# Reaction Front Induced Roughness in Developed Chemically Amplified Photoresists

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## INTRODUCTION

The effect of line edge roughness (LER) is an increasingly important problem as lithographic feature dimensions shrink to the sub-100 nm level. Previous experiments have demonstrated several key material properties that influence LER, such as incompatibility between protected and deprotected components [1], casting solvents, base additives and photoacid generators [2], as well as process conditions such as X-ray or UV dosage to mask and post-exposure bake protocols [3]. Due to the chemical amplification process, line edges are polymer-polymer interfaces, hence are precursors to the LER problem. These interfaces have a distinct and measurable interfacial width and will be present regardless of lithographic feature shape. Thus model interfaces may be used to understand sources of LER.

In the feature development step one component is preferentially dissolved from this buried interface with an aqueous base solution. This development step is critical to the final feature as the developer is anticipated to resolve features by dissolving polymer through this buried concentration gradient interface. It has been demonstrated using neutron and X-ray reflectivity that the buried interfacial width in model line edges is broadened during the post-exposure bake (PEB) step. Subsequent development reveals that the average surface roughness is much less than the prior interfacial width, yet greater than the as-spun photoresist [4]. This highlights the ability to develop features in the presence of a deprotection gradient. From reflectivity studies, height and lateral fluctuations are averaged to provide only a one-dimensional estimate for the surface roughness. However, with tapping-mode atomic force microscopy (AFM) these correlations are able to be distinguished.

We will present recent experimental work regarding the effect of PEB times and developer on surface roughness using model interfaces of deuterium-labeled poly(tert-butyloxycarbonyloxy styrene) and poly(hydroxystyrene), d-PBOCSt and PHOSt, respectively. This study compliments X-ray and neutron reflectivity experiments, which measure the profile width as functions of PEB time and temperature.

## EXPERIMENTAL

Bilayer structures were prepared on cleaned silicon wafers primed with hexamethyldisilazane vapor (HMDS). The lower layer consisting of the d-PBOCSt [4] ($M_{r,n}$ = 21000, $M_{r,w}/M_{r,n}$ = 2.1) was spin-coated from a propylene glycol methyl ether acetate (PGMEA) solution and post-apply baked (PAB) for 90 s on a 130 °C hotplate to remove residual solvent. The corresponding deprotected polymer, PHOSt ($M_{r,n}$ = 5260, $M_{r,w}/M_{r,n}$ = 1.12), was spin-coated from a 1-butanol solution directly onto the lower layer. The PHOSt layer is loaded with a 5 % mass fraction of the photoacid generator, di(*tert*-butylphenyl) iodonium perfluorooctanesulfonate. The bilayer is subjected to another PAB for 90 s at 130 °C. The model bilayer stack was exposed with a dose of 1000 mJ/cm$^2$ to broadband UV radiation to generate acid within the top PHOSt layer followed by PEB at 110 °C for varying times of 15 s, 20 s, 30 s, and 90 s. The original PHOSt layer and the soluble deprotected d-PBOCSt reaction products were removed (developed) by immersion in a 0.26 N tetramethylammonium hydroxide (TMAH) solution for 30 s followed by a rinse with deionized water.

## DISCUSSION

After a blanket UV exposure, the bilayers were baked for varying times from (10 to 90) s. The variation in bake time serves to control the depth of penetration of the acid and hence the profile of the deprotection front. Larger bake times result in larger interfacial widths between the two layers. Measurements of this front by reflectivity provide an average profile. To investigate the surface roughness induced by this propagating reaction-diffusion front, the developed bilayer interfaces were subsequently measured using AFM in tapping mode with a silicon nitride tip.

The images shown in Fig. 1 demonstrate the evolution of the resulting surface morphology, representative of a line edge, as the width of the deprotection front increases. As bake time increases, the average surface roughness increases from (1 to 5) nm, however the surfaces are not laterally homogeneous. Initially, the bilayer is smooth with residual particulates remaining from the developing stage. Further washing with water did not remove these particulates. After short bake times, the surface possesses a dual morphology with deep pits within a shallow variable topology. The variable topology is characteristic of developed surfaces in uniformly deprotected films, independent of the level of deprotection.

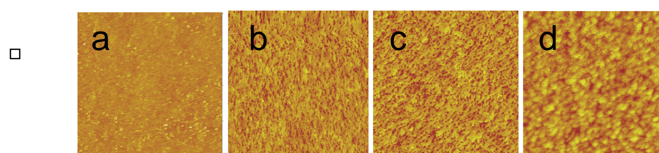


**Figure 1.** Tapping mode AFM images from model bilayers [Si/HMDS/d-PBOCSt/(PHS/PFOS)] after development following PEB times of a) 15 s b) 20 s c) 30 s and d) 90 s. Dimensions of AFM images are 30 nmx30 nm.

The morphologies in Fig.1 have been further quantified using a histogram of depths, shown in Fig. 2. This analysis demonstrates that as the width of the deprotection profile increases, the profile broadens asymmetrically, producing a bimodal distribution. However, at long bake times, the overall width of the distribution has doubled the initial, unbaked, roughness and recovered a symmetrical shape. The images demonstrate that the deprotection front is spatially inhomogeneous during short bake times and evolves into a homogeneous broad front. The origin of the spatial inhomogeneity and the dual morphology are still unknown.

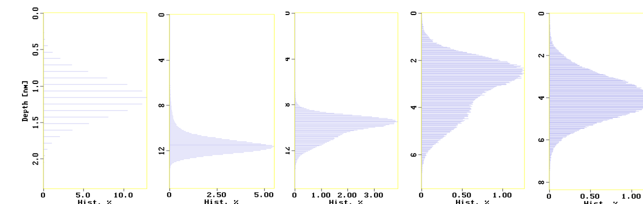

**Figure 2.** Depth histograms from the AFM topology images from developed bilayer films after development following varying PEB times, from L to R, a) pure PBOCSt film b) 15 s c) 20 s d) 30 s e) 90 s.

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