Study of acid transport using IR spectroscopy and SEM

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ABSTRACT

The migration of acid catalyst molecules from exposed regions into unexposed regions in chemically amplified photoresists and the resulting image blur, has long been recognized as an important topic requiring close study. A fuller understanding of acid transport mechanisms occurring during the post exposure bake is important to help guide the development and formulation of photoresists capable of reliably resolving the increasingly small features required by the semiconductor industry. This paper reports the direct measurement of diffusion coefficients for perfluorobutane sulfonic (nonaflate) acid in poly(4-hydroxystyrene) at several elevated temperatures. These results show that the Fickian diffusion coefficient for nonaflate acid in poly(4-hydroxystyrene) is too small, at typical post exposure bake temperatures, to account for observed isofocal bias. Also reported is a new technique for investigating acid transport properties of photoresist films. This method uses selective silylation to decorate cleaved resist film stacks, so that the extent of acid catalyst migration can be measured directly by scanning electron microscope (SEM). Acid transport distances from the SEM method are compared to those obtained from infrared (IR) spectroscopic techniques.

Keywords: Acid diffusion, CD bias, isofocal bias, post exposure bake, infrared spectroscopy, SEM

1. INTRODUCTION

The image blur in chemically amplified photoresists, resulting from migration of acid catalyst from exposed regions into unexposed regions, has been recognized for several years as an important area of research for the semiconductor industry. Each time device features decrease in size, acid diffusion becomes a proportionately larger consideration in critical dimension control. Several attempts to quantify the contribution of acid diffusion to critical dimension bias have been made previously ¹⁻⁴, but the actual phenomena controlling acid transport during the post exposure bake step remain poorly understood. A better understanding of the mechanisms of acid transport in a chemically amplified resists could be a valuable guide for formulating photoresists capable of reliably resolving the smaller features required for future generations of semiconductor devices. A physical understanding of the acid transport mechanisms would also be useful for developing microlithographic simulators that would not have to rely on empirical fitting parameters, but instead could rely on certain easily measurable physical properties. These more powerful simulators would be valuable tools for the entire microlithography community.

Previously, a reaction front propagation mechanism hypothesis was proposed to explain the observed lithographic behavior of APEX-like deep UV photoresists.^{5,6} The reaction front hypothesis explains observed acid transport behaviors including the nearly linear dependence of feature width on post exposure bake time for short (less than 200 seconds) bake times ^{2,7} by postulating a zone of locally enhanced acid mobility at the interface between exposed and unexposed regions. The local enhancement of acid mobility results from the deprotection reaction that occurs when acid moves into the unexposed regions. Local enhancement could result from of excess free volume that is generated by the gaseous evolution of deprotection by-products or, perhaps, mobility enhancement could result from plastization of the film by the same gaseous by-products. Another possible enhancement mechanism could result from the exothermic deprotection reaction locally responsible for the enhancement.

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The enhancement of mobility in the reaction front, due to whatever factors, can explain the rapid change in line width that occurs at the initial stages of the bake, but it can not explain the drastic slowing down in line-width spread that has also been experimentally observed ^{6,7} at longer bake times. The reaction front mechanism explains this observed slowing down by noting that the enhancement of acid mobility resulting from the deprotection reaction is likely to be transient in nature. A short time after the reaction has been completed in any volume element, the mobility enhancement will dissipate. The polymer film will relax removing excess free volume, the gaseous by-products will evolve from the film thereby ending the plasticization effect, or the heat from the reaction will flow to the surroundings lowering the local temperature back to the bulk temperature. If normal (unenhanced) mobility in deprotected regions is low, the result of transient enhancement is that the acid concentration in the reaction zone (deprotected/protected interface) must quickly deplete. Figure 1 depicts the depletion that occurs as the reaction zone travels through unexposed regions. Initially the acid concentration in the reaction zone is relatively high, but as the front travels into the unexposed region, the concentration in the zone decays as acid molecules get left behind in already reacted regions. Acid molecules that, due to the statistical nature of molecular motion, happen to exit the reaction zone and enter the already reacted region become enmeshed (trapped) in a slow diffusion, low mobility region. Acid left behind will be unable to catch up with the reaction front; thus the concentration in the front decays and the rate of propagation slows drastically. An attempt to simulate this decay has previously been described.⁸



Figure 1. Pictorial representation of the reaction front propagation model. Acid molecules in the reaction zone experience transient enhanced mobility due to the reaction. Mobility in already reacted regions is low, so acid molecules that gets left behind as the front advances are permanently lost to the front.

Clearly, one of the underlying assumptions of the reaction front propagation hypothesis is that diffusion in deprotected regions is very slow. The work presented in this paper experimentally verifies that this assumption is correct. Diffusion coefficients for an acid in poly(4-hydroxstyrene) (PHS) were determined at temperatures in the range of 165°C - 185°C using an FT-IR "sandwich" experiment. Extrapolation of these results to more reasonable temperatures for an actual post exposure bake shows that acid diffusion in PHS is far too slow to keep up with the reaction front. The extrapolated diffusion coefficients are so small that simple Fickian diffusion can not account for any significant fraction of critical dimension bias observed in semiconductor device manufacturing.

The FT-IR "sandwich" approach to determining acid diffusion coefficients in thin polymer films has been reported previously.^{6,9} The "sandwich" or polymer film stack consists of the polymer being studied (e.g. PHS) sandwiched between a photoacid feeder layer and an acid detector layer. The stack is created on a mirror backed silicon wafer, which allows for real-time FT-IR monitoring of the stack while it bakes on a hotplate. Acid is generated in the feeder layer by exposing the stack with ultraviolet light. Once the acid traverses the analyzed polymer layer and reaches the detector layer, it catalyzes a reaction that clearly alters the IR absorbance of the sample and the acid arrival time can thereby be determined. Diffusion coefficients can then be calculated from the Fickian relation:

$$D = L^2 / 2t_{diffusion}$$

where L is the thickness of the analyzed layer and $t_{diffusion}$ is acid transit time.

Also presented in this work is a new analytical method for measuring acid transport distances. This approach is complementary to the FT-IR approach in that it gives information concerning the spatial distribution of deprotected sites that can only be inferred from the FT-IR method. This new method is based on a silylation decoration technique that allows the extent of deprotection caused by the acid front to be visualized using scanning electron microscopy (SEM). This SEM method corroborates previous conclusions drawn from FT-IR results. SEM results also strengthen the case for the reaction front propagation model by showing that deprotection is confined to a reasonably sharp band and not distributed throughout the bulk film.

2. EXPERIMENTAL

2.1 Materials

Poly(4-hydroxystyrene) (PHS) used in this experiment was synthesized from the base-catalyzed hydrolysis of poly(4-acetoxystyrene) (Mw = 8,000), which was made from the free-radical (AIBN) polymerization of 4acetoxystyrene monomer supplied by Triquest Chemical Co. Poly(4-methoxystyrene) (PMOS) was synthesized from the reaction of PHS, potassium carbonate, and methyl iodide in acetone. The high-temperature detector layer, poly(4-(1,2-dihydroxy-1,2-dimethylpropyl)styrene) (PSDIOL) was prepared from the free-radical (AIBN) polymerization of the corresponding monomer. This monomer was synthesized from the Grignard reaction between freshly prepared 4-chloromagnesiostyrene (2 equivalents) and 3-hydroxy-3-methyl-2-butanone in THF. The structure and the acid-catalyzed rearrangement of PSDIOL are shown in Figure 2. The photoacid generators used in this study were bis(4-t-butylphenyl)iodonium perfluorobutane-1-sulfonate (nonaflate) and triphenylsulfonium perfluoromethanesulfonate (triflate). The nonaflate PAG was obtained from Midori Kagaku Co. The triflate PAG was prepared according to standard procedures in our labs. Poly(4-t-butyloxycarbonyloxystyrene) (tBOC) used in the SEM experiments was prepared from the polymerization of 4-t-butyloxycarbonyloxystyrene monomer using AIBN. This monomer was obtained from Triquest Chemical Co. The spin-casting solvent for the PMOS, tBOC, and PSDIOL layers was propylene glycol methyl ether acetate (PGMEA), which was obtained from Aldrich Reagent-grade ethanol was used as the casting solvent for PHS. Chemical Co. The silvlating agent, dimethylsilyldimethylamine, used in the SEM decoration technique was obtained from Silar Laboratories.

2.2 Sample preparation

Films stacks for PHS trilayer experiments were prepared on double-polished silicon wafer pieces, one side of which had been coated with approximately 100 nanometers (nm) of aluminum metal to facilitate collection of IR data in mirror-backed reflection mode. Film stacks were created on the silicon side of the wafer piece. The first layer formed on the wafer piece was the acid feeder layer. The acid feeder layer consisted of PMOS and nonflate PAG in a 20:1 weight ratio. The feeder layer was spin cast at 2500 rpm, then baked on a hotplate for two minutes at 90°C to yield a film 550 nm thick. The PHS layer was spin cast from ethanol directly onto the feeder layer. PHS layers were spin cast at speeds ranging from 4500 rpm to 1500 rpm to give the various thicknesses required by the experimental design. After coating with PHS, the wafer piece was baked at 90°C for two minutes. The third layer, the detector layer, consisted of the PSDIOL polymer. PSDIOL was spin cast onto a glass microscope slide substrate and, after a ten second bake on a 90°C hotplate, was floated from its glass substrate onto the surface of de-ionized water. The floating detector layer was then picked up onto the silicon substrate coated with the previous two layers. A two-minute bake at 40°C was used to remove water caught between the PHS and detector layers. After the 40°C bake, a two-minute bake at 90°C was used to drive off residual casting solvent. Completed samples were then exposed with 60 mJ/cm² of 248 nm ultraviolet light. Exposed samples were then placed on a hotplate attached to a Fourier-transform infrared spectrometer. The FT-IR setup used for real-time monitoring of the bake process is the same as was previously reported.^{6,9}

Film stacks for the SEM based experiments were created using methods similar to those previously stated. Feeder layers of PMOS with PAG were spin cast onto silicon substrates and then post apply baked at 90°C for two minutes. The tBOC detector layer was spin cast on a glass microscope slide, then floated onto de-ionized water after a ten second, 90°C bake. The film was then picked up on a silicon substrate coated with the feeder layer. A twominute bake a 40°C was used to evaporate residual water. The bilayer stack consisting of both feeder and detector layer was then baked at 90°C for two minutes. Samples with nonaflate PAG in the feeder layer were exposed with 100 mJ/cm² of 248nm light. Samples with triflate PAG in the feeder layer were exposed with 15 mJ/cm². After exposure, samples were baked for 35 minutes at 60°C, 75°C, or 90°C. The sample wafer pieces were then cleaved into two halves to expose the layer profile. Samples containing triflate PAG were then placed under vacuum at 20 millitorr for ten hours to remove volatile triflic acid. One half of each cleaved sample was silvlated for one minute at 90°C with dimethylsilvldimethylamine at a pressure of 50 millitorr. Silvlated samples were then etched, edge on, in a Plasma Technology Oxford μ 80 reactive ion etch chamber for twenty seconds in oxygen plasma. The etcher settings were 10 sccm of O₂, 30 millitorr pressure and 45 watts RF power. These settings and etcher configuration were set to minimize horizontal etching. Etched samples were then prepared for the SEM by coating with gold/palladium. A Hitachi 4500 SEM was used to generate all micrographs appearing in this work.

3. RESULTS AND DISCUSSION

3.1 High-temperature acid detector layer

Earlier attempts to use the sandwich FT-IR experimental method to directly measure acid migration times through PHS films were limited to temperatures below 125°C. Above this temperature, the tBOC being used as an acid detector layer begins to decompose due to uncatalyzed thermolysis. This decomposition occurs whether acid is present or not, and thus makes tBOC useless as an acid detector layer at temperatures above 125°C. A new detector layer had to be found to investigate the transport properties of PHS at higher temperatures, say near its glass transition temperature (T_g) of 170°C. Several different polymers were tried before finally settling upon the PSDIOL polymer. PSDIOL was found to be stable up to at least 200°C and acid reactive at temperatures above 160°C. Arrival of acid at the PSDIOL layer can been seen in the IR as an increase in the carbonyl signal at 1710 cm⁻¹, caused by the Pinacol rearrangement of the diol into a ketone. The mechanism for this reaction is shown in Figure 2.



Figure 2. Acid catalyzed Pinacol rearrangement reaction of PSDIOL serves as the basis for a high-temperature acid detector layer.

Once a suitable high-temperature acid detector layer was found, transport of acid through PHS films could be investigated at temperatures above 125°C. The first PSDIOL experiment measured the acid transit time for nonaflate acid through PHS films of varying thickness at 180°C. (Thickness was varied from 0.3 microns to 1.1 microns.) As shown in Figure 3, the time it took for acid to traverse the PHS layer scales linearly ($R^2 = 0.96$) with the square of layer thickness. This is behavior to be expected from classical Fickian diffusion. The diffusion coefficient for nonaflate acid, determined from this method, is $5x10^{-5} \mu m^2/s$. A diffusion coefficient of this magnitude would give over 50 nm of acid displacement during a ninety-second post exposure bake. This rapid diffusion rate can be explained by noting that PHS is ten degrees above its glass transition temperature and is, therefore, in a rubbery state where segmental polymer chain motion can occur.



Figure 3. Measured times required for nonaflate acid to diffuse through PHS layers of various thickness at 180°C.

Experiments at 180°C were able to show that the trilayer method was a valid approach for measuring diffusion coefficients in PHS, but diffusion properties of PHS at 180°C are not particularly useful for microlithography since most post exposure bakes are carried out at much lower temperatures. Another experiment using the PSDIOL detector layer was performed to investigate the effect of bake temperature on acid transport times through PHS layers of fixed thickness. Acid transit times were determined at post exposure bake temperatures of 185°C, 180°C, 175°C, 170°C and 165°C for samples with a 510 nm thick intermediate PHS layer. Figure 4 shows the results of this series of measurements. The mid-point glass transition temperature of 170°C for PHS, as measured by differential scanning calorimetery on the dry polymer powder, was used in the generation of Figure 4. These results show that molecular transport time has a sharp dependence on the relationship of the bake temperature to the glass transition temperature. This strong dependence is a widely observed phenomenon in polymer science.



Figure 4. Acid transit time through 510 nm of PHS at different bake temperatures. The difference between the bake temperature (T_{bake}) and the glass transition temperature (T_g) is used as the x-coordinate. Film stacks consisted of 680 nm of PSDIOL over 510 nm PHS on 425 nm of PMOS+5wt% nonaflate PAG.

The lowest bake temperature presented in Figure 4 is still significantly higher than that typically used for an APEX photoresist post exposure bake. When experiments where carried out at 160°C, no acid arrival was detected even through the samples were monitored for over twenty-four hours. It is likely that the acid did arrive, but the response of the detector layer was not great enough to register above the random noise limit of the FT-IR. A simple linear extrapolation from gathered data suggests acid arrival should occur after some fourteen hours, but no acid arrival was detected over the course of a twenty-four experiment. The lower temperature limit for PSDIOL as an acid detector layer is likely limited by its own diffusion properties and reaction kinetics.

Even though diffusion data was not collected below 165°C, methods of extrapolation exist that can estimate diffusion coefficients for lower temperatures. One such extrapolation method is the Williams-Landel-Ferry (WLF) equation originally developed to describe the kinetics of relaxation in polymers.¹⁰ WLF analysis takes into account the change in rotational mobility of polymer chain segments occurring at the glass transition. Using the WLF analysis, diffusion data can be plotted using the following equation:

$$\ln\left(\frac{t_{diffusion}}{t_{T_g}}\right) = \frac{-C_1(T - T_g)}{\left(C_2 + \left(T - T_g\right)\right)}$$

where $t_{diffusion}$ is the acid transit time, t_{Tg} is the acid transit time at the glass transition temperature, T is the bake temperature, and T_g is the midpoint glass transition temperature. The value of constant C_2 is usually taken to be 50°C. The slope of the fitted line gives C_1 , but the typical C_1 value for most polymers is reported to be near 17.4.¹¹ As seen in Figure 5, the experimentally determined value of C_1 for PHS is 14.9 which is within fifteen percent of the accepted value.



Figure 5. WLF fit for nonaflate acid in PHS.

Tabulated results for both the experimentally measured and WLF extrapolated diffusion coefficients are given in Table 1. The WLF extrapolation was carried with both the experimentally determined C_1 value and the reported generic C_1 value. It can be seen in Table 1 that both C_1 values give diffusion coefficients with roughly the same order of magnitude over most of the extrapolated range. As seen in Table 1, at 150°C (20°C below the glass transition temperature), the magnitude of the nonaflate acid diffusion coefficient in PHS is estimated to be 10⁻¹⁰ μ m²/s. A diffusion coefficient with this order of magnitude would lead to only 0.26 nm to 0.80 nm of total line width spread during a 90 seconds post exposure bake. Previously, IBM researchers have reported a diffusion coefficient of nonaflate acid in PHS at 85°C with a magnitude of $10^{-8} \mu m^2/s$.⁴ This value, which was extracted from simulation, is dramatically higher than the extrapolated values reported here. For example, the WLF extrapolated value at 155°C (just 10°C below the last measured value) is already of the same magnitude as the IBM reported value at 85°C. According to WLF analysis, the change in segmental mobility occurring at glass transition is the controlling factor in penetrant mobility; so for equivalent differences between T and Tg, it would be expected that acid diffusion coefficients in any polymer system would be similar in magnitude to those estimated for PHS. Acid mobility in any non-reactive polymer matrix will be extremely low when the bake temperature is significantly (more than 10°C) below the glass transition temperature of the polymer. Similar values were in fact observed for the polymers poly(ethylmethacrylate) and poly(methylmethacrylate).⁹

Temperature (°C)	$D_{measured} (\mu m^2/s)$	$D_{WLF} (C_1 = 14.9) (\mu m^2/s)$	$D_{WLF} (C_1 = 17.4) (\mu m^2/s)$
185	5.4 x 10 ⁻⁴	4.0 x 10 ⁻⁴	7.1 x 10 ⁻⁴
180	1.3 x 10 ⁻⁴	1.5 x 10 ⁻⁴	2.3 x 10 ⁻⁴
175	4.3 x 10 ⁻⁵	5.0 x 10 ⁻⁵	6.2 x 10 ⁻⁵
170	1.3 x 10 ⁻⁵	1.3 x 10 ⁻⁵	1.3 x 10 ⁻⁵
165	3.3 x 10 ⁻⁶	2.5 x 10 ⁻⁶	1.9 x 10 ⁻⁶
160	-	3.1 x 10 ⁻⁷	1.7 x 10 ⁻⁷
155	-	2.2 x 10 ⁻⁸	7.4 x 10 ⁻⁹
150	-	6.3 x 10 ⁻¹⁰	$1.2 \ge 10^{-10}$
145	-	$4.4 \ge 10^{-12}$	3.6×10^{-13}
140	-	2.6×10^{-15}	5.9 x 10 ⁻¹⁷

Table 1. Measured and extrapolated diffusion coefficients for nonaflate acid in PHS

3.2 Diffusion and amplification

For chemically amplified photoresists it is assumed that there is some trade-off between acid diffusion and catalytic amplification. The acid must be mobile enough to move around to catalyze several reactions, but not so mobile as to allow significant catalyst migration into unexposed regions. According to our analysis, diffusion of nonaflate acid at 90°C in PHS would give much less than a nanometer of acid displacement during a ninety-second post exposure bake. With typical PAG loadings, this small amount of movement could not give sufficient amplification to cause complete deprotection of an exposed photoresist film. If the proton was able to separate significantly from its counter ion, full deprotection might still be possible, but coulombic attraction between the proton and its conjugate anion makes significant separation unlikely. Xuelong Shi has analyzed this effect and showed that the movement of the acid and its anion are strongly correlated and, in fact, is "ambipolar" in nature.¹² Quantum mechanical simulations reported in a companion paper also suggest that separation of the acid/anion pair in media with dielectric constants similar to resist materials is unlikely to be much more than a nanometer.¹³ If, as it appears, the acid is tied closely to its anion, amplification must occur by diffusion of the acid/anion pair, but estimated diffusion coefficients are apparently too small to account for experimentally observed amplification. To say that amplification occurs because the reaction has a long catalytic chain length is to state the obvious, but ignores an important point; the catalytic chain length can not be greater than the number of accessible reaction sites. In a glassy polymer, movement of the polymer chains is basically precluded, so the number of accessible reaction sites must be governed by the distance the acid can migrate. In order to explain the catalytic chain lengths observed experimentally, the acid/anion complex must have higher than expected mobility. The local enhancement of mobility postulated in the reaction front propagation model to explain line width spread in reactive systems can also be used to explain the anomalously high amplification. According to the reaction front propagation model, the deprotection reaction causes a local enhancement in acid mobility in the regions where the reaction is in progress. This enhancement effect allows for a temporary increase in the acid/anion mobility, which in turn allows a larger number of reaction sites to become accessible to the acid for some short, finite time. A greater number of accessible reaction sites allows for greater amplification.

3.3 Silylation/SEM method

The silylation/SEM method relies on the digital silylation scheme described previously by MacDonald, et al.¹⁴ In this scheme the silylating agent reacts only with phenolic sites. Protected phenolic sites (tBOC sites) do not react with the silylating agent, thus silicon is only incorporated into deprotected regions. The silylation/SEM method directly shows where acid deprotection has occurred in the film stack. The IR method can not give information about the spatial distribution of the deprotection sites because the IR beam must interrogate the entire film stack thickness. If one considers a film of tBOC with a PAG dispersed throughout, it is clear that the IR method would be unable to distinguish partial deprotection homogeneously distributed throughout the film from deprotection that was localized to a band. These two possibilities would be readily distinguishable when the silylation/SEM method is used.

The silylation/SEM method was developed to confirm that the acid migration distances inferred from IR experiments on bilayer (tBOC on acid feeder layer) samples were accurate and that acid was indeed confined to a definite region and not distributed throughout the entire tBOC layer. Figure 7 shows SEM micrographs of a bilayer sample with nonaflate PAG in the PMOS feeder layer that was exposed and baked at 90°C for 35 minutes. Figure 8 shows SEM micrographs of a control experiment sample that was not exposed to UV light, but otherwise was processed exactly like the exposed sample. Two distinct layers are evident in Figure 8 and the interface between the two layers is sharp, showing that the two layers did not mix during sample preparation. In Figure 7, a third layer is present that is not evident in the control sample experiment. The new middle layer corresponds to the PHS layer that was generated as the acid catalyst migrated from the feeder layer into the tBOC detector layer and catalyzes the deprotection reaction. As measured in the SEM, the thickness of the deprotected region is 60 nm; this corresponds well with the 65 nm thickness predicted by IR experiments.



Figure 7. SEM micrographs of an exposed bilayer sample. From bottom up the four layers evident in Picture A are the silicon wafer, the PMOS feeder layer, deprotected/silylated region, then the remaining tBOC detector layer. Picture B is a close-up of the interface region between feeder layer and detector layer. The granularity seen in these micrographs is an artifact of the decoration process.



Figure 8. SEM micrographs of an unexposed bilayer sample. From the bottom up the three layers evident in picture A are the silicon wafer, the PMOS feeder layer and the tBOC detector layer.

The acid transport distance expected and observed in the nonaflate bilayer samples is small so this means that measurement errors will remain significant in the measurement of total transport distance. When the triflate PAG was used in the acid feeder layer, transport distances increased significantly, making measurement errors less significant. The triflate PAG was therefore chosen for an experiment designed to compare the distances measured in the SEM to the distances estimated from the IR method. Bilayer samples were constructed on mirror-backed silicon wafer pieces. Samples were exposed, then placed on a FT-IR equipped bake plate and monitored continuously for 35 minutes at three different temperatures. Acid transport distances were determined as a function of bake time and temperature. Final acid transport distances determined by IR at bake temperatures of 60°C, 75°C, and 90°C were 120 nm, 176 nm, and 334 nm, respectively. IR method results for the three samples are shown in Figure 9. At the

end of the 35-minute post exposure bake, the samples were promptly removed and cooled. Samples were then cleaved and decorated according to the procedures given in the Experimental section. Figure 10 shows the SEM profiles for each of three different sample temperatures. Acid transport distance measured in SEM for bake temperatures of 60°C, 75°C, and 90°C were 129 nm, 230 nm and 415 nm, respectively.



Figure 9. Acid transport distances as a function of bake time at three different temperatures.



Figure 10. Transport distances of triflic acid into tBOC after 35 minutes at three different temperatures. Picture A: T_{bake} = 60°C, Picture B: T_{bake} = 75°C, Picture C: T_{bake} = 90°C.

A comparison of results from the two different methods shows that the SEM method gives consistently higher values for acid transport distances. The difference between measured values from SEM and IR at 60°C was about 7%. At 75°C and 90°C the difference between the two methods amounted to 26% and 22%, respectively. This difference could arise from extra, unmonitored diffusion occurring during the silylation bake of the decoration procedure. The samples were held under vacuum for extended periods to remove the triflic acid, but it is possible that this did not completely remove the acid. Also, the film shrinkage that occurs as a result of the deprotection reaction and the swelling that occurs when the silylating agent is incorporated into the film was not accounted for rigorously in the SEM measurements. Future work will take these considerations into account.

4. CONCLUSIONS

Diffusion coefficients for nonaflate acid through PHS, extrapolated from high-temperature trilayer experiments to lower bake temperatures, are far too small to account for a significant fraction of observed isofocal bias. The acid catalyzes reactions as it moves through a real photoresist system and this reaction temporarily enhances diffusion. This transient, reaction enhanced diffusion can explain the extent and speed of acid migration observed in real photoresists. The specific mechanism by which migration is promoted by the reaction requires

further investigation, but any promotion mechanism that is transient in nature can be incorporated into the reaction front propagation model which has been presented to explain experimentally observed behaviors.

The silylation/SEM method confirms that deprotection in our bilayer experiments is confined generally to a definite band and is not distributed throughout the entire detector film. Transport distances measured by SEM are typically larger than distances determined by IR methods. This discrepancy likely results from incomplete removal of acid from the film stack prior to the silylation bake step of the SEM decoration process. Neither the film shrinkage due to the deprotection reaction or the swelling due to the silylation was accounted for during the experiment.

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