Measurement of Acid Induced Blur in Polymer Films by Single-Molecule Fluorescence Microscopy

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Chemically amplified (CA) resists represent a major component in the semiconductor industry's ability to continue to pattern smaller features onto silicon wafers to allow for faster, more powerful devices. The chemical amplification, achieved through the catalytic deprotection of labile blocking groups attached to a polymer chain by photochemically generated acid, has afforded lithographers the ability to utilize lower intensity light sources while maintaining the high throughput required of an industrial scale process. However, this catalytic process does have drawbacks. It relies upon the diffusion of an acid to cause deprotection of a sufficient number of acid labile groups to realize a developable change in the solubility of the polymer. This also means that the acid can diffuse out of the originally exposed area. This results in blurring of the latent image which, due to the stochastic nature of diffusion, means that the line edge becomes less uniform. The ability to analyze the deviation from the intended pattern resulting from acid diffusion alone will allow the processes of latent image formation and resist development to be deconvolved, enabling more effective design of the resist components.

Fluorescence microscopy is ideally suited for this task for three reasons: 1] acid sensitive fluorophores have been developed that can be used to indicate acid generation in resist films; 2] very few fluorophores need to be activated in order to provide an accurate representation of the acid diffusion profile; 3] fluorescence microscopes are widely available and inexpensive. While this technique has been attempted previously,[1] the fluorophore utilized required a more complicated setup and did not provide an on/off fluorescence response to acid generation. Additionally, new techniques have been developed recently that allow for sub-wavelength resolution,[2] offering the possibility that this method could be extended to view the diffusion blur at resolutions approaching 10 nm. In this paper, measurement of the acid image and latent images from e-beam patterned resist will be shown through the use on an inverse stochastic optical reconstruction microscopy (STORM) technique. Using a centroiding algorithm, fluorophores found in these patterns are located to sub-5 nm accuracy and these positions are then subsequently utilized in a maximum likelihood estimator to reconstruct the initial written pattern as well as the blur associated with the post exposure bake step. This work should allow for the decoupling of effects from acid diffusion, deprotection and development, which to this point have been exceedingly difficult.

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[1] G. D. Feke, Q. Wu, R. D. Grober, *Appl. Phys. Lett.* **1998**, *73*, 408.
[2] X. Zhuang, *Nature Photonics* **2009**, *3*, 365.

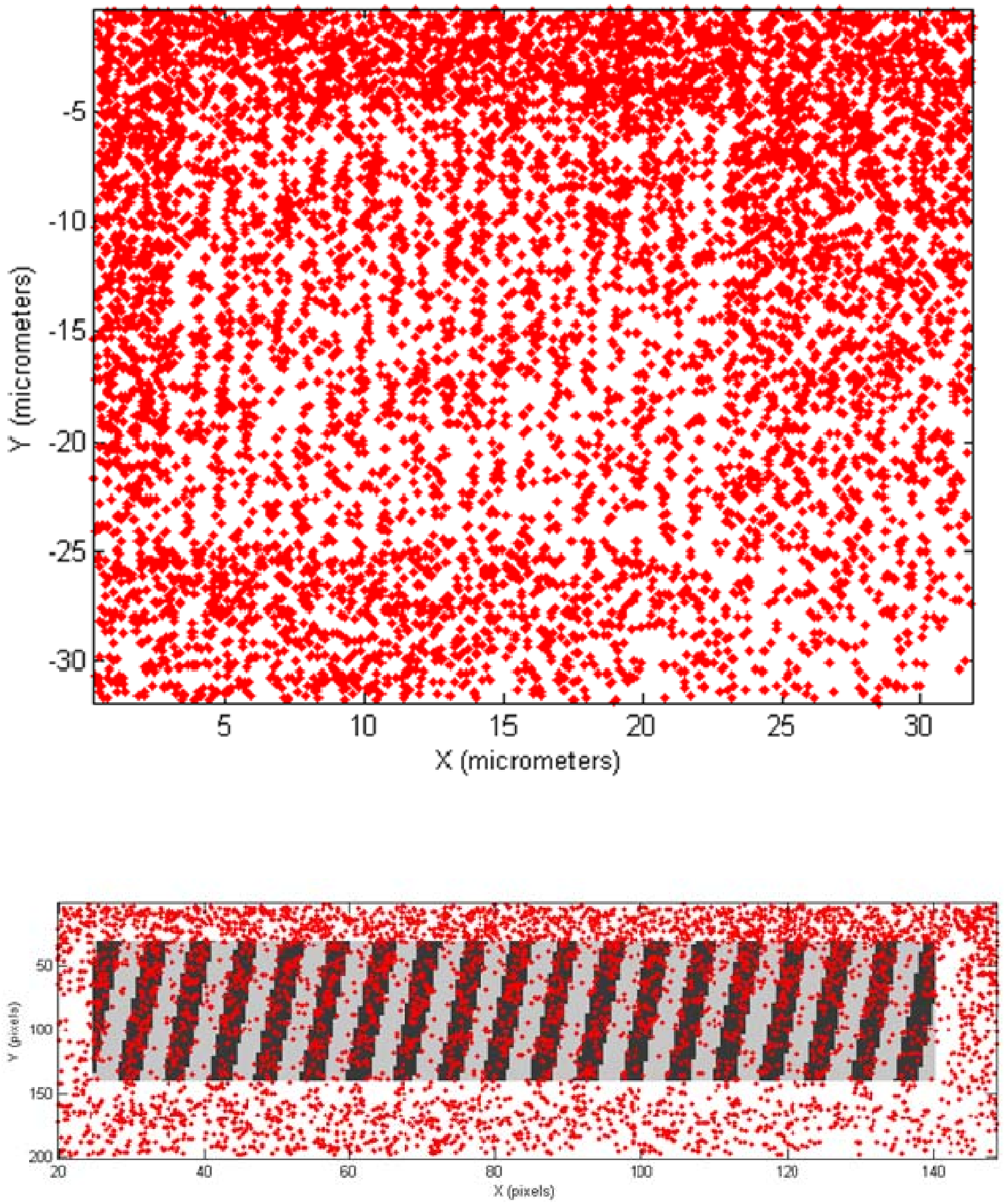

Figure 1: Inverse STORM image before application of maximum likelihood estimator (top) and after (bottom). The vertical scale in the bottom image has been compressed to make the alignment of the data points (red) with the features calculated by the maximum likelihood estimator more apparent.