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Moisture absorption into ultrathin hydrophilic polymer films on different substrate surfaces

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Abstract

Moisture absorption into ultrathin poly(vinyl pyrrolidone) (PVP) films with varying thickness was examined using X-ray reflectivity (XR) and quartz crystal microbalance (QCM) measurements. Two different surfaces were used for the substrate: a hydrophilic silicon oxide (SiO_x) and a hydrophobic hexamethyldisilazane (HMDS) treated silicon oxide surface. The total equilibrium moisture absorption (solubility) was insensitive to the surface treatment in the thickest films (≈ 150 nm). However, strong reductions in the equilibrium uptake with decreasing PVP film thickness were observed on the HMDS surfaces, while the SiO_x surface exhibited thickness independent equilibrium absorption. The decreased absorption with decreasing film thickness is attributed a depletion layer of water near the polymer/HMDS interface, arising from hydrophobic interactions between the surface and water. The diffusivity of water decreased when the film thickness was less than 60 nm, independent of the surface treatment. Changes in the properties of ultrathin polymer films occur even in plasticized films containing nearly 50% water.

Keywords: Thin films; Swelling; Interfaces

1. Introduction

Moisture absorption in polymeric films is important for a variety of industries ranging from microelectronics to adhesives and coatings. In many applications, water absorption leads to reliability problems such as the degradation of dielectric properties, corrosion or delamination [1]. A significant number of studies covering many polymer systems have focused on characterizing the absorption and diffusion properties of water in polymer films. However, many of the significant problems observed are due to interfacial effects and have not been fully examined. For instance, the water concentration within a supported polymer film may not necessarily be uniform through the thickness of the film; concentration gradients are sometimes observed near the interfaces [2–4]. For moderately hydrophobic polymer films supported on silicon oxide substrates, there can be a 30 Å thick water-rich layer near the substrate [3,5]. Neutron reflectivity (NR) measurements show that the concentration of deuterium labeled water (D_2O) at this polymer/silicon interface is noticeably greater than the bulk, approaching 30% by volume. We recently demonstrated that the total amount of water in this excess layer can be inferred, albeit not as quantitatively as from NR, from simple swelling experiments as a function of film thickness using X-ray reflectivity (XR) [5]. The total swelling is a linear combination of equilibrium or bulk-like swelling and a thickness independent excess swelling near the interface. Combined, these effects lead to an increase in the degree of swelling with decreasing film thickness. It is possible to reduce the concentration of interfacial water by modifying the surface with a silane coupling agent [2,6]. However, even with the silane coupling agents, the interfacial concentrations were larger than the water concentration in the bulk polymer.

It is also important to understand the kinetics of moisture absorption into thin polymer films. The moisture absorption mechanisms into polymers can be complex and numerous models have been formulated to describe these processes [7,

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8]. Recently, thin film confinement effects have been explored by several groups [9–11]. In one study, the diffusivity of water decreased by five orders of magnitude when the film thickness decreased from 200 to 3 nm [10]. The decreased diffusivity is thought to reflect a coupling of the water transport with the local chain dynamics, which also become strongly suppressed in thin films [12]. However, in another study, there was no change in the swelling kinetics for films ranging from 45 to 20 nm thick [9]. The qualitatively different thin film confinement effects on the moisture absorption kinetics suggest that the effect is not universal across all polymers and substrates. This observation is consistent with changes in other thermophysical properties of thin films, such as the glass transition temperature (T_g), that are also polymer thickness and substrate dependent. For example, in thin films the T_g has been found to increase, decrease or remain constant as the film thickness approaches the radius of gyration (R_g) of the polymer chain, depending on the polymer and the substrate surface energy [13,14].

Understanding the interfacial and confinement effects on the moisture absorption properties of polymers is becoming increasingly important. Polymers are frequently used in thin film applications where the total film thickness continues to decrease. A clear example is lithography where the advent of immersion processing places a liquid in direct contact with a thin polymeric photoresist. As the film thickness decreases, the interfacial properties can dominate the material response. Likewise, highly filled or multi-layer polymer structures can be modeled by a thin film interface. For example, multi-layers of nanometer thick polymers and inorganic desiccant materials are utilized as barrier coatings to prevent moisture absorption into microelectronics packaging or organic electronic devices. These structures are composed almost entirely of interfacial material. Here, we measure the equilibrium uptake and diffusion coefficient of water into hydrophilic, uncharged ultrathin polymer films with varying thickness. The moisture absorption into poly(vinyl pyrrolidone) (PVP) films was measured using X-ray reflectivity (XR) and quartz crystal microbalance (QCM) on both hydrophilic (silicon oxide) and moderately hydrophobic (hexamethyldisilazane (HMDS)) substrates.

2. Experimental section

2.1. Materials and film preparation

PVP with a relative molecular mass ($M_{n,r}$) of approximately 10,000 g/mol was purchased from KAF[1]. All films were prepared by spin-coating from filtered (0.45 μm) 1-butanol solutions ranging from (0.001 to 0.05) mass fraction polymer. For the XR measurements, films were spun onto silicon wafers. Prior to spin coating, two distinct treatment methods were used to create either hydrophilic or hydrophobic surfaces on the silicon wafers. All wafers were initially cleaned in oxygen plasma for approximately 5 min, followed by a 1 min buffered oxide etch (a 7:1 ratio by mass of NH_4F/HF) to remove the native silicon oxide layer. A thin (less than 20 Å) uniform silicon oxide surface layer was re-grown with a 3 min exposure in an ultraviolet light ozone (UVO) chamber. Some PVP films were immediately spun-cast on these hydrophilic (oxide) substrates. To create hydrophobic surfaces, wafers were further treated with HMDS vapor for 2 min at 120 °C immediately following the UVO oxide growth. The HMDS treated wafers were rinsed with toluene prior to spin coating. For the QCM measurements, quartz crystals with SiO_x surface sputtering were used as the supporting substrate for the polymer films. The crystals were cleaned with UVO for 5 min prior to spin coating for the oxide surfaces. For hydrophobic surface, a HMDS treatment identical to the silicon wafer preparation was employed following UVO cleaning. The water contact angle for the HMDS treated surface was found to be $63.5 \pm 3.5°$, whereas water completely wets the oxide surface. Prior to measurement, all samples were annealed at 180 °C under vacuum for greater than 12 h.

2.2. Measurement procedure

Film thickness in the dry and hydrated states was measured using XR. For thin films (<120 nm), the reflectivity measurements were made in a θ/θ geometry using Ni filter Cu K_α radiation ($\lambda = 1.54$ Å) and Soller slit collimation on the incident and reflected beams. The sample environment was controlled in an aluminum chamber with beryllium windows. Measurements could be performed under vacuum or at set humidity levels using saturated salt solutions. The relative humidity was regulated from (11 to 100)% using the salt solutions shown in Table 1 [15]. Each measurement was made after at least 6 h of equilibration at a given relative humidity or after such time that the film thickness remained constant (± 0.2 nm). For thicker films (>120 nm), reflectivity measurements were made in a $\theta/2\theta$

Table 1
Relative humidity from various saturated salt solutions at 25 °C

Saturated salt solution	Relative humidity (%)
$LiCl$[a]	11.3
$MgCl_2$[a]	32.7
$NaHCO_3$	53
$NaCl$[a]	75.1
KCl[a]	84.2
$CuSO_4$[a]	97.2

[a] From Young.

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[1] 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.

geometry with a finely focused Cu K_α X-rays collimated with a focusing mirror and a 4-bounce Ge (220) crystal monochromator. The reflected beam was further collimated with a 3-bounce channel cut Ge (220) crystal before entering a proportional gas detector. An attractive feature of PVP in this study is the high mass density (1.66 g/cm^3). Because of this high density, there is modest contrast or difference in the scattering length density (SLD) between PVP (SLD $=1.53\times10^{-5}$ Å^{-2}) and water (SLD $=9.46\times10^{-6}$ Å^{-2}). This is not generally true for most polymers where the physical densities are closer to 1 g/cm^3 and SLDs are comparable with water. This contrast allows for potential gradients in the water concentration in the film to be observed in the PVP film with XR, but confidence in the absolute concentration profile is limited by the rather modest contrast. Otherwise neutron reflectivity is typically required to observe such gradients, where the contrast between the water and polymer can be significantly enhanced through deuterium labeling [2–4].

The mass uptake of moisture into the films was measured using a quartz crystal microbalance (Q-Sense) with dissipation (QCM-D). The crystals were 5.0 MHz quartz resonators with SiO_x coated gold electrodes. During the course of the swelling experiment, the fundamental resonance and three overtone frequencies ($n=1$, 3, 5 and 7) were measured at intervals of approximately 2 s. Since the PVP films are hydrophilic, the hydration should plasticize the films from the glassy to rubbery state. This change in the rigidity of the film raises concerns about the applicability of the Sauerbrey equation to analyze the QCM-D data [16]. However, the validity of the Sauerbrey equation for these systems has been confirmed under circumstances encountered in these experiments [10,17,18]. Under these conditions, the amount of water absorbed into the film can be determined from the change in the resonance frequency using the Sauerbrey equation [19], relating the frequency shift, Δf, to the change in mass, Δm.

$$\Delta f = -\frac{2f_o^2\Delta m}{nA(\mu_q\rho_q)^{0.5}} = -C_f\frac{\Delta m}{nA} \qquad (1)$$

where f_o is the measured resonant frequency or overtone, n is the number of the overtone, A is the electrode area (0.25 cm^2), μ_q and ρ_q are the shear modulus (2.95×10^6 N cm^{-2}) and the density (2.65 g/cm^3), respectively, of the quartz, and C_f is the integral sensitivity constant (57 Hz cm^2 μg^{-1}). The agreement in mass uptake between the primary resonance and the three overtones is within ± 5%[2]. All measurements were performed at 25 ± 0.5 °C.

Instead of using a static system, the moisture was introduced into the QCM sample chamber through a flow system that bubbles dry air through distilled water, exposing the PVP film to 100% RH. We have chosen to use a flow system here in these kinetic experiments as the relative humidity in the static system rises slowly as the water from the source evaporates to saturate the atmosphere. In these static systems, the swelling kinetics is convoluted by the rate of equilibration of the water vapor. Although the films are small such that the absorption should not influence the humidity level, hygroscopic surfaces of the chamber can adsorb appreciable amounts of water vapor, which can prolong the equilibration time significantly [20]. We have observed a significant decrease in the apparent adsorption rate using the stagnant water source technique with X-ray reflectivity, but the absorption rate is highly dependent on the pre-conditioning of the X-ray chamber indicating that the absorption rate is controlled by the chamber, not the polymer. The apparent swelling rate increases by several orders of magnitude if the X-ray chamber is exposed overnight to saturated vapor prior to the introduction of sample. With the flow system on the QCM cell, the vapor in contact with the sample is nearly saturated immediately as determined by a relative humidity meter on the effluent stream. Due to the variation in relative humidity at short times in the XR chamber, only the QCM measurements are used for kinetic data.

3. Results

3.1. Substrate effect on the total equilibrium moisture absorption

The moisture absorption from saturated vapor was measured as a function of film thickness on both HMDS and silicon oxide surfaces. The average volume fraction of water from the total amount absorbed determined from the degree of swelling (relative thickness change) using XR is shown in Fig. 1. The water concentration can also be determined from the shift of the critical angle of the film with water absorption. In this case the swelling was determined from the thickness change due instrumental resolution issues ($\Delta\lambda/\lambda=0.01$) with the thin film measurement resulting in significant uncertainty (±10%) in the critical angle. This is based on the volume change being one dimensional through the thickness of the film, which is a reasonable assumption based on the large area to thickness ratio. On silicon oxide, absorption is independent of film thickness, reaching an equilibrium volume fraction of 0.47 ± 0.01. However, for PVP on HMDS-treated substrates, the moisture absorption is significantly depressed when the film thickness is less than 60 nm. In previous studies of model photoresist films on HMDS treated surfaces, a depletion of water near the buried substrate interface was observed for the hydrophilic photoresist, but an excess of water was found for the hydrophobic analog [21]. These concentration gradients were observed directly using neutron reflectivity and indirectly through XR

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

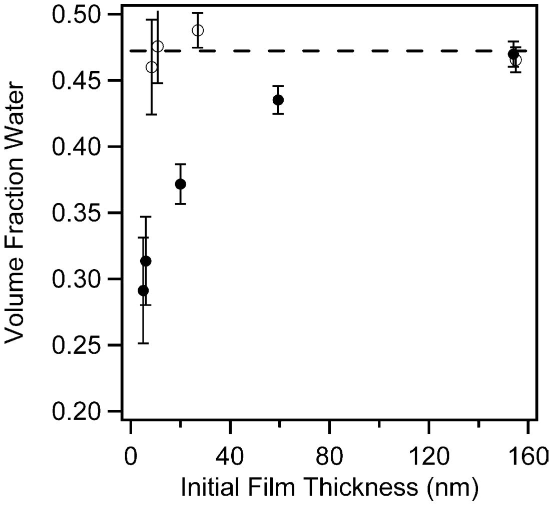

Fig. 1. Influence of film thickness on moisture absorption as measured by reflectivity. The water volume fraction absorbed in the films from saturated vapor is dependent for the thin films upon the substrate, either (○) SiO_x or (●) HMDS treated silicon. The dashed line is a guide to show that the absorption in PVP on the silicon oxide substrate is independent of film thickness.

swelling measurements. The PVP shows a similar thickness dependence of the swelling as the previous hydrophilic photoresist when both polymers are supported on a HMDS-treated surface [21], consistent with the presence of a depletion layer or a decrease in water concentration near the hydrophobic HMDS interface.

The accumulation or depletion of water near the polymer/substrate interface is dependent on the chemical nature of the substrate and the solubility of water in the polymer film. Water at buried interfaces has been studied in detail for only a few systems [2–6]. The most commonly studied substrate is silicon oxide which water, in the absence of a polymer film, will wet. In the case of relatively hydrophobic polymer films, the water concentration near the buried interface was observed to increase relative to the bulk with a maximum concentration of approximately 30% by volume at the interface [3,5]. This accumulation at the interface is expected as the silicon oxide is hydrophilic and is more attractive to the water than the polymer. If the affinity for water at the interface is reduced by applying a silane coupling agent to the substrate, the excess interfacial water in a hydrophobic film (if the film is still more hydrophobic than the interface) can be reduced to 10–20% by volume [2,3]. For hydrophobic polymer films the interfacial moisture content is dictated by the affinity of water for the substrate. However, very hydrophilic films behave differently. Recent confinement studies on moisture absorption in polyelectrolyte films show equilibrium absorptions that are independent of film thickness [10]. The equilibrium swelling invariance with film thickness implies that the water concentration is uniform throughout the polyelectrolyte film. A similar trend is observed with neutral PVP films on silicon oxide surfaces where an invariance in swelling ratio with respect to film thickness for ultra-thin films as shown in Fig. 1.

The water concentration in a polymer film near a hydrophobic HMDS treated surface is also examined. For the PVP films in Fig. 1, the swelling decreases as the film thickness decreases due to a depletion of water near the HMDS-treated interface. The hydrophobic interactions from the methylation of the surface hydroxyls of the oxide repel water absorbing in the PVP film near the interface. The depletion of water near an HMDS treated surface has been directly observed using neutron reflectivity for poly(4-hydroxystyrene) (PHOSt), which absorbs approximately 25% water in the bulk rather than the nearly 50% for PVP [21]. For PHOSt, a decrease in swelling was observed as the film thickness drops below 40 nm. The swelling behavior of the PVP films on the HMDS, has the same thickness dependence as the PHOSt system. It is important to note that the bulk equilibrium concentration in both polymers is greater than the maximum excess concentration 10–20% observed at the polymer/HMDS interface when the polymer is hydrophobic [21]. From the thickness dependence of the PVP swelling, we estimate the concentration at the interface by extrapolating logarithmically to zero thickness. This results in a concentration of 21%, which is consistent with neutron reflectivity estimates for the interfacial moisture concentration for the hydrophobic polymers near an HMDS substrate (10–20%) [21]. The thickness dependence of the PVP and PHOSt swelling on HMDS surfaces is controlled by the equilibrium interfacial accumulation of water at the polymer–substrate interface.

In general, the relative hydrophobicity (hydrophilicity) of the surface relative to the polymer determines the moisture concentration gradient near the substrate. If the surface has a stronger affinity for water than the polymer film, a surface excess is observed with an apparent increase in the relative swelling as film thickness decreases. If the surface is more hydrophobic than the polymer film, a depletion of moisture is found at the interface with an apparent swelling that decreases with film thickness. The only ‘exceptions’ to these observations are the highly hygroscopic films (neutral PVP in Fig. 1 and polyelectrolyte films [10]) on the silicon oxide substrates that absorb nearly 50% water, independent of film thickness. All of the other silicon oxide supported films cited above indicate that the preferred moisture content near the substrate approaches 30%.

The total amount of water absorbed is also affected by the elasticity of the film [22]. High modulus films resist increasing their volume in the presence of water. The observation that the moisture content does not rise above 30% at the interface could be related to an elastic resistance to swelling. Likewise, the observation that the moisture content exceeds 30% at the interface with the oxide surface for hygroscopic (PVP and polyelectrolyte) films might reflect a reduced elastic resistance to swelling. At a water concentration of 50%, both materials are plasticized and will be in the rubbery state with a lower modulus than glassy films. A detailed separation of elastic and solvation contributions to the moisture absorption profiles in thin polymer films is beyond the scope of this manuscript and remains to be clarified.

The presence of this water concentration gradient in the PVP films on the HMDS-treated substrates was evidenced by the thickness dependence of the swelling response. The same type of information can be inferred from the raw XR data, shown in Fig. 2 as a function of the momentum transfer vector (q), where $q=(4\pi/\lambda)\sin\theta$ and θ is the incident angle. These data are for a 20.8 nm thick PVP film on an HMDS-treated wafer during several different exposure steps. The film expands as the relative humidity is increased from vacuum (20.8 nm) to 53% (27.8 nm) to 100% (33.1 nm), as expected. The film thickness can be determined by the change in the Kiessig fringe spacing, Δq, which is inversely proportional to the film thickness, $t(\Delta q=2\pi/t)$. Upon exposure to moisture, the persistence of the Kiessig fringes decreases, indicative of a gradient in the SLD of the film. This gradient can result from either a physical roughing of a sharp interface or a uniform density gradient through the film itself; specular XR is not sensitive to lateral structure within the plane of the film, only an average across the entire film. Typically for polymer–solvent systems, the contrast in electron SLD is sufficiently small, such that variation in the solvent concentration profile are not directly observable [6]. For the PVP/water system, this is not the case due to the large mass density of PVP (1.66 g/cm^3). The electron *SLD* can be calculated as:

$$\mathrm{SLD}=\frac{\sum_{i=1}^{n}\rho_i}{v_\mathrm{m}} \tag{2}$$

where ρ_i is the electron scattering length for the i^th atom in the molecule and v_m is the molecular volume. This results in a SLD of 1.53×10^{-5} Å^{-2} and 9.46×10^{-6} Å^{-2} for PVP and water, respectively. As a comparison, the SLD of polystyrene is 9.6×10^{-6} Å^{-2}, which is nearly identical to water. The contrast between the PVP and water combined with the rapid decay in the persistence of the fringes in the hydrated sample is consistent with the water concentration gradient estimated from Fig. 1. Without additional information, the reflectivity profile could be fit equally well by physical roughening of the free interface or by introducing a depletion of water near the HMDS/polymer interface. However, examination of the reflectivity profile of the film after moisture exposure and subsequent evacuation reveals that the gradient in the SLD is lessened in comparison to the hydrated case. This is clear from the comparison of the persistence of the Kiessig fringes in the three profiles in Fig. 2. It should be noted that there is a slight increase in the roughness in the dry film after hydration. In combination with the film thickness dependent swelling, this result suggests there is depletion of water at the HMDS interface.

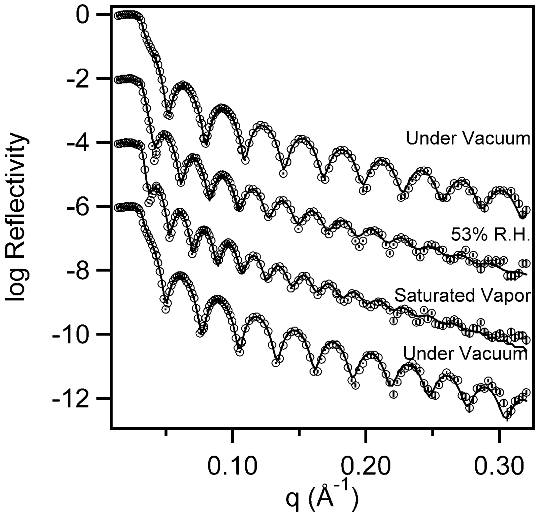

Fig. 2. X-ray reflectivity profiles of 20.6 nm thick PVP film. The sample is first evacuated, then exposed to 53% relative humidity, then saturated vapor, and finally evacuated. Each reflectivity profile is offset by two decades for clarity.

The film thickness was also determined by fitting the reflectivity profiles using a recursive multi-layer method with a non-linear least-squares fitting routine, as shown by the solid lines in Fig. 2. The agreement between the two methods is generally within ±5 Å for thin films. After exposure and subsequent drying (evacuation), the film shrinks (21.6 nm), but does not return to its original thickness. This offset between the initial and final dry thickness can be attributed to the vitrification of the film during solvent removal, thus preventing the film from relaxing to its equilibrium thickness. The initial thickness can, however, be recovered by annealing the sample above T_g for several hours.

3.2. Effect of relative humidity on interfacial water concentration

The study of water near buried interfaces to this point has been limited to either saturated vapor or liquid exposure [2–5,21]. To further probe the influence of the substrate on the swelling of ultrathin PVP films, the level of hydration in the films was varied by changing the relative humidity. Not only does relative humidity influence the amount of water absorbed within the film, it also influences the amount of water at the interface. For water adsorbing on bare silicon oxide, the thickness of the adsorbed water layer varies with the relative humidity [23]. The moisture absorption in several thin PVP films supported on HMDS treated substrates is shown as a function of relative humidity in Fig. 3. The shape of the absorption isotherm is different from predictions with Flory–Huggins theory, which reasonably describes the swelling behavior of many other hydrophilic polymers such as polysaccharides as a function of relative humidity [24]. For the PVP films examined here, the swelling is small at low humidity (<50%), but then

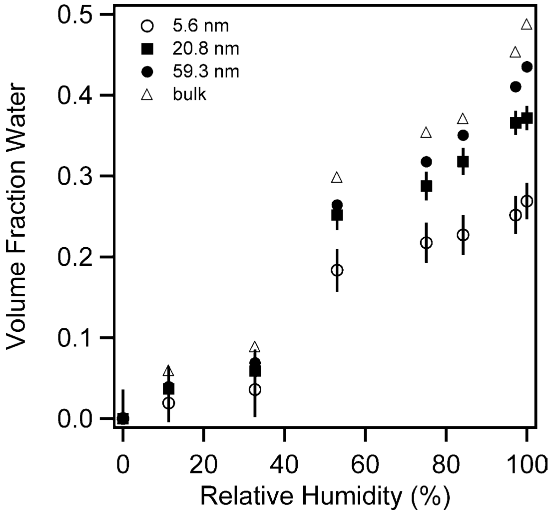

Fig. 3. Thickness dependence of moisture absorption in PVP on HMDS surface at various humidity levels. The absorption into (○) 5.6 nm, (■) 20.8 nm and (●) 59.3 nm thick films is decreased as the films become thinner. The swelling of the bulk PVP (△) is shown as a comparison.

rapidly increases between 32.7 and 53% relative humidity. This jump in swelling corresponds with the change from the glassy to the rubbery state [25,26]. After this region, the swelling increases at a slower rate. Similar swelling behavior has been observed for polyglycols where an increase in swelling was observed near 50% relative humidity [27].

Although the shape for the absorption isotherms is similar for different film thickness, the absolute swelling is dependent on film thickness at all relative humidities examined as shown in Fig. 3. At all levels of hydration, the thinnest film absorbs the least water. The swelling of the films supported on the HMDS-treated substrates is most significantly depressed at low humidity (<50% RH). As the relative humidity is increased above 50%, the swelling in the supported films in comparison to the bulk reaches a constant value. This ratio is dependent on the initial film thickness, ranging from approximately 0.6 for the 5.6 nm film to 0.95 for the 59.3 nm film. This suggests that the extent of the surface depletion layer of moisture also reaches a plateau with relative humidity.

3.3. Substrate and thickness dependence of absorption rate

The substrate surface chemistry has been shown to have an impact on the total equilibrium moisture uptake. In this section, the influence of film thickness and the substrate on the moisture absorption rate is examined. The substrate surface energy is known to influence T_g shifts in thin films [13,28–31] and thus the dynamics of the polymer chains. The diffusion of water molecules into the film during the absorption process may be used as a probe of the segmental polymer dynamics. In addition, in the PVP polymer studied here, chains must rearrange their packing through molecular (polymer) motions to accommodate the large volumes of absorbed water. In supported thin films, the presence of the rigid substrate leads to the polymer being physically bound in the plane of the substrate and confines the swelling to occur normal to the substrate [31]. The local chain swelling near the substrate interface due to water absorption can be controlled by the surface energy, as shown above. These experiments help determine if different extents of chain stretching due to swelling also affect the moisture absorption kinetics.

The moisture absorption kinetics was measured using QCM. The simplest case for water absorption into a polymer is a Fickian process where the time resolved mass increase for a thin film on an impermeable substrate is [32]

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{h^2}\right)^{0.5}\left(\frac{1}{\pi^{0.5}+2}\sum_{n=1}^{\infty}(-1)^{\mathrm{n}}\, ierfc\,\frac{nh}{2(Dt)^{0.5}}\right) \quad (3)$$

where M_t and M_∞ are the mass gains at time, t, and at equilibrium, respectively. D is the diffusivity of the penetrant, and h is the film thickness. It is assumed that the penetrant absorption is one dimensional, which should be valid given the large surface area to volume ratio and the impermeable substrate. At short times, this expression can be simplified to

$$\frac{M_{\mathrm{t}}}{M_\infty} = \frac{2}{h}\sqrt{\frac{Dt}{\pi}} \quad (4)$$

that results in a simple expression for the diffusivity:

$$D = \frac{\pi}{4}\left(\frac{\frac{M_{\mathrm{t}}}{M_\infty}}{\frac{\sqrt{t}}{h}}\right)^2 \quad (5)$$

The diffusion coefficient is determined from the initial slope of the absorption curve plotted in the form of M_t/M_∞ versus $t^{1/2}/h$. We extract a single diffusion coefficient for simplicity and to illustrate trends with film thickness. A complete description would account for the potential transition from a glassy to rubbery response with increasing amounts of absorbed water. The moisture absorption into a 20.8 nm thick PVP film on both the silicon oxide and HMDS surfaces is shown in Fig. 4. Recall that the total moisture absorption (M_∞) was dependent on the substrate (SiO_x versus HMDS). However, the substrate surface does not significantly influence the absorption rate. At short times, both absorption curves are well represented by the Fickian model. For the samples on silicon oxide, there is a slight inflection in the absorption profile for all film thickness, which is absent in samples on HMDS surfaces. This is similar to phenomena observed in two-stage absorption (non-Fickian) [33]. However, the difference in the absorption rate between films on each substrate is small considering the effect of the substrate surface on the total absorption.

The influence of film thickness on the water diffusion rate in poly(4-ammonium styrenesulfonic acid), a charged

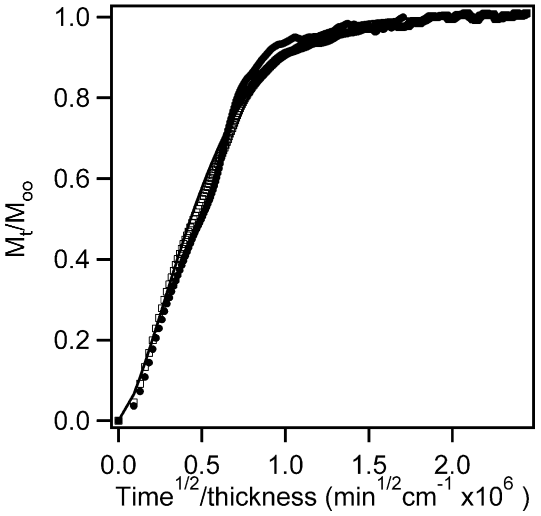

Fig. 4. Moisture absorption for saturated vapor into 20.8 nm thick PVP film on (□) HMDS and (●) SiO_x surfaces. The absorption rate is nearly independent of film thickness. The solid line is a Fickian fit ($D=2.3\times10^{-13}$ cm^2/min).

hydrophilic polymer, was determined previously [10]. The diffusivity decreased by five orders of magnitude when the film thickness was decreased from 200 to 3 nm. A similar result was found for the uncharged PVP films, as shown in Fig. 5. The diffusivity decreased by three orders of magnitude as the film thickness decreases from 155 to 5.6 nm. When comparing films initially of equal thickness, the substrate surface energy does not play a significant role in the water absorption rate, despite the large influence on the equilibrium uptake. One explanation for the lack of substrate influence on the water diffusivity is that the diffusion coefficient calculations depend primarily on the initial uptake, which emphasizes transport near the free interface.

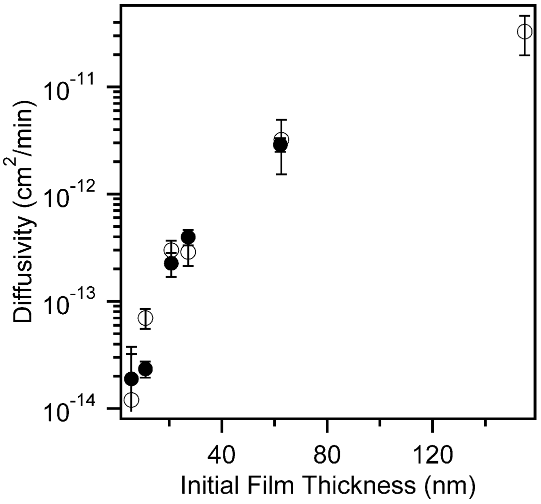

Fig. 5. Effective water diffusion coefficients in PVP films. The diffusivity decreases by three orders of magnitude as the film thickness decreases from 155 to 5.6 nm. There is no discernable effect of the substrate, (●) SiO_x or (○) HMDS, on the diffusivity.

A decrease in the diffusivity of water in ultrathin polymer films has been observed for both charged and neutral polymers on both hydrophobic and hydrophilic surfaces. There are several possible reasons for the origin of the decrease in the mobility of the small molecules in ultrathin polymer films. Guest molecules have previously been used to investigate polymer mobility in thin films with inconsistent results [34–36]. Thickness dependent through-plane chain mobility has been observed using polymer interdiffusion experiments, which find a decrease in the mobility as the film thickness approaches R_g [37,38]. This decrease is similar to the mobility change observed for the water absorption presented here. However, the transport of small molecules through polymers is not coupled with the large-scale motion of polymer chains, such as those measured in the interdiffusion experiments. Since the water swelling of the PVP substantially changes the film dimensions, polymer chain motion will be important. But initially during the absorption, local segmental motion along the polymer chain will determine the absorption rate. These local motions can be suppressed in ultrathin films [12,39,40], and there have been correlations with the suppression of these motions and reduced transport kinetics [39]. However, the mechanism(s) for deviations in the dynamics of confined polymer films remains an area of much conjecture, due in part to the complexity of the coupling of confinement and interfacial effects [41]. Several theories have been developed to attempt to describe the experimental deviations in the T_g in thin polymer films involving free volume and percolation concepts or heterogeneity in the density profile [42,43]. The diffusivity of small molecules in thin polymer films is related to these parameters and provides additional data to test these ideas. The observation of decreased diffusivity in ultrathin PVP films shows that decreased transport rates of small molecules are observed even with large amounts of absorbed water.

4. Conclusions

The influence of film thickness and the substrate surface on the moisture absorption in PVP was examined. The equilibrium moisture concentration absorbed from saturated vapor was independent of PVP film thickness for films supported on silicon oxide surfaces with film thickness as small as 5.6 nm. This thickness independence of swelling is consistent with previous measurements for a polyelectrolyte on silicon oxide [10] and suggests that physical confinement of the polymer chains does not significantly influence the equilibrium absorption of small molecules. Additionally, the results show that when the substrate and polymer both have an affinity toward to water, there are no concentration gradients within the film induced by the substrate. However, if the substrate was modified with HMDS, the measured water absorption decreased with decreasing film thickness when the initial film thickness was less than 60 nm. The apparent solubility change can be significant. For example, for a film initially 154 nm thick, the film swells in saturated water vapor such that the water concentration is 0.47 ± 0.01 by volume fraction, whereas for a film initially 5.6 nm thick, the film only contains a water volume fraction of 0.29 ± 0.04. The apparent solubility in the thin film is decreased by nearly 40%. This decrease is attributed to a depletion of water near the HMDS/polymer interface as suggested by the thickness dependent absorption in the thin films and the X-ray reflectivity profiles of the hydrated films that indicate a gradient in water concentration through the film. This depletion is expected to be a result of the hydrophobic interactions between the HMDS surface and the absorbing water. The chemistry of the substrate can thus significantly influence the water concentration near the buried interface with implications for adhesion in moist environments [3]. In addition to the equilibrium absorption, the influence of the substrate on the absorption kinetics was also examined. Although the total uptake was substrate dependent, there was no significant influence of the substrate on the absorption rate, even for films as thin as 5.6 nm. This result is not surprising as the water diffuses into the film from the free interface, but for the thin films, this limits the chemistry of the substrate influence to less than 5.6 nm. However, the film thickness did affect the measured water diffusivity with the diffusion coefficient decreasing by 3 orders of magnitude as the film thickness decreased from 155 to 5.6 nm. This decrease in the diffusivity is attributed to the coupling of the water mobility within the polymer film to the local chain motion, which has been found to be retarded in thin films [12]. In summary, the concentration of water near an interface can be influenced by the chemistry of the substrate, while the absorption kinetics are relatively unaffected by the chemical nature of the substrate, but film confinement leads to a decrease in the mobility of the absorbing species.

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