Water immersion of model photoresists: interfacial influences on water concentration and surface morphology

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Abstract. The emergence of immersion lithography as a potential alternative for the extension of current lithography tools requires a fundamental understanding of the interactions between the photoresist and an immersion liquid such as water. The water concentration depth profile within the immersed photoresist films is measured with neutron reflectometry. The polymer/substrate interface affects both the water concentration near the interface and the surface morphology of the film. Immersed films are not stable (adhesive failure) over the course of hours when supported on a silicon wafer with a native oxide surface, but are stable when the substrate is first treated with hexamethyldisilazane (HMDS). The bulk of the polymer films swells to the equilibrium water concentration, however, a gradient in water concentration is observed near the polymer/HMDS substrate interface with a concentration of approximately 17% by volume fraction and extending up to 50 Å into the film. Thus, polymers that absorb more than this amount exhibit depletion near the interface, whereas polymers that absorb less exhibit a water excess layer. These concentration gradients extend approximately 50 Å away from the interface into the film. As the total film thickness approaches this length scale, the substrate-induced concentration gradients lead to a film-thickness-dependent swelling; enhanced or suppressed swelling is witnessed for the excess or depleted interfacial concentrations, respectively. The substrate also influences the surface morphology of immersed thin films. The film surface is smooth for the HMDS-treated substrate, but pin-hole defects with an average radius of 19 ± 9 nm are formed in the films supported on the native oxide substrates. [DOI: 10.1117/1.1861852]

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1 Introduction

The development of immersion lithography is of growing interest due to the challenges facing the next generations of optical lithography. Immersion lithography enables an increase in optical resolution without changing the exposure radiation wavelength by introducing a high-refractive-index fluid between the optics and the photoresist film.[1] For 193-nm immersion lithography, water has been selected as the high-index fluid due to its optical transparency at the exposure wavelength and compatibility with current processing protocols (aqueous developer, deionized water rinse). However, exposure to water could introduce additional difficulties that are not encountered for dry photoresists. For example, variations in the water content in a photoresist film can change the rate of the deprotection reaction.[2] More importantly, it is necessary to understand the uniformity of the water absorption in the photoresist during immersion. Heterogeneities in the concentration profile throughout the film thickness could lead to spatial variation in absorbance, nonuniform acid diffusion, large sidewall roughness, or other undesired features. Uniformity of the small molecule additives, such as photoacid generators (PAGs), within photoresists remains an issue because segregation of material to either interface potentially cause effects such as undercutting, T-topping, and/or residual layers.[3] Absorbed moisture can increase the mobility of these molecules or extract them from the resist, potentially exasperating segregation problems. Finally, the immersion of the film may induce defects in the film that could lead to device failure.

The distribution of water within thin polymeric films has been studied previously for applications such as adhesion,[4] electronics packaging,[5] and microelectronics.[6] In all these cases, excess water was observed at the polymer/substrate interface. However, these studies involved the absorption of water vapor into the film. In this paper, we present the first direct measure of the water concentration in a model photoresist using true immersion conditions, where the sample resides in a liquid environment. The photoresist polymers used in this study are model 248-nm resists, poly(4-hydroxystyrene) (PHOSt) and its protected analog, poly(4-*tert*-butoxycarbonyl-oxystyrene) (PBOCSt). Although these polymers are not directly used for immersion lithography, they are well-understood systems and useful for addressing a fundamental understanding of immersion issues.

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In this paper, the influence of the silicon wafer substrate on the moisture absorption profiles in and surface morphology of PBOCSt and PHOSt films is explored under both immersion (liquid water) and saturated water vapor. Both hydrophilic silicon wafers with the native oxide surface and hydrophobic wafers treated with hexamethyldisilazane (HMDS) were studied. HMDS is used as an adhesion promoter in the semiconductor industry to prevent the resist from delaminating from the wafer under the action of the aqueous base developer. The water distribution normal to the film is probed using neutron reflectivity (NR). The lateral heterogeneity is probed using an atomic force microscope (AFM) through changes in the surface topology on immersion in liquid water. Together these results illustrate several important considerations for immersion lithography irrespective of any particular resist and immersion fluid.

2 Experiments

The PHOSt ($M_{r,n}=8000$ g/mol) used in this study was obtained from Triquest. (Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standard and Technology nor does it imply that the materials or equipment are necessarily the best available for the purpose.) The PBOCSt was synthesized by protecting the PHOSt via free radical addition of t-butylene 4-vinylphenyl carbonate to the para position of the aromatic ring.[7] The films were prepared by dissolving PHOSt or PBOCSt in propylene glycol methyl ether acetate (PGMEA), filtering through 0.2-μm-pore-size solvent-resistant filters and subsequently spin coating onto silicon wafers with either native oxide or HMDS-treated surfaces. The wafers were prepared by first cleaning in oxygen plasma for approximately 5 min, followed by oxide etch using buffered HF solution (a 7:1 NH_4F:HF ratio by mass), and then a thin, uniform oxide layer was regrown in an ultraviolet ozone (UVO) chamber with approximately 3 min of exposure. The films denoted with native oxide surfaces followed this procedure. For HMDS-treated substrates, the same cleaning procedure was used, but following the UVO step, the wafers were exposed to controlled pressure of HMDS vapor for approximately 3 min at 120°C. The water contact angle was found to be 69 ± 4 deg for the HMDS-treated substrates. The water used for the immersion was either purified by a MilliQ filtered system (Millipore Corporation) for AFM measurements or deuterium oxide (99.9%, Aldrich) for NR measurements. Prior to all measurements, the films were baked at 120°C for 2 h under vacuum to remove residual solvent.

The NR measurements were performed at the Center for Neutron Research (NCNR) on the NG-7 reflectometer at the National Institute of Standards and Technology (Gaithersburg, Maryland) in the following configuration: wavelength (λ) = 4.768 Å and wavelength spread ($\Delta\lambda/\lambda$) = 0.025. The reflectivity was measured with the beam passing through the bottom side of the wafer, rather than the top that may be covered with water. The reflectivity of the films were measured both in the dry state and after the film was immersed in D_2O for greater than 4 h. With HMDS treatment, delamination of the films from the silicon substrate was not observed over the course of 12 h. The uncertainties are calculated as the estimated standard deviation of the mean. In the case where the limits are smaller than the plotted symbols, the limits are left out for clarity. Fits of the reflectivity data are made by a weighted least-squares regression algorithm.

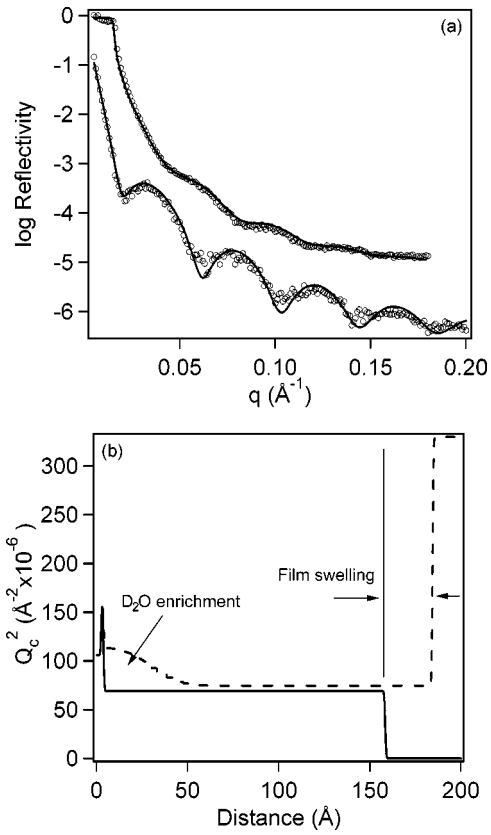

Fig. 1 (a) NR profile for 15.5-nm-thick PBOCSt film before (bottom) and after (top) immersion in liquid D_2O. The profiles are not offset. (b) SLD profiles as a function of distance from the substrate corresponding to the best fit of the NR profiles for dry (solid) and wet (dashed) films.

A Digital Instruments AFM (Dimension 3100) was used for the AFM measurements. The images were obtained in contact mode using a spring constant of 0.12 N/m^2. For the measurements in water, the sample was immersed in a very large water droplet. A fluid cell was used to protect the electronics from the liquid environment. Samples were imaged at 25°C.

3 Results and Discussion

Figure 1 shows the reflectivity profiles (symbols) and corresponding fits (lines) for a 15.5-nm-thick PBOCSt film on a HMDS-treated substrate, both before and after immersion in liquid water. The inset indicates the scattering length density (SLD) profiles in terms of Q_c^2 (with units of Å^{-2}) corresponding to the best NR fit. In this inset, the origin is assigned to be at the polymer/substrate interface and increasing with distance into the resist film. The value of Q_c^2 rapidly decreases to $Q_c^2 = 0$ Å^{-2} or increases to $Q_c^2 = 3.3 \times 10^{-4}$ Å^2, indicating either the dry or immersed in D_2O film surface, respectively. From Fig. 1, the film swells from

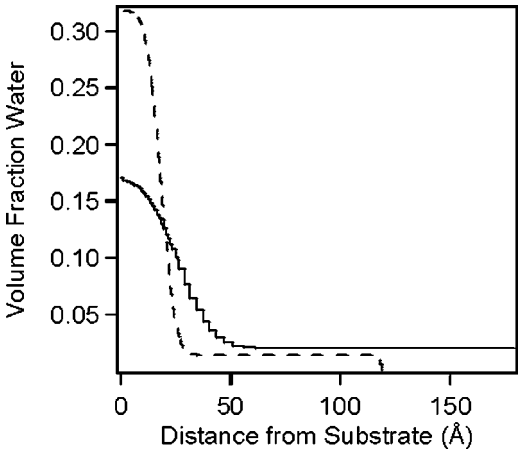

Fig. 2 Water concentration profile within PBOCSt films on bare silicon (dashed lines) or HMDS-treated surface (solid line) as determined by NR. The interfacial water concentration is depressed by the presence of HMDS. The bare silicon data is from Ref. 6.

15.5 to 18.1 nm on immersion, as clearly shown from the SLD profile. Note that the SLD in the bulk of the film increases on absorption, and that this increase becomes more pronounced near the polymer/silicon interface. Thus, the immersed data could not be quantified by a single layer of uniform SLD contrary to the dry film. The observed increase in SLD arises from the absorbed D_2O, which has a significantly higher SLD than the PBOCSt. The volume fraction of absorbed D_2O at any given distance into the film is a linearly weighted average of the pure component SLDs. Therefore, these data suggest an excess concentration of absorbed water near the interface.

Previously, a similar excess was found at the polymer/silicon interface for water absorption from the vapor state into PBOCSt films supported on untreated silicon wafers.[6] Water accumulation at the silicon oxide interface is not surprising because the oxide surface is very hydrophilic, creating a thermodynamic driving force for water to accumulate at the surface interface. The HMDS-treated surface is generally viewed as hydrophobic however (nonwetting water contact angle of 69 ± 4 deg), making the excess water accumulation at the surface less obvious. (Note that the data throughout this paper and the figures are presented along with the standard uncertainty ($\pm$) involved in the measurement based on one standard deviation.) However, the water accumulation at the HMDS surface is rationalized when realizing that the water contract angle on a pure PBOCSt film is 83 ± 2 deg; the HMDS-treated surface is actually more hydrophilic than the PBOCSt polymer. Thus, water accumulates at the PBOCSt/substrate interface for the HMDS as well. The water affinity for the HMDS surface is reduced from native oxide, as expected. This is best illustrated by a comparison of the water concentration profile in PBOCSt on either the HMDS (solid line) or native oxide (dashed line) surface shown in Fig. 2. These concentration profiles were determined using the fitted SLD profiles and a rule of mixtures between pure D_2O and dry PBOCSt. Figure 2 shows that the water concentration within the bulk of the film is less than 2% by volume. However, near the polymer/substrate interface, there is a

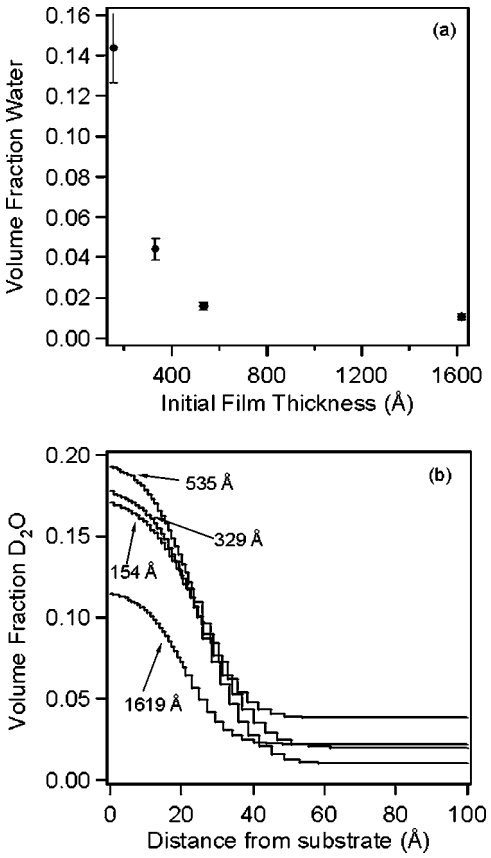

Fig. 3 NR results on PBOCSt film show that the (a) film-thickness-dependent swelling is a result of a (b) thickness-independent excess layer. The values in (b) correspond to the initial film thickness.

significant increase in the water concentration. The amount of excess water at the interface decreases from approximately 30 to 17% by volume between the native oxide and HMDS-treated substrates. This reduced interfacial water is consistent with the improved adhesion of the HMDS surface treatment photoresist development.

Excess moisture absorption presumably leads to excess swelling of the interface. This implies that the excess interfacial water can also be determined indirectly by measuring the film thickness dependence of the moisture-induced swelling. For relatively thick films, the contribution of the interfacial excess is negligible and the measured film swelling would be close to expected values for the bulk material. However, deviations from the bulk-like swelling are expected as the film thickness approaches the size of the excess layer. The thickness-dependent absorption is shown in Fig. 3(a). Note that the changes in film thickness have been converted to a volume fraction by assuming the ''mixing'' of the water and the polymer are additive; this facilitates comparison with the SLD measurements, which are on a per volume basis. As anticipated, the degree of swelling increases as the film thickness decreases due to the interfacial excess. The relative invariance of the water excess profile (both in magnitude of the excess and thickness of the interfacial layer) with decreasing film thickness was confirmed with NR, corroborating the notion that the enhanced swelling with decreasing film thickness reflects the interfacial excess moisture. Figure 3(b) shows a series of four

PBOCSt films on the HMDS substrate, ranging in thickness from 15.4 to 161.9 nm, revealing very similar interfacial excess regions. Over all four films, the average concentration at the interface was determined to be 0.17 ± 0.03 by volume fraction with a width of 40 ± 10 Å. In the thickest film, there was some difficulty fitting the reflectivity profile because the film thickness approached the instrumental resolution. The water concentration profile of the thickest film, which appears to have substantially less water at the interface, is therefore not as reliable as that of the thinner films; the reduced interfacial excess in the thick film could either reflect difficulties in fitting the data or possibly surface energy variations due the quality of the HMDS coating. There is good agreement in the interfacial water distribution for the other films, confirming the generality of the interfacial segregation effect.

Knowledge of an interfacial region of excess moisture absorption could be extremely important in lithography or other thin film applications. While NR measurements may be difficult from a logistical perspective, NR is not required to measure the thickness-dependent swelling behavior. Apparent enhancements in the thin film behavior swelling from simple thickness measurements, such as x-ray reflectivity or spectroscopic ellipsometry, appear to be general signatures of the phenomenon. However, NR is required to verify and quantify the characteristics and profile of the excess layer.

Previously, it was found that the water concentration at the interface was independent of the polymer coating for both PHOSt and PBOCSt films on native oxide surfaces.[6] The extension of these results to HMDS surfaces is shown in Fig. 4 with the reflectivity profile and corresponding fit for a PHOSt film before and after immersion in liquid water. As seen from the corresponding SLD profile shown in the inset, there is no longer an excess of water at the interface. In fact, the SLD decreases near the substrate, indicating interfacial water depletion. This indicates that the surface is less hydrophilic than the polymer film. If this mechanism is correct, there should be a decrease in the extent of water-induced swelling as the total film thickness is reduced and becomes comparable to the thickness of the interfacial deplete zone. Figure 5 confirms this reduced swelling in the thin PHOSt films on the more hydrophobic (relative to PHOSt) HMDS substrates.

The moisture absorption of PHOSt from the liquid phase on the HMDS surfaces reported here is qualitatively very different from the vapor phase absorption on the silicon oxide substrates reported earlier. For the oxide, enhanced absorption in the thinner films indicates excess water at the interface,[6] whereas on HMDS surfaces, the absorption is diminished in the thinnest films. Additionally, the equilibrium absorption in the thickest films (where interfacial effects are negligible) is significantly different between the two data sets. The vapor state leads to an equilibrium uptake of 0.062 ± 0.011 volume fraction, whereas the liquid state results in a volume fraction of 0.236 ± 0.031. The reduced uptake in the saturated vapor in comparison to the immersed liquid could arise from the heat of adsorption corresponding to this initial step of by water molecules diffusing from a vapor into a solid film. The difference between the liquid and saturated vapor swelling in the thick PBOCSt films, however, was within experimental error.

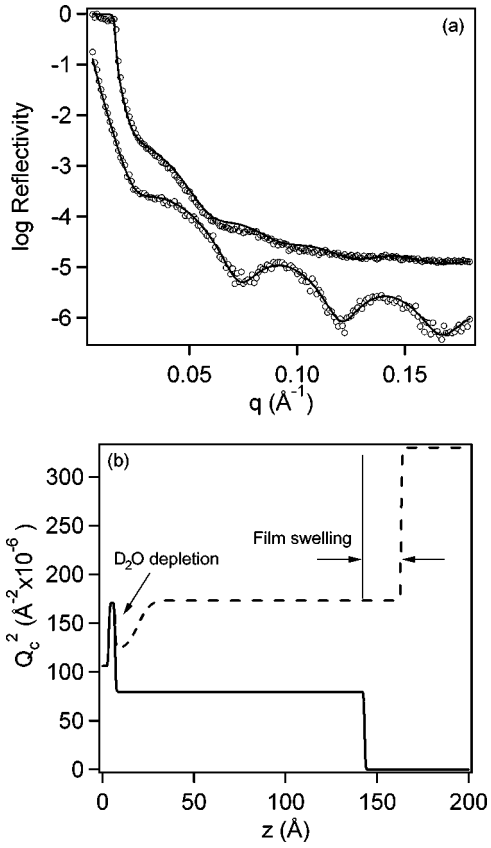

Fig. 4 (a) NR profile for 13.6-nm-thick PHOSt film before (bottom) and after (top) immersion in liquid D_2O and (b) SLD profiles corresponding to the best fit of the NR profiles for dry (solid) and wet (dashed) films.

The difference between PHOSt and PBOCSt could be attributed to strong hydrogen bonds between PHOSt and water that are not present within PBOCSt. However, it is important to realize the potential for this discrepancy in immersion applications if the film swelling is an issue; the swelling associated with the saturated vapor does not necessarily correspond with the swelling from immersion in the liquid.

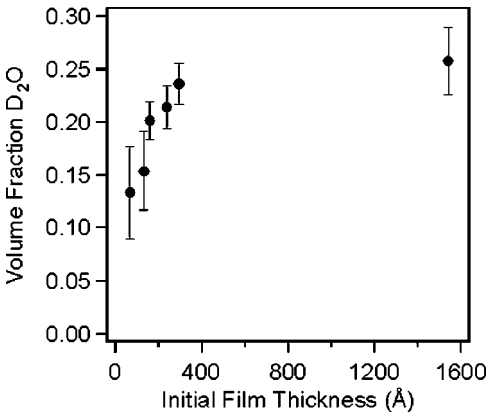

Fig. 5 Film-thickness-dependent moisture absorption for PHOSt immersed in D_2O. Depletion near the polymer/substrate interface leads to the decrease in absorption for the thinner films.

Quantifying the water concentration depth profile through the PHOSt film is not as straightforward as in the the PBOCSt case. It is readily understood that the PHOSt hydroxyl group can exchange its proton with the deuterium in the D_2O, meaning that the SLD no longer increases according to simple rule of mixtures. It is not possible to quantitatively extract the water concentration from these films. In the previous vapor phase work, it was assumed that all the hydroxyl protons exchanged, giving a lower limit on the water concentration that corresponded well to the average water concentration determined by the film swelling.[6] In this case, however, the depletion of water near the interface limits the ability for the PHOSt acidic proton to exchange with D_2O, leading to a concentration depletion near the interface. An additional difficulty is that the SLD difference between the silicon substrate and the depletion layer is small. Nevertheless, the interfacial layer size can be constrained by physical limitations. Despite these problems, qualitatively the existence of water depletion near the HMDS surface is obvious from the NR through results, as evidenced by the decrease in the scattering length density of the film near the substrate and the reduced swelling with decreasing film thickness. The depletion layer was found to extend 15 to 50 Å into the film, irrespective of the film thickness, indicative of a substrate-controlled concentration.

To understand this phenomenon, it is helpful to first examine the simple, but related HMDS-treated surface interaction with water. The effect of HMDS treatment on the surface interactions with water has been well studied (see Ref. 8 and the references therein) with the surface coverage of the silica surface sterically limited to 2.5 μmol/m^2.[9] This leads to a substantial residual concentration of surface silanols, which are active site for water adsorption on silicon oxide (see Ref. 8 and references therein and Ref. 9). HMDS leads to a decrease in the available silanol sites for water adsorption. However, due to the incomplete coverage, the heterogeneous surface is polarized through the variation in charge between the hydrophilic and hydrophobic regions. The polymer dependence on water depletion or excess at the buried interface is due to the interplay between these competing interactions and the water concentration present in the bulk of the film. For the native oxide of silicon, approximately 30% by volume of water was located at the interface,[4,6] but this excess concentration is decreased here to 0.17 ± 0.03 when the surface is modified with HMDS. As for the polymer/silicon oxide interface, it appears that the maximum water concentration at the interface is largely unaffected by the polymer coating. This is difficult to fully confirm due to problems in resolving the concentration profiles for the immersed PHOSt. Nonetheless, the depletion of water at the interface for PHOSt would be expected as the solubility in the bulk ($\approx 25\%$) is greater than the interfacial concentration ($17 \pm 3\%$) observed for the PBOCSt.

The concentration gradients near the polymer/substrate interface can potentially limit lithographic resolution. From the NR measurements, the depth profile of the water concentration was determined as a laterally averaged concentration in the plane of the film as a function of the distance from the substrate. The morphology of the excess layer in the lateral dimension, to which NR is largely insensitive, is also important. An AFM can be used to examine the lateral homogeneity of immersed films, but it is sensitive primarily to the top surface. From the NR measurements, only the buried interface is affected by the concentration gradient. However, this buried interface may influence the surface morphology. The influence of surface treatment on the surface morphology during immersion was examined using two ultrathin PHOSt films (≈ 15 nm), one on HMDS and the other on native oxide. The AFM micrographs are shown in Fig. 6 for these PHOSt films. The film on the HMDS surface remains smooth on immersion but holes are observed across the film on the oxide surface. These features appear almost instantaneously on immersion and do not appreciably change dimension with time. Dynamics of the feature formation are not accessible due to the limited scanning rate of the AFM cantilever, which limits the time scale to several minutes. The holes in Fig. 6 are circular with an average diameter of 19 ± 9 nm. Prior to immersion, the film showed no visible defects, as determined by the AFM. After immersion, the hole formation is irreversible. Similar results have been shown for water immersion of polystyrene supported on a silicon substrate where the surface "blisters."[10] Although the physical mechanism for the feature formation on immersion of the PHOSt films on the silicon oxide surface is not understood fully, we infer from the combination of the NR results and AFM measurements on different surfaces that these features are associated with

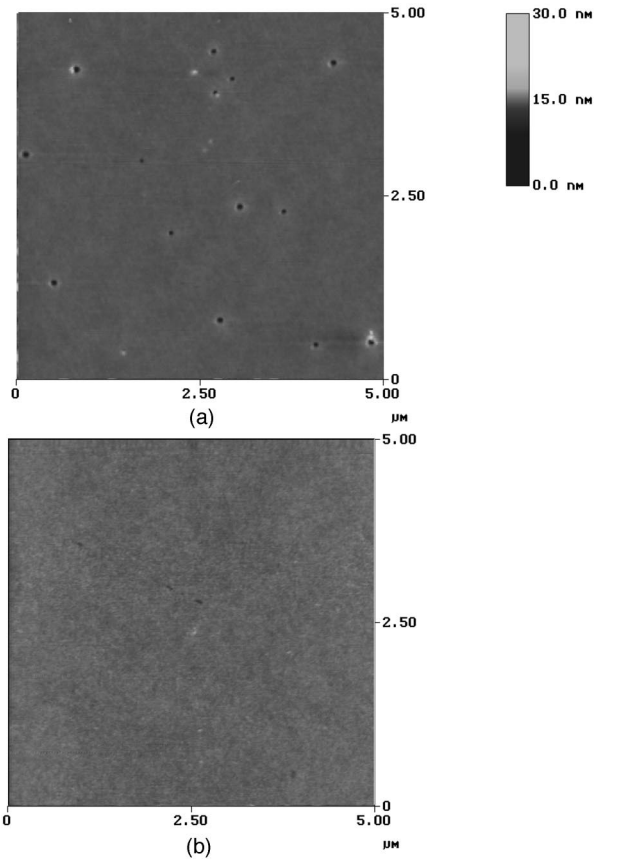

Fig. 6 Surface morphology of 8K PHOSt film immersed in water on native oxide (a) and HMDS-treated (b) substrates. The micrographs are 5×5 μm.

excessive water near the polymer/substrate interface. We suggest that these structures result from an in-plane phase separation between water and polymer to create patterns similar to those observed in thin polymer blend films undergoing phase separation.[11] It is unlikely that the phenomenon is a result of dewetting due to the stability of the holes in time. The displacement of PHOSt from the substrate by water during the phase separation, mediated by the surface energy of the wafer, could mechanically induce instabilities in ultrathin films and manifest as irreversible defects in the film. It is, however, important to realize that the holes are not the source of excess interfacial moisture evidenced by NR. It is true that NR lacks the lateral resolution to determine if the interfacial excess is uniformly distributed across the film or an average of pockets of pure water (touching the interface through the holes) and bulk like water in the rest of the film. Such a mechanism would be inconsistent with the x-ray reflectivity (XR) swelling studies which are not sensitive to the occasional pin-hole; the enhance swelling is indeed uniform laterally across the entire surface.

4 Conclusions

The surface treatment of the substrate has a significant influence on the water concentration profile and the surface morphology for PHOSt films immersed in water. The treatment of the silicon substrate with HMDS results in a surface-induced water depletion layer for the PHOSt films that extends 15 to 50 Å into the film. This water depletion phenomenon was directly observed from the neutron scattering length density profile determined by NR. A decrease in the film swelling with decreasing film thickness was found in association with this phenomenon. Conversely, an excess of water near the HMDS/polymer interface was observed for PBOCSt films with a maximum concentration of 0.17 ± 0.03 by volume and the gradient extends 40 ± 10 Å into the film. Note, however, that the maximum water concentration near the interface decreased in comparison to that observed for PBOCSt on native silicon oxide from approximately 30% for the oxide to 17% for the HMDS-treated surface.[6] These different water distributions near the buried polymer/substrate interface have potential influences on the processing of these resists through the nonuniform optical constants of the immersed film and the moisture enhanced acid diffusion rate during the postapply bake.[2] The moisture excess at the interface is especially worrisome as the enhanced acid transport could lead to undercutting. The free surface morphology of the polymer film can also be influenced by the chemical nature of the underlying substrate. For PHOSt films on HMDS-treated substrates, immersion in water does not change the surface morphology. However, if the substrate surface is not modified from the native oxide, defects are observed in the immersed film. These defects with an average dimension of 19 ± 9 nm are not acceptable for the feature sizes anticipated for structures produced by immersion lithography.

Acknowledgments

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