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Deposition of Ultrathin Polythiourea Films by Molecular Layer Deposition

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Molecular layer deposition (MLD) is a film growth technique which utilizes self-saturating surface chemistry to deposit organic films layer-by-layer. In this study we report a new MLD coupling chemistry to grow oxygen-free films with polythiourea groups. 1,4-Phenylene diisothiocyanate and ethylenediamine are reacted to form thiourea moieties. The films exhibit a constant growth rate and show saturation behavior in dosing each of the precursor molecules. The chemical composition of the films is probed by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and density functional theory, which confirm that the expected polythiourea films are formed by the MLD process. Transmission electron micrographs demonstrate conformal coating of SiO_2 nanoparticles. Thermal stability studies reveal that the thiourea films are stable to 200 °C, and indicate that desorption likely occurs at the SiO_2/organic interface.

Introduction

Molecular layer deposition (MLD) is a promising film growth technique that has gained increased interest in recent years as a method to deposit ultrathin organic films.[1] This interest stems largely from the potential to integrate organic films into a wide range of applications. These include areas where organic films have been the standard, such as organic electronics,[2] chemical sensors,[3] and bioresistant coatings,[4,5] as well as areas where organic films are less conventional, such as adhesion promoters,[6,7] gas diffusion barriers,[8] and copper diffusion barrier layers.[9−12] In all of these applications, the ability to precisely control film thickness, ordering, and composition is of paramount importance. MLD allows for an unprecedented level of control over these parameters in the deposition of organic films.

Analogous to atomic layer deposition (ALD),[13] MLD utilizes self-saturating surface reactions to construct films in a layer-by-layer fashion. Whereas ALD deposits a single layer of atoms per cycle for inorganic films, MLD deposits a single layer of organic molecules per cycle for organic films. By limiting the film deposition rate to no more than one molecular layer per cycle, MLD has many of the same advantages as ALD systems, including a precise control over the film thickness, conformal coating of substrates, and the ability to vary film chemistry to make blended films. It is this level of fine control that makes MLD attractive for advanced technologies: as relevant device dimensions approach the atomic scale, a film deposition technique with the capacity to make modifications on the single molecule scale is necessary.

Another advantage of MLD is that, by building upon organic chemistry, the vast library of organic molecules is available to select film precursors. By utilizing self-assembled monolayers (SAMs) to create initial surface functionalization, MLD films can be grown on a wide variety of substrates. Likewise, the terminus of the film can be varied by substituting a desired functionality into the final molecule of the MLD sequence. Within the film itself, there are two ways to modify the composition: through the film backbone and through the film coupling chemistry. Typically, MLD reactants are bifunctional organic molecules. The backbone of these molecules can be changed, to incorporate heteroatoms or select alkyl, allyl, or aryl groups, while maintaining the two reactive

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moieties necessary for MLD. Alternatively, the backbone can be preserved while the reactive moieties are changed, thus altering the coupling chemistry of the MLD scheme.

Several MLD coupling chemistries have been reported to date. The vacuum environment of MLD limits the types of organic reactions that can be utilized. In the absence of a solvent, the pH cannot be varied, a catalyst cannot be easily employed, and simple proton exchanges become non-trivial. For this reason, MLD coupling chemistries involve highly reactive groups that form exceedingly stable products. Examples of reported MLD chemistries include the reaction of acyl chlorides and amines to form polyamides,[8,14] the reaction of anhydrides with amines to form polyimides,[15] the reaction of aldehydes and amines to form polyazomethines,[16] the reaction of isocyanates and alcohols to form polyurethanes,[17] and the reaction of isocyanates and amines to form polyureas.[18,19] Reactive organometallic precursors have also been incorporated into MLD schemes, resulting in hybrid organic/inorganic films.[1,20−26]

In this study, we report a new MLD coupling chemistry: the reaction of isothiocyanates and amines to form polythiourea films. These films demonstrate a constant growth rate, and saturation behavior is observed for each of the reactants. Fourier transform infrared (FTIR) spectra agree well with spectra calculated with density functional theory (DFT), and X-ray photoelectron spectroscopy confirms that the film composition is close to the theoretical value. This vapor-phase thiourea chemistry brings new capabilities to the growth of films by MLD, providing a route to ultrathin, oxygen-free organic films and the ability to incorporate sulfur via thiocarbonyl moieties.

Experimental Section

MLD films were deposited in a reactor with a base pressure of 1 mTorr that has been described in detail elsewhere.[18] Films were grown on silicon substrates containing a 4 nm thick chemical oxide. Before initial functionalization, samples were cleaned for 15 min in a piranha solution with a 7:3 ratio of 98% sulfuric acid:30% hydrogen peroxide. The samples were rinsed in deionized water and then dried with compressed air before loading into the reactor. 3-Aminopropyltriethoxysilane (APTES) (99% Sigma-Aldrich) was deposited from the vapor phase using a method described previously.[18] Following APTES deposition, the reactor was held at 50 °C for MLD cycling. 1,4-Phenylene diisothiocyanate (PDITC) (98% Sigma-Aldrich) is a solid below 129 °C, so the precursor vial was submerged in a silicone oil bath held at 50 °C to increase vapor pressure. The gas manifold line was also heated to 50 °C, to prevent condensation of the PDITC in the line. To allow for greater PDITC pressures in the reactor, the pump was isolated during doses, and the chamber backfilled with PDITC for the desired dosing time. Ethylenediamine (ED) (99% Sigma-Aldrich) is a liquid at room temperature, and has sufficient vapor pressure for MLD dosing without heating. During ED doses, the chamber was backfilled with 1 Torr of ED vapor and held for the dose time. The nominal dose times for growth rate and saturation studies were as follows: 960 s PDITC dose, 10 s ED dose, and 240 s nitrogen purges. A single MLD cycle consisted of a sequence of the following: PDITC dose, nitrogen purge, ED dose, nitrogen purge. This sequence was repeated for the desired number of MLD cycles. Following MLD, samples were removed from the reactor for ex situ analysis.

Ellipsometry measurements were performed on a Gaertner L116C Ellipsometer using a 70° angle of incidence and the polarizer set to 45°, with 632.8 nm light. The instrument software calculated the ellipsometric angles Δ and ψ, and iteratively solved for film thickness values. Sample thickness was measured in no fewer than 3 spots on the sample, to ensure film uniformity. Because of the similarity in the index of refraction for SiO_2 and that of the organic film,[27−29] a single film thickness was determined using an index of refraction of $n_f = 1.46$, since a solution could not be found for a double-layer film model. For each experiment, the SiO_2 thickness of piranha-cleaned silicon samples was measured, and this value used as a baseline oxide thickness, which was subtracted from the subsequent total film thickness values to yield the thickness of the deposited organic film. X-ray photoelectron spectroscopy (XPS) was performed on a Surface Science Instruments S-Probe spectrometer. The excitation source was Al Kα radiation, which has an energy of 1486.6 eV. Survey scans used an energy step of 1 eV, while fine scans used an energy step of 0.1 eV. Atomic percentages were calculated by finding peak integrals, and peaks were fit using pure Gaussian profiles with a Shirley background. Multiple peaks within a single fine scan were fit while constraining the peak widths from the different species to be identical. FTIR spectroscopy measurements were made in a transmission geometry on a Thermo Nicolet 6700 FT-IR spectrometer using a MCT-A detector. Spectra were taken with 200 scans, at 4 cm^{-1} resolution. Piranha-cleaned samples were used as a background reference unless otherwise specified. Water and carbon-dioxide peaks were subtracted as necessary during the baselining process. Bright field transmission electron microscopy (TEM) images were obtained on a 200 kV FEI Tecnai G2 F20 X-TWIN microscope. For TEM studies, MLD films were deposited on silica nanoparticles (7 nm dia., Sigma-Aldrich), which were dispersed onto a carbon TEM grid (Ted Pella) using ethanol as a solvent.

Density functional theory calculations were performed using the Gaussian 03 software suite.[30] All calculations were performed

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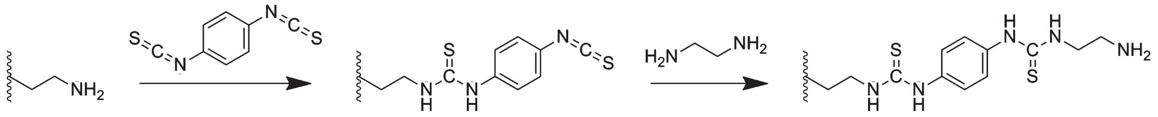

Figure 1. Schematic of a polythiourea MLD cycle. An amine-terminated surface is exposed to PDITC to yield an isothiocyanate-terminated surface, which is exposed to ED to regenerate the amine-termination.

using the B3LYP functional[31,32] with the 6-311++G** basis set. Optimizations were performed without constraints on any atoms, and vibrational frequencies were calculated to simulate IR absorption spectra. All simulated IR absorption spectra have frequencies scaled by a factor of 0.9614,[33] and an arbitrary full-width-half-max of 4 cm^{-1} is assigned to calculated peaks, to better represent FTIR spectra.

Results and Discussion

The base MLD reaction employed for deposition of polythiourea films consisted of alternating doses of PDITC and ED, and is depicted in Figure 1. In this scheme, the initial surface is amine-terminated, and becomes isothiocyanate-terminated after the reaction of PDITC. The subsequent reaction of ED completes the binary cycle, regenerating the amine-termination. Nitrogen purges between reactant doses, although not depicted in Figure 1, ensure that the two reactants are not present in the deposition chamber at the same time, preventing uncontrolled chemical vapor deposition (CVD) from occurring.

To test the growth characteristics of the polythiourea MLD process, films of different numbers of MLD cycles were deposited, and the film thicknesses were measured by ellipsometry. The results are shown in Figure 2a, where film thickness is given as a function of number of cycles. As can be seen from the plot, film thickness increases linearly with increasing number of cycles, resulting in a constant growth rate of 0.19 nm/cycle. This value is lower than the combined molecular length of PDITC and ED, which was calculated to be 1.38 nm by DFT, but a similarly low growth rate was observed for polyurea films by MLD.[18] The low deposition rate could indicate that the molecular chains are growing at a large angle of 82° from the surface normal, resulting in a small amount of vertical film growth per binary cycle. Another possibility is that the film is depositing with submonolayer coverage per cycle, as is often observed for ALD reactions.[13] This submonolayer growth could result from dual reaction of the bifunctional monomers, which has been shown to occur for other MLD systems.[1,24] In this case, linear film growth can still proceed by generation of nucleation sites within the film, possibly by uptake of precursor into the film.[1,24]

In addition to a constant growth rate, MLD requires saturation behavior in the reactant dose steps. To test the growth rate as a function of reactant dose time, a series of experiments were carried out in which all parameters were held constant while a single reactant dose time was varied. The results of these saturation studies are given in Figure 2b and 2c. As can be seen in the plots, both ED and PDITC demonstrate saturation behavior, with a region of increasing growth rate with increasing dose time, which plateaus to a region of constant growth with increasing dose time. For ED, this plateau occurs quickly, and dose times as low as 5 s result in the saturation growth rate. PDITC has a much slower response, likely because of the much lower vapor pressure of the solid, and the saturation growth rate is not reached until a dose time of 960 s. Even so, the final growth rates achieved in both the ED and the PDITC saturation studies are in agreement, at a value of 0.16 nm/cycle. Interestingly, this value is slightly lower than the value of 0.19 nm/cycle measured in the linear film growth study. We believe the higher growth is due to the nature of the film growth experiments: for

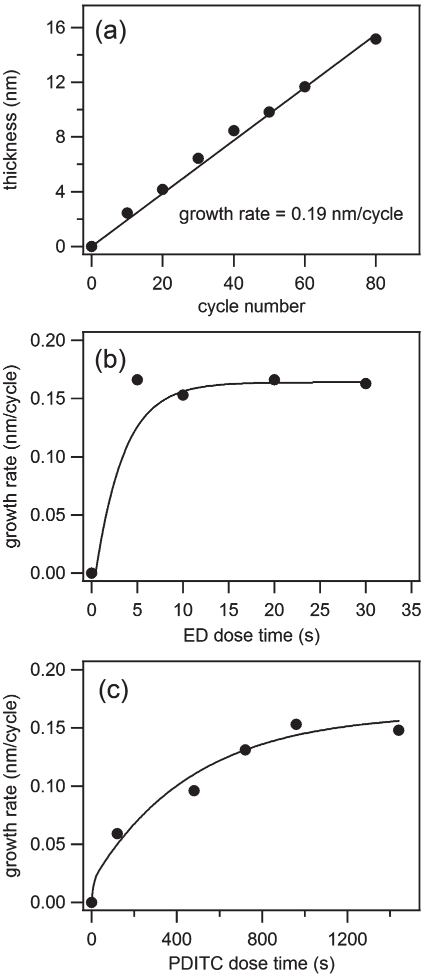

Figure 2. (a) MLD film thickness as a function of increasing number of cycles, with saturation curves showing the growth rate dependence on (b) ED dose time and (c) PDITC dose time.

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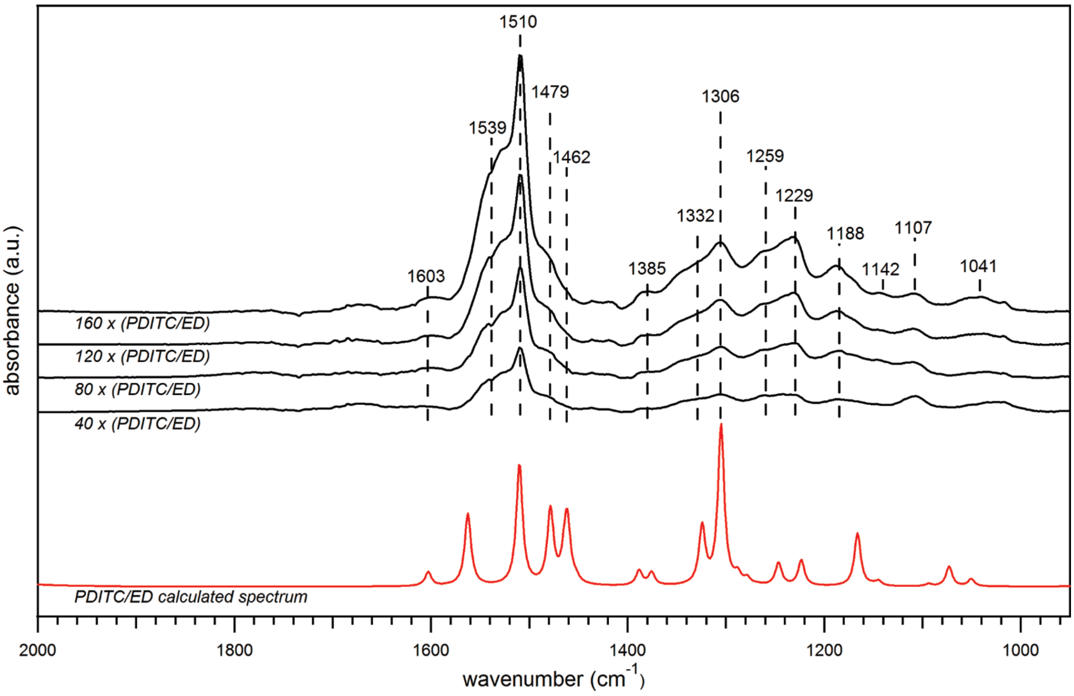

Figure 3. Transmission FTIR spectra for increasing MLD cycles, with a calculated spectrum given for comparison.

each thickness measured, the samples were removed from the reactor, analyzed, and then replaced in the reactor for further MLD cycling. This repeated exposure to atmosphere has the potential for slight contamination of the surface, for example by adventitious carbon. Such contamination did not lead to an attenuation of the growth rate over time, but may have led to the slight increase in measured growth rate observed in comparison to the saturation studies.

Following demonstration of a constant growth rate and saturation behavior for the reactants, the chemical nature of the MLD film was probed using FTIR spectroscopy. Films with varying numbers of MLD cycles were sampled by transmission FTIR spectroscopy. The resulting spectra are given in Figure 3. For comparison, a theoretical spectrum for a polythiourea chain segment, calculated by DFT, is also shown. The molecular vibrational modes for the calculated spectrum are listed in Table 1, with the corresponding peak positions for the experimental spectra. As seen from Figure 3, most of the spectral features increase in intensity with increasing number of MLD cycles, indicating that these features correspond to the characteristic modes of the MLD film. The major peak in these spectra occurs at 1510 cm^{-1} and results from a δ(NH) mode, which is known to be general to polythiourea films, and is in good agreement with the analogous "amide II" mode in polyurea films.[18] The close spacing of other modes for the thiourea films results in an overlap of peaks, observed in the region from 1400 to 1100 cm^{-1}. These features are due to various C$-$H bending modes from the alkyl chain and phenyl ring, as well as skeletal stretching modes of the C$-$C and C$-$N bonds in the chain. A second key feature of the thiourea films is evident at 1188 cm^{-1}, and is due to the ν(C=S) of the thiocarbonyl. Several of the peaks at lower frequencies, specifically at 1142, 1107, and 1041 cm^{-1}, show little variation between the spectra, and do not demonstrate the same degree of intensity increase observed with increasing coverage for modes associated with the organic. Peaks in this region have been previously observed for organic layers on SiO$_2$, and are attributed to Si$-$O$-$Si and Si$-$O$-$C modes.[29,34,35] Because these modes are due solely to the SiO$_2$/organic interface and SiO$_2$ substrate, they are unchanged by additional MLD cycling, and the constant peak intensities are as expected. Overall, we observe excellent agreement between the experimental and the calculated spectral features, especially considering that the calculated spectrum is for a single chain, and does not account for multiple chain interactions.

Table 1. Vibrational Modes Associated with Calculated Frequencies, and Corresponding Peak Frequencies in Experimental Spectra

Infrared Peak Assignments		
experimental freq (cm^{-1})	calculated freq (cm^{-1})	mode
1603	1603	δ(NH$_2$) scissor
1539	1563	δ(NH) bend + ν(C$-$C) ring mode
1510	1510	δ(NH) bend
1479	1479	ν(C$-$C) ring mode
1462	1464	δ(CH$_2$) scissor
1385	1388	δ(C$-$H) ring mode
1306, 1332	1305, 1324	δ(CH$_2$) wag + skeletal mode
1259	1247	skeletal mode
1229	1223	δ(C$-$H) ring mode
1188	1166	ν(C=S)

To further characterize the chemical nature of the MLD film, XPS was used to determine its atomic composition. Fine scans of the N(1s), S(2s), and C(1s) orbitals are given in Figure 4. Calculation of the composition using the

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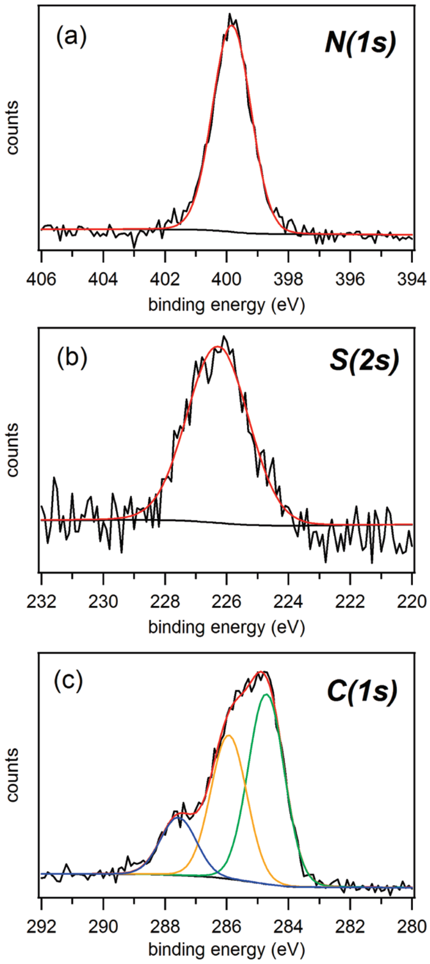

Figure 4. XPS fine scans of 12 cycle MLD films for the (a) N(1s), (b) S(2s), and (c) C(1s) core levels.

integrated peak areas reveals C:N:S ratios of 5.9:2.1:1, in close agreement with the theoretical values for the thiourea film of 5:2:1. The slight excess of carbon is likely due to adventitious carbon resulting from the transfer of samples from the reactor to the analysis chamber. In the fine scans, both the N(1s) and the S(2s) spectra can be fit to a single peak, indicating a single form of each element within the film. A single form of sulfur is expected, as the only atoms in the film are found in the thiocarbonyl moieties. There are two distinct nitrogen atoms in the MLD film: the amide nitrogen bonded to the alkyl carbon, and the amide nitrogen bonded to the aryl carbon. From the N(1s) spectrum, it is apparent that these nitrogen atoms are too electronically similar to be resolved by this XPS system. Similar results were observed for the case of MLD polyurea films.[18]

While only one peak is present in the N(1s) and S(2s) spectra, the C(1s) fine scan contains three distinct features. The peaks can be attributed to the three types of carbon within the film. The highest binding energy peak is due to the thiocarbonyl. Although the sulfur is not as electronegative as an oxygen atom, the thiocarbonyl carbon is still electrophilic and displays a distinct chemical shift. The middle peak of the C(1s) spectrum is due to alkyl carbons in the MLD film, while the lowest binding energy peak is due to aromatic carbons which have the highest electron density because of the phenyl ring conjugation. The ratio of the peak intensities of the thiocarbonyl/alkyl/aromatic carbons is 1:2.5:3.3, which indicates that the sample contains more alkyl carbon than the expected ratio of 1:1:3. This difference results primarily from adventitious carbon, which was observed in atomic composition of the film and is expected to increase the alkyl carbon content of the film. With this excess carbon taken into account, the ratios fall within the experimental accuracy of the XPS system. The C(1s) spectrum for the polythiourea films agrees closely with the results for the similar polyurea films,[18] with the main difference being a shift in the high energy peak toward lower binding energy for the polythiourea films, because of the thiocarbonyl, as discussed above. Overall, the XPS studies paired with the FTIR spectroscopy confirm the MLD film identity as the expected polythiourea film.

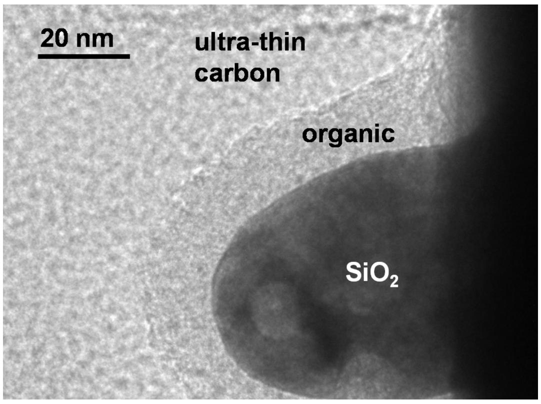

Figure 5. TEM image of 50 MLD cycle polythiourea film on a silica nanoparticle, deposited on a TEM grid coated with ultrathin carbon.

To test the conformality of the thiourea MLD process, 50 cycle films were deposited on silica nanoparticles supported on a TEM grid. A micrograph obtained by TEM is given in Figure 5. In the image, a film of light contrast surrounding the SiO_2 nanoparticle is apparent, with its morphology following the contours of the particle. The thickness of the film around the particle determined from the TEM image is 14 nm. This value agrees well with the film thickness of 13.7 nm measured by ellipsometry for monolithic control substrates in the same deposition. This film thickness corresponds to a growth rate of 0.28 nm/cycle which is higher than the previously measured growth rate of 0.19 nm/cycle. The higher growth rate for this sample may result from a chemical vapor deposition (CVD) component during deposition, perhaps because of insufficient purge times, or from temperature instabilities within the reactor, as the growth rate for MLD systems has been observed to depend strongly on deposition temperature.[18,20,23] Despite the increase in growth rate, it is evident that the MLD film conformally coats the nanoparticles, with a film thickness that matches that observed for monolithic silica substrates. Conformal coating by MLD films allows for uniform deposition in high aspect ratio features and on nanoporous substrates, and is advantageous for applications in the microelectronics industry such as organic copper diffusion barrier layers.[12]

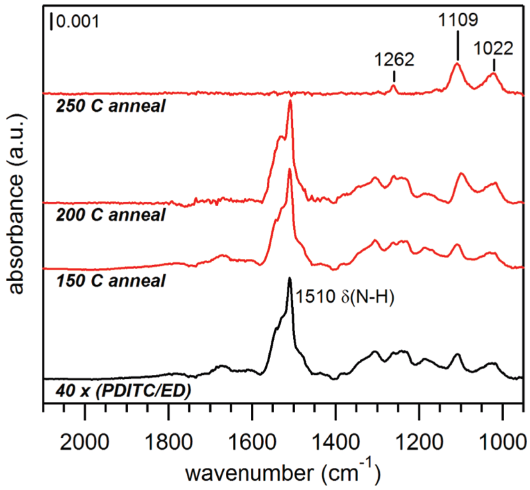

Figure 6. FTIR spectra of MLD film after 20 min vacuum anneals.

To test the thermal stability of the polythiourea films, a 40 cycle MLD film was subjected to a series of 20 min vacuum anneals under 50 mTorr of flowing N_2. FTIR spectra were taken after each anneal, to measure the chemical integrity of the film. The resulting spectra are given in Figure 6. In these spectra, little change is observed after the 150 °C anneal, but a sharpening of the high frequency shoulder for the δ(NH) mode at 1510 cm^{-1} is apparent after the 200 °C anneal. This may reflect an ordering of the film involving alignment of the chains upon anneal. There is also an increase of the features at 1109 and 1022 cm^{-1}, which are assigned to Si$-$O$-$C and Si$-$O$-$Si modes.[29,34,35] Thus, changes occur at the interface during the anneal, but it is unclear whether the new Si$-$O$-$Si bond formation is due to bonding between the organosilane and the surface or two surface Si atoms. After the 250 °C anneal the characteristic peaks of the polythiourea films are gone, indicating that the MLD film is no longer present. The only peaks remaining after this anneal are the peaks at 1109 and 1022 cm^{-1}, as well as a small peak at 1262 cm^{-1}. This small feature is likely due to a $\delta(CH_2)$ mode, and could be due to a small number of hydrolyzed ethoxy groups reacting with the surface. While such a peak could arise from film decomposition, it is unlikely that the feature would be so small if the film was readily decomposing at this anneal temperature.

The thermal stability of ≤250 °C is slightly lower than values previously measured for organosilanes at the SiO_2 surface,[36] and similar to the value measured for polyurea films.[18] The clean FTIR spectrum of the surface after the 250 °C anneal indicates that the film is likely lost because of combination of desorption and decomposition. This result in turn suggests that the organic-surface bond, that is, the APTES-SiO_2 linkage, may be the easiest bond to break thermally. This conclusion is consistent with other studies of MLD films involving the APTES/SiO_2 interface;[12] however, for desorption of the MLD chains to take place, some decomposition of the polythiourea chains is likely needed as well. Recent studies by Gandhi et al. suggested that the thermal stability of organosilanes is limited by incomplete reaction of the silane chains with the surface hydroxyl groups.[7] This work showed that annealing these films with an overlayer in place can trap the organic, preventing desorption, and allowing for further reaction of the silane with the SiO_2 surface, resulting in increased adhesion values. While adhesion does not always correlate with thermal stability, in this case, where one of the limiting factors in the stability is the bonding at the interface, increasing the bonding may help to increase the thermal stability and allow for a more accurate assessment of the inherent stability of the polythiourea MLD films.

Conclusion

We have shown the ability to deposit polythiourea films at room temperature from PDITC and ED precursors using MLD. The films exhibit the necessary MLD growth characteristics of a constant growth rate and saturation behavior in both of the precursor dose times, with conformal film deposition demonstrated by TEM. The deposited films contain vibrational modes consistent with polythiourea films, and show excellent agreement with a theoretical DFT vibrational spectrum. XPS studies of the film revealed a film composition that closely matches the expected atomic ratios, and peak splitting within the N(1s), S(2s), and C(1s) corresponded to the anticipated polythiourea films. Thermal stability studies gave evidence for an ordering of the film at 200 °C, and subsequent film desorption was observed at 250 °C. This desorption likely occurs by bond breakage at the SiO_2/organic interface because of insufficient bonding of the silane to the substrate, and masks the actual thermal stability of the MLD polythiourea chains.

This work introduces a new MLD coupling reaction, and allows for incorporation of a thiocarbonyl moiety, differing from the carbonyl and imide coupling chemistries that have previously been demonstrated. The reaction proceeds at low temperature, and takes place without byproduct. The incorporation of sulfur into organic films could find specific use in organic copper diffusion barrier layers, as sulfur is expected to form strong bonds with copper and has been shown to have desirable barrier properties.[37] Organic sulfur molecules have also been used to promote adhesion between dissimilar materials, forming a "nanoglue".[7] The thiourea MLD coupling reaction could also find use in applications that are sensitive to oxidation. Neither precursor contains oxygen, so it eliminates the possibility for oxygen release from the MLD films. This could be an important factor for incorporating MLD with materials that oxidize readily, or organic electronic systems where carbonyls function as electronic traps, as even small degrees of oxidation can have a large effect on device performance. As the field of MLD expands, the versatility of the deposited films becomes greater. Now, with another coupling chemistry, the ability to insert thiocarbonyls into films at desired locations

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(36) Senkevich, J. J.; Yang, G. R.; Lu, T. M. *Colloids. Surf., A* **2002**, *207*, 139.

(37) Gandhi, D. D.; Tisch, U.; Singh, B.; Eizenberg, M.; Ramanath, G. *Appl. Phys. Lett.* **2007**, *91*, 143503.

or as laminate layers diversifies the types of ultrathin organic films that can be deposited by MLD.

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Supporting Information Available: Complete ref 30. This material is available free of charge via the Internet at http://pubs.acs.org.