Lateral length scales of latent image roughness as determined by off-specular neutron reflectivity

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A combination of specular and off-specular neutron reflectometries was used to measure the buried lateral roughness of the reaction-diffusion front in a model extreme ultraviolet lithography photoresist. Compositional heterogeneities at the latent reaction-diffusion front has been proposed as a major cause of line edge roughness in photolithographic features. This work describes the experimental observation of the longitudinal and lateral compositional heterogeneities of a latent image, revealing the buried lateral length scale as well as the amplitude of inhomogeneity at the reaction-diffusion front. These measurements aid in determining the origins of line edge roughness formation, while exploring the material limits of the current chemically amplified photoresists.

The ability to form lithographic features exhibiting line-edge roughness (LER) below 2 nm is a major challenge in the formation of sub-32-nm lithographic features.1 In an effort to understand the material and processing origins of LER, a great deal of research has been directed at comprehending the impact of exposure,2–4 latent image formation,5,6 and development7–9 on roughness formation. It has been surmised that all of these steps can influence the LER of developed features, although the individual contributions from each of these interdependent processing steps are poorly understood. In particular, the reaction step, in which activated photoacid molecules catalyze reactions in the exposed regions of the photoresist, has been linked to roughness formation through diffusion of acid molecules into unexposed areas.10–14 Here, we present the first direct measurement of the composition distribution both across and parallel to a reaction-diffusion front in a photoresist film. These measurements will provide crucial insight into the role of the reaction-diffusion process in determining the material limits of LER in lithographic features.

In this work, a model extreme ultraviolet lithography (EUVL) photoresist copolymer is used in a polymer-polymer bilayer geometry that mimics an ideal exposure line edge.15,16 The bottom layer is a polymer loaded with photoacid generator (PAG) molecules, which acts as the exposed portion of the film. The top layer is the photoresist copolymer in which the protecting group was deuterated to provide neutron scattering length density contrast between protected and deprotected forms of the resist. Bilayer thin films of poly(hydroxystyrene-co-d9- tert-butyl acrylate) (PHOST-co-d9-TBA) on poly(hydroxyladamantyl methacrylate) (PHAdMA) were prepared on 76.2 mm (3 in.) diameter by 5 mm (0.197 in.) thick float glass substrates using subsequent spin coating steps, as described previously.16 The PHAdMA bottom layer contained 6% by mass of triphenylsulfonium perfluorobutane sulfonate photoacid generator. Postapply bake steps were performed at 130 °C for 60 s to remove residual solvent. This initial, unexposed bilayer film was characterized using specular and off-specular neutron reflectivity, as described below. The same bilayer film was then exposed to a broadband 248 nm light for 10 s (Oriel Instruments), resulting in a dose of 2.6 ml/cm2 and postexposure baked (PEB) at 90 °C for 180 s. Specular and off-specular neutron reflectivity measurements were then completed in an identical manner to the unexposed bilayer.

Specular and off-specular reflectivity measurements were performed at the NIST Center for Neutron Research on the Advanced Neutron Diffractometer/Reflectometer (AND/R) beam line.17 The neutron wavelength (\(\lambda\)) was 5.00 Å with a wavelength divergence (\(\Delta\lambda/\lambda\)) of 0.02. Specular measurements were done over a \(Q_z\) range of 0.012–0.120 Å−1, where \(Q_z=(4\pi/\lambda)\sin(\theta)\) and \(\theta\) is the specular angle of reflection. Fits to the data were calculated using NIST REFLFIT software18 to determine the interfaces width \(\alpha_{\text{spec}}\).

During the PEB step, the photoacids in the PHAdMA layer diffuse into the photoresist layer, catalyzing deprotection reactions. The t-butyl protecting groups are deuterated labeled, thus allowing the direct observation of the deprotection reaction-diffusion front propagation using neutron reflectometry. Specular neutron reflectometry measurements were done to determine the shape and spatial extent of the reaction-diffusion front. Shown in Fig. 1 is the deprotection front, both before and after PEB. The deprotection extent was calculated from the scattered length density profile, which was determined from fits to the reflectivity curves. The reaction-diffusion front width \(\sigma_{\text{spec}}\) was found to be 79 Å, determined from the measured interfacial width of the reacted sample minus the initial bilayer interfacial width. This result was consistent with observations from our previous measurements on the same photoresist copolymer,16 where the reaction front shape was modeled as an exponen-

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apparent decrease in roughness upon reaction is largely caused by an increase in the width of the reaction front; from a step function to one with a 79 Å width. In order to quantify the interplay between interface width and roughness, the fitting parameters were systematically changed to obtain the most reliable fit to the data. Figure 3 shows calculations of the diffuse scattering compared to data taken after PEB at a $Q_z$ of 0.022 Å$^{-1}$. If the entire 79 Å interfacial width is modeled by a lateral compositional inhomogeneity, the result (dotted curve) overestimates the diffuse scattering intensity. In the other extreme, if the reaction front is modeled as a smooth reaction gradient without any lateral compositional inhomogeneity, the result (dashed curve) underestimates the diffuse scattering. The best fit was obtained by a combination of these extremes whereby a lateral compositional inhomogeneity was added at the leading edge of the reaction front while the backend or the region with high degree of reaction stays laterally smooth. The result, shown as the solid curve in Fig. 3, is calculated with a combination of a smooth 75 Å wide compositional gradient and a 25 Å amplitude roughness superimposed at the leading edge of the reaction front. In all cases, $H$ was kept fixed at 0.3. The dotted line in Fig. 3 is the neutron wavelength, $2\pi/\lambda$, the scattering angle, and $\omega$ is the angle of incidence.
1 marks the depth where the deprotection level is at 0.2. For \(\text{P(Host-co-}d_4\text{-TBA)}\) to dissolve in 0.26 mol/L tetramethylammonium hydroxide (TMAH), which is a typical base developer used in lithographic processing, the deprotection level has to be 0.2 or above.

The lateral length scale \((\xi)\) of the compositional inhomogeneity is estimated by comparing the experimental results to the theoretical curves calculated with different values of \(\xi\), as shown in Fig. 4. At \(\xi\) equal to 8000 Å the calculated result fits well not only the diffuse scattering around the specular peak but also the intensity of the Yoneda peak. For the initial bilayer before reaction, the value of \(\xi\) is 15 000 Å. A lateral correlation length of 8000 Å is considered to be very large in semiconductor applications where the relevant length scale is between 500 and 2000 Å.

Off-specular reflectivity provides a complete picture of the buried deprotection reaction-diffusion front in a model EUV photoresist copolymer. These measurements show the latent image possesses a low-amplitude, low-frequency inhomogeneity or roughness at the tip of the reaction wave front. This inhomogeneity occurs at a depth beyond the solubility switch for the resist in 0.26 mol/L TMAH, which may diminish the role it plays in roughness formation. Instead, other processes in lithographic feature formation, such as the swelling and deswelling that occur during development, may play more of a role in determining feature quality. Measurements of the lateral length scales at the solid-fluid interface during development will be key in understanding this effect.

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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.

Fig. 3. (Color online) Off-specular transverse scan at \(Q_z\) of 0.022 Å\(^{-1}\) with calculations for a rough interface (dotted), a smooth gradient interface (dashed), and a combination of the above two (solid).

Fig. 4. (Color online) Off-specular transverse scan at \(Q_z\) of 0.022 Å\(^{-1}\) with calculations of the diffuse scattering of various correlation length \(\xi\).