Characterization of Ultra-Thin Polymer Films by Polarization Modulation FTIR Spectroscopy

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SUMMARY: Self assembly monolayers of octadecyltrichlorosilane Cl_3-Si-$(CH_2)_{17}$-CH_3 and 17-cyanopentadecyltrichlorosilane Cl_3-Si-$(CH_2)_{17}$-CN on silicon wafers have been prepared by adsorption from solution. The molecular orientation within the monolayers was investigated by using Polarisation Modulation FTIR spectroscopy. Quantitative analysis reveals that both types of silanes - monofunctionalised and bifunctionalised - form highly ordered monolayers. A high degree of ordering as well as a small tilt angel of the molecular backbones with respect to the surface normal are indicated by the strength of the Si-O-Si stretching modes and the weakness of the CH_2 stretching modes. The decomposition of the terminal nitrile group of the substituted silane into a carboxyl group could be identified. The decomposition is caused by a high local HCl concentration, which develops upon binding of 17-cyanopentadecyltrichlorosilane to the OH groups of the silicon surface.

Introduction

Ultra-thin polymer films have attracted attention in surface chemistry. Self assembled monolayers (SAM) play a particular role in devices like opto-electronic components, sensors, in coatings or during etching processes[1,2,3,4]. The most common methods to form SAMs are the Langmuir Blodget (LB) technique and adsorption by self assembly of molecules on surfaces. Widespread examples for spontaneous adsorptions are thiols and silanes. SAM of thiols are formed via gold-sulfur chemistry [5,6] whereas silanes adsorbs via silanisation onto silicon or glass surfaces[7]. The molecular arrangements have been investigated by various methods like Fourier transform infrared (FTIR) spectroscopy[8], X-ray spectroscopy[9,10,11], impedance spectroscopy[12], conoscopic microscopy[13], scanning probe microscopy[6,14], surface plasmon resonance (SPR)[15,16,17], atomic force microscopy (AFM)[18,19] and in-situ scanning tunneling microscopy (STM)[20].

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The infrared reflections absorption spectroscopy (IRRAS) at grazing incidence has been one of the best approaches to investigate the chemical structure and molecular orientation of thin polymer films because the sample does not have to be modified or to be exposed to ultra high vacuum[22)]. However, the detection limit of IRRAS is not sufficient for the characterization of monolayers. It has been shown that polarization modulation (PM) of the occurring IR radiation results in an increase of the detection capabilities of IRRAS [21,22,23,24,25)]. Within scan times of a few minutes, PM-IRRAS provides spectra of monolayers of a high signal to noise ratio. Such spectra may be quantitatively analyzed with respect to orientation and conformation of the molecules.

Experimental

Octadecyltrichlorosilane (OTS) Cl_3-Si-$(CH_2)_{17}$-CH_3 and 17-cyanopehtadecyltrichlorosilane (CTS) Cl_3-Si-$(CH_2)_{17}$-CN were synthesized as described in [26,27)]. Commercial silicon wafers of 10 x 10 mm were immersed in a solution of concentrated H_2SO_4 and 30% H_2O_2 (known as piranha-solution) at 90°C for approximately 1 hour. After cooling to room temperature, the substrates were rinsed with deionized water and dried with a nitrogen stream. SAMs of OTS and CTS were prepared by adsorption from solutions of 1 mM silane in toluene. The adsorption time under atmospheric condition was 12 hours. After adsorption the samples were rinsed with toluene and dried under nitrogen.

Transmission spectra of bulk samples were recorded using a capillary cell with KBr windows. The cell was placed into the sample compartment of a FTIR spectrometer Nicolet 205 (Nicolet, Offenbach, Germany). 100 scans were averaged at a resolution of 2 cm^{-1}.

PM-IRRAS spectra were recorded using a FTIR spectrometer IFS 88 (Bruker Optik, Ettlingen, Germany) equipped with a MCT detector. After the infrared beam passed the interferometer it was linearly polarized by a wire grid polarizer and subsequently modulated by a ZnSe photoelastic modulator (PEM-90, HINDS Instrumentation, Hilsboro/OR, USA). Polarizer and modulator together with the reflection unit (Graceby Specac, Fairfax/VA, USA) fit into the purged sample compartment. All IRRA spectra were recorded at an incident angle of 80°. At a resolution of 4 cm^{-1}, 512 scans were coadded in order to achieve a good signal to noise ratio. A silicon wafer was used to obtain the reference spectrum.

The theory of PM-IRRAS is described elsewhere[28,22)]. Basically, the detector signal consists of two components $R^{\sim}$ and R^{-}, recorded simultaneously:

$$R^{\sim} = J_2(R_{\parallel} - R_{\perp}) \quad ; \quad R^{-} = (R_{\parallel} + R_{\perp}) \quad . \qquad (1)$$

$R_{\parallel}$ and $R_{\perp}$ are the reflectivities for parallel and perpendicular polarized light, respectively. J_2 is the second-order Bessel function resulting from the double modulation of the detected light. The two components $R^{\sim}$ and R^{-} can be recorded individually by means of a multiplexer and a lock-in amplifier. After co-adding all scans, the two interferograms are successively Fourier transformed. From the ratio of the two spectra the actual IRRA spectrum R is calculated:

$$R = \frac{R^{\sim}}{R^{-}} = \frac{J_2(R_{\parallel} - R_{\perp})}{(R_{\parallel} + R_{\perp})} \quad . \qquad (2)$$

Molecules of isotropic orientation will cause identical absorptions for parallel and perpendicularly polarized light. As a result the numerator in (2) becomes zero, i.e. no absorption band can be observed. Upon increasing anisotropy of the molecular orientation (increasing molecular ordering) the value $(R_{\parallel}-R_{\perp})$ grows correspondingly. Thus, PM-IRRAS reveals the degree of orientation order of molecules bound to the surface of the solid.

Results

Octadecyltrichlorosilane (OTS)

The transmission spectrum of neat OTS in liquid state together with a PM-IRRAS spectrum of an OTS monolayer on silicon are shown in Fig. 1. Band positions and assignments are summarized in Table 1. OTS shows a strong and broad Si-O-Si stretching band between 1130 – 1040 cm^{-1}, which is in good agreement with other studies[29)]. Compared to the intensity of the Si-O-Si band, the CH_2 stretching modes are much weaker in the PM-IRRA spectrum than in the transmission spectrum. Furthermore, the PM-IRRA spectrum reveals a series of CH_2 wagging progression bands in the 1380 – 1250 cm^{-1} region [28)].

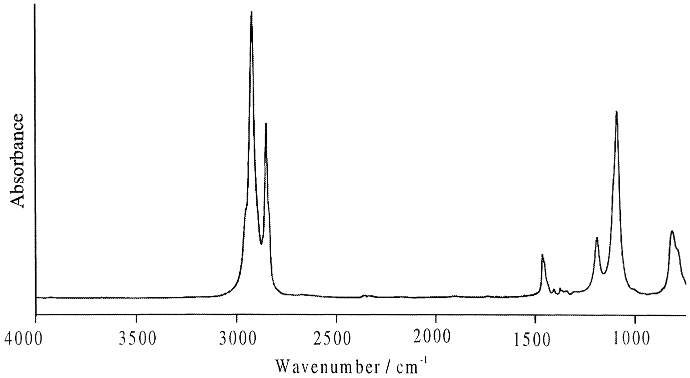

Fig.1a: FTIR transmission spectrum of neat OTS in a KBr capillary cell.

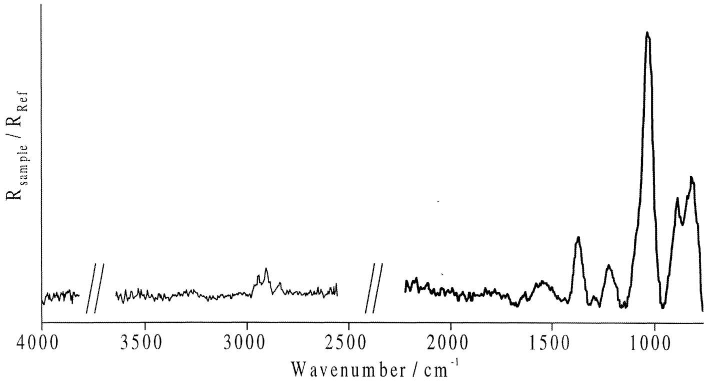

Fig.1b: PM-IRRAS spectrum of an OTS monolayer on silicon. Regions in the PM spectra obscured by the Bessel function have been cut out.

Table 1. Assignments and positions of vibrational modes of trichlorosilane.

wavenumber [cm^{-1}]	assignment
2970	$\nu_{as}(CH_3)$
2930	$\nu_{as}(CH_2)$
2850	$\nu_s(CH_2)$
1460	$\delta(CH_2)$
1380-1250	progression bands
1130-1040	ν(Si-O-Si)
1010- 900	ν(Si-O-Si)

17-cyanopentadecyltrichlorosilane (CTS)

The transmission spectrum of liquid CTS together with a PM-IRRAS spectrum of a CTS monolayer on silicon are shown in Fig. 2. The most striking differences in these spectra are the missing absorption band of the C≡N stretching mode at 2250 cm^{-1} and the appearance of some "negative" absorption bands in the PM-IRRA spectrum. The "negative" absorption bands arise from a increase in $R_{\perp}$ upon adsorption of CTS on the silicon surface. Such effects have also been observed by other authors[24)]. The broad band between 3800 – 3400 cm^{-1} reveals adsorbed water molecules. The origin in CTS of the C=O stretching mode at $1730cm^{-1}$ will be discussed below.

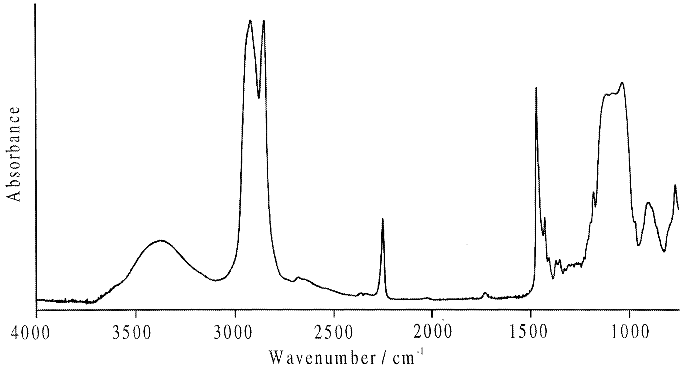

Fig 2a: FTIR transmission spectrum of neat CTS in a KBr capillary cell.

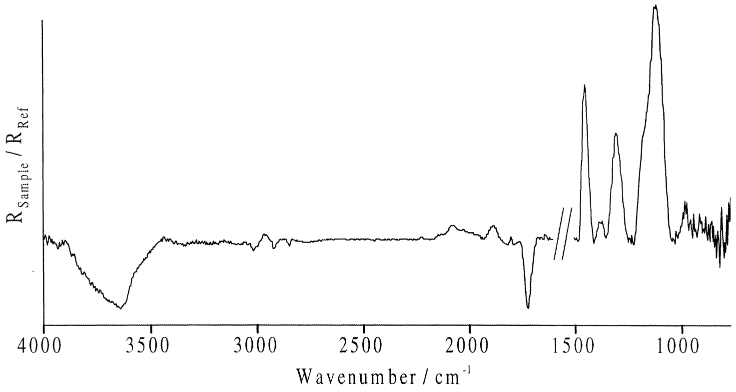

Fig 2b: PM-IRRAS spectrum of a CTS monolayer on silicon. Regions in the PM spectra obscured by the Bessel function have been cut out.

Discussion

Any appearance of an absorption band in a PM-IRRA spectrum indicates differences in absorbance between parallel and perpendicular polarization for the particular vibrational mode. Such differences are only observed in case of some degree of ordering among the molecules, i.e. the appearance of absorption bands in our PM-IRRA spectra indicates the formation of a SA monolayer. Within such a monolayer, the Si-O-Si linkages have to adopt an invariant orientation at the surface, hence the Si-O-Si modes will always be strong. On the other hand, the CH_2 bending and wagging modes of well-ordered molecules should not exhibit strong absorptions in the PM-IRRA spectra. The reason is the orientation of the hydrocarbon backbone. If the alkyl chains would be oriented exactly perpendicular to the silicon surface, the symmetric and antisymmetric CH_2 stretching modes could not be seen at all because the molecular transition dipole moment was compensated by the opposite dipole moment, which is induced within the silicon surface (30,31). For well-assembled monolayers formed by trichlorosilane on silicon surfaces, published values for the alkyl chain tilt do not exceed the range 0 – 15° off the surface normal (32,13,33), i.e., the slight deviation from the normal enables a small transition dipole to be excited. The monofunctionalised OTS is a well suited reference for the behavior just discussed (Fig.1). The strong Si-O-Si band indicates the chemical linkage of OTS to the surface. The very weak excitation of the CH_2 transition dipoles in the PM-IRRA spectrum reveals the preferential orientation of the hydrocarbon backbone in to before-mentioned direction, hence a high degree of ordering within the monolayer.

The spectra of the bifunctionalised CTS exhibit an additional feature. The C≡N stretching band is only seen in the transmission spectrum of the bulk material. It disappears in the PM-IRRA spectrum, instead a C=O stretching mode appears at 1730 cm^{-1}. This observation reveals the decomposition of the nitrile group upon formation of the SA layer. During formation of the Si-O-Si linkages, the trichlorosilane hydrolyses, and a relatively high local HCl concentration develops. The highly acidic conditions right at the surface cause the nitrile group of the adsorbed CTS to hydrolyze. The hydrolysis proceeds via an amide group to a carboxyl group.

Conclusion

PM-IRRA spectroscopy has been applied to study structural information about octadecyltrichlorosilane (OTS), 17-cyanopentadecyltrichlorosilane (CTS). Self assembly monolayers on silicon surface were prepared from solution. The results indicate a high degree of order within the self assembled layers. Structural changes due to conformational transitions as well as chemical changes within functional groups upon formation of the monolayer could be observed.

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