From Nanorough to More Robust: Using FT-IR Spectroscopy to Monitor the Surface Topography of Chemically Modified Silicon

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Introduction

The chemical modification of silicon surfaces has been studied due to the metal's importance in the semiconductor industry and its numerous biological applications, which include serving as a surface of attachment for biomolecules and proteins[1] and for cell adhesion.[2]

This project used primarily surface infrared spectroscopy to explore the chemistry of H-terminated Si(100) following oxidation by different methods. The studies presented here focus on the effects of using SC-1, SC-2, and P-Clean on water-etched Si(100) surfaces that have a unique, nanoscale roughness characterized by the presence of hillocks. Contact angle goniometry was also used to determine the effectiveness of silanization on the water-etched Si(100) samples.

Why Study the Surface Changes in Si(100)?

Previous work has shown that water-etched Si(100) leads to regular nanoscale roughness on the nanoscale,[3] but we wanted to obtain a more useful surface chemistry than Si-H bonds. One method to achieve this was was to make a siloxane monolayer. However, we first had to determine whether in the process of making a more useful Si(100) surface, the roughness of the original water-etched sample could be maintained.

Figure 1: Silanization of water-etched Si(100) with dimethylchlorooctylsilane

Experimental

Experiments used double-side polished Float Zone Si(100) of high resistivity. H-terminated surfaces were prepared using a modified RCA Clean (SC-1, HF, SC-2, HF). All samples were then etched in argon-purged deionized water. One sample served as an H_2O reference, and the remaining samples were modified by: SC-1,SC-2, or piranha clean. The final HF immersion prepared H-terminated surfaces for IR spectroscopy. The mode of interest is ν(Si-H), which can be analyzed in the frequency range of 2072-2135 cm^{-1}.

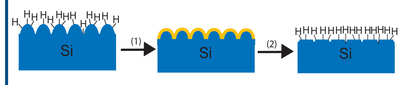


Figure 2: Water-etched Si(100) is oxidized (1) by SC1, SC2, or P-Clean leaving an SiO_2 layer. HF removes the oxide,leaving it H-terminated (2).

In the silantization experiments, dynamic contact angle goniometry was used to provide data on the surface features of the Si(100) post-modifications.

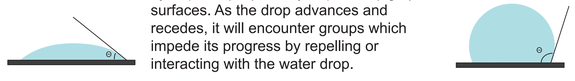


Figure 3: Typical contact angle measurement for the hydrophilic (left) and hydrophobic (right) surfaces. As the drop advances and recedes, it will encounter groups which impede its progress by repelling or interacting with the water drop.

Evolution of the Si-H Stretching Mode in Chemically-Modified Si(100)

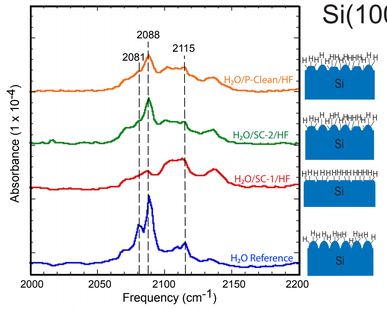


Figure 3: Comparison of the Si-H stretching modes in the control and a Si(100) sample that was water-etched and HF-etched.

FT-IR spectroscopy analysis showed that SC-2 best maintained the hillocks seen in the n(Si-H) mode. The SC-1 oxidized surface least resembled the reference, suggestingthat much of the nanoscale roughness had been etched away. Although SC-2 and P-Clean produced similar spectra, the intensity of the peak at 2088 cm^{-1} is greater in the SC-2 spectrum.

A Control to Monitor the Effects of HF

It is known that HF etches the surface of silicon;[4] thus, the spectrum of a water/HF-etched sample was compared to that of a reference in order to determine the impact of hydrofluoric acid on the nanoscale roughness of the surface.

Overall, HF did not affect the hillocks on the water-etched Si(100) surface significantly. A slight difference is seen at 2081 cm^{-1} where the peak visible in the spectrum water/HF-etched sample is less intense, possibly indicating a small decrease in the surface area of {111} facets.

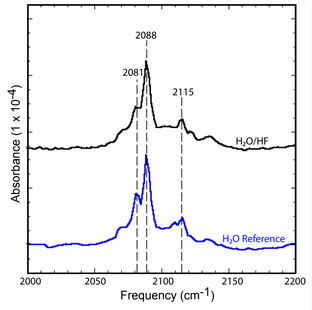
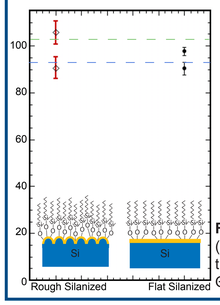


Figure 4: Comparison of the SiH stretching modes in the control and a Si(100) sample that was water-etched and HF-etched.

Contact Angle Data Show Successive Silanization of Rough Surface



The silane layer on flat surface is SLIGHTLY less homogeneous than for the P-Cleaned surface, since SC2 treatment produces a lower density of hydroxyls. Research using contact angle goniometry on rough and flat surfaces has shown that roughness increases contact angle measurements.[5] The rough silanized sample showed higher measurements for the advancing and receding contact angles than the flat silanized sample, indicating the presence of roughness.

Figure 5: Dynamic contact angle measurements of water-etched Si(100) (rough silanized) and non-etched Si(100) (flat silanized). As reference, the optimal silanized surface has an ΘA ~ 103˚ (green dotted line) and a ΘR ~ 94˚ (blue dotted line).

Preliminary AFM Imaging Shows Roughness

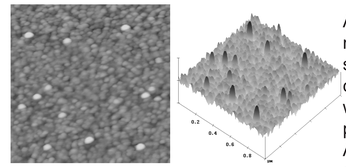


Figure 6: AFM images of the top (left) and side (right) views of a Si(100) sample following silanization.

AFM imaging showed that roughness is PRESERVED during silanization, meaning that a chemically functionalized surface with nanoscale roughness is possible. However, preliminary AFM data was not sufficient to determine whether the water-etched samples were successfully silanized.

Conclusions

Spectra obtained by FT-IR spectroscopy showed that all oxidation methods tested, SC-1, SC-2, and P-Clean caused apparent changes to the hillocks of water-etched Si(100). In the cases of SC-2 and P-Clean, the effects were less drastic, but in SC-1, there were significant differences between that spectrum and the reference spectrum. SC-2 appeared to cause the least perturbation to SiH species associated with the faceting on the hillock sides as evidenced by the peaks at 2088 cm^{-1} and 2081 cm^{-1}.

IR spectra on its own cannot determine what exactly is happening to the hillocks due to oxidation. While decreased intensities of peaks suggest that the hillocks are being etched away, this is an assumption that can be further supported by contact angle and AFM analyses.

In the silanization experiments, SC-2 was used to oxidize the water-etched Si(100) surface. Contact angle data showed that silanization of the surface was possible and that nanoscale roughness was present. AFM imaging also showed that roughness was preserved throughout the chemical modification process, but further studies will need to determine conclusively whether the images showed silanization as well.

References

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