluded that the sample actually showed a UDAME self-assembled monolayer, the characteristics of which are displayed in Table 1. The similarities between the data obtained on the UV exposed, when compared with the dark exposed, are clear indications of such a film. There was no possibility of UDAME remnants from the exposure because the sample was thoroughly cleaned after the two-hour exposure by sonication with methylene chloride and afterwards with methanol.

Approach

Given these results, it was clear that the process leading to UDAME monolayer formation needed to be analyzed. If a monolayer formed under an omission in the procedure, what other variations could yield the same result? The ultimate goal of this research was to minimize the steps for the synthesis of a UDAME monolayer, with the hope of decreasing the time required. The preparation of the hydrogen-passivated silicon surface was not varied, and its procedure can be found in many published articles.[2] One variation introduced in this study was that etch pits that form during hydrogen passivation were avoided by tilting the sample during the acid and base baths. Surface etch pits cause an unequal distribution of UDAME and can make it more difficult to analyze the film produced.

Following the formation of a monolayer under dark exposure, experiments were conducted to test the possible cause of the radical-chain step. Samples prepared under different variations of the procedure were first analyzed using an atomic force microscope (AFM). The goal was to keep the number of samples analyzed using X-ray reflectivity to a minimum because of the time needed to analyze samples using this method. Images taken at 3 microns show that a sample with a UDAME monolayer demonstrates the same characteristics as that of a bare hydrogen-passivated surface (Figure 2). Substrates that did not appear to have a monolayer were not analyzed using X-ray reflectivity, as the focus was to form UDAME monolayers.

Once the existence of a monolayer is confirmed through AFM imaging, more detailed information is needed to further characterize the structure of the film, such as its electron density and roughness. Such data can be collected using X-ray reflectivity, which is sensitive to changes in the average electron density along the momentum transfer vector Q. From derivations of Fresnel reflectivity, information regarding the density of the film perpendicular to the surface, film thickness, and interface roughness can be gathered by carrying out a single experiment. This makes reflectivity a powerful technique for analyzing films and solid surfaces. The setup of the 18KW machine has already been documented extensively.[3]

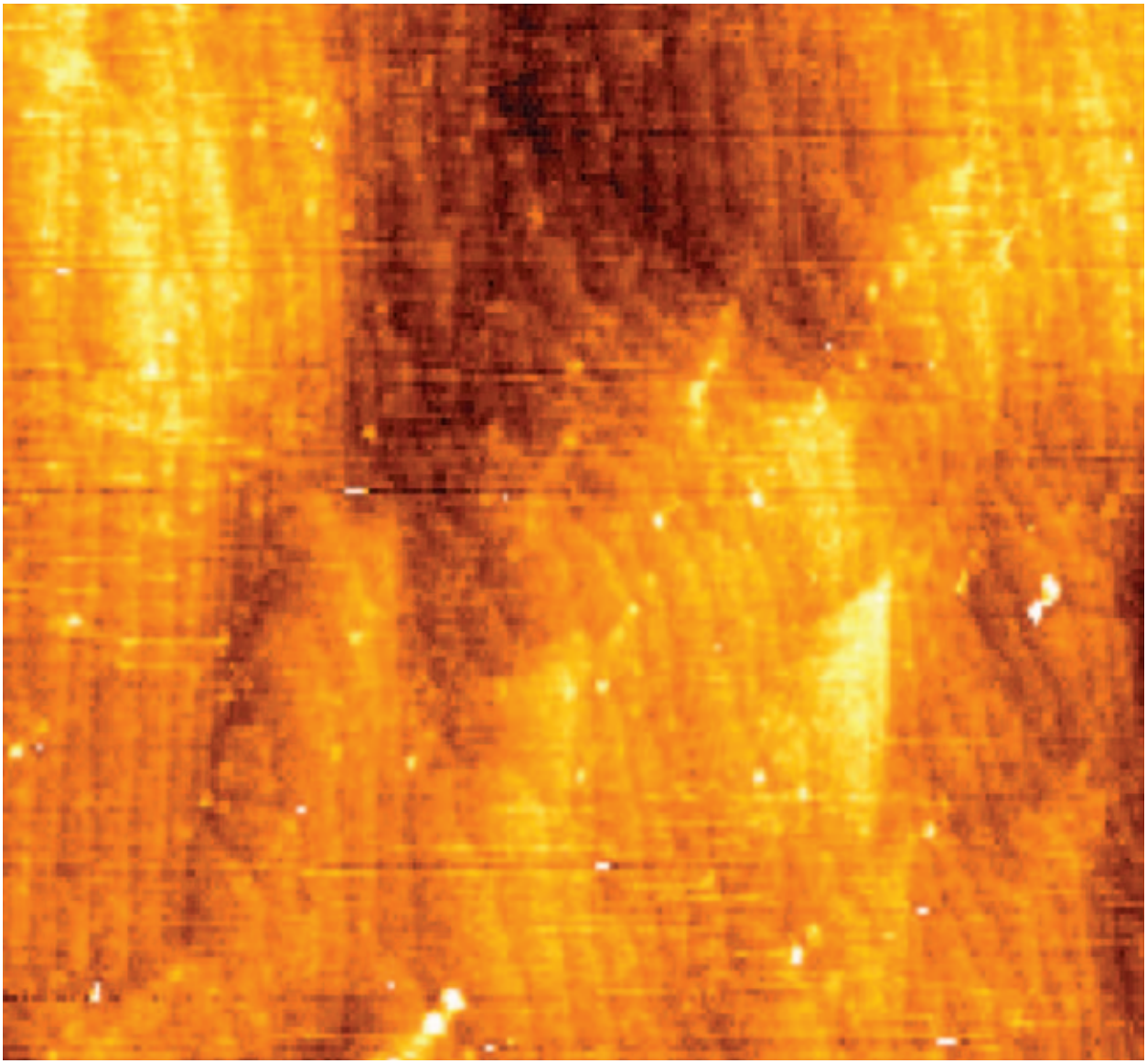

Figure 2: AFM image (3 micron scan) of a H-passivated Si surface. Identical to image of sample with UDAME monolayer.

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Table 2: Compilation of results

Sample	ρF (e^-/ Å 3)	T (Å)	σS (Å)	σI (Å)
UV treated	0.35	12.2	2.3	3.20
Dark exposure	0.40	12.5	3.0	3.12
5-min exposure	0.24	19.5	7.0	3.00

ρF: Film-electron-density
T: Film-thickness
σI: Si-Film interface-roughness
σS: Film-Air interface-roughness
α: Molecular tilt-angle

Results

Images obtained through the AFM showed that only two variations of the aforementioned UDAME-synthesizing method produced any monolayer on the substrates. The variations in these samples were as follows:

1) Sample was not exposed to ultraviolet illumination for two hours. However, it was kept in dark exposure for two hours (contained in aluminum in a nitrogen-rich environment).

2) Sample had a total exposure time to UDAME of five minutes in ambient conditions before sonication in methanol to remove any superfluous UDAME.

Analysis of these samples using X-ray reflectivity shows that they both have a monolayer bonded to the Si(111) surface. The characteristic peak in the spectra indicates the presence of a film on the substrate.

The spectrum obtained from the sample prepared under two hours of dark exposure is shown in Figure 3. The red points represent the data gathered, while the blue line shows the spectra of a model that fits the given data. The monolayer formed under these conditions has an electron density of 0.28 e^-/Å3, a thickness of 12.5Å, and an interface roughness of 3.1Å. These results are of special interest because they are extremely similar to those obtained through ultraviolet illumination, suggesting that UV illumination is not required for the formation of a UDAME self-assembled monolayer.

The spectrum of the sample that was exposed to UDAME for a total of five minutes is shown in Figure 4. This illustrates that the substrate has a film attached to it, but that the film thickness exceeds that of the molecular length of UDAME. The resulting data suggest that the film's structure is different from that of a monolayer.

Discussion

The X-ray reflectivity results clearly show that a film is present when the procedure is varied. In both those cases, there should not be anything but a hydrogen-passivated surface. While it is contrary to published literature, a monolayer of UDAME appears on a sample that has been dark exposed, as opposed to illuminated with ultraviolet light. Because energy must be provided to the bonds for them to break, unless the breaking of the initial H-Si bond is just a statistical occurrence, these results raise questions about the chemical processes that form this monolayer. Specifically, it implies that the determining factor in the synthesis of a UDAME monolayer is time exposure to UDAME rather than UV illumination.

The five-minute exposure results, however, may be showing the consequences of improper cleaning. That the sample was sonicated only in methanol means that UDAME residue may have remained on the surface. That, and exposure to ambient light while in storage, could produce the film structure with the characteristics mentioned above. AFM images of this sample were limited due to time restrictions, and those taken were not indicative of a monolayer due to adverse conditions during use of the atomic force microscope. Nonetheless, these results could provide important information about decreasing the synthesis of films on the silicon(111) substrate.

Conclusion

This experiment indicates that the monolayer previously produced under dark conditions was not an anomaly, and that the results are reproducible. The spectra produced by the sample under X-ray reflectivity analysis shows that the characteristics of this film differ minimally from that of a UV-treated UDAME monolayer (Table 2).

Despite possible solutions (stated above) as to why a film formed on the five-minute exposure, particular note should be made of this procedural variation. These results suggest the formation of a film of unknown structure, even though a film formed under merely five minutes of exposure to UDAME. This could provide insight into more efficient methods of creating monolayers by sonication and replace the lengthy process of waiting two hours for the UDAME to attach itself to the substrate.

To expand knowledge about the factors affecting the self-assembly of a monolayer, it is suggested that samples be prepared under dark exposure ranging in time from zero to two hours in order to determine the minimum time required for the synthesis of a UDAME monolayer. Given the results of this study, it would seem necessary to investigate whether the phenomena reported here are specific only to UDAME, or whether they apply to other unsaturated carbon compounds.

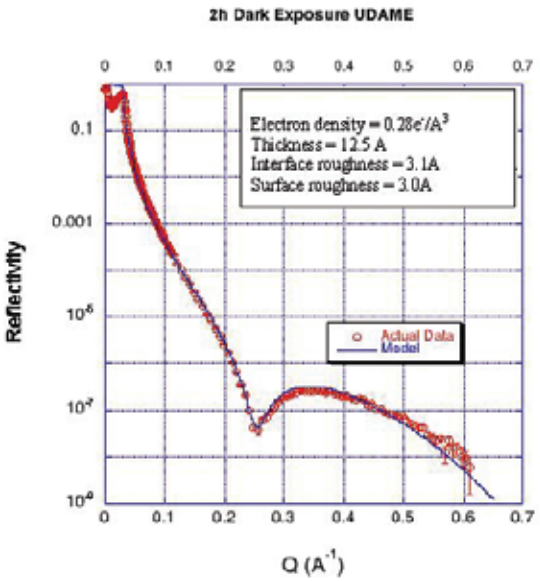

Figure 3: X-ray reflectivity spectra of two-hour dark exposed sample.

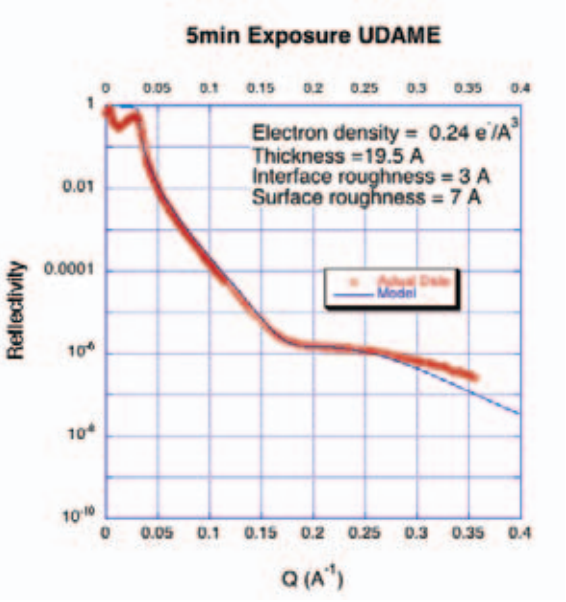

Figure 4: X-ray reflectivity spectra of five-minute exposed sample.

References

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