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A Protocol for the Verification of Acid Generation in 157 nm Lithography

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The quest for feature size reduction has triggered the need for microlithographic imaging processes at very short wavelengths. In the past few years attention has been devoted to 157 nm laser pulses, produced from a fluorine excimer laser and perhaps the shortest practical wavelength for optical lithography.[1−5] Imaging at 157 nm presents numerous experimental challenges largely related to the undesirable high absorbance of most imaging materials, optical components, and many chemicals, including oxygen and water vapor.[6,7] These problems are gradually being solved, but many of these solutions are based on a trial-and-error, largely empirical approach. This may lead to usable materials but contributes little to a rational progression toward the design of new materials with improved performance. For example, while many polymeric materials with low absorbance at 157 nm have been developed, the lithographic process is largely based on photoacid generation from molecules that have never been demonstrated to yield acid upon 157 nm exposure. While this may not be an unreasonable extrapolation from work at other wavelengths (such as 248 nm), the high energy at 157 nm (182 kcal/mol or 7.88 eV) is sufficient to photoionize many compounds and/or cause fragmentation of “normally” photostable chemical bonds; in fact, there is sufficient energy to produce “hot” intermediates in many cases.[8,9]

Thus, a protocol that would validate the acid generation assumptions and that could prove useful in testing or designing new, exclusive VUV photoacid generators (PAGs) would be highly desirable.[10−17] With this in mind, we decided to evaluate possible acid-monitoring schemes, employing both commercial VUV resists and PAG−polymer homemade compositions. While the work in this Communication concentrates on qualitative aspects of acid generation and acid imaging, it is clear that the approach lends itself to future quantification in aspects such as acid yield and dose required to neutralize base content in the resist.[18−20]

The dye selected for these tests was Coumarin 6, which has proven useful in earlier acid-monitoring studies.[10] Naturally, the ideal dye for this work would be one that is transparent at the excitation wavelength. At 157 nm it is impossible to meet this criterion; however, the fact that (a) other components generally have significant extinction coefficients and are present in greater amount, (b) the high sensitivity of fluorescence techniques requires minimal dye concentrations, and (c) films for this work are generally quite thin (≤ 200 nm) all contribute to minimize any interference from dye absorption.

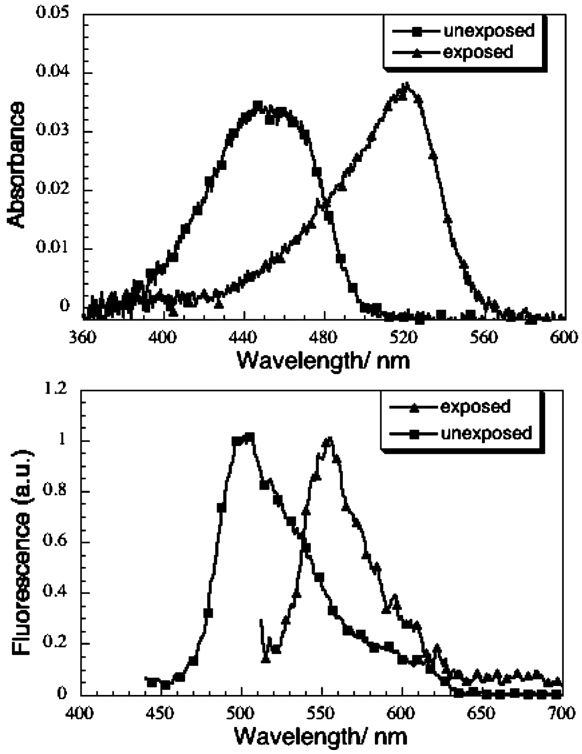
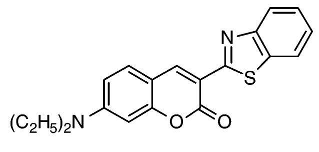


Figure 1. Absorbance (top) and fluorescence (bottom) of both neutral (unexposed, ■) and protonated (exposed, ▲) forms of Coumarin 6. For the fluorescence spectra, $\lambda_{ex} = 410$ nm for the unexposed resist and $\lambda_{ex} = 500$ nm for the exposed resist.



Coumarin 6

As a control experiment, we started by monitoring the absorption and fluorescence of Coumarin 6 in a film under conditions of flood exposure at 254 nm, a wavelength region where acid generation from onium type photoacid generators (PAGs) is well established. Figure 1 shows the absorption and fluorescence spectra obtained from 143.9 nm thick films of exposed and unexposed Shipley resist XP1215Aa, which contains an onium salt as the PAG and has been developed for 157 nm lithography. The photoresist contains a fluorinated polymer from DuPont that has been described elsewhere.[21] In this control experiment 254 nm exposure was achieved with a HTG exposure unit. The film was exposed for 2 min, enough to cause extensive protonation of the dye. The spectra in Figure 1 agree well with those recorded in solution.

Examination of Figure 1 reveals that the differences in absorption and emission spectra for the protonated and unprotonated forms of Coumarin 6 are such as to offer adequate discrimination for imaging purposes. The rest of this Communication takes advantage of this

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characteristic and deals with thin films deposited by spin-coating, followed by a postapply bake (PAB) step and exposure at 157 nm.

The substrates used as support were calcium fluoride or silica disks as well as silicon wafers. The spatial resolution in the figures that will follow does not reflect a limitation in the dye or resist, but rather the local availability of masks and imaging equipment for 157 nm applications. The mask used is of the type employed in X-ray applications, where the transparent features are hexagonal holes in a metallic self-supporting film. The mask used had holes with 62 μm center-to-center distances. Exposure at 157 nm employed an MSX-250 laser from MPB Technologies coupled with the exposure chamber maintained under dry nitrogen. The laser is rated to produce pulses of about 6 mJ; under our exposure conditions it normally delivered approximately 4 mJ per pulse to the sample, and the geometry was such that the actual dose was about 2 mJ cm^{-2} per pulse. At this preliminary stage no effort was made to condition the beam to optimize exposure homogeneity. Approximate film thickness was determined with a Luzchem TFA-11 thin film analyzer, UV−vis dye spectra with a Cary-1 spectrometer, and fluorescence spectra with a Perkin-Elmer luminescence spectrometer LS 50. Film absorbances were determined using the 157 nm laser as a light source and measuring transmitted power through CaF$_2$ substrates with and without the resist film. Fluorescence microscopy employed a Zeiss Universal microscope. Further experimental details are provided in the Supporting Information.

Exposure at 157 nm through the mask gave the images of Figure 2A,B when monitored by fluorescence microscopy using a filter that only allows detection of emission at ≥520 nm for negative images and ≥590 nm for the positive image, ranges mentioned also in the figure caption. The negative and the positive images are shown in parts A and B of Figure 2, respectively. The color in the images reflects the band positions in Figure 1, in combination with the filter systems used (see Supporting Information).

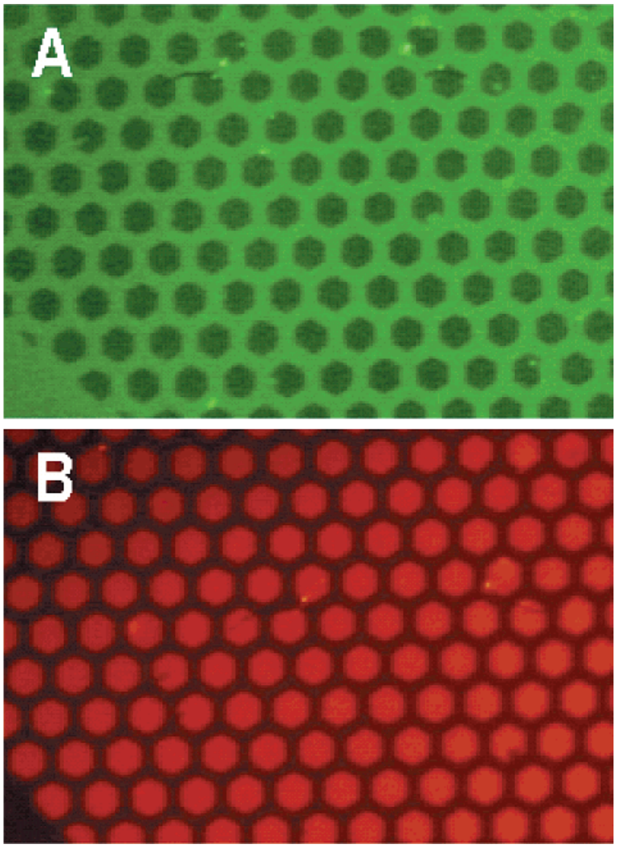

Figure 2. Fluorescent images (true color) of fluorine-containing resist exposed at 2.3 mJ cm^{-2} per shot for 35 shots at 157 nm taken with the fluorescent microscope at excitation wavelengths 485 ± 12 nm (A) for the “negative” image and 546 ± 12 nm (B) for the “positive” image. The edge of the mask perforation pattern is visible at the bottom left of the pictures.

Despite the arguments presented above against potential interference due to dye absorption at 157 nm, it is clear that a negative image could conceivably be obtained by destroying the dye either by direct photolysis or, possibly, by yet unrecognized energy or electron transport mechanisms following 157 nm laser excitation. Thus, it is important to also obtain a positive image and confirm the presence of the protonated dye. This was achieved with fluorescence excitation centered at 546 ± 12 nm and monitoring the emission with a cutoff filter at 590 nm, which only passes light from the red edge of the fluorescence from the protonated dye (see Figure 1). The image is shown in Figure 2B. The choice of excitation wavelength and monitoring of emission was a limitation of the equipment available at the time of the measurements. The fact that both negative and positive images can be obtained from the same exposure by simply adjusting the spectroscopic parameters proves that acid is being generated. We note that while the doses for the onset of fluorescence and for image development are not required to be the same, we generally find them to be quite similar. The dose in Figure 2 was larger than required for imaging; the Supporting Information includes examples where only a few laser shots were used. At high doses and without PAG in the resist formulation, the protonated form of C6 was detected, presumably due to formation of HF following photolysis of the polymer. However, at small energy doses protonation of C6 did not occur, unlike in the case of resist containing PAG where the protonated form of C6 was detected after only one shot (~2 mJ/cm^2), obviously due to formation of acid following PAG photolysis.

It is a common practice to add a small amount of base to photoresist compositions as a tool for contrast enhancement. In this case with Shipley resist XP1215Aa, the first laser shot did not produce a fluorescent image, while subsequent shots did. This also provides confirmatory evidence that fluorescence imaging results from acid generation in the exposed regions because one laser shot did not produce enough acid to neutralize the base present.

Acid-specific imaging was explored in a variety of resist compositions and polymers/PAG mixtures (see details in Supporting Information). The film thickness ranged from ca. 70 nm up to >2 μm; imaging was successful in all cases, although we note that in the case of a 2342 nm thick PMMA film the resolution was poor compared with the images in Figure 2. The absorbance of this film at 157 nm was 8.5/μm, thus leading to excessive absorbance and an unacceptable exposure gradient, with virtually no light penetrating to the substrate−polymer interface.

In summary, the results of Figure 2 and of the Supporting Information confirm that the 157 nm photodecomposition of aryl sulfonium salts generates acid in much the same way as it does at longer wavelengths. The methodology shown here may prove useful as a tool to establish and measure acid generation in novel PAGs designed for 157 nm applications as it can be calibrated for the quantitative evaluation of acid generation and base neutralization studies.

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Supporting Information Available: Description of the experimental setups and procedures, absorbance measurements using the 157 nm laser, more images, and comments. This material is available free of charge via the Internet at http://pubs.acs.org.

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