Investigation of self-assembled monolayers on silicon wafer by terahertz spectrometry

Introduction

Silicon wafer surface needs to be modified for different chemistry in preparation of processes such as patterning of waveguides or CMOS process with different functionalities, etc. Common surface modification involves making a wafer hydrophilic or if it is already hydrophilic then converting it to hydrophobic. This is uniquely done by various self-assembled monolayers (SAMs). However, a major difficulty is to characterize the SAMs with common laboratory instruments (e.g., UV/Vis, Raman or FTIR). SAMs being only one molecule thick layer, physical characterization between different SAMs applied on wafer surfaces is challenging. Terahertz spectrometry offers an advent of characterizing molecular systems – even with closely spaced structural differences – owing to its ultra-high sensitivity stemmed from the fact that terahertz photons interact with the entire molecule as opposed to a bond or a charge states as used by its predecessors. In this note, silicon wafer coated with two different SAMs have been discussed. The spectra shows shows clear identifying characteristics between the two species.

Samples

Here, two different SAMs were formed on double side polished silicon wafer surface:

(1) (C18): n-OCTADECYLTRICHLOROSILANE (CH$_3$(CH$_2$)$_{17}$SiCl$_3$); Mw = 387.93 g/mol

(2) (C8): 7-OCT-1-ENYLTRICHLOROSILANE (H$_2$C=CH(CH$_2$)$_6$SiCl$_3$); Mw = 245.65 g/mol
Procedure

As supplied samples\(^1\) were used to measure their THz response at room temperature and normal ambient conditions. The wafer pieces coated with the SAMs were placed on a sample holder orthogonal to the THz beam path. Spectra of each specimen were acquired repeatedly over ~1700 seconds by the TeraSpectra front end. The spectrometer is shown in Fig. 1.

![Terahertz Spectrometer, TeraSpectra (AR Photonics, Harrisburg, PA 17111).](image)

Fig. 1. Terahertz Spectrometer, TeraSpectra (AR Photonics, Harrisburg, PA 17111).

Results and Discussion

Fig. 2 shows the temporal signal of the empty spectrometer. The max and min values as defined in Fig. 2 are plotted in Fig. 3. This shows the stability of the spectrometer. Since acquisition of each spectrum takes only a few seconds, the spectrometer is sufficiently stable over the entire length of measurements. All measurements were done in transmission mode. The temporal signal of the wafer coated with C-18 SAM (C-18 SAM-wafer) is shown in Fig. 4 and the corresponding max and min plot of C-18 SAM-wafer is shown in Fig. 5. Both the max and min values exhibit similar kinetics indicating the SAM is undergoing some kind of change and then reaching saturation. The details of

\(^1\) Samples were obtained from Dr. Theresa McIntire, Chemistry Dept. of UC Irvine.
this kinetics are not known yet but indicative of some interaction of the C-18 SAM coated surface with atmospheric oxygen. The Fourier transform frequency spectrum corresponding to Fig. 4 is shown in Fig. 6 (discussed later).

Fig. 7 exhibits the temporal pulse of C-8 SAM coated wafer (C-8 SAM-wafer) and Fig. 8 shows the kinetics of max and min. Unlike the C-18 SAM-wafer, C-8 SAM-wafer has different trend. Also, as seen from Fig. 9, C-8 SAM-wafer has higher transmission than that of C-18 SAM-wafer. This is expected because C-8 having lower Mw have lower thickness than C-18; as such C-8 exhibits higher transmission than C-18.

The Fourier transform absorbance spectra of both specimens are shown in Fig. 10. Here too the C-18 SAM-wafer exhibits higher absorbance than that of C-8 SAM-wafer; consistent with the higher Mw of C-18. Fig. 11 shows several peaks identified by their frequency that may be used as distinguishing features between the two SAMs.

![Fig. 2. Temporal signal of empty spectrometer](image)
Fig. 3. Stability of empty spectrometer min (pink) and max (blue) power

Fig. 4. Temporal Signal or interferogram of SAM C-18 coated Si-wafer (measured in transmission)
Fig. 5. C-18 coated wafer exhibits time dependent changes. Both min (pink) and max (blue) have the same trend. The time dependent change is presumably due only to the SAM (C-18).

Fig. 6. Fourier transform absorbance spectrum of C-18 coated Si-wafer.
Fig. 7. Temporal Signal of SAM C-8 coated Si-wafer

Fig. 8. C-8 coated wafer exhibit time dependent change in transmitted power that is quite different than C-18 coated wafer (see Fig. 5).
Summary

This note outlines an initial attempt of characterizing different SAM coated silicon wafers for identifying different SAM species. Two SAM used are C-18 and C-8 as defined before. Both species exhibit time dependent change in the transmitted power, but with different kinetics. The C-18 SAM-wafer exhibit higher absorbance than C-8. This is assigned to the higher molecular weight of C-18. The Fourier transform absorbance spectra of both specimens also exhibits higher absorbance for C-18 than that of C-8 SAM-wafer. This is consistent with the higher Mw of C-18. Further investigations will be carried out to arrive at conclusive results.
Fig. 10. Comparison of absorbance of C-8 and C-18. C-18 SAM-wafer exhibits higher absorbance compared to C-8 SAM-wafer. This is consistent with C-18’s higher Mw.
Fig. 11. The absorbance spectra of both SAMs (same as Fig. 10, but X-axis truncated to 20 THz). Several peaks may be identified for characteristic differences between the two SAM species.

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