Measurements of the Latent Image in Chemically-Amplified Resists

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Projection lithography is the primary technology used for patterning semiconductor devices. High-throughput manufacturing requires resists that are highly sensitive to radiation, and this demand is satisfied through a process termed chemical amplification (CA). CA resists are based on a polymer resin (reactant) blended with a photoacid generator (catalyst). Image resolution is controlled by slow diffusion of the ionic catalyst. Ionic diffusion in polymer matrices is highly sensitive to free volume and segmental motion, and these dynamical properties are coupled to extent of reaction, temperature, film thickness, and strength of polymer-substrate interactions.[1] Currently, there are no experimental methods that provide feedback for image formation with three-dimensional spatial resolution. The lack of data makes it difficult to build quantitative models for reaction front propagation in thin films.

We demonstrate that transmission X-ray diffraction can measure spatial extent-of-reaction in ultrathin films of a model CA resist. The CA resist is poly(4-hydroxystyrene-co-tertbutylacrylate) (PHOST-PTBA, 60% PHOST) loaded with 4 wt% triphenylsulfonium sulfonate photoacid generator. Thin films are cast on silicon nitride membranes. The spatial distribution of photoacid is generated with electron beam lithography (0.3 nC/cm at 30 keV), and deprotection reactions are completed at temperatures in the range of 90-100°C. The lithographic process generates a pattern of deprotected polymer nanolines in a protected polymer matrix, and a measurement of the line grating surface is included in Figure 1a. Transmission X-ray diffraction data are acquired at the Advanced Photon Source of Argonne National Laboratory. The latent image structure is calculated from diffraction data through an inverse solution method:[2] First, we build a model for the structure of deprotected polymer patterns that includes the size, shape, and periodicity of the nanolines, as well as the average width of the deprotection interface. Second, we refine each model parameter through nonlinear regression to obtain agreement between simulated and experimental diffraction profiles. Examples of X-ray diffraction data with the best-fit to a trapezoidal shape model (Figure 1b) are included in (Figure 1c). We find evidence of faster reaction front propagation at the free surface than the polymer-substrate interface, and this behavior generates a sidewall angle of approximately 36° (Figure 1d). We also find that the width of the deprotection interface is nearly independent of post exposure bake (PEB) time but increases with PEB temperature (Figure 1e). To our knowledge, these data offer the first feedback for image formation in thin films of CA resists. These data are very valuable for understanding the effects of interfaces on the coupled reaction-diffusion process.

[1] International Technology Roadmap for Semiconductors, 2009.
[2] Tengjiao Hu, Ronald Jones, Wen-li Wu et al., Journal of Applied Physics **96** (2004) 1983-1987.

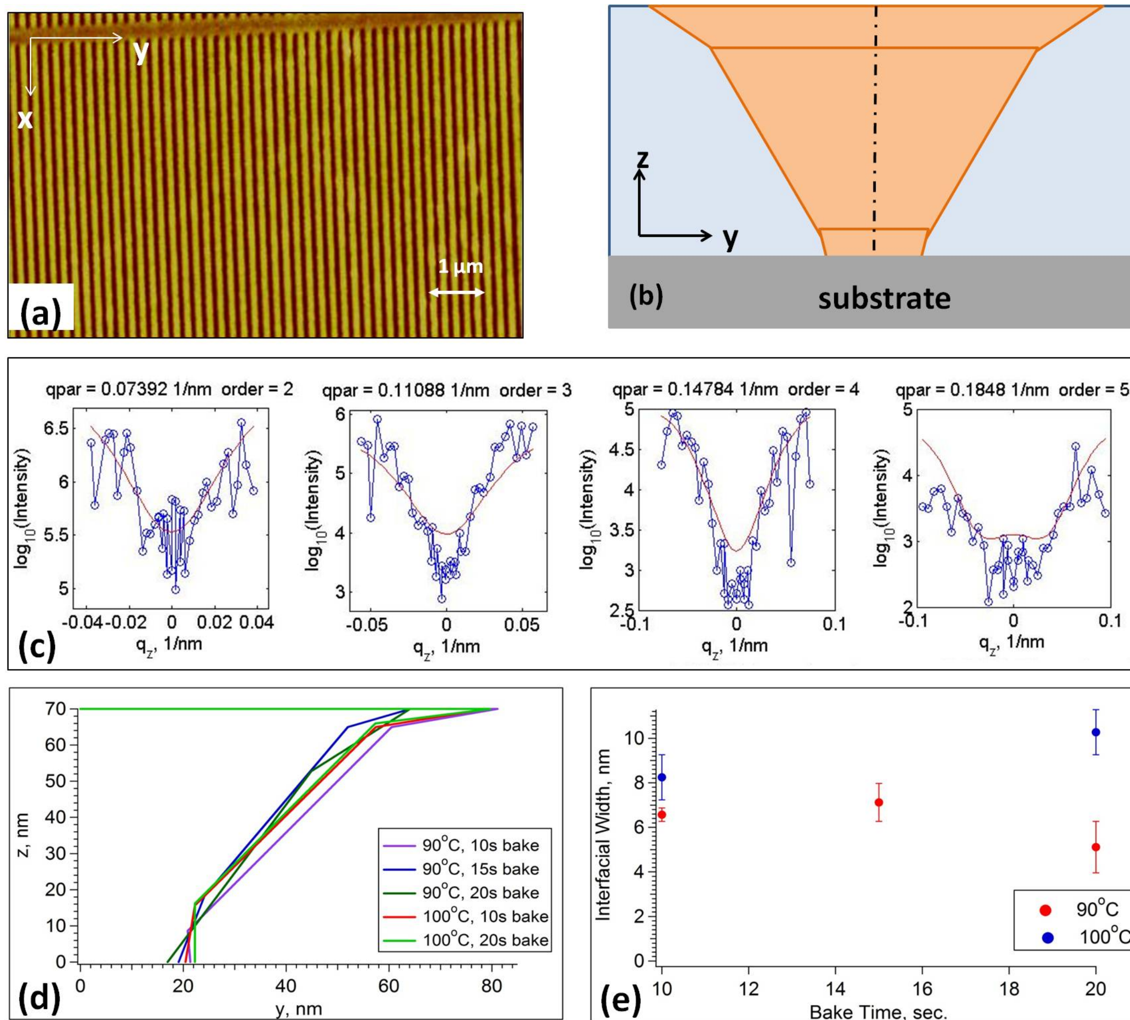

Figure 1: (a) AFM micrograph of a 170 nm pitch line grating. Post-exposure bake temperature was 90°C. (b) Schematic of the trapezoidal model. (c) Diffraction data for a 170 nm pitch line grating that was post-exposure baked for 20 sec at 90°C. Solid line is the best fit to a model based on a stack of three trapezoids. (d) Resulting domain shapes from the best-fit model at post-exposure bake temperatures 90 - 100°C and bake times 10, 15 and 20 sec. (e) Width of the deprotection interface as a function of post-exposure bake temperature and time.