

Imaging of photogenerated acid in a chemically amplified photoresist

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Chemically amplified photoresists are widely used throughout the semiconductor industry due to the need for high throughput in the lithography process. Knowledge of the location of acid molecules in chemically amplified resists is of paramount importance for the process control of the image formation of almost all the lithographic techniques used in the semiconductor industry today. We have demonstrated a technique based on *pH*-dependent fluorescence which can measure *directly* the spatial distribution of the photoacid in photoresist films without the need of any other subsequent process after exposure. By adding a small amount of fluorescent material to the resist, a latent image can be formed when photogenerated acid molecules quench the fluorescence in exposed areas. We demonstrate images formed after exposure of SAL605 resist films to x-ray radiation, with no post-exposure bake, and show that the optical contrast is a function of dose. We also show that the same technique can be utilized for rapid evaluation of photoacid generator efficiency. © 1998 American Institute of Physics. [S0003-6951(98)02429-2]

As the exposure wavelength of modern microlithographic tools continues to decrease, chemically amplified photoresists¹ are becoming more important. Chemical amplification serves to increase the sensitivity of photoresists by creating a photogenerated catalyst (typically a strong acid) during exposure. During a post-exposure bake (PEB), this acid acts as a catalyst for further reactions. Thus, one incident photon can be responsible for many chemical events.

Knowledge of the location of the photogenerated acid is crucial for understanding resist behavior. Issues such as acid diffusion during bake steps can affect critical dimension and linewidth variation in a level. Since it is extremely difficult to make optical contact with the acids directly, their location is generally inferred from scanning electron microscopy (SEM) images of developed patterns. These exposed images, however, are convolved with subsequent processes such as resist chemistry, baking, and chemical development. For this reason, it is desirable to have a method of detecting latent images in exposed photoresist which allows direct determination of acid location.

Previous studies of latent images have been undertaken with a variety of methods, including atomic force microscopy² and photon tunneling microscopy.^{3,4} These techniques rely on contrast mechanisms resulting from topographic and/or refractive index variations in exposed resist. It would be desirable, however, to have an imaging technique which is sensitive directly to the presence of the photogenerated acid molecules. This is the focus of the experiments in this letter.

In biological applications, it is often desired to have a quantitative measure of proton concentration in a material. In order to make this measurement, fluorescent molecules have

been developed whose fluorescence intensity is a strong function of *pH*.⁵ These fluorophores may be good candidates for use as detectors for photogenerated acids in chemically amplified photoresists. In this letter, we describe experiments performed on an undyed formulation of SAL605⁶ (and similar formulations), an e-beam/x-ray, negative tone, chemically amplified photoresist. This resist system is extremely well characterized^{7,8} and has higher environmental stability than many positive-tone resists.

The experimental technique we have developed involves adding a small amount of *pH*-sensitive fluorescent material to the photoresist casting solution, and then processing the resist in the standard fashion. After exposure, locations where acid molecules have been created exhibit lower fluorescence, revealing the latent image. The resist is illuminated with the 514 nm line of an argon-ion laser, using a 0.8 NA 100× microscope objective. It should be noted that the resist is insensitive to this wavelength; only the fluorophores are excited. The fluorescence is collected with the same optic, and is imaged onto an avalanche photodiode. Two holographic notch filters remove the pump wavelength from the detector. The background signal on the detector is dark-count limited at approximately 20 counts/s, while the measured fluorescence is orders of magnitude larger. The wafer sits on a scanning platform which is controlled by a computer. Images are formed by rastering the wafer through the pump beam and collecting fluorescence at each point. Due to amplitude fluctuations in the laser, there is an inherent uncertainty of $\pm 0.5\%$ in the laser power during the measurements.

Since the as-spun *pH* of SAL605 films is slightly acidic (effective *pH* = 4),⁹ it is important to choose a fluorophore with an appropriate pK_a . We have investigated the Rhodol derivative Cl-NERF^{10,11} (pK_a = 3.8 in water), whose fluorescence intensity is reduced in the presence of acids. Since we do not want to influence the basic resist performance, small

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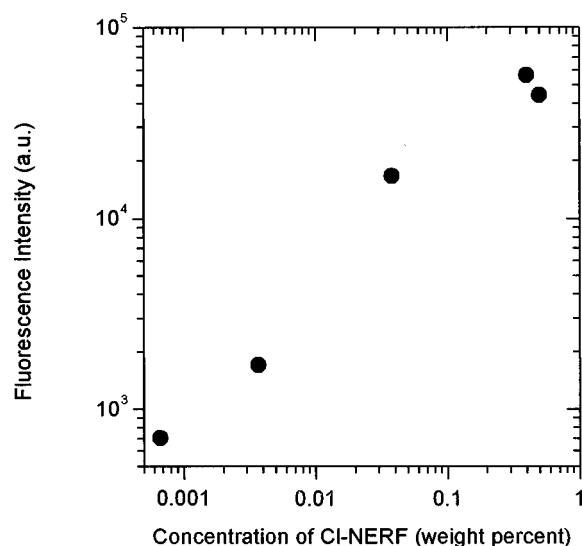


FIG. 1. Fluorescence intensity as a function of CI-NERF concentration in $0.5 \mu\text{m}$ thick SAL605 films. At higher weight percents, the fluorescence intensity is reduced by self-quenching of the fluorescent molecules. The error at each data point is $\pm 0.5\%$ due to laser fluctuations. The uncertainty in fluorophore concentration is $\pm 2.5\%$.

amounts of the fluorescent molecule were added to the resist formulation. The fluorophore is added to the resist casting solution prior to spin coating the resist on the wafer. The wafers were then baked at 118°C for 72 s. Since the dye in SAL605 was found to reduce the measured fluorescence, an undyed formulation of the resist was used.

Figure 1 shows the results of adding various amounts of CI-NERF to $0.5 \mu\text{m}$ thick films; each data point is the average of 50 measurements. The intensity of fluorescence increases as more fluorophores are added to the films, but drops off at high weight percents. We attribute this effect to self-quenching of the fluorophores when the intermolecule spacing is less than $\sim 10 \text{ nm}$.^{12,13} To avoid this problem, as well as to minimize the fluorophores interfering with the resist, we have chosen to use approximately 0.07 wt % of CI-NERF in the resist films for this study.

The samples used to test whether the *pH*-dependent fluorescence of CI-NERF could reveal latent images were 4 in. wafers coated with $0.5 \mu\text{m}$ thick resist films. The wafers were exposed at various doses on an x-ray stepper at the University of Wisconsin, and then imaged on the fluorescence apparatus at Yale University. Figure 2(a) shows a SEM image of exposed and developed photoresist. Figure 2(b) shows a latent image acquired by fluorescence microscopy with a pump power of 50 nW. The image is $10 \mu\text{m}$ on a side, and consists of 100×100 pixels acquired at 100 Hz. The difference in fluorescence between exposed and unexposed regions is approximately 20% for an exposure dose of $350 \text{ mJ}/\text{cm}^2$ measured at the x-ray mask used for the results shown in Fig. 2. This reduction in fluorescence changes with dose accordingly—the contrast drops to 10% for a $200 \text{ mJ}/\text{cm}^2$ exposure, and to 5% for $125 \text{ mJ}/\text{cm}^2$. It should also be noted that latent images are detected without a PEB; this is important if this technique is to be used for photoacid diffusion experiments.

We have also verified that the reduction in fluorescence intensity in the exposed regions is truly due to interaction of

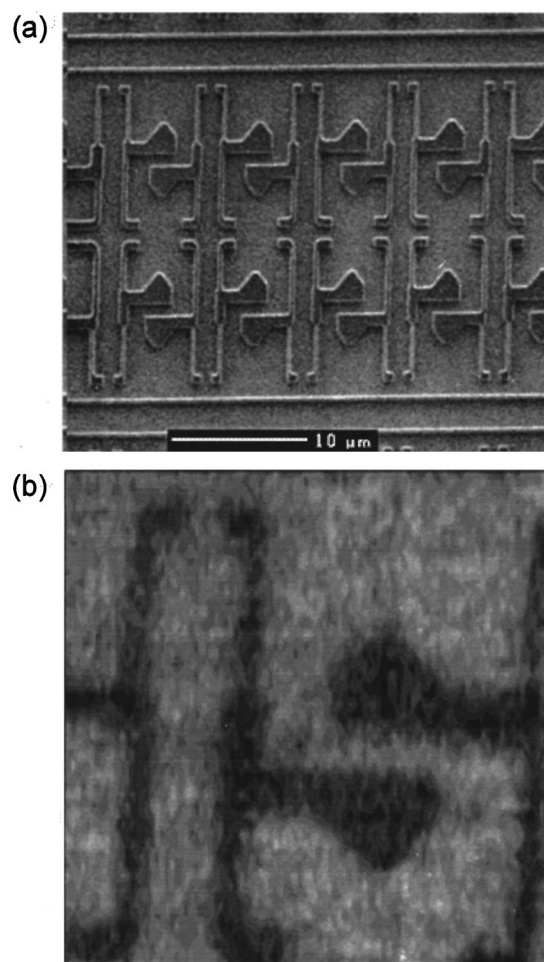


FIG. 2. Images formed by x-ray exposure of $0.5 \mu\text{m}$ SAL605 films. In (a), a SEM image of developed photoresist is shown; the smallest features on the mask are $0.25 \mu\text{m}$ lines. In (b), a $10 \times 10 \mu\text{m}$ latent image is shown, formed by the *pH*-dependent fluorescence of CI-NERF. The fluorescence in the exposed regions has been reduced by the formation of photogenerated acid molecules.

the photogenerated acid molecules with the fluorophores. Two resist samples were formulated, one containing a photoacid generator (PAG) and one without. The PAG was 4,4'-isopropylidene bis(2,6-dibromophenol)^{14,15} 8 wt % against solids in a novolac/hexamethoxymelamine resist. The samples with and without the PAG were processed identically and exposed at various doses. The sample without the photoacid generator showed no optical contrast even at doses as high as $600 \text{ mJ}/\text{cm}^2$. The sample with the photoacid generator showed images at all doses. Thus we are confident that the optical contrast is not due to photobleaching of the fluorophores with exposure.

The spatial resolution of our optical system is 400 nm using 514 nm illumination. However, this technique is scalable to using near-field scanning optical microscopy (NSOM).¹⁶ With the enhanced resolution of this technique, measurement of photoacid diffusion in small lines could be undertaken. NSOM would also be useful for image modeling verification and studies of features as a function of mask/wafer gap and other parameters.

Another area in which this technique can be useful is determination of the efficiency of photoacid generators. When evaluating the response of a PAG, it is necessary to

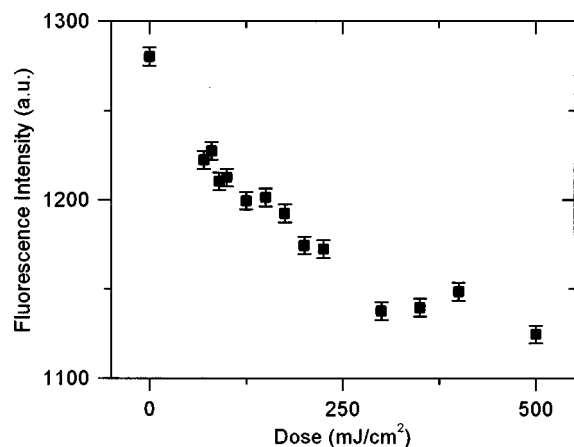


FIG. 3. Fluorescence vs dose for a 0.5 μm thick SAL605 film with 0.07 wt % CI-NERF added. The error bars represent a $\pm 0.5\%$ uncertainty in the laser power during the measurement.

know how many acid molecules are created as a function of dose. This is commonly accomplished by spectrophotometric titration.^{7,17} To map out the response of the PAG as a function of dose can take days. Using our technique, the time to compare the efficiency of one PAG versus another can be reduced to hours. In order to perform this “fluorescence optical titration,” a dose matrix is printed on a single wafer, and the fluorescence at each field is measured. In each field, a $10 \times 10 \mu\text{m}$ area is scanned, and the fluorescence is averaged over all of the pixels. This provides some statistical improvement in the data. The results of this experiment for SAL605 are shown in Fig. 3. This experiment measured the fluorescence from 0.5 μm films with approximately 0.07 wt % CI-NERF added. As the exposure dose increases, more photogenerated acid molecules are created, and the fluorescence decreases. This information could be used to quickly compare the efficiency of two different PAGs, or differing amounts of the same PAG.

The error in this type of measurement is due to two factors: the laser fluctuation noise, and the statistics associated with the photon counting process. Since a large number of data points are averaged, it is appropriate to use a large-sample confidence interval for the mean fluorescence at each point. Due to the extremely large sample size (10 000 measurements at each point), this error is much smaller than the laser fluctuation noise.

Although the amount of photogenerated acid created as a function of dose is linear over the range of doses measured,⁷ the fluorescence data is nonlinear at higher doses. This is likely due to the fact that we are titrating the indicator fluorophore well past its equivalence point. In addition, the overall change in fluorescence we observe from unexposed to exposed pads is approximately 10%. This is less than the optical contrast we observe in the fluorescence images. This could be due to the long time delay between exposure and measurement of this sample due to shipment of samples between Wisconsin and Yale.

In addition, we comment that even though the environmental stability of chemically amplified resists can be quite poor in unfiltered environments, the fluorescence images we see are surprisingly stable with time. Even though the wafers are not stored in a clean room, there is little degradation in

the images for about 24 h after exposure. After a few days, however, the optical contrast begins to decrease, and small features become washed out. This time scale could likely be increased by storing the wafers in a controlled environment.

In summary, we have demonstrated a fluorescence technique for mapping pH gradients in chemically amplified photoresists. This allows the study of latent images formed in the resist, after exposure and without baking or developing the resist, for almost any lithographic technique used in the semiconductor industry today. In addition, this technique has the potential for the rapid determination of photogenerated acid yield among a variety of photoacid generators. Due to the low level of fluorophore required (0.01–0.1 wt %) and high signal-to-noise ratio, it can be used for photoacid yield determination in resists without altering the absorbance characteristics of the film. This is especially important in 193 nm lithography, or exposures using extreme ultraviolet lithography where the exposure depth is only about 200 nm.¹⁸ The technique is also flexible enough to measure other catalysts besides acids; fluorophores sensitive to many different species are available.

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