Direct measurement of the spatial extent of the *in situ* developed latent image by neutron reflectivity

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The spatial distribution of polymer photoresist and deuterium labeled base developer highlights a fraction of the line edge that swells but does not dissolve. This residual swelling fraction remains swollen during both the *in situ* aqueous hydroxide dissolution (development) and water rinse steps uncovering that the final lithographic feature is resolved by a collapse mechanism during the drying step. These new insights into the mechanism of lithographic feature formation were enabled by contrast variant neutron reflectivity methods with nanometer resolution. [DOI: 10.1116/1.2800329]

I. INTRODUCTION

The drive to sub-32-nm critical dimensions places an increasing reliance on photolithography with chemically amplified photoresists.[1] The process by which an imposed photoacid distribution reacts with photoresist to form a chemical latent image is controlled by a combination of optical and photoresist design parameters. However, a possible trade-off among resolution, exposure dose sensitivity, and line-edge roughness (LER) may limit photoresists from reaching sub-2-nm LER.[2–7] A central assumption in these resolution limit models is a direct transfer of photoacid distribution and chemical deprotection reaction-diffusion heterogeneity on the feature quality.[8,9] This statistical approach to photoresist resolution limits is supported by computer simulation[10] and lithographic measurements.[11] The specific role of image development was not considered but typically applies a threshold development.

The bulk of photoresist thin films dissolves via reactive dissolution kinetics involving a well-defined steady-state swollen layer.[12–14] This swollen layer must approach the nominally unreacted and unexposed areas as the bulk development ceases.[15] This crucial transition zone results from the initial deprotection latent image which can be controlled by aerial image, polymer chemistry, photoacid generator and base additives, and post-exposure bake conditions.[16–19] The mechanism of how the advancing swelling dissolution front faces the transition of soluble to insoluble species (solubility switch) is crucial to understand resist resolution limits.

In this article, we provide a direct measurement of the residual swelling fraction (RSF) at a model lithographic line edge, as shown in Fig. 1. This fraction of material is defined by an average deprotection level that dissolves (solubility switch) and a lower composition limit for swelling without dissolution. The line-edge region remains diffuse over length scales exceeding the single chain dimensions upon completion of hydroxide development and water rinse steps and collapses upon drying. This experimental evidence supports a dynamic interface with physical grounds extendable to modern simulations[8,20,21] and perhaps can lead to rational approaches to minimize the residual swelling fraction by resist design and additive-based approaches to smooth and reduce LER.

II. EXPERIMENT

A well-defined latent image was prepared by successive spin coating of a photoresist/acid feeder layer bilayer structure. This provides a sharp initial photoacid step profile and subsequent acid catalyzed deprotection of the underlying photoresist polymer. This reaction front was previously characterized with nanometer resolution.[18] Here, we use these model line-edge systems for the *in situ* development, rinse, and subsequent drying of the samples; this enables direct measurements of the line-edge structure in contact with the developer.

A. Materials and sample preparation

The acid feeder layer/photoresist polymer bilayer films were prepared with one slight modification; an antireflective coating (ARC) was applied to improve the adhesion of the photoresist polymer to the clean silicon substrate for the *in situ* development studies. Therefore, the trilayer is used for *in situ* development, as shown in Fig. 2. The ARC was a diluted form of CD2326 (Brewer Science Inc.) spun coated onto the cleaned silicon wafer with regrown native oxide and post-apply baked (PAB) at 200 °C for 5 min under a N_2 atmosphere. The model photoresist polymer poly(methyladamantyl methacrylate) (PMAdMA) with number-average molecular mass (M_n) of 8800 g mol^{-1} and polydispersity index of 1.18 (DuPont Electronic Polymers) was spin casted from toluene onto this ARC layer followed by a PAB of 130 °C/60 s. The acid feeder layer consists of

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FIG. 1. Schematic of the deprotection profile (solid line) that appears as a gradient line edge with "solubility switch" for development and residual swelling fraction appearing between nonswelling and dissolving photoresist regions.

FIG. 2. Sample processing from UV exposure, post-exposure bake, *in situ* development and rinse steps, and final dried state.

poly(4-hydroxystyrene) (PHOSt) (DuPont Electronic Polymers, $M_n = 8000$ g mol^{-1}) with 5% by mass of triphenylsulfonium perfluorobutanesulfonate spun coated from 1-butanol and PAB at 130 °C/60 s. This trilayer is then exposed to broadband ultraviolet (UV) radiation and post-exposure baked at 130 °C for 15 s. The deprotection reaction scheme for the PMAdMA is provided in Fig. 3. The deprotection reaction extent into methacrylic acid (MAA) and residual methylene adamantane was characterized by infrared spectroscopy.[18,22] Control samples without UV exposure and post-exposure baked were prepared to characterize the initial sharp trilayer structure. Excellent reproducibility of film thickness between different samples processed under the same conditions was achieved and observed by characterization by infrared spectroscopy and neutron reflectivity.

B. Neutron reflectivity

Neutron reflectivity measurements were performed on the NG-7 reflectometer at the NIST Center for Neutron Research. The absolute reflected neutron intensity was measured as a function of the scattering wave vector (Q) normal to the film, $Q = 4\pi\lambda^{-1} \sin \theta$, where λ is the fixed incident neutron wavelength of 4.75 Å and θ is the angle of reflection. The reflected intensity as a function of wave vector provides nanometer resolution depth profile of the film due to the neutron scattering length density variations between components.

The dry trilayer sample was characterized by neutron reflectivity on unexposed and post-exposure baked samples following procedures described elsewhere.[18] As the deprotection reaction proceeds, the difference in hydrogen content between PHOSt and PMAdMA and subsequent deprotection reaction provide sufficient neutron contrast to measure the

reaction front[18] and film profile. The physical thickness (mass density) and surface roughness of the films are measured using x-ray reflectivity.

In situ development was performed on the well-defined latent image reaction fronts. These samples were placed into a custom liquid cell and a single sample was subjected to *in situ* development and rinse. Two trilayer separate samples were measured to characterize the polymer segmental profile and the deuterium labeled tetramethylammonium profile using a full contrast and zero-average contrast approach, respectively.[23]

Full contrast experiments used protonated 0.065 mol/L tetramethylammonium hydroxide (TMAH) prepared from the salt form in D$_2$O (99.9% isotopic purity, Aldrich) to maximize the scattering length contrast between polymer and solvent. Once the developer was introduced into the cell, the acid feeder layer and portion of the reaction front dissolved, as observed visually through a view port in the liquid cell. The film remaining in contact with the developer was measured by specular neutron reflectivity. Subsequently, the developer was removed from the cell, rinsed, and filled with D$_2$O to mimic the rinse step.

The zero-average contrast experiment used a D$_2$O/H$_2$O mixture of 0.197 volume fraction D$_2$O which contrast matches the dry polymer film (Q_C^2 of 4.0×10^{-5} Å^{-2}), containing 0.065 mol/L deuterium labeled d_{12}-tetramethylammonium (d-TMA) hydroxide prepared from the salt form (Cambridge Isotopes, Andover, MA). Analogous to the full contrast experiment, the sample was measured after development but then subjected to two types of *in situ* rinses. The first used a zero-average contrast solvent to detect any trapped d-TMA and the second used D$_2$O.

After development, the films were removed from the liquid cell, tilted to allow the water to drain easily, and dried in

FIG. 3. Acid catalyzed deprotection reaction for the model 193 nm photoresist polymer poly(methyladamantyl methacrylate) into poly(methacrylic acid-co-methyladamantyl methacrylate) and methylene adamantane residual products.

FIG. 4. Neutron reflectivity of unexposed (○) and post-exposure baked (●) (offset by one decade for clarity) samples along with model fits. (Inset) Scattering length density profile change due to the deprotection reaction at the PMAdMA/acid feeder interface with distance relative to silicon/silicon oxide interface.

open air. The change in film thickness from the original trilayer was observed visually and subsequently measured by neutron and x-ray reflectivity.

These experimental data are fitted to reflectivity profiles calculated from model scattering length density profiles ($Q_C^2 = 16\pi\Sigma b_i/v$) using the Parratt algorithm,[24] where the scattering length of each repeat unit is determined by the sum over the atomic scattering lengths b_i within molar volume (v) leading to the absolute scattering length density, an intensive absolute quantity. In general, this approach uses successive layers (a box model) of constant Q_C^2 with interfaces smeared by a Gaussian function leading to error function interfacial width profiles. For dry films, each component layer (silicon, silicon oxide, ARC, and polymer) is quantified using layers of constant absorption coefficient, scattering length density, and thickness. However, for liquid and base immersed films, the polymer and base profiles are inadequately represented by one layer, so two to three layers are needed to describe the nonuniformities at the solid/liquid interface. The calculated reflectivity from the trial Q_C^2 profile is fitted to the experimental data using a Levenberg-Marquardt nonlinear least-squares method with adjustable thickness, scattering length density, and interfacial width of the unknown layers with a least-squares statistics (χ^2). These Q_C^2 profiles can be directly converted to volume fraction profiles. Uncertainties are calculated as the estimated standard deviation from the mean. In the case where the limits are smaller than the plotted symbols, the limits are removed for clarity.

III. RESULTS AND DISCUSSIONS

A. Latent image

The photoacid catalyzed deprotection reaction front broadens an initially sharp interface (model line edge) due to photoacid diffusion. The resulting deprotection profile can be characterized by neutron reflectivity, as shown in Fig. 4 for unexposed and post-exposure baked samples. The reflectivity fringes reveal the multilayer structure such that the silicon, silicon oxide, ARC, PMAdMA, and PHOSt acid feeder layers are resolved in the scattering length density profiles (inset). The dry film thickness corresponds to 26 nm of ARC, 124 nm of PMAdMA, and 61 nm of acid feeder layer. The deprotection profiles in terms of fraction of MAA are obtained by combining neutron reflectivity with infrared spectroscopy.[18] Figure 5 highlights the main results of the photoresist latent image comprised of an initial sharp MAdMA profile (solid line) and MAA deprotection fraction (dotted line) formed by the photoacid catalyzed reaction of Fig. 3. The photoacid diffuses from the feeder layer (not shown for clarity) into the PMAdMA and catalyzes the deprotection reaction that results in the broad latent image profile.

B. Developed image: Contrast variant neutron reflectivity

The *in situ* developed, rinsed, and dried samples are shown in the composite plots of Fig. 6. The developed sample in contact with 0.065 mol/L TMAH in D_2O was

FIG. 5. Neutron reflectivity results analyzed in terms of volume fraction profiles for initial sharp MAdMA profile (solid line, left axis) and partially deprotected (MAA) (dotted line, right axis) profiles after a post-exposure bake at 130 °C of 15 s. The photoacid reaction diffusion from the acid feeder layer partially deprotects PMAdMA as shown by the smooth MAA profile as a function of distance from the underlying antireflective coating.

measured by a full contrast study, as shown at the topmost data set. The reflectivity arises from the interferences from the developer/resist, resist/ARC, and ARC/silicon substrate interfaces. The four prominent fringes that appear after the critical edge correspond to the thinnest ARC layer which gives rise to the longest wavelength fringes due to the inverse relationship between film thickness and fringe period. However, additional fringes of higher frequency are convoluted near the maxima of the long-wavelength fringes. These

correspond to the total film structure which is resolved by a multilayer stack model shown as the scattering length density profile to the immediate right in Fig. 6(b). The ordinate is the absolute scattering length density plotted versus distance whereby the abscissa has been shifted to place the ARC/resist interface at zero. The silicon substrate has a Q_C^2 of 1.06×10^{-4} Å^{-2} which transitions through the silicon oxide, ARC, resist polymer, and finally the developer ($Q_C^2 = 3.16 \times 10^{-4}$ Å^{-2}).

The thin ARC layer fringes of thickness of 28 nm are persistent due to the large Q_C^2 difference and sharp interfaces with the silicon substrate and resist polymer. The ARC/resist interface remains sharp with interfacial width of 12 Å indicating negligible intermixing as expected between cross-linked network/polymer interfaces. However, a very diffuse resist/developer interface is required to fit the data. This provides a first indication that the initial broad latent image remains highly diffuse even upon development. The experimental sign of the diffuse resist/developer interface is the lack of fringe persistence associated with the thicker layer. The two interference fringes between 0.025 and 0.035 Å^{-1} convoluted with the first ARC-associated fringe are reduced to a weak doublet near $Q \sim 0.05$ Å^{-1} which flattens the primary fringe. The nonswelling portion of the resist polymer has a scattering length density equal to the dry state indicating no appreciable water sorption in this phase.

The *in situ* rinse with D$_2$O is shown as the third reflectivity curve from the top in Fig. 6(a). In this case the features look similar to the *in situ* developed films; however, slight

FIG. 6. (a) Neutron and x-ray reflectivity measurements with fits in order from top to bottom: 0.065 mol/L TMAH *in situ* development, 0.065 mol/L deuterium labeled TMAH in D$_2$O/H$_2$O mixture, *in situ* rinse in D$_2$O, and *ex situ* dried film. The corresponding scattering length density profiles are shown directly to the right in (b) highlighting the silicon substrate, native silicon oxide, antireflective coating (ARC), and overlying polymer thin film in contact with aqueous solutions for *in situ* development conditions or air for the dried film. All distances are relative to the ARC/polymer interface.

differences appear in the prominence of the interference fringes between (0.025 and 0.035) Å^{-1} and mid-Q region. The Q_C^2 profiles have identical substrate and ARC profiles when compared to the developed case. However, the modification of the resist/developer interface accounts for the subtle reflectivity differences in terms of a reduced swelling by 2 nm, but maintaining a diffuse interface.

The weakly acidic MAA groups must sustain interfacial swelling in D$_2$O; therefore, the predominant resist residual swelling fraction collapse does not occur during this rinse step. In fact, the final dry feature shows reflectivity fringes associated with the total film thickness as measured by x-ray reflectivity in the bottom of Fig. 6. The persistence of the fringes indicates relatively low physical roughness when compared to the *in situ* conditions. The scattering length density profile for x rays is shown in Fig. 6(b). In this case the silicon substrate appears with Q_C^2 of 1.02×10^{-3} Å^{-2} and transitions through the silicon oxide, ARC, polymer, and finally air ($Q_C^2=0$). The physical density profile of the polymer layer is significantly thinner than the *in situ* compositional profiles from neutron reflectivity. Therefore, the highly extended residual swelling fraction undergoes a collapse mechanism to the final feature critical dimension and roughness during drying.

The previous experiments highlighted the total film behavior by using deuterium oxide as the solvent which provides a large scattering length density difference with the film components. However, if the scattering length density of the solvent is reduced to the polymer photoresist, via isotopic mixtures, the film is contrast matched. Therefore, the resist film is invisible to neutrons due to lack of contrast with the solution.[23] Upon addition of deuterium labeled developer to this contrast matched solution, its local distribution may enhance reflectivity because the *d*-TMA molecule has a high Q_C^2.

The reflectivity for this contrast matched condition for development with 0.065 mol/L *d*-TMAH is shown in Fig. 6(a) in the second data set from the top. In this case, lack of a critical edge is because the Q_C^2 of the solvent is lower than that of silicon. However, reflectivity is still observed due to the presence of the ARC layer that provides contrast with the substrate and polymer film. The ARC layer was within 0.5 nm in thickness with the full contrast study experiment. The first reflectivity maxima are distorted, appearing as a doublet. In order to accommodate the additional fringe detail, the contrast must appear in the vicinity of the developer/resist interface, as shown in Fig. 6(b). The solvent and nonswelling resist zone have the same Q_C^2, but an interface with extrema is required to resolve the features of the reflectivity data. The interfacial enhancement is provided by the deuterium labeled tetramethylammonium cations. Therefore, at the developer step, an excess of *d*-TMA ions appears within the residual swelling fraction. This is consistent with the acid-base titration of the weakly acidic MAA groups due to the strong coupling between polyion and counterion observed in model cases of polyelectrolytes in this films[23] as well as in semidilute solutions.[25] These measurements complement the

real-time Fourier transform infrared study within the steady-state gel layer[12] but within the final developer residual swelling fraction.

C. Concentration profiles

The segmental volume fraction profiles are obtained by combining the full contrast and zero-average contrast experiments. The Q_C^2 profile as shown in Fig. 6(b) for the polymer and deuterium labeled TMAH experiments can be expanded into contributions from the polymer (ϕ_p), solvent (ϕ_s), and base (ϕ_B) such that

$$Q_{C,\mathrm{FC}}^2(z) = \phi_p Q_{C,p}^2 + \phi_s Q_{C,s}^2 + \phi_B Q_{C,h\text{-TMA}}^2, \tag{1}$$

$$Q_{C,\mathrm{ZAC}}^2(z) = \phi_p Q_{C,p}^2 + \phi_s Q_{C,s}^2 + \phi_B Q_{C,d\text{-TMA}}^2 \tag{2}$$

for the full contrast and zero-average contrast experiments, respectively. The Q_C^2 of the deuterium labeled base *d*-TMA (4.2×10^{-4} Å^{-2}) differs from that of the protonated TMA (-3.2×10^{-5} Å^{-2}) and in the zero-average contrast experiment, the isotopic solvent mixture scattering length density equals that of the polymer. The physics of the problem should lead to equivalent volume fraction profiles between the two experiments. Using an incompressible assumption for the mixing of the species ($\phi_p + \phi_s + \phi_B = 1$), the base and polymer profiles are determined by

$$\phi_B(z) = \frac{Q_{C,\mathrm{ZAC}}^2(z) - Q_{C,p}^2}{Q_{C,d\text{-TMA}}^2 - Q_{C,p}^2}, \tag{3}$$

$$\phi_p(z) = \frac{Q_{C,\mathrm{FC}}^2(z) - Q_{C,s}^2 - \phi_B(Q_{C,h\text{-TMA}}^2 - Q_{C,s}^2)}{Q_{C,p}^2 - Q_{C,s}^2}. \tag{4}$$

The base profile is obtained directly because $Q_{C,p}^2$ and $Q_{C,s}^2$ are equal, while the volume fraction profile of the base is required to analyze the polymer profile in the full contrast experiment. The raw experimental data in Fig. 6(b) provide all the physical length scales. However, the conversion to the volume fraction profiles highlights the concentration regimes that occur at the line edge due to the residual swelling fraction, as illustrated in Fig. 7(a).

The volume fraction profiles (ϕ_i) for each component are plotted as ϕ_i versus distance from the ARC/resist interface. The polymer segment profile resolves the dense nonswollen region and transitions to the RSF. The concentrated phase ($\phi \approx 1$) to semidilute and dilute regimes is observed by these profiles, whereby the long tail in polymer concentration occurs in a dilute solution regime assuming a homogeneous phase. This implies that the low molecular weight polymers must associate to form the swollen line edge reminiscent of associating polymers. In such a case, the entropy gained by dissolving into the solution cannot overcome the association energy due to the hydrophobicity.

The lower composition limit for swelling from the polymer segment profile [Fig. 7(a)] appears at a depth of 54 nm corresponding to a MAA fraction of 0.095 from the dry latent image (Fig. 5). Therefore, the deprotection limit for the residual swelling fraction is lower than that determined from

FIG. 7. (a) *In situ* development volume fraction profiles for the polymer segment, D_2O, and deuterium labeled tetramethylammonium counterion (*d*-TMA⁺) as a function of distance from the antireflective coating/polymer interface. (b) *In situ* rinse and *ex situ* dry polymer composition profiles measured by neutron and x-ray reflectivity, respectively.

single layer films, which was near 0.30 mol fraction MAA. In the single layer case, the initial photoacid distribution is uniform and the deprotection process leads to chemically heterogeneous films, which at low deprotection extents are comprised of well-separated deprotection domains.[26] These diffuse deprotection domains percolate and overlap with longer post-exposure bake reaction time.[27] The percolation of MAA domains was correlated with the onset of swelling. However, at the feature line edge, the photoacid diffusion will lead to a highly connected or percolated structure as the photoacid follows multiple diffusion paths defined by the protected and deprotected species.[28] The resulting broad interface completely dissolves at the solubility switch, but the water and developer will swell to the lower composition limit (0.095 volume fraction MAA). Below this deprotection level, the water and developer are effectively excluded. This may arise from randomly distributed MAA groups leading to films that are too hydrophobic to allow unfavorable water-MAdMA contacts. Alternatively, the hydrophilic MAA may be nonuniformly distributed into isolated pockets[21] or channels,[29,30] such that while water can find a pocket of hydrophilic moieties, the surrounding stiff hydrophobic matrix prevents volume expansion.

The *d*-TMA profiles achieve a peak concentration of 5% by volume and are enriched over the bulk volume fraction (0.55% by volume) because of the high concentration of weakly acidic MAA groups within the residual swelling fraction. The process by which *d*-TMA is enhanced is partially due to the local titration of the high concentration of MAA segments. The decay of the *d*-TMA profile to zero may come as a surprise considering the finite deprotection extent toward the substrate (Fig. 5) expected by the latent image. The further suppression of TMA in addition to water within the RSF is likely due to the additional requirement for the TMA ion to carry its hydration shell.[31,32] The effect of image charge is also possible due to the dielectric constant difference between the pure MAdMA polymer and water. In this case, the free and mobile ion responds to an effective repulsive potential set up by the dielectric constant difference. The decay of *d*-TMA to the bulk is expected by the low concentration of polymer segments, as well as dilute bulk solution concentration.

The *in situ* water rinse of Fig. 7(b) shows the persistence of swelling with slight shrinkage, but the RSF remains highly diffuse. This behavior was not previously known due to the few measurements available to depth profile the nanometer scale solid/liquid interface. Materials which exhibit true etchlike development fall into a separate class, as noted by Hinsberg *et al.*[12] In the present case, the MAA, a hydrophilic moiety, ionizes in water, as demonstrated in model polyelectrolyte systems such as brushes and gels. In the present case, both the developer and the water rinse may be regarded as good solvents for the RSF. In previous photoresist generations, such as those incorporating hydroxystyrene, the water should be a poor solvent, since poly(hydroxystyrene) is not water soluble. Therefore, the swelling collapse should occur more prominently during the water rinse step.

Lastly, the RSF collapse occurs during the drying process [Fig. 7(b)] whereby the physical mass density profile was determined by x-ray reflectivity [Fig. 6(b)]. In this experiment, the thin films were permitted to air dry, causing the substantial collapse of the swollen phase. The area under the segmental profiles is the total volume of the polymer. Therefore, the final thickness obtained from an ideal collapse can be calculated from a line that partitions equal areas. The calculated final thickness with ideal collapse and no interfacial roughness should be 78 nm. However, the experimental data show the film thickness of 75 nm with a surface roughness of 7 nm. Therefore, the roughening at the interface contributes to a nonideal film collapse.

This final roughness may limit future device scaling; therefore, material approaches are required if chemically amplified photoresists are to be used for sub-32-nm features. These fundamental measurements support a mechanism by which resist polymer chains can rearrange in a dilute swollen phase, as well as segregate to the surface. Therefore, the nonideal collapse can cause segregation of polymer groups based on chemical mismatch (hydrophobicity) or possibly through the intrinsic mechanism of film drying. Controlling the swelling and collapse via polymer chemistry, solvent quality, and molecular weight are crucial areas of interest with regards to these chemically gradient interfaces.

IV. CONCLUSIONS

An improved insight into the mechanism of development, rinse, and drying at a gradient line edge was provided by *in situ* neutron reflectivity. The direct measurements highlight a

residual swelling fraction during the development and rinse processing steps with a lower composition limit for swelling at a gradient interface. Evidence directs to a highly associated and swollen phase present at the line-edge region during development. The swelling persists during the water rinse step and collapses during the drying process which leads to the final surface roughness. A mechanism of a simple transfer of roughness from the latent image to the developed image is challenged by these data due to the surface swelling polymer layer. In order to capture these nanometer scale effects, both percolation and penetration of developer and polymer associative behavior are required. These results may provide needed insights to line-edge roughness and defect reduction as the feature half-pitch approaches the swelling layer thickness.

ACKNOWLEDGMENTS

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