

Measurements of water distribution in thin lithographic films[§]

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1. ABSTRACT

Neutron and x-ray reflectivity measurements quantify the non-uniform distribution of water within poly(4-*tert*-butoxycarbonyloxystyrene) (PBOCSt) and poly(4-hydroxystyrene) (PHOST) thin films on silicon wafer substrates. Two contrasting surface treatments were examined, silicon oxide, representing a hydrophilic interface and a trimethylsilane primed surface, representing a hydrophobic interface. The distribution of water in the films was sensitive to the surface preparation and photoresist relative hydrophilicity. Depending upon the water contact angle of the substrate in comparison to the polymer film, an excess of water near the interface occurs when the substrate is more hydrophilic than the photoresist. Likewise, interfacial depletion results when the photoresist is more hydrophilic than the substrate. These non-uniform water distributions occurs within (50 ± 10) Å of the photoresist/substrate interface.[1] The water concentration in this interfacial region appears to be independent of the photoresist properties, but is strongly dependent upon the substrate surface energy.

Keywords: thin films, neutron reflectivity, x-ray reflectivity, water immersion

2. INTRODUCTION

The drive to print smaller feature dimensions with photolithography necessitates decreases in the total film thickness of the photoresist. This is due to design criteria for a maximum aspect ratio, height-to-width on the order of 3:1, beyond which buckling instabilities upon rinsing can lead to pattern collapse. This pattern collapse problem dictates that the film thickness must decrease proportionally to the minimum feature widths. Likewise, smaller features necessitate a shift to shorter wavelength UV radiation, for instance from 248 nm to 193 nm and 157 nm. This is problematic as most polymers strongly absorb at these wavelengths. Thinner resist films designed with optically transparent functional groups reduces UV absorption and ensures illumination throughout the film. With critical dimensions reaching the sub-100 nm mark for chemically amplified photoresist, the influence of the unperturbed dimensions of the polymers that comprise the resist, confinement, and interfacial issues must be considered. It is well known that thin film confinement of a polymer affects several of the basic thermo-physical properties [2-4]. Additionally as films become thinner, the fraction of the film that is near the interfaces increases; thus, interfacial phenomenon such as segregation of components [5] is an important consideration for lithography in thin films.

Interfacial effects on moisture absorption from both the vapor and liquid phase are becoming increasingly important as immersion lithography becomes a viable alternative to enhance resolution. Current 193 nm immersion technology uses deionized water as an immersion fluid to effectively extend tool set applicability down to the 45 nm node [6]. Thus, understanding the interactions of water with the photoresist is important to realize the technical feasibility of immersion lithography. Resist swelling would clearly affect resist performance. However, bulk swelling may not sufficiently explain why certain resist systems fail. Interfacial effects, such as T-topping, footing, and undercutting, commonly have been shown to interfere with the production of high quality features. Moisture content has been found to influence the

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reaction-diffusion process of the photogenerated acid within chemically amplified resists [7]. Variations of water content throughout the film could lead to loss of resolution. Additionally, moisture has been found to be a destabilizing agent to adhesion [8]. Water accumulation at the buried interface during the immersion process could lead to photoresist delamination. In all these cases, information about the interfacial distribution of water within a thin polymer resist is needed to evaluate and understand its affect on lithographic performance.

Here we measure the distribution of water within model photoresist films and the influence of surface chemistry on the distribution. The water distribution can be directly quantified using isotopic labeling and neutron reflectivity. However, neutron reflectivity is not required to identify the excess or depletion of water near the substrate. We use a series of x-ray reflectivity measurements over different film thickness to show that for ultrathin films ($< 500 \text{ \AA}$) there is a thickness dependence on the swelling if the water distribution is non-uniform.

3. EXPERIMENTAL METHODOLOGY

3.1. Samples

This study uses model 248 nm resists: poly(4-*tert*-butoxycarbonyloxystyrene) (PBOCSt) and poly(4-hydroxystyrene) (PHOSt). While this resist will not be utilized for sub-100 nm lithography because of transparency limitations, it provides a model system for demonstrating general thin film deviations and has been the subject of numerous studies for bulk and thin film effects in the dry state. The PHOSt ($M_{n,r} = 8,000 \text{ g mol}^{-1}$) was purchased from Triquest [9], while PBOCSt was prepared by protecting PHOSt with a *tert*-butoxycarbonyl group (t-BOC) using routes described elsewhere.[10] The chemical structures are identified in Figure 1.

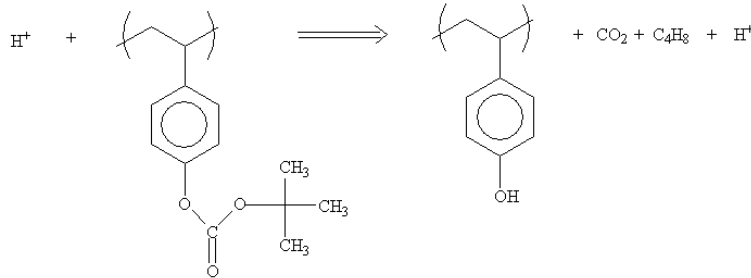


Figure 1. Simplified reaction schematics depicting how a photoacid (H⁺) reacts with the protected PBOCSt to yield the deprotected and base soluble PHOSt. The photoacid is regenerated by the reaction in addition to evolution of gaseous carbon dioxide and isobutylene..

Either PBOCSt or PHOSt were dissolved in propylene glycol methyl ether acetate (PGMEA) at different mass loadings. The solutions were filtered through a 0.45 μm PTFE filter and spun cast at 209 rad/s (2000 rpm) onto silicon substrates. The silicon substrates were pre-treated with either UV ozone (UVO) to produce a hydrophilic surface or hexamethyldisilazane (HMDS) vapor at 120 $^{\circ}\text{C}$ for 5 min for a hydrophobic surface. Static water contact angle measurements were performed. Water wets the UVO treated oxide surface. The contact angle was $69^{\circ} \pm 4^{\circ}$ for the HMDS treated surface. Each sample, spun coat from different mass fractions to achieve variable film thickness, was post-apply baked 120 $^{\circ}\text{C}$ for 2 h under a vacuum of 0.1 Pa. We have confirmed that these conditions do not induce significant thermal deprotection.

3.2. Methods

The neutron reflectivity measurements were performed on the NIST Center for Neutron Research (NCNR) NG-7 reflectometer using a wavelength (λ) = 4.768 \AA and wavelength spread ($\lambda/\Delta\lambda$) = 0.2. Neutron reflectivity is capable of probing the neutron scattering length density at depths of up to several thousand \AA , with \AA depth resolution. All

reflectivity measurements were performed at 25 °C for dry films, films equilibrated with saturated deuterium oxide (D₂O) vapor, or films immersed in liquid D₂O. To ensure equilibration, films were exposed to moisture for greater than 4 h. The water distribution vertically through the film can be observed using neutron reflectivity because of the large difference in scattering length density between deuterium and protonated polymers. The immersion experiments utilize an inverted geometry as shown in Fig. 2. The neutron beam is incident through the thick silicon wafer and reflected off the thin polymer film. This inverted geometry is used because Si is highly transparent to the neutrons, especially in comparison to the D₂O. In this inverted geometry on the HMDS treated Si, the films were stable for more than 12 h, without signs of moisture-induced delamination. However, the silicon oxide supported film delaminated quickly in the liquid D₂O meaning that exposure to saturated D₂O vapor was the only recourse. In this case reflectivity geometry was inverted such that the incident beam passed through the vapor phase (or air) before reflecting off the thin polymer film; this is because D₂O saturated vapor is more transparent to the neutrons than solid Si. Whether the incident neutrons first pass through the Si or the vapor is inconsequential in terms of extracting the D₂O absorption profiles in the thin polymer films.

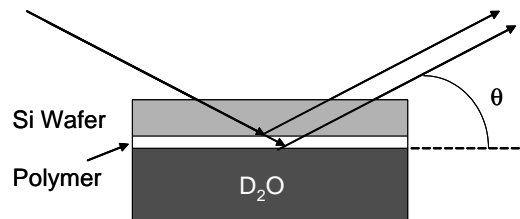


Figure 2. Schematic of neutron reflectivity setup for the immersed samples.

The film thickness for both dry and vapor-exposed films were independently corroborated by specular x-ray reflectivity incident through the air/vapor phase; similar measurements are not feasible on the immersed films because both the liquid D₂O and the Si are not transparent to x-rays. For thin films (< 120 nm), the reflectivity measurements were made in θ/θ mode with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) using two sets of collimation slits. The humidity was controlled using an aluminum chamber with beryllium windows either under vacuum or closed with an excess of liquid water in the chamber to produce nearly saturated vapor. Each sample measurement was allowed at least 6 h to equilibrate or after which time the film thickness remained constant ($\approx 0.1 \text{ nm}$). For thicker films (> 120 nm), reflectivity measurements were made in $\theta/2\theta$ mode with a finely focused Cu-K α beam of radiation using a focusing mirror and a 4-bounce Ge (220) crystal monochromator. The reflected beam then passes through a 3-bounce channel cut Ge (220) crystal into a proportional gas detector.

4. RESULTS AND DISCUSSION

In order to quantify the influence of immersion on the water distribution in thin films, the dry state must be compared with the immersed state. A typical neutron reflectivity result is shown in Fig 3, for a PBOCSt film on HMDS treated wafer with initial thickness of 535 Å for both the dry and immersed in D₂O case. The reflectivity is shown as a function of the momentum transfer vector, $Q = 4\pi/\lambda \sin(\theta)$. The reflectivity results from the interference of reflected neutrons between the substrate and film and provides detailed information with respect to the neutron scattering length density profile. This profile is modeled by a series of slabs with varying neutron scattering length density and absorbance coefficients. These density profiles are presented in units of Q_c^2 as a function of distance (Z) through the film. Q_c^2 is a scattering length density, with dimensions \AA^{-2} , and is proportional to the average atomic scattering length, b ($Q_c^2 = 16 \pi N b$), where N is the number of nuclei. The scattering length density profile for the PBOCSt film illustrates several of the film properties that can be extracted from the reflectivity profile. First, the thickness of the film in the dry and immersed state can be determined. For the PBOCSt on HMDS illustrated here, the film swells from an initial thickness of 535 Å to 543 Å. The scattering length density of each of the layers can also be determined. From the silicon substrate, there are three distinct layers in both the dry and immersed state. First, the oxide layer (near $Z = 0 \text{ \AA}$) on the silicon that remains unchanged by the immersion. The average Q_c^2 of the polymer film (beyond $Z = 0 \text{ \AA}$ out to approximately $Z = 535 \text{ \AA}$) increases slightly upon immersion due to the large Q_c^2 of pure D₂O; this is seen by the high Q_c^2 plateau in the immersed profile (solid line). However, the increase in Q_c^2 is not constant across the film as an

increase in scattering length density near the HMDS treated silicon oxide surface is observed. This can be attributed to an excess of D₂O at the interface. The maximum D₂O concentration is 17 % by volume at the solid interface and this decays smoothly to the bulk value within 40 Å from the interface. This is significantly greater than the concentration expected from the total film swelling (1.5 % by volume).

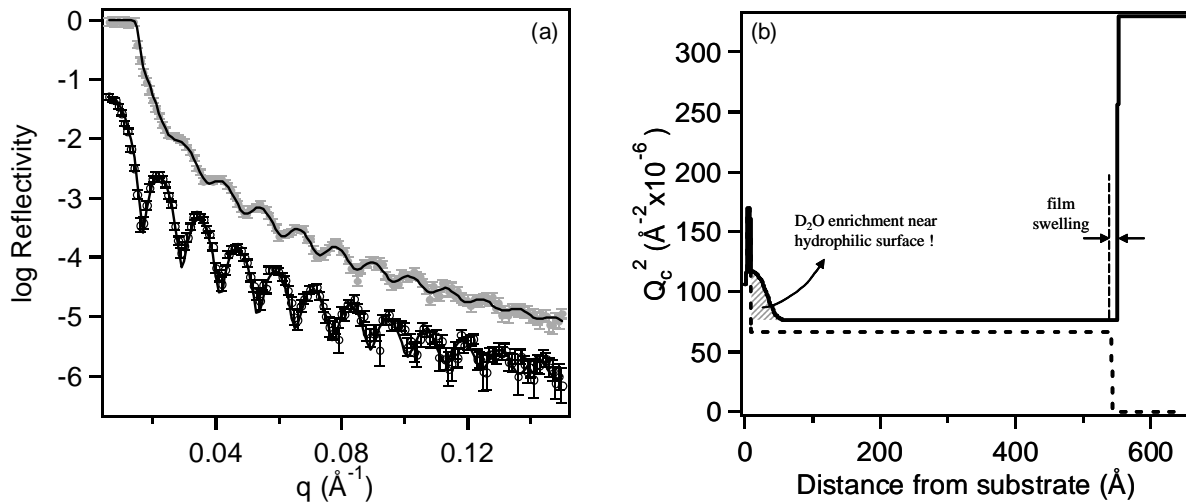


Figure 3. Neutron reflectivity and corresponding fit for initially 535 Å thick PBOCSt film before and after immersion in D₂O. (a) Reflectivity profiles in the dry (open symbols) and immersed (closed gray symbols). The line through the data corresponds to the best fit. The scattering length density profile from the reflectivity fits is shown in (b) for both the dry (dashed line) and immersed (solid line) cases. The enhanced D₂O concentration at the silicon oxide interface is indicated by the hatched region.

The water distribution within PHOSt was also measured in the dry and immersed states on HMDS treated wafers. The reflectivity profiles and corresponding scattering length density profiles for an initially 295 Å thick PHOSt film are shown in Fig. 4. Similar to the PBOCSt results, a total film thickness increases due to the absorption of D₂O was observed as the film swelled to 386 Å. A greater extent of swelling is observed, as expected due to the presence of the more hydrophilic hydroxyl groups.

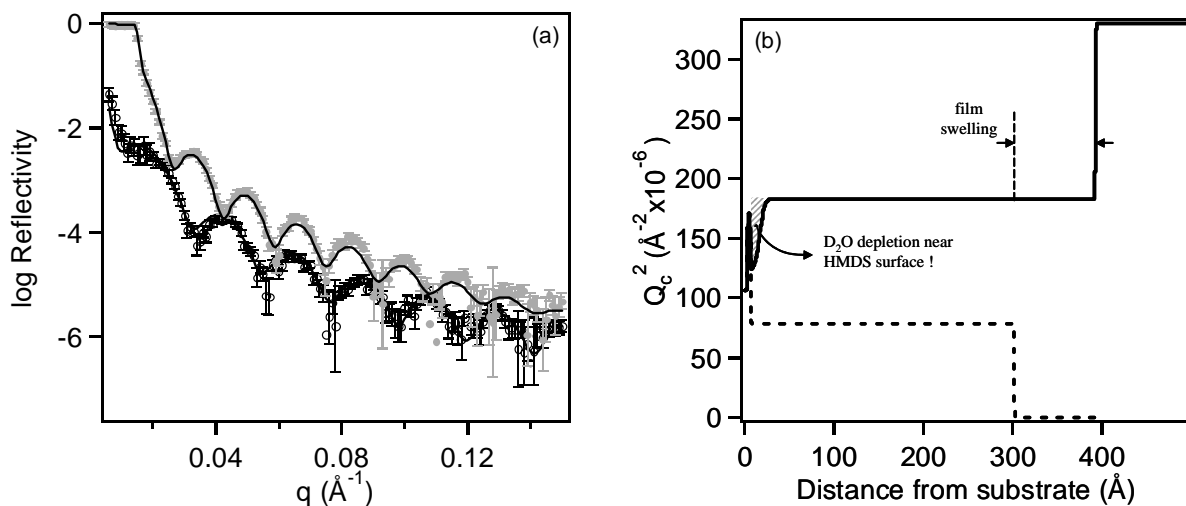


Figure 4. Neutron reflectivity and corresponding fit for initially 295 Å thick PHOSt film before and after immersion in D₂O. (a) Reflectivity profiles in the dry (open symbols) and immersed (closed gray symbols). The line through the data corresponds to the best fit. The scattering length density profile from the reflectivity fits is shown in (b) for both the dry (dashed line) and immersed (solid line) cases. The D₂O depleted region is indicated by the hatched area.

One consequence of the increased swelling in the PHOST is the greater increase in the scattering length density of the film (compare Figs. 3b and 4b). However, the more significant increase in Q_c^2 for the PHOST is not only due to greater absorption of D_2O , but also to the exchange of hydroxyl protons with deuterium. This proton exchange complicates quantifying the exact water concentration through the film. The largest complication occurs from the decrease in scattering length density near the HMDS surface. This indicates a depletion of water, but the lack of water also limits the proton exchange. Regardless, it is clear that for PHOST immersed in D_2O on an HMDS treated substrate there is a depletion of water near the substrate, whereas for PBOCSt under the same condition there is an excess of water near the substrate. From this data alone, the determining factor for excess or depletion cannot be distinguished.

In order to understand the cause of the non-uniform water distribution near interfaces, measurements were performed on both PHOST and PBOCSt on silicon wafers with a more hydrophilic silicon oxide surface. One problem encountered with this system was delamination of the film during the immersed measurement. To circumvent this problem, the films were exposed to saturated D_2O vapor. The use of vapor rather than liquid should not significantly influence the results because the chemical potentials of the saturated vapor and liquid (assuming saturated) are equal. However, the absorption process from the vapor state first requires an adsorption at the free interface that is not necessary in the immersed case, which may lead to differences. Although the absolute concentrations may change, the trends observed from the equilibrated vapor state should hold.

Neutron reflectivity was again used to measure the water concentration profiles through the film. Using a simple rule of mixtures for the scattering length densities based upon the pure polymer and D_2O scattering length densities, a water concentration profile can be determined. The depth profile of water through PHOST and PBOCSt films are shown in Fig. 5. The PHOST concentration is calculated assuming all the labile hydroxyl protons are exchanged (this is the minimum concentration). As can clearly be seen, the water concentration near the silicon oxide interface is independent of polymer despite the nearly order of magnitude difference in solubility between PHOST and PBOCSt. A concentration maximum of roughly 30 % by volume is observed at the interface for both films. This value is consistent with recent results of Kent and coworkers for the water concentration at a silicon oxide interface that is covered with a silane.[11] The water concentration profile in the immersed PBOCSt on HMDS prepared silicon is also shown in Fig. 5. This indicates that the moisture concentration at the interface can be tuned by controlling the surface chemistry, whereas a change in the polymer itself does not appear to significantly alter the interfacial water concentration.

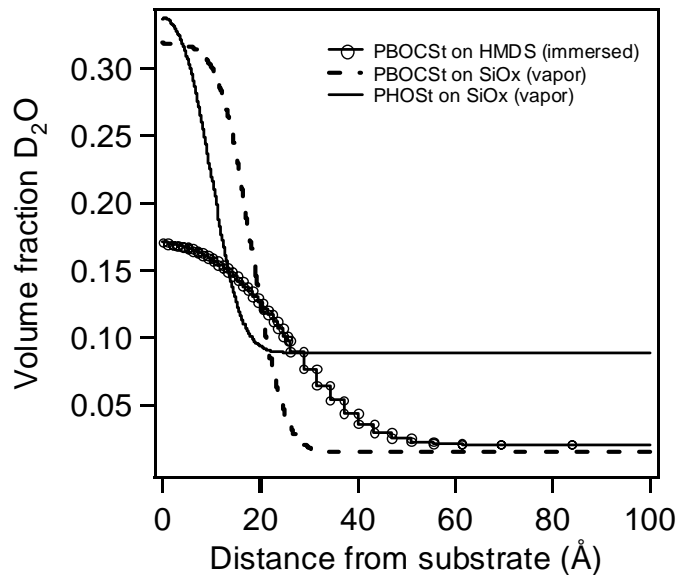


Figure 5. Concentration profiles near the silicon substrate obtained directly from neutron reflectivity measurements similar to those shown in Figs 3 and 4 (reflectivity curves not shown here). The volume fraction of D_2O is determined from the critical angle of the two pure components (polymer and D_2O) using a simple rule of mixtures.

The presence of excess interfacial water in these systems can be indirectly determined by x-ray reflectivity. The swelling of thin films can be monitored accurately with x-ray reflectivity. As the film becomes thinner, the swelling due to water at the interface dominates the total film swelling. Thus by monitoring the film swelling as a function of initial film thickness (h_0), the presence of an interfacial excess or depletion can be determined. The swelling of thin PBOCSt and PHOSt films supported on silicon oxide surfaces in the presence of saturated water vapor is shown in Figure 6 displays the degree of film swelling ($\Delta h/h_0$) as a function of the initial thickness (h_0). As can be clearly observed, the swelling of thick films is independent of film thickness as the interfacial water only accounts for a small fraction of the total absorbed water in the film. However as the initial film thickness decreases below 1000 Å, the observed swelling increases with decreasing thickness. When the film thickness is less than 100 Å, the interfacial water excess dominates the swelling. The lack of polymer influence on the excess water at the interface can be observed by the similarity in swelling between PBOCSt and PHOSt in these ultrathin films. Although the thick films do not exhibit any thickness dependence, this does not preclude the presence of excess water at the interface. We have observed directly with neutron reflectivity the presence of excess water at the buried interface for films as thick as 1500 Å. Additionally, the thickness dependence of the swelling of both PBOCSt and PHOSt can be explained with a simple, zero fit parameter model that assumes that the swelling consists of two parts: a thickness dependent swelling that is based upon the water solubility in the bulk, and a constant excess concentration at the silicon oxide / polymer interface that is independent of film thickness. The fit of this model to the data is shown with the dashed lines in Figure 6. Thus even if a thickness dependence is not observed in the film thickness range of interest, a non-uniform distribution of water within the film cannot be discounted, unless the swelling is measured down to the thickness range of 100 Å.

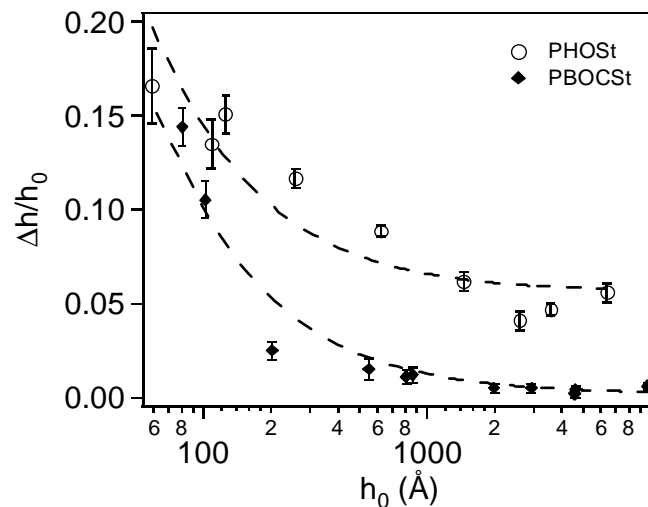


Figure 6. Film thickness dependent swelling, as measured by x-ray reflectivity, for both PBOCSt and PHOSt films. The enhanced swelling with decreasing film thickness stems from excess water adsorption at the buried interface. The lines through the data are not fits, rather predictions based on the level of excess moisture perceived by the neutron reflectivity experiments (see text).

One potential tool for predicting whether depletion or excess near the substrate will be observed is the water contact angle measurements. For PBOCSt, the contact angle is greater than for the HMDS treated surface. For PHOSt, the contact angle is less than for the HMDS surface and the contact angle for both photoresists is greater than the silicon oxide. Thus from the neutron reflectivity measurements, it appears that an excess of water will be present at the interface if the contact angle for the photoresist is greater than that of the substrate. Conversely, if the contact angle of the photoresist is less than the substrate, the water concentration near the substrate is less than the bulk (depletion). This result may be coincidental and requires additional data, but if this trend holds, it allows for a straightforward and simple technique to determine if concentration gradients exist near a buried interface.

5. CONCLUSIONS

The distribution of deuterium oxide within model photoresist films has been probed directly using neutron reflectivity. There is a region near the buried interface where the water concentration deviates from the bulk. Both an increase and decrease in relative concentration has been observed depending upon the polymer and substrate. For PHOSt and PBOCSt supported on silicon oxide surface substrate, there was an excess of water at the interface observed with a maximum concentration of approximately 30 % by volume in both cases for saturated D₂O vapor equilibration. For immersed PBOCSt supported on HMDS-treated silicon wafer, an excess concentration was observed as well, but the maximum concentration at the interface was only 17 % by volume. The depletion of water was observed for PHOSt on HMDS treated wafers for the D₂O immersion experiment. Thus, the absolute interfacial concentration is highly dependent upon the chemistry of the supporting surface, but does not appear strongly dependent upon the photoresist itself. The excess water for the films on the oxide surfaces also manifests itself as a thickness dependent swelling for thin films. However, this thickness dependence is not seen in films thicker than 1000 Å, but the water concentration deviation at the interface can still be present. A trend in the data suggests that the presence of an excess or depletion of water near the buried interface can be estimated by examining the relative water contact angles.

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