Control of Moisture at Buried Polymer/Alumina Interfaces through Substrate Surface Modification

Bryan D. Vogt,*,† Vivek M. Prabhu,† Christopher L. Soles,† Sushil K. Satija,‡
Eric K. Lin,† and Wen-li Wu*,†

Polymers Division and Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899

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Moisture absorption in poly(4-*tert*-butoxycarbonyloxystyrene) (PBOCSt) films supported on Al_2O_3 sputter coated silicon wafers is measured using neutron and X-ray reflectivity. Accumulation of water at the interface during moisture exposure results in an apparent film-thickness-dependent swelling for ultrathin PBOCSt films. The swelling of a film on Al_2O_3 is less than the swelling of a film of the same thickness on SiO_x for films thinner than 20 nm. This is due to comparatively less moisture accumulation at the Al_2O_3/PBOCSt 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 describes the thickness-dependent swelling quantitatively. The influence of four different Al_2O_3 surface treatments on the moisture distribution within PBOCSt films was examined: bare Al_2O_3, *tert*-butylphosphonic acid, phenylphosphonic acid, and *n*-octyltrichlorosilane. Both the phenyl and the octyl surface treatments reduce the accumulation of water at the polymer/substrate interface. The *tert*-butyl treatment does not reduce the interfacial water concentration, presumably due to insufficient surface coverage.

1. Introduction

Ambient moisture absorption is a concern in many technical applications and can lead to undesired outcomes such as corrosion,[1] loss of adhesion,[2] and material degradation.[3] Ability to control moisture absorption is desirable for economic reasons. For example, it is estimated that material replacement costs due to corrosion approach 4% of the U.S. gross national product.[1] To a first approximation, a hydrophobic coating (such as paint) on a metal surface would seemingly be sufficient to prevent corrosion as the water solubility in the polymer is extremely small. However, in many cases, a simple coating is insufficient and moisture absorption can lead to blisters[4] and adhesion loss.[2] The source of these problems is rooted in moisture accumulation at the polymer/metal interface.[5−9] The metal's high surface energy oxide layer is believed to be the culprit. The hydrophilic nature of this oxide layer causes moisture to accumulate, leading to a water-rich layer at the buried interface. Thus, a methodology to control the moisture at an interface to the application demands is highly desirable.

Although polymer coatings and their interactions with water have received a large degree of attention,[10,11] there are only a few studies that directly examine the influence of interfaces.[5−9] The importance of these interfaces grows in the near future as coating properties are enhanced using nanotechnology;[12] nanoparticle modifiers present enormous surface/interfacial areas. The moisture accumulation at buried polymer/metal (oxide) interfaces has been studied for a limited number of substrates and polymer systems.[5−9] There are two trends from the data: (1) the interfacial water concentration is dependent upon the surface energy of the substrate and (2) changes in the polymeric coating composition have no apparent influence on the water concentration at the buried interface.

It is suspected that, as the hydrophobicity of the substrate increases, the interfacial water concentration should decrease. However, as the surface becomes increasingly hydrophobic, the dry adhesion between the substrate and the polymer decreases significantly. If the surface becomes highly hydrophobic, the polymer solution may not even wet the substrate meaning that a smooth film cannot be formed, depending upon the polymer/solvent pair. There is, therefore, a balance between an extremely hydrophilic substrate that allows for easy coating but is unstable in moist atmospheres and an extremely hydrophobic substrate that prevents interfacial water accumulation but leads to adhesion issues and unstable films. It has been shown that siloxane coupling agents are effective at reducing the interfacial water concentration for polymers supported on silicon wafers.[5,8] There are other surface treatments where covalent bonding is not present. For the case of a hydrophobic polymer coating, the dispersion forces involved are not strong enough to prevent significant accumulation of moisture at the interface.

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* Corresponding authors. E-mail: bryan.vogt@nist.gov (B.D.V.); wenli@nist.gov (W.-l.W.).

† Polymers Division, National Institute of Standards and Technology.

‡ Center for Neutron Research, National Institute of Standards and Technology.

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The surface modification of silicon with silane coupling agents[13] or gold with alkanethiols[14] is well established. However, the use of these surface modification methods with other metal (M) substrates is limited due to the specific nature of the thiol interaction and the stability of certain M−O−Si bonds. One approach to modify many engineering surfaces is through bonding alkyl phosphonic acids to the metal (oxide) surface.[15] The stability of these phosphonic acid layers has been found to be much greater than for silane coupling agents on TiO_2 and ZrO_2 substrates.[15] The alkyl phosphonic acid is bound to the oxide surface by strong electrostatic interactions. Previously, it has been shown that covalent bonding (through silane coupling agent) is effective at mitigating the interfacial water concentration, but the effectiveness of electrostatically bound modifiers has not been determined.

Here, we examine how the water concentration at the polymer/substrate interface can be modified and potentially controlled by choice of surface modification. The moisture accumulation at the buried interface of poly(4-*tert*-butoxycarbonyloxystyrene) (PBOCSt) films on silicon oxide and hexamethyldisilazane (HMDS) treated silicon substrates has been studied previously.[7,8] The maximum water concentration at the interface decreased from approximately 30 vol % to nearly 15 vol % by treatment of the silicon surface with HMDS. In this work, we examine moisture accumulation at a PBOCSt/alumina interface using neutron reflectivity (NR). The interfacial water concentration is controlled using three different surface modifications with a large range of hydrophobicity. These surface modifying agents include *tert*-butylphosphonic acid, phenylphosponic acid, and *n*-octyltrichlorosilane (OTS).

2. Experimental Section

A. Sample Preparation. Moisture swelling experiments were performed using PBOCSt. The PBOCSt was synthesized by protecting poly(4-hydroxystyrene) (PHOSt) via post-polymerization addition of *tert*-butylene 4-vinylphenyl carbonate to the para position of the aromatic ring, resulting in greater than 95% conversion of the hydroxyl group.[16] The PHOSt with an average relative molar mass ($M_{n,r}$) of 8000 g/mol was obtained from Triquest Chemical Co.[19] PBOCSt films were prepared by spin coating from propylene glycol methyl ether acetate (Aldrich) solutions at various concentrations.

The substrates were prepared by sputtering Al_2O_3 onto the surface of the silicon wafer. The nominal thickness for the Al_2O_3 layer was 40 nm in all cases. To remove any adsorbed organic contaminants, the Al_2O_3 substrates were cleaned with UV ozone exposure for 2 min. To modify the surface of the Al_2O_3, different treatment protocols were used prior to spin coating. For the surface treatments with alkanephosphonic acids, the acid was dissolved in ethanol (Aldrich, 200 proof) to obtain a 1 mmol/L solution. The phosphonic acids, *tert*-butylphosphonic acid and phenylphosphonic acid, were obtained from Aldrich and used as received. The Al_2O_3 substrates were soaked in the acidic solution for 30 min. The substrates were then dried and baked at 130 °C and subsequently rinsed with ethanol to remove excess alkylphosphonic acid prior to spin coating. The OTS (Aldrich) treatment of the Al_2O_3 surface was carried out in the vapor phase. The substrate was exposed to OTS vapor for 6 h and rinsed liberally with toluene to remove excess silane, which was followed by 130 °C baking. The static water contact angle on the different surfaces was 59.7 ± 1.2° for the bare Al_2O_3, 72 ± 1.4° for the *tert*-butyl treated surface, 76.3 ± 1.3° for the phenyl treated surface, and 97.3 ± 5.4° for the OTS treated surface.[20] The PBOCSt solution was then filtered (0.45 μm) and spun at 209 rad/s (2000 rpm) onto the substrates. After spin-coating, a 2 h post-apply bake at 120 °C under a vacuum (<0.1 Pa) was used to remove residual solvent.

B. Measurement Methods. The water distribution in the films was determined by specular NR. NR measurements were performed at the Center for Neutron Research NG-7 reflectometer at the National Institute of Standards and Technology (Gaithersburg, MD) utilizing cold neutrons with a wavelength (λ) = 4.768 Å and wavelength spread ($\Delta\lambda/\lambda$) = 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 several angstroms. The humidity at room temperature was controlled inside an aluminum chamber with silicon windows that was first evacuated (dry sample) and then backfilled with the equilibrium vapor from heavy water (deuterium oxide; Aldrich, 99.9% pure) The water was vacuum degassed through three freeze−thaw cycles (freeze under a vacuum) prior to exposing the sample in the neutron reflectometer chamber. The NR of the films was first measured in a dry state under a vacuum (<0.1 Pa) and then subsequently after exposure to saturated D_2O vapor at ambient temperature.

The total moisture absorption was determined by using specular X-ray reflectivity (XR) as a function of applied polymer film thickness. The reflectivity measurements were made with a θ/θ diffractometer with Ni filtered Cu Kα radiation (λ = 1.54 Å) and Soller slit collimation on both the incident and the reflected beams. The environmental control for the XR experiments was identical to the NR experiment, except that the sample chamber was equipped with beryllium windows and distilled, deionized water (Milli-Q Millipore, Molsheim, France; 18.2 MΩ·cm) was used in place of D_2O. All measurements were performed at ambient temperatures.

3. Results and Discussion

The NR profiles for a thin PBOCSt film on the bare Al_2O_3 substrate before and after exposure to D_2O vapor are shown in Figure 1. The reflectivity is shown as a function of the momentum transfer vector, q, where $q = 4\pi \sin(\theta)/\lambda$, θ is the incident angle, and λ is the neutron wavelength. The reflectivity profiles (Figure 1a) show multiple beating patterns due to competing constructive and destructive interferences from both the Al_2O_3 and PBOCSt layers. Exposure to moisture alters these correlations from the swelling of the PBOCSt film and D_2O accumulation at the buried interface. These changes are expected based upon previous results for the absorption into PBOCSt supported on silicon wafers with native oxide.[7] The aluminum oxide surface is much rougher than the silicon oxide surface. This roughness is apparent in the real space density profiles in Figure 1b. The density profiles are obtained by fit of the reflectivity data using a multilayer least-squares fitting algorithm. The profiles are presented in terms of the scattering length density, Q_c^2, as a function of distance through the film. Q_c^2 is proportional to the average atomic scattering length, b, where $Q_c^2 = 16\pi Nb$ and N is the number of nuclei. The Q_c^2 profile in Figure 1b begins at 0 in the vacuum (or approximately zero for the D_2O vapor) and increases first to the scattering length density for PBOCSt as one moves along the thickness axis. Notice that this increase in Q_c^2 is relatively sharp, indicative of a smooth film (the roughness for all polymer films examined here is less than 10 Å). The surface roughness of the polymer film is unchanged within error by exposure to D_2O. Q_c^2 then increases more gradually (indicative of the roughness) to that of Al_2O_3, followed by a decrease to the native silicon oxide, and finally to the scattering length density of the silicon substrate. The roughness of the top Al_2O_3 surface and the Al_2O_3/silicon interface was confirmed with XR for a film without a polymer overcoat. The roughness at the Al_2O_3/silicon interface is expected to be due to the sputtering process where high-energy ions bombard the

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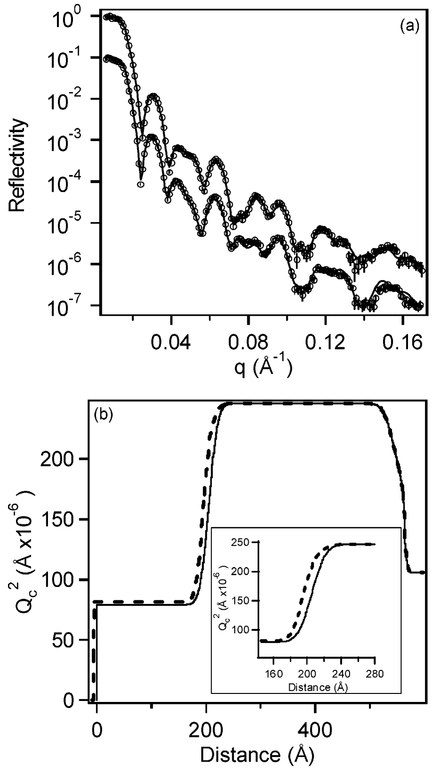

Figure 1. (a) NR profile for 20.5 nm thick PBOCSt film on Al_2O_3 coated substrate under a vacuum (top curve) and exposed to saturated D_2O vapor (bottom curve). The solid lines correspond to the best fit of the data. The exposed data is offset for clarity. (b) Neutron scattering length density profiles corresponding to the best fits of the reflectivity data under a vacuum (solid line) and exposed to saturated D_2O vapor (dashed line). The inset better illustrates the accumulation of moisture at the interface.

silicon surface. This leads to an interfacial width that is typically between 2 and 4 nm.

In the dry state, the total applied thickness (Al_2O_3 and PBOCSt) is 54.8 nm, comprised of 34.3 nm Al_2O_3 and 20.5 nm PBOCSt. After exposure to D_2O, the total applied thickness swells to 55.4 nm. Assuming that the aluminum oxide does not swell, this corresponds to 2.8% swelling of the PBOCSt, which is significantly greater than the bulk swelling ($\approx$0.5%). This is consistent with the enhanced swelling in thin films due to accumulation of water (D_2O) at the buried interface.[7] From the NR experiment, the excess interfacial water can be directly observed because the scattering length density of the D_2O (3.3×10^{-4} Å^{-2}) is large in comparison to the PBOCSt (7.86×10^{-5} Å^{-2}). The absorption of D_2O within the PBOCSt film leads to an increase in Q_c^2 as shown in Figure 1b where the Q_c^2 of the PBOCSt film after exposure to D_2O is greater (dashed line) than in the dry state. The accumulation of D_2O at the interface leads to an increase in Q_c^2, which appears to be an increase in the thickness of the Al_2O_3 layer. This is because the Q_c^2 of D_2O is not significantly different from that of Al_2O_3 in NR; from NR alone it would be difficult to distinguish an increase in the Al_2O_3 thickness from excess D_2O at the interface. However, the Q_c^2 of H_2O in XR is very similar to that of PBOCSt, not that of Al_2O_3. Independent XR measurements confirm that the Al_2O_3 thickness is invariant during the swelling experiments.

Quantifying the excess water at the interface is more complicated than doing so at the previous silicon interfaces because of the broad interface between Al_2O_3 and PBOCSt. The water concentration profile can be calculated from the change in the scattering length density profiles between the dry and the wet states. There are three components whose concentration each must be determined. First, the concentration of the Al_2O_3 as a function of distance into the PBOCSt film was determined for the dry state as follows:

$$\phi_{Al_2O_3}(x) = \frac{{Q_c}^2(x) - {Q_{c,\mathrm{PBOCSt}}}^2}{{Q_{c,Al_2O_3}}^2 - {Q_{c,\mathrm{PBOCSt}}}^2} \qquad (1)$$

where $Q_c^2(x)$ is the scattering length density at position x in the film, $Q_{c,Al_2O_3}^2$ is the scattering length density of the pure Al_2O_3, and $Q_{c,\mathrm{PBOCSt}}^2$ is the scattering length density of pure PBOCSt. With the assumption that the Al_2O_3 concentration profile does not change upon D_2O exposure, the water concentration profile can then be calculated as

$$\phi_w(x) = \frac{{Q_c}^2(x) - [1 - \phi_{Al_2O_3}(x)]{Q_{c,\mathrm{PBOCSt}}}^2 - \phi_{Al_2O_3}(x){Q_{c,Al_2O_3}}^2}{{Q_{c,D_2O}}^2 - [1 - \phi_{Al_2O_3}(x)]{Q_{c,\mathit{PBOCSt}}}^2 - \phi_{Al_2O_3}(x){Q_{c,Al_2O_3}}^2} \qquad (2)$$

where $\phi_w(x)$ is the water concentration at position x in the film and Q_{c,D_2O}^2 is the scattering length density for pure D_2O. The water concentration profile obtained is shown in Figure 2a. The distance axis is measured from pure Al_2O_3 into the PBOCSt as determined using eq 1. The water concentration determined by eq 2 goes through a maximum as shown by the shaded area in Figure 2a. This maximum is resultant from two competing factors. First, the proximity to hydrophilic Al_2O_3 increases the D_2O concentration. However, there is a decrease in the accessible volume to D_2O due to the presence of Al_2O_3 protruding into the PBOCSt film (solid line in Figure 2).

The moisture concentrations at the different Al_2O_3-modified surfaces were determined in a similar manner and are also shown in Figure 2. It is clear that different phosphonic acids affect interfacial moisture concentrations especially for the phenylphosphonic acid where the water concentration has been decreased by almost a factor of 5. This is analogous to the covalently attached silane coupling agents on silicon surfaces reported elsewhere.[5,8] Thus, the electrostatic attractions of the phosphonic acid toward the Al_2O_3 surface are large enough to suppress the accumulation of water at the interface, driven by the dispersion forces between the water and metal oxide. However, the change in the concentration at the interface does not follow the degree of hydrophobicity (from the water contact angle) to the extent that might be expected {Al_2O_3 (59.7 ± 1.2°) → *tert*-butylphosphonic acid (72 ± 1.4°) → phenylphosphonic acid (76.3 ± 1.3°)}. There is no decrease in the total water accumulation with the *tert*-butyl treated surface in comparison to the bare aluminum oxide. From the static water contact angles, it is clear that the *tert*-butyl coverage is incomplete because the completely methylated surface results in a contact angle close to 90°. This is in contrast to a phenyl surface, which has a contact angle near 80°, suggesting near complete coverage of the phenylphosphonic acid. The effectiveness of the surface treatment at blocking moisture accumulation at the interface is related to both the hydrophobicity and the surface coverage. The partial coverage of the *tert*-butylphosphonic acid treatment may result from steric effects, similar to the limited surface coverage obtainable

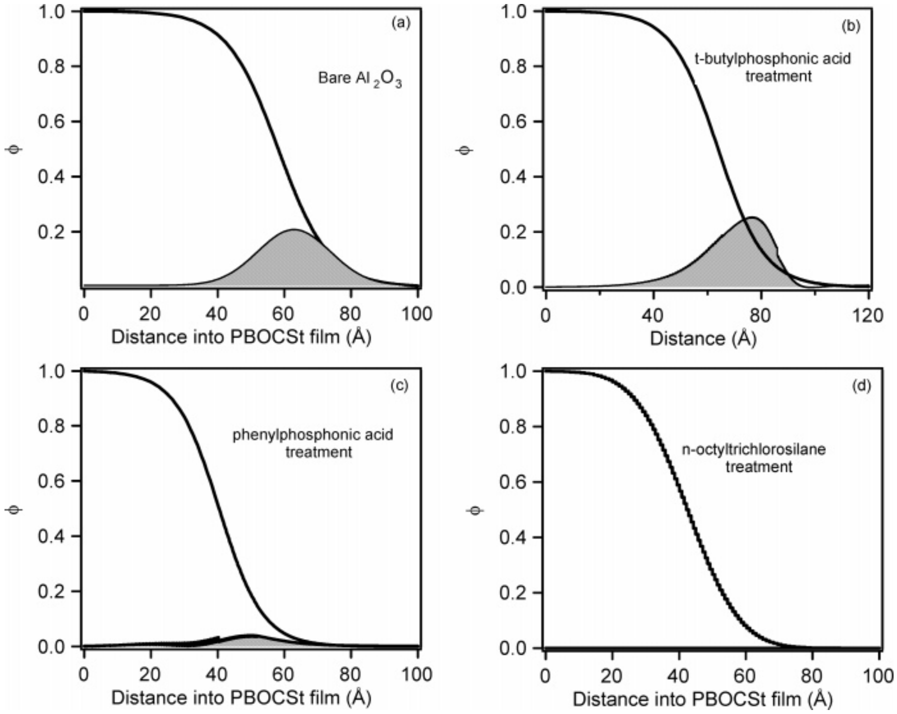

Figure 2. Concentration profiles determined from the NR data for PBOCSt films supported on Al_2O_3. The total concentration of D_2O (filled) is shown as a function of distance from solid Al_2O_3. The difference between these two curves is a result of the diffuse Al_2O_3/polymer interface. The Al_2O_3 concentration in the dry film is shown by the solid line. The influence of different surface treatments is clearly visible: (a) neat Al_2O_3, (b) *tert*-butylphosphonic acid, (c) phenylphosphonic acid, and (d) *n*-octyltrichlorosilane (OTS).

for HMDS.[17] The rotor rotations of the *tert*-butyl moiety result in a substantial volume inaccessible to other adsorbing species, thus, limiting the surface coverage. Imperfections in the surface coverage allow water accumulation at the Al_2O_3 interface as well as water coordination with the phosphonic acid, which may be responsible for the skewed water distribution in the *tert*-butylphosphonic acid treated sample (Figure 2b). In phenylphosphonic acid, there are no rotations available, which allows for substantially better coverage than for the case of *tert*-butylphosphonic acid. The phenylphosphonic acid is much more effective in blocking water accumulation at the interface as would be expected for the greater surface coverage. But even for phenylphosphonic acid, there is a small amount of water accumulation at the interface. It is initially surprising that water does not accumulate at the ionic interface between the phosphates and oxide. However, alkanephosphonic acids bind strongly to alumina (potentially through formation of M−O−P bonds) and aggressive aqueous environments are necessary for removal from the surface.[18] Thus, the interaction between the phosphonic acid and alumina is more favorable than that for water with either species.

In addition to the phosphonic acids, OTS was used to modify the Al_2O_3 surface. One difficulty in working with the OTS-modified surface was subsequent PBOCSt film coating on the surface. For the all the other surfaces, the same solution was used to prepare films of similar thicknesses (20.3 ± 0.6 nm). However, for the silane treated surface, this PBOCSt solution did not adequately wet the surface to yield a high-quality film. To produce a reasonable PBOCSt film, a much larger PBOCSt concentration was required, resulting in a thicker PBOCSt film (156 nm). This should not influence the ability to observe the interfacial D_2O accumulation because thicker films have been previously measured with NR.[8,9] The NR profiles for PBOCSt supported on OTS-modified Al_2O_3 are shown in Figure 3 before and after exposure to D_2O. Upon exposure, the PBOCSt film swells from 156.4 to 159.6 nm, an increase of approximately 2%. The OTS surface treatment results in a low Q_c^2 film near the Al_2O_3 surface, due to the high density of protons in the surface modification. This treatment is effective at preventing the accumulation of D_2O at the interface within the resolution limits ($<1\%$). The concentration profile is shown in Figure 2d and illustrates the effectiveness of the OTS treatment in comparison to other treatments used in this study to prevent moisture accumulation at the buried interface. These results suggest that the only requirement for preventing moisture accumulation at inorganic oxide interfaces is to cover all the surface hydroxyls with a hydrophobic moiety that cannot be displaced by water. The effectiveness of the surface treatment depends on the surface coverage and strength of the interaction with the inorganic oxide (or hydroxide).

The accumulation of water at the buried interface has previously been shown to be the source of an apparent enhanced swelling in thin films.[7,8] As the total film thickness decreases, the swelling in ultrathin films of PBOCSt is dominated by the accumulation of water at the interface. Using XR, the swelling of PBOCSt supported on Al_2O_3 sputtered substrates upon exposure to saturated water vapor was measured as a function of film thickness

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(20) The data throughout the manuscript and the figures are presented along with the standard uncertainty (±) involved in the measurement based on one standard deviation.

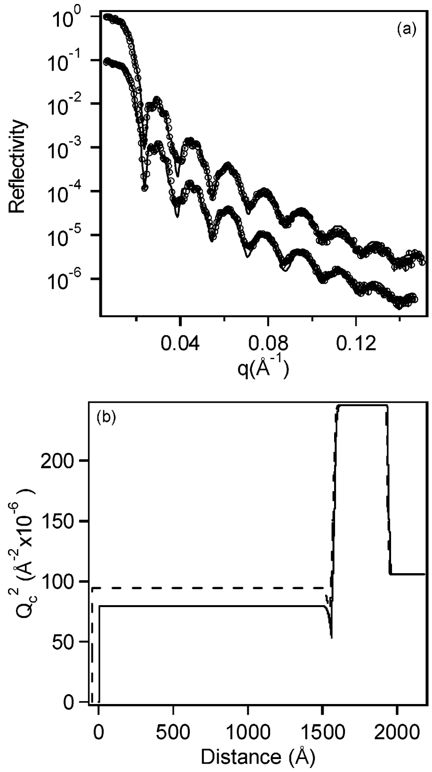

Figure 3. (a) NR profile for 156 nm thick PBOCSt film on OTS treated Al_2O_3 coated substrate under a vacuum (top curve) and exposed to saturated D_2O vapor (bottom curve). The solid lines correspond to the best fit of the data. The exposed data is offset for clarity. (b) Neutron scattering length density profiles corresponding to the best fits of the reflectivity data under a vacuum (solid line) and exposed to saturated D_2O vapor (dashed line). There is no observable accumulation of D_2O at the buried interface.

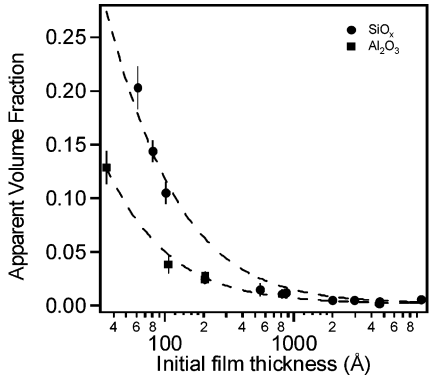

Figure 4. Film-thickness-dependent swelling for PBOCSt on (■) Al_2O_3 coated substrate and (●) Si substrate when exposed to saturated water vapor. The Si data is from ref 7. The dashed lines are fits to eq 3.

as shown in Figure 4. As the PBOCSt film thickness decreases, the relative film swelling increases due to the accumulation of water at the interface. Thus, the swelling in the thin films should be dependent upon the substrate. This is shown by a comparison of the swelling of PBOCSt on SiO_x and on Al_2O_3.[7] There is significantly less swelling for the film on the Al_2O_3. Previously, the thickness-dependent swelling was found to be well represented by a zero-adjustable parameter model, consisting of an excess layer at the polymer/substrate interface and bulk swelling of the polymer. The total apparent volume fraction of water (ϕ_w) within the polymer film can be written as

$$\phi_w = \frac{t_f - t_i}{t_f} = \frac{\Delta t_{eq} + t_{excess}}{t_i + \Delta t_{eq} + t_{excess}} \quad (3)$$

where t_f is the swollen film thickness, t_i is the initial film thickness, Δt_{eq} is the thickness change from bulk swelling, and t_{excess} is the equivalent water thickness corresponding to the accumulation at the interface. From the XR measurements, both t_f and t_i are determined, but t_f can be predicted from t_i if the equilibrium swelling and excess are known. t_{excess} can be determined from integration of the excess water from one NR experiment such as that shown in Figure 1. This integration is represented by the area under the total D_2O concentration curve (shaded area in Figure 2a). There is significantly less total water accumulation at the Al_2O_3 interface in comparison to that at the SiO_x interface. This is responsible for the difference in the swelling in the thin PBOCSt films. The fit of the data to eq 3 is shown by the dashed lines in Figure 4. There is good agreement between the predictions from this simple model and the experimental results. This provides additional verification of the accumulation of water at a polymer/Al_2O_3 interface.

4. Conclusions

The influence of surface modification on the accumulation of water at a buried polymer/substrate interface was determined using NR. The interfacial water concentration could be effectively controlled by changing the surface chemistry of aluminum oxide with alkylphosphonic acids and alkylchlorosilanes. The electrostatic interactions of the phosphonic acid with the Al_2O_3 surface appear to be strong enough to prevent accumulation of moisture at the interface if complete surface coverage is obtained. For *tert*-butylphosphonic acid treatment, the coating is ineffective at shielding the interface from water due to poor surface coverage. For phenylphosphonic acid treatment, the total water accumulation is decreased by more than a factor of 5. The most effective substrate treatment for preventing moisture accumulation at the buried interface was OTS. No measurable water accumulation was detected for substrates with this treatment. Although the treatment was effective at screening water from the interface, the film preparation on this surface was difficult in comparison to that on the other surfaces examined. Moisture accumulation at the Al_2O_3 surface was compared to that of SiO_x for PBOCSt using complementary NR and XR experiments. Considerably less moisture accumulates at the Al_2O_3/PBOCSt interface. Water accumulation at the buried polymer/substrate interface can be controlled by changing the chemistry of the substrate.

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