Oligomer Orientation in Vapor-Molecular-Layer-Deposited Alkyl-Aromatic Polyamide Films

Qing Peng,† Kirill Efimenko, Jan Genzer, and Gregory N. Parsons*

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

ABSTRACT: The surface-limited molecular-layer deposition of alkyl-aromatic polyamide films using sequential doses of 1,4-butanediol (BDA) and terephthaloyl dichloride (TDC) is characterized using in situ quartz crystal microbalance and ex situ spectroscopy analysis. For the first time, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is used to offer insight into molecular orientation in films deposited via molecular-layer deposition (MLD). The results show that the oligomer units are lying nearly parallel to the surface, which differs from the linear vertical growth mode often used to illustrate film growth.

INTRODUCTION

There is growing interest in vapor-phase molecular-layer deposition (MLD) to synthesize oligomers/polymers1−11 and organic−inorganic thin-film materials.12−21 MLD follows a cyclic surface-limited reaction scheme used in atomic-layer deposition (ALD)22,23 to produce highly conformal coatings.22−25 Whereas ALD is typically focused on inorganic materials,22−25 MLD processes are designed to use organic reactants to incorporate the organic component intentionally into the deposited layer.2−21 Binary surface reactions between a metal−ligand reactant and an organic reactant can yield a hybrid organic−inorganic film, whereas the reactions between two organic coreactants result in a thin film comprising organic oligomeric or polymeric materials. To date, researchers have studied MLD processes leading to the formation of molecular orientations in MLD films. NEXAFS is a powerful tool for determining the orientation of molecules on substrates.31,32 The K-shell excitation energy provides elemental specificity, and the final-state unoccupied molecular orbital provides chemical bonding information. (Note that L and M edges for elements with higher atomic numbers can provide similar information; however, they are not accessible in our experiments owing to the lower-energy (250−800 eV) X-ray used.) The partial electron yield (PEY) intensity in the NEXAFS spectra identifies the chemical bonds and their relative population density near a sample surface (the probe depth is 2 to 3 nm).31,32 More importantly, because the incident X-ray beam is linearly attributed to the thermally driven desorption of precursors. A higher deposition rate implies that the growing film will attain a higher film density, corresponding to a layer of a more densely packed oligomer layer, which tends to orient the molecules parallel to the substrate normal because of van der Waals forces.

In this article, the in situ quartz crystal microbalance (QCM) was used to study the surface-limited behavior of the MLD process of alkyl-aromatic polyamides. Importantly, for the first time, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy25,26 was employed to analyze the molecular orientation in MLD films. NEXAFS is a powerful tool for determining the orientation of molecules on substrates.31,32 In NEXAFS, a resonant soft X-ray excites a K-shell electron to an unoccupied low-lying antibonding or π* state.31,32 The K-shell excitation energy provides elemental specificity, and the final-state unoccupied molecular orbital provides chemical bonding information. (Note that L and M edges for elements with higher atomic numbers can provide similar information; however, they are not accessible in our experiments owing to the lower-energy (250−800 eV) X-ray used.) The partial electron yield (PEY) intensity in the NEXAFS spectra identifies the chemical bonds and their relative population density near a sample surface (the probe depth is 2 to 3 nm).31,32 More importantly, because the incident X-ray beam is linearly attributed to the thermally driven desorption of precursors. A higher deposition rate implies that the growing film will attain a higher film density, corresponding to a layer of a more densely packed oligomer layer, which tends to orient the molecules parallel to the substrate normal because of van der Waals forces.

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polarized, collecting NEXAFS spectra at various incident X-ray beam angles ($\theta$) between the surface normal and the X-ray polarization vector provides direct information regarding the orientation of molecules on the substrate surface.\textsuperscript{31,32} Specifically, we varied the incident angle ($\theta$) between 20 and 90$^\circ$ and analyzed trends in the PEY NEXAFS spectra to quantify the details of the molecular orientation within the film.

## EXPERIMENTS

For molecular-layer deposition, 1,4-butane diamine (BDA) (>98%), terephthaloyl dichloride (TDC, >99%), and anhydrous toluene were used as received (Sigma-Aldrich). In addition, 3-aminopropyltriethoxysilane (APTES, >98%) was purchased from Gelest Inc. Alkyl- aromatic polyamide MLD deposition was carried out on a homemade hot wall vacuum reactor as described previously.\textsuperscript{14} The deposition temperatures investigated here ranged from 75 to 155 °C. The BDA and TDC precursors were evaporated at 40 and 60 °C, respectively. The processing pressure during the reaction was $\sim$0.75 Torr. Between reactant exposures, the reactor was purged using 100 sccm of argon (99.999%) purified with a filter (Gatekeeper) to remove residual water vapor. Silicon (100) wafers (1 × 1 cm$^2$) with a thin native oxide layer were used as substrates and were prepared by wet cleaning with a solution of BakerClean JTB-100, followed by rinsing in deionized water and then drying with a flow of N$_2$. In some cases, Si wafers with an APTES-terminated surface were used. To form the APTES-terminated substrate, the cleaned Si wafer was exposed to UV-ozone for 20 min, resulting in a hydrophilic surface with a high density of $-$OH groups. Then the UV-ozone-treated Si wafer was immersed in a 1 vol % APTES solution in toluene for 5 min at 60 °C, followed by three rinsing steps in toluene, methanol, and deionized water. An in situ QCM\textsuperscript{23} was used to monitor the adsorption and desorption behavior during half cycles of each reactant in MLD. Ellipsometry (Rudolf/Auto EL) provided information about the film thickness after deposition. A refractive index of 1.56 was used for polyamide films.\textsuperscript{33} Transmission Fourier transform infrared (FTIR) spectroscopy of polyamide films provided chemical information about the film composition. A ThermoNicolet IR bench with a deuterated triglycine sulfate detector (KBr beam splitter) was used in transmission mode; the measuring chamber was purged with purified dry air. A background spectrum was collected using the same wafer before deposition. Contact angle measurements (model 200 Rame-Hart goniometer) were employed to analyze the surface wettability after APTES treatment.

NEXAFS spectroscopy was used to probe the chemical and molecular orientation information of the as-formed polyamide film. NEXAFS analysis was performed at the NIST/Dow Soft X-ray Materials Characterization Facility of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.\textsuperscript{31} Experimental details have been described previously.\textsuperscript{31} The incident photon source applied during analysis has a resolution of 0.2 eV, an intensity of 5 × 10$^{13}$ photon/s, and an energy of 300 eV. The typical storage current is around 500 mA. From our past experience, hydrocarbons are not as susceptible to damage as other materials (e.g., fluorocarbons), particularly for short run times (about 8 min for each scan). Each scan (different geometries) was performed on a fresh spot on the sample.

## RESULTS AND DISCUSSION

Figure 1 depicts the reaction mechanism scheme for 1,4-butane diamine reacting with terephthaloyl chloride in the MLD reaction sequence. These two reactants can react with one another without a catalyst at room temperature with the generation of HCl vapor.\textsuperscript{2,4,30} After the BDA half cycle, the surface becomes amine-terminated.\textsuperscript{2,5} The amine groups then react during the TDC half cycle to form an amide bond and a carboxylic chloride terminus.\textsuperscript{2,5} The stepwise repetition of the above reactions results in the oligomeric amide on the substrate.

The saturation behavior of the BDA and TDC half-reaction steps measured by QCM at 75 °C is shown in Figure 2. In Figure 2a, TDC exposure on the BDA-treated surface shows the reaction and net mass gain. Repeating the TDC/Ar steps (10 s/120 s) (without the BDA half cycle) shows continued mass uptake and near saturation after approximately three

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Mechanism of the MLD reaction between BDA and TDC. * indicates a surface-bonded ligand.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Behavior of the adsorption/desorption of monomers onto a Au-coated quartz crystal surface at a reaction temperature of 75 °C. (a) Adsorption behavior of TDC evaporated at 60 °C. After the dosing of BDA (at $t = 7$ min, duration = 7 s, solid arrow), TDC was dosed every 2 min, with a duration of 10 s of exposure (dotted arrow). Argon gas was purged in between doses. This procedure was repeated 10 times. The adsorption of TDC is almost saturated after 60 s of dosing. Two minutes of Ar purging is enough to remove physically absorbed TDC. (b) Saturation curve of BDA evaporated at 40 °C, which shows a pulse at 40 °C with 7 s of saturation at a reaction temperature of 75 °C.}
\end{figure}
subpulses. The net mass gain from the TDC half cycle corresponds to the condensation reaction between carboxylic acid chloride groups in TDC and surface amino groups, as shown in Figure 1. For the case of BDA exposure on a TDC-treated surface, the QCM results in Figure 2b exhibit different behavior. A large mass gain occurs during BDA exposure owing to the physisorption and chemisorption of BDA. In the following purging step, there is significant mass loss owing to the desorption of physically absorbed BDA. The net mass gain after the half cycle of the BDA dose/purge step is ascribed to covalently grafted BDA during the reaction steps. Repeating the BDA dose/purge steps (without the TDC half cycle) leads to significant physisorption but decreased chemically adsorbed BDA. However, it takes a long time (∼240 s) to remove most of the physisorbed BDA molecules. The QCM data shown in Figure 2 provide direct evidence of the surface-limited growth behavior in the alkyl-aromatic polyamide MLD process.

The thickness per cycle during MLD of the alkyl-aromatic polyamide film was studied at different reaction temperatures. On the basis of the QCM analysis (cf. Figure 2), for real growth, pulsing times 60 and 7 s were used for TDC and BDA, respectively. A purging time of 300 s was employed for both reactants. The growth rate of MLD film decreases with increasing growth temperature. At 85 and 125 °C, the growth rates are ∼2 and 0.5 Å/cycle, respectively, whereas at 155 °C the growth rate is almost zero. This trend is consistent with the temperature-dependent growth rates reported in the literature.4,7,12 Pretreatment of the silicon substrate with a monolayer of APTES was investigated as a means to modify MLD nucleation. The as-formed APTES monolayer had a thickness of ∼8–10 Å (based on ellipsometry) with a static water contact angle of ∼45–50°. These values are consistent with those reported previously.34 Interestingly, the presence of APTES did not significantly affect the nucleation and growth of the oligoamide. The growth rate of the MLD film thickness on the −NH2-terminated silicon substrate at 85 °C was ∼2 Å/cycle, which is indistinguishable from the growth rate for MLD directly on silicon coated with native oxide. This result indicates that polyamide MLD growth can nucleate on both the −OH- and −NH2-terminated surfaces.4,7

Figure 3 shows a transmission FTIR spectrum for a film prepared at 85 °C on native oxidized silicon. The spectrum features peaks for (C==O)−N−H bending and C−N stretching at 1543 cm−1, C==O stretching (amide I) at 1638 cm−1, and N−H stretching at 3310 cm−1, all consistent with the characteristic IR spectrum of polyamide.2,4,5,30 Additionally, C−H stretching modes are detected at 2800–3000 cm−1. The absence of any −COCl mode near ∼1786 cm−1 suggests that no carboxylic acid chloride monomer remains inside the deposited film.9 The small absorption peak centered at ∼2100 cm−1 may result from nitriles formed from the dehydration of amide during deposition or air exposure.4

The NEXAFS spectra of the as-deposited alkyl-aromatic polyamide on a Si wafer coated with native oxide collected at various incident angles of the X-ray beam relative to the sample surface (θ) are shown in Figure 4. The film was deposited at 85 °C for 100 cycles, producing a ∼20-nm-thick film. All NEXAFS spectra exhibit a sharp peak at 284.6 eV, with the signature of the 1s → σ* C−C transition originating from the phenyl group.35–37 The peak at 287.6 eV is attributed to 1s → σ* C−H transitions.35 The peaks centered at 289.4 eV are ascribed to the 1s → π* C−O transition.56,58 Peaks at 296 and 302 eV are associated with the 1s → σ* C−C transitions. The presence of the various peaks confirms the chemical composition of the film. The change in peak intensity with varying the angle between the incident X-ray beam and the sample provides evidence that the oligomer is oriented on the surface. The positions of the peaks in the PEY NEXAFS spectra were determined using the method outlined below.

To gain more quantitative insight into the molecular orientation, the NEXAFS spectra shown in Figure 4 were analyzed according to the procedure developed by Outka and co-workers.32,59,40 Specifically, the presence of the NEXAFS signals corresponding to the various 1s → σ* and 1s → π*
excitations was established from a difference spectrum obtained by subtracting the NEXAFS spectra collected at θ = 90° (i.e., normal incidence) and θ = 20° (i.e., glancing incidence). The positions and widths of the Gaussian peaks used to fit the difference spectra were then employed to establish a background signal from the NEXAFS spectrum collected at θ = 50°. NEXAFS spectra collected at various values of θ were then fitted to the series of Gaussian peaks established earlier and the carbon excitation step edge (placed at 290.2 eV, a typical value for hydrocarbons) by varying the intensities of the Gaussian peaks through an in-house simulated annealing fitting routine. In Figure 5 we plot the experimental PEY NEXAFS spectra (thick black line), Gaussians and (thick red line), which are summarized in Figure 4, and the calculated NEXAFS spectra (thick black line) and background (not shown) with sample/beam angles of (a) 20°, (b) 30°, (c) 40°, (d) 50°, (e) 60°, (f) 70°, (g) 80°, and (h) 90°.

where z is an axis normal to the film surface and x and y are orthogonal axes in the plane of the surface whereas α is the angle between the z axis and the direction of the σ* orbital (along the σ bond) or the π* orbital (orthogonal to the π bond), and dΩ is the differential solid angle. The molecular axis distribution function f(α) is normalized so that ∫ f(α) dΩ = 1 (i.e., f_x + f_y + f_z = 1), as apparent from eq 2.

The PEY NEXAFS intensity I_XY(θ) originating from an X–Y bond adopts the following form

\[ I_{XY}(θ) = A_{XY} + B_{XY} \sin^2(θ) \]  

where \( A_{XY} \) and \( B_{XY} \) are constants. Further following Stöhr and Samant, one can write

\[ f_x,XY = A_{XY} + B_{XY} \]  

\[ f_y,XY = \frac{A_{XY} + B_{XY}}{I_{tot}} \]  

\[ f_z,XY = \frac{A_{XY} + B_{XY}(1 - \frac{1}{P})}{I_{tot}} \]  

where P is the polarization factor of the X-ray beam and \( I_{tot,XY} \) is the total integrated intensity originating from the X–Y bond given by

\[ I_{tot} = 3A_{XY} + \left(3 - \frac{1}{P}\right)B_{XY} \]  

as apparent from eqs 2, 4, and 5.42 Hence

\[ f_z,XY = \frac{A_{XY} + B_{XY}(1 - \frac{1}{P})}{3A_{XY} + \left(3 - \frac{1}{P}\right)B_{XY}} \]  

Stöhr and Samant have shown that a uniaxial orientation order parameter S can be defined as

\[ S = \frac{1}{2} \left(3f_z - 1\right) \]  

where S ranges from +1 (σ* or π* aligned perfectly along z) to −1/2 (σ* or π* lying in the plane of the surface). The above treatment assumes that there is molecular symmetry normal to the plane of the surface (i.e., there is no preferred direction in the plane). This condition is very likely fulfilled in our samples given that no preferential in-plane orientation was established during deposition. The order parameter defined in this way is analogous to the Herman orientation parameter of X-ray diffraction.41 Orientation order parameter \( S_{XY} \) can be determined from the values of \( A_{XY} \) and \( B_{XY} \) by combining eqs 7 and 8 as follows:

\[ S_{XY} = -\frac{B_{XY}}{3A_{XY} + \left(3 - \frac{1}{P}\right)B_{XY}} \]  

We have obtained the values of \( A_{XY} \) and \( B_{XY} \) as the intercept and slope in the experimental data corresponding to each bond detected in the NEXAFS spectra (cf. Figures 4 and 5). By using \( P = 0.85 \) (relevant for the setup at BNL), we have calculated the corresponding values of \( S_{XY} \); these are listed in Table 1.

Using the values of the orientation parameters listed in Table 1, we construct the conformation of the molecule on the surface. Let us consider first the orientation of the phenyl groups. The value of orientation parameter (0.274) suggests that the transition dipole moment is oriented toward the sample normal but not aligned perfectly with it. Considering

![Figure 5. PEY NEXAFS spectra collected from the sample in Figure 4 (thick red line) and the corresponding model fits (thick black lines) using the Gaussian peaks and the ionization edge (thin black line) and background (not shown) with sample/beam angles of (a) 20°, (b) 30°, (c) 40°, (d) 50°, (e) 60°, (f) 70°, (g) 80°, and (h) 90°.](image-url)
that the π* orbitals are oriented orthogonal to the plane of the phenyl rings, the phenyls are lying in the plane of the sample surface but are not perfectly aligned with it. We note that any other orientation of the phenyl ring (i.e., edge-on or standing up) would result in a negative value of S. We now turn to the orientation of the oligo(ethylene) spacer. The large negative values of the orientation factor at peak energies of 296.0 and 302.0 eV imply that the transition dipole moment associated with the 1s → σ* C−C transition lies within (or close to) the plane of the surface. Taking into account that the σ* C−C antibonding for a C−C bond is oriented along the C−C bond, this would suggest that the planar zig-zag of the oligo(ethylene) spacer is oriented close to parallel with respect to the surface plane. Overall, the conformation of the topmost 2 atoms is consistent with the measured growth rate orientation and high packing density within the molecular film. The low oligomer density likely results from double reactions during the MLD sequence. In a double reaction, both reactive end groups on the TDC or BDA monomers react with available surface sites, consuming and/or blocking surface reactive sites that would otherwise be available during the following surface reaction step. In addition, whereas a higher temperature may be expected to help increase the packing density, we find that increasing temperature acts to reduce the growth rate. The reduced growth rate is ascribed to a smaller sticking coefficient of adsorbed precursors at higher temperature, which therefore decreases the molecular density on the surface. With a shorter surface residence time at higher temperature, it is more difficult for reactants to find a favorable reaction site to react. Moreover, even when the starting surface has a high density of reactive sites, the size of the molecular chain introduces a steric hindrance effect that will decrease the number of available reaction sites and the oligomer packing density as the film reaches steady-state growth.

**CONCLUSIONS**

Surface-limited MLD growth of alkyl-aromatic polyamide films was confirmed by using in situ QCM analysis. For the first time, the alignment of the molecular chain in the MLD films was characterized using NEXAFS spectroscopy. The results reveal significant tilting of the grown oligomer units with respect to the substrate normal. As the MLD field continues to advance, a more detailed understanding of the molecular structure inside the material is essential to adjusting the film properties to meet the desired function. NEXAFS, as demonstrated here, is a powerful technique for this purpose.

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: qing.peng@duke.edu; parsons@ncsu.edu.
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**REFERENCES**


