Structural Characterization of Self-Assembled Multilayers by FTIR

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We have used attenuated total reflection infrared spectroscopy (ATR-IR) to probe the structural order in zirconium–phosphonate self-assembled multilayers. Very well-ordered alkylsiloxane anchor layers can be prepared on silicon substrates after suitable etching. However, the IR spectra indicate that zirconium–organophosphonate multilayers deposited onto the anchor layer are disordered. The disorder correlates with introduction of zirconium and appears to be a result of the poor match of the hydrocarbon lattice with the stronger inorganic Zr–phosphonate lattice. There is no additional degradation in packing order with the deposition of multiple layers. Ramifications for possible device application are discussed.

Introduction

The evaluation and investigation of self-assembled films have become prevalent in the past several years.[1] The deposition techniques are straightforward and simple, and many of the films exhibit excellent mechanical and thermal stability.[2] Most importantly, the application of self-assembly techniques allows the user to create custom-designed materials with functionality engineered at the molecular level. This property, combined with the advantage that their fabrication is compatible with planar processing, makes self-assembled molecular films exciting candidates for use in a wide variety of devices.

One class of materials in particular has received much attention for potential device applications. Zirconium–organophosphonate self-assembled multilayers have been shown to be extremely versatile toward repetitive layering of a wide variety of molecular species.[3-7] The success of this particular assembly strategy can be traced to its effective use of the inorganic metal–phosphonate structure as a template upon which the organic multilayer is constructed. This approach allows total sequential and spatial control of the material, and, in addition, because the network is strongly bonded, the films exhibit high thermal stability. Potential applications of zirconium–organophosphonate multilayers have been demonstrated in such areas as nonlinear optics,[4] molecular recognition and chemical sensing,[2] vectorial electron transfer,[8] and electrical insulation.[9]

To function as active devices, self-assembled multilayer materials must meet two criteria. Besides exhibiting the correct microscopic chemical, electrical, or optical properties, the bulk films must be stable and have a low density of defects such as pores, incomplete layers, and unoriented regions. The question of film quality and density, i.e., molecular packing, in the multilayer structures is therefore critical to their assessment as materials for device fabrication.

An ideal technique for assessing layer quality and density in these films is infrared spectroscopy, which has proven to be a powerful diagnostic for the determination of packing order in a variety of linear hydrocarbon materials, including phospholipid membranes,[10,11] *n*-alkane solids,[12] and self-assembled monolayers.[13-17] The power of this technique is due to the sensitivity of the C–H stretching modes to molecular configuration and environment. Preliminary infrared studies of zirconium–phosphonate multilayers on silicon have been reported by Mallouk and co-workers.[2,18] On the basis of the constancy of the IR line widths with additional layers, they show that each new layer has the same degree of structural order as the preceding one.[2] However, such studies do not address the degree of order in any one layer. Recently, Frey et al.[19] reported an infrared study of zirconium phosphonate multilayers on germanium and gold surfaces, with similar results to that

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reported here for silicon.

In the present work, we present an infrared study in which we probe IR frequencies, linewidths, and integrated intensities throughout the stepwise deposition process and compare them with a well-ordered monolayer on the same sample. Using this approach, we are able to determine that the packing in each Zr–alkylphosphonate layer, while unchanged from layer to layer in agreement with Mallouk et al.,[2] is *relatively disordered in each layer*. Furthermore, we estimate that the zirconium phosphonate layers are only approximately half as dense as fully packed alkylsiloxane monolayer, indicating that the alkyl chains are not tightly packed in the Zr films. The analysis of difference spectra over the sequential deposition process allows us to conclude that it is the zirconium–phosphonate lattice which plays a key role in controlling the packing in the hydrocarbon layer.

Experimental Methods

Deposition and syntheses are described in detail in ref 20. Briefly, the multilayer samples were prepared by first depositing a monolayer of (triethoxysilyl)nonadecyl acetate (C_{19}) onto a freshly cleaned silicon internal reflection plate, based on chemistry initially developed by Sagiv and co-workers.[21] Cleaning was performed either by simple piranha etch using a mixture of H_2O_2 and H_2SO_4 or alternatively by a three-step procedure whereby the piranha etch was followed by immersing the substrate in HF and in a basic hydrogen peroxide solution. The C_{19} acetate was then reduced to the alcohol, phosphorylated, and zirconated in a stepwise fashion.

The substrate in this form is now ready for sequential deposition of a bisphosphonic acid and zirconium. The phosphonic acid depositions were made from freshly made 1 mM solutions in ethanol/5% H_2O. We have found this solvent to be superior to either DMSO or pure ethanol, according both to ellipsometry measurements on the resultant films and to visual assessment of the deposition solution, which can develop cloudiness over time.[22] Samples were zirconated in a 5 mM aqueous solution of zirconium oxychloride. Since bulky components may act to prohibit the formation of well-oriented layers by interfering with lateral packing, we consider here the simpler case of a straight-chain hydrocarbon, hexadecanediylbis(phosphonic acid) (C_{16}), which we have found previously to make better layers than either a C_{12} or C_{20} chain.[20] This allows us to assess the structural limitations of the zirconium–phosphonate system under the most straightforward conditions. The formation of multilayers was monitored by measuring the ellipsometric thickness after each deposition step with a Gaertner rotating-analyzer ellipsometer.

The infrared spectra were obtained with a Nicolet 800 FTIR spectrometer using unpolarized light from a globar infrared source, a cooled HgCdTe detector, and attenuated total reflection (ATR) geometry. The silicon internal reflection plates (Harrick) were 50 mm × 20 mm × 1 mm with both edges bevelled at 45°, yielding 25 reflections each from the front and back faces (see inset to Figure 1). Spectra were recorded under nitrogen at 2-cm^{-1} resolution. Averages over 128 scans led to excellent signal-to-noise for monolayer films.

Under the present experimental geometry, perpendicular and parallel components of the transition dipole are detected with similar sensitivity. It can be shown that for internal reflection in a silicon substrate using perfectly unpolarized light, all the field components at the surface, E_x, E_y, and E_z, are close in amplitude over a wide range of angles.[23] The infrared intensities are then largely independent of the effect of chain reorientation to within 20–30%.[13,24,25] Additional factors such as unequal s- and p-polarization components, submonolayer coverage,[13] and large changes in refractive index may reduce the correlation between FTIR band intensities and film coverage. Within such uncertainties, changes (especially large changes) in infrared absorption intensities may be qualitatively used to compare relative amounts of deposited material.

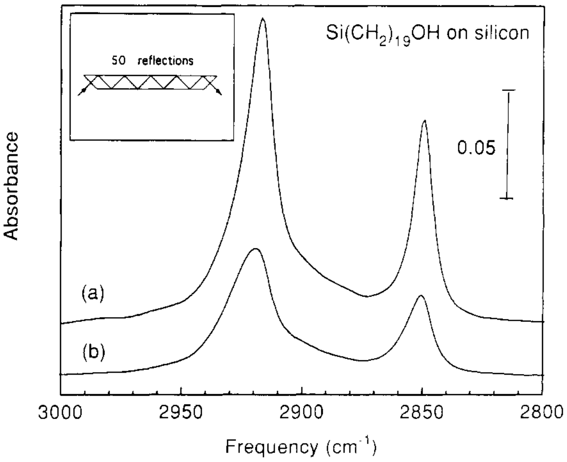

Figure 1. Infrared spectra obtained for monolayers of the alcohol-terminated nonadecyl siloxane, $Si(CH_2)_{19}OH$, adsorbed on silicon that was etched by (a) an optimized, three-step procedure and (b) piranha etch. The spectra shown are referenced to background spectra of the clean, freshly etched ATR plates. A schematic illustration of the ATR sample geometry is shown in the inset.

We will take advantage of the observation that the peak position[12] and width[26,27] of the methylene C–H stretching modes are sensitive probes of the two-dimensional packing order in the material. The symmetric and asymmetric C–H methylene stretches are designated d^+ and d^-, respectively. In crystalline hydrocarbons, these modes appear at 2850 and 2920 cm^{-1} but are blue-shifted to 2856 and 2928 cm^{-1}, respectively, for a liquid *n*-alkane.[12a] In self-assembled monolayer systems, frequencies as low as 2917 cm^{-1} have been measured for the d^- mode on well-ordered samples; increased disorder, introduced for example by heating the sample[28,29] or incorporating short chains,[15,27] is accompanied by blue-shifts of several wavenumbers. Shifts of the methylene stretching modes to higher energy are thus an indication of increased conformational disorder of the chains. The lower frequency bending modes are also commonly used to probe the degree of order in condensed phase alkanes; however, under our present experimental setup, we are unable to detect vibrational frequencies of less than ~1400 cm^{-1} due to strong absorption in this region by bulk silicon.

Results and Discussion

Typical infrared spectra obtained for monolayers of the alcohol-terminated nonadecylsilyl group deposited on the silicon ATR plates are shown in Figure 1. This monolayer is the starting point, or anchor layer, onto which the zirconium–phosphonate structure is built. The spectrum in Figure 1a is from a layer deposited on a silicon substrate that was prepared by the three-step etching sequence. Strong, narrow d^+ and d^- symmetric and asymmetric CH_2 modes are evident, with peak positions of 2850 and 2917

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cm^{-1}, respectively. We assign this spectrum to a dense, well-ordered crystalline layer based on a variety of factors, including the sharpness and low frequency (2917 cm^{-1}) of the d$^-$ mode, the good agreement of the spectrum with other well-ordered self-assembled monolayers of siloxanes[13,17] and thiols[14–16] (especially those in which a high degree of order has been confirmed by other diagnostic measures including ellipsometry[20] and helium diffraction[30]), and the fact that these films represent the best, reproducible layers obtained as a result of extensive optimization of the deposition conditions.

To illustrate the last point, Figure 1b reveals how a different cleaning procedure results in films which, according to their infrared spectra, are clearly less ordered and less dense. The monolayers studied in Figure 1 differed only in the etching procedure undertaken on the silicon substrate prior to deposition. The film deposited on a substrate prepared by a simple piranha etch (Figure 1b) exhibits CH_2 peaks that are blue-shifted and broadened compared to those shown in Figure 1a, with the asymmetric d$^-$ mode shifted by 3 cm^{-1} (2920 cm^{-1}). Most striking is the decrease in d$^+$ and d$^-$ peak intensities. Given the magnitude of the intensity decrease, we attribute the lower absorbance primarily to a decrease in deposited material rather than to a change in chain orientation, as discussed in the previous section. Using the peak intensity integrated over the CH_2 stretch region as a measure of the relative amount of material present, we find a 50% reduction in material as compared to the substrates prepared by the optimized etch sequence. Both the lower intensity and the higher frequency of the methylene peaks are consistent with the formation of a less dense, more poorly ordered monolayer.

Subsequent experiments have been carried out using the highly ordered siloxane anchor layers. The presence of this densely packed, ordered layer on the substrate provides us with an ideal basis with which to compare subsequent Zr–phosphonate layers. The most sensitive way to probe the difference between the films is to look at the incremental spectral changes occurring at each deposition step leading from the siloxane layer to the Zr–phosphonate layers.

Figure 2 shows the difference spectra for several subsequent steps in the deposition process. The data were obtained by taking the difference of the spectra recorded just before and just after the noted chemical treatment and are obtained on the well-ordered, densely packed C_{19} monolayer. Shown in Figure 2a is the spectrum of the initial C_{19} primer layer (from Figure 1a) reproduced on a reduced scale for purposes of comparison. Figure 2b shows the combined effect of phosphorylation of the C_{19} alcohol followed by zirconation of the layer. Subsequent spectra were taken after alternating (1) deposition of the C_{16} bisphosphonic acid and (2) zirconation.

The spectral changes occurring after both zirconation and C_{16} deposition steps reveal a deterioration of the layer crystallinity compared to the initial siloxane monolayer. The analysis of these changes is straightforward. First, the spectra suggest that the zirconation step degrades layer quality. This effect is evidenced by the negative peaks at the frequency associated with ordered hydrocarbon chains and a broad positive absorption increase at the higher frequencies associated with disordered chains. Furthermore, we found in general that the total integrated CH_2 mode peak intensities did not differ systematically within experimental error before and after zirconation, indicating that the difference spectrum is characteristic of a *shift* in peak intensity to higher frequencies rather than a net loss of material. This observation is consistent with ellipsometric analysis, which reveals no decrease in film thickness after zirconation. Zirconation appears to reduce the order in the underlying hydrocarbon layer primarily in the densely packed anchor layer but also to a lesser extent in the subsequent C_{16} layers. A possible mechanism for the role of the Zr is that the formation of the larger zirconium–phosphonate lattice (see below) onto a layer causes a distortion of the hydrocarbon lattice.

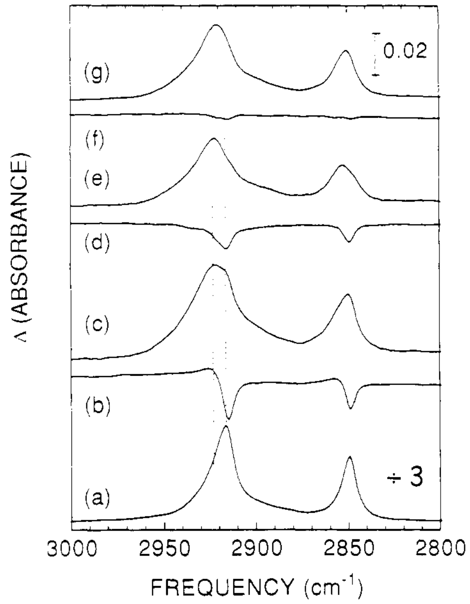

Figure 2. Difference spectra in the CH_2 stretch region obtained for a sequential series of steps in the deposition procedure. The spectrum of the initial $C_{19}OH$ primer layer is shown in (a). The spectrum in (b) is taken after phosphorylation of the $C_{19}OH$ followed by zirconation. Deposition of a C_{16} bisphosphonic acid layer (c), followed by zirconation (d), C_{16} deposition (e), zirconation (f), and C_{16} deposition (g) are also shown. The dotted lines are to aid the eye, and correspond to frequencies of 2917 and 2922 cm^{-1}.

Table 1. Peak Positions and Line Widths for Spectra of Figure 2 (in cm^{-1})

spectrum	ν (d$^-$)	fwhm (d$^-$)	ν (d$^+$)	fwhm (d$^+$)
a	2917	15	2849	10
c	2922	30	2850	16
e	2922	26	2853	18
g	2921	24	2850	15

Experiments in which we looked separately at phosphorylation and zirconation of the first layer (combined in spectrum b) indicated that phosphorylation of the alcohol groups has only a weak effect on the order in the C_{19} anchor layer. Although small, the effect is toward increased disorder, possibly because the bulkier phosphate groups interfere with the close, crystalline-like packing found for the alcohol.

It is also evident from Figure 2 that there is greater disorder in the multilayers compared to that of the first monolayer. The incremental spectra of the C_{16} layers are much broader, blue-shifted, and less intense than that of the C_{19}–siloxane primary layer on the same sample. Table 1 contains the peak positions and line widths from the spectra in Figure 2 for comparison. We note that a small

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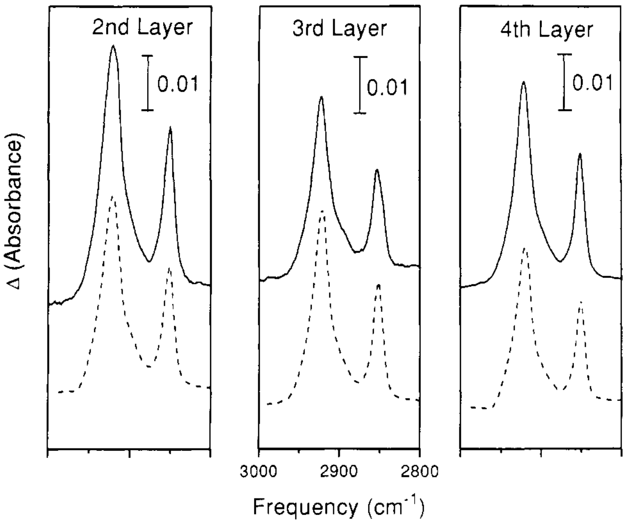

Figure 3. Difference spectra for incremental depositions of C_{16} zirconium–phosphonate layers onto both well-ordered (solid curves) and poorly ordered (dashed curves) monolayers of C_{19}.

blue shift can be attributed to the decrease in alkyl chain length (e.g., a 1-cm^{-1} shift between $n = 21$ and $n = 17$ C_n alkanethiol monolayers was noted by Porter et al.[15]), but the magnitude of the shift that we observe is too large to be accounted for by only this effect without the additional role of disorder. Interestingly, on some samples (not shown) we were able to resolve a bimodal d$^-$ difference peak, indicating that perhaps some quantity of well-ordered C_{16} was deposited along with disordered C_{16}. The decrease in CH_2 peak intensities by a factor of approximately 3 for the multilayers compared to the primer layer suggests a decrease in film density. After accounting for both the broadening of the peaks and the chain-length dependence on the intensities,[31] we estimate that the molecular coverage in the zirconium–phosphonate layers is only approximately half that of the siloxane monolayer.

To address the importance of the role of the first layer in determining the order in subsequent multilayers, we have probed C_{16} multilayer films deposited on both well-ordered and poorly ordered C_{19} monolayers. Figure 3 shows C_{16} difference spectra for films deposited on both types of monolayers (solid curves for well-ordered, dashed curves for poorly ordered initial layers), where the different siloxane anchor layers were prepared by the different etching procedures. Within experimental error, no difference is detected in peak positions or widths. Small (~20%) differences in peak intensities are observed between the two types of preparation for the second and fourth layers, but this deviation is within the range of the experimental scatter. It appears that the packing quality of the C_{16} organophosphonate layers is largely independent of the integrity of the primer layer, for the degree of variation in primer layer density that we were able to prepare. Work by Hong et al.[18] on Zr–phosphonate films deposited on fumed silica also suggests that the structure is independent of the anchoring step. However, Frey et al.[19] have found recently on Ge substrates that changing the chemical structure of the primer layer does influence the resulting zirconium phosphonate multilayer structure.

Finally, Figure 3 illustrates that the packing order of zirconium–organophosphonate layers appears relatively constant with increasing number of layers. Although we have followed the spectra only as far as three C_{16} layers, the implication is that in multilayer assemblies of alkyl chains, the layer quality does not further degrade with increasing deposition. This is consistent with the conclusion reached by Mallouk and co-workers from an analysis of IR peak widths of multilayers.[2,18] Much thicker (>25 layer) zirconium–phosphonate multilayers have been studied by techniques such as ellipsometry, which indicate good layer-to-layer reproducibility in the deposition of thick films.[2,32]

It is clear from the data that multiple layers built up using zirconium–phosphonate linkages are less highly ordered and less dense than single siloxane monolayers. The density of these layers appears to be only about half of that achieved with siloxane self-assembly. Furthermore, the data suggest that the film quality of multilayer materials is limited by virtue of the strong linking groups, in this case zirconium phosphonate, necessary to assemble the layers. These effects are evident from (1) the ability of Zr to introduce disorder into even the well-packed siloxane anchor layer (Figure 2), (2) the relatively broad, blue-shifted spectra of subsequent zirconium–organophosphonate layers, and (3) the weak dependence of zirconium–organophosphonate structure on the density or quality of the underlying layer (Figure 3).

It is instructive to compare films prepared by other self-assembly techniques with the zirconium–phosphonate films presently under study. It has been demonstrated previously that high quality, single-layer films can be prepared by both organosulfur/gold[14–16] and siloxane/silicon[13,17] linkages. Experimental work on the organosulfur/gold class of materials, for example, has shown that these monolayers are densely packed, highly oriented films. Infrared data indicate a nearly all-trans alkyl configuration with spectra closely resembling that of the bulk hydrocarbon crystal.[14–16] Helium diffraction studies on *n*-alkane thiols self-assembled on Au(111) have confirmed that a high degree of order exists in the films.[30] Siloxane self-assembly, which is used in the present work to bind the anchor alkyl layer to the silicon substrate, clearly also can produce dense, crystalline monolayers.[17]

In comparison to monolayer films, however, it might be expected that the packing in *multilayer* assemblies will be more complex. Because alkane chains in multilayers are tethered at both ends to linking groups, the molecules have less freedom to arrange into their preferred solid packing arrangement. Studies on other self-assembled systems indicate, however, that poor packing is not a necessary characteristic of multilayer assembly, but rather that it is dependent upon the particular linking chemistry. Infrared experiments of siloxane multilayers show no spectral shifts over the CH_2 stretch region from a monolayer up to 8 layers (although complementary contact angle measurements do indicate some increase in disorder at the higher layers).[17] The order in the zirconium–phosphonate films compares rather unfavorably with other types of multilayers, such as the siloxane and Langmuir–Blodgett films, which have been shown by infrared measurements to be ordered.[17,33–35]

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It appears that the degree of order is closely tied to the match of the lattice spacing of the linking atoms with the crystal spacing of the organic layer. The present infrared results suggest that the Zr–phosphonate linking structure is not well-matched to the preferred alkane crystal packing. This is supported by measured cross-sectional areas of 25 Å^2 for the ideal Zr-phosphonate salt[36] versus 18 Å^2 for neat crystalline polyethylene.[37] Furthermore, work by Frey et al.[19] shows that phosphorylation of the terminal hydroxy groups of the primer layer results in a mixture of phosphate mono- and diesters, which may further increase the spacing of active sites for bonding. As observed by Cao et al. for layered metal phosponate salts,[2] the bonding is primarily dictated by the requirements of the metal and insensitive to the nature of the attached organic group. Although other factors such as steric constraints or incomplete deposition may also contribute, much of the decreased density in the zirconium phosphonate layer can be accounted for by the lattice mismatch.

These results suggest that selecting a metal atom of appropriate size and valency to form a metal–phosphonate lattice correctly matched to that of the organic layer of interest might be a useful approach for improving the order in the organic layers.[2] Another possible strategy, recently illustrated by Byrd et al.[38] is to preorganize the organic layer by combining molecular self-assembly with Langmuir–Blodgett techniques.

The present results should serve as a starting point for studies of other organic layers based on the same zirconium–phosphonate chemistry. We have shown that the molecular ordering within alkyl layers is not as good as can be obtained in single monolayer films or in crystalline materials. However, similar structural studies must be performed on zirconium–phosphonate multilayers of more complex functionalities, e.g., aromatic molecules, to directly assess the degree of order attainable in an application-specific system. The challenge will be to characterize these structures without the benefit of the infrared-active alkyl CH_2 modes which are so sensitive to crystal structure.

Clearly, the issue of disorder in the multilayers is important to the use of these materials in devices. Disorder may not only prohibit the formation of dense films, but may also reduce the magnitude of any phenomena that rely on directional properties, such as dichroism or second harmonic generation. On the other hand, for many applications, packing effects may be relatively unimportant in light of other useful properties of the zirconium–phosphonate films. These properties include, for example, the lack of intermixing between layers, which allows for control of spatial separation and is important for electron-transfer and energy-storage devices,[8] the resistance to solvents and thermal degradation,[2] and the ability to incorporate polar order into the organic layer with only a simple modification of the deposition technique.[2,39] Finally, the ability to deposit many layers without degradation of the layer quality, as confirmed by the present infrared results, is critical to the fabrication of multilayered devices in real applications.

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