# **Interfacial Effects on Moisture Absorption in Thin Polymer Films**

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Moisture absorption in model photoresist films of poly(4-hydroxystryene) (PHOSt) and poly(tertbutoxycarboxystyrene) (PBOCSt) supported on silicon wafers was measured by X-ray and neutron reflectivity. The overall thickness change in the films upon moisture exposure was found to be dependent upon the initial film thickness. As the film becomes thinner, the swelling is enhanced. The enhanced swelling in the thin films is due to the attractive nature of the hydrophilic substrate, leading to an accumulation of water at the silicon/polymer interface and subsequently a gradient in concentration from the enhancement at the interface to the bulk concentration. As films become thinner, this interfacial excess dominates the swelling response of the film. This accumulation was confirmed experimentally using neutron reflectivity. The water rich layer extends  $25 \pm 10$  Å into the film with a maximum water concentration of  $\sim 30$  vol %. The excess layer was found to be polymer independent despite the order of magnitude difference in the water solubility in the bulk of the film. To test if the source of the thickness dependent behavior was the enhanced swelling at the interface, a simple, zero adjustable parameter model consisting of a fixed water rich layer at the interface and bulk swelling through the remainder of the film was developed and found to reasonably correspond to the measured thickness dependent swelling.

## **1. Introduction**

Moisture absorption in polymeric films has been studied in great detail with applications in coatings, sensors, and microelectronics, as examples.<sup>1</sup> However, the influence of the film interfaces has been generally neglected.<sup>2–4</sup> The determination of the water distribution in films is much more difficult to resolve than just the total moisture content. There have been a number of different methods used to probe this distribution, with varying degrees of success.<sup>5,6</sup> However, for these techniques, detailed concentration profiles cannot be obtained for ultrathin films. Neutron reflectivity has been used to characterize moisture at interfaces in thin films.<sup>2,4,7</sup> In these cases, an excess of water, dependent upon the substrate hydrophilicity, was observed at the substrate/polymer interface.<sup>2,3</sup> In some instances, a nonuniform water distribution can have significant implications for lithographic imaging, where moisture content influences the reaction in chemically

amplified resists.<sup>8</sup> Proof of this importance is that moisture absorption has been measured recently in several photoresist systems.<sup>9,10</sup> However, in these cases, the influence of interfaces was ignored.

With the push toward thinner lithographic films and smaller device features in the semiconductor industry, interfaces have become a significant portion of the total photoresist film and can lead to apparent changes in physical properties. Over the past decade, deviations in the thermal and transport properties have been observed when the film thickness approaches the bulk radius of gyration  $(R_g)$ .<sup>11–20</sup> Previously, the role of confinement on the properties of model photoresist films was studied in detail. The effect of confinement on the thermal properties

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of poly(4-hydroxystryene) (PHOSt) has been examined.<sup>21,22</sup> The thermal expansion coefficient was found to be highly dependent upon the substrate surface energy.<sup>21</sup> Additionally, the atomic mobility in PHOSt and poly(tert-butoxycarboxystyrene) (PBOCSt) was probed using incoherent neutron scattering.<sup>23</sup> The changes in the mobility upon confinement were dependent upon the polymer; for PBOCSt, suppression in molecular motion was observed at all measured temperatures, even those deep in the glassy state, whereas, for PHOSt, significant changes were only observed above the glass transition temperature  $(T_g)$ .<sup>23</sup> This is important for lithographic applications, as the decreased chain mobility manifests itself as a decrease in the reaction kinetics in these chemically amplified resists.<sup>24</sup> Here, we examine film thickness effects on the amount of moisture absorption in PHOSt and PBOCSt films. This is motivated by the observation that moisture content has been found to influence the reaction rate in chemically amplified photoresists. A distribution of water within the photoresist film may also lead to interfacial patterning defects such as T-topping and/or footing. Finally, the interactions of water with a photoresist film are anticipated to be increasingly important with the introduction of immersion lithography as a viable alternative to the extension of current lithographic tools.

#### 2. Experimental Methods

A. Sample Preparation. Moisture swelling experiments were performed on model 248 nm resist formulations of poly(tertbutoxycarboxystyrene) (PBOCSt) and its unprotected analogue, poly(4-hydroxystyrene) (PHOSt). PHOSt with an average relative molar mass  $(M_{n,r})$  of 8000 g/mol was obtained from Triquest Chemical Company. (Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.) PBOCSt was formed by protecting PHOSt via free radical polymerization of tert-butylene-4-vinylphenyl carbonate to the para position of the aromatic ring.<sup>25</sup> Films were prepared by spin-coating from propylene glycol methyl ether acetate (PGMEA) solutions at various concentrations. All solutions were filtered (0.45  $\mu$ m) and spun at 209 rad/s (2000 rpm) onto silicon (100) wafers. Prior to spin-coating, the wafers were cleaned in an oxygen plasma for 5 min succeeded by a 1 min etch in an aqueous HF bath, after which a smooth, clean silicon oxide layer was regrown on the wafer through a UV ozone exposure for 2 min. After spincoating, a 2 h postapply bake (PAB) at 120 °C under vacuum (<0.1 Pa) was used to remove excess solvent.

**B. Measurement Methods.** The total moisture absorption was determined by using specular X-ray reflectivity (XR). For thin films (<120 nm), the reflectivity measurements were made with a  $\theta/\theta$  diffractometer with Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) and soller slit collimation for both the incident and the reflected beam. The humidity at room temperature was controlled inside an aluminum chamber with beryllium windows that was first evacuated (dry sample) and then backfilled with the equilibrium vapor from distilled and deionized water (Milli-Q Millipore, Molsheim, France; 18.2 M $\Omega$  cm). The water was vacuum degassed through three freeze—thaw cycles (freeze under



**Figure 1.** X-ray reflectivity profile for PBOCSt film before and after moisture exposure. The reflectivity of the exposed film is offset by two decades for clarity. The scattering length density profiles corresponding to the fit of the data are shown in the inset for the film under vacuum (dashed line) and after exposure to saturated water vapor (solid line).

vacuum) prior to exposing the sample in the X-ray reflectometer chamber. For thicker films (>120 nm), the reflectivity was collected in a  $\theta/2\theta$  geometry using Cu K $\alpha$  radiation focused by a bent crystal mirror into a four-bounce Ge(220) crystal monochromator. The reflected beam was further collimated through a three-bounce channel-cut Ge(220) crystal prior to detection. The XR of the films was first measured in a dry state under vacuum (<0.1 Pa) and then subsequently exposed to saturated water vapor. All measurements were performed at ambient temperatures.

The water distribution in the films was determined by specular neutron reflectivity (NR). NR measurements were performed on the Center for Neutron Research NG-7 reflectometer at the National Institute of Standards and Technology (Gaithersburg, MD) utilizing cold neutrons with a wavelength ( $\lambda$ ) of 4.768 Å and a wavelength spread ( $\Delta\lambda/\lambda$ ) of 0.2. NR is capable of probing the neutron scattering density at depths of up to several thousand angstroms, with an effective depth resolution of a few angstroms. The environmental control for the NR experiments was identical to the XR experiment except that the sample chamber was equipped with silicon windows and that heavy water (deuterium oxide; Aldrich, 99.9% pure) was used in place of H<sub>2</sub>O.

#### 3. Results and Discussion

The X-ray reflectivity profiles of a PBOCSt film before and after exposure to saturated water vapor are shown in Figure 1 as a function of *Q*, where  $Q = 4\pi \sin(\theta)/\lambda$ ,  $\theta$ is the incident angle, and  $\lambda$  is the X-ray (or neutron) wavelength. Exposing the dry film to the moisture vapor decreases the distance between the interference fringes, indicating swelling of the film. The reflectivity data are fit using a multilayer least-squares fitting algorithm<sup>26</sup> to extract the thickness and the real space density profiles. displayed in the inset of Figure 1. These density profiles are presented in terms of  $Q_c^2$  as a function of distance through the film.  $Q_c^2$  is a scattering length density, with dimensions of  $Å^{-2}$ , and is proportional to the average atomic scattering length (b)  $(Q_c^2 = 16\pi Nb)$ , where N is the number of electrons for X-rays or the number of nuclei for neutrons. For the XR data in Figure 1, the angle  $\theta_{\rm c}$ corresponding to  $Q_c^2$  is proportional to the electron density  $(\rho_{\rm e})$  (and thus the mass density) through the relation  $\theta_{\rm c}$  $=\lambda(\rho_{\rm e}r_{\rm e}/\pi)^{0.5}$ , where  $r_{\rm e}$  is the classical radius of an electron. The  $Q_c^2$  profile is 0 above the sample in a vacuum. As the thickness axis increases, the scattering length density increases first to that of PBOCSt, next to that of native silicon oxide, and finally to that of pure silicon. The film initially 6.3  $\pm$  0.2 nm thick expands to 7.5  $\pm$  0.2 nm after exposure to saturated water vapor. (The data throughout the paper and the figures are presented along with the standard uncertainty  $(\pm)$  involved in the measurement

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**Figure 2.** Swelling of PBOCSt film with saturated water vapor. The fractional uptake increases as the film thickness decreases below 100 nm. The dashed line is the prediction from eq 3 using the swelling of the thickest film as the bulk water concentration (eq 5) and using the excess water thickness found using neutron reflectivity (eq 4). The data are well represented by this excess layer model.



**Figure 3.** X-ray reflectivity profile for PHOSt film before and after moisture exposure. The reflectivity of the exposed film is offset by two decades for clarity. The scattering length density profiles corresponding to the fit of the data are shown in the inset for the film under vacuum (dashed line) and after exposure to saturated water vapor (solid line).

based on one standard deviation.) Notice that the scattering length density does not change significantly upon moisture exposure. This is because the  $Q_c^2$  of  $H_2O$  (4.76  $\times 10^{-4} \text{ Å}^{-2}$ ) is not too different from that of PBOCSt (5.0  $\times$  10^{-4} Å^{-2}) for X-rays. Later, we will see how this limits any attempt to directly determine inhomogeneity in the moisture distribution from XR. Nevertheless, the total water content in the film can be determined by the vertical swelling given that the lateral swelling is constrained (prohibited) by the rigid substrate. The fractional swelling as a function of the PBOCSt film thickness is shown in Figure 2. The swelling increases markedly for the thinnest films, by almost an order of magnitude greater than that of the thickest films. For films thicker than  $\sim$ 80 nm, the fractional swelling appears constant irrespective of film thickness.

The X-ray reflectivity and corresponding density profiles for the swelling of a PHOSt film are shown in Figure 3. The PHOSt film expands from  $12.6 \pm 0.2$  nm to  $14.6 \pm 0.2$ nm upon moisture exposure, corresponding to a  $15.4 \pm$ 5.2% film swelling. As seen with PBOCSt, the absorption appears to be enhanced as the films become progressively thinner, as illustrated in Figure 4. However, notice that the swelling in the thicker films is greater for PHOSt compared with PBOCSt. This is consistent with expectations from the chemical structure, with the increase in hydroxyl groups corresponding to an increase in water affinity. We note that the swelling of the thickest films is less than that previously reported by Berger and Henderson,<sup>9</sup> but the film processing is significantly different



**Figure 4.** Swelling of PHOSt film with saturated water vapor. The fractional uptake increases as the film thickness decreases below 100 nm. The data can be predicted from the excess water found using neutron reflectivity and the swelling in the thickest film as the bulk equilibrium concentration (dashed line).

and probably the reason for the discrepancy. Berger and Henderson<sup>9</sup> used a relatively gentle PAB (115 °C for 3 min in air) in comparison to the more aggressive conditions (120 °C for 2 h in a vacuum) utilized here. Under the former PAB, the film retains significant amounts of solvent.<sup>27</sup> Since PGMEA and/or ethyl lactate are mildly polar, these casting solvents occupy some of the potential  $H_2O$  interaction sites (hydroxyls) in PHOSt. In effect, the soft PAB film is "preswollen" by residual solvent in comparison to the case of the more aggressive PAB. Ito shows that H<sub>2</sub>O will rapidly replace residual PGMEA in a PHOSt film.<sup>27</sup> However, for the soft PAB, this leads to an apparent reduction of the moisture induced swelling because of the solvent preswelling effect. Therefore, it is reasonable that Berger and Henderson<sup>9</sup> observed a smaller uptake in the thicker films. Also consistent with larger amounts of residual solvent, Berger and Henderson<sup>9</sup> observed faster H<sub>2</sub>O diffusion coefficients (consistent with a solvent plasticization effect) than our own measurements.<sup>28</sup> Finally, we repeated the measurements of Berger and Henderson,<sup>9</sup> using their PAB conditions and our X-ray reflectivity technique, and then obtained comparable results.

The film thickness dependent absorption could be described by interfacial effects on the absorbed water concentration, that is, an excess of water at the hydrophilic silicon oxide substrate. This is further suggested by the observation that the excess swelling in thin PBOCSt and PHOSt films is similar despite the greater water affinity for PHOSt. The segregation of water near silicon oxide would not be surprising, given the hydrophilic nature of this interface. It is understood that a water layer will form on silicon oxide when exposed to a given vapor pressure due to surface ionization.<sup>29</sup> However, even for bare silicon oxide, quantitative predictions of the water layer thickness involve assumptions about hydration forces.<sup>30</sup> Additionally, the water distribution near buried interfaces has been a topic of debate in the adhesion field for a number of years. There are conflicting interpretations indicating that water resides at the interface in either heterogeneous condensed droplets or a homogeneously distributed layer.<sup>31</sup> These conflicting interpretations make quantitative predictions of the excess water at the silicon

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**Figure 5.** Scattering length density profiles ( $Q_c^2$ ) for (a) PHOSt and (b) PBOCSt films before (dashed line) and after exposure (solid line) to saturated D<sub>2</sub>O vapor. The reflectivity profiles with fits corresponding to the density profiles are shown in parts c and d for PHOSt and PBOCSt, respectively. The reflectivity for the exposed films is offset by two decades for clarity.

oxide/polymer interface difficult, but the qualitative presence of the interfacial water can be explained rationally. In the case of silicon oxide, the substrate is attractive toward water. The chemical potential of the system can be written as a summation of external potentials (surface) and internal potentials (intrinsic).

$$\mu = \sum \mu_{\text{external}} + \sum \mu_{\text{internal}} \tag{1}$$

Far from the surface, the external potential contribution is negligible. This results in bulklike swelling of the polymer film, as the total chemical potential is internal. At the interface, additional contributions to the chemical potential from the substrate are important. These include contributions from van der Waals and electrostatic interactions, although other forces such as hydration are also important. The attractive nature of silicon oxide for water results in a positive external contribution. This leads to an apparent increase in the chemical potential near the substrate, which should manifest itself as an increase in water concentration. The attractive force (toward the water) is at a maximum near the interface and then decays as the distance (D) from the interface is increased. The distance dependence on the decay is dependent upon the exact combination of forces acting on the system (i.e., 1/Dfor van der Waals forces,  $1/D^2$  for electrostatic forces, and e<sup>-D</sup> for hydration forces).<sup>29</sup> The decay in chemical potential as a result of these forces will cause a water concentration gradient to occur.

Due to the difficulties described previously, it would be useful to experimentally determine the excess water concentration. Previously, Wu and co-workers used neutron reflectivity to characterize the excess water concentration at a silicon/polyimide interface.<sup>4</sup> The water distribution can be ascertained by isotopic substitution, namely, by using perdeuterated water. The neutron scattering length density for D<sub>2</sub>O ( $3.3 \times 10^{-4} \text{ Å}^{-2}$ ) is significantly higher than that for any other component in the sample, including the silicon ( $1.06 \times 10^{-4} \text{ Å}^{-2}$ ) and the polymers ( $8.19 \times 10^{-5} \text{ Å}^{-2}$  and  $7.86 \times 10^{-5} \text{ Å}^{-2}$  for PBOCSt and PHOSt, respectively). Here, we take a similar approach and directly measure the water distribution in the PBOCSt and PHOSt films.

The neutron reflectivity profiles and corresponding scattering length density profiles are shown in Figure 5 for both PBOCSt and PHOSt. The  $Q_c^2$  (scattering length density) profiles read like the X-ray data in Figures 1 and 3 except that  $Q_c^2$  now reflects the neutron scattering length density profiles. For the NR experiments,  $Q_c^2$  depends on both the composition and the mass density. Upon exposure to  $D_2O$ , there are changes in the  $Q_c^2$  profile that were not observed by XR due to the large scattering length density of D<sub>2</sub>O. The film thickness increases, as observed in the XR measurements, but the  $Q_c^2$  profile of the polymer films can increase appreciably and there is an especially large increase in  $Q_c^2$  near the silicon/photoresist interface. For the PBOCSt film, the thickness increases from 104  $\pm$  3 Å to 120  $\pm$  3 Å with an increase in  $\it Q_c^2$  from 8.19 imes 10  $^{-5}$  $\rm \AA^{-2}$  to 8.55 imes 10<sup>-5</sup>  $\rm \AA^{-2}$ . The PHOSt film shows a more pronounced change in the NR profile than that observed for PBOCSt, with an expansion from 110  $\pm$  3 Å to 124  $\pm$ 3 Å and an increase in  $Q_c^2$  from 9.06 imes 10<sup>-5</sup> Å<sup>-2</sup> to 1.50  $\times$  10<sup>-4</sup> Å<sup>-2</sup>. Notice the larger increase (besides the interfacial region) in  $Q_c^2$  upon  $D_2O$  exposure for PHOSt in comparison to PBOCSt. This is because the labile -OHproton in PHOSt readily exchanges with deuterium from  $D_2O$ , resulting in a greater increase in  $Q_c^2$  than what simple absorption, without exchange, would predict. However, this can be accounted for by assuming all of the hydroxyls in PHOSt are replaced with -OD.

The increase in  $Q_c^2$  can be correlated to the  $D_2O$  concentration in the film. The water concentration profile can be determined from the scattering length density profile determined from the best fit of the neutron reflectivity profile.

$$\phi_{\rm w}(x) = \frac{Q_{\rm c}^{2}(x) - Q_{\rm c}^{2}_{\rm (poly)}}{Q_{\rm c}^{2}_{\rm (D_{2}O)} - Q_{\rm c}^{2}_{\rm (poly)}}$$
(2)

where  $Q_c^2(x)$  is the scattering length density at a position *x* from the substrate,  $Q_c^2_{(poly)}$  is the scattering length density of the pure polymer, and  $Q_c^2_{(D_2O)}$  is the scattering length density of pure D<sub>2</sub>O. For the PHOSt samples,  $Q_c^2_{(poly)}$  is taken as the scattering length density for a completely

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**Figure 6.** Water concentration profiles for PHOSt and PBOCSt films as determined by neutron reflectivity. The water accumulation at the silicon interface is independent of the polymer coating within experimental error.

-OH to -OD exchanged sample. The resulting concentration profiles are shown in Figure 6. As expected, the water absorption in PBOCSt is considerably lower than that in PHOSt in the bulk of the film. However, as the silicon substrate is approached, the water concentration increases in a manner that is independent of the polymer within the uncertainty. The thickness of the excess interfacial water layer,  $25\pm10$  Å, is nominally consistent with the value obtained for polyimide films.<sup>4</sup> The exact thickness is difficult to quantify, as the water concentration profile near the substrate is a gradient rather than a discrete layer. The maximum concentration is slightly different (30 vol % here vs 17 vol % for the polyimide), but this may be a result of curing the very rigid polyimide film, which could inhibit swelling. The results also agree with water adsorption measurements in silane treatments on silicon wafers.<sup>7</sup> Both the thickness of the excess layer  $(\approx 30 \text{ Å})$  and the maximum concentration  $(\approx 30 \text{ vol }\%)$  are very consistent with the results for the photoresist polymers presented here. The lack of polymer influence on the interfacial excess water distribution can be attributed to the forces controlling the adsorption at the interface. Near the silicon oxide/polymer interface (D =0), the electrostatic and solvation forces dominate the maximum water uptake due to their  $1/D^2$  and  $e^{-D}$ dependencies, respectively. The van der Waals interactions near the substrate have very little effect due to their 1/Ddependence. In fact, this helps rationalize why changing the polymer medium, which changes the nature of the van der Waals interactions, does not significantly affect the interfacial moisture content. The solvation and electrostatic interactions between water and silicon oxide are affected very little by the polymer medium.

With this knowledge of the excess concentration at the silicon/polymer interface, the anomalous thickness dependent swelling behavior of the photoresists can be modeled. The observed water volume fraction ( $\phi_w$ ) absorbed in the film is written as

$$\phi_{\rm w} = \frac{t_{\rm f} - t_{\rm i}}{t_{\rm f}} = \frac{\Delta t_{\rm eq} + t_{\rm excess}}{t_{\rm i} + \Delta t_{\rm eq} + t_{\rm excess}}$$
(3)

where  $t_{\rm f}$  is the final film thickness,  $t_{\rm i}$  is the initial film thickness,  $\Delta t_{\rm eq}$  is the thickness change expected from *bulk* swelling, and  $t_{\rm excess}$  is the equivalent thickness of the water excess layer. From the XR measurements,  $t_{\rm i}$  and  $t_{\rm f}$  are directly determined to calculate the volume fraction. The second expression in eq 3 can be evaluated independently of any XR results.  $t_{\rm excess}$  is calculated by integration of the excess portion of the concentration profile as determined by eq 1 and illustrated by the increased concentration

near the interface in Figure 6 as follows:

$$t_{\text{excess}} = \int_0^T (\phi_{\text{w}}(x) - \bar{\phi}) \, \mathrm{d}x \tag{4}$$

where *T* is the total film thickness and  $\overline{\phi}$  is the water concentration far away from the interface (the plateau in Figure 6) and represents the bulklike concentration. As a reminder, the water concentration profile ( $\phi_w(x)$ ) is determined by the change in the scattering length density due to D<sub>2</sub>O absorption.  $t_{\text{excess}}$  is assumed to be constant irrespective of film thickness. The thickness change from bulk swelling is calculated using the water concentration away from the interface as

$$\Delta t_{\rm eq} = \frac{\bar{\phi}}{1 - \bar{\phi}} t_{\rm i} \tag{5}$$

Using these results solely from NR, the water concentration in a photoresist film of any given thickness can be calculated.

Strictly speaking, the resolution in  $Q_c^2$  is  $\pm 10\%$ , stemming from the uncertainty in the angular and wavelength divergences. This means that, for small changes in the scattering length density, the uncertainty in the concentration can actually be greater than the concentration of interest. This manifests itself in this case in large uncertainty in the bulk concentration ( $\phi$ ). However, the concentration at the interface can be determined with much greater certainty due to the large change in  $Q_c^2$ . Likewise, the uncertainty in the *increase* in  $Q_c^2$  upon absorption is comparatively small; the inherent reflectometer uncertainties do not change upon the exposure to  $D_2O$ , meaning that the increase in  $Q_c^2$  and the sample thickness accurately reflects absorption. Stated otherwise, the accuracy with which the absolute density of an unknown film can be determined from NR is poor compared to the ability to perceive a relative change in density due to absorption. To illustrate the reasonable values of the interfacial excess water concentrations predicted by NR, we use a simple, independent predictive model based on the XR swelling data presented in Figures 2 and 4. The equilibrium water concentration ( $\phi_{eq}$ ) within the bulk of the sample was assumed to be the minimum observed swelling in the thicker films from XR measurements because, for sufficiently thick films, the excess thickness is negligible and  $\Delta t_{eq} \approx t_{\rm f} - t_{\rm i}$ . Instead of using eq 5, the thickness change from bulk swelling is calculated as

$$\Delta t_{\rm eq} = \frac{\phi_{\rm eq}}{1 - \phi_{\rm eq}} t_{\rm i} \tag{6}$$

By using eqs 3 and 6 to calculate the terms to predict the water absorption, the excess layer model (eq 3) at least semiquantitatively represents the film thickness dependence of the XR swelling data, as shown by the dashed lines in Figures 2 and 4. The majority of the thickness dependence of the swelling appears to be due to the increased interfacial film fraction as the film thickness decreases; however, other factors such as chain stretching at the interface or confinement effects might contribute to the thickness dependent behavior.

The phenomenon of excess interfacial moisture absorption near a hydrophilic surface appears to be general and dependent on the surface energy rather than the film material. It is seen here with both hydrophilic (PHOSt) and hydrophobic (PBOCSt) polymers, as well as with the previous cases of the polyimide films.<sup>4</sup> In this respect, the enhanced swelling as a function of decreasing film thickness might be a general phenomenon when moisture, or presumably any other solvent, wets the underlying substrate. If this generalization is true, the existence of excess interfacial  $H_2O$ /solvent can be detected by a variety of techniques sensitive to film thickness, like X-ray reflectivity or ellipsometry, and not just neutron reflectivity. This would be useful, since neutron reflectivity studies are limited by access to neutron facilities and are also expensive if deuterium-substituted materials are required. In closing, it remains to be seen if the opposite condition, absorption near a hydrophobic interface and an interfacial  $H_2O$  depletion, occurs in comparison to the case of the bulk. Such experiments are in progress.

#### 4. Conclusions

The influence of an interface on the absorption properties of two model photoresist polymers was determined by complementary neutron and X-ray reflectivity experiments. These results show an accumulation of water at the silicon/polymer interface with the interfacial water concentration independent of the polymer. The polymer independence is initially quite surprising given the difference in the bulk swelling between PBOCSt and PHOSt. However, if van der Waals forces are the dominant polymer influence, the lack of polymer influence on the interface can be predicted. This has not been shown previously and illustrates the importance of chemically tethering modifiers to the substrate to prevent moisture accumulation at the interface. Furthermore, the deviations in the absorption observed in the thinnest films can be explained primarily by this excess interfacial concentration. This is an important consideration for the study of thin polymer films because any thickness dependent behavior in polymer films could be attributed to factors other than solely confinement.

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