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Infrared Characterization of Interfacial Si−O Bond Formation on Silanized Flat SiO_2/Si Surfaces

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Chemical functionalization of silicon oxide (SiO_2) surfaces with silane molecules is an important technique for a variety of device and sensor applications. Quality control of self-assembled monolayers (SAMs) is difficult to achieve because of the lack of a direct measure for newly formed interfacial Si−O bonds. Herein we report a sensitive measure of the bonding interface between the SAM and SiO_2, whereby the longitudinal optical (LO) phonon mode of SiO_2 provides a high level of selectivity for the characterization of newly formed interfacial bonds. The intensity and spectral position of the LO peak, observed upon silanization of a variety of silane molecules, are shown to be reliable fingerprints of formation of interfacial bonds that effectively extend the Si−O network after SAM formation. While the IR absorption intensities of functional groups (e.g., >C═O, CH_2/CH_3) depend on the nature of the films, the blue-shift and intensity increase of the LO phonon mode are common to all silane molecules investigated and their magnitude is associated with the creation of interfacial bonds only. Moreover, results from this study demonstrate the ability of the LO phonon mode to analyze the silanization kinetics of SiO_2 surfaces, which provides mechanistic insights on the self-assembly process to help achieve a stable and high quality SAM.

Self-assembly of silane molecules on flat oxidized silicon (SiO_2/Si) surfaces is widely used for construction of functional surfaces in a variety of device[1−4] and sensor[5,6] applications. Although silanization reaction is simple to carry out, the formation of reproducible, high quality self-assembled monolayers (SAMs) by alkylchlorosilanes or alkylalkoxysilanes is difficult to achieve due to many competing processes, such as polycondensation or physical adsorption of silane molecules on the SiO_2 surfaces (Scheme 1).[7,8] Indeed, the degree of self-assembly strongly depends on the reaction conditions, such as trace of water, temperature, solvent and silane concentrations.[9,10] Although silanization reactions have been successfully characterized in silica powder samples (e.g., by ^{1}H/^{29}Si NMR and thermogravimetric methods),[11−13] the characterization methods used for powders are not applicable for SiO_2/Si films due to the insolubility of films and small weight ratio of surface functional groups to the bulk sample. Among the current techniques, Fourier transform infrared (FT-IR) spectroscopy has proven to be a powerful method for surface characterization. Despite numerous studies,[6] lack of extensive and precise characterization of the SAM/(SiO_2/Si) interface has made it difficult to fully understand and control the self-assembly processes. Previous FT-IR studies have been primarily focused on the modes of $>CH_2$ and other functional groups such as >C═O and $-NH_2$. However, these modes do not provide direct information to distinguish physically adsorbed silanes from chemically conjugated SAM molecules. A direct characterization of the interfacial Si−O bond formation is critically important to understand the surface reaction mechanisms and improve the quality of the SAM. IR spectroscopy has previously been used for the silica powder surface silanization studies for monitoring Si−O−Si bond formation,[14] and has shown that it is possible to use the Si−O−Si region to distinguish between covalently bound organosilanes through Si−O−Si surface bonds and an organosilane polymer deposited on the surface.[15] However, this study cannot determine whether the newly formed organosilanes are parts of the silica network or just attached through one bond. The difficulty in uncovering the nature of the interfacial Si−O bonds arises in part due to the complexity of this spectral region as characterized by a broad absorption at 1000−1260 cm^{-1}, where modes of Si−O bonds from silica, silane/silica interface, and silane−silane polymer overlap.

Here we report that detection of the longitudinal optical (LO) phonon mode of thin SiO_2 films makes it possible to characterize

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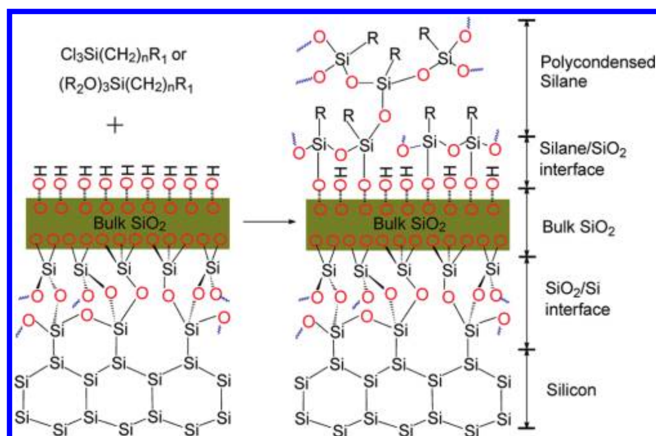
Scheme 1. Surface Modification of SiO_2/Si by Silane Molecules and Associated Layer Structures[a]



[a] R_1 represents functional groups such as $-CHO$, $-NH_2$, $-COOH$, $-SH$, etc., and $R = -(CH_2)_nR_1$; R_2 represents methyl or ethyl groups. The newly formed Si−O−Si bonds at the silane/SiO_2 interface extend the SiO_2 network, which can be detected by the LO phonon mode using a differential IR method.

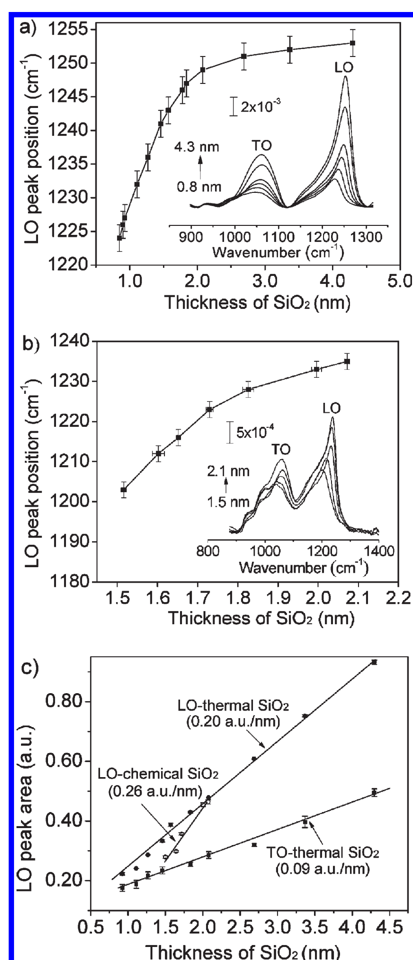


Figure 1. LO peak frequency as a function of SiO_2 thickness for (a) thermal SiO_2 and (b) chemical SiO_2. The insets are IR spectra showing the TO/LO peaks for different thicknesses of SiO_2 with H−Si as reference. (c) Integrated areas of LO or TO peaks as a function of SiO_2 thickness. The error range represents an upper and lower limit of the integrated areas from multiple baseline evaluations.

the newly formed Si−O bonds at the SAM/(SiO_2/Si) interface. This mode can be measured by using oblique incidence at the

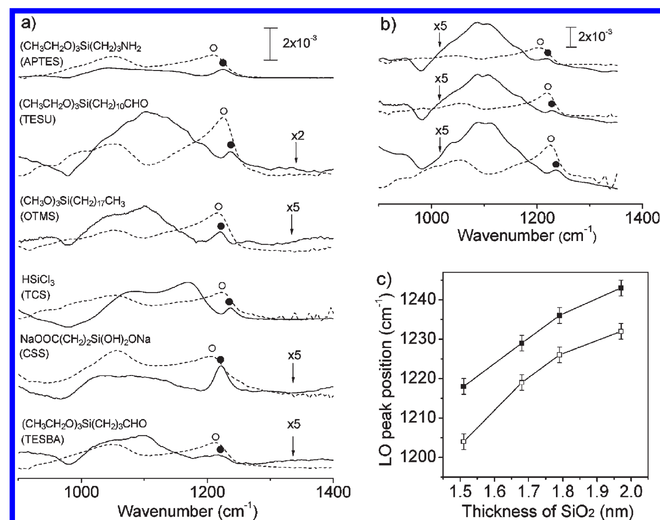


Figure 2. (a) Differential IR spectra of initial SiO_2 surfaces (dashed lines) and after surface silanization with different silane molecules (solid lines). The abbreviation for each silane molecule is shown in parentheses. (b) Differential IR spectra of TESU-silanized SiO_2 with different initial thicknesses of SiO_2 substrate. Initial chemical SiO_2 spectra are shown as dashed lines, and silanized SiO_2 spectra are shown as solid lines. Filled and open circles represent the LO peaks in the silanized and initial SiO_2, respectively. In both (a) and (b), SiO_2 spectra were referenced to H-terminated silicon surfaces and silanized SiO_2 spectra were referenced to initial SiO_2 surfaces. (c) Increase of LO peak frequency (cm^{-1}) after TESU silanization for chemical SiO_2 with different thicknesses.

Brewster angle when *p*-polarized radiation is preferentially transmitted.[16−18] Figure 1 shows the dependence of the intensity and frequency shift of the LO band on the thickness of the oxide for thermally (1a) and chemically (1b) prepared SiO_2 (see Supporting Information for preparation procedures). For both types of oxides, an increase in SiO_2 thickness leads to a blue-shift (1a and 1b) and an increase in LO intensity (1c). These observations are well explained by considering the work of Chabal and co-workers on thermal SiO_2 studies.[19−22] At comparable SiO_2 thickness, the LO peak frequency is higher for thermal SiO_2 than for chemical SiO_2, suggesting that thermal SiO_2 is more compact than chemical SiO_2. Compared to the LO peak, the intensity and frequency variations of the transverse optical (TO) band are much weaker. Figure 1c confirms that the integrated absorbance of the LO mode is linearly correlated to the SiO_2 thickness. The slopes are 0.20 and 0.26 absorbance units (au)/nm for thermal and chemical SiO_2, respectively. Thermal SiO_2 has a smaller absorption coefficient than that of chemical SiO_2, probably due to its more compact and crystalline structure.

Figure 2a shows the IR absorption induced (differential spectra, solid curves) by functionalizing the initial SiO_2 by different silane molecules, including triethoxysilyl undecanal (TESU), trichlorosilane (TCS), aminopropyltriethoxysilane (APTES), triethoxysilyl butyraldehyde (TESBA), *n*-octadecyltrimethoxysilane (OTMS), and carboxyethylsilanetriol sodium (CSS). The black

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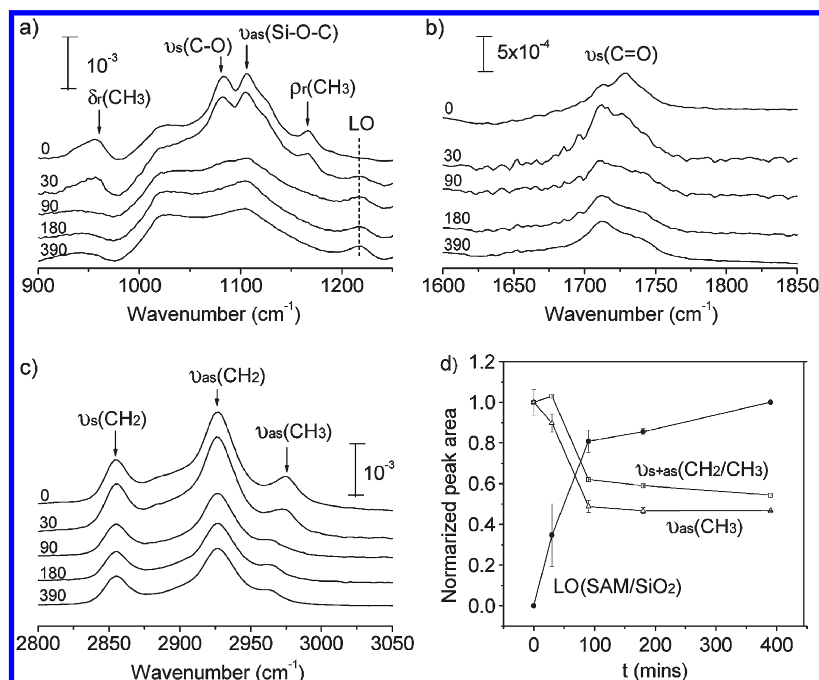

Figure 3. IR spectra of (a) Si−O−Si, (b) >C=O, and (c) CH_2/CH_3 vibration modes as a function of reaction time. At $t = 0$ min, TESU is physically adsorbed on the chemical SiO_2 surface by vapor deposition. After immersion in the PBS buffer (pH 7.4) for different times (30, 90, 180, 390 min), IR spectra were obtained. (d) Normalized peak area of LO and CH_2/CH_3 vibration modes plotted as a function of silanization time. The LO peak was normalized to its maximum value at 390 min, while the CH_2/CH_3 peaks were normalized to its initial value at 0 min.

circles indicate the position of the newly induced LO absorption, which arises from the formation of interfacial Si−O bonds between silane and SiO_2. The intensity of these induced spectra is lower (see scale factor) than the intensity of the spectra of the initial SiO_2 layer (dashed lines) recorded prior to SAM modification. The spectra of the initial oxides are characterized by two absorbance features: a TO band at 1000−1150 cm^{-1} and a LO band at 1200−1260 cm^{-1}. The differential spectra after SAM modification show a highly variable TO band at ~1000−1200 cm^{-1} and a sharper LO feature at 1200−1260 cm^{-1}. The peak assignment in the TO band is difficult because of contributions from several species, including Si−O−Si and Si−O−C vibrations.[10−12,14] In contrast, the sharp LO band appears consistently in the differential spectra as new Si−O bonds are formed at the silane/SiO_2 interface.

This conclusion is reached by noting that no new LO peaks are observed when the initial oxides (SiO_2) are immersed in the solution without the silane molecules. Furthermore, simple polycondensation of silane films on any of these SiO_2 surfaces does not lead to any absorption in the LO band region despite considerable signal increase in the TO band (see Supporting Information Figure S1). In contrast, all the silanized samples do show an increased absorbance and a blue-shift of the LO peak upon SAM formation (Figure 2a, Supporting Information Table S1 lists the quantitative values of LO shifts). These results corroborate our previous data (Figure 1) and literature reports[19,21,23] whereby LO modes intensify and blue-shift when the oxide thickness is increased. In summary, only direct bonding of the silane molecules to SiO_2 can add intensity to the LO band, and polycondensed silanes do not contribute any additional features in the region of the SiO_2 LO mode.

The dependence of the LO frequency of the newly formed Si−O bonds on the SiO_2 thickness was investigated for TESU reacted with chemically prepared SiO_2. For this model system, SiO_2 thickness was varied from 1.5 to 2.1 nm by adjusting the immersion time of Si substrates in the piranha solution. Figure 2b shows the spectra of SiO_2 with three different initial thicknesses (dashed lines) and the corresponding differential spectra obtained after TESU treatment (solid lines). If more Si−O bonds are added to the existing oxide by TESU adsorption, the LO frequency is expected to increase (according to Figure 1b). Indeed, increased intensity featuring a blue shift is observed in all three cases in the LO spectral range after TESU silanization. A similar trend is also observed for thermal SiO_2 (Supporting Information Figure S2), suggesting that in all cases TESU adsorption extends the SiO_2 network. In the case of very thin chemical oxides, the magnitude of LO frequency shift ($\Delta LO = LO_{TESU\text{-}SiO_2} - LO_{SiO_2}$, unit: cm^{-1}) is relatively constant (12 ± 2 cm^{-1} for the four different SiO_2 samples used). The LO frequency shift becomes smaller when the film thickness becomes larger as in the case of thermal oxide (Supporting Information Figure S2). The increase in SiO_2 film thickness can be estimated from measurements of the integrated areas added to the LO band. The average value is measured to be 0.022 ± 0.005 au. Based on the LO slope of 0.26 au/nm for chemical SiO_2 (Figure 1c), the thickness of the newly formed silane/SiO_2 interface is estimated at 0.8 ± 0.2 Å. This value is approximately half of the theoretical Si−O bond length (1.60−1.63 Å).[24] This indicates that not all of the newly formed Si−O bonds from TESU can truly add to the underlying SiO_2 layer thickness. Lateral Si−O bonds between the TESU molecules are also formed as evidenced by the considerable increase in TO intensity (1000−1200 cm^{-1}), and these bonds do not contribute to the LO peak intensity because they are not part of the SiO_2 network. While the initial density of surface Si−OH groups is important to establish the Si−O−Si linkages (Scheme 1) as reported in atomic layer deposition[25] and SiO_2 powder studies,[11−13] it is

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difficult to quantify their concentrations and degrees of reaction in this study. The difficulty in correlating the OH surface density to the nature of the interfacial bonds underscores the usefulness of the LO absorption band to determine the amount of Si−O formation contributing to the SiO_2 film thickness (i.e., formation of strong chemical bonds expanding the silica network).

The study of vapor phase deposition for silanization provides another means to investigate the ability of the LO mode to monitor interfacial Si−O bond formation. In a series of experiments, TESU was first deposited onto chemical SiO_2 by a dry vapor process. The physically adsorbed TESU molecules do not yield any LO peaks in the IR differential spectrum (Figure 3a, $t = 0$ min), although the TESU molecules are clearly on the surface since their other vibrational modes (e.g., >C=O and CH_2/CH_3) are detected (Figure 3b and c, $t = 0$ min). Silanization could then be induced by immersing the TESU/SiO_2 sample in the phosphate buffer (pH 7.4), leading to the observation of a LO peak at 1217 cm^{-1}. Over time, the LO peak frequency remains constant while its intensity increases. This behavior differs from the previous case, in which the LO frequency increases with increasing initial SiO_2 thickness (Figure 2b and c). In this case, the initial TESU layer does not contribute to the SiO_2 thickness until a reaction is initiated in the phosphate buffer. To follow the reaction kinetics, we integrate the LO peak area and plot it as a function of immersion time. The results show that Si−O bond formation is rapid during the first 90 min and then stabilizes. Interestingly, the behaviors of the >C=O and CH_2/CH_3 bands are different from that of the LO mode. After water exposure, the >C=O mode shows two bands at 1726 and 1714 cm^{-1} that are assigned to aldehyde and carboxyl groups, respectively. Their time dependence suggests that aldehydes are partly converted into carboxylic groups in the buffer solution during the first 30 min (increase of the overall area of the >C=O mode), followed by a monotonous decrease of all >C=O species after 30 min (Figure 3b). The intensity increase is due to the stronger dynamic dipole of the carbonyl group in the carboxylic form than aldehyde configuration, and not to a density increase. Moreover, the intensities of the CH_2 and CH_3 modes first decrease by 40−50% during the first 90 min and then reach a plateau (Figure 3d). The decrease in the $\nu_{as}(CH_3)$ signal at 2975 cm^{-1} and combined CH_2/CH_3 signals as well as the one of the >C=O modes (Figure 3b) can be attributed to two primary processes: desorption of physically adsorbed TESU molecules and/or loss of the ethoxy residues upon formation of Si−O bonds.[26,27] Notably, the kinetics of CH_2/CH_3 signal loss coincides with the LO peak increase, with a stabilization of its overall intensity when the LO peak intensity reaches a plateau. The beginning of this plateau corresponds to the time required to form a stable SAM surface.

In summary, this work shows that the self-assembly processes of silane molecules on flat oxidized silicon surfaces can be monitored by the LO absorption band that arises from the formation of Si−O bonds at the SAM/SiO_2 interface only. Such a direct characterization of interface bond formation using the LO feature allows for in-depth study of the interaction between self-assembled (mono)layers and surfaces. In particular, it makes it possible to distinguish silanes that form a strong chemisorbed bond to the surface from weakly adsorbed molecules, and thus to optimize processing conditions for sensor and other devices.

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Supporting Information Available: Materials and experimental details including SiO_2 preparation, characterization, and surface silanization. This material is available free of charge via the Internet at http://pubs.acs.org.

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