

Infrared reflection absorption spectroscopy for characterization of alkylsilane monolayers on silicon nitride surfaces

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1 Introduction

Infrared reflection absorption spectroscopy (IRRAS) is a well-established technique for the characterization of surfaces and adsorbate films, which provides specific information on the chemical composition and structure of thin surface layers and adsorbed molecules. Most of the investigations have been carried out on metal substrates due to the high reflectivity and the ease of the spectra interpretation. Only since the 1980s the method has also been used for dielectric substrates with high refractive index, weakly reflection and vanishingly small absorption in the mid-IR region [1].

The formation of silane-based self-assembled monolayers (SAMs) on silicon oxide surfaces has attracted an increasing amount of interest since three decades. A number of previous works have focused on the formation mechanism, the thermal, mechanical and chemical stability of the silane-based adlayers [2,3]. Silicon nitride is one of the most common materials used in semiconductor industry and has been due to its unique biocompatibility the topic of a few studies and applications in biotechnology. In comparison to silicon oxide the formation process of silane-based SAMs is not completely understood [4,5].

2 Results

In the present work, we used IRRAS to determine the film quality of SAMs formed on antireflective coated silicon nitride substrates

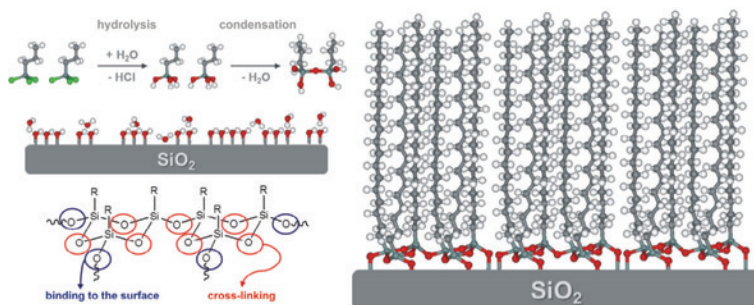


Figure 8.1: Formation of the silane film on the SiO_2 surface.

for state-of-the-art applications in industry. The formation of SAMs made of *n*-alkylsilanes (*n*-octadecyltrichlorosilane $\text{C}_{18}\text{SiCl}_3$, *n*-dodecyltrichlorosilane $\text{C}_{12}\text{SiCl}_3$ and *n*-dodecyltriethoxysilane $\text{C}_{12}\text{Si}(\text{OEt})_3$) on silicon oxide and silicon nitride surfaces has been investigated. The resulting films were characterized with IRRAS to improve the detailed parameters for the preparation. The IRRAS spectra have been taken with polarized light using a Bruker Optics VERTEX 80 FT-IR spectrometer in combination with an optimized variable angle reflection sample accessory (A513) equipped with an automated polarizer rotation unit (A121). All IRRAS data were recorded with a resolution of 2 cm^{-1} using p- or s-polarized radiation with different incidence angles. All data were normalized by subtracting a spectrum recorded for the same substrate (clean Si_3N_4 or SiO_2). The substrates have been pretreated with ethanol and chloroform in an initial wet cleaning step. Subsequently, they were placed in an UV/Ozone chamber ($\lambda=185$ and 254 nm) for 30 min to remove residual organic contaminations. In our studies we realized the most important treatment to be the following, final step, wet chemical oxidation with piranha solution. This step consists of immersing the SiO_2 or Si_3N_4 substrate in a freshly prepared piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 4:1) for 30 min at $70\text{ }^\circ\text{C}$, followed by rinsing with deionized water (Caution! Piranha solution should always be handled with great care and can react explosive with organic solvents). This preparation process fabricates hydroxylated and highly hydrophilic substrate surfaces.

The silane-based SAMs were prepared generally by immersing the pretreated Si_3N_4 or SiO_2 substrate in the corresponding silane solutions. For the formation of the silane-based SAMs not only reactions between the silane monomers and the surface but also reactions occurring within the solution have to be considered, as schematically depicted in Fig. 8.1. The velocity of the hydrolysis reaction depends strongly on the leaving group. In the next step, the silanols formed in the hydrolysis reaction will either react with each other to form polysiloxanes or bind to surface OH-groups. These two reactions, condensation in the solvent and binding to the surface compete with each other. In principle, for the formation of well-defined silane-based SAMs on the surface the condensation reaction between silanol molecules in solution leading to oligomerization, polymerization and deformation of siloxane patches is unwanted. Different preparation parameters, such as the temperature, the water content in the solution, the concentration of the silane solution, the solvent, the immersion time and the pretreatment of the substrate, have been shown to be critical for the kinetics of the SAM formation process and for the quality of the final SAM. As shown in Fig. 8.1, the silanol molecules condensed on the silicon surface are not only covalent bonded to the substrate, but also lateral linked to each other within the monolayer. This covalent cross-linking is characteristic for silane films and determines the stability and toughness of the formed silane-based SAMs.

With the help of the achieved IRRA spectra (see Fig. 8.2) we could make a statement for the ordering, the density and even for the orientation of the adsorbed molecules on the substrate surface and hence optimize the preparation conditions. The asymmetric (ν_{as} CH_2) and the symmetric stretching modes (ν_s CH_2) of the CH_2 groups in the alkyl chain are located at 2918 cm^{-1} and 2850 cm^{-1} . The position and the intensity ratio of the both vibrational bands are in good agreement with those reported in the literature [1]. The band positions and shapes demonstrate the presence of well-ordered, densely packed with the alkyl chains mostly in an all-trans conformation. Since the position of ν_{as} CH_2 vibrational mode is very sensitive to the ordering of the alkyl chains or rather of the monolayer, we use it as an indication of the film quality. According to previous work the presence of a highly ordered densely packed *n*-alkylsilane SAM with the alkyl chains in an all-trans conformation is indicated by a CH_2 vibrational frequency of

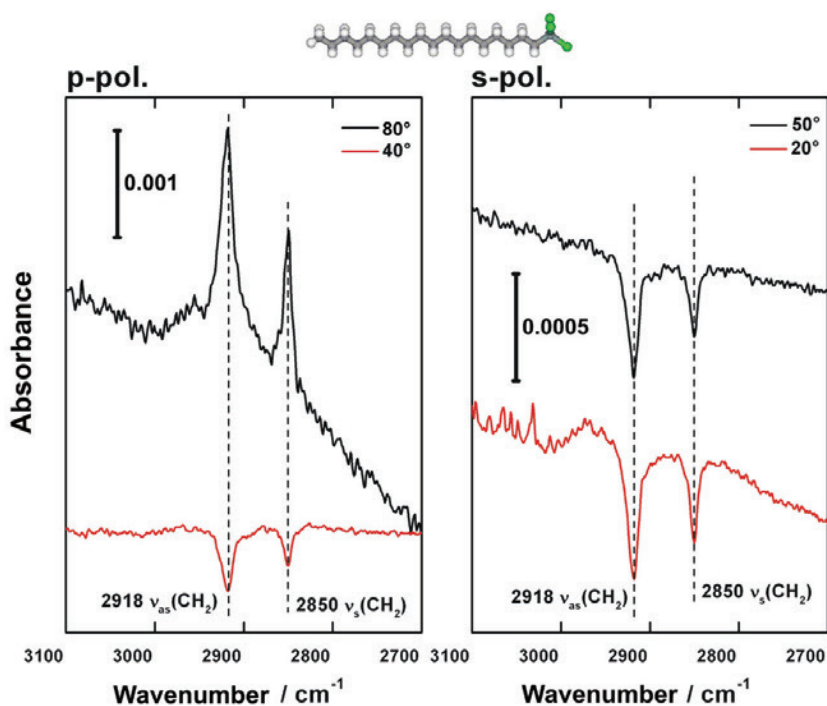


Figure 8.2: IRRA spectra of *n*-octadecyltrichlorosilane (structure shown above)-based SAM on silicon oxide surface measured with p- (left) and s-polarized light (right) each with two different incident angles using a Bruker Optics FT-IR VERTEX 80 spectrometer. The region of the CH₂ stretching modes is presented.

2919 cm⁻¹. As a consequence of a less dense packing, where the alkyl chains are disordered and exhibit high density of Gauche defects, the ν_{as} CH₂ band will be shifted towards higher energies (blue-shifted) by a few wavenumbers. The data shown in Fig. 8.2 reveal that there is a pronounced dependence of both band intensity and polarity, on IR-light incidence angle. With s-polarized light only negative absorption bands are observed with higher intensity at lower incident angle, whereas with p-polarized light an inversion of the absorbance from negative to positive at incident angles higher than 75° is characteristic for these ab-

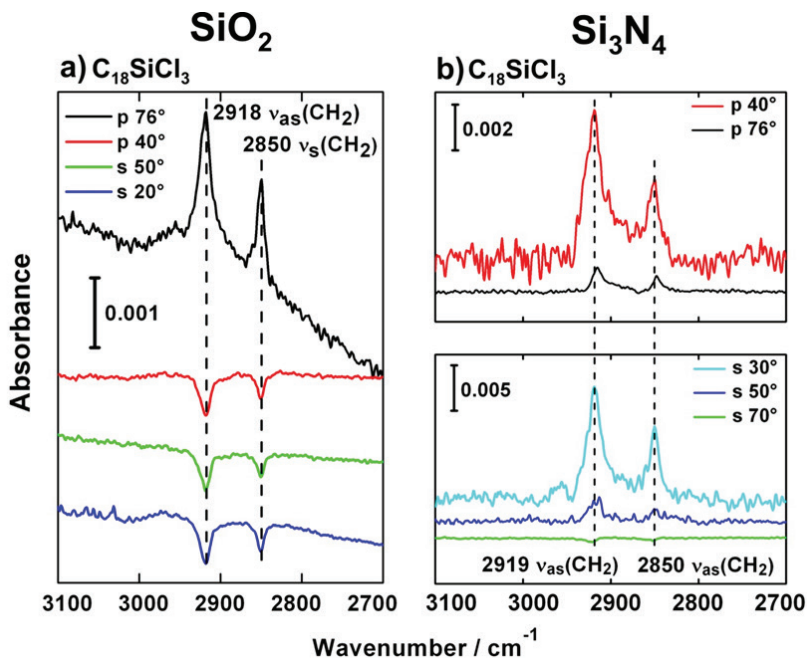


Figure 8.3: IRRA spectra of $C_{18}SiCl_3$ SAM a) on silicon oxide and b) on silicon nitride with p- and s-polarized light and different incident angles using a Bruker Optics FT-IR VERTEX 80 spectrometer.

sorption modes in a well-ordered anisotropic silane based monolayer on silicon oxide. A successful coupling of *n*-alkyltrichlorosilane on the rarely passive silicon nitride surface and the optimized preparation parameters of a well-defined silane-based SAM on this substrate could be achieved (see Fig. 8.3).

3 Summary

In our application of the IRRAS method using the novel setup provided by the Bruker Optics FT-IR spectrometer technology, highest sensitivity in combination with detailed structural information also on weakly re-

flecting, nonmetal surfaces was demonstrated. IRRAS was proved to be a steady, reliable and effective technique to control the quality of ultra-thin films on dielectric surfaces.

References

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