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Vapor Phase Self-Assembly of Fluorinated Monolayers on Silicon and Germanium Oxide

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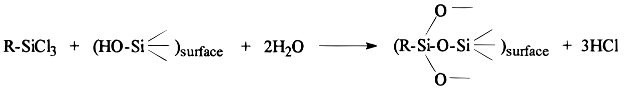
Molecular orientation in monomolecular thin organic films and surface coverage on Ge/Si oxide was measured by attenuated total reflectance Fourier transform infrared spectroscopy. A gas phase reactor allowed for precise control of surface hydration and reaction temperature during the deposition of monofunctional perfluorated alkylsilanes. It is therefore considered superior to solution-based silylation procedures commonly employed.

Introduction

Chemical modification of surfaces by silylation is a promising approach for a wide range of applications such as construction of low-energy surfaces, lubrication, biocompatible surfaces, and monolayer lithography.[1−5]

Extensive research on surface silylation and its dependence upon parameters like oxidation, surface hydration,[6−9] and silylation conditions,[10] has not yet elucidated the mechanism of monolayer formation, especially in the case of silylation of planar surfaces. In particular there is considerable interest in the extent of covalent bonding of the silane molecules to the surface via siloxane bonds versus adsorption of laterally polymerized oligomers through hydrogen bonding.[9]

Silylation with trifunctional silanes according to



$$\mathrm{R\text{-}SiCl_3 + (HO\text{-}Si\lessdot)_{surface} + 2H_2O \longrightarrow (R\text{-}\overset{O-}{\underset{O-}{Si}}\text{-}O\text{-}Si\lessdot)_{surface} + 3HCl}$$

is very sensitive to both surface adsorbed water and ambient moisture and easily forms three-dimensional polysiloxane networks rather than perfect monolayers of surface-bonded molecules. In contrast, monofunctional silylating agents, as used in this study which react according to

$$\mathrm{R\text{-}Si(Me)_2Cl + (HO\text{-}Si\lessdot)_{surface} \longrightarrow (R\text{-}Si(Me)_2\text{-}O\text{-}Si\lessdot)_{surface} + HCl}$$

can only bind to a surface silanol group or form a dimer which does not adhere to the surface and hence can be easily removed by desorption at about 100 °C and 10^{-2} Torr. We report here the use of a gas flow reactor to investigate the influence of surface cleaning, oxidation, and hydration parameters on the quality of the surface silylation. This reactor allows for precise temperature control and flow control of the gas above the substrate surface and is compatible with standard semiconductor process technology with high reaction temperatures in the range of 200−300 °C being achievable. Fluoroalkyl compounds were used since they are potentially interesting for the fabrication of low surface energy surfaces and in addition they exhibit very strong IR absorption bands. In particular the C−F stretching vibrations allow for the evaluation of surface coverage and molecular orientation at coverages as low as 10% as is reported below.

Experimental Section

In this work, surface coverage and molecular orientation within surface monolayers of a semifluorinated alkylsilane were determined with polarized attenuated total reflectance Fourier transform infrared (FTIR-ATR) spectroscopy.[11−13] Germanium crystals with thermally grown germanium oxide or with evaporated silicon oxide which was thermally cured in an oxygen atmosphere were used as substrates.[14] ATR crystals made from germanium rather than silicon had to be used to gain access to the C−F stretching vibrations located in the fingerprint region of the IR spectra. The layer of native oxide was removed by immersing the substrate in a 50% HF solution in water for approximately 30 s. In order to determine the relationship between monolayer coverage and preparation methods, a wide range of preparation parameters was used. For the hydration step the substrate temperature was varied between 60 and 100 °C at a water vapor pressure of 400−550 Torr and a treatment duration of 2−48 h. This was followed by a desorption/drying step at 130 °C and pressures (1−5) × 10^{-2} Torr. Silylation was performed at substrate temperatures between 50 and 200 °C and 1−20 Torr vapor pressure of the silylating agent for up to 0.2−24 h. Silylation with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFTES) on Ge/Ge oxide and 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane (PFDCS) on Ge/Ge oxide and Ge/Si oxide substrates was investigated with the unreacted residue being removed by a desorption step at 130 °C and (1−5) × 10^{-2} Torr for 1−6 h.

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(14) Evaporation of silicon monoxide was performed at an oxygen pressure of 5 × 10^{-4} Torr at a rate of 0.2−0.5 Å/s. The films were cured for 2 h at 400 °C in an oxygen atmosphere at $p = 400$ Torr. In a control experiment the stoichiometry of freshly evaporated silicon monoxide and of a cured oxide layer on silicon wafers was determined with X-ray photoelectron spectroscopy as 1.8 ± 0.1 and 1.9 ± 0.1, respectively. These surfaces are expected to exhibit similar surface chemistry properties as silicon/silicon oxide substrates but are, in contrast, IR transparent down to 1100 cm^{-1}.

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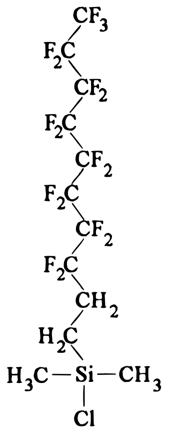
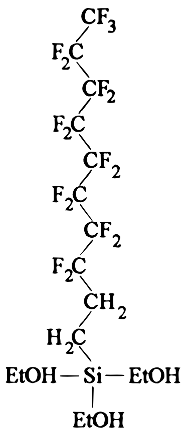


1H,1H,2H,2H-Perfluorodecyldimethylchlorosilane (PFDCS)



1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFTES)

Spectra were evaluated using the commercially available software, LabCalc (Galactic Industries). Its peak fitting feature uses the Levenberg−Marquardt algorithm.[15] Great care was applied to ensure that the results obtained from peak fitting were actually insensitive toward the choice of initial guesses. The standard deviation of fitting results obtained with different initial guesses was between 5 and 15% in all cases.

Results and Discussion

Dynamic contact angle measurements were performed and advancing contact angles for water of 75−115° were obtained in qualitative agreement with the coverage determined from FTIR-ATR measurements which will be described in detail in a later section. The hysteresis between advancing and receding contact angles was 15−25°, indicative of surface coverages <1 and/or residual surface roughness. Very low receding contact angles (<10°) were observed in some cases on Ge/Ge oxide surfaces and may be due to the dissolution of the Ge oxide and thus the production of a wettable surface.[16] Ge/Si oxide surfaces did not show this behavior, and both advancing and receding contact angles correlated well with the coverage measured by FTIR spectroscopy.

In the choice of suitable substrates for these experiments, a number of considerations had to be addressed. Ge/Ge oxide substrates are transparent in the IR down to 630 cm^{-1} compared to a lower limit of 1100 cm^{-1} (s-polarized light) and of 1250 cm^{-1} (p-polarized light) for Ge/Si oxide and 1500 cm^{-1} for Si/Si oxide substrates. However, less is known about the surface chemistry of Ge oxide relative to Si oxide surfaces. Due to the choice of molecules, the spectral region of interest for the experiments reported herein extended down to about 1100 cm^{-1}; and hence Ge/Ge oxide and Ge/Si oxide surfaces were used for the IR experiment.

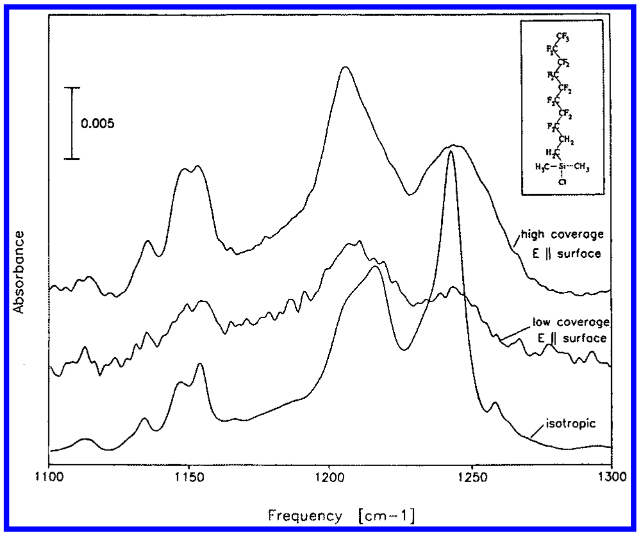


Figure 1. Spectra of PFDCS (chemical structure shown in insert) in CCl_4 solution (isotropic) and on Ge/Ge oxide ATR crystals with the electric field, **E**, being polarized parallel to the surface. Note the difference in relative absorbance of the C−C stretching vibration at 1217 cm^{-1} and the CF_2 stretching vibration at 1206 cm^{-1} in the case of the isotropic spectrum and for the anisotropic spectra, respectively.

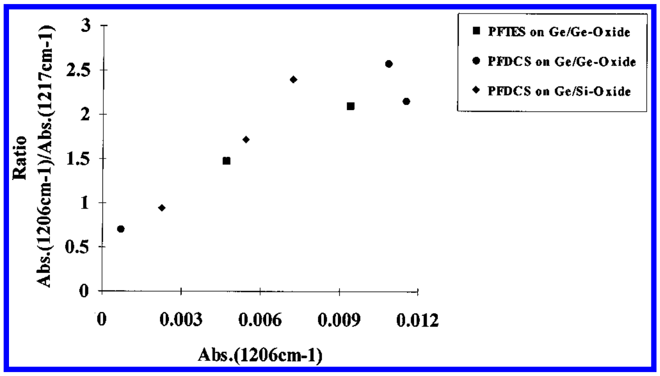


Figure 2. Ratio of absorbance at 1206 cm^{-1} (CF_2 stretching, perpendicular with respect to molecule axis) and 1217 cm^{-1} (almost parallel to molecule axis) displayed as a function of the absolute absorbance at 1206 cm^{-1}. Only the components of the change in molecular dipole moment oriented parallel to the surface result in the absorption of light because **E** is polarized parallel to the surface (insert).

In contrast to the common approach of varying the polarization of the incident light, we employed only s-polarized light (E || surface) and evaluated two bands with almost orthogonal orientation of the respective changes of dipole moment in order to determine average orientation and monolayer coverage.[13,17,18] In the case of the previously assigned[19] C−C stretching (and CCC bending) vibration at 1217 cm^{-1}, the change in dipole moment is oriented almost parallel to the molecule axis, while for the CF_2 stretching vibration at 1206 cm^{-1} it is oriented perpendicular to the molecule axis. Therefore these two bands are a good choice to assess the extent of molecular orientation on the surface.

In Figure 1 are found the isotropic (bottom) and polarized IR spectra from samples with low (middle) and high (top) coverage. The relative intensities at 1206 and 1217 cm^{-1} are reversed in the polarized spectra compared to the isotropic spectrum, and their ratio (A_{1206}/A_{1217}) increases qualitatively with increasing coverage (Figures 1 and 2). Some caution must be exercised in comparing an isotropic liquid spectrum with that of an oriented solid spectrum due to the additional conformational disorder that may occur in the former. However, by measuring the intensity ratio (A_{1206}/A_{1217}) as a function of coverage in the monolayer ATR spectrum, one gets, at least, a semiquantitative measure of the extent of molecular orientation, i.e., average tilt angle. Conceivably one would obtain the same results if the symmetric CF_2 stretching vibration at 1153 cm^{-1} or the asymmetric CF_2 stretch at

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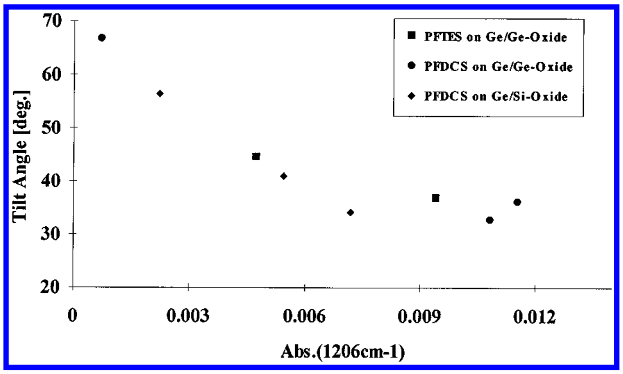

Figure 3. Average tilt angles as a function of absorbance at 1206 cm^{-1} calculated assuming a uniaxial model for the molecular organization and a small component of the change in dipole moment of the C−C stretching vibration perpendicular to the molecule axis.

1243 cm^{-1} was used, since their change in dipole moment is perpendicular to the molecular axis and both have significant intensity in the ATR monolayer spectra (upper 2 traces in Figure 1). Since all band shapes are somewhat complex in these spectra, the choice of the 1206/1217 cm^{-1} pair was dictated by the ability to adequately curve fit the spectra in this region with two bands. The peak intensities determined from spectra obtained from samples prepared by different methods yielded coverages ranging from 0.05 to 0.6 (Figure 4). Values of monolayer coverage as given herein relate to the density in a close packed monolayer of fluorocarbon chains assuming a cross sectional area of 25 Å^2/molecule.[20] From isotropic spectra of the silylating agents in CCl_4 solution, the absorption coefficients, $k(\nu)$, for the most pronounced peaks were determined for use in these calculations.

Average tilt angles were calculated using a uniaxial model that allows for rotation of the change of dipole moment around the molecular axis and rotation of the chain around the surface normal.[13,21] The angles used in the calculation were $\alpha_{1206} = 90°$ and $\alpha_{1217} = 15°$.[22] From average tilt angles and absorbances at 1206 cm^{-1}, the monolayer coverage was calculated.[23] It should be emphasized that in contrast to the average tilt angles, which are calculated from a ratio of absorption intensities, the coverage depends on the absolute value of the absorption coefficient and is thus affected by any uncertainty in the area/molecule of the fluorocarbon chain. Using a higher area/molecule in this calculation would yield lower absorption coefficients and higher values of monolayer coverage. The value assumed in this paper (25 Å^2/molecule) is at the lower end of values of the cross sectional area of a fluorocarbon chain reported in the literature.

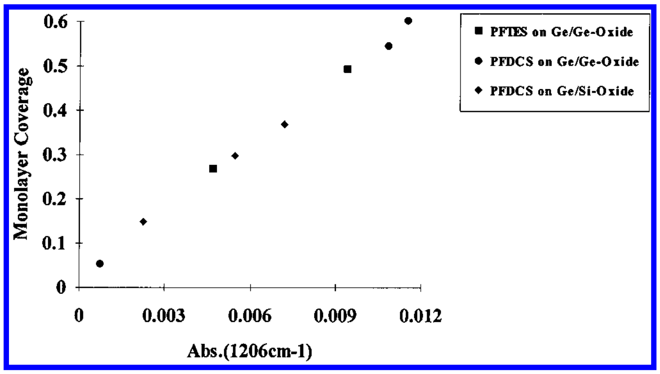

Figure 4. Coverage as a function of the measured intensity of the band at 1206 cm^{-1}. Coverage was calculated as the ratio between the peak intensities determined from s-polarized spectra by curve fitting and the calculated absorbance of a complete monolayer of fluorocarbon chains oriented perpendicular to the surface (chain cross section 25 Å^2). An effective absorption coefficient for the monolayer sample was calculated[21,23] from the isotropic spectra while taking into account the tilt angle determined from the ratio A_{1206}/A_{1217}.

In Figure 2 the ratio A_{1206}/A_{1216} is displayed as a function of the *monolayer* coverage since any unreacted monomer or dimer has been removed by a desorption step.[24] Clearly, the ratio increases with increasing overall absorbance, i.e., coverage, θ. This can be explained in terms of a change of the average orientation of the molecular axis from mostly parallel to perpendicular with respect to the surface as the packing density increases. Since the electric field is polarized parallel to the surface (s-polarization), only components of the change in dipole moment parallel to the surface result in an absorption of IR light. The average tilt angle varies from 67° in the case of very low coverage to 33° for high coverage (Figure 3). The latter value seems to be a minimum tilt angle because it does not vary considerably between medium and high coverage. This finding may be explained by the fact that the dimethylsilane group in PFDCS exhibits a larger cross section than the fluorocarbon chain and no close packing of the chains can therefore be achieved. This is supported by a report on the chemisorption of decyldimethylsilane on silica where a maximum coverage at an area of 40 Å^2/molecule was found although the alkyl chain cross section is known

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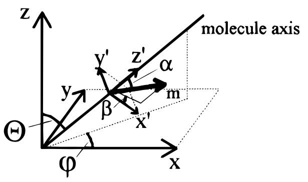
(21) The measured absorption A is proportional to $(\mathbf{E}^*\mathbf{m})^2$ with $\mathbf{E}$ being the electric field strength and $\mathbf{m}$ the change in molecular dipole moment associated with the observed band (both are given with respect to the lab system (x,y,z)). The following model accounts for the measured absorbance in the case of a uniaxial orientation of the molecular chains, i.e., a preferred tilt angle of the molecule axis with respect to the surface normal and free rotation around the molecular axis. Here, α and β determine the orientation of $\mathbf{m}$ relative to the molecular axis in the coordinate system $x'y'z'$ tied to the molecule, while θ is the tilt angle of the molecular axis relative to the surface normal and φ is its azimuthal angle in the xyz system (substrate). The y' axis is oriented parallel to the xy-plane.



In the case of a polarization of the electric field parallel to the surface, $\mathbf{E} = (0,E_y,0)$, i.e., s-polarized light, the measured absorption is

$$A \propto \frac{1}{4}\sin^2\alpha\cos^2\theta + \frac{1}{4}\sin^2\alpha + \frac{1}{2}\cos^2\alpha\sin^2\theta$$

if free rotation around the z-axis and the z'-axis (molecule axis) is assumed.

(22) We assume from the geometry of the fluorocarbon helix that the change of the dipole moment for the CC stretching vibration contains a small component perpendicular to the molecular axis. This is accounted for in the calculation by a tilt angle between the change in molecular dipole moment associated with the C−C stretching vibration and the molecule axis of 15°.

(23) Coverage was calculated as the ratio between measured absorption and the value calculated from

$$A_{\mathrm{calc}}(\alpha,\theta,\nu) = \frac{4\pi\nu}{2.303}\, k_{\mathrm{eff}}(\alpha,\theta,\nu) d_{\mathrm{layer}} N d_{\mathrm{eff}\perp}$$

were d_{layer} is the layer thickness, N the number of reflections within the ATR crystal, d_{eff} is the effective thickness due to electric field enhancement near to the surface in the case of s-polarized light, and $k_{\mathrm{eff}}(\alpha,\theta,\nu)$ is the effective absorption coefficient.

(24) Substrate temperature 100−200 °C, pressure (1−2) × 10^{-2} Torr, duration 1−4 h.

to be only 20 Å^2/chain in a close packed monolayer.[25] Thus, the maximum coverage of 0.6 observed here is very close to the limiting coverage achievable with the particular silylating agent used in this work. Although a precise quantitative relation between a particular preparation procedure and the surface coverage achieved thereby is not yet established, it is nevertheless obvious that the reported process conditions yield monolayers covering the whole range from 0.05 to virtually maximum coverage.

An important measure of the strength of the covalent bonds to the substrate is the tenacity with which these molecules are chemisorbed. The monolayers produced in this study exhibit higher temperature stability than alkanethiol monolayers on gold surfaces. While the latter are completely desorbed after 10 min at 220 °C and 10^{-2} Torr as observed by FTIR-ATR (data not shown), no significant change in FTIR-ATR absorbance is detected for PFDCS monolayers after this procedure. Similar results have been reported by Severin and co-workers.[26] This superior stability is potentially important for high-temperature applications in semiconductor fabrication processes as for example selective metalization of surfaces using monolayer lithography and CVD.[5]

Conclusion

In summary this work has demonstrated that oriented monolayers can be deposited from the vapor phase onto Ge and Si oxide surfaces by direct attachment through the formation of siloxane bonds. High coverages of oriented molecules can be achieved with proper surface hydration and proper choice of reaction conditions in a gas phase process. The films which are formed from PFDCS have low surface energies and bind tenaciously to the surface. Further quantitative studies are necessary in order to become able to correlate the surface concentration of hydroxyl groups before and after silylation respectively and the surface coverage achieved thereof. While this seems hardly possible when conventional solution-based silylation processes are employed, in-situ surface analysis is certainly compatible with a gas phase process.

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